

# FUMIGATION AND CONTROLLED ATMOSPHERE STORAGE OF GRAIN



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# **Fumigation and Controlled Atmosphere Storage of Grain**

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*Editors:* **B.R. Champ, E. Highley, and H.J. Banks**

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## Overview of Conference

### The Topic

Fumigation and controlled atmospheres (CA) are pest control technologies based on the application of gases to stored grain. Key objectives of both processes are to control pests, particularly insects, while maintaining the inherent quality of the stored product. It is essential to the success of both fumigation and CA that they be carried out in grain enclosures that are gastight, the aim being to keep the fumigant or CA in, and the outside atmosphere out.

Fumigation is critical to the grain industries of most countries. Nevertheless, fumigation practices are often poor, leading to failures and commodity losses. Also, poor fumigation practices accelerate the development of resistance of insects to fumigants, and the discovery of resistance to phosphine among grain pests is a serious threat to the safe storage of grain in the region. Phosphine is the most useful of the very few fumigants currently available and no replacements for it are in sight.

### Organisation and Objectives

Against this background, ACIAR and the National University of Singapore (NUS) agreed to cosponsor a conference with the following overall objectives:

- to assess the current status of gas application techniques for pest and quality control in stored grain and related products around the world;
- to examine — from technical and other viewpoints — the advantages and potential of emerging fumigation and CA technologies, particularly to the Asian region.

In short, the task was to present the technologies that are available and those that are in the pipeline.

The conference was held with the support of the International Steering Committee on Controlled Atmosphere Conferences. This committee (Chairman: H.J. Banks; Secretary: S. Navarro) organises conferences on fumigation and CA techniques every 4 years. The Singapore conference was effectively the third in the series, previous meetings having been held in Rome in 1980\* and in Perth, Western Australia in 1984†.

The conference had two subsidiary objectives.

The first of these was to present, for comment and discussion, drafts of the first two parts of 'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region', a fumigation 'code of practice' whose development is being sponsored by the Kuala Lumpur-based ASEAN Food Handling Bureau (AFHB) and ACIAR. Part 1 of the fumigation recommendations (the main volume) is headed 'Principles and General Practice', while Part 2, the first of a series of manuals covering specific types of fumigations in detail, covers long term storage of bag stacks in sealed plastic

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\* Shejbal, J., ed., 1980. Controlled atmosphere storage of grains. Amsterdam, Elsevier, 616 p.

† Ripp, B.E., et al., ed. 1984. Controlled atmosphere and fumigation in grain storages. Amsterdam, Elsevier, 812 p.

enclosures following fumigation with carbon dioxide. The final version of Part 1 has since been published.

The second subsidiary objective was to present the final results of ACIAR Project 8307 on long-term storage of grain in sealed plastic enclosures. This project, begun in 1984, came to a successful conclusion at the end of 1988 following extensive field and laboratory research in Malaysia, the Philippines, Thailand, and Australia.

The conference program was developed in consultations between ACIAR, NUS, other ASEAN regional research groups, the staff of the CSIRO Stored Grain Research Laboratory in Canberra, and a representative of the International Steering Committee on Controlled Atmosphere Conferences.

The Singapore Ministry of Trade and Industry, and the ASEAN Food Handling Bureau based in Kuala Lumpur, provided logistic support for the meeting.

### **Conference Program**

There were 20 invited papers grouped by topic area into six sessions, as follows:

- Background to current use of fumigation-CA technology
- Biological responses to treatment with gases
- Physical processes in fumigation and CA storage
- Application methodology
- Sealed storage of bag stacks
- Issues relating to the application of fumigation-CA.

In addition, a call for poster papers elicited a good response and there were 15 such presentations.

A number of commercial presentations were made at the conference, that by Rentokil of its 'bubble fumigation system' generating perhaps the most interest. The complete system was demonstrated to participants.

A field trip to Johore Bharu in nearby Malaysia was part of the program. On this excursion, participants were able to inspect, at a National Paddy and Rice Authority warehouse, the opening of a 200-tonne bag stack of milled rice which had been held for nine months in a sealed plastic enclosure following an initial fumigation with carbon dioxide. This storage trial was part of ACIAR Project 8307. The rice was found to be of good quality and free of pests.

To give participants a further opportunity to develop and crystallise any major issues arising from the main conference sessions, a series of informal parallel workshops was held on one evening. These workshops, hosted by the chairmen of the six sessions, proved to be a useful adjunct to the program.

### **Participation**

The importance of fumigation and controlled atmosphere technologies to the grain industries in the region and elsewhere was reflected in strong interest in the conference from industry, the R&D community, and government agencies of various types. There were some 140 participants, from Australia, Canada, France, West Germany, Hong Kong, India, Indonesia, Israel, Japan, Korea, Malaysia, Nepal, Philippines, Singapore, South Africa, Thailand, U.K., USA, and Zimbabwe. The private sector accounted for some 40% of participants.

### **Major Discussion Points**

A number of key points or issues could be identified from presentations and discussion. These were as follows.



- Robust fumigation and CA technologies are available, but good management and trained operators are essential for their successful application.
- Controlled atmosphere storage is, in general, good for grain. The quality of the product emerging after long-term CA storage is invariably superior to that of grain subjected to repeated ad hoc fumigations or other methods of pest control.
- The storage design parameters for successful fumigation or CA application are well established. The degree of sealing achieved is a critical factor
- There is much activity in the field of fumigation and CA application technology around the world, a great deal of it aimed at refining existing techniques to overcome problems of leakiness and insure against the further spread of resistance to fumigants among storage pests.
- The plastic enclosure technique developed the collaborative research undertaken in ACIAR Project 8307 is ready for commercial use and has, indeed, already been taken up by private sector millers in Thailand and BULOG in Indonesia. It appears to represent a technology very appropriate to preservation of strategic reserves of grain in the region.
- US Environmental Protection Agency regulations may threaten the availability of currently accepted fumigants, few as these materials are. This highlights the need for development of CA technologies based on non-toxic and environmentally relatively benign materials such as carbon dioxide.
- There remain many R&D needs in the area of fumigation–CA storage. Further fumigants are needed and, given the unlikelihood, because of the high costs involved, that any new materials will be even sought let alone found, it may be opportune to look again at some of the older materials that have, for one reason or another, passed out of use. Finally, information about the amounts of fumigant sorbed by various commodities is sorely needed, particularly for phosphine.
- More effort needs to be put into technology transfer so that useful new methods developed have an increased chance of adoption. Conversely, support should not be provided to research yielding results that have no identifiable end-users or beneficiaries.
- Countries in the Asian region are beginning to take seriously the need for regulation, labelling of materials, and education and training of operators in the context of fumigation. The code of fumigation practice presented at the conference stands on the twin precepts of effectiveness and safety. Good fumigations not only kill the target pests but also ensure the absolute safety of workers, the surrounding community, and the environment at large.

# **Opening Addresses**

## Address of Welcome

IT GIVES me great pleasure and is an honour to welcome you, on behalf of the National University of Singapore, to this International Conference on Fumigation and Controlled Atmosphere Storage of Grain.

The storage of grain free from insect infestation and damage is of the utmost importance to many nations. Millions of dollars could be lost if grain is not protected from pest attack. I am glad that we have here with us a group of distinguished scientists whose expertise is in the field of fumigation and controlled atmosphere storage of grain. I look forward, as you no doubt do, to meeting them and to learning of the advances that have been made in this most important field over the past few years.

It is gratifying to see the large number of participants in this conference, and to know that most of the continents of the world are represented among them. Our delegates come from academic institutions, research organisations, and trade and industry, as well as government agencies. I am particularly pleased to note that the Department of Zoology of the National University of Singapore is well represented. Our Department is deeply involved in research in insect control in grain storage. We work closely with industry so that the outcome of the research can be applied to trade and commerce in a tangible way.

Besides contributing to the various topics of discussion, which I believe you will find fruitful and challenging, I hope you will take the opportunity to do some sightseeing during your stay in Singapore. I would also like to urge you to participate in two activities that Singaporeans enjoy doing in their leisure—eating and shopping.

Welcome to Singapore. May your stay be enjoyable, and may the conference be stimulating and productive for you. Thank you.

*Dr S.H. Ho*  
Department of Zoology  
National University of Singapore

## Objectives of Conference

LADIES and gentlemen, it is a pleasure for me, on behalf of the Australian Centre for International Agricultural Research, to outline the objectives of this conference to you before we begin what I am sure will be five extremely stimulating days of formal and informal discussion.

The establishment of ACIAR represented an important innovation for Australia's foreign aid program with the Centre being dedicated explicitly to mobilising Australia's unique agricultural capacity for the benefit of developing countries. Australia has a first-rate reputation in agricultural research in areas of relevance to many developing countries with compatible climatic environments.

ACIAR is an Australian Government statutory authority in its seventh year of operation, being established under its own Act of Parliament which was passed in mid-1982. ACIAR reports direct to the Minister for Foreign Affairs and Trade and has a Policy Advisory Council and Board of Management. The Centre's budget is derived from Australia's global aid allocation.

ACIAR's policy needs to be consistent with Australia's foreign policy objectives, and is this connection the Centre relates closely to AIDAB and the Department of Foreign Affairs and Trade.

In essence, ACIAR has a threefold purpose or objective:

- to identify and help solve agricultural research problems in fields where Australia has a demonstrated comparative advantage and which represent a high priority for our developing country partners;
- to assist in developing the research capacity of the scientists in these countries; and
- to help communicate the results of this research in ways that will facilitate its adoption.

ACIAR does not command large financial resources. However, we believe we have something valuable to offer, namely access to experienced scientists to participate in a partnership in research. We believe that we share many agricultural problems in common with our Asia-Pacific neighbours because of our climatic similarities—half of Australia lies in the tropics and subtropics—and common interest in many agricultural commodities. We are anxious to respond to problems as defined by our partners and respond in areas where we believe that we have special capabilities to assist.

Due to limitation of resources, ACIAR aims to do fewer things well, and thus adopts a focused approach to collaborative research problems.

ACIAR's style of operation is based on linking commissioned organisations in developing countries. The relationship is based on an equal partnership, with each partner contributing to the solution of problems. The partnership is based on mutual interest and benefits. ACIAR seeks to build onto existing priority research programs and to strengthen the research effort in participating countries.

ACIAR has funded a total of 131 projects since it began operations in 1982. These projects, while representing priority problems in our partner countries, also fall within the framework of ACIAR's research priorities. These emphasise: (i) a geographic focus on Southeast Asia and the South Pacific, which together represent

about two-thirds of ACIAR's portfolio; (ii) an assessment of the likely national and regional economic impact of projects; and (iii) Australia's particular skills in agricultural research. ACIAR is honoured to have the National University of Singapore as its partner in cosponsoring this conference. I would also like to thank the Ministry of Trade and Industry here in Singapore for its assistance in organising what I am sure will be a very successful meeting.

Ladies and gentlemen, this conference is about fumigation and controlled atmosphere storage of grain and related staple foodstuffs to protect them from the ravages of pests, particularly insects. Populations of grain pests, if left unchecked, can seriously reduce the quality, quantity, and value of grain stocks, and thereby have a substantial impact on social and economic life at levels ranging from the individual farmer to nations as a whole.

Both fumigation and controlled atmosphere techniques rely for their effect on the modification of the gaseous atmosphere in the grain store. They are widely used around the world and have their roots in ancient history. The grain stewards of the Pharaohs of Egypt were most likely the first practitioners of controlled atmosphere storage of grain. They hermetically sealed the corn harvest in pits. The respiration of the grain and any pests present progressively depleted the oxygen in the pit's atmosphere thereby leading to the self destruction of the pests. By this means the Egyptians were able to safely store grain for many years and, by all accounts, the corn remained of good quality when the time came to consume it.

Fumigation is a faster acting approach to the disinfection of grain in that it involves the direct application of a gas that is harmful to pests. In most circumstances in our part of the world it is the only practical method of treating grain found to be infested and is therefore central to storage management throughout the region.

There have been significant advances in both fumigation and controlled atmosphere technologies over the past decade. Some of these advances have been made in our region and are therefore of direct relevance to grain management strategies here. The relevance to our storage problems of developments in other parts of the world also needs to be assessed.

This international conference therefore has the twin objectives of:

- assessing the current status of gas application techniques for pest and quality control in stored grain and related products around the world; and
- examining — from technical and other viewpoints — the advantages and potential of emerging fumigation and CA technologies, particularly in relation to the Asian region.

These are no mean objectives to achieve over just five days but, on looking through the list of titles and authors of the 20 invited papers to be presented and of those for the large number of submitted poster papers, I feel confident that they will be met. The response to this conference, as reflected in the number of participants, the number of poster papers, and the strong commercial representation, has been little short of enthusiastic, and is extremely gratifying to the organisers.

From ACIAR's point of view, the conference has at least two more objectives.

The first of these is to launch a fumigation 'code of practice' for the region that it has been developing over the past few years in conjunction with the ASEAN Food Handling Bureau. All relevant agencies and authorities in ASEAN have been consulted on and have contributed to this code. We will be presenting the first part of the code to this forum as a 'pre-publication draft', cleared by all contributors. We are taking this opportunity to invite your comments before we proceed to final printing and distribution.

ACIAR's second supplementary objective is to, in effect, round-off its collaborative research project on 'Long term storage of grain under plastic covers'. Work in this project was finalised at the end of 1988, following some four years research in Malaysia, the Philippines, and Thailand, as well as Australia.

The main result of that research has been the proving of a technique for long term storage of bag stacks that involves an initial fumigation with either carbon dioxide or phosphine, followed by enclosure in a sealed plastic membrane that is impenetrable to pests.

As you will hear and see at this conference this project has been — from all points of view — extremely productive. It has proven a new method of storage that is particularly suited to this part of the world. It has built up research and technical skills in the project teams involved and it has forged links in research and friendship that will remain intact for many years to come. These are just the sorts of benefits that ACIAR seeks in its 'partnership' approach to the identification and solution of agricultural problems in developing countries.

Finally, this conference has, of course, a third unwritten objective, and that is to guide funding agencies and researchers towards those areas that are likely to yield greatest benefits in the future. This sort of guidance becomes more and more critical as research funds shrink, something that has been happening, at least to us in Australia, for some years now.

So, we are looking for value for money in the research we support.

One of the ways that we have been able to do this in the past is by acting on the recommendations of conferences such as this where the views of a broad spectrum of research and development, government, industry, international agencies, and the community at large are represented. We at ACIAR will therefore be looking to this meeting for some solid recommendations to help us plan future directions for our postharvest work. I am sure that the same will apply to other donor agencies. This approach has certainly stood us in good stead in the past, as is evidenced by the success of our Postharvest Research Program.

Ladies and gentlemen, be you invited speakers, poster presenters, commercial representatives, chairmen, rapporteurs or, last but not least, participants in general, these are your objectives. I am sure that you will work strenuously to achieve them and I wish you well in your efforts. Thank you.

*C.D. Thurlow*  
Centre Secretary, ACIAR

## Opening Address

ON BEHALF of the National University of Singapore let me again welcome all delegates to this International Conference on Fumigation and Controlled Atmosphere Storage of Grain.

The University is pleased to be the cosponsor of this conference organised by the Australian Centre for International Agricultural Research (ACIAR).

I understand ACIAR has been involved in grain storage research and development programs in Southeast Asia for many years. A major project in the postharvest program has been concerned with the safe long-term storage of grain. This project has come to a successful conclusion and a conference was proposed to pass the results on to grain industries in general. The International Steering Committee on Controlled Atmosphere Conferences suggested a joint conference with Singapore as the venue, and NUS as the cosponsor of the conference. I wish to congratulate the Committee for taking the initiative in getting this worthwhile conference under way.

I understand that there are 20 invited speakers whose papers will cover a broad range of aspects of the science and application of fumigation and controlled atmosphere techniques. There will also be a poster session in which scientists other than the invited speakers will present their papers. In addition, various companies will display their commercial products. There will also be a field trip on the last day of the conference to see a field demonstration of fumigation and CA technology. All in all, I believe an interesting program has been prepared for participants and I hope it will prove also to be useful.

In the context of world food and agriculture, the safe storage of cereal grains and foodstuffs must be a topic of considerable importance, especially to developing countries, for the most deep-seated and severe food problems are those of developing countries, not the developed countries or even of the USSR and Eastern Europe. According to the FAO study 'Agriculture: Towards 2000', it is estimated that in developing countries as a group, excluding China, food supplies now hover at no more than about 100% of minimum nutritional requirements.

In other words, at this aggregate level, this group of countries has no margin to buffer itself against unequal distribution of food and no margin to absorb the impact of serious interruptions to food supplies. On the other hand, the developed countries have a margin of around 30% above their minimum nutritional requirements, as well as a second line of defence in their capacity to switch potentially appreciable quantities of grains from livestock to human use. Inequalities in the distribution of income found in all societies demand that there be a reasonable margin of supplies over minimum requirements if virtually everyone is to have enough food.

Dr James O'Hagan, Chief of Global Perspective Studies at FAO in Rome, has pointed out that there is one very cogent reason why improvement in the world food agricultural system must be hastened: population growth, together with rising incomes, will continue to drive upwards the demands on world food and agriculture throughout at least the first half of the 21st century. Recent projections suggest that by around the middle of the next century, world population may be nine thousand million. Reasonable assumptions indicate that around the year 2050 world food production will need to be three times its 1980 level. The present developing countries, however, would need to increase their 1980 food and agriculture output approximately five-fold in order to meet demand at that time. Growth rates of

output would have to be at their highest during the next two decades and the early part of the succeeding period.

Given this probable scenario, every possible way of protecting our food supplies must take on added significance and importance.

Fumigation is a method of killing pests using 'a chemical which, at a required temperature and pressure, can exist in the gaseous state in sufficient concentration to be lethal to a given pest organism'.

In controlled atmosphere storage, the normal atmospheric gas composition in a storage is intentionally altered in order to provide a better storage environment than air. The atmosphere within the storage is usually altered by introducing nitrogen, carbon dioxide, or a mixture of these gases.

Fumigation and controlled atmospheres are technologies that are widely used to protect stored products from attack by insects and other pests.

Much attention has been given to developing methods for modifying the storage atmosphere so that pests cannot survive. This can be done either by altering the relative concentrations in the air of gases that are already present, or by introducing toxic vapours, that is, by fumigating the grain. The former method averts the problems of chemical residues in the grain but needs long exposure periods. Fumigation as such requires shorter exposure periods and is often the only option where grain can be held in storage for only short periods.

The two technologies are basically similar, and some would even say they are, in fact, aspects of one and the same technology. Whatever view one takes, the common feature of fumigation and controlled atmosphere techniques is the application, at one stage or another during the storage period, of gases that kill grain pests.

Of course, no technology is ever perfect and so, throughout the world, research and development teams are currently working to improve and refine methods of gas application and maintenance. In general, they have two main objectives:

- to improve the effectiveness of fumigation and CA storage methods; and
- to improve their safety.

There are at least two aspects to the matter of effectiveness. First, we seek to ensure that the dosages of gases we apply are sufficient to kill all pests present. This is critical, not just because we want to avoid repeating the process, but also to remove the likelihood of tolerance or resistance developing among members of the pest population treated. The development of insect resistance to the main fumigants currently in use is seen as a major threat.

The other aspect to effectiveness is cost. We need methods that take account of the financial resources—generally limited—of all who might seek to use them.

Safety also has two aspects, both of them arising from the fact that the gases used to kill pests can also harm humans. We are concerned therefore with the safety of individual fumigation workers and people working or living close to commodities being fumigated, and of the eventual consumers of the grain or products made from it. We are also concerned with the impact of fumigation practices on the wider environment.

The net result of research to improve the effectiveness and safety of fumigation and controlled atmosphere storage has been the development and application of more robust techniques that can be integrated with other management and pest control practices in grain stores.

Over the past few years, national grain storage research and development agencies, often working in conjunction with international agencies, have been investigating the problems besetting current fumigation and related practices in the region.



In Singapore, where commodity trading is important and we are totally dependent on imported grain, we have had some experience in maintaining our rice stocks in controlled atmosphere storage. However, the existing technology is not entirely practical and cost effective. More efforts are being made in this direction to develop an appropriate system to suit our needs.

In the National University of Singapore, research is being undertaken at the Zoology Department with the cooperation of the Ministry of Trade and Industry, on the feasibility of using controlled atmosphere storage of grain in terms of the cost-effectiveness, effectiveness against various species of insects, and the maintenance of the quality of the grain. An area of research that will be looked into is the effect of moisture migration in stacks of bagged grain on the quality of the grain in sealed storage, particularly in the humid tropics.

An important outcome of fumigation and controlled atmosphere studies in ASEAN sponsored by ACIAR is the development of a new technology—storage of bag stacks in sealed plastic enclosures. This technology involves initial fumigation of bag stacks held in a plastic enclosure which is then sealed for long-term controlled atmosphere storage. Storage in sealed plastic enclosures is a robust and cost-effective technology that should pass into widespread commercial use in ASEAN. Indeed, it has already done so in Indonesia and Thailand.

One of the main problems with fumigation has been seen to be the lack of a code of practice applicable to the circumstances prevailing in our part of the world. Following some years of work by authorities and specialists from all countries of the region, we are launching at this conference the first part of 'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region', a regional fumigation code of practice whose development has been sponsored by the ASEAN Food Handling Bureau and ACIAR.

With the broad spectrum of interests represented by participants —research and development centres in academia, government agencies of various types, and industry—it is unlikely discussions will proceed without some divergence of views. The challenge will be to accommodate any such divergence in a set of recommendations that can point us along a united path for the future because, despite the great advances we have made in fumigation and controlled atmosphere storage in recent years, there is still much to be done.

I wish you all a successful conference.

*Professor Huang Hsing Hua*  
Deputy Vice-Chancellor  
National University of Singapore

# **Background to Current Use of Fumigation – CA Technology**

# Requirements for Fumigation and Controlled Atmospheres as Options for Pest and Quality Control in Stored Grain

P.C. Annis\*

## *Abstract*

Fumigation may be thought of as having two roles: one to allow rapid removal of live insects to meet short-term goals, and the other as a preliminary to, or component of, long-term storage. While fumigation of grain is primarily for insect control, good control of insects also makes possible the better preservation of other quality parameters. Both fumigation and controlled atmospheres, if used correctly, can give a very high level of insect control. Although similar principles apply to the use of both processes, details of adding, distributing and retaining the gases vary. This paper uses a range of well-documented treatments to demonstrate how these general principles have been employed with a variety of gases and storage structures. These show that many enclosures can be used for successful gaseous treatments if an appropriate level of sealing is attained. This level of sealing depends to some extent on the gas distribution and introduction methods. Methods of continuous gas addition are under development. These may allow gaseous treatment in enclosures currently considered impossible to seal economically.

BOTH controlled atmosphere (CA) storage and fumigation are techniques that rely on a gas or a mixture of gases as a means for controlling the effects of biological agents that may cause quality degradation. This paper aims to show that both gaseous processes have much in common and their uses overlap substantially. However, individual controlled atmospheres and fumigants have properties that make them more appropriate for particular roles. The specific details of these properties are discussed elsewhere in these proceedings (Banks 1990; Graver 1990). Here, discussion will be general and aims to identify the role of fumigation and controlled atmospheres as options for pest and quality control, by identifying the agents of quality change and how CA and fumigation may affect them. The general criteria for a successful gaseous treatment, and the consequences of failure to meet them, are considered. Specific discussion on how to

ensure success by setting treatment targets gives a background to adapting treatment techniques to meet the targets. A series of examples is presented to show how these targets can be reached in practice and to demonstrate that fumigation and CA are options for pest and quality control in a wide range of storage enclosures.

Controlled atmospheres (CAs) as used in grain storage are mixtures of those gases normally found in the storage atmosphere: nitrogen, oxygen, and carbon dioxide. In CAs, the oxygen concentration is reduced and/or the carbon dioxide concentration increased. Specific CAs are generally named by their means of production, maintenance or active component, and are usually designated as one of the following types of atmosphere: modified, oxygen deficient, low oxygen, carbon dioxide enriched, high carbon dioxide, nitrogen, burner gas and hermetic storage.

CAs have not had extensive usage in modern commercial grain storage, despite hermetic stor-

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\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

age — one of the variants of CA — being one of the methods of grain storage with the longest continuous history of use (Bowen and Wood 1986; Sigaut 1980). Where CAs have been used, they have normally formed part of a disinfection and physical protection system (Shejbal (1980) gives many examples). In this, the atmosphere controls the quality degrading biological agent and the containing enclosure acts as both a barrier against gaseous interchange and insect reinfestation.

Fumigants, on the other hand, are highly toxic gases (or vapours) unlikely to form a normal part of the storage atmosphere. They are added to the storage specifically to kill a target organism or group of organisms. These organisms are usually, but not always, insects. Over the years, a fairly wide range of compounds has been used as fumigants either singly or in combination. These have included the following: ethylene dichloride, carbon tetrachloride, carbon disulphide, ethylene dibromide, chloropicrin, hydrogen cyanide, ethylene oxide, methyl chloride, methyl bromide, and phosphine. For a variety of reasons, only methyl bromide and phosphine remain in widespread use.

Traditionally, fumigation has been used as a rapid method of killing insects, either to meet a specific requirement such as quarantine, or as part of a continuing program of insect suppression, applied when insect numbers pass some nominal threshold. In these cases, there is no aim for continuous protection. Rather, the aim is to reduce insect damage as much as possible and to market a commodity at a level of infestation acceptable to the market or its regulatory authorities.

### **Agents Affecting Quality in Stored Grains**

There is a large range of quality changes that may occur during the storage of grains. These changes may be brought about by physical, biological, or chemical agents.

The primary aim of most gaseous treatments of stored grain is to control the biological agents causing quality change within the stored commodity or its containing structure. These agents are normally animal pests, usually insects, but may include rodents. The biological agents themselves can cause substantial physi-

cal damage to the grain quality by completely or partially consuming it, or through contamination. Killing the biological agents will eliminate direct damage and may also lead to a reduced risk of consequential quality degradation by other biological, chemical and physical factors.

Controlled atmospheres with substantially reduced oxygen concentration have the potential to kill animals (insects, mites and rodents), reduce other biological activity (moulds, fungi, and grain respiration), and to reduce oxidative degradation. However, CAs with high carbon dioxide concentrations in air, and which have a significant oxygen content, act as a toxic gas only. While able to kill pest animals they are unlikely to have any other direct quality preserving effects (Banks 1981). Because the component gases of controlled atmospheres are normal components of the storage atmosphere, it is unlikely that they will directly cause quality degradation by residue formation. There is, however, some evidence that, although high CO<sub>2</sub> atmospheres generally have no adverse effect on germination, there are specific circumstances when germination may be affected (Peterson et al. 1956; Ponton and Briggs 1969; Banks and Gras 1982).

Fumigation on its own is unlikely to have any direct positive effect on grain quality other than control of biological degradation. Fumigants may have negative effects on grain quality by reducing germination or by forming detectable and/or deleterious residues (Plimmer 1977).

### **Similarities between CAs and Fumigants**

Fumigants and controlled atmospheres are gaseous treatments and have much in common in both the theory and practice of their application. They require similar facilities, can have a similar role in an integrated commodity management system (Annis and Graver 1987) and their use has indirect but important consequences leading to quality maintenance.

If a storage enclosure is well sealed and adequately dosed with an insecticidal atmosphere, the gas has the potential to come in contact with every grain in the storage, thereby giving a high probability of complete disinfection. If the grain is dry enough to store safely, and is protected from further infestation and the effects of physical agencies such as excessive

moisture, it may be stored for extremely long periods with little risk of significant quality degradation. Gaseous treatment, therefore, if properly carried out in an adequately sealed and gas-proof enclosure, not only gives reliable disinfestation but allows a high degree of continued physical protection from external biological and physical agents that may otherwise degrade the stored commodity.

The use of a semi-permanent enclosure for physical protection has been advocated before (e.g. McFarlane 1980). However, without thorough disinfestation and a reliable means of protection against reinfestation it may lead to significant quality degradation. Live insects can cause substantial localised heating and water production. This heat will lead to moisture migration that cannot escape from an unventilated system, leading in turn to the formation of wet areas of grain close to the inside of the fabric of the enclosure, if this is in contact with the grain. If the grain is not in contact with the fabric, water from the high humidity air may condense on the inside of the enclosure and otherwise come into contact with the grain. In both cases there is a significant likelihood of mould growth, sprouting, etc. These biological processes themselves produce further heat and water, thus exacerbating the problem.

However, a sealed enclosure that does not lead to significant moisture migration can be left safely in place. The enclosure then forms a barrier, which if properly maintained should stop reinfestation by insects, help protect the commodity from rodents, dirt and dust (Tilton 1961), reduce the impact of ambient humidity (Annis and Greve 1984) and aridity, and offer some protection against water ingress, be it from roof leaks or low level flooding.

## **Criteria for a Gaseous Treatment**

The first objective of a gaseous treatment should be to kill all target organisms. This is equally true whether the treatment is for quarantine or is a component of long-term storage. A complete kill can be assured only by maintaining an adequate concentration of active gas for long enough and throughout the storage to achieve the required effect (in the case of oxygen-deficient atmospheres, a sufficiently low oxygen concentration is the objective). In insect control, this means 100% mortality in all stages of all species present. It is often difficult to be

certain which insect species are present. The dosage, in terms of time and concentration, has therefore to be set so as to ensure a complete kill of the most tolerant insects likely to be present.

Most existing grain storage facilities were designed to be well ventilated. Gaseous treatments require a sealed enclosure. Thus, there are very few existing storage facilities in which very reliable gaseous treatments can be carried out without some modification to either the storage and/or existing fumigation practices. The modifications necessary are in three main areas: sealing, dosing and distribution. The general specification of these modifications is given later and the details for particular treatments are given elsewhere (AFHB/ACIAR 1989). If these specifications cannot be met, a gaseous method of quality control should not be considered. If, for some reason, a gaseous treatment has to be carried out in suboptimal conditions, the risks associated with the treatment failing need careful consideration and a plan made to cope with the consequences of the almost certain failure.

## **What is a Failure?**

There are a number of criteria for a treatment failure (Banks and Annis (1984a) discuss criteria for a successful fumigation). In commercial practice, the least stringent of these is finding significant numbers of insects after the fumigation. The most stringent, rarely considered in commercial fumigation, is identification of localised areas in the grain where dosages would have been inadequate for a complete kill had insects been present. In this paper, a practical definition of failure is used: that there is survival by the target organisms at such a level that there is a possibility of population resurgence from these survivors.

## **Risks Associated with Failure**

The immediate impact of insect resurgence depends on the reason for treatment. In traditional treatments, a failure is often considered merely as a nuisance that requires retreatment. In long-term sealed storage a failure may compromise the quality of the enclosed commodity. In quarantine treatments, failure may lead to the loss of whole markets. A less immediate but more serious long-term risk is that survival may lead to insects developing tolerance/resistance

to the treatment, thus making the requirements for successful treatments in the future harder or, in the worst case, impossible to meet. The problems created by resistance are many but some of them are: the cost of using higher doses; increased exposure times requiring continuous or repeated fumigant application; and production of unacceptable levels of residue with some fumigants.

## The Prerequisites for Quality Control Using Gases

In the simplest of terms, the most important requirement for a successful gaseous treatment is to maintain at least a minimum gas concentration for a required period throughout the enclosure. Guidelines for these requirements are shown in Table 1. The idea of requiring a minimum concentration at the end of exposure is not a well-recognised concept in fumigation. It is used in this paper to eliminate problems associated with assuming that the  $c \times t$  products for a given response are constant for gases such as carbon dioxide, phosphine and low oxygen.

The minimum concentration goals are set at levels appropriate to current good fumigation practice, but other combinations of concentration and time can be equally effective (see Winks (1987) for phosphine and Annis (1987) for low oxygen and carbon dioxide).

None of these targets can be achieved or maintained if:

- inadequate gas is added;
- there is excessive leakage leading to dilution by air;
- poor gas distribution occurs; or
- other processes occur that delay the establishment of an even concentration.

Theoretically, any of these can be accommodated by adjusting one or more of the three factors controlling gas concentration, namely level of sealing, method of gas distribution, and gas application methodology. Examples of the relationship between sealing and concentration distribution are discussed by Banks and Annis (1984a). They showed that with a single-shot addition of fumigant (phosphine in the case in point) it was essential that the gas be retained well enough to ensure adequate concentration distribution before losses reduced the average concentration to non-efficacious levels.

The interaction between application methodology and sealing is complex and not well documented, although it is considered by Annis elsewhere in these proceedings (Annis 1990). Generally, in a single-shot fumigation, it is not possible to increase applied dosage enough to overcome the effect of very high leakage rates. For example, a loss rate of 50% per day means a reduction to 1/33 of the original concentration during a fumigation of 7 days (the time of a phosphine fumigation) and a reduction to 1/1808 in 15 days (the time of a carbon dioxide treatment). In both cases, the required initial concentration would need to be impossibly high to meet the target.

Loss rates of 50% or higher are common in unsealed storages. Unacceptably large initial dosages may be required, even when some attempt, albeit inadequate, has been made to achieve gas-tightness. For example, the method of fumigation of bagstacks using gas-proof sheeting and sand-snakes may well not give adequate sealing to reduce the CO<sub>2</sub> loss rate to the 7.0% per day required for a single-shot treatment where the upper concentration possible is 100% and a minimum of 15 days above 35% is needed. On the other-hand, in a well-sealed storage it may be possible to ensure that

**Table 1.** Suggested dosage targets for gaseous treatments of grain at 25°C

Gas	Days <sup>a</sup>	Concentration	Ct product	Reference
carbon dioxide	15 days	> 35%	–	Annis 1987
low oxygen	20 days	< 1%	–	Annis 1987
phosphine	7 days	100 mg/m <sup>3</sup>	–	<sup>b</sup>
methyl bromide	1–2 days	–	150 g h/m <sup>3</sup>	AFHB/ACIAR 1989
hydrogen cyanide	1 day	<sup>c</sup>	–	–

<sup>a</sup> In cases of slow gas introduction or poor gas distribution it is necessary to increase the exposure period to ensure the required time above the minimum concentration is achieved throughout the enclosure.

<sup>b</sup> Based on the dosage to ensure high mortality in *Sitophilus granarius* pupae (Winks 1987).

<sup>c</sup> Concentration that needs maintaining not defined.

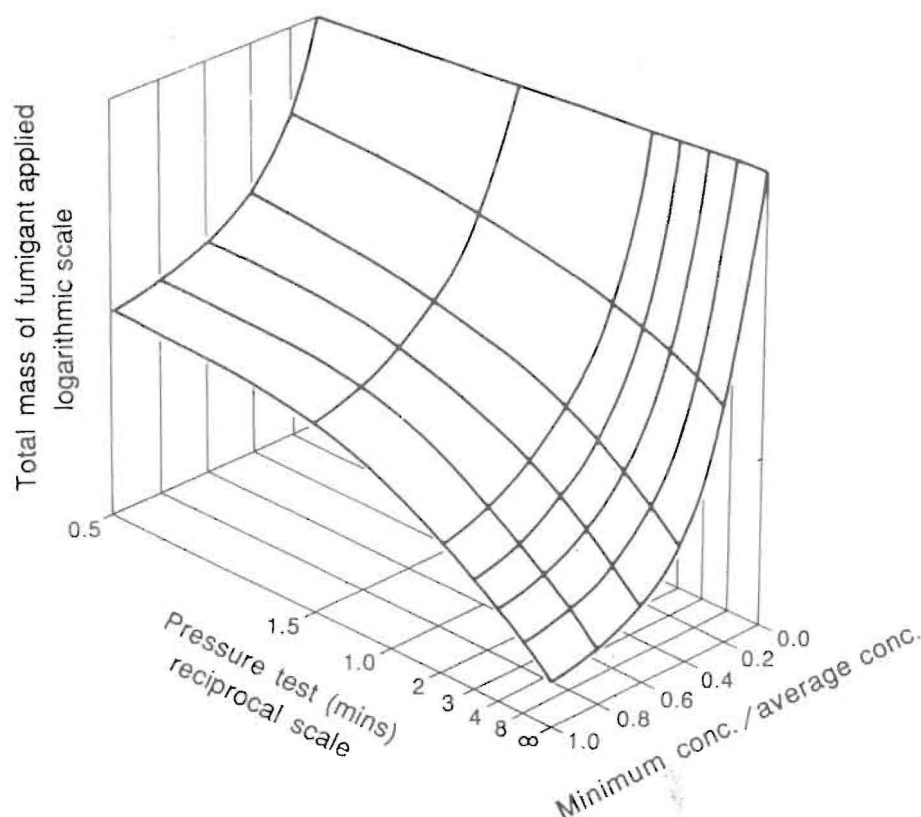
target dosage regimes are reached even if the dose is decreased substantially from those normally recommended. The actual minimum applied dose required in these circumstances is correlated with the level of sealing as assessed by a pressure test (Banks 1987; Annis 1990).

It is possible to approximate the combination of distribution, applied dose, and level of sealing required to meet the dosage schedules given in Table 1. This can be done by applying the method of Banks and Annis (1984b) to both one-shot and continuous-application fumigations to give the treatment surfaces of the type shown in Figure 1. Combinations of dose and pressure, and distribution above the surface, will meet the requirements of Table 1, those below will fail.

Toxicological constraints may make the restrictions on increasing the initial concentration even more severe. The response of insects to high concentrations of some fumigants may be significantly different in terms of concentration and time requirements than would be predicted from

the response at lower concentrations. This may make treatments at high concentration less desirable than at lower ones and, in some cases, may necessitate prolonging the treatment rather than reducing it for high concentrations. Fumigants reported to display different effects at high and low concentration include phosphine (Winks 1984) and carbon dioxide (Annis 1987).

One further limitation to simply increasing concentration by adding more gas initially is that it does nothing to overcome the effects of unidirectional leakage. This type of leakage is caused by two major phenomena, a difference in the density of internal and external gases (chimney effect) (Banks and Annis 1984b) and by differential wind-induced pressure between the base and top of (or across) the enclosure (Mulhearn et al. 1976). Both phenomena can cause substantial and continuous ingress of air thereby reducing the gas concentration in localised areas. This type of unevenness in concentration can be reliably countered only by either one of two methods. Either the leaks are identi-



**Fig 1.** An example of a surface plot showing the combinations of pressure test, total dose, and distribution needed to ensure that a fumigation meets a defined minimum concentration at a specified time. Combinations falling below the surface will fail, those above will pass. This example is based on the data for a horizontal grain shed in Banks and Annis (1984b).

fied and sealed, or all areas inside the enclosure must be held at a constantly positive differential pressure compared with the external environment. If the second method is employed then gas loss during pressurisation must be replaced.

On the other hand, uneven distribution of concentration resulting from poor initial distribution of gas may be overcome by one or other of the following four ways:

1. better initial gas distribution by ducting, etc.
2. gas distribution assisted by ducts and fans
3. additional sealing to allow uniform distribution before loss
4. continuous/repeated addition of gas to make up for losses.

There is no single prescription for meeting concentration/time requirements. In theory at least, they can always be met by one or many combinations of sealing, distribution method and dosage (method and quantity). The balance between these will depend on a variety of operational factors, with those most commonly taken into consideration being cost and convenience. In some circumstances it may well be that, although a theoretical prescription can be produced, no economically acceptable solution can be derived. In this case, an alternative to a gaseous treatment will have to be considered.

The following examples taken from reports of well-monitored gaseous treatments show that it has been possible to achieve target schedules in a wide range of storage enclosures. Although all are based on Australian work, similar work has been reported from elsewhere, e.g. China (Lu Quianyu 1984) and USA (Jay et al. 1990).

### Case 1

*Type of structure:* well-sealed bag-stack.

*Load:* 100–200 t rice, paddy, and maize.

*Enclosure material:* a PVC membrane tailored to stack dimensions, sealed to PVC floor sheet (indoor storage).

*Level of sealing:* pressure halving time 100–50 Pa > 10 min (typically > 20 min).

*Treatment method:* single addition of carbon dioxide or phosphine generating preparation.

*Distribution:* **a.** With carbon dioxide, initial purge plus time for natural convection to ensure all parts were above 35% for 15 days before leakage made this unattainable.

**b.** With phosphine, natural convection and diffusion to ensure all parts were above 100 mg/m<sup>3</sup> for 7 days before leakage made this unattainable.

*Proven protection:* with CO<sub>2</sub> up to 18 months with milled rice, up to 1 year with paddy and maize. With phosphine up to 6 months for milled rice and maize.

*References:* Annis and Graver 1986; Sukprakarn et al. 1990; Sabio et al. 1990; Anon. 1984; Annis 1990.

### Case 2

*Type of structure:* bunker storage bulk grain.

*Load:* 10 000 t Australian standard white (ASW) wheat.

*Enclosure material:* PVC membrane top-cover, bitumenised paper floor cover.

*Level of sealing:* pressure halving time 100–50 Pa approx. 3 min.

*Treatment method:* single addition of phosphine generating preparation at a rate of 0.75 g PH<sub>3</sub>/t.

*Distribution:* natural convection and diffusion ensure all parts are above  $c \times t$  product > 20 g h/m<sup>3</sup> in 28 days.

*Proven protection:* 10 months.

*Reference:* Banks and Sticka 1981.

### Case 3

*Type of structure:* very large shed—bulk grain storage.

*Load:* **a.** 176 000 t wheat; **b.** 278 000 t wheat.

*Enclosure material:* concrete walls and floor, aluminium cladding, sealed after construction (Ripp 1984).

*Level of sealing:* **a.** Pressure halving time 170–85 Pa 28 min. **b.** Pressure halving time 200–100 Pa > 30 min.

*Treatment method:* **a.** Single addition of phosphine generating preparation at a rate of 0.88 g PH<sub>3</sub>/t. **b.** Initial purge followed by daily addition of carbon dioxide to keep concentration above 35%.

*Distribution:* fan-assisted recirculation between base and head space such that **a.** all parts above 100 mg/m<sup>3</sup> phosphine for 7 days; **b.** all parts above 35% CO<sub>2</sub> for 23 days.

*Proven protection:* not stated

*Reference:* Green 1987.



#### Case 4

*Type of structure:* large shed — bulk grain storage.

*Load:* **a.** 16 000 t wheat; **b.** 16 000 t wheat.

*Enclosure material:* steel cladding walls and roof, sealed after construction.

*Level of sealing:* pressure halving time 100–50 Pa 5 min.

*Treatment method:* **a.** Initial purge with 100% CO<sub>2</sub>. **b.** Single addition of phosphine preparation at a rate of 1.6 g PH<sub>3</sub>/t.

*Distribution:* **a.** Fan-assisted recirculation between base and head space such that all parts above 35% CO<sub>2</sub> for 15 days. **b.** Natural convection and diffusion so that all parts above 100 mg/m<sup>3</sup> PH<sub>3</sub> for 7 days.

*Proven protection:* **a.** 3–4 months; **b.** >4 months

*References:* Sealing: Banks et al. 1979; CO<sub>2</sub> results: Banks et al. 1980; PH<sub>3</sub> results: Banks and Annis 1984a.

#### Case 5

*Type of structure:* ISO general purpose shipping container (6.1 m).

*Load:* various dry commodities about 18 t.

*Enclosure material:* steel walls and roof, plywood floor.

*Level of sealing:* pressure test decay time of >10 sec.

*Treatment method:* initial charge of dry ice for purging. Continuous addition of gas by controlled sublimation of dry ice.

*Distribution:* natural convection.

*Proven protection:* duration of domestic transit and voyage to Europe, 1–2 months.

*Reference:* Banks 1987.

#### Case 6

*Type of structure:* sealed steel vertical cells.

*Load:* 1900 t ASW wheat.

*Enclosure material:* welded steel.

*Level of sealing:* pressure halving 1500–750 Pa 3.6 min.

*Treatment method:* single addition carbon dioxide.

*Distribution:* recirculation base to head-space.

*Proven protection:* 4.5 months.

*Reference:* Wilson et al. 1980.

#### Case 7

*Type of structure:* sealed steel vertical cells.

*Load:* 1900 t wheat.

*Enclosure material:* welded steel.

*Level of sealing:* pressure halving > 5 min.

*Treatment method:* continuous addition nitrogen.

*Distribution:* aeration ducts at base.

*Proven protection:* not stated.

*Reference:* Banks et al. 1980.

In all these cases, sealing and proving the level of sealing were major aspects of ensuring the maintenance of target gas concentrations. All rely to some extent on adequate initial dosing, but in case 3b (very large shed with CO<sub>2</sub>), case 5 (ISO shipping container with CO<sub>2</sub>) and case 7 (vertical silo with nitrogen), some form of concentration maintenance was also necessary.

In the very large shed, the large volumes of purge gas needed to attain the initial high concentration required for a single-shot treatment were logistically very difficult to apply. In this case, however, addition of CO<sub>2</sub> when required for maintenance at >35% presented no difficulties.

Treatments of shipping containers with CO<sub>2</sub> presents a problem because it is almost impossible to select a container that can be sealed well enough for a conventional single-shot treatment. It is therefore necessary to select containers to a lower level of gas-tightness and, over several days after the initial gassing, add make-up CO<sub>2</sub> produced by the controlled sublimation of dry ice.

In treatments relying on low oxygen it is not feasible, because of pressure build up, to seal sufficiently to use a single-shot treatment of gas to maintain <1.2% O<sub>2</sub> for 21 days or more. This means that in low oxygen treatments, continuous or on demand addition of low-oxygen gas is needed to displace the oxygen gained by leakage.

Recent advances in atmosphere generation technology may well alter the balance of effort between sealing, addition, and distribution in such a way as to remove some of the emphasis from sealing towards constant introduction of gas. Although these changes have been foreshadowed, e.g. phosphine addition (Winks 1990) and low cost, burner-generated, low oxygen atmospheres (Banks 1984), they have

not yet been reported as being either widely or readily available.

Until these processes become widely and economically available, sealing remains the most reliable, currently available method of ensuring efficacious gaseous treatments. Because of this a good starting point for any gaseous treatment is to aim for an enclosure sealed to the highest standard that is economically and logistically possible. Sealing is neither as hard nor as complex as it appears, although it does require some experience. Given the correct experience, common sense and a reasonable range of sealing materials there are a very few enclosed structures that can not be well sealed (Ripp 1980).

## Conclusion

The foregoing discussion implies that many gaseous treatments (as currently carried out) are not up to the required standard. The three or four gases we have available today as major agents for quality control are all we are likely to have for a long time. Methyl bromide, phosphine, carbon dioxide and, possibly for some applications, hydrogen cyanide, all live a precarious life. Each has its weaknesses in terms of potential for resistance, perceived danger to the environment, expense, residues, and operational difficulties. More care is therefore needed to ensure their availability as fumigants is preserved for as long as possible. This implies that they have to be used in a manner safe to the environment, workers, and consumers, as well as being 100% effectively against insect pests. In practical terms that means minimum emission to the environment, the lowest possible residue in the commodity and well-planned and executed treatments in suitable facilities. The simplest way of achieving this at present is to make the fumigation enclosure as gas-proof as possible.

In a limited number of applications it will not be possible to achieve targeted concentration regimes solely by a combination of sealing and single dosage. In these cases, a method of external concentration maintenance will be needed. Even then, however, a substantial level of sealing will be required to ensure reliable treatments. Where the targeted concentration regimes cannot be achieved, fumigation and controlled atmospheres are not options for quality control and other methods must be employed.

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# Current Scope and Usage of Fumigation and Controlled Atmospheres for Pest Control in Stored Products

E.J. Bond\*

## Abstract

The prospects for controlling stored product pests with modified or controlled atmospheres (CA) has taken on new dimensions in recent years as increasing numbers of basic scientific and applied studies have pointed up the advantages and feasibility of using such procedures. Both the technology for producing and maintaining controlled atmospheres, and the protocols for applying treatments more effectively and efficiently, are gradually emerging from this research. A somewhat similar technology with similar protocols and similar objectives has been used in the fumigation of grain and food products so that the two processes have often seemed competitive and the choice has been determined by relative efficacies and costs of the two approaches.

For the fumigants, where public concern to reduce or eliminate highly toxic chemicals from the environment is increasing, current research has been directed mainly towards an increased assurance for safety and efficacy. The development of insect resistance to the fumigant phosphine threatens to reduce effectiveness of this very widely used compound. Incorrect or careless usage of phosphine and other fumigants is also a matter of serious concern, particularly for reasons of safety and public acceptance. For the fumigant methyl bromide, the residues and reaction products remaining in treated food must be shown to be relatively innocuous for this product to be reregistered by the U.S. Environmental Protection Agency.

New developments in CA technology, such as the use of oxygen absorbing systems to establish oxygen deficient atmospheres, the development of hollow fibre, selectively permeable membranes to separate oxygen from nitrogen, and the use of new sealing materials and techniques, plus the increasing flow of new information on the toxicity of various atmospheres to pests in various stages and conditions, promises to increase the feasibility of adopting CA treatments for some routine requirements.

THE development of pest control procedures for stored products has been greatly complicated in recent years by rapidly changing practices. Changes in the types and quantities of commodities, in the methods of handling and processing, and in socioeconomic requirements all have had pronounced influence on infestation problems. New species of insects that were formerly of only minor significance have become serious economic pests: for example, the larger grain

borer (*Prostephanus truncatus*), a little known insect from Central America, has become a serious pest in several parts of Africa (Hodges 1986). Also, the Khapra beetle (*Trogoderma granarium*) has spread and created problems that have necessitated large and costly eradication programs. All of these changes have made pest control a formidable and continuing challenge. The question is: how can stored products best be protected under these constantly changing conditions?

Various methods have been used for controlling stored product insects in the past.

\*Research Centre, Agriculture Canada, 1400 Western Road, London, Ontario N6G 2V4.

## Fumigants and Fumigation Techniques

One very successful approach has been to modify the atmosphere so that the pest organism cannot survive in it. Atmospheres have been modified mainly in two ways: either by changing proportions of normal components, e.g. oxygen and carbon dioxide, or by injection of toxic gases. Both of these processes have been used in one form or another and with varying degrees of success since time immemorial. However, it is only in recent times that comprehensive studies have been made to understand the dynamics and the potential of the processes. Fumigants have been studied on a scientific basis for just over 100 years and controlled atmosphere storage since the work of Dendy and Elkington (1918a, b). Over the intervening years much research has been done to define the various physical and physiological parameters central to effective pest control. The current usage and potential for future use of these processes is directly dependent on this research. Basic understanding of the parameters of the processes is essential to the development of effective, economic techniques.

Fumigation has been by far the dominant method of pest control in stored products; it has been given preference in many cases because of ease of application and relatively low cost. Sometimes fumigation has been so easy and successful that it has been used to obviate basic requirements of good sanitation. However, as a result of overuse and abuse, and certain adverse features, its popularity has declined in recent years and the need for other approaches has become more apparent.

Controlled atmospheres offer attractive alternatives to the practice of fumigation. The manipulation of normal atmospheric constituents to create conditions lethal to insects is far more compatible with modern philosophies of pest control than is the use of toxic pesticides. However, further information and improved technology is required to exploit the full potential of controlled atmospheres.

Much information on the use of controlled atmospheres and fumigation was brought together and discussed at the two previous conferences on this subject (Shejbal 1980; Ripp et al. 1984). This paper is intended to provide information on research and development in the field since the last conference and to relate this to current pest management strategies.

The number of fumigants available for pest control in stored products has decreased in recent years and is now limited mainly to the two compounds methyl bromide and phosphine. The continued use of even these two compounds is largely dependent on their continued acceptability to registration authorities and the general public. Misuse, adverse publicity, the discovery of hazardous effects (or even the fear of such effects), all serve to jeopardise continued use of these two materials. Some hazards may be alleviated by research and new data on properties, but misuse and adverse publicity present problems that are almost insoluble. Nevertheless, it is important to know of these problems and accommodate their effects and implications in future plans for fumigants.

### Misuse of Fumigants

Fumigants are misused when they are improperly applied or when they are applied for the wrong reasons. Fumigants have in the past sometimes been used in place of good sanitation procedures as well as for other purposes for which they are not intended, such as fulfilling terms of contracts without regard to efficacy in controlling insects. Misuse not only causes excessive waste of materials but can also greatly weaken the main objective in registering fumigants for pest control.

The safe and proper application of fumigants is the responsibility of all of those associated with their production and use. The manufacturers of the materials, the managers that plan for their use, and the fumigators themselves, all have a responsibility in ensuring that the materials are employed with the greatest efficiency and safety. The manufacturer is required to label the product with detailed information indicating the conditions for proper use and safety. In most developed countries, such labels are legal requirements and they must be printed in the official languages of the countries concerned. However, in many of the developing parts of the world these same pesticides are supplied and used without labels in official national languages. This means that the pesticides are very often handled and used by people who are unaware of their properties

and hazards and, as a result, accidents—sometimes fatal—occur. Such accidents are more frequent than may be generally known and they would not be tolerated in many developed countries.

In addition to the labelling, the usage of the fumigant is important. Although the intended objective of a fumigation is to control or eliminate insects in commodities, fumigants are sometimes applied to fulfill the terms of a contract without regard to efficacy or control. For example, I recently observed the fumigation of a cargo of rice on a ship where the treatment was conducted not to control insects but merely to satisfy the terms of a contract. The dosage used was considerably below the recommended level and no assessment of efficacy was made: all that was sought was the certificate indicating that the treatment had been carried out. Also, in this particular treatment, safety precautions were grossly deficient. The applicators had gas masks available but did not wear them, despite the presence of dense clouds of white smoke emanating from open packages of the phosphine-producing formulation that was used. The labelling instructions on these packages were in four European languages (German, English, French, and Spanish) but not in the national language of the country concerned. The applicators were unfamiliar with any of these foreign languages and hence were unable to read of the hazards involved.

Accidents are also known to occur in fumigation of barges where families live and work. People, especially children, are particularly vulnerable and are sometimes injured or killed by improper use of fumigants, but occurrence of such accidents seems to go largely unreported. The Intergovernmental Maritime Organization (I.M.O. 1980; 1984) has published 'Recommendations on the Safe Use of Pesticides on Ships' to help overcome such problems but, unfortunately, these recommendations are not always followed.

The misuse of fumigants is a matter of great concern to all, regardless of what part of the world it occurs. Accidents and adverse publicity are likely to have serious implications for the future acceptance of these materials for use on food commodities.

### **Repercussions from Misuse of Fumigants**

The adverse publicity given to fumigants

seems already to be producing considerable reaction against their application to stored products. Environmentalists and other reaction groups are questioning the use of any of these toxic materials because of possible long-term effects on human health and the environment.

The State of California in the United States already has a law (Proposition 65) requiring that warning signs be posted by food distributors when food or other materials containing any carcinogenic agent are being sold or retained on the premises. This means, for example, that foods treated with a pesticide shown to have any carcinogenic properties would need to be so labelled. Further developments that could emanate from such policies can easily be envisaged.

Resistance to phosphine is another serious consequence of improper use of fumigants. A number of reports in the past have alluded to the possibility of resistance to phosphine and Taylor and Halliday (1986) have confirmed the geographical spread of resistance to phosphine in several coleopterous pests of stored products. Unsatisfactory sealing of storages, leading to rapid loss of gas and consequent inadequate exposure of the insects, was proposed as the reason for resistance and some strains have been widely dispersed in certain regions of the world.

The fact that most occurrences of resistance have been in tropical regions will no doubt have serious consequences for stored product pest control in those areas but the phenomenon also has long-term implications for temperate areas where tropical commodities are traded. A solution to resistance problems is not likely to be easily found. The possibilities and consequences of resistance to phosphine have been known for some time: part of the answer to them lies in proper management and careful, effective use of the fumigant.

### **Research on Fumigants and Fumigation**

#### *Dosage response studies on insects*

Some investigations in this area have been carried out since the previous conference on controlled atmospheres and fumigation in 1983. They have been directed at both efficacy in controlling insects and safety in use. Studies on the toxicity of phosphine to tolerant stages of the very serious stored product pest

*Trogoderma granarium* have shown that larvae of several stocks (in diapause) can be completely controlled in a 6-day exposure at 20°C to 1.4 mg/L of phosphine. Control could also be achieved in 4 days when 2.0 mg/L methyl bromide was mixed with the phosphine (Bell et al. 1984). These authors concluded that use of the mixture of the two fumigants reduced the chance of selecting for resistance to phosphine.

Laboratory investigations on the relationship of concentration of phosphine and exposure time to toxicity have shown that mortality of at least some species of stored product insects may decline at concentrations above 0.5 mg/L (Winks 1984). Exposure to concentrations above this level can cause insects to become narcotised, so that they are more tolerant to the fumigant. This finding has some relevance, particularly for laboratory studies on dosage response of insects to this fumigant, and it should help to alleviate problems of data inconsistencies that have been encountered by investigators in toxicity studies.

#### *Flammability of phosphine at reduced pressures*

Phosphine is normally applied at atmospheric pressures, under which condition there is no risk of flammability due to pressure changes. However, there has been some concern about its stability in forced circulation systems where the use of fans to disperse the fumigant is known to create pressure changes in certain regions of the system. Phosphine has not been recommended for use under such conditions in the past because of uncertainty about its stability at reduced pressures.

Bond and Miller (1988) investigated the problem. They found that the lowest concentration at which flammability occurred was 1.67% at a pressure of 150 mmHg. Below this concentration no reaction occurred at any pressure in the range of 760–150 mmHg.

Since a concentration of 1.67% phosphine is far greater than the level used for pest control, there does not seem to be a significant risk of fires or explosions due to reduced pressures. This information may be of some value for improving efficacy of phosphine: the use of recirculation systems to promote rapid and uniform distribution of the gas could be effective in improving the treatment so that resistance cannot develop.

#### *Dispersal of methyl bromide around flour mills after a fumigation*

Over the years that fumigants have been used for pest control some concern has been raised about the dispersal and hazard of the residual fumigant exhausted into the atmosphere from fumigated facilities. This concern was highlighted recently in the Province of Ontario in Canada when regulatory authorities applied severe restrictions to the aeration of flour mills after fumigation. One of the main questions was whether or not the gas was moving to residential areas in concentrations above permitted threshold limits. No information was available on the levels of exhausted fumigant that might occur in the vicinity of fumigated buildings during the aeration period and patterns of dispersal of the gas were not known.

An investigation of this matter in three different flour mills showed that concentrations inside the mills dropped by 85% or more during the exposure period, even when the initial dose was supplemented by additional fumigant (Bond and Dumas 1987). Thus, only a small proportion of the original dosage remained to be exhausted into the outside atmosphere during the aeration period. Measurements of the concentrations outside one flour mill showed a maximum concentration of 27 ppm at 25 m distance in the first 5 minutes of the aeration, and 7 ppm at 20 minutes. The results obtained in these tests suggested that dispersal of the fumigant was likely to be erratic and transitory, but when treatments were carried out according to recommended procedures the risk of toxic exposure to personnel outside the mill was not great.

#### *Residues of methyl bromide in treated commodities*

The reregistration in the United States of methyl bromide as a fumigant of food commodities is dependent on the availability of information on the nature and safety of its residues. Because methyl bromide is known to have mutagenic potential the U.S. Environmental Protection Agency required data on both the presence of unchanged methyl bromide in food commodities and on products formed by reaction with methyl bromide for the reregistration process.

It is known that proteins are the major site of

methylation when commodities are treated with this fumigant. The sites of methylation in several commodities—wheat, oatmeal, peanuts, almonds, apples, oranges, maize, alfalfa and potatoes—were studied by Starratt and Bond (1989). Differences were observed in levels of the major products of *O*- and *S*-methylation (methanol, dimethyl sulphide, and methyl mercaptan) that resulted from treatment of the fumigated materials with 1N sodium hydroxide. In studies of maize and wheat, histidine was the amino acid which underwent the highest level of N-methylation.

The possibility of methyl bromide methylating DNA in foodstuffs, thereby posing a hazard to the genetic constitution of the consumer, was also studied (Starratt and Bond 1988). Methylated purines and/or pyrimidines, nucleotides, and other methylated fragments of nucleic acids might possibly be reincorporated into the DNA, potentially leading to faulty pairing of the bases and consequent mutation. The results showed that methylation of DNA occurred to a significant extent in maize and wheat, the two commodities studied. Major products identified were 7 methylguanine and 1 methyladenine, along with lesser amounts of 3 methyl cytosine and 3 methyladenine. Of the guanine residues in the DNA, 0.5–1% were methylated during treatment with 48 mg/L methyl bromide for 72 hours. The significance of these results is not completely known, but the products of the treatment are naturally occurring materials not normally associated with mutagenicity or carcinogenicity.

## Controlled Atmosphere Storage

Controlled atmosphere treatments depend for their effectiveness in controlling insects on removal of life-supporting oxygen or addition of toxic levels of carbon dioxide, or a combination of the two. The underlying mechanisms that convey effectiveness of the two processes are quite different and, to be clearly understood, they must be considered separately in laboratory experiments. However, investigation of the combined effects of the two processes is also needed, in order to assess joint action and determine total effectiveness. In practical control treatments, the levels of both oxygen and carbon dioxide are frequently changed so that toxicity may be enhanced by the combined effects of the two (Bell 1984).

## Oxygen Deficient Atmospheres

Insects can survive without oxygen or with depleted oxygen for varying lengths of time depending on species of insect, stage of development, temperature, previous history of the population, and other factors. Oxygen concentrations around 1% or less are usually recommended for control, but some species can be controlled with oxygen concentrations as high as 4% (Reichmuth 1986). Eggs of *Ephestia elutella* and *Plodia interpunctella*, and adults of *Oryzaephilus surinamensis* and *Tribolium confusum*, were controlled in 10 days at 15°C and 6 days at 20°C in 3% oxygen, and in 18 days using 4% oxygen. However, the granary weevil *Sitophilus granarius* at various stages of development required up to 41 days at 20°C and 55 days at 15°C. The pupal stage was most tolerant at both temperatures. In an atmosphere completely devoid of oxygen, the granary weevil has been shown capable of surviving for more than 4 days at 25°C (Bond 1961) and this survival rate has been extended to over 11 days when insects were selected for tolerance to anoxic conditions over a number of generations (Bond, unpublished data).

In a review of controlled atmosphere requirements, Annis (1986) has concluded that, while the majority of stored product insects are killed in 10 days with oxygen deficient atmospheres, dosage regimes should be based on the response of the pupae of *Sitophilus oryzae*. Control of this very tolerant insect would give control of other species present. He has suggested a provisional dosage regime of 0–1% oxygen for 20 days for grain temperatures of 20°–29°C.

## Carbon Dioxide Enriched Atmospheres

Since the addition of carbon dioxide (CO<sub>2</sub>) to storage atmospheres usually involves simultaneous depletion of oxygen, the toxicity of carbon dioxide to insects is frequently studied in association with some degree of oxygen deficiency. Consequently, the response of the insects may be due to both anoxia and the toxicity of carbon dioxide: oxygen deficiency may give an enhanced effect but complete anoxia may reduce or nullify the effectiveness of carbon dioxide.

Using a range of low oxygen atmospheres Krishnamurthy et al. (1986) have shown that CO<sub>2</sub>, at levels which alone would not be



effective in controlling insects, substantially reduced the length of the exposure period necessary for control. In all of the five species tested except one (*Sitophilus granarius*) mortality increased as the concentration of CO<sub>2</sub> was increased and that of oxygen decreased down to 0.5%. With *S. granarius*, adult survival in CO<sub>2</sub> declined with decreased oxygen down to 1.5% but at oxygen concentrations below 1% more insects survived. Some requirement for oxygen seems necessary for the carbon dioxide to exert its maximum effect on this insect.

Following studies of the effect of high concentrations of CO<sub>2</sub> on the Khapra beetle, *Trogoderma granarium*, Spratt et al. (1985) suggested that insects can be classified into two categories according to their response to modified atmospheres. Some insects, e.g. *Sitophilus* spp., are more susceptible to CO<sub>2</sub> in atmospheres with some oxygen, while others are more susceptible in completely anoxic atmospheres. The Khapra beetle was found to belong to the latter group and very low oxygen atmospheres gave more effective control than mixtures of CO<sub>2</sub> with higher levels of oxygen.

The data of both Reichmuth (1986) and Krishnamurthy et al. (1986) show that effectiveness of CO<sub>2</sub> is appreciably increased with reduced oxygen concentrations, at least down to the 1% level. The reversal in response shown by *Sitophilus* species, and possibly others, at very low oxygen concentrations may simply indicate that these insects have some appreciable tolerance to anoxia and that the toxic effects of CO<sub>2</sub> are dependent on some functioning of aerobic metabolic systems. Other factors such as water loss from the insects could also be involved.

From the point of view of practical application of controlled atmospheres, these investigations, plus many previous studies, are providing the biological information necessary to fully exploit these types of treatments. Although some of the information may not be directly applicable to field situations, it does provide greater understanding of the way that insects respond and the conditions that will give control. We now have a reasonable knowledge of the dynamics and potential of CA in providing effective insect control and safe food storage. The challenge for the future seems to centre mainly on the technology of establishing and maintaining controlled environments in an efficient and economical manner.

## Developments in the Technology of CA Storage

The success of the CA process is heavily dependent on the technology that is developed coincident with scientific research on toxicity. Considerable progress has been made in the past few years on the technology of both producing and maintaining modified atmospheres. A variety of methods for establishing atmospheres of nitrogen and/or carbon dioxide in sealed spaces (from pressure cylinders or tanks, by using exothermic generators, by using oxygen absorbants, or by metabolism of microorganisms) has been tested and developed. Much information on these developments has been brought together in the proceedings of the two previous conferences on CA and fumigation (Shejbal 1980; Ripp et al. 1984) and in other publications such as Banks and Sharp (1979), Banks et al. (1979), Banks and Annis (1981), and Fleurat Lessard and Le Torc'h (1986). A comprehensive assessment of sealant systems for treatment of concrete grain storage bins to permit their use with fumigants or controlled atmospheres has been compiled by Banks (1984).

Small containers for storage and shipment of 50 kg quantities of peanuts in low oxygen or CO<sub>2</sub> enriched atmospheres have also been developed and tested (Slay et al. 1982). These containers, which had a laminated plastic liner, were found to maintain integrity for several months after shipment and storage, with no sign of insect or mould contamination. An oxygen absorbing material for producing oxygen deficient atmospheres within small packages has also been tested (Ohguchi et al. 1983). With such a material inside packages the contents could be preserved for long periods without deterioration or unwanted residues.

One problem encountered with the use of carbon dioxide in concrete storages has been reaction of the gas with the concrete (carbonation). Investigation of the reaction by Banks and McCabe (1988) suggested that the risk of corrosion of reinforcing steel was low under normal conditions of grain storage at 9.5 to 13.5% moisture content. However, in well-sealed enclosures, the CO<sub>2</sub> in the atmosphere might be rapidly depleted thereby reducing its insecticidal effect and also causing substantial, possibly hazardous, pressure reductions. They recommended that carbona-

tion and associated risks be considered during the design and operation of storages built of reinforced concrete.

Research has also been carried out on the recirculation-rate requirements for adequate distribution of carbon dioxide in grain bins (Navarro et al. 1986) and on the coefficient of diffusion of carbon dioxide through samples of cereals and rapeseed (Singh et al. 1984).

Perhaps one of the most pressing needs for the CA process is the means to generate the atmosphere effectively and economically at the storage site. Recent developments in separating oxygen and nitrogen from the air by the use of hollow fibre membrane separators show great potential in this regard. With this technique, oxygen deficient atmospheres can be produced on site as required, with little or no adverse effect on the commodity and with no appreciable risk to the environment.

The technique relies on the phenomenon of selective permeation of gases through a membrane. Each gas has a characteristic rate of permeation thus permitting 'faster' gases such as oxygen to be separated from 'slower' gases such as nitrogen. Bundles of semipermeable membranes formed into tiny hollow fibres are attached to a manifold and pressurised air is applied. Oxygen permeates the fibres, leaving mainly nitrogen in the exit gas stream. The efficiency of the system in separating oxygen and nitrogen is dependent on its size and operating conditions, and on properties of the membrane. The Prism Alpha nitrogen system produced by Permea Inc. of St. Louis, Missouri, U.S.A. comes in a variety of standard sizes with product flows ranging from less than 200 SCFH (5.7 m<sup>3</sup>/h nitrogen) to over 2500 SCFH (670 m<sup>3</sup>/h nitrogen). It can operate on compressed air pressures of 80–150 psig but special systems can be designed for pressures up to 600 psig. Nitrogen product from 95–99% oxygen-free can be drawn off at the exit of the system.

The future prospects for the CA technique as a result of this and similar technological developments seem increasingly promising. Procedures that improve efficacy, facilitate application and maintenance, and promote greater economy are of great importance to the CA process. With such developments, CA will be more acceptable as an additional technique or as an alternative to the use of fumigants and other pesticides.

## Conclusions

Current trends in stored product insect pest management point to increasing emphasis on prevention and control without traditional pesticides. Public concerns with toxic chemicals in food and the environment are growing, and justifiably so, reflecting a more generally perceived need to restrict their production and use.

While fumigants are likely to be needed for many more years to come, their use must be much more carefully regulated. Manufacturers, fumigators, and government regulatory authorities and, indeed, the stored food industries that benefit from the use of fumigants, all have a great responsibility in ensuring that these materials are not misused or abused. For some situations, because of ease of application and rapid action, fumigants appear to be the only feasible means available for controlling stored product insects.

There remains, however, a pressing need for alternative control measures that do not require toxic chemicals. In the boardrooms of many food storage and processing industries, decisions are, more and more, being directed away from the use of toxic pesticides. The consumer is demanding food that is free from pesticide residues and this demand is likely to become increasingly forceful in the future. Controlled atmospheres, which have minimal adverse effects on either the commodity or the environment, have many of the features that suit current philosophies and requirements. In addition, new techniques and developments are providing expanding possibilities for increasingly efficient and economical procedures for stored products pest control and preservation. Increased emphasis on CA and the research and technology that is required to fully exploit these techniques is likely to provide great benefit to the food storage and processing industries of the future.

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# Fumigation and Controlled Atmospheres as Components of Integrated Commodity Management in the Tropics

J.E. van S. Graver\*

## *Abstract*

This paper outlines fumigation practices in central storage systems handling bagged commodities in the tropics. Problems caused by failure of whole-store treatments leading to recommendations for more extensive use of sheet fumigation are described. The requirements for successful sheet fumigation are defined in terms of final gas concentration for carbon dioxide, methyl bromide, and phosphine. Practical methods to achieve these targets using sealed stacks and improved sheet fumigation practice and alternate fumigation methods are described. The paper concludes with a short account of alternative infestation control methods and the need to integrate them into commodity storage systems as a means to ensure the continued effective use of fumigation.

IN the tropics almost all grain and other durable commodities held in central storage are stored in bags (Halliday and Calverley 1986), without the protection of admixed insecticides. If held in keeping with good storage practice, stocks are usually disinfested when they enter storage. This is usually achieved by fumigating the bags immediately before or after they are stacked. Thereafter, a combination of preventive measures, comprising both good storage hygiene and regular spray treatments with residual insecticides may be used to protect the commodity against reinfestation (Webley 1986a,b). This treatment eventually fails, because it does not provide an effective barrier to insects passing through the treated surfaces into the centre of the stacked commodity where populations can build up (Webley 1986b). Other insecticidal methods for protecting bag-stacked commodities, such as layer-by-layer treatments (Dick 1987), insecticide impregnated textile stack covers (Hayward 1984) or permanently enclosing a stack under unsealed plastic sheets (McFarlane 1980), are

more effective, but are still unable to provide complete protection against infestation. Eventually insect numbers build up to levels at which the damage that they cause is unacceptable and curative action must be taken.

Fumigation is the preferred method of infestation control in many instances, because the process is rapid and can be undertaken without moving the commodity. Fumigation is usually carried out by temporarily enclosing the stack under gas-proof sheets while the fumigant is applied using a technique known as 'sheet fumigation'.

In bag storages, this cycle of preventive, or prophylactic, treatments with insecticides followed by curative, or intervention, fumigations may be repeated a number of times whilst a commodity is stored.

Frequently, there is a need to simultaneously fumigate most or all of the stacks in a storage when these either become infested (Mathur 1986), or there is a requirement to eradicate pests subject to quarantine restrictions. Under such circumstances, whole-store fumigation offers a number of advantages over conventional 'sheet fumigation' and has consequently

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\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

attracted considerable attention. Unfortunately, the majority of storages in the tropics are unsuitable for this technique because they cannot be sealed and made sufficiently gas-tight for effective fumigation (Hayward 1984; Harnisch 1988). Despite this, whole-store fumigations have been carried out. Where the technique has been applied in poorly sealed storages over a period of time, high levels of fumigant resistance to phosphine have been reported in a number of stored product pest insects (Tyler et al. 1983).

A small but increasing quantity of grain is stored in bulk, as opposed to bag, in the central storage systems operating in the tropics (Champ and Highley 1988; Anon 1988a). A wide range of storage structures is in use for this purpose.

Airtight underground storages were successfully utilised for hermetic storage of bulk maize in Tanzania and Malawi from 1949 to 1955 (Hall et al. 1956; Pattinson 1969). Underground hermetic storages with capacities for up to 1000 tonnes of grain are still in use in Somalia (de Lima 1990; Watt 1969), the People's Republic of China (Zhu Renkang 1988) and Argentina. Semi-underground, hermetic 'Cyprus' bins are used in Kenya for long-term, bulk storage of strategic food reserves (de Lima 1980a).

Where sealable silos have been erected, the option to seal has not usually been exercised. Sealed vertical steel silos of various designs with the potential for hermetic storage have been installed in Morocco and Venezuela and in several West African francophone countries (Ransome 1960). In the Ivory Coast, a number of these are presently in use with controlled atmospheres (H.J. Banks, pers. comm.). Similar silos have been installed elsewhere in the tropics, where their potential for use either as hermetic storages or with controlled atmospheres has not been utilised. The practical difficulties of maintaining the required air-tightness in hermetic structures has led to declining interest in this method of storage in the tropics (Halliday and Calverley 1986).

There has, however, been a greater interest in the use of controlled atmospheres, e.g. in Cameroon, where Lipp silos have been used with controlled atmospheres (Fleurat-Lessard 1986). Use of controlled atmospheres has also been extended to bag storage. In Indonesia, grain held in conventional bag storages is stored under controlled atmospheres retained within well-sealed plastic enclosures (Yun C.

Nataredja and Hodges 1990) known as 'sealed stacks' (Annis 1990b). Elsewhere in Southeast Asia, sealable bag storages have been constructed specifically for use with controlled atmospheres (Muda et al. 1988; Samarasinghe et al. 1987).

When a commodity is finally removed from storage, it may again have to be disinfested to comply with international regulatory or trade requirements. This final fumigation is usually carried out in-store; though it can also be undertaken in-transit (Bond 1990; Davis 1986) for which controlled atmospheres are also used (Adamovsky and Mordkovich 1989).

## Current Fumigation Practice

The technique of fumigation under gas-proof sheeting, or 'sheet fumigation' (Burns Brown 1954), is the most widely used method for disinfesting bagged commodities stored in the tropics. The process was formerly carried out with hydrogen cyanide, but use of this gas diminished as supplies of methyl bromide became more abundant in the 1940s (Ismail bin Shamsudin et al. 1981). Phosphine, introduced widely in the 1960s, is now the most commonly used fumigant in the tropics, because of its low cost, ease of handling and effectiveness (Hayward 1984; Krishnamurthy 1973). It is normal in areas some distance from regional centres and capital cities to find that choice of fumigant is restricted to phosphine, whereas methyl bromide is used only in larger centres where the required expertise for its application is available. Phosphine tends now to be presented as the fumigant of first choice (Anon 1985; Webley 1984; Reichmuth 1988) and in some countries has totally replaced methyl bromide (Taylor 1986). One long-term consequence of this trend, both in the public and private sectors, has been an increasing use of phosphine by fumigators lacking experience of the more rigorous requirements of methyl bromide fumigation. Inexperience of the requirement for good sealing, in particular, has contributed to the substandard fumigations that have been the cause of considerable concern (GASGA 1986).

Harris (1981) and Harnisch (1988) list a number of reasons for unsatisfactory fumigations in tropical countries including:

- poor equipment;
- lack of fumigator training;

- need for management awareness;
- poor fumigation techniques;
- incorrect exposure periods;
- underdosing;
- the need to integrate pest control operations;
- poor stack preparation; and
- failure to monitor fumigant concentrations.

Substandard fumigation practices continue to occur. It is common to find fumigations where:

- sheets are simply laid flat over one another, with no attempt made to roll and seal them together;
- sheets are not sealed to the floor; and
- phosphine-generating compounds are applied directly to a commodity without the use of any form of enclosure.

While many of these problems are directly attributable to poor training and lack of management awareness, the economic pressures exerted on private fumigation contractors are also important and infrequently reported. For example, the necessity to reduce fumigant loss downwards through the floor by building stacks on a gas-proof surface, is well known (Burns Brown 1954) but often overlooked in practice. In central storages, where fumigators are frequently involved as stacks are built, there is usually an awareness of this requirement (U Hla Myint and U San Maung 1986). In the private sector, however, contract fumigators rarely view a stack before treating it, and it is not unusual to find them built on pallets laid directly onto the ground.

Those in charge of the commodity are normally reluctant to restack correctly and, in the event of a fumigator's unwillingness to undertake the work, the services of another less professional operator will be sought. Competing contractors may also attempt to recoup price cuts by reducing the dose of fumigant applied to well below the recommended dosage. Additionally, influenced by the claims of manufacturers of phosphine-generating compounds, fumigators have tended to reduce exposure periods to compete with rival products (Winks 1986a) and the speed of methyl bromide fumigations. More recently the introduction of magnesium-based phosphine-generating compounds has been accompanied by further rec-

ommendations for reduced exposure periods (private communication). These recommendations are spurious because they cannot produce a complete kill of the tolerant stages of pest insects (Winks 1986a).

Such malpractices are not only the direct cause of fumigation failures but can eventually lead to the development of fumigant tolerance in pest insects by repeated exposure to sub-lethal doses. This has already occurred where whole-store fumigations have been carried out in improperly sealed storages.

Whole-store fumigation has been seen to be simpler to implement than 'sheet fumigation' but was cumbersome when applied using methyl bromide. The advent of phosphine, with its ease of application (Hayward 1984), made it possible to use the technique in situations, where formerly it had been impractical. Whole-store fumigations have been successfully carried out with methyl bromide since 1966 in Nigeria, in cocoa storages built specifically for this purpose. However, whole-store fumigations carried out in conventional bag stores modified for this purpose have not always yielded good results (Calverley 1984a).

The technique of whole-store fumigation using phosphine has been applied over a period of years to poorly sealed godowns in Bangladesh and Pakistan. Serious fumigation failures have been reported as a result of the reduced exposure periods to lethal fumigant concentrations resulting from this malpractice (Tyler et al. 1983). The situation has been exacerbated by the development of high levels of phosphine tolerance in a number of stored product pest insects in the Indian region. However, practical strategies have been devised to retain the use of whole-store fumigation in partially sealed storages and also control these resistant strains. In very leaky storages that cannot be sealed to meet even these requirements for gas retention, 'sheet fumigation' of individual bag stacks is recommended (Friendship et al. 1986; Hafiz Ahmed et al. 1986). It is now recognised in some countries that it is impossible to undertake whole-store fumigations in existing storage structures, and that 'sheet fumigation' is the only effective method for disinfecting bag-stacks (Prachak Charoen and Ito 1986).

Similarly, in West Africa, whole-store fumigations of small 'banco' stores, of mud brick and plaster construction are not considered to have

been successful (Banks 1986a), even after repairs and sealing in an attempt to render them sufficiently gas-proof (Webley and Harris 1979). Whole-store fumigations of similar small-scale village grain stores, designed and built to be sealed have, however, performed satisfactorily (Harnisch and Krall 1986; Hayward 1984).

Some bulk storages in the tropics are now designed to permit fumigation, and the opportunity that silos offer for efficient and effective fumigation is recognised (Newman 1988; Newman 1990; Shukla and Patil 1989). Operational problems have, in some situations, made fumigation difficult to execute (Umar Khan Balouch and Asim Rahim Kazmi 1988). In some complexes where old concrete silos are in use, considerable gas loss has been observed to occur through their walls (Conway & Mohiuddin 1984). Elsewhere, silos are known to have cracked sufficiently to prevent effective fumigation. Where bunkers have been adopted, disinfestation may be carried out using phosphine (Banks and Sticka 1981) or controlled atmospheres (Jay et al. 1990).

## Requirements for Successful Fumigation

Fumigation plays a key role in the control and management of infestation in commodities stored in the tropics. It has proven to be a versatile technique and great reliance has been placed on it to underpin the success of other pest and quality control measures, particularly in countries where admixture of protectants to grains is prohibited. It is used throughout the storage system:

- as an adjunct to storage hygiene to ensure that stocks entering storage are free of infestations;
- as a curative treatment when other physical and chemical pest control measures fail to control infestations; and
- for regulatory purposes to comply with international quarantine or trade requirements.

The increased dependence on fumigation in the tropics since the introduction of phosphine has matched the increasing agricultural use of pesticides evinced in a swing away from traditional pest management techniques towards reliance on routine pesticide application (Putter 1984). Similarly in commodity storage, the

increased dependence on fumigation has led to reduced awareness both of alternative infestation control strategies and of fumigants other than phosphine.

Use of substandard fumigation techniques has led to phosphine resistance and is causing concern that further abuse of this fumigant may have a damaging long-term effect on its future availability (Winks 1986b; Bond 1990). The potential for resistant strains to be spread through international trade (Conway 1986), with the concomitant problems of controlling them, may present problems in export markets (Rassman 1988; Reichmuth 1988).

In order to ensure the continued use of fumigation in the tropics, it is essential to establish a target, or standard, for effective fumigations. Effective fumigations are those in which there is a total kill, i.e., no survivors from the original infestation. For practical purposes such fumigations can be defined in terms of the gas concentration attained at the end of the exposure period:

- for phosphine — a minimum exposure period of 7 days ending with a final gas concentration at, or above, 80 ppm (Annis 1990a). *In practice, this may involve a 10-day fumigation.*
- for methyl bromide — in normal commodity fumigations requiring exposures between 24–48 hours carried out at temperatures:
  - between 25°–29°C: a final Ct product of 150 g hours/m<sup>3</sup>
  - at or above 30°C: a final Ct product of 100 g hours/m<sup>3</sup> (AFHB/ACIAR 1989)
- for carbon dioxide — a minimum exposure period of 15 days, ending with a final gas concentration at, or above, 35% (Annis 1990b).

Prevention of resistance is an integral consideration in the continued use of fumigation in the tropics (Winks 1980), particularly as the prospects for developing new fumigants appear very poor (Banks 1987). Choice of fumigant is not limited to methyl bromide and phosphine. Both carbon dioxide (Jay 1986) and hydrogen cyanide (Banks 1987) are available, and the technology for their use well established. They should both be brought into service, along with methyl bromide, phosphine and the formates (Banks 1987), so that their advantages may be



used in alternation within storage systems as a tactic to prevent fumigant resistance (Roush 1989). Another tactic involves an extension of the requirements for effective fumigation, demanding high standards of gastightness and increased exposure periods, to control strains of insects resistant to phosphine (Winks 1986b).

Bag-stacks can be enclosed to the standards of gastightness required for effective fumigation using the sealed stack system (Annis 1990b), which at the same time provides long-term protection against reinfestation. This system, which can be sealed to the stringent requirements for disinfestation with carbon dioxide, has also been used for phosphine fumigation and can extend exposure periods for this fumigant (Annis 1990b). An added operational feature of the technique is the pressure test. This provides an accurate, practical means of predicting the outcome of a fumigation, something which remains impossible with sheet fumigation.

Effective 'sheet fumigation' of bag-stacked commodities with methyl bromide and phosphine is possible indoors, provided all measures to prevent gas loss are taken. Leakage downwards can be avoided by routinely building bag stacks on gas-proof floor sheets. Techniques for sheeting and sealing bag-stacks (Anon 1974; Stout 1983) should be rigorously implemented. Particular attention is required where sheets must be joined, for which timber laths and carpenters' 'C' clamps provide a more effective seal than rolling and clipping. When a floor sheet is used, the seal at floor level is greatly improved when this is folded over with the cover sheet and weighted down.

Loose sand, or sand snakes, are the preferred means of sealing at floor level. Where sand snakes are used, these should not be filled to more than two-thirds of their capacity, so that they can lie flat filling any depressions in the floor to make the best possible seal. Care must be taken to ensure that sand snakes are placed closely side-by-side and flattened so no gas loss can occur through gaps that might be left between them. Chains and timber baulks should not be used as these do not provide an effective seal, and can cause extensive damage to fumigation sheets.

The seal produced by these methods must be judged as inadequate by modern standards, as gas losses from enclosures of this type can still be substantial (Banks 1986b). However, gas loss can be significantly reduced by checking

for, and sealing leaks, a practice that has largely fallen into disuse with the widespread adoption of phosphine. For methyl bromide fumigations, halide detector lamps continue to provide an effective means for this purpose (Bond 1984), though a more reliable and safer electronic instrument (Riken) is now available. For phosphine fumigations, detector tubes provide a simple means for leak detection although electronic detectors are becoming available (Ducom and Bourges 1986).

Torn or holed fumigation sheets should be promptly repaired and maintained in a gas-proof state. Fumigation sheets made of PVC can be very effectively patched using glue made from PVC dissolved in methyl ethyl ketone\*. This makes a strong permanent and flexible bond (Banks 1986b), surpassing the patching usually carried out with other glues or self-adhesive insulating tapes.

The practice of using two 'leaky' sheets, one on top of the other to obtain a gas proof enclosure, should be avoided, as significant gas loss will still occur. There is the additional risk that insects finding harbourage between the sheets will survive and subsequently reinfest the commodity, with the likelihood of resistance developing.

Almost complete gas loss can occur very rapidly where sheeted stacks are exposed to wind, and every step should be taken to reduce its effects in a storage where sheet fumigation is being carried out. Stacks built outdoors are particularly at risk in this respect (Banks 1986b). In situations where excessive gas loss occurs and fumigant concentrations fall below expected values, top-up doses can be added to ensure that the correct final level is obtained (Annis 1990b; Stout 1983). Thus, to ensure the successful outcome of a sheet fumigation, it is essential that fumigant concentrations are monitored at intervals during the exposure period, and finally when it is terminated. To do this effectively, fumigators must be provided with the appropriate equipment and materials.

Effective sheet fumigation on a routine basis should always be possible — given the basic requirements for success: management awareness of the need for fumigation; good, well

\* In the People's Republic of China a glue consisting of dichloroethane and perchloroethane (4:1) is used to patch PVC sheets (Wang Han Bin & Tang Zhenjia 1986a).

maintained equipment; and well-trained fumigators. With these requirements assured, then a combination of careful attention to detail and common sense should ensure the successful outcome of a fumigation.

## **Alternative Fumigation Techniques**

Effective fumigation requires a gastight enclosure, which in bag storage is most commonly provided by temporarily enclosing bag-stacks under gas-proof sheeting whilst in storage. Alternative techniques, large- and small-scale, have been developed to permit the use of controlled atmospheres. These also offer protection against reinfestation. Elsewhere in the storage system, practical opportunities to make use of gas-tight enclosures have been recognised and applied.

### **Bag Storage in Sealed Plastic Enclosures**

This technique is compatible with existing bag storage practices and makes few extra demands of them. It provides a method for long-term storage that has the advantages of improving the efficacy of fumigation, reducing fumigant use and at the same time protecting stacks from reinfestation. It eliminates the penalty of repeated spray applications and fumigations, and the possibility of residue accumulation (Ong 1985; Anon 1986; Anon 1988b; Hayward 1984) normally associated with long-term storage. It also has strategic value by providing the means for using an 'alternative' fumigant, i.e. carbon dioxide, when the need arises: for example, either when there is a requirement for a residue-free treatment, or to eliminate fumigant resistant insect strains. Furthermore it can be integrated into existing commodity management systems (Annis and van S. Graver 1987).

In Australia, the technique has been adopted for storing groundnut seed, providing protection against infestation and moisture uptake (M. Read, pers. comm.) and in Indonesia it is used by BULOG as one of a range of storage options (Conway et al. 1990; Yun C. Nataredja and Hodges 1990). In the People's Republic of China, PVC membranes are likewise used with controlled or hermetic atmospheres to store rice (Wang Han Bin and Tang Zhenjia 1986a); while in Pakistan a simple sealed polyethylene enclousure

has been used with phosphine for long-term storage of wheat (Hafiz Ahmed et al. 1986). A variation of the standard sheet fumigation technique, using multiple applications of hydrogen cyanide to 'permanently' sheeted stacks, has been applied for long-term storage of bag-stacked polished rice in the United States of America (Tilton 1961). On a smaller scale, Volcani Cubes can also be used for indoor storage (Navarro and Donahaye 1990).

### **Whole-Store Fumigation**

This technique has a number of advantages: it is simpler than sheet fumigation, particularly where stores can be sealed; it maximises the space available in a bag-storage by permitting an increase in stack size and allows stacks to be built around obstructions that otherwise prevent sheet fumigation; it eliminates the expense of gas-proof sheeting; and, in well-sealed stores, it prevents reinfestation. In well-sealed (Banks and Annis 1980), or purpose-built storages the technique has performed well (Green 1987), but it is not recommended for storages that cannot be sealed. In situations where there is no alternative means of disinfestation and the technique must be implemented, it is essential that insects are exposed to lethal levels of fumigant throughout the required exposure period. This may be achieved by a multiple-dosing treatment that accepts a degree of gas loss from these poorly sealed storages and compensates for it by the addition of extra fumigant at two- to three-day intervals (Friendship et al. 1986; Wang Han Bin and Tang Zhenjia 1986b).

### **Hermetic Storages**

When dry, lightly infested grain is hermetically stored, infestation control may be a lengthy process. Under such circumstances very small doses of fumigant have been used to hasten the rate of insect control achieved by oxygen depletion (de Lima 1984). Similar results can be obtained with bagged grain stored in flexible silos (Kenneford and O'Dowd 1981).

### **In-Transit Fumigation**

Barges, lighters and ocean-going vessels have been used as fumigation enclosures (Bond 1990; Davis 1986; Prachak Charoen and Ito 1986). Despite concern about the safety aspects

of the technique (Snelson and Winks 1981), in-transit fumigation continues to be practiced. In Thailand, a recirculatory system for in-transit fumigation of grain with phosphine, as described by Leesch et al. (1986), is currently used for grain exported in bulk carriers (R.P. Sririrak, pers. comm.). Recent developments in fumigation technology (Winks 1990) may find application to greatly improve the safety aspects and efficacy of in-transit shipboard fumigations.

Carbon-dioxide-rich controlled atmospheres have been applied for in-transit disinfestation of commodities in barges (Jay et al. 1990) and in standard ISO shipping containers (Banks 1988). In Australia the technique is used to export groundnuts to Japan and New Zealand with considerable cost savings over the standard fumigation treatment. Controlled atmospheres have also been used to disinfest commodities in LASH barges (Banks 1979) and bulk carriers (Adamovsky and Mordkovich 1989).

### **Bag Liners**

Polyethylene bags placed as liners inside woven jute or polypropylene bags provide a gastight enclosure, making it possible to fumigate the contents of individual bags and also providing a physical barrier against reinfestation (Proctor and Ashman 1972). Groundnuts have been stored safely in such lined bags without moisture migration for up to three months. The system has application for a number of commodities, particularly those of high value, e.g. well-dried cocoa (Prado et al. 1988). Similarly, 'Joseph Sacks' (Anon 1988c) made of sealable laminated plastic can be used for this purpose.

### **Fumigation Tents**

There is frequently a need to undertake small-scale fumigations for which sheets, on account of their size, are inappropriate. Portable fumigation enclosures, such as the the Rentokil Bubble (Smith 1990) and the Volcani Cube (Navarro and Donahaye 1990), are effective for this purpose.

An application in storage practice is disinfestation of used bags, pallets, and spillage recovered during the course of storage hygiene. All provide a source of reinfestation that is frequently overlooked.

## **Alternatives to Fumigation**

The relative ease with which fumigation can now be undertaken has in many places led to a reduced awareness of the alternatives. The need to delay the development of fumigant resistance by avoiding unnecessary fumigant use, combined with concern about residues in commodities exported from the tropics (Anon 1986; Anon 1988b; Hayward 1984), make it important to recognise and utilise alternatives to fumigation.

### **Hygiene**

A well-managed program of storage hygiene can do much to reduce infestation levels using the simplest of tools — the brush and the shovel. Storage hygiene provides the foundation for the success of all other infestation control procedures because it reduces the possibility of uninfested commodities being infested 1. by contact with other infested commodity or 2. by migration of insect pests. Hygiene should be rigorously monitored by regular inspection and effective stock control. Lack of hygiene can result in strong selection for resistance caused by reinfestation leading to the necessity for repeated refumigation at short intervals.

Storage hygiene is pivotal to the implementation of integrated commodity management. Inspection, as commodities are first taken into a storage, provides the basic information upon which action thresholds and infestation control options are selected: grain variety, moisture content, presence or absence of infestation, dockage, degree of processing, end use, value and duration of storage. With these factors established and constantly monitored, control options can be selected, timed for maximum efficiency and changed to suit circumstances.

Stock control based on the principle of first-in/first-out can, on its own, be a very effective infestation control method. In Papua New Guinea, bagged rice is largely imported from Australia. The organisation handling the supply and distribution of this commodity has, by means of very efficient stock control, virtually eliminated the need for fumigation from its operations and is still able to deliver a high quality product to the market. A key component of this strategy has been maintenance of rigorously high standards of hygiene from source of supply to wholesale outlet.

## Drying

The most important factor determining the storability of a commodity in the tropics is its moisture content. Drying is not only the best preventive measure to counter infestation but also a good control measure. The moisture content of a commodity also affects other control measures: thus the biological activity of protectant insecticides may be affected by commodity moisture content (Samson and Parker 1986) and, in varieties of cowpeas resistant to insect infestation, it has been shown that resistance decreases as moisture content increases (Anon 1988d).

Provided bag-stacks are built on pallets, natural ventilation will remove a considerable amount of moisture. Various drying processes involving special stacking procedures are well known. Nevertheless, neither these nor traditional sun drying methods are sufficiently reliable, or convenient, to handle wet-season grain harvests (Acasio 1982). Using existing mechanical drying facilities, effective strategies have been developed to rapidly dry such grain to levels at which they can be safely stored (Adamczak et al. 1987; Driscoll 1987).

## Hermetic Storage and Controlled Atmospheres

Large-scale hermetic stores provide a low energy means for long-term pesticide-free storage of bulk grain. Operational losses have been lower than those normally encountered in conventional bag storage (de Lima 1980a). Effective stock rotation is possible by integrating the operations of a bag-storage with those of a hermetic storage system (de Lima 1980b).

Controlled atmospheres provide a very effective means of storing commodities to provide a residue-free product acceptable to overseas markets and discriminating domestic markets in the tropics. Controlled atmospheres have application both in bag and bulk storage. In West Africa, controlled atmospheres are in use for bulk storage of cocoa, coffee, and paddy in silos (H.J. Banks, pers. comm.).

Despite the more stringent technical and management requirements for this form of storage (Calverley 1984b), it is being adopted for bag storage in the tropics (Samarasinghe et al. 1987). These storages, being well-sealed, may also be used with conventional fumigants, thereby allowing alternation of fumigants, and

can meet the fumigation requirements of differing commodities.

Controlled atmospheres have applications on a smaller scale. In India, cashew nuts are packed in controlled atmospheres contained in airtight 20 L tins. This application ensures that the commodity is infestation free, and prevents quality deterioration while providing a robust container suitable for export trade.

## Insecticides

For bagged commodities prophylactic use of grain protectant insecticides (Bengston 1986) is commonly the only practical alternative to fumigation. They may be applied as fabric treatments, space sprays or to the bag-stack as surface sprays (Webley 1986a,b). Such treatments will reduce, but not eliminate infestations and it is essential to combine them with rigorous hygiene measures to keep insect numbers low. In the Sahel, long-term protection of bagged grain has been achieved by covering stacks with insecticide-impregnated cotton sheets. This technique has reduced insecticide usage to about 25% of that required for conventional treatments (Hayward 1984).

Insecticides are relatively cheap and recent work has established application rates for admixture that are applicable to the moisture contents at which grains are stored in the tropics (Bengston 1988; Samson and Parker 1989; Samson et al. 1988). In bulk storage situations, the option to admix protectants is available as a first treatment that can be integrated with fumigation or use of controlled atmospheres where sealed storages are available. In bag storage systems, the option of admixing protectants is restricted to the time when a commodity is first bagged, as failure can result if protectants are admixed when infestation levels are high. A method to integrate insecticide admixture and sealed storage of bagged commodities has been proposed as a means to extend the use of bag storage (Annis and van S. Graver 1987).

## Processing

A commodity's storability can be altered by processing it. Some commodities in their raw state are more resistant to infestation, or less susceptible to change in quality. However, this advantage is gained at the expense of an increased requirement for storage space, thus:

coffee may be stored in parchment, which is less likely to suffer change in quality — an advantage in remote areas where transport is unreliable; groundnuts may be stored in-pod with protection against most of the insects that attack unprotected groundnut kernels; and rice may be stored as paddy (Haines 1982a).

In general, the products of milling a commodity, e.g. grits, flour, etc. are more susceptible to infestation. An exception is rice: well polished, milled rice, as a whole grain, is less susceptible to infestation (McFarlane 1978).

### **No Control Implemented**

The option to exercise no control methods (other than hygiene) may be selected with a knowledge of the end use of a commodity, the desired quality standard, remaining duration of storage and the potential for cross infestation. Thus, some commodities can be disinfested during further processing, e.g. paddy to polished or parboiled rice, or whole grains to flour, or where established levels of infestation may be acceptable for stock feeds. Similarly, in situations where the expected duration of storage is short, no control measures may be deemed necessary. In some circumstances, natural occurrences of predatory insects may effect adequate control that may be recognised and utilised.

Absence of infestation control may be enforced by market prices that make it uneconomic. In the South Pacific islands, for example, copra may be stored unprotected for long periods, during which time it becomes heavily infested and presents a major source of infestation for both imported and exported commodities.

### **Conclusion**

There has been a tendency in most postharvest systems towards major dependence on a small number of disinfestation procedures (Haines 1982b). In this respect, extensive reliance has been placed on fumigation following the introduction and widespread adoption of phosphine. The development of resistance to this fumigant (Champ and Dyte 1976; Tyler et al. 1983) has, however, led to concern about its continued availability (GASGA 1986). It has therefore become important to ensure that fumigation is used to maximum effect, in order to prevent the spread of resistance in the tropics and preserve its key role in commodity storage.

Integration of fumigation into a commodity management system (Evans and van S.Graver 1987) is based on applying knowledge of the interactions (de Lima 1987; Heselhurst et al. 1987) that affect the manner by which a commodity is stored. Application of this information will differ from storage to storage within a system, from commodity to commodity and according to end-use. At the national level, there can be interaction between different commodity storage systems, which may be complicated when high- and low-value commodities, with conflicting infestation control standards, are produced as part of the same farming system, e.g., cocoa and copra. Many commodities grown and stored in the tropics are exported, and further interactions at the international trade level must be taken into consideration when formulating infestation control programs.

The development of practical techniques for applying controlled atmospheres to bagged commodities provides an alternate gaseous disinfestation technique which, combined with higher standards of gastightness, offers a means for continued and efficient use of conventional fumigants. Opportunities to make effective use of fumigants and controlled atmospheres within commodity storage systems must be recognised and utilised.

Alternate control measures, or actions to supplement the efficiency of gaseous treatments, should be utilised particularly where they offer greater chances of success. These may even involve management decisions to relocate and centralise storages to maximise the impact of climate, logistics, etc. on infestation control measures (McFarlane 1988).

Adoption of good fumigation practice is dependent on the relevant technology being available so that it can be used effectively. Government policy, in the form of regulations to enforce quality standards in commodity exports or plant quarantine criteria on imports, is an incentive towards the goal of good fumigation practice (Horrihan 1987). Enforcement of both domestic and international regulations can improve fumigation practice to ensure their successful outcome.

In the ASEAN region, action has been taken to develop a workable code of practice for fumigation (AFHB/ACIAR 1989), aimed at ensuring that all fumigations carried out within the region attain at least a minimum standard for success—a complete kill of all insects

present. Implementation of the code throughout the region is intended to prevent the development and spread of resistance and may permit fumigators to refuse to carry out fumigations under substandard conditions. For successful implementation, such a code must be supported by enforceable legislation to ensure management awareness and cooperation, and registration of trained fumigators. For example, domestic phytosanitary regulations may be invoked to prevent the spread of pests through domestic and international trade, e.g. The Plant Protection - Control of *Prostephanus truncatus* Rules 1986 in Tanzania (McFarlane 1988).

International regulations can also affect the conduct of fumigation in the tropics. Some countries that import commodities enforce strict domestic quarantine regulations requiring all infestable imported goods to be fumigated to specified standards before export. Failure to comply with these standards can involve costly refumigation at the ports of destination. International fumigation contractors are now responding to these problems by enforcing high standards in their overseas operations (Bert Prinsen, pers. comm.). Concern about the problems that might be caused by the introduction of fumigant-resistant strains of insects on imported commodities has prompted calls for stricter implementation of quarantine regulations in some European countries (Rassman 1988; Reichmuth 1988).

The successful outcome of a fumigation is dependent upon the knowledge and skill of the personnel undertaking this work. Fumigation should be carried out only by well-trained fumigators who are fully aware of its objectives — and any impediments to its successful outcome. Training should be relevant to the practical applications of fumigation and involve the transfer of as much 'proven experience' as possible.

The lessons of training must be supported by regular supervision to ensure that the standards required for effective fumigations are maintained.

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# Report on Session 1: Background to Current Use of Fumigation/CA Technology

Chairman: Dr C.H. Bell, Ministry of Agriculture, Fisheries and Food, U.K.

Rapporteur: Dr R.P. Garcia, University of the Philippines, Los Baños

THE three papers of this opening session summarised the use of fumigation and controlled atmosphere procedures round the world, and discussed their advantages and disadvantages.

The first paper, by Mr P.C. Annis of the CSIRO Division of Entomology, Canberra, stressed that with fumigation and controlled atmosphere treatments there is a need to kill all stages of all target organisms. Both types of treatment can control pest insects and rodents effectively but only if used correctly. Good insect control leads to the preservation of a wide range of grain qualities.

A number of published research reports were cited to compare and contrast how fumigation and controlled atmospheres had been used under a variety of conditions in various storage structures. It was apparent that widely different structures and enclosures could be used for successful treatments if an appropriate level of sealing could be obtained. This level depended on the methods of gas application and distribution chosen. Most existing storage structures are not airtight and hence procedures need to be modified to avoid failures. Currently, research is underway into methods of continuous gas flow that may extend, under carefully controlled conditions, the number of enclosures that can be successfully used for gaseous treatments. It was recognised that unless all known impediments to achieving of uniform distribution within the bulk have been eliminated, some enclosures cannot hold gas for long enough to get 100% kill with a high degree of reliability, in spite of having made all reasonable efforts to seal them and having chosen the correct dose and application method for gassing.

For modified atmosphere (MA) and phosphine the length of exposure is critical. In a leaky structure, there is no point in merely increasing the dose applied. Even with repeated application the chance of success is poor. The duration of exposure is very much dependent on temperature. In warm climates, 10 days are required to guarantee control by phosphine of all insect pests so far tested and 14–15 days for controlled atmospheres.

A question was raised on the humidity limit necessary for sealed storages. It was stressed that the water activity of the commodity under the sheet should not exceed the level promoting mould growth (0.65–0.7) and that this also applied to unsheeted commodities.

The second paper was given by Dr E.J. Bond of Agriculture Canada. He highlighted some new developments in MA technology and problems arising from the use and misuse of fumigants, including the current need for the fumigant methyl bromide to be re-registered by the United States Environmental Protection Agency. He noted a marked increase in the use of MA techniques for pest control. Such uses followed similar principles and procedures to those used in fumigation for many years. In the past, MA technology has been hampered by cost.

Some recent developments in MA technology, including the use of new generating

devices, sealing materials and methods were described, and the need for new information and development was identified for MA toxicity to insects, in the light of the long survival times in low oxygen atmospheres and the possibility of resistance. Also required was further information on the sorption of  $\text{CO}_2$  by concrete.

Public awareness of the potentially adverse effects on non-target organisms and the environment of the use of fumigants was increasing but was being biased by sensational media reporting, resulting in pressure being brought to bear from legislative sources to limit the chemicals available for use. Some recent research on the effect of methyl bromide on DNA was described indicating that methylation of nitrogen but not oxygen sites occurred. Further residue data for a wider range of commodities was also presented.

Use, misuse, and abuse of fumigation as a control measure has led to problems in pest resistance and public alarm, and current research was thus closely geared towards improving safety and efficacy. One aspect highlighted was the need for information in the right language for the country concerned where fumigants and pesticides were made available for use by handlers in developing countries. Another aspect which was the subject of discussion at question time was the effect of reduced pressure—such as may occur when gas is distributed by fan-powered ventilation—on the flammability limit for phosphine.

Dr Bond concluded by acknowledging that it was what the consumer demands that is likely to determine the future in the field of control by chemicals or gases.

The third paper by Mr J. van S. Graver of CSIRO, Canberra, concentrated on the role of fumigation and controlled atmospheres in the tropics. Fumigation was identified as currently the most important single means of controlling an infestation. Use of phosphine had extended from treatment of individual bags to whole stores but now, because of resistance problems arising from poor practice in whole store treatments, there was a return to the treatment of bags, particularly in sheeted stacks. The pressing need for education, both of handlers and managers, is apparent if the more successful sheeted bag stack technique is to be practised more widely and the incidence of failure reduced.

Some further points were emphasised. As dosages are temperature dependent for phosphine treatments, measurements needed to be made of the commodity temperature at an appropriate position and time of day to determine the exposure required. It was also recognised that the length of exposure for control was species dependent.

The need for gas concentration measurements at the end of exposures was emphasised and attention was focussed on the need for suitable, cheap equipment for gas sampling in developing countries, such as the potassium hydroxide absorption kit for  $\text{CO}_2$  and electrochemical cells for phosphine.

Finally it was recognised that the status of and progress in fumigation control and technology in developing countries is determined by social and political issues rather than by technical ones and that the implementation of new technology is always controlled by market forces.

# **Biological Responses to Treatment with Gases**

# Toxic Gas Treatment Responses of Insect Pests of Stored Products and Impact on the Environment

Ch. Reichmuth\*

## *Abstract*

Both preventative and curative processes are used in integrated pest management of stored product pests. Use of toxic gases (fumigants) may be a final measure. The chemicals used must have particular qualities to make them suitable as fumigants, viz.:

- toxicity to the target pest
- high diffusion and penetration potential
- little reaction with treated produce
- harmless metabolites
- easy to handle
- easily detectable
- chemically unstable in the atmosphere
- harmless to the environment.

On the basis of this list, it is easy to conclude that only a few substances meet these requirements. Phosphine, methyl bromide, and hydrogen cyanide are the only fumigants remaining in widespread use in stored product pest control. The inert gases nitrogen and carbon dioxide are beginning to replace the toxic fumigants, particularly where storages to be treated are gas-tight or can economically be made so, and the length of the exposure period is not a limiting factor.

This paper discusses and compares the toxicity of these gases to various insects. Mode of action and occurrence of resistant strains are covered. Emphasis is placed on the environmental impact of these chemicals and possible risks to human health. New developments in fumigation techniques are discussed.

KEY activities in protecting stored products from insect pests are:

- creation of a pest and weatherproof enclosure for the product;
- monitoring the quality of the stored product, including detection of any pest infestation; and
- where pests are detected, employing appropriate methods of controlling their populations.

Commodities are sometimes disinfested before being placed in storage.

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\* Institute for Stored Products Protection, Federal Biological Research Centre for Agriculture and Forestry, Koenigin Luise Strasse 19, D-1000 Berlin 33, Federal Republic of Germany.

The use of toxic gases, smokes, and vapours to control pests, especially insects, in stored agricultural products has a very long history. These chemical substances have a common ability to penetrate and distribute themselves through the products being treated.

Other types of chemicals, such as contact insecticides, have to be mechanically mixed with the product and their use is thus inconvenient or impractical. Moreover, treatment of products with residue-producing protectants before they are stored, although widely practiced is, for health and environmental reasons, becoming less acceptable to consumers.

Gases used as fumigants should have the following attributes:

- they are toxic to the target pests over short exposure periods
- they consist of small molecules with great potential to diffuse throughout the product to wherever pests may be located
- they leave insignificant or tolerable amounts of residues or metabolites in treated goods following ventilation
- they are easy to handle
- their presence is easy to detect, and concentrations can be readily monitored by fumigation personnel
- they are chemically unstable in the atmosphere after aeration
- they decompose into compounds harmless to the environment.

Gases meeting all these requirements are scarce and, due to the high standards of safety demanded, only a few chemicals are currently available for application as fumigants for pest control.

## Hydrogen cyanide (HCN)

Hydrogen cyanide is renowned for its high toxicity, especially to mammals. It is still used for rodent control in ships, mills, and other food- and feed- processing factories. In the past, HCN has been used to treat citrus trees for control of scale insects and was also used for stored product insect pest control. However, the following serious disadvantages have led to preference being given to other compounds:

- high toxicity to humans
- high solubility in water, a problem in treatment of materials stored in damp cellars and of products with high moisture content
- arthropods displaying a protective stupefaction mechanism, which can result in their surviving treatment with the gas.

Peters and Ganter (1935) examined the mortality of adult *Sitophilus granarius* after treatment with HCN over a concentration range of 3.5–30 g/m<sup>3</sup> of HCN at temperatures of 17° and 35°C (Fig.1). The experiments included constant concentrations during treatment as well as variable concentrations, the latter, due to evaporation and diffusion (increasing concentration) and leakage and sorption (decreasing concentration), being characteristic of practical fumigations. Comparing all mortality results from the

experiments with constant concentrations with those from varying concentrations showed clearly the applicability of Haber's rule to all dose mortality data.

Haber (1924; page 92) stated that for toxic gases the product of the amount of inhaled gas and the time during which an animal is inhaling the toxic air-gas mixture gives a good basis on which to assess the comparative toxicities of different fumigants. The rule itself states that, for a certain level of mortality, the product of the concentration and the exposure time is a constant. Peters and Ganter (1935) defined

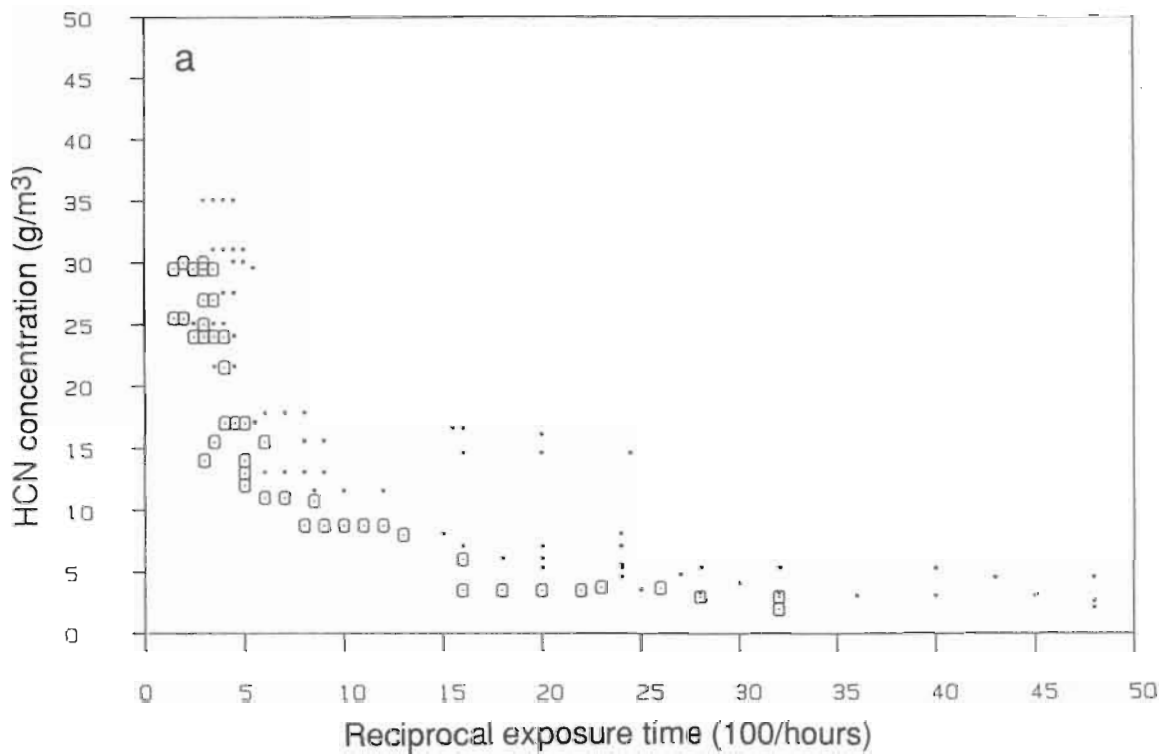
$$W = C \times t \quad (1)$$

where  $W$  is the coefficient of efficacy (now known as the  $Ct$  product),  $c$  is the concentration of HCN in g/m<sup>3</sup>, and  $t$  is the time in hours.

When plotting concentration versus time (Fig. 1), and marking the corresponding value that indicated 100% control and less than 100% control, they found that a hyperbola was formed between these two sets of points. At high temperatures the insects were more susceptible. The  $Ct$  product for complete kill at 35°C (between 20–30 g.hours/m<sup>3</sup>), that at 25°C (about 60 g.hours/m<sup>3</sup>), and that at 17°C (between 90 and 100 g.hours/m<sup>3</sup>) showed a proportion of 1:2:3. Experiments at 0°C led, unexpectedly, to almost the same results as those at 17°C. Indeed, the  $Ct$  product was slightly reduced at 0°C. The possibility of protective stupefaction in this context was not deemed by Peters and Ganter to be sufficiently manifested. The cold as such did not have any pronounced influence, because weevils exposed at 0°C for 6 days without HCN were immobilised but showed no ill effects after removal from the low temperature. Experiments with changing concentrations had maxima of 12 g HCN/m<sup>3</sup> and 5 g HCN/m<sup>3</sup>, respectively, and were combined with corresponding high or low concentration decay rates. Mortality rates closely approximated the  $Ct$  model when the integral of the concentration with time was used instead of the  $Ct$  product. The conclusion was, that Haber's rule described the dose-mortality relationship for adult *S. granarius* treated with HCN.

This result seems to contradict the results of Lindgren (1938), Pratt et al. (1931), and Gray and Kirkpatrick (1929). These authors described the occurrence of protective stupefaction for





**Fig. 1.** Mortality of adult *Sitophilus granarius* after exposure to HCN at 17°C (● 100% mortality; ○ less than 100% mortality): (a – above) concentration of HCN in g/m<sup>3</sup> versus time in hours; (b – next page) concentration of HCN in g/m<sup>3</sup> versus reciprocal time in 100/hours (data of Peters and Ganter 1935).

As expected from Haber's rule a clear hyperbola can be drawn in Figure 1(a) between the two groups of data for 100% and less than 100% mortality.

Because the hyperbola can be given in the form

$$Y = K \cdot 1/x,$$

the inverse function must be a line:

$$y = k \cdot z; \text{ with } z = 1/x \text{ and the slope } s = k.$$

Applied to the data of Peters and Ganter it follows that:

$$C = k \cdot 1/t = k \cdot z.$$

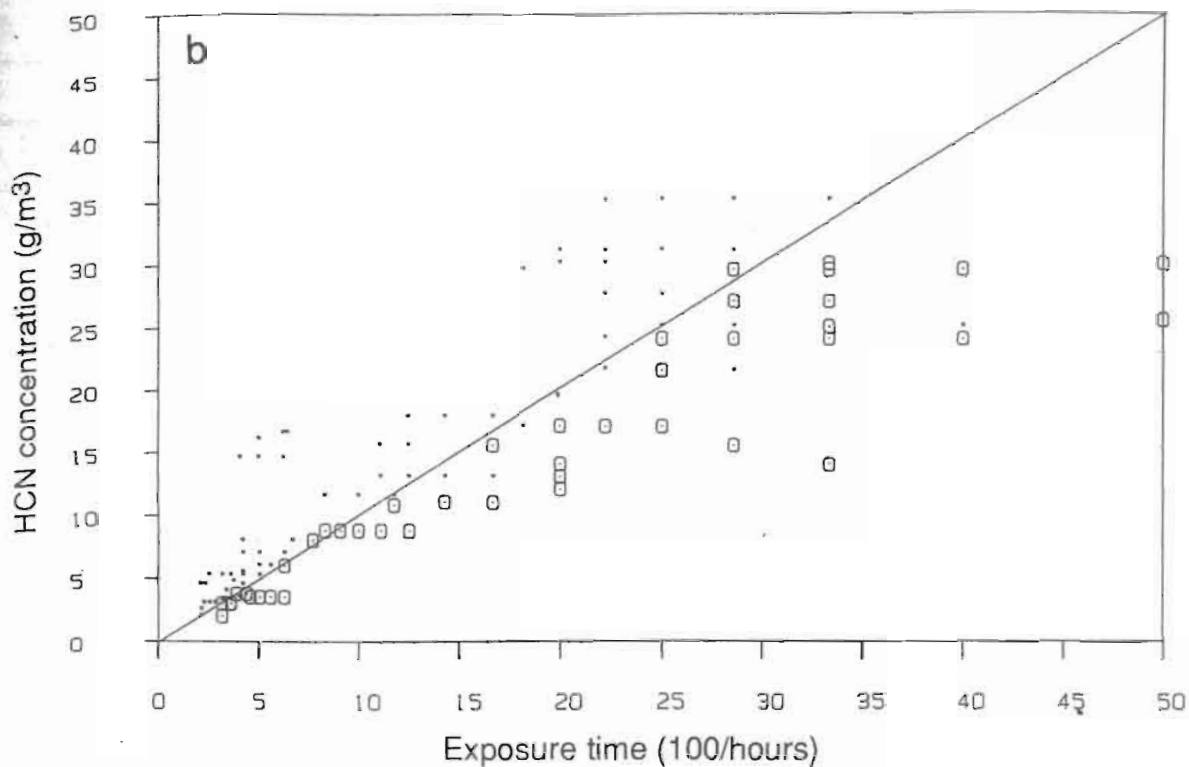
In Figure 1(b) the data are plotted in this reciprocal form. The result is a closely fitting line: between the two groups of data. The line is extrapolated to facilitate calculation of its slope which contains the Ct product for 100% mortality. As can readily be seen the slope is unity, multiplied by 100, which is the transformation factor of the time axis. The slope  $s$  follows as:

$$s = 100 \text{ g.hours/m}^3.$$

This is about the value of the Ct product derived by Peters and Ganter from their data.

some important arthropod pests including scale insects and *S. granarius*. The explanation is that the tolerance is increased when the insects are first stupefied with a fairly low dose approximately one hour before actual fumigation takes place. These parameters were used by Lindgren (1938), Pratt et al. (1931), and Gray and Kirkpatrick (1929), and were markedly different from the experimental conditions of Peters and Ganter. Bond (1963) described the important role of oxygen in the

toxicity of hydrogen cyanide. Exclusion of oxygen from adult *S. granarius* prior to fumigation (48 hours fumigation to achieve LD<sub>50</sub>, mortality count after 5 days, temperature not given) increased their susceptibility by a factor of 20. Price (1985, 1986b) discussed broadly the known facts and theories concerning the mode of action of fumigants. He suggested that the action of HCN is not merely a matter of respiratory inhibition, since the gas has an influence in the absence of oxygen.



### Resistance to Hydrogen Cyanide

Resistance of insects to hydrogen cyanide has been discussed by Lindgren and Vincent (1965) and Bond (1984). The level of resistance reported is no more than a factor of 3. It should not be confused with protective stupefaction.

### Methyl bromide

Haber's rule holds for methyl bromide over a wide range of temperatures, concentrations, and exposure periods. This, combined with the high specific toxicity, makes the gas a favourite candidate for pest control. It is relatively convenient and safe to handle. Limitations are:

- its boiling point of 4°C and condensation problems;
- a tendency to build up residues, especially in products with high fat content; and, last but not least,
- the suspicion that it is carcinogenic.

If the last limitation proves to be unfounded, methyl bromide will continue to be one of the most widely used fumigants. This seems unlikely, however, when all other halogenated hydrocarbon fumigants are currently banned because of health risks. It may remain useful and acceptable for disinfesting empty stores if

the gas can be removed from the effluent air during ventilation after fumigation is complete.

In a recent paper, Bell (1988) gave the results of studies on minimum lethal concentrations of methyl bromide below which Haber's rule no longer applies. In the temperature range 15–25°C the efficacy threshold was found to lie between 0.5 and 4 g/m<sup>3</sup> for adults of 12 strains of stored-product beetles. At both temperatures, strains of *Tribolium castaneum* and *T. confusum* were more tolerant than strains of *Oryzaephilus surinamensis*, *Rhyzopertha dominica*, *Sitophilus granarius*, and *S. zeamais*. An increase in temperature from 15° to 20°C consistently almost doubled the efficacy threshold concentration levels. Bell indicated that further work is needed to determine minimum effective concentration levels. If flow-through methods for phosphine fumigation, such as those proposed by Winks (1986), are adapted to methyl bromide application it would be interesting to focus on the effective concentrations for 2–4 week exposures even though these concentrations lie outside the range of Haber's rule. Bell's work does not include methyl bromide concentrations of more than 4 g/m<sup>3</sup>. Clearly, these concentrations have to be investigated, because of the variable concentrations characteristic of field fumigations (Fig. 1). For those concentrations above the efficacy threshold level, the mortal-

ity can be calculated by using the integral of the concentration versus time characteristic. However, the minimum lethal concentration, below which Haber's rule no longer applies, has to be determined in advance.

Howe and Hole (1966), working with *Sitophilus granarius*, found the early pupa to be the developmental stage of this species most tolerant to methyl bromide at 25°C, using concentrations of 3–9 g/m<sup>3</sup>. It was estimated that *Ct* products of more than 50 g.hours/m<sup>3</sup> were needed to kill 99.9% of a population of *S. granarius* at 25°C. Fumigation leads to delay in emergence. Fortunately, if the lethal response to methyl bromide fumigation is extrapolated from experiments with low concentrations to those with high concentrations the amount of gas actually needed is less than calculated. The corresponding probit lines are curved, leading to overestimation of the dose required (Howe and Hole 1967). Thus, 52.5 g.hours/m<sup>3</sup> (10 g/m<sup>3</sup>) gave total kill of developing *S. granarius* at 25°C, in contrast to the 75 g.hours/m<sup>3</sup> estimated. Furthermore, the survivors of sub-lethal treatments were short-lived and infertile when the dose was close to 100% effective.

Since gas is always lost by leakage and/or absorption by the product treated, the dosage must be increased to allow for these losses. Because it is possible to meter gas concentration during a fumigation, it is feasible to add fumigant if low values are found (Howe and Hole 1967). In addition, a check for gastightness should be part of the pre-fumigation routine.

### Resistance to Methyl Bromide

Using a methyl bromide concentration of 4 g/m<sup>3</sup>, Hole (1981) found many field strains of stored product Coleoptera from all over the world to be about twice as tolerant as laboratory strains. This is in accordance with results of the FAO survey by Champ and Dyte (1976), and of Monro and Upitis (1956) who selected for resistance in the laboratory. Monro et al. (1961) subsequently reported that this artificially induced tolerance was retained for at least 23 generations after cessation of exposure to the fumigant and so could be defined as resistance. This high tolerance could be transferred to hybrids by crossing resistant and susceptible strains.

## Phosphine

Phosphine is currently the most widely used fumigant in stored product protection. Its chemical properties and use are described elsewhere (Fluck 1973; Bond 1984; Reichmuth 1988). Phosphine fulfills many of the requirements of a fumigant for pest control, but has some disadvantages, viz:

- exposure times are relatively long
- it has a high specific toxicity for mammals
- it corrodes various metals
- high levels of resistance are prevalent due to poor fumigation practices.

Phosphine's advantages explain its widespread use:

- formulations of metal phosphides are safe and easy to handle
- the gas may be associated with a strong warning smell (sometimes masked!)
- it is efficacious at very low concentrations
- it leaves low levels of residues
- it is metabolised rapidly, leaving harmless metabolites
- if properly applied, it has no deleterious effect on the environment.

Bell et al. (1985) gave the following *Ct* products for 100% kill of *Trogoderma granarium* including the very tolerant diapausing larvae and young eggs: 75 g.hours/m<sup>3</sup> (8 days exposure), 100–200 g.hours/m<sup>3</sup> (6 days exposure) at 15°C; 0.7–1.4 g.hours/m<sup>3</sup> at 20 °C; and 45 g.hours/m<sup>3</sup> for 2 days exposure at 25°C. Winks (1982, 1984, 1986) exhaustively investigated the toxicity of phosphine to adults of *Tribolium castaneum* at 25°C and 70% R.H. A *Ct* relationship:

$$C^{0.9} \cdot t = W \quad (2)$$

provided a good description of toxicity. The beetles became narcotised and were partially protected from the effects of phosphine at concentrations greater than 0.5 mg.hours/L. Narcosis was defined as a state of immobility.\*

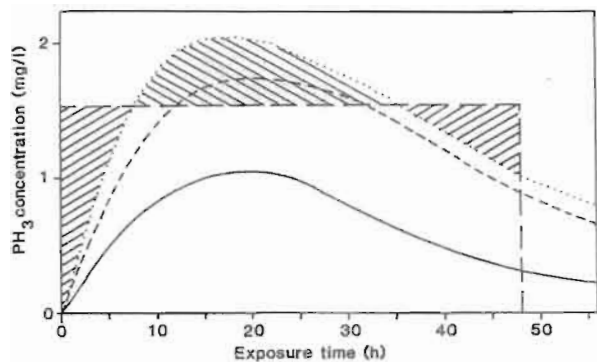
Reichmuth (1985) compared the *Ct* products required to achieve a specified mortality of

\*In populations exposed to concentrations producing narcosis, it is the insects that are not immobilised that are likely to survive. Narcotised insects usually succumb. Eds.

adult *S. granarius* after exposure to constant concentrations with those of exposure to increasing and decreasing concentrations. With phosphine, in contrast to hydrogen cyanide (Peters and Ganter 1935), Haber's rule did not apply to both types of experimental conditions (Figs 2 and 3). The values of the integrals over concentration/time curves leading to the same mortality were much greater in the case of changing compared with fixed concentrations. The difference was by a factor of about 20. The same difference in response applied also to immature stages of *S. granarius* (Reichmuth 1986). In general terms it can be concluded that increasing the concentration of phosphine does not increase the mortality by nearly as much as would be expected. This has often been observed (e.g. Bell 1986). Equation (2), given earlier and used by Winks (1984, 1986), shows clearly that exposure time is the more important parameter in achieving a specified insect mortality. In logarithmic scales for both axes, the influence of the exponent can be judged from the slope of the graph  $\log t$  versus  $C$  (Winks 1984):

$$\log t = -W - 0.9 \log C \text{ (i.e. slope} = -0.9) \quad (3)$$

Increasing steepness of the slope of the graph expresses growing influence of the exposure period. Equation (3) applies only to the linear part of the probit plane and not to the concentration/time area, which is defined to be 'the

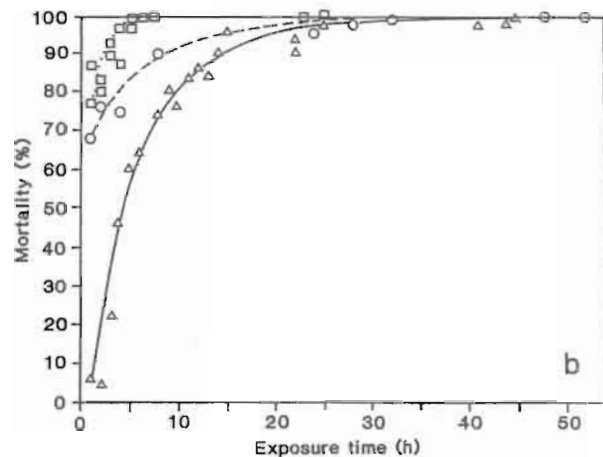
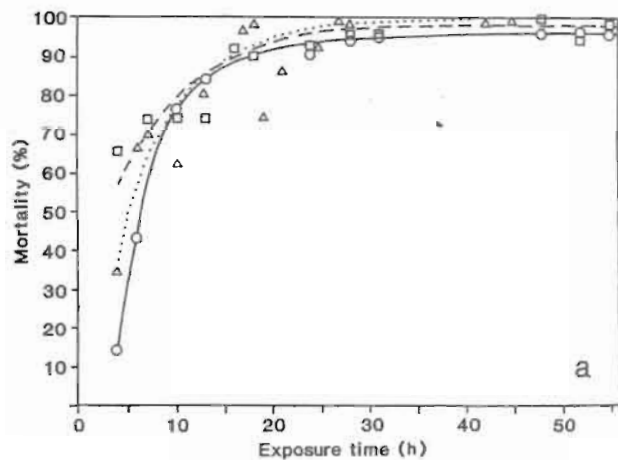


**Fig. 2.** Gas concentration characteristics of phosphine fumigations with adult *Sitophilus granarius* following an initial dosage of 6 (.....), 4 (---), and 2 (—)  $\text{g/m}^3$  of phosphine at  $20^\circ\text{C}$ , 76% RH, and a leakage rate of 5% of the volume of the treated enclosure per hour. The two shaded areas of the rectangle are equivalent to the shaded area under the dotted curve, so that the rectangle corresponds to the integral of the dotted curve.

narcotic region' (Winks 1984) (Fig. 4). As already indicated, this deviation should not be considered as 'protective stupefaction' which involves pretreatment before the actual exposure.

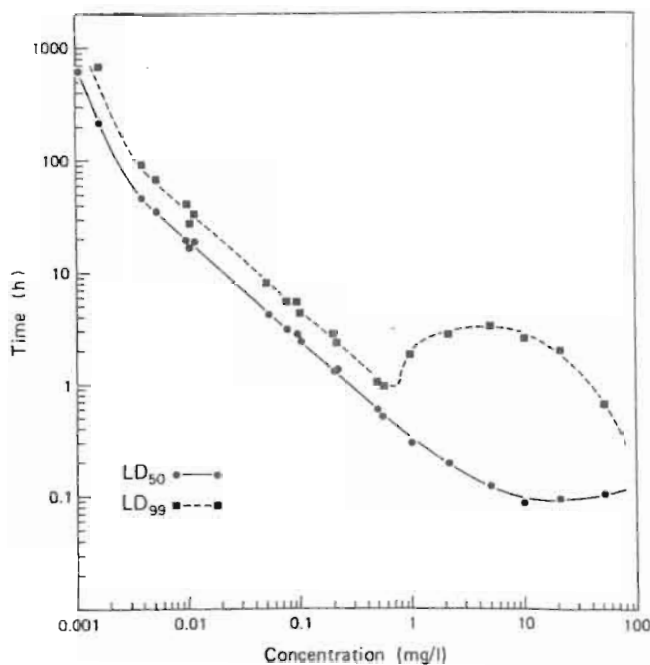
### Resistance to Phosphine

It is clear that immobilised insects continue to take up phosphine. With adult *Tribolium castaneum* it was shown that resistant insects took up phosphine at a lower rate than susceptibles. This was investigated in vivo using radiolabelled phosphine (Figs 5 and 6). The amount of phosphine that needed to be incorporated to kill resistant insects was greater than the corresponding amount for susceptible insects. The



**Fig. 3.** (a) Mortality results from phosphine treatment of adult *Sitophilus granarius* with 6 ( $\Delta$ ), 4 ( $\square$ ), and 2 ( $\circ$ )  $\text{g/m}^3$  aluminium phosphide formulation at  $20^\circ\text{C}$ , 75% RH, and a leakage rate of 5% of the volume of the treated enclosure per hour.

(b) Mortality results from phosphine treatment of adult *Sitophilus granarius* with at 1.55  $\text{g/m}^3$  ( $\square$ ), 0.90  $\text{g/m}^3$  ( $\circ$ ), and 0.08  $\text{g/m}^3$  ( $\Delta$ ) at  $20^\circ\text{C}$  and 75% RH.



**Fig. 4.** The concentration  $\times$  time relationship at the LD<sub>50</sub> and LD<sub>99</sub> levels for *Tribolium castaneum* adults exposed to a range of fixed concentrations for various exposure periods (data of Winks 1984). The data for LD<sub>99</sub> indicate very clearly that, for concentrations of phosphine above 0.7 g/m<sup>3</sup>, Haber's rule does not apply in this so-called narcotic range. Moreover, increasing concentration beyond 0.7 g/m<sup>3</sup> requires an increase in exposure time to achieve the same mortality as at lower concentrations. This agrees with the finding of Reichmuth (1985) that steadily increasing concentrations of phosphine gradually became less effective against *S. granarius*.

reduced uptake by resistant insects is in accordance with findings of Price (1985), who suggested that active exclusion is a characteristic of phosphine resistant strains of *Rhyzopertha dominica*. One of the clear findings of studies using radiolabelled phosphine was that those insects that tend to stay active for the longest time (i.e. those not narcotised) are those that will most probably survive. This is especially true with resistant adult beetles and was observed during the experiments. The same phenomenon is described by Price (1986a).

### New Aspects of Phosphine Fumigation

For fumigation during cold weather, Sullivan (1985) proposed use of magnesium phosphide rather than aluminium phosphide because of more rapid evolution phosphine from the magnesium formulation at low temperatures. Insect control data were not given. Cook (1980),

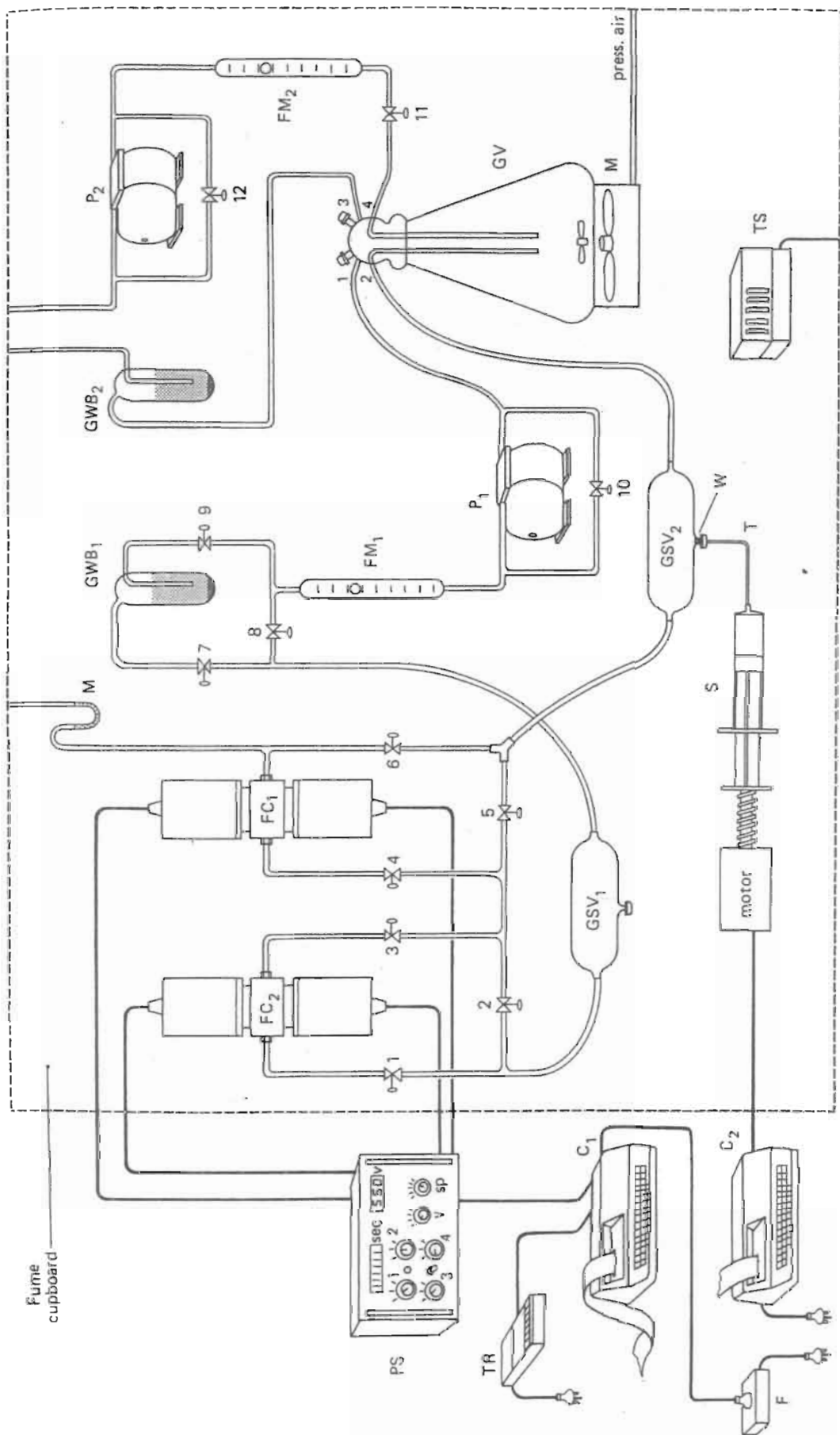
Reichmuth (1985), Sullivan (1985), Banks (1986), Winks (1986), and Wohlgemuth (1986) all dealt with the question of recirculating the gas through bulk grain or using a flow-through method. The great advantage of these techniques is that the stored product need not be turned to add the formulation. Uniform distribution of the gas is easily achievable given a specified degree of gastightness. In the case of flow-through techniques, exposure time must be some weeks to ensure complete kill at low concentrations. In any case, because time of exposure is the governing factor in phosphine toxicity, long exposure periods are preferable to minimise the dosage. Moreover, concentration needs to be low to avoid environmental risks. A further development might be the sorption of the gas in some way as it is purged from the bulk rather than venting it to the air. These ideas are stimulated by the increasingly stringent regulations on fumigation being imposed in the Federal Republic of Germany.

### Controlled Atmospheres

Due to growing concern on the use of toxic materials, gases such as nitrogen and carbon dioxide have come back into focus for stored product pest control. Annis (1987) surveyed insect pest control with these fumigants at temperatures above 20°C. Reichmuth (1987) did likewise for the temperature range 15°–20°C. Lethal exposure times for immature *S. granarius* are shown in Table 1. At 15°C, older larvae and pupae had to be exposed to high nitrogen atmospheres for about 60 days for 95% mortality, a less effective regime than 16–19% CO<sub>2</sub>. In high carbon dioxide atmospheres, only 35–40 days were necessary for complete control. At 20°C these times were reduced to 30–40 days and to 25–38 days, respectively.

The future potential of these gases as 'Controlled Atmospheres' (CA) is strongly dependent on the level of gastightness of the treated premises. Love et al. (1983) have given figures that indicate the economic range for their use when warehouses are made gastight and used over a period of years.

Generally speaking, exposure time is not a limiting factor with CAs. At 30°C a few days are sufficient, at 20°C a week or two, and at 15°C about a month is needed to control various species of stored product pests, with pupae of *S. granarius* being most tolerant. Normally, one



purge of the whole volume is necessary to remove the air from the product. The purge rate during the exposure period depends on the gastightness, although in some cases only an initial purge is necessary, making CA-application very economic.

Since the gases are costed by weight, it is worth noting that 1 kg of liquefied nitrogen produces 1 m<sup>3</sup> of gas, while 1 kg CO<sub>2</sub> yields only 0.5 m<sup>3</sup> of gas. This fact—along with other parameters such toxicity, availability, safety, sorption, and quality of treated product—may influence the choice of the gas. With nitrogen the oxygen concentration must be depressed below about 4% by volume, while carbon dioxide is lethal below an oxygen content of about 6% by volume. Insects, like mammals, are rapidly narcotised by carbon dioxide at low oxygen contents and low levels of resistance to carbon dioxide, established by selection in the laboratory, have been reported. Bond and Buckland (1979) found tolerance factors between 1.8 (LT<sub>99</sub>, 4 generations at 75% CO<sub>2</sub>) and 3.3 (LT<sub>99</sub>, 7 generations at 42% CO<sub>2</sub>) with adult *S. granarius*, and Navarro et al. (1985) determined factors of 2.2 (LT<sub>95</sub>, 7 generations at 40% CO<sub>2</sub>) and 3.3 (LT<sub>95</sub>, 10 generations at 75% CO<sub>2</sub>) with *S. oryzae*.

The use of pressurised CO<sub>2</sub> in high-pressure chambers was recently demonstrated for insect

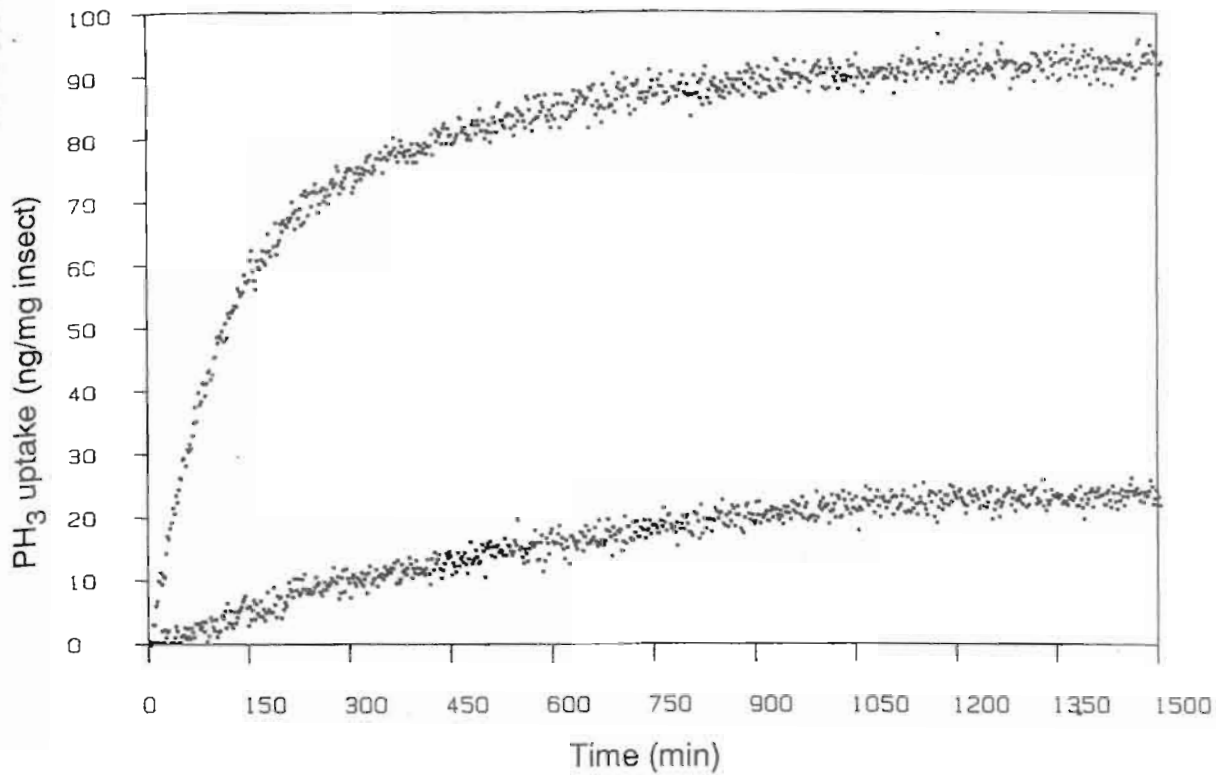
control (Gerard et al. 1988) (Figs 7 and 8). This costly method has only a limited market for treating high-value products such as drugs, tea, and cocoa, its advantage being that only short exposure periods—of the order of hours—are needed.

## Environmental and Health Aspects of Fumigation in Stored Products Protection

Some 10 years ago Reichmuth et al. (1981) began a project to assess the likely risks of the application and emission of fumigants used in stored product protection. Measurements in and around fumigated structures such as flour mills, warehouses, and granaries led to the conclusion that only within 10 m of such facilities would values of more than 0.15 mg/m<sup>3</sup> of phosphine (the German TLV) be detectable on a regular basis (Reichmuth and Noack 1983). In the event of an accident, higher concentrations might occur at greater distance from a structure being fumigated, but only for a very short period. This study involved large granaries, warehouses, and mills with an average level of sealing quality. The results for methyl bromide and HCN were very similar. The German TLVs were very rarely exceeded at distances more than 10 m from the structure. These results con-

**Fig. 5** (previous page). Diagram of apparatus for monitoring phosphine uptake by insects at constant or varying concentrations.

FC<sub>1</sub> and FC<sub>2</sub> are fumigation chambers (≈ 100 mL) and FC<sub>1</sub> contains the insects; power supply (PS) and counting device (Computer C<sub>1</sub>) for the Geiger tubes; the voltage of the Geiger tube (550 V) can be adjusted with switch V for the four tubes 1, 2, 3, and 4; the time relative to the beginning of the experiment is indicated in seconds or minutes; this can be selected with the switch between voltage potentiometer 3 and 4; time reset button between voltage potentiometer 1 and 2; select switch SP for a loudspeaker to indicate acoustically radioactivity at the four Geiger tubes, fifth position is off-position; filter F saves the computer from spikes derived from the main voltage supply; pump P<sub>1</sub> circulates the gas; flow adjustment at tube clamp 10, flow indication at flowmeter FM<sub>1</sub>, humidification of the gas in a gas-washing bottle GWB<sub>1</sub> which contains a saturated NaCl solution and some residual NaCl salt at the bottom, regulation with clamps 7, 8, and 9; monitoring of the gas concentration at gas sampling vessel GSV<sub>1</sub> with syringe through the septum of this vessel, clamps 1 to 6 determine the actual flow path of the gas, manometer M shows the pressure in the system; a septum in gas sampling bottle GSV<sub>2</sub> can be used to introduce gas slowly from a syringe S, the plunger being driven by a motor according to a gas release characteristic which can be programmed into Computer C<sub>2</sub>, the tip of the syringe inside GSV<sub>2</sub> is covered with water W to avoid free diffusion from the tip, the gas in the gas mixing vessel GV containing 2 septum ports for injection or withdrawing of gas is stirred by a magnet which is driven by another magnet outside on top of a rotor M being driven by pressurised air; for simulation of leakage port 3 and 4 of GV can be used to withdraw gas with pump P<sub>2</sub>, regulated with clamp 12, the flow is indicated at flowmeter FM<sub>2</sub>; the withdrawn gas is continuously replaced by fresh humidified air (gas washing bottle GWB<sub>2</sub>); the temperature of the installation is regulated constantly to 25 ± 0.3°C using a thermosensor TS which is placed close to the apparatus inside a fume cupboard which is sucking continuously air outside the laboratory because of safety reasons; the leads of the electrical equipment are led through holes in the walls of the cupboard.

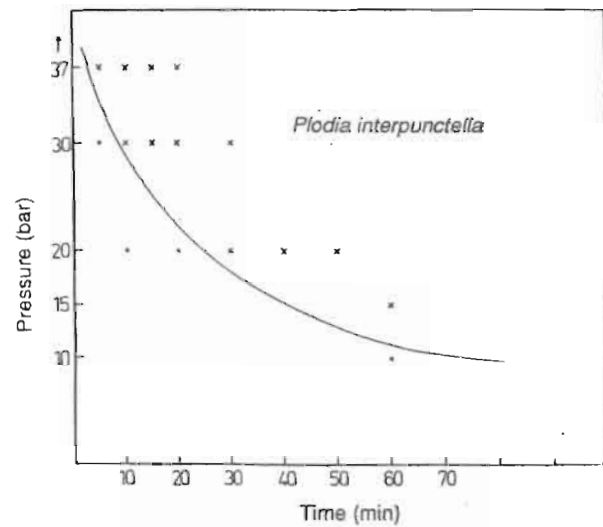


**Fig. 6.** Phosphine uptake by 10 resistant (IR) and 10 susceptible (II S) adults of *Tribolium castaneum* during exposure to 1 g/m<sup>3</sup> phosphine at 25°C. The change in uptake rate (flattening of the curves) is correlated to mortality of the insects. The horizontal parts of the lines indicate uptake by moribund or dead insects.

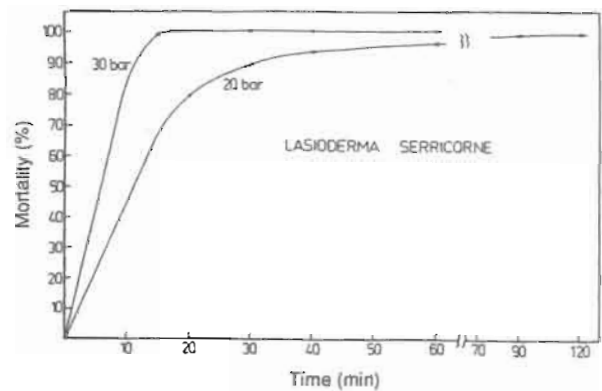
firmed those of Arendt et al. (1979). Meanwhile, due to changing public health consciousness in the FRG, stimulated by environmental accidents involving chemicals, a concentration level of 1/5 of the German TLV (0.02 ppm v/v) has

been declared the critical level. This value must not be exceeded during a fumigation at places where people live. The fumigator-in-charge has to measure and make sure that no persons are exposed to higher concentrations. If needs be, he must evacuate the the area (at the cost of the fumigation firm) to ensure that young children, and ill, elderly, or other sensitive persons are not placed at risk.

In the course of the study, the possibility of



**Fig. 7.** Survival (•) and 100% mortality (x) of eggs of *Plodia interpunctella* after exposure to high pressure and carbon dioxide. At room temperature good results can be achieved in less than 1 hour.



**Fig. 8.** Response of adult and immature *Lasioderma serricorne* to high pressure and carbon dioxide at room temperature.



**Table 1.** Lethal exposure time (LT95) in days for immature *Sitophilus granarius* exposed to varying concentrations of nitrogen and carbon dioxide at 15°C and 20°C and oxygen contents of 1–4% by volume. B1 ... B5: 3 day age cohorts\* of various developmental stages cultured at 70% RH and 25°C.

Oxygen content (vol %)	Gas mixture	Lethal exposure times (days)									
		15°C					20°C				
		B1	B2	B3	B4	B5	B1	B2	B3	B4	B5
1% O <sub>2</sub>	+99% N <sub>2</sub>	30	40	40	40	45	20	13	21	30	30
	+80% N <sub>2</sub> +19% CO <sub>2</sub>	30	35	45	60	39	16	27	29	30	32
	+4% N <sub>2</sub> +95% CO <sub>2</sub>	30	9	15	22	35	16	2	11	20	24
2% O <sub>2</sub>	+98% N <sub>2</sub>	30	40	40	60	52	12	13	25	31	25
	+80% N <sub>2</sub> +18% CO <sub>2</sub>	20	35	35	53	49	14	14	14	25	21
	+8% N <sub>2</sub> +90% CO <sub>2</sub>	13	12	25	15	27	10	5	5	7	19
3% O <sub>2</sub>	+97% N <sub>2</sub>	30	31	45	65	53	17	12	28	35	30
	+80% N <sub>2</sub> +17% CO <sub>2</sub>	32	33	40	50	41	15	18	25	42	45
	+12% N <sub>2</sub> +85% CO <sub>2</sub>	21	11	9	24	34	10	2	9	15	26
4% O <sub>2</sub>	+96% N <sub>2</sub>	40	25	60	60	55	32	18	25	40	40
	+80% N <sub>2</sub> +16% CO <sub>2</sub>	46	32	40	48	49	18	7	18	31	32
	+16% N <sub>2</sub> +80% CO <sub>2</sub>	45	15	31	39	40	23	18	25	40	38

\* Age cohorts are: B1, eggs, 0–3 d old; B2, larvae, 7–10 d old; B3, larvae, 14–17 d old; B4, pupae and larvae, 21–24 d old; B5, pupae, 28–31 d old.

harmful effects of low concentrations on plants and animals was also investigated (Noack and Reichmuth 1981, 1982). It was found that 0.1 ppm v/v phosphine in air is about the limit value for significant damage to *Drosophila melanogaster*, which is classed as a very susceptible animal. The threshold concentration of phosphine in air for harmful effects on growing lettuce (a highly sensitive plant species) was determined to be between 3 and 8 mg/m<sup>3</sup> (20 and 53 ppm v/v). In another experiment, a common ornamental plant (*Diefenbachia*) was unharmed by exposure to 10 ppm v/v phosphine for 14 days at room temperature (22°C) and 80–90% RH.

The concentration limit below which there will be no harm to exposed persons is problematic. The issue is discussed in general terms by Jackson et al. (1988). Klimmer (1969) found that 1.4 and 3.5 mg/m<sup>3</sup> of phosphine applied for 4–6 hours per day, for 6 days a week, for a total of more than 800 hours over a 24-week period produced no clinical, laboratory, or pathological evidence of effects on exposed cats, guinea-pigs, and rats. Pazynich et al. (1984) exposed white rats to 0.05, 0.2, 1.5, and 8 mg/m<sup>3</sup> of phosphine. Changes in blood cholinesterase, peroxidase, and catalase activity and in phagocyte behaviour were found. They were not generally dose-related. The authors recom-

mended mean exposure limits for urban air, for exposure durations of 24 hours, one month, and one year of 0.004, 0.0015, and 0.001 mg/m<sup>3</sup> phosphine, respectively, with a ceiling value of 0.01 mg/m<sup>3</sup>. This recommendation has been adopted in the USSR. In a similar study, Atchbarov et al. (1984) found significant medical changes in rats inhaling 0.1 and 0.05 mg/m<sup>3</sup> phosphine.

From the available literature on human toxicity (e.g. Waritz and Brown 1975; Amoores and Hautala 1983; Jackson et al. 1988) the conclusion can be drawn that very low concentrations of phosphine inhaled over periods of several hours or days might have minimal toxic effects. In practice, the periods of exposure are very short and sporadic for fumigation personnel and for persons close to a facility being fumigated and therefore not critical when gas concentrations are regularly checked and gas masks are at hand in case of complications. Serious accidents have occurred only when persons slept immediately outside a treated premises—which is strictly forbidden—or where safety precautions were not taken. It must be added that during certain weather conditions (e.g. inversions) gas might diffuse from the premises and drift away without turbulent mixing. On these rare occasions care must be taken to check gas concentrations at greater than usual distances from the fumigated premises.

Due to these uncertainties surrounding granary fumigation it is suggested that the emission of gas might be prevented by continuously sucking the free air out of the treated premises and purging it through a sorbing unit. The gas which is diffusing through the plastic cover of the grain into the airspace is thus continuously removed. During the period of aeration the same principle could be used. Using this strategy, only minute amounts of the gas would escape into the environment.

Fritz et al. (1982) investigated the stability of phosphine in the atmosphere and found a median lifespan of less than one day: conversion to hypophosphoric acid was suggested. Experiments to determine the rate of hydrolysis of methyl bromide showed that light enhances it markedly (Castro and Belser 1981). From these results it can be concluded that the stability of methyl bromide in the atmosphere is of the order of days or less. On the other hand, Singh (1988) reported the occurrence of methyl

bromide in stratospheric air but not (yet) in the stratosphere of middle or lower latitudes. This methyl bromide might originate from the catalytic destruction of ozone by ClO<sub>x</sub> and BrO<sub>x</sub> radicals.

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# Responses of Fungi to Modified Atmospheres

Ailsa D. Hocking\*

## Abstract

The use of controlled atmospheres (CA) for insect control in the bulk storage of grains can have the added benefit of controlling mould growth and mycotoxin production. Mould deterioration accounts for significant losses in stored grains, particularly in tropical countries where the temperature and relative humidity are high. The problem is exacerbated where grains are inadequately dried before entering storage.

Atmospheres high in CO<sub>2</sub> are more effective in controlling fungal growth than those which exclude O<sub>2</sub> by replacement with nitrogen. Although most fungi require some oxygen for growth, many spoilage species are efficient scavengers and are capable of near normal growth in O<sub>2</sub> concentrations of <1%. Atmospheres containing about 20% CO<sub>2</sub> generally inhibit mould growth, but >80% CO<sub>2</sub> may be required to prevent fungal deterioration of high moisture commodities. Some *Fusarium*, *Aspergillus*, and *Mucor* species are particularly tolerant of high levels of CO<sub>2</sub>. Mycotoxin production is more sensitive than fungal growth to low O<sub>2</sub> and high CO<sub>2</sub>. Concentrations of CO<sub>2</sub> between 20 and 60% have been demonstrated to prevent or significantly reduce mycotoxin production by some *Fusarium*, *Aspergillus*, and *Penicillium* species. Reduction of O<sub>2</sub> content is less effective in preventing mycotoxin formation.

MEDIUM to long term storage of grains in tropical regions presents many problems, as grain is frequently stored at a higher moisture content than is desirable, and invasion pressure from insects is often high. Both these factors will also encourage mould growth, and postharvest losses in stored grains due to insects and other pests, and fungal spoilage are considerable.

The introduction of controlled atmosphere storage of commodities for insect control also offers considerable scope for control of fungal deterioration. However, many storage fungi are capable of growth in low partial pressures of oxygen, and reduction of available oxygen is often not sufficient to prevent moulding, particularly of high moisture grains. Elevated levels of CO<sub>2</sub> are more inhibitory to mould growth, but other factors, such as temperature and moisture content, will affect the degree of inhibition exerted by controlled atmospheres.

\*Food Research Laboratory, CSIRO Division of Food Processing, P.O. Box 52, North Ryde, NSW 2113, Australia.

## Effect of Controlled Atmospheres on Mycoflora of Stored Commodities

Investigations into the effects of reduced O<sub>2</sub> and increased CO<sub>2</sub> on moulds in stored commodities date back at least to the early 1950s, when hermetic storage of grains was proposed as a new technology (Vayssi re 1948). The earliest studies were undertaken with maize (Bottomley et al. 1950) and wheat (Peterson et al. 1956) and dealt mainly with spoilage by storage fungi. Studies undertaken after the mid 1960s were more concerned with the proliferation of mycotoxigenic fungi, and the effects of controlled atmospheres on mycotoxin production.

### Maize

Storage of high moisture content maize presents a significant problem in many parts of the world, including the USA. Bottomley et al. (1950) investigated the effects of reduced

oxygen on maize stored at relative humidities between 75 and 100%, and temperatures from 25 to 45°C, but their storage period was only 12 days. They found that mould growth was significantly reduced but not prevented by storage in an atmosphere of 0.1% O<sub>2</sub> and 21% CO<sub>2</sub>. Different moulds predominated depending on the storage conditions. At 80% relative humidity, *Penicillium* species were dominant at 25°C, *Aspergillus flavus* at 30°C, and *Eurotium* species at 35°C (Table 1). Mould growth was less at 40 and 45°C, but *Mucor* was predominant at 45°C, especially when the oxygen concentration was 5% or less. In maize at 90% ERH or higher, *Candida* species proliferated in the 0.1% O<sub>2</sub> and 21% CO<sub>2</sub> atmosphere at 25°C, but not at higher temperatures.

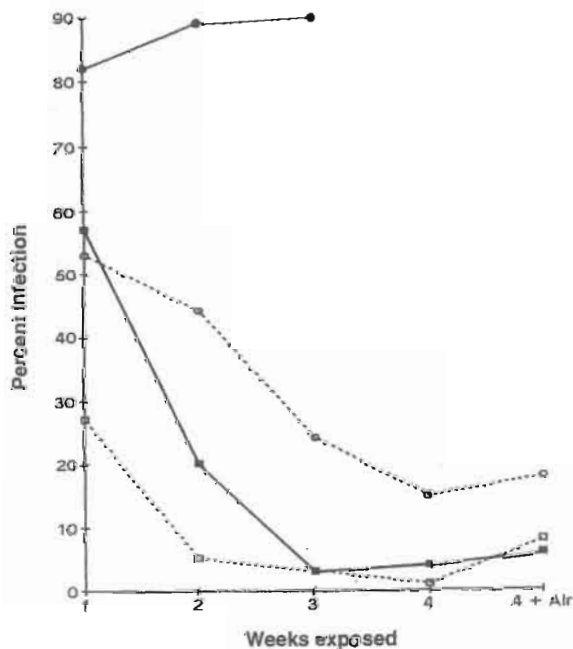
Wilson et al. (1975) investigated the effects of modified atmospheres on the survival of the toxigenic moulds *A. flavus* and *Fusarium moniliforme* in freshly harvested high moisture maize (moisture content 29.4%) and maize rewetted to 19.6% moisture. The maize was inoculated with *A. flavus* and exposed to atmospheres of air, N<sub>2</sub> (99.7%, balance O<sub>2</sub>), CO<sub>2</sub> (61.7%) and low O<sub>2</sub> (8.7%), and a CA mixture of 13.5% CO<sub>2</sub>, 0.5% O<sub>2</sub> and 84.8% N<sub>2</sub>. In the freshly harvested maize, *A. flavus* levels increased in the air control to 90% kernel infection after 2 weeks, but with the other treatments kernel infection rate was only 5-18% after 4 weeks (Fig. 1). *F. moniliforme* was recovered from 21% of the kernels initially, but in subsamples exposed to modified atmospheres for four weeks, then held for 1 week in air, was present in 100% of kernels

**Table 1.** Predominant mycoflora in maize stored for 12 days at 80% ERH in 20% CO<sub>2</sub> and 0.1% O<sub>2</sub>. Data of Bottomley et al. (1950).

Temperature (°C)	Species (%)
25	<i>Penicillium</i> (55)
	<i>A. flavus</i> (45)
30	<i>A. flavus</i> (90)
35	<i>Eurotium</i> (50)
	<i>Penicillium</i> (50)
40	<i>Eurotium</i> (70)
	<i>A. flavus</i> (25)
45	<i>Mucor</i> (25)
	<i>Penicillium</i> (50)
	<i>A. flavus</i> (15)

from all three treatments. The CO<sub>2</sub> + low O<sub>2</sub> sample developed an unpleasant odour, and was visibly overgrown with an unidentified yeast. In the rewetted maize, *A. flavus* did not decrease in any of the treatments, and increased in the N<sub>2</sub> and CA treatments. The incidence of *F. moniliforme* increased from 67% to near 90% in all treatments. The incidence of other fungi (*Penicillium*, *Eurotium*, other *Aspergillus* species, *Rhizopus* and *Mucor*) was low, and did not increase during modified atmosphere storage.

In a longer term experiment, Wilson et al. (1977) used maize with a moisture content of 18.8% for a storage trial in an atmosphere of 14-15% CO<sub>2</sub> and 0.5-1.0% O<sub>2</sub>. Maize stored for 35 and 109 days in this atmosphere was tested for aflatoxins and the presence of *A. flavus* and *F. moniliforme*. No aflatoxin was detected after 35 or 109 days, whereas a control sample stored in air contained 472 µg/kg total aflatoxins. A significant proportion of the kernels contained *A. flavus* (30-47%) and *F. moniliforme* (35-47%), after both storage periods, and 27% of kernels contained a *Penicillium* species after 109 days storage. The



**Fig. 1.** Effects of modified atmospheres on *Aspergillus flavus* infection of inoculated high-moisture maize. Data of Wilson et al. (1975).

- (●) Air (0.03% CO<sub>2</sub>, 21% O<sub>2</sub>, 78% N<sub>2</sub>)
- (○) CO<sub>2</sub> + low O<sub>2</sub> (61.7% CO<sub>2</sub>, 8.7% O<sub>2</sub>, 29.6% N<sub>2</sub>)
- (■) N<sub>2</sub> (99.7% N<sub>2</sub>, 0.3% O<sub>2</sub>)
- (□) CA (13.5% CO<sub>2</sub>, 0.5% O<sub>2</sub>, 84.8% N<sub>2</sub>)

maize was not assayed for *Fusarium* or *Penicillium* toxins.

Controlled atmosphere storage of high moisture maize in atmospheres containing <1% O<sub>2</sub> could be used for temporary holding before drying, or, at lower temperatures, for longer-term storage, the main advantages being residue-free insect control and retardation of fungal growth. However, because most fungi are not killed by low O<sub>2</sub> atmospheres, the safe storage period for high moisture maize is limited and the maize will deteriorate rapidly upon exposure to the normal atmosphere.

## Peanuts

Much attention has been paid to control of aflatoxin production in stored peanuts by use of controlled atmospheres, and this aspect will be addressed later in this paper. However, relatively little has been published on the mycoflora changes that occur in peanuts stored under controlled atmospheres over long periods.

The effects of CO<sub>2</sub> on growth and sporulation of *A. flavus* on high moisture peanuts were reported by Landers et al. (1967) and Sanders et al. (1968). Growth and sporulation were reduced with each 20% increase in CO<sub>2</sub> from 20% to 80%, with no growth occurring in 100% CO<sub>2</sub>. Growth was much reduced in atmospheres of < 5% O<sub>2</sub>, and almost completely inhibited at < 1% O<sub>2</sub>. Concentrations of CO<sub>2</sub> in excess of 20% were required before there was any inhibition of growth of *A. flavus* in high moisture peanuts. However, Jackson and Press (1967) reported that incidence of *A. flavus* at 27°C on shelled peanuts of 5.0% moisture content (m.c.) or unshelled peanuts at 7.5% m.c. was not reduced by storage in atmospheres containing 3% O<sub>2</sub> or 82% CO<sub>2</sub> in air compared with air storage over 12 months.

Wilson et al. (1985) used pilot scale experiments to determine if long-term storage of peanuts was practical in modified atmospheres with minimal deterioration due to mould spoilage, aflatoxin contamination and insect infestation, without use of refrigeration or pesticides. Two large bins of peanuts (1996 kg and 6451 kg) were stored in an atmosphere of approximately 60% CO<sub>2</sub> (balance air), at a moisture content of 6–7% for one year.

The smaller (metal) bin experienced moisture migration due to condensation of water on or near the surface at night, the moisture content

of the peanuts at the top rose to 11.1% and they were visibly mouldy after 16 weeks. After this time, the atmosphere was recirculated, and moisture contents rapidly equilibrated throughout the bin. The most common species at the top of the bin were *A. flavus*, *Eurotium* species, and an unidentified white yeast, possibly a *Candida* species (Table 2). Other *Aspergillus* species (*A. candidus*, *A. ochraceus* and *A. niger*) were also recorded on 18% of kernels, while *Rhizopus* and *Penicillium* were less frequently isolated. The same species of fungi were isolated from kernels at the bottom of the bin, but in much lower numbers (Table 2). Despite the high incidence of *A. flavus*, no aflatoxins were detected.

In the second trial with the larger (fibre-glass) bin of peanuts, the atmosphere of 55–60% CO<sub>2</sub> was recirculated, and there was no moisture migration. The only major change observed in the mycoflora was a decrease in superficial *Penicillium* contamination for 64 to 16%. Aflatoxins were not detected during the 54 week trial.

## Wheat

The mycoflora of wheat differs from that of maize and oilseeds. Wheat is usually drier when harvested, and in general *A. flavus* and *F. moniliforme* cause fewer problems in this commodity.

Petersen et al. (1956) stored wheat of 18% m.c. for 16 days at 30°C under atmospheres with varying concentrations of oxygen and carbon dioxide. In 4.3% O<sub>2</sub>, the mycoflora was dominated by *Eurotium* species (80%), with *Penicillium* species and *A. flavus* also present (10% each). When O<sub>2</sub> was reduced to 2.3%,

**Table 2.** Fungal colonisation of peanut kernels stored at 7% m.c. in 50–60% CO<sub>2</sub> in an outside bin at ambient temperatures for 12 months. Data of Wilson et al. (1985).

Species	Percent kernel invasion	
	Top of bin	Bottom of bin
<i>A. flavus</i>	95	18
<i>A. candidus</i>	5	1
<i>A. niger</i>	9	20
<i>A. ochraceus</i>	4	1
<i>Eurotium</i>	87	21
<i>Penicillium</i>	3	4
<i>Rhizopus</i>	12	38
<i>Candida</i>	100	11

only *Eurotium* (67%) and *Penicillium* (33%) were present (Table 3). In 0.2% O<sub>2</sub> only *Eurotium* species were detected, and their numbers were much reduced (Table 3). With gas mixtures containing 21% O<sub>2</sub> and varying concentrations of CO<sub>2</sub>, there was no significant change in numbers of fungi present in up to 18.6% CO<sub>2</sub>. However, growth was almost completely inhibited by 50% and 79% CO<sub>2</sub> (Fig. 2). *Eurotium* species were the most tolerant of elevated levels of CO<sub>2</sub>.

Shejbal and Di Maggio (1976) and Di Maggio et al. (1976) stored wheat of 18% m.c. in pure nitrogen, and found that mould growth was inhibited, and fungi gradually decreased with time. After 30 weeks, there was an increase in *Aspergillus candidus*. After 54 weeks, the total mould count was 6 x 10<sup>4</sup>/gram, a quite acceptable level for wheat. Under 0.2% O<sub>2</sub>, mould growth at 18-26°C on wheat of 17.4% m.c. was substantially inhibited in comparison with the air control. However, with both treatments, *A. candidus* eventually proliferated, reaching counts of 6 x 10<sup>5</sup>/gram after 3 and about 20 weeks, respectively.

## Rice

In a study on naturally contaminated rice, Richard-Molard et al. (1986) investigated the effects of oxygen deficiency on microflora of grain rewetted to 0.87 and 0.94 a<sub>w</sub> and stored for 2-4 months. They found that in the samples where the moisture content was low enough to prevent bacterial growth (0.87 a<sub>w</sub>), most storage

fungi, including *Penicillium* and *Aspergillus* were inhibited by atmospheres of less than 1% O<sub>2</sub>. However, yeasts (*Candida* spp.) and the yeast-like fungus *Aureobasidium pullulans* were able to develop, even with less than 0.5% O<sub>2</sub>, and the higher the a<sub>w</sub>, the more rapid the growth. In the complete absence of O<sub>2</sub> (under 100% CO<sub>2</sub> or N<sub>2</sub>), there was no fungal growth. At a<sub>w</sub> values higher than 0.90, lactic acid bacteria proliferated, and were not inhibited by any of the atmospheres studied.

## Effect of Gas Mixtures on Growth of Fungi

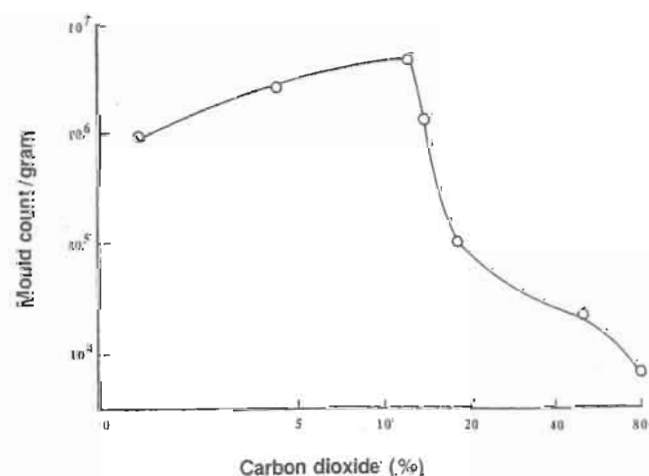
The two factors that need to be considered in preventing fungal growth in controlled atmospheres are (1) the minimum amount of oxygen required for fungal growth and (2) the inhibitory effects of high levels of CO<sub>2</sub>. Atmospheres high in nitrogen are only effective because of their low O<sub>2</sub> content, as nitrogen itself has no inhibitory effects.

## Oxygen Requirements

Many fungi are able to grow in the presence of very small amounts of oxygen (Miller and Golding 1949; Follstad 1966; Wells and Uota 1970; Walsh 1972; Yanai et al. 1980; Gibb and Walsh 1980; Magan and Lacey 1984). Anaerobic growth has also been reported for several fungi, for example, *Fusarium oxysporum* (Gunner and Alexander 1964) and some species of *Mucorales* that are used as starter cultures for

**Table 3.** Effect of oxygen concentration on mould population and distribution in wheat stored for 16 days at 18% moisture and 30°C. Data of Peterson et al. (1956).

Oxygen (%)	Moulds/g	Species
0.2	7.0 x 10 <sup>3</sup>	<i>Eurotium</i>
2.3	1.9 x 10 <sup>5</sup>	<i>Penicillium</i>
	2.9 x 10 <sup>5</sup>	<i>Eurotium</i>
4.3	1.0 x 10 <sup>5</sup>	<i>Penicillium</i>
	8.0 x 10 <sup>5</sup>	<i>Eurotium</i>
	1.0 x 10 <sup>5</sup>	<i>A. flavus</i>
8.0	1.0 x 10 <sup>5</sup>	<i>Penicillium</i>
	5.6 x 10 <sup>5</sup>	<i>Eurotium</i>
20.6	6.8 x 10 <sup>5</sup>	<i>Penicillium</i>
	3.9 x 10 <sup>5</sup>	<i>Eurotium</i>
	5.6 x 10 <sup>4</sup>	<i>A. flavus</i>



**Fig. 2.** Effect of CO<sub>2</sub> tension on mould count in wheat incubated 20 days at 30°C and 18% moisture. All gas mixtures contained 21% O<sub>2</sub>. Data of Peterson et al. (1956).



food fermentations in Asia (Hesseltine et al. 1985). Tabak and Cook (1968) reported 'good to very good' growth of a range of species under 100% nitrogen. The strongest growth was exhibited by *Geotrichum candidum*, a yeast-like fungus, *Mucor beimalis*, *Fusarium oxysporum*, and *F. solani*. However, 'good' growth was observed in *Aspergillus niger*, *A. fumigatus*, *Penicillium aurantiogriseum*, and *P. brevicompactum*, and the black yeast-like fungus *Aureobasidium pullulans*. Such anaerobic growth can take place only if a number of growth factors (vitamins, oxygen donors in the form of higher oxidation states of certain elements) are supplied.

What is perhaps more relevant to CA storage of commodities, is the ability of many common field and storage fungi to grow in atmospheres containing <1% O<sub>2</sub> (Fig. 3). Of the field fungi present on grains at harvest, e.g. *Fusarium* species, *Alternaria*, other dematiaceous

hyphomycetes, *Rhizopus*, yeasts, etc., some grow very well in low levels of oxygen. *Fusarium moniliforme*, *F. oxysporum*, *F. culmorum*, and *F. solani* all grow strongly in atmospheres containing 1.0% to 0.1% O<sub>2</sub> or even less (Gunner and Alexander 1964; Tabak and Cook 1968; Walsh 1972; Gibb and Walsh 1980; Magan and Lacey 1984), provided that other growth conditions such as temperature and water activity are favourable. Some *Rhizopus* and *Mucor* species can also grow at low oxygen tensions (Wells and Uota 1970; Gibb and Walsh 1980; Yanai et al. 1980) or even anaerobically (Hesseltine et al. 1985), and can proliferate in high moisture commodities stored under low oxygen atmospheres (Bottomley et al. 1950; Wilson et al. 1975). Other field fungi such as *Alternaria* and *Cladosporium herbarum* are more sensitive to reduced oxygen tensions (Magan and Lacey, 1984) and gradually die out during storage.

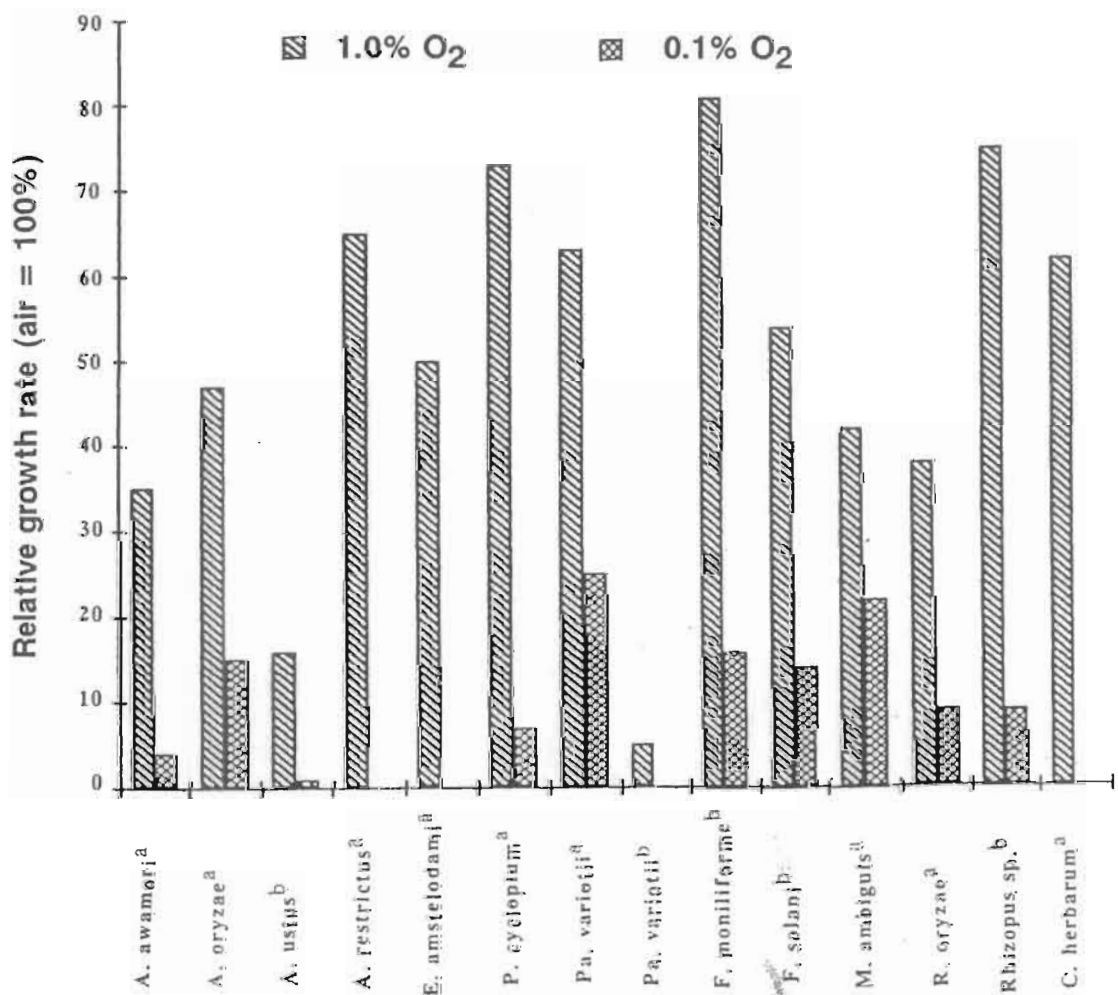


Fig. 3. Effects of reduced O<sub>2</sub> tensions on growth of some field and storage fungi. Data of a. Yanai et al. (1980); and b. Gibb and Walsh (1980).

Storage fungi such as *Penicillium* and *Aspergillus* species are generally more sensitive to low levels of  $O_2$  than the more tolerant field fungi. With the exception of *P. roquefortii*, the growth rates of most *Penicillium* species are reduced by more than 50% in atmospheres of 1%  $O_2$  or less (Yanai et al. 1980; Magan and Lacey 1984). Of the *Aspergillus* species, *A. candidus* is the most tolerant of reduced  $O_2$  conditions (Magan and Lacey 1984) and thus can proliferate in CA stored wheat (Shebjal and Di Maggio 1976; Di Maggio et al. 1976). Some *Eurotium* species are also reasonably tolerant of low  $O_2$  levels (Petersen et al. 1956; Yanai et al. 1980).

In our laboratory, studies on a number of spoilage fungi isolated from low  $O_2$  environments have shown that most are inhibited only slightly when grown in nitrogen atmospheres, with 0–1.0%  $O_2$  (Fig. 4). Isolates of *Penicillium corylophilum* and *P. glabrum* from vacuum-packed jams were able to grow at 66–90% of their control rate (air) when sealed

in barrier film with an atmosphere of nitrogen. *Fusarium equiseti* and *F. oxysporum* which caused fermentative spoilage of UHT fruit juices grew at 88–97% of their normal rate. A *Cladosporium* species isolated from the inside of a UHT pack of apple juice was little affected by lack of oxygen, growing at 95–100% when sealed in an atmosphere of nitrogen. *Mucor plumbeus* and *Absidia corymbifera* also grew strongly in nitrogen. The xerophilic fungus *Eurotium repens* grew at 60–90% of the control rate, depending on the growth medium, and the extreme xerophile *Xeromyces bisporus* grew at the same rate in air and in nitrogen (Fig. 4).

#### Effects of Increased Carbon Dioxide Levels

Levels of  $CO_2$  from 4% to 20% can be stimulatory to growth of many fungi in atmospheres containing low levels of  $O_2$  (Wells and Uota 1970; Gibb and Walsh 1980), conditions that may well arise during sealed storage of commodities. However, elevated  $CO_2$

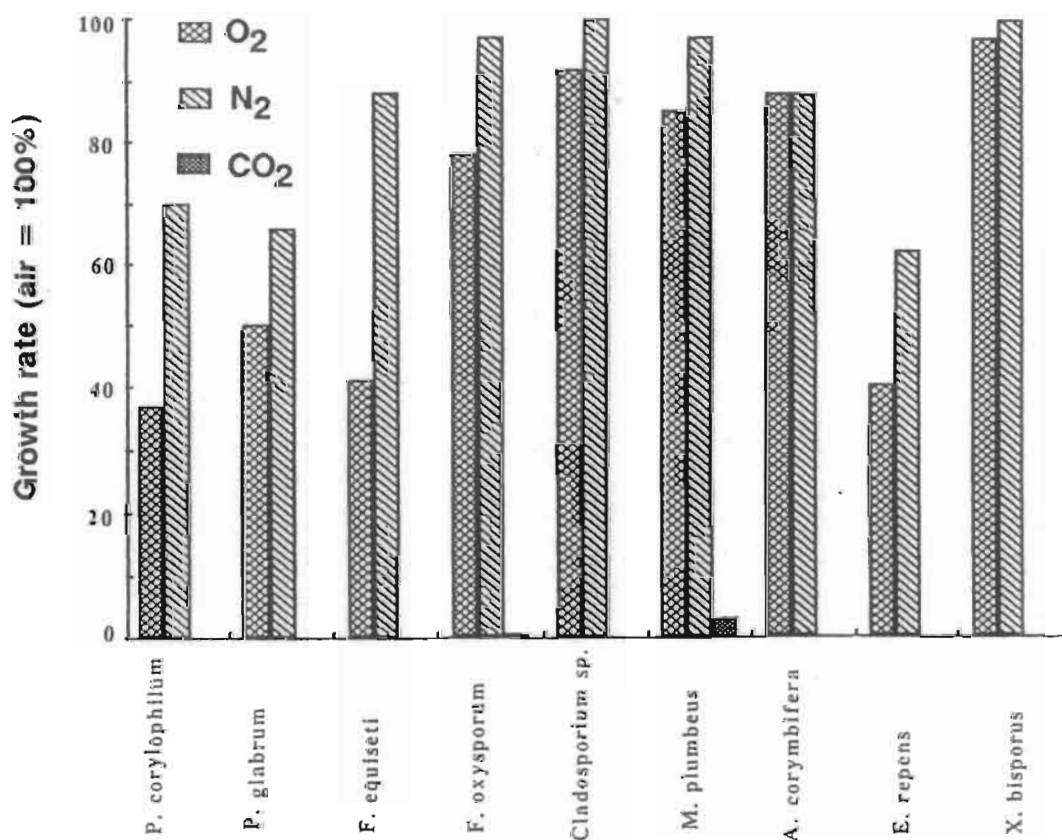


Fig. 4. Growth rates (relative to air) of nine fungi in  $O_2$ ,  $N_2$ , and  $CO_2$ . Fungi were grown in pure culture on Petriplates (Millipore Corp.) sealed inside barrier film containing the appropriate atmosphere, and incubated at 25°C. Growth was measured by radial growth rate of colonies.

concentrations are generally much more effective in controlling fungal growth than oxygen depletion. Thus, atmospheres rich in CO<sub>2</sub> are more likely to prevent mould deterioration of CA stored high moisture commodities than atmospheres of nitrogen with traces of O<sub>2</sub>. Typical insecticidal atmospheres used for grain storage are 1% O<sub>2</sub> in nitrogen and 60% CO<sub>2</sub> 40% air (Banks 1981), and while both may be equally effective in controlling insect populations in stored grain, the CO<sub>2</sub>-enriched atmosphere would be more effective in controlling fungal growth in high-moisture commodities.

Atmospheres containing > 50% CO<sub>2</sub> will substantially inhibit growth of most spoilage fungi (Petersen et al. 1956; Wells and Uota 1970) but there is little information in the literature on their actual CO<sub>2</sub> tolerances. Stotzky and Goos (1965) recorded slight growth of *Rhizopus stolonifer*, *Mucor hiemalis*, and a *Trichoderma* species in 100% CO<sub>2</sub>. The same three species grew well in an atmosphere of 50% CO<sub>2</sub>, 45% N<sub>2</sub>, and 5% O<sub>2</sub>. *Fusarium oxysporum* grew in 95% CO<sub>2</sub>, 5% N<sub>2</sub> but not in 95% CO<sub>2</sub>, 5% O<sub>2</sub>. *Paecilomyces lilacinus* did not grow in either of these atmospheres, but grew reasonably well in 50% CO<sub>2</sub>, 45% N<sub>2</sub>, and 5% O<sub>2</sub>.

Magan and Lacey (1984) reported that >15% CO<sub>2</sub> was required to halve the linear growth rate of most of the 14 species of field and storage fungi tested at 0.98–0.90 a<sub>w</sub> and 23°C. The species most sensitive to elevated CO<sub>2</sub> concentrations were *Penicillium brevicompactum*, *Aspergillus fumigatus*, *A. nidulans*, and *A. versicolor* (Table 4). However, no upper limits of CO<sub>2</sub> tolerance were determined, as the maximum concentration of CO<sub>2</sub> tested was 15%.

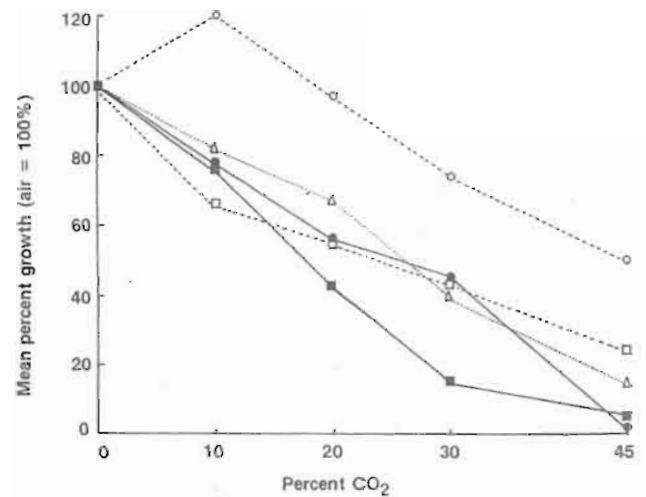
Nine species were tested in our laboratory for their ability to grow in an atmosphere of 97–99% CO<sub>2</sub> with trace amounts of O<sub>2</sub> and N<sub>2</sub>. Only *Fusarium oxysporum* and *Mucor plumbeus* grew, and their growth rates were only 0.5–4% of those in air (Fig. 4).

Wells and Uota (1970) showed that growth of *Alternaria alternata*, *Botrytis cinerea*, *Rhizopus stolonifer*, and *Cladosporium herbarum* in atmospheres of 10, 20, 30, and 45% CO<sub>2</sub> plus 21% O<sub>2</sub> decreased linearly with increasing CO<sub>2</sub> concentrations and was inhibited about 50% in an atmosphere of 20% CO<sub>2</sub> (Fig. 5). Growth of a *Fusarium* species, cited as *F. roseum* was stimulated at 10% CO<sub>2</sub>, and inhibited 50% at 45% CO<sub>2</sub>

**Table 4.** Concentrations of CO<sub>2</sub> required to halve the linear growth rate of field and storage fungi at 23°C. Data of Magan and Lacey (1984).

	Water activity		
	0.98	0.95	0.90
Field fungi			
<i>A. alternata</i>	>15.0	>15.0	>15.0
<i>C. cladosporioides</i>	>15.0	>15.0	>15.0
<i>C. herbarum</i>	13.0	>15.0	>15.0
<i>E. nigrum</i>	>15.0	>15.0	>15.0
<i>F. culmorum</i>	14.0	13.5	>15.0
Storage fungi			
<i>P. brevicompactum</i>	11.5	8.5	15.0
<i>P. aurantiogriseum</i>	4.5*	4.0*	>15.0
<i>P. bordei</i>	>15.0	8.5	9.5
<i>P. piceum</i>	>15.0	>15.0	14.5
<i>P. roquefortii</i>	>15.0	>15.0	4.5
<i>A. candidus</i>	>15.0	>15.0	>15.0
<i>A. fumigatus</i>	>15.0	5.2	2.5
<i>A. nidulans</i>	>15.0	6.5	13.5
<i>A. versicolor</i>	12.0	>15.0	14.5
<i>E. repens</i>	>15.0	>15.0	>15.0

\* Stimulation of growth occurred at higher CO<sub>2</sub> concentrations.



**Fig. 5.** Growth of five fungi in 21% O<sub>2</sub> with different levels of CO<sub>2</sub>, cultured on liquid media at 19°C. Growth was measured by dry weight of mycelia. Data of Wells and Uota (1970). (O) *Fusarium roseum*; (Δ) *Rhizopus stolonifer*; (□) *Alternaria alternata*; (●) *Botrytis cinerea*; (■) *Cladosporium herbarum*.

The effects of CO<sub>2</sub> concentrations on fungi growing in stored commodities, rather than in pure culture, seem to vary. Landers et al. (1967) and Sanders et al. (1968) reported that growth of *A. flavus* on high moisture peanuts was inhibited by 80% CO<sub>2</sub>/20% O<sub>2</sub>, but Jackson and Press (1967) found no reduction in *A. flavus* on peanuts stored at 5% m.c. (approximately 0.7 a<sub>w</sub>) in 82% CO<sub>2</sub> in air for 12 months. This perhaps indicates that although 80% CO<sub>2</sub> will inhibit growth of *A. flavus*, conidia of this species are not killed by exposure to high levels of CO<sub>2</sub> at low a<sub>w</sub>. Peterson et al. (1956) reported that *Eurotium* species survived and grew in wheat stored in 50% CO<sub>2</sub>/21% O<sub>2</sub> and 79% CO<sub>2</sub>/21% O<sub>2</sub>. However, there is little evidence that *Eurotium* species are particularly tolerant of high concentrations of CO<sub>2</sub> in pure culture. Magan and Lacey (1984) found that >15% CO<sub>2</sub> was required to halve the linear growth rate of *E. repens*, but this species will not germinate or grow in an atmosphere of 85% CO<sub>2</sub>, 12% N<sub>2</sub>, and 3% O<sub>2</sub> (Hocking, unpublished).

The exact mechanisms of CO<sub>2</sub> inhibition of microbial growth are unknown. It is obvious that it is not simply an oxygen displacement effect. Most studies have been carried out on bacteria, and little is known of the effects on fungi. Research on mechanisms of inhibition of bacterial growth have been summarised by Daniels et al. (1985) as follows: (a) the exclusion of oxygen by replacement with CO<sub>2</sub> may contribute slightly to the overall effect; (b) the ease with which CO<sub>2</sub> penetrates cells may facilitate its chemical effects on the internal metabolism; (c) carbon dioxide is able to produce a rapid acidification of the internal pH of cells with possible ramifications relating to metabolic processes; and (d) carbon dioxide appears to exert an effect on certain enzyme systems, though these effects differ for different species and with differing growth conditions.

## Effects of Gas Mixtures on Mycotoxin Production

### Aflatoxins

A number of studies have investigated the effects of various atmospheres and other environmental conditions on aflatoxin production, both in stored commodities and in pure culture. Landers et al. (1967), investigating

aflatoxin production in stored peanuts, reported that aflatoxin production decreased with increasing concentrations of CO<sub>2</sub> from 0.03% (air) to 100%, and that, in general, reducing the O<sub>2</sub> concentration also reduced aflatoxin production, particularly from 5% to 1% O<sub>2</sub> (Fig. 6). The inhibitory effect of CO<sub>2</sub> was greater at 15°C than at 30°C. At 15°C, aflatoxin production in 20% CO<sub>2</sub>, 5% O<sub>2</sub>, and 75% N<sub>2</sub> was less than 1% of that in air, and was barely detectable in an atmosphere of 40% CO<sub>2</sub>, 5% O<sub>2</sub>, and 55% N<sub>2</sub>. Sanders et al. (1968) reported similar results in storage experiments with peanuts at reduced a<sub>w</sub> and temperature. They found that aflatoxin levels decreased as a<sub>w</sub> decreased from 0.99 to 0.86. At a constant temperature, an increase in CO<sub>2</sub> concentration caused a decrease in aflatoxin formation, and lowering the temperature also decreased the amount of toxin formed.

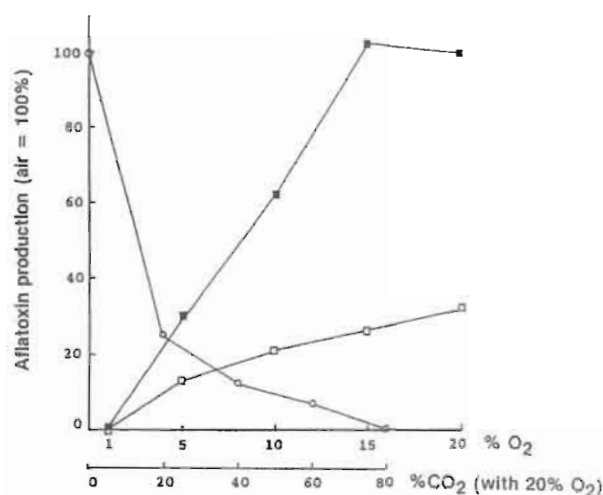


Fig. 6. Influence of various concentrations of O<sub>2</sub> and CO<sub>2</sub> on aflatoxin production in peanuts with kernel moisture content of 27-30% held at 30°C for 2 weeks. Data of Landers et al. (1967). (O) CO<sub>2</sub> with 20% O<sub>2</sub>; (■) O<sub>2</sub> with no CO<sub>2</sub>; (□) O<sub>2</sub> with 20% CO<sub>2</sub>

Epstein et al. (1970) studied the effects of controlled atmosphere (10% CO<sub>2</sub>, 1.8% O<sub>2</sub>, and 88.2% N<sub>2</sub>) on aflatoxin production in liquid medium and in inoculated maize at room temperature (which varied from 25 to 35°C) and at temperatures from 29°C to 1°C. At room temperature, *A. flavus* grew well and produced toxin in both air and CA. At 15°C, aflatoxin production, but not growth, was inhibited in CA. Aflatoxin was not produced at 12°C, and there was little growth at this temperature in air and none in CA. The minimum temperature for

aflatoxin production varies with strains, but is generally 10–12°C (Northolt et al. 1977).

Wilson and Jay (1975) found that maize inoculated with *A. flavus* and stored at 27°C for four weeks in three different modified atmospheres accumulated less than 20 µg/kg total aflatoxin compared with up to >1021 µg/kg for the air control. Remoistened maize was more susceptible to aflatoxin production than freshly harvested high moisture maize. Aflatoxin production in moistened (18.5% m.c.) wheat incubated at 32°C for up to 21 days was minimal (<1 µg/kg) in an atmosphere of N<sub>2</sub> compared with 123 µg/kg in air (Fabbri et al. 1980). Clevström et al. (1983) also found that small quantities of aflatoxins were produced when *A. flavus* was cultured under an atmosphere of nitrogen, and that production increased approximately 15-fold with the addition of B vitamins and a supply of traces of air. Carbon dioxide enrichment hindered aflatoxin formation on a defined medium even in the presence of B vitamins, but small quantities (5 to 15 µg/litre) were formed when formic acid was added.

Carbon monoxide can also suppress growth of *A. flavus* and aflatoxin formation. Buchanan et al. (1985) reported that after growth of *A. flavus* for 32 days in cooked rice medium or raw pistachio nuts in an atmosphere containing 2% O<sub>2</sub> and 10% CO, aflatoxin production was <2% of the production in an atmosphere containing 2% O<sub>2</sub> or air without CO.

### Other *Aspergillus* Toxins

Ochratoxin is the only other *Aspergillus* toxin that has been studied under modified atmospheres. Paster et al. (1983) grew *A. ochraceus* on solid synthetic medium at 16°C±1°C for 14 days in atmospheres containing various concentrations of O<sub>2</sub> and CO<sub>2</sub> (Fig. 7). In atmospheres of 1% and 5% O<sub>2</sub> without CO<sub>2</sub>, ochratoxin production was similar to the air control. Increasing the O<sub>2</sub> level up to 40% reduced ochratoxin production by 75%, whereas at 60% O<sub>2</sub>, ochratoxin production was enhanced. In atmospheres of 10% and 20% CO<sub>2</sub>, ochratoxin production decreased when O<sub>2</sub> concentrations were below 20%, and was enhanced when they were 40% or 60%. Ochratoxin production was completely inhibited by 30% or more CO<sub>2</sub>, regardless of the oxygen concentration. Colony growth was partially inhibited at 60% CO<sub>2</sub>, and there was no growth in 80% CO<sub>2</sub>.

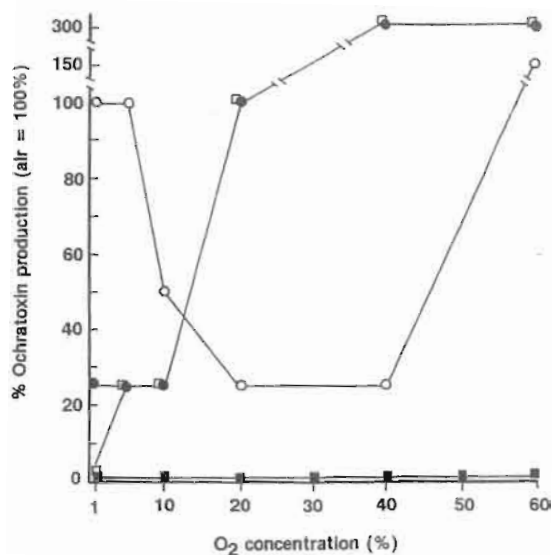
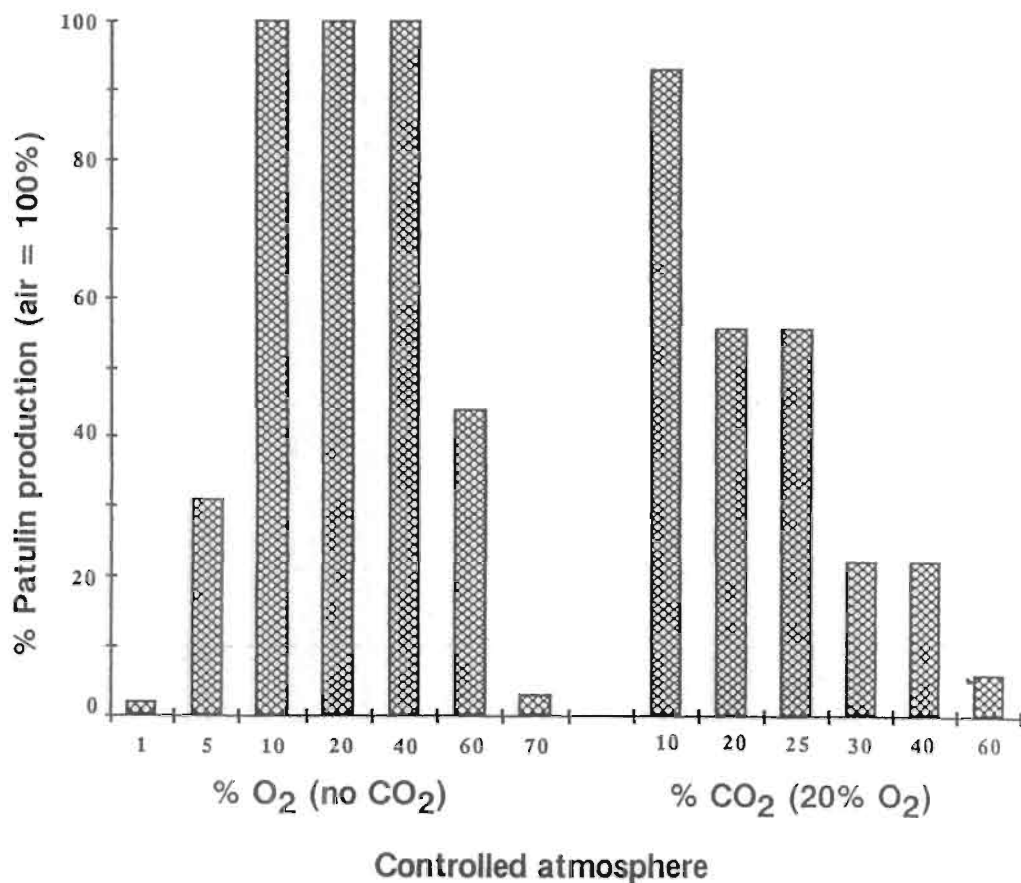


Fig. 7. Ochratoxin production by *Aspergillus ochraceus* grown under modified atmospheres on solid synthetic medium at 16°C±1°C for 14 days. Data of Paster et al. (1983). (○) 0% CO<sub>2</sub>; (●) 10% CO<sub>2</sub>; (□) 20% CO<sub>2</sub>; (■) 30% CO<sub>2</sub>.

### *Penicillium* Toxins

The effect of modified atmospheres on growth and toxin production by *Penicillium* species has not been thoroughly investigated, and there are few reports in the literature. However, in general, it can be assumed that elevated levels of CO<sub>2</sub> will inhibit toxin production to some degree. The effect of limiting O<sub>2</sub> supplies is less predictable. The effect of modified atmospheres on patulin production by *Penicillium patulum* (now *P. griseofulvum*) has been investigated by Paster and Lisker (1985) (Fig. 8). Cultures grown for 7 days in 1% or 5% O<sub>2</sub> but no CO<sub>2</sub> produced less toxin than the control (1 and 14 mg/40 mL compared with 45 mg/40 mL for the control). In 10% O<sub>2</sub> without CO<sub>2</sub> patulin production and mycelial dry weight were similar to the controls. Increasing the O<sub>2</sub> content to 60% or 70% decreased patulin production to 20 and 1.3 mg/40 mL respectively. Toxin production was also inhibited when CO<sub>2</sub> concentration was raised to 20% or more in the presence of 20% O<sub>2</sub>. Spores incubated in 100% CO<sub>2</sub> or N<sub>2</sub> did not germinate, but grew normally and produced patulin in amounts comparable to the controls when subsequently exposed to air.

Penicillic acid production by *Penicillium martensii* (now *P. aurantiogriseum*) was studied in mould inoculated maize over a



**Fig. 8.** Effects of controlled atmospheres on patulin production by *Penicillium aurantiogriseum* grown for 7 days in Czapek agar at 26°C. Data of Paster and Lisker (1985)

temperature range of 5° to 20°C in air and in atmospheres containing 20%, 40% or 60% CO<sub>2</sub>, with 20% O<sub>2</sub> (Lillehoj et al. 1972). Penicillic acid production decreased with increasing CO<sub>2</sub> concentration. Toxin production was greatest in air at 5°C, but was completely blocked at this temperature by 20% CO<sub>2</sub>, and by 40% CO<sub>2</sub> at 10°C over a four week incubation period.

### **Fusarium Toxins**

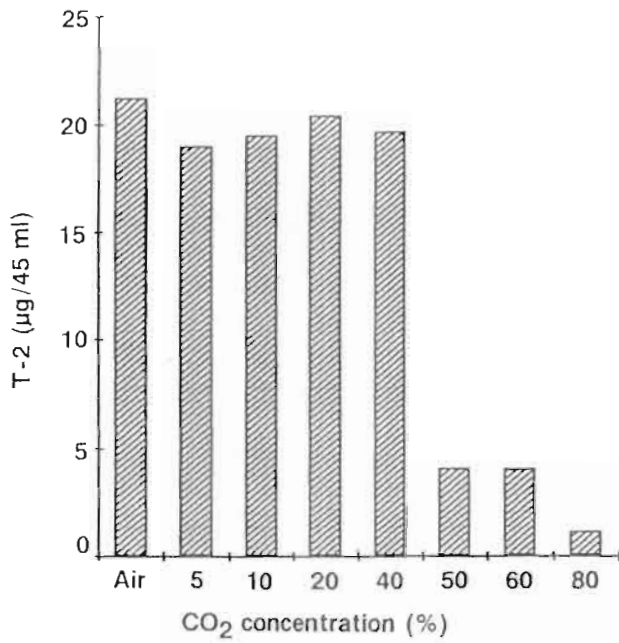
As with *Penicillium* species, little work has been done on the effects of modified atmospheres on toxin production by *Fusarium* species, although it is known that many *Fusarium* species are tolerant of low O<sub>2</sub> tensions and high CO<sub>2</sub> concentrations.

The effects of MA on production of T-2 toxin by *F. sporotrichioides* has been investigated both in synthetic media (Paster et al. 1986) and in remoistened irradiated maize (Paster and Menasherov, 1988). In the synthetic medium, T-2 production after 7 days at 27°C in an atmosphere of 50% CO<sub>2</sub>/20% O<sub>2</sub> was reduced

to about 20% of the air control (Fig. 9). At 60% and 80% CO<sub>2</sub> with 20% O<sub>2</sub>, there was a significant reduction in fungal growth. Toxin production in 80% CO<sub>2</sub> was only 1.1 µg/45 mL. When the same strain of *F. sporotrichioides* was grown for 14 days at 26°C±1°C on irradiated maize remoistened to 22% m.c., the production of T-2 toxin was totally inhibited under 60% CO<sub>2</sub>/20% O<sub>2</sub>, and only trace amounts were detected when the gas combination was 40% CO<sub>2</sub>/5% O<sub>2</sub> (Fig. 10). Fungal growth was not inhibited by any of the gas mixtures examined, and the growth rate was identical to that for grains kept under air.

### **Implications for CA Storage of Commodities**

Storage of commodities in controlled atmospheres containing high (>60%) levels of CO<sub>2</sub> to prevent insect infestation can also inhibit mould growth and mycotoxin production, while atmospheres of nitrogen need to contain <1% O<sub>2</sub> to retard fungal growth. Mycotoxin produc-



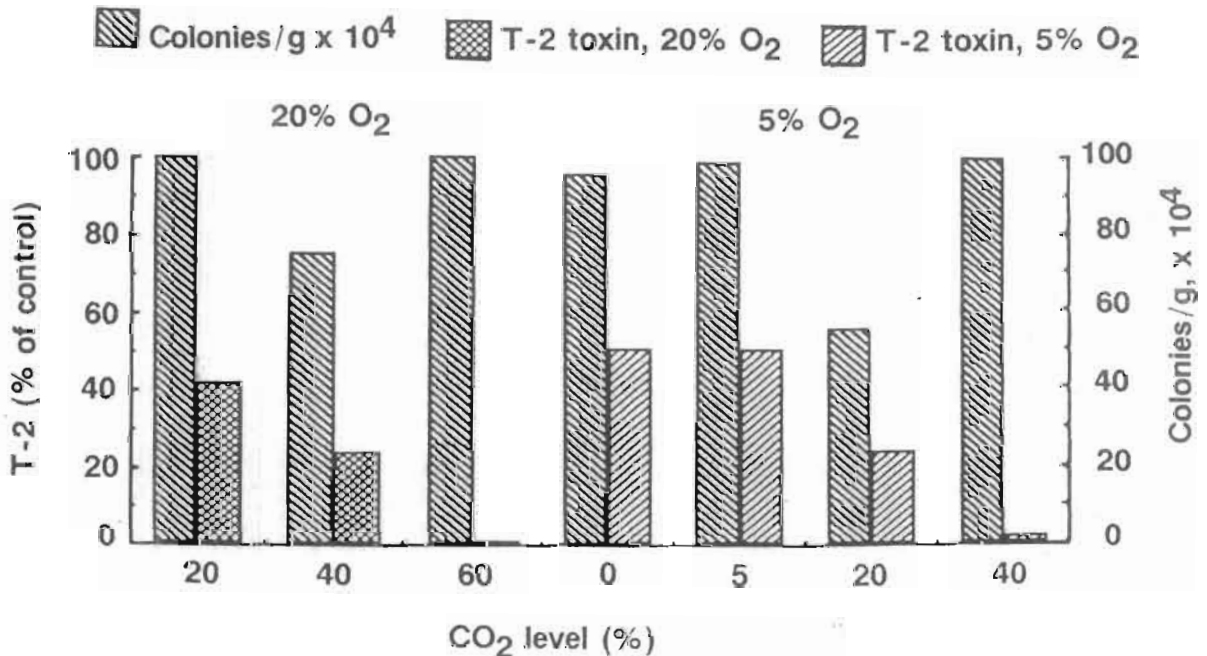
**Fig. 9.** T-2 toxin production by *Fusarium sporotrichioides* under controlled atmospheres containing various concentrations of CO<sub>2</sub> in 20% O<sub>2</sub>. Cultures were grown on potato dextrose agar for 7 days at 27°C. Data of Paster et al. (1986)

tion is more sensitive than fungal growth to CA conditions, but may still occur if other conditions (temperature and  $a_w$ ) are favourable.

Fungal deterioration cannot be completely prevented in high moisture commodities ( $a_w$  between about 0.90 and 0.80) by CA storage, as some fungi, particularly some *Fusarium*, *Mucor* and *Aspergillus* species, are tolerant of levels of 60–80% CO<sub>2</sub>. Yeasts and yeast-like fungi can also develop in CA stored high moisture commodities, causing rancidity and off odours. At very high moisture levels, above 0.90  $a_w$ , lactic acid bacteria may develop, irrespective of the concentrations of CO<sub>2</sub> or O<sub>2</sub> used in the storage atmosphere.

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**Fig. 10.** Effects of various levels of CO<sub>2</sub> and O<sub>2</sub> on colony counts of *Fusarium sporotrichioides* and T-2 toxin production in maize stored under modified atmospheres at 26°C±1°C for 14 days. Data of Paster and Menasherov (1988)

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# Biochemical Effects of Storage Atmospheres on Grain and Grain Quality

P.W. Gras\* and M.L. Bason\*

## *Abstract*

Developments in grain storage technology have meant that insect damage may now be reduced to minimal levels by modifying the storage atmosphere. In these atmospheres, the commodity and its environment (storage atmosphere, temperature, and water activity) are the major factors determining the changes in quality that take place during storage. Recent work has shown that, given knowledge of temperature, water activity, atmosphere, and duration of storage, changes in the quality of both paddy and milled rice (as measured by change in kernel yellowness) can be predicted. This model of change in quality may also be useful in understanding some aspects of postharvest yellowing of paddy rice and other damp-harvested commodities prior to storage. Other research has shown that the model can be used to predict quality changes in wheat, and that similar models may be applicable to maize (corn), barley, and mung and soybeans. Storage temperature has the greatest effect on quality, with water activity also very important. Carbon dioxide has generally little effect on grain quality, whilst increases in oxygen concentration have a small deleterious effect. A quantitative appreciation of the effects of these factors will allow design of storage systems that will best retain grain quality.

INSECT resistance to pesticides and consumer aversion to pesticide residues have prompted considerable research into alternative pest control techniques in the last decade. Developments in the technology of long-term storage of grain have meant that it is now possible to store dry cereals for long periods completely free of insect infestation without the use of residual pesticides. The use of either controlled atmospheres (CA) or fumigants in sealed storages offers economically attractive alternatives to pest control procedures based on the use of residual pesticides. In both CA and fumigation, an insecticidal atmosphere is maintained in a sealed storage enclosure for sufficient time to kill all insects present. The grain is subsequently maintained sealed in the enclosure, which provides a barrier to reinfestation. High levels of carbon dioxide,

low levels of oxygen, or the addition of phosphine can all be used as the insecticidal atmosphere.

When properly used, these techniques provide grain storage free from insects and residues. For example, the use of carbon dioxide sealed under plastic covers has been shown to be highly effective for milled rice and paddy rice (Annis et al. 1987). Long-term storage (greater than six months) using this technique has been implemented in Indonesia to provide buffer stocks and to help regulate domestic rice prices (Suharno 1986). The technique is being used with considerable success in Western Australia for the protection of wheat destined for export (Ripp 1984; Anon. 1987). In a properly constructed enclosure, no live insects can be found after storage, and grain held in this way seems to remain in good condition for long periods.

Until a timely review on the quantitative effects of controlled atmospheres (CA) on the

CSIRO Division of Plant Industry, Wheat Research Unit, P.O. Box 7, North Ryde, NSW 2113, Australia.

quality of stored grain (Banks 1981), there was a notable lack of quantitative information on the interaction between grain quality and the storage environment. The need for better estimates of the effects of oxygen and carbon dioxide on grain quality, and their interactions with temperature and moisture content were highlighted (Banks 1981; Faure 1986). Since Banks' review, considerable progress has been made in quantifying the effect of storage on quality changes in wheat, rice, maize, and barley for atmospheres containing lowered concentrations of oxygen or increased concentrations of carbon dioxide. Large scale trials, and in some cases commercial development of CA storage have been carried out in Australia (Anon. 1987), China (FAO 1982; Wang and Tang 1986), Indonesia (Suharno 1986), Singapore (Annis, personal communication), U.S.A. (Jay and D'Orazio 1983), Malaysia, the Philippines, and Thailand (Annis 1990). The aim of this paper is to briefly summarise some of this progress in the maintenance of quality, and to outline a possible general approach to understanding the changes in quality which take place in storage in the absence of insects and moulds.

There are many potential advantages of developing a quantitative understanding of the effect of storage on quality. Some of the more important aspects are listed below.

1. Changes in the quality of grain in storage could be predicted from knowledge of the grain storage temperature, moisture, atmosphere, and initial grain quality. This is particularly relevant for sealed storage where monitoring quality changes during storage is impractical.

2. This would then provide a rational basis for manipulation of the commodity or storage environment to enhance the development of desirable quality factors or to retard the development of undesirable traits (Gras et al. 1989). For example, in some parts of the Philippines, slightly aged rice ('Laon') is said to display better organoleptic properties and commands a price premium in the marketplace. Careful commodity management could exploit this opportunity for 'adding value' to rice in storage.

3. Quantitative data on the rate of change of grain quality are necessary for benefit-cost analyses of the various pest control strategies, such as fumigation, pesticide treatment, and CA storage. Work to relate quality to price is under

way in the Philippines (Umali and Duff 1988; Abansi and Duff 1988), but more research is required in this area. In practice, CA techniques involve higher capital outlay but can have lower maintenance costs and yield more grain of higher quality at the end of prolonged storage. Consequently, CA storage is usually considered a long-term storage option.

4. A quantitative description of the storage processes may provide a better understanding of the underlying chemical processes involved in grain quality change. This information will enable rational assessment of which strategies provide optimal management of grain in storage. This understanding may also be applicable to changes which take place during postharvest handling processes, such as during drying, handling while wet, or the delays before drying which are common in humid tropical regions. The model of the effects of drying processes on grain quality could be incorporated into models of grain drying processes to help optimise the design of grain drying systems.

## **Approaches to Quantifying Changes in Grain Quality**

The objective of quantifying quality data is to enable characterisation of changes in quality over the possible range of storage parameters. In CA storage, these parameters include the grain and quality of interest, storage temperature, grain moisture content, atmospheric composition, and storage period. In order to assess the effects of each factor, it is necessary to vary one storage factor whilst holding the others constant. This implies taking measurements of quality at various times throughout storage under each set of storage conditions. Further, there is a need for replication given the usual inherent variation in grain quality data. Consequently, any serious attempt to quantify the effect of storage conditions on grain quality requires a large body of experimental work. The data are then fitted to a mathematical model, which allows the calculation of quality changes for situations within the range of conditions covered by the experimental work.

There are two general approaches to this type of modelling. The first is empirical model fitting where the best model that can be found is applied to the data. An example of this approach is the model used by Ellis and

Roberts (1980a) to describe declining germination in various grains (equation 1),

$$v = a - t / (10^{b-c.m-d.T}) \quad (1)$$

where  $v$  is the probit of the percentage viability,  $t$  is storage time,  $m$  is moisture content (percent wet basis),  $T$  is temperature ( $^{\circ}\text{C}$ ),  $a$  is a constant dependent on the seed lot, and  $b, c, d$  are species dependent constants. Whilst this technique usually describes the data well, it provides no understanding of the underlying processes involved.

The second approach is the adoption of models with a theoretical basis. Recently, Gras et al. (1989) described yellowing in rice during storage using the model shown in equation (2),

$$k = ae^{b/T}(a_w)^c[\text{O}_2]^d \quad (2)$$

where  $k$  is the rate of change (Hunterlab b units/day),  $T$  is absolute temperature (K),  $a_w$  is water activity,  $[\text{O}_2]$  is the oxygen concentration in mole/ $\text{m}^3$ , and  $a, b, c, d$  are constants. This model is derived from simple chemical kinetics theory and is commonly used to describe the rate of a reaction in terms of the concentrations of reactants.

With either approach to modelling, the change in quality is quantified in terms of the storage conditions. The end result is an equation which can be used (subject to experimental limits and error estimates) to assess the effects of various storage conditions on changes in the quality factor of interest.

The methods of modelling represented by equations (1) and (2) incorporate the effects of water in different ways. The use of moisture content in equation (1) is attractive because moisture content is readily and commonly measured. The use of the water activity, as shown in equation (2), has the advantage that water activity reflects the actual availability of the water in the grain, both to microorganisms which might grow on the grain, and for chemical and biochemical processes within the grain. At water activities below 0.65, the growth of storage fungi is virtually eliminated, a very desirable state for grain that is to be stored for long periods of time.

The relation between moisture content and water activity is commodity dependent. This can be seen for such diverse crops as maize, flaxseed, milled rice, and white wheat, which

have moisture contents of 12.9, 7.9, 13.4, and 11.8% respectively at  $25^{\circ}\text{C}$  and 60% equilibrium relative humidity (Hukill 1963). Commercially, the moisture content of cereals has particular value for the grain trade because it provides a guide to the amount of dry matter being bought and sold. For traders or agencies involved in the storage of grain, the water activity ( $a_w$ ) or equilibrium relative humidity (ERH) of the grain is a more relevant quantity.

## Effect of CA Storage on Quality in Rice

### Germination

Viability of cereals during storage typically declines in a sigmoidal manner as a function of time. In most cases, this trend is well represented by the cumulative normal curve (Ellis and Roberts 1980b; Moore and Roos 1982). A commonly used measure of the rate of loss of germination is the reciprocal of the time for a 50% loss in viability ( $1/t_{50}$ ), calculated using the probit transformation (Finney 1980).

Roberts (1961) stored rice at a range of temperatures and moisture contents, and hermetically sealed in air, nitrogen, oxygen, and carbon dioxide, and measured loss of viability as a function of time. The effects of the storage gases were not included in the mathematical model, but it was found that lowered oxygen levels were generally beneficial, whereas the effect of carbon dioxide was ambiguous. More recently, Bason et al. (1987) stored two cultivars of Australian paddy at a range of temperatures, one water activity (0.6), and a graded series of oxygen and carbon dioxide levels that were held constant throughout storage. Grain viability data were fitted to the equations

$$\ln(t_{50}) = a + b/T + c[\text{O}_2] \quad (3)$$

and

$$\ln(t_{50}) = d + f/T + g[\text{CO}_2] \quad (4)$$

where  $[\text{O}_2]$  is the percent oxygen and  $[\text{CO}_2]$  is the percent carbon dioxide in the storage atmosphere (dry basis),  $T$  is absolute temperature, and  $a, b, c, d, f,$  and  $g$  are constants. It was found that low oxygen slightly increased the mean lifespan retention period, whereas

atmospheres containing carbon dioxide were slightly deleterious to lifespan compared to those without. The magnitude of these effects was minimal compared with that of temperature, and unlikely to be of sufficient concern to either warrant the technically difficult maintenance of low oxygen atmospheres (<1% oxygen) or prohibit the use of carbon dioxide in large scale storage.

Further work (unpublished) has indicated that the rate of loss of germination (i.e.,  $k = 1/t_{50}$ ) can be fitted to a model in the form of equation (2), which also incorporates the effects of water activity. As before, the effects of temperature and water activity were large compared with that of gas concentration. This implies that strategies to maintain grain viability should focus on cooling and drying, whilst altered atmospheres may be used to maintain insect control.

### Yellowness

Gras et al. (1989) stored two cultivars of milled rice under controlled conditions where the temperature range was 35°–60°C, water activity 0.4–0.8, oxygen concentrations 0.2–100% (dry basis), and carbon dioxide 7.5–60% (dry basis). They demonstrated that yellowing, as measured by the Hunterlab b value, was well described by the rate equation (2). The kinetics of the yellowing were consistent with non-enzymic browning as the cause of the overall increase in yellowness. The coefficients indicated that, over the range of storage conditions used, temperature was the major determinant of the rate of yellowing, followed by water activity. Oxygen concentration had a minor effect, and carbon dioxide no significant effect. This has allayed previous concerns that carbon dioxide may induce yellowing in rice.

Recent work (Bason et al. unpublished) has indicated that yellowing rate in stored paddy c.v. Pelde is very similar to that of milled Pelde. Further, the model predicts rates of yellowing reasonably consistent with the limited data available in the literature. These results suggest that the model may be applied generally to other cultivars of rice, but further work is required to confirm this.

The model has several applications. For example, the common problem of 'stackburn' results from heating in paddy which has been allowed to stand in moist piles. The model

indicates that temperature is the most important factor in yellowing of grain, so some method of cooling the grain bulk (for example, by increasing the surface area to volume ratio or by turning the grain piles) would reduce the incidence of the problem when drying is impossible. Alternatively, controlled heating could be used to accelerate the formation of 'aged' characteristics (such as reduced stickiness) which are preferred in countries such as the Philippines and Singapore. The problems of yellowing before drying are highlighted by the model, which predicts that significant yellowing can be expected in very wet rice held for as little as 24 hours at 45°C. This can be judged from Figure 1, where the calculated time to minimum discernible change in colour (0.3 b\* units; Billmeyer 1962) is plotted against the storage temperature for selected storage water activities.

Under the conditions of the studies described above, the growth of fungus could not have been a factor in the colour development. This is not to say that fungal infection does not play a part in the yellowing process. Indeed, fungal infection would be expected to lead to the accumulation of reducing sugars and amino groups as the result of the action of amylolytic and proteolytic enzymes released during the normal course of the growth of the fungus. The increased concentration of the reacting materials would be expected to lead to accelerated

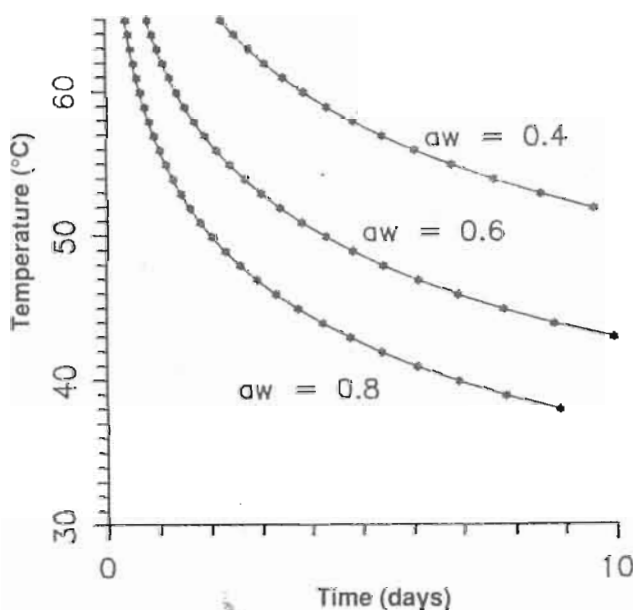


Fig. 1. Calculated time to minimum perceptible change in colour (0.3 Hunterlab 'b' units).

yellowing in the affected kernels. This is probably the basis of the successful 'Potential Yellows' test (Phillips et al. 1984, 1988), in which incubation at elevated temperature and water activity is used to predict the proportion of grains which might turn visibly yellow during extended storage.

### Available Lysine Content

Lysine is the first limiting amino acid in rice (Juliano 1985). Widespread experience in the livestock industry has shown that not all the lysine in some cereals and feedstuffs is biologically available (Sauer and Ozimek 1986). Measurements of 'available lysine' provide an estimation of the lysine available for metabolism (Hurrell and Carpenter 1976; Walker 1979). Although controversial, such measurements are routinely made in the livestock industry. Measurements of available lysine in samples of milled rice with a range of yellowness resulting from varying periods of storage confirmed that changes in the yellowness of the rice (Minolta  $b^*$  value) were closely correlated ( $r = -0.77$ , 32 samples) with the levels of available lysine (Fig. 2). The loss of available lysine concurrent with the development of the yellow coloration provides support for non-enzymic browning as the mechanism of the yellowing reaction. This reaction is widely observed in many food products and consists of a complex series of reactions between protein or non-protein amino groups and reducing sugars. It requires some mobility of the reacting species, and

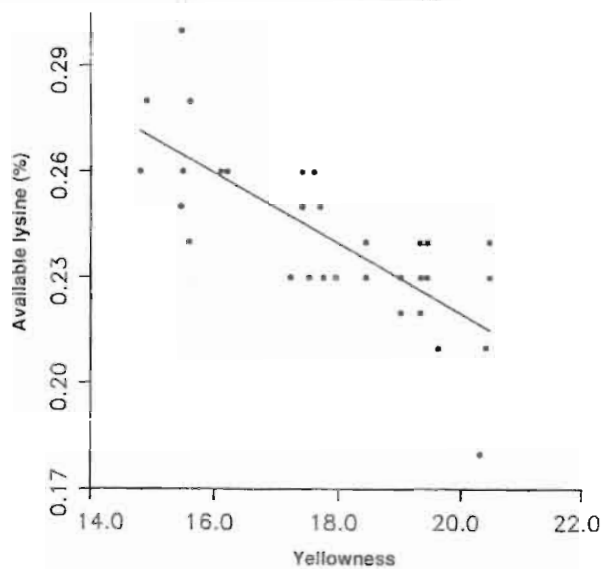


Fig. 2. Relation between available lysine and yellowness (Minolta  $b^*$  units) in milled rice stored under a range of controlled conditions.

would be assisted by elevated levels of reducing sugars and basic amino acids. These conditions exist even in sound grain, and are consistent with the kinetics observed.

The results also imply that there may be some loss in the nutritive value of rice which has yellowed extensively. This has public health implications, particularly for children on marginal diets, in areas where rice forms the major part of the diet.

### Sensory Evaluation

The acceptability of the product to the consumer is the ultimate quality test of any product. Recently, sensory evaluation has been carried out using rice consumers in the Philippines to assess the effects of storage under a range of temperatures, water activities, and concentrations of oxygen and carbon dioxide on rice acceptability (Gras et al., 1990). Preliminary analyses of the results suggest that panel ranked preference data can be fitted to the same form of model as equation (2). In this case, no significant effect of either oxygen or carbon dioxide could be detected, but well over 90% of the variation in ranked preference scores was explained by the temperature and water activity components. Yanai et al. (1979) have reported slightly superior retention of the organoleptic properties of rice when stored in nitrogen or carbon dioxide rather than in air, which is consistent with the results given here.

In both of the above studies, altered atmospheres did not lower the perceived quality of stored rice. On the results so far obtained, the increasing use of carbon dioxide as a storage atmosphere for rice seems well justified.

### Other Quality Parameters

Other quality parameters of rice include milling yield, proportion of broken grains, cooking parameters (water uptake, volume expansion, cooking time, hardness, stickiness, etc.), gelatinisation temperature, gel consistency, amylose content, and fat acidity. The quantitative effect of altered atmospheres on these properties is under investigation. The few data in the literature suggest that the effect is minimal (Iwasaki and Tani 1967; Yanai et al. 1979; Ory et al. 1980), but further work is required.

## **Effect of CA Storage on Quality in Maize**

### **Germination**

Bason et al. (1987) stored white dent maize at a range of temperatures (35°–60°C) and one water activity (0.6) under a graded series of carbon dioxide levels (7.5–60%) which were held constant throughout storage. The data were fitted to equation (4). It was found that carbon dioxide had no significant effect on the mean lifespan retention period. Recent results (unpublished) have indicated that lowered oxygen levels generally extend lifespan in this cultivar. However, under some conditions the lowest oxygen level used (0.2%) gave lower than expected lifespans, presumably because there was insufficient oxygen to support respiration.

### **Physical Properties**

There is still a lack of information on the effect of controlled atmospheres on the physical properties of maize. In large scale experiments in the Philippines, stacks of bagged white flint maize stored under carbon dioxide showed an average percentage weight loss of 0.1% compared to 2.0% for similar storage under air (Esteves et al. 1988). This was due to effective insect control under carbon dioxide but not in the control stacks stored in air. Other associated physical changes included a significantly larger amount of yellowing and increase in redness for grain stored in air compared with that stored in carbon dioxide.

In tropical regions, maize is often milled into grits and consumed much like rice. The yield of grits is an important physical quality parameter, since it reflects the amount of edible material that can be recovered from the maize. Laboratory studies (unpublished) have indicated that the yield of edible grits increases with storage time. The effect of altered atmospheres on yield of maize grits is under investigation, but as yet is not established.

### **Chemical Properties**

Sowumni et al. (1982) stored yellow maize under nitrogen in small airtight silos and in air for three months. By comparison with storage in air, storage under nitrogen retarded changes

in proximate constituents, carbohydrate fractions, and lipids. However, the moisture content increased in the samples stored in air but not in nitrogen, and therefore the changes may have been due to a greater water activity rather than a lower oxygen content. Esteves et al. (1988) found a significantly lower increase in fat acidity of white maize stored in carbon dioxide compared with air.

Further work is required under more tightly controlled conditions to quantify the effect of CA storage on all aspects of maize quality. It would appear likely, however, that storage under either low oxygen or high carbon dioxide levels is not worse than storage under air, and therefore is an acceptable storage option for this grain in terms of quality preservation.

## **Effect of CA Storage on Quality in Wheat**

### **Germination**

In accelerated aging experiments, Banks and Gras (1982) exposed three cultivars of wheat to a range of oxygen concentrations (0.2%–100%) and to one atmosphere containing 60% carbon dioxide. The effect of each gas mixture was determined at three water activities (0.4, 0.6, 0.8) at 60°C. Average lifespan generally increased with decreasing oxygen concentration at all three water activities. A model was developed which satisfactorily quantified the effects of oxygen and water activity on viability. There was a linear relation between viability and the logarithm of the oxygen concentration, and between the viability and the logarithm of the water activity, which is consistent with the results for rice and maize germination. Storage under carbon dioxide was slightly detrimental to retention of viability, but the quantitative effect could not be determined from the single atmosphere used. Data from a more extensive range of CA storage experiments are currently being compiled.

### **Dough and Baking Quality**

Subsequent work by Gras (unpublished data) has demonstrated that there is a correlation between germination and various dough and baking properties in wheat. Storage under conditions that were detrimental to germination

also led to a longer time to peak dough development and lower peak resistance in mixograph tests, and reduced loaf volume in microbaking tests. Quantification of the relative contributions of storage time, temperature, water activity, and gaseous environment is in progress, but it appears that the storage gas composition has only a minor effect on wheat quality.

## **Effect of CA Storage on Quality in Barley**

### **Germination**

Barley needs to be at least 95% viable to be classified as malting grade. The effect of storage on germination is therefore critical to the value of the product. Shejbal and Di Maggio (1976) reported longer retention of viability in barley stored in nitrogen than when stored in air. Duff et al. (1986) stored three cultivars of barley under a range of oxygen concentrations (0.2%–100%) and one atmosphere containing 60% carbon dioxide in air, and at three water activities (0.4, 0.6, 0.8) at 47°C. All varieties indicated an inverse relation between lifespan and oxygen concentration, consistent with results for the other cereals mentioned previously. In similar experiments over an extended range of temperatures (35°–60°C), Konik and Gras (1988) reported a temperature dependence in the effect of carbon dioxide in that it may be deleterious at higher storage temperatures but not at 35°C. Whilst lowered oxygen generally increased lifespan, it was noted that grain viability was often retained for less time in 0.2% than in 2.0% oxygen, similar to observations for maize. There is a need for further research to determine minimum oxygen requirements in barley. It is worth noting that the effect of the gaseous atmosphere was much smaller than that of storage temperature and water activity.

### **Malting Properties**

Storey et al. (1977) and Storey (1980) reported storing barley under reduced oxygen conditions and in air at 27°C and 50% RH for up to 6 months. Results were somewhat inconsistent, but overall the reduced oxygen environment appeared neither beneficial nor detrimental to malt quality. Gras et al. (1988) reported that the

malting quality of barley stored in carbon dioxide under normal storage temperatures (up to 35°C) and water activities (up to 0.6) was at least as good as that of barley stored under similar conditions in air. Therefore, storage of barley under carbon dioxide appears to be an acceptable option under normal conditions.

### **Alternative Insecticidal Atmospheres**

There are various fumigants available that provide effective insect control within a sealed enclosure. The advantages of low oxygen or carbon dioxide enriched atmospheres are that their effect on quality is minimal and they leave no toxic residues on the grain. Recently phosphine has been used in place of conventional CA gases. There has, as yet, been no systematic study of the effects of phosphine (or other fumigants for that matter) on grain quality: this is urgently required. •

## **Conclusions**

Quantification of the changes in grain quality have been particularly useful in the study of yellowing of rice in storage. These studies suggest that the mechanism of the yellowing may be non-enzymic browning, and that this process may be independent of direct yellowing resulting from the growth of fungi. It is quite possible that residual enzymes, small peptides, and simple sugars resulting from fungal invasion may thus potentiate the yellowing process. It is equally clear that sound rice will become yellowed given sufficient time under normal tropical storage conditions. The quantitative model of the yellowing of rice may also be useful for the prediction of quality changes to be expected from drying, and also for predicting the consequences of poor postharvest handling.

Quantification of the effects of storing cereals under controlled atmospheres has provided valuable information on the utility of these atmospheres for maintaining grain quality. Practical storage atmospheres with low levels of oxygen or high levels of carbon dioxide have only minimal effects on the quality of rice, maize, wheat, and barley. In general, storage under atmospheres containing reduced concentrations of oxygen provides slightly improved retention of quality, whereas carbon dioxide can reduce viability in some cases,



most importantly in barley at high temperatures and water activities. The effects are not sufficiently large, however, to be of commercial concern in most cases. Thus, from the quality perspective, the increasing use of these atmospheres as an alternative insect control technique is quite acceptable. The effects of other insecticidal atmospheres such as phosphine on stored grain quality requires further research.

## Acknowledgments

The authors express their gratitude to Dr H.J. Banks of the Stored Grain Research Laboratory, CSIRO Division of Entomology, who provided advice and assistance in work reported in this paper, and to Ms Sharee McCammon, CSIRO Division of Plant Industry and Mrs Lyn Esteves, NAPHIRE, Philippines for technical assistance. This work was supported by grants from the Australian Centre for International Agricultural Research (ACIAR), the Wheat Industry Research Council (WIRC), and the Barley Industry Research Council (BIRC).

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## Report on Session 2: Biological Responses to Treatment with Gases

Chairman: Dr E. Jay, U.S. Postharvest Consultant  
Rapporteur: Dr M. Sidik, Bulog, Indonesia

THE first paper in this session was presented by Dr C. Reichmuth, Institute for Stored-Product Protection, Ministry of Agriculture, Berlin, Federal Republic of Germany (FRG). It covered the effects of toxic gas treatments on arthropods and their impact on the environment. The introduction included the qualities necessary for a chemical to become suitable for use as a fumigant.

His discussion on hydrogen cyanide included coverage of its use to further develop the Ct concept, which was initially postulated in 1924.

This was followed by a treatment of the widely used fumigant, methyl bromide, including information on resistance to this compound.

A discussion on the use of phosphine followed, including its advantages and disadvantages and some Ct products developed for this fumigant by several researchers. Exposure time is the important factor to be considered when using this fumigant as high concentrations can lead to narcosis. Studies on phosphine resistance have led to the discovery that those insects exhibiting resistance take up less of the fumigant than susceptible insects.

The author conducted studies on the effects of controlled atmospheres on immature *Sitophilus granarius* at low temperatures. At 15°C an LT95 was obtained only after 45 days when the insects were exposed to 1% O<sub>2</sub> and 99% N<sub>2</sub>. The LT95 at this temperature was reduced to 27 days when the immatures were exposed to an atmosphere containing 90% CO<sub>2</sub>, 8% N<sub>2</sub> and 2% O<sub>2</sub>.

The author has been interested in concentrations of fumigants found outside treated flour mills, grain storage facilities, and warehouses, and has taken measurements relating to this in the FRG for the past 10 years. He has found that the concentration of phosphine rarely exceeds 5 ppm outside a line 10 m from the treated structure.

A thorough discussion of the effects of fumigants leaking from these buildings was presented. The problem of fumigants leaking from storage facilities is not limited to the FRG and more emphasis will have to be placed on the containment of gases inside the structures being treated in the near future in order to satisfy national, state, and local safety regulations.

The second paper in this session was written and presented by Dr A.D. Hocking of the CSIRO Division of Food Processing, Sydney, Australia. It was entitled 'Responses of Microorganisms to Modified Atmospheres'.

Dr Hocking reported that the introduction of controlled atmospheres for preventing insect infestation of commodities also provided a certain degree of protection against fungal invasion and subsequent mycotoxin production. Among physical factors affecting mould development in stored grains, it seems that temperature, relative humidity, and moisture content are very important in determining storage characteristics of maize, peanuts, wheat, and rice.

Commodities stored under controlled atmospheres containing high levels of carbon dioxide (>60%) were protected to some extent from mould development and

mycotoxin production, while atmospheres of nitrogen need to contain <1% oxygen to retard fungal growth, as nitrogen itself has no inhibitory effects on fungi.

Various common species of field and storage fungi were able to grow in commodities stored under modified atmospheres. These included *Aspergillus*, *Fusarium*, *Penicillium*, and *Mucor* which develop in high moisture commodities (water activity factor 0.80–0.90). Their development could not be completely prevented by controlled atmosphere storage as some of these species were tolerant to high concentrations of carbon dioxide (60–80%).

Mycotoxin production, however, was more sensitive than fungal growth to controlled atmosphere conditions, although it might occur if temperature and water activity were favourable. The production of mycotoxins by some species of *Fusarium*, *Aspergillus*, and *Penicillium* was significantly reduced if high levels of carbon dioxide could be achieved and maintained.

The final paper in this session was written by Dr P.W. Gras and Mr M. Bason, CSIRO Division of Plant Industry, Sydney, Australia, and presented by Dr Gras. It dealt with the biochemical effects of storage atmospheres on grain and grain quality.

The paper revealed that quantifying the effects of storage on the quality of grain was very important in predicting changes in quality of stored grain. We need to know such things as the initial and final quality of the grain, temperature, moisture content, and the storage atmosphere. Quantification of effects will also provide a rational basis for manipulation of the commodity or storage environment to enhance the development of desirable qualities. Cost-benefit analyses of the various pest control strategies, such as fumigation, pesticide treatment, or use of controlled atmospheres could be carried out if quantitative data on the rate of change of grain quality were known.

Two types of mathematical models have been used to quantify changes in grain quality: empirical models and models having a theoretical basis. The modelling approach requires accurate information on water absorption isotherms and rates of yellowing of a wide range of varieties if it is applied to stored rice. The results of this mathematical modelling in predicting the changes in rice quality suggest that yellowing of rice in storage occurs by a process which is independent of direct yellowing resulting from the growth of fungi. It is quite possible that residual enzymes, small peptides, and simple sucrose resulting from fungal invasion might be present in quantities larger than usual and thus potentiate the yellowing process, but it is equally clear that even sound rice will eventually become yellowed given sufficient time under tropical storage conditions.

Controlled atmospheres with low levels of oxygen or high concentrations of carbon dioxide have only minor effects on the quality of rice, maize, wheat, and barley, in terms of germination, and physical and chemical properties. Generally, improved retention of quality of grain was observed if it was stored under low oxygen concentrations, whereas carbon dioxide could reduce viability in some cases, most importantly in barley at high temperatures and water activities. However, these effects were not of economic significance in most cases.

Therefore, the increasing use of controlled atmospheres as an alternative insect control measure appears warranted in terms of quality effects. Further research is needed on the effects of other insecticidal atmospheres, such as phosphine, on the quality of stored grain.

The evening workshop on topics presented in session 2 was lightly attended. However, the participants enjoyed a spirited discussion led by Dr Gras. Recommendations developed at this workshop include:

1. Efforts should be made to widely inform farmers that they should keep their grain as cool and as dry as possible.
2. Newsletters relating to grain storage should be translated into local languages and efforts made to distribute these translated newsletters to as many farmers as is possible.

# **Physical Processes in Fumigation and CA Storage**

# Behaviour of Gases in Grain Storages

H.J. Banks\*

## *Abstract*

Understanding gas behaviour is fundamental to theory and practice of both fumigation and controlled atmosphere (CA) techniques. The actual gaseous concentration to which pests are exposed determines the outcome of the treatment. This is affected by processes on three length scales, all of which interact to give the observed concentration distribution. On the molecular level, sorption/desorption and diffusional effects predominate; on the scale of the stored grains, forced or natural dispersion is important; and on the scale of the store itself, gas interchange with the environment is the main influence. This paper reviews progress towards a sound qualitative and quantitative appreciation of the fate of gases (CO<sub>2</sub>, methyl bromide, nitrogen, oxygen, phosphine) applied to stored grain. Some of the sorption/desorption effects have been quantified recently, but new, unexpected observations relating to fumigant residues show that more work is required before an acceptable mathematical model for this can be elaborated. Larger scale phenomena are better understood qualitatively, although full-scale data for testing of theoretically based models are scarce. Examples are given of neglected and recently noted aspects of behaviour of gases in grain storages relevant to pest control by CA and fumigation, including evolution of methyl chloride during methyl bromide treatments and rapid sorption of phosphine by paddy rice.

A proper appreciation of the techniques of controlled atmospheres (CA) and fumigation must be based on an understanding of the behaviour of gases: how gases disperse in stores and interact with the commodity or pests. The objective is to be able to describe the variation in concentration over time of the active agent or agents at any point within the treatment enclosure, since the concentration-time regimen experienced by pests determines the success or failure of the treatment. Even in regions free of pests, it is necessary to know the concentration and its variation, as this affects production of residues, and gain or loss into regions that are infested or must otherwise be protected.

The problem of describing gas behaviour is complex. Relevant phenomena include sorp-

tion/desorption, diffusion, natural convection and, often, forced distribution. These phenomena, in turn, are influenced by factors such the grain condition, type, history, grade, temperature, moisture content, etc., how the grain is stored (e.g. bag stack or bulk), shape of store, and external inputs such as gas quantities added, use of fans and environmental effects on the enclosure. Furthermore, there are interactions between the various phenomena. For instance, solar heating of an enclosure heats part of the stored commodity and alters internal convection currents, both of which will affect the rate and magnitude of sorption. Nevertheless, without knowledge of the details of the gas-related processes involved in fumigation and CA, treatments can at best be carried out only by recipe. They cannot be predictably optimised for new situations or changed regulations; treatment failures often cannot be explained and appropriate remedial action

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\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

taken; particular instructions cannot be justified; and research and development of new techniques cannot be rationally planned or carried out.

This paper reviews current knowledge on the behaviour of gases relevant to CA and fumigation. Only processes involving cereal grain within an enclosure are considered. Related phenomena exterior to the enclosure — such as the fate of vented fumigant in the environment — are not considered. The processes described, in principle, operate with any stored commodity, though parameter values may change. A general outline of phenomena and leading references are given, rather than detail and a comprehensive review. Mathematical approaches to the description of gas behaviour in fumigation and CA will be referred to without mathematical detail. Many persons find mathematical modelling abstruse and of no obvious utility. However, it should be noted that it does provide a means of integrating knowledge into a formal framework and, inevitably, will affect thinking on fumigation and CA. Successes and failures in modelling serve to measure how close or far away we are to understanding real processes.

The descriptive system used in this paper is based on consideration of phenomena occurring on different 'length scales', usually in isolation. Various phenomena are influenced by different scales. Three scales are used, summarised in Table 1. These are: the 'molecular' scale, where chemical interactions and the movement of individual molecules are important; the 'grain' scale, where the arrangement of individual grains and local inhomogeneities are important; and the 'store' scale, where large-scale effects such as wind and fan-forced ventilation predominate. This view of gas behaviour is similar to that on which the mathematical modelling must be based. It should thus provide a common basis on which practitioners of CA and fumigations, and theoreticians, can talk.

## Molecular Scale Phenomena

Phenomena of particular interest to fumigation and CA on the molecular length scale involve gas diffusion and film permeation, sorption/desorption effects and chemical reaction. All of these directly influence important variables such as the residues formed by treatments,

**Table 1.** Length-scales

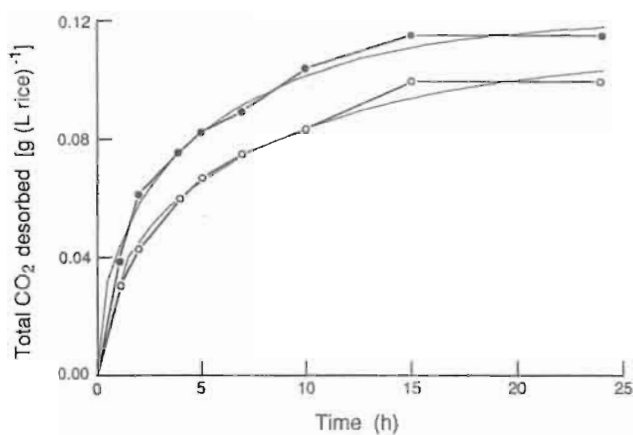
Names used	Typical dimension (m)	Typical phenomena
Molecular scale	$10^{-10}$ – $10^{-5}$	Diffusion, chemical reaction, physical sorption
Grain scale	$10^{-3}$ – $1$	Convection, boundary layer problems, local effects of inhomogeneities
Storage scale	10–100	Bulk air movement, environmental effects

the concentration of fumigant or CA composition experienced by target pests, and how rapidly gases are dissipated after a treatment.

## Diffusion

The phenomenon of diffusion controls the travel of individual gas molecules over short distances, typically less than about 1 mm. The rate at which the gas disperses by diffusion depends on temperature and the environment, usually described in terms of the concentration gradient of the gas and a temperature-dependent diffusion coefficient,  $D$ . The magnitude of  $D$  has a major influence on fumigation and CA. It determines the rate at which gases travel into and within grains (and insects) and thus the rate at which fumigant molecules are taken out of the free gas phase, either temporarily, through reversible sorption, or permanently, by irreversible chemical reaction, giving alteration products or fixed residues of some kind. Removal from the free gas phase reduces the gas concentration available to act on pests. Note, however, that the magnitude of  $D$  does not directly determine the magnitude of a process such as sorption, only the rate of approach to completion. The desorption of  $\text{CO}_2$  from grains (Fig. 1) is an example of a diffusion-controlled system.

In fumigation and CA, four principal values of  $D$  for a given gas are important: that in air; the effective value in grain in a grain mass; the apparent value within a grain; and the value for permeation through plastic film. Table 2 gives



**Fig. 1.** Desorption of  $\text{CO}_2$  from brown (O) and milled (●) rice (data of Mitsuda et al. 1973). Faint curves show fitted trend based on diffusion kinetics.

some values of  $D$  for the first three of these. The effective rate through bulk grain appears to be about one-third that in free air. It should be noted that the values of  $D$  given for travel within a single grain are derived from curve-fitting results of fumigations under controlled conditions. Because of the simplifications assumed in this analysis, the values obtained are approximate only. Nevertheless, they are the best estimates available until experiments conducted specifically to measure  $D$  are carried out. The effect of temperature on  $D$  for unrestricted gases is predictable theoretically. The variation with temperature for diffusion within a single grain has not been determined for any cereal but is known for phosphine into hazelnuts (Noack et al. 1984).

Permeation through films is of topical interest with the development of film packaging on both a small (ca 1 kg retail packs) and large

**Table 2.** Diffusion coefficients ( $\text{m}^2/\text{s}$ ) for fumigants in grain and air ( $25^\circ\text{C}$ )

Medium	$\text{PH}_3$	MeBr	$\text{CO}_2$
in air <sup>a</sup>	$1.7 \times 10^{-5}$	$0.94 \times 10^{-5}$	$1.5 \times 10^{-5}$
in bulk grain <sup>b</sup>	$5.3 \times 10^{-6}$	—	$4.7 \times 10^{-6}$
within milled <i>japonica</i> rice <sup>c</sup>	$5.9 \times 10^{-12}$	—	$2.2 \times 10^{-12}$

<sup>a</sup> Calculated from data in Weast (1986) and Barker (1974) using Graham's Law and assuming  $D$  proportional to absolute temperature.

<sup>b</sup> from Barker (1974) and Singh et al. (1984) with adjustment for temperature. Values will include some contribution from sorption phenomena.

<sup>c</sup> from data in Banks (1986), assuming rice to be of spherical grains, diameter 1.8 mm.

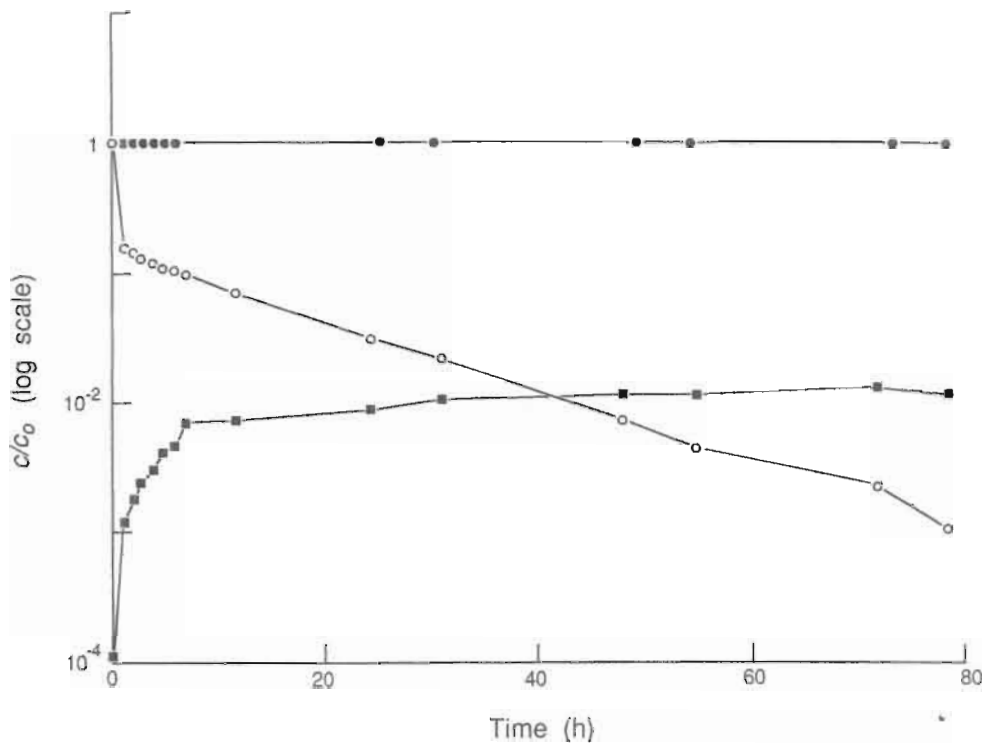
(ca 100 t bag stacks) scale as a means of protecting grain. The concentration of gases within the pack or enclosure is dependent on diffusion across the film and thus on the diffusion coefficient, in this situation referred to as the permeation coefficient or constant. A large number of films are available with a wide range of permeabilities to atmospheric gases. The permeation coefficients for fumigants are known for only a few films (Williams et al. 1980; Phillips and Nelson 1957), but those for atmospheric gases have been determined for a wide variety of membranes (Bixler and Smeeting 1971). These coefficients vary somewhat with both humidity and temperature but this variation is seldom described. It is small compared with the differences between films and the effect of thickness.

Grains appear to be solid particles. However, they are actually microporous, having small channels or pores running through them. The diameter of these pores has been estimated for wheat ( $10^{-8}$ – $10^{-4}$  m (Stawinski and Szot 1976)) and rice (half volume being less than  $3.5 \times 10^{-8}$  m (Mitsuda and Yamamoto 1980)). The effective diffusion coefficient for travel within a grain is a combination of diffusion through those pores and presumably from permeation through liquid and solid components and from physical sorption. The size of these pores is relevant to fumigation. It may restrict entry of large molecules. For instance, sulphur hexafluoride is almost completely unadsorbed (Fig. 2) suggesting that it cannot penetrate into the capillary space important for sorption of small fumigant molecules and atmospheric gases. Fumigants with boiling points at or above ambient temperatures, e.g. hydrogen cyanide, may liquefy within the pores ('capillary condensation') resulting in high losses through sorption. Overall, the effect of the microporous nature of grain in fumigation has largely been ignored, but deserves detailed research attention.

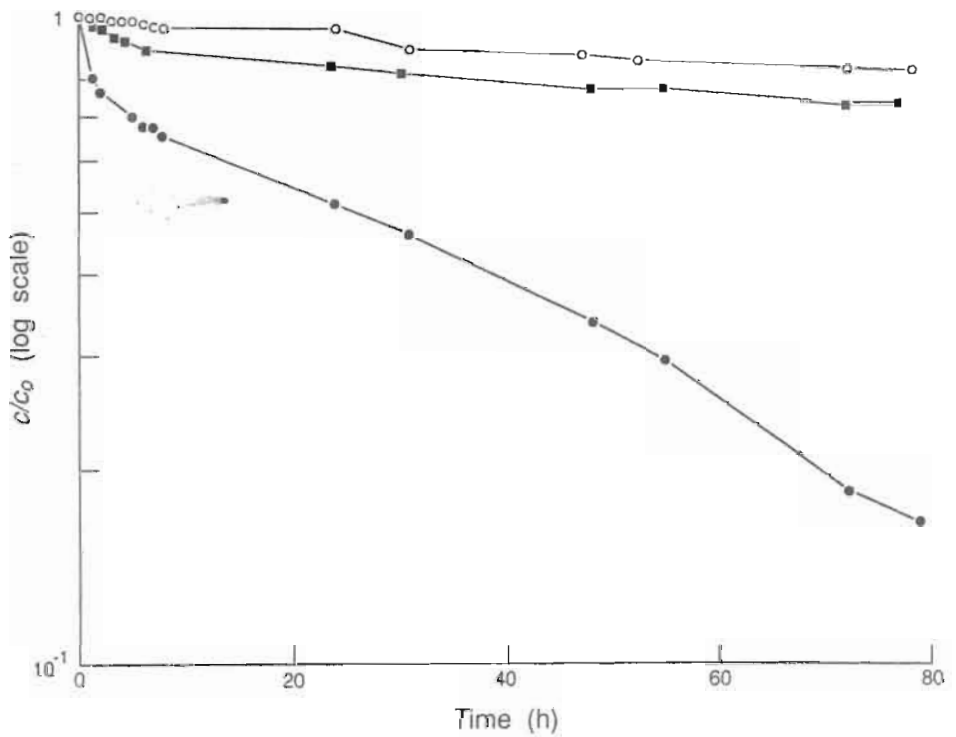
### Sorption, Reaction, and Residues

The rate of uptake and release of gas into grain may be limited either by diffusion or by the rate of reaction with grain constituents. Thus, the loss of methyl bromide and phosphine from the gas phase of a closed system containing grain is typically very rapid, initially corresponding to diffusion-dependent uptake and declining to a semilogarithmic decay after a few hours (e.g. Figs 2 and 3) when reaction predominates.





**Fig. 2.** Uptake of sulphur hexafluoride on whole wheat (●) and methyl bromide (○) with concurrent release of methyl chloride (■) by ground wheat. 25°C, 60% relative humidity (H.J. Banks and J.A. Gorman, unpublished data).



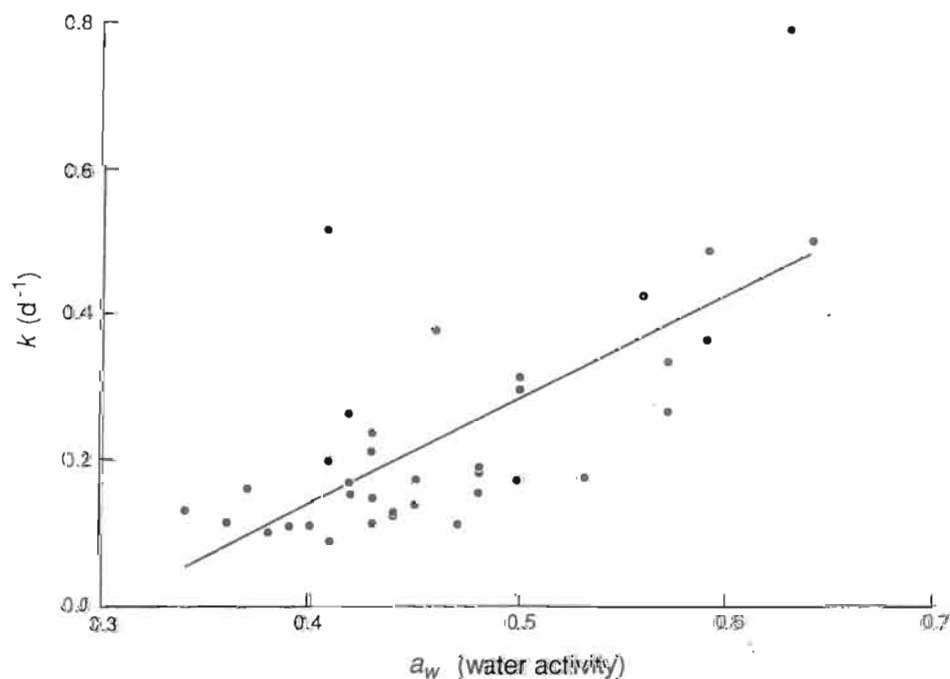
**Fig. 3.** Phosphine uptake by paddy (●), brown (■), and milled (○) rice. Initial dosage 3 g/m<sup>3</sup>, 25°C, 60% relative humidity with 70 g rice in 100 mL vessel (H.J. Banks and J.A. Gorman, unpublished data).

The magnitude of uptake of gas is determined by the type of grain, its condition, and the relative quantities of gas to grain. It is described by a mathematical expression, a 'sorption isotherm', relating the concentration in the gas phase to that in the solid. These are equivalent to the more familiar water sorption isotherms. Apparent sorption isotherms are available for methyl bromide and phosphine (see Banks 1986). In neither case are they truly sorption isotherms. Some of the material is taken up irreversibly and cannot be counted as unchanged, yet no allowance has been made for this. A crude isotherm has been given for CO<sub>2</sub> on rice (Mitsuda et al. 1973), but isotherms for oxygen or nitrogen on grain are not available.

Indeed, detailed data on uptake of oxygen and nitrogen into grain is generally not available, though it is known that some oxygen desorbs only slowly from grain (Bailey 1965). Complete desorption takes about 24 hours after the atmosphere is changed from air to nitrogen. After a rapid purge of a grain mass with nitrogen, if the system remains sealed, the interstitial

oxygen concentration will rise to about 1%. Carbon dioxide is absorbed more extensively on grain, with the rate apparently diffusion controlled. Uptake is complete in about 48 hours on wheat (e.g. Mitsuda et al. 1973). Crude figures are available for the quantity of CO<sub>2</sub> sorbed on several grains (Mitsuda et al. 1973), but systematic studies are lacking. Typically, about 10% of the applied CO<sub>2</sub> is absorbed by grains. In all probability, the mechanism of sorption is largely by reversible chemical bonding to basic groups in proteins (Mitsuda et al. 1975).

The uptake of phosphine has in the past been regarded as part simple reversible physical sorption and part loss by oxidation leading to innocuous residues of phosphorus oxyacids such as phosphate. The recent WHO review (Anon. 1988) discusses the fate of phosphine in these terms. However, some other pathways apparently operate too. Unchanged phosphine, or materials releasing unchanged phosphine on treatment, can be detected in grain long after exposure (Dumas 1980), suggesting that at least



**Fig. 4.** Reaction rate constants ( $k$ ) for sorption of phosphine on samples of wheat obtained soon after harvest from various receipt sites in New South Wales, shown as a function of water activity ( $a_w$ ). Line shown corresponds to  $k = 1.41 a_w - 0.43$  (H.J. Banks and C.M. Ahern, unpublished data).

some chemical reaction is involved in uptake. Phosphine can also bond to protein in some form, though this is a minor part of the total sorbed (Tkatchuk 1972). Phosphine also appears to react with several vegetable oils, causing them to solidify. Further research is needed on these aspects, as they are relevant both to understanding and quantifying of residues produced in phosphine treatments and to the kinetics of phosphine uptake and, more importantly, desorption. Without a satisfactory understanding of the reaction scheme, it is not possible to measure the fundamental parameters such as *D* and the isotherms.

The rate of phosphine sorption onto dry grains in general is similar in magnitude to losses expected from a well-sealed enclosure caused by environmental forces, i.e. 0.05–0.20 per day (see Fig. 4). However, the sorption rate is much less than the loss rate from poorly sealed systems in which phosphine is frequently used. As a result, loss rates have overshadowed sorption, and recommendations for phosphine use have ignored its effect. Nevertheless, allowance may have to be made for sorption in dosage schedules. Paddy rice, but not brown or milled rice (see Fig. 3), and high moisture grain, absorb phosphine very rapidly and, occasionally, so too do apparently normal samples of wheat (Fig. 5). Sorption onto paddy rice is so extensive that an adequate fumigation may not be achieved under normal dosages, even in a perfectly sealed system. The occasional occurrence of high sorption rates presents a clear demonstration of the need to monitor fumigations.

The sorption and residue production behaviour of methyl bromide has been extensively studied. Some progress has been made towards relating bromide ion concentration, produced as residue, with constituents of grain, in the hope of finding some measure of reactivity independent of grain type (see Banks 1986). However, most studies on methyl bromide sorption have not been sufficiently systematic to allow generalisation. Kinetic studies have hitherto assumed that loss of methyl bromide from the gas phase, after the initial rapid loss, directly reflects reaction of methyl bromide to give bromide residues. Unfortunately, methyl chloride is released during methyl bromide treatment of grain (Fig. 2 and Dennis et al. 1972). Unless special precautions are taken, usual analytical methods determine methyl

chloride erroneously as methyl bromide. This leads to incorrect residual methyl bromide estimations and incorrect reaction rate constants. Consequently, published rate constants (e.g. Scudamore and Heuser 1970) are likely to be incorrect, sometimes substantially so, and require checking. The continued production of methyl chloride from methyl bromide-treated materials can be quite prolonged, extending over several days. This is clearly relevant to studies on methyl bromide desorption, field quantitation of methyl bromide concentrations and on practical definition of ventilation periods after fumigation (methyl chloride is much less toxic to humans than methyl bromide). No desorption studies taking methyl chloride production into account are yet available.

Table 3 gives some typical rate constants for reaction of phosphine and methyl bromide with grains.

**Table 3.** Typical apparent first-order rate constants (per day) for sorption of fumigants on wheat and rice at 25°C, 60% relative humidity, for a full system (estimated from Banks 1986, and H.J. Banks and J.A. Gorman, unpublished data).

Commodities	PH <sub>3</sub>	MeBr
Whole wheat	0.4	0.6
Paddy rice	0.8	0.4
Milled rice	0.1	0.7

## Grain Scale

The most intractable problems in gas behaviour occur over the grain length scale. This is because, at this scale, the effect of inhomogeneities become most apparent. With few exceptions, models of gas behaviour on the molecular and store length scales treat phenomena in what are considered to be homogeneous units. For instance, reaction rates are taken to apply to the grain, with due allowance for temperature and humidity, and grain is assumed to be uniformly porous throughout the store. In practice, even individual grains differ in properties and bulk grain includes regions containing different quantities of foreign matter, dust, hulls, etc., that substantially alter the properties of the region relative to clean grain (e.g. Lai and Fan 1976; Lai 1978).

These regions may well be of practical importance as they may be more easily colonised by

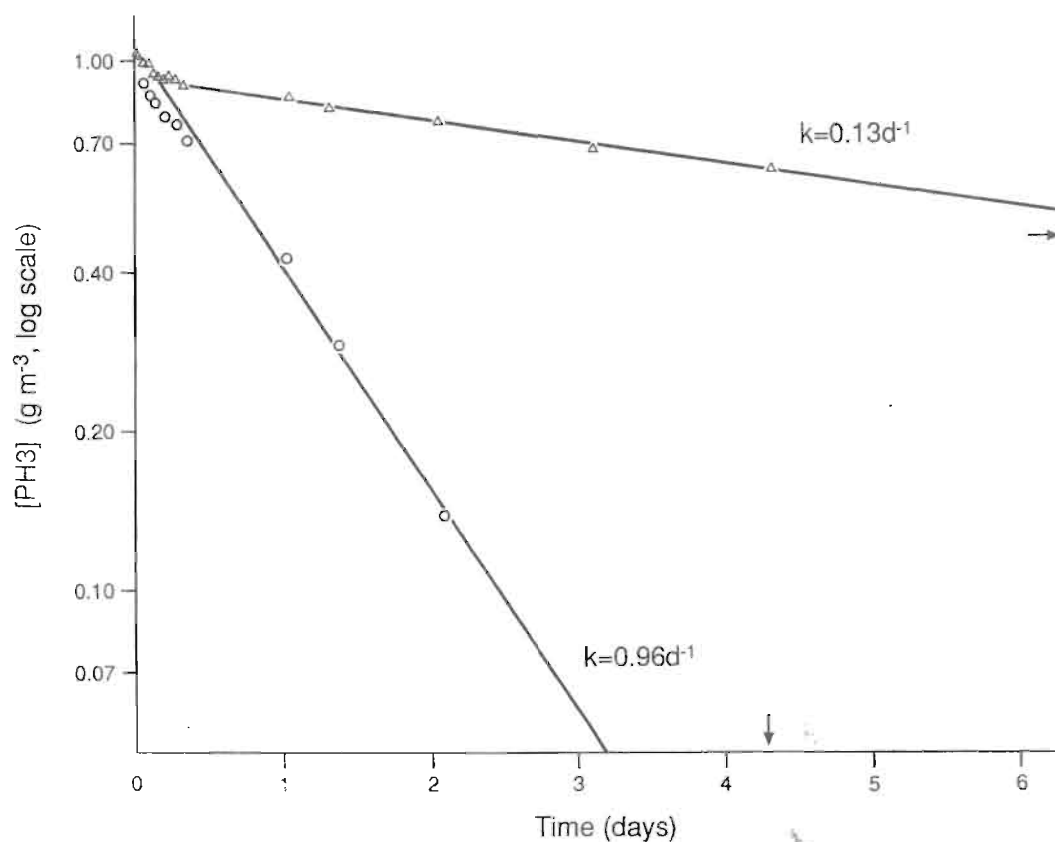
pests or affected by moulds, or even be created by the activities of the pests and moulds themselves. There is remarkably little documentation on how inhomogeneous the grain in store actually is, yet it is well known to those who store grain that variation within a bulk or bag stack can be dramatic. The presence, particularly of dust and matter other than whole grains, can cause major storage problems, as demonstrated by the better storage obtained when grain is cleaned (e.g. maize in 'Cyprus' bins (de Lima 1980)). Clearly, if mathematical treatment of gas behaviour is to be useful it must be able to illuminate what happens in other than perfectly clean grain. As yet, this has not been done (but see Lai 1978).

Study of the way that CAs are formed in grain can provide some demonstration of intermediate-scale problems that must be addressed. For instance, unexplained, inadequate penetration of regions of grain under fumigation is sometimes observed in practice, though the results are not usually published.

Fig. 6 shows, however, such a problem during

the purging of barley with nitrogen where there was slow displacement of oxygen in one region where husks may have accumulated.

Another area of concern on the intermediate scale involves the formation of 'havens', i.e., regions of the grain mass or enclosure under treatment where, because of dilution of the fumigant or CA through leakage of air into the region, pest control fails. Regions around poorly sealed valves in silo bins are an example of such havens (e.g. Bond et al. 1977). Here the chimney effect may draw in sufficient air to dilute the fumigant and allow pests to survive. Wind may displace fumigant from critical regions, such as from the windward corner of a bunker (Fig. 7). Where havens form by air ingress, this problem can, in theory, be overcome by maintaining a positive pressure differential with respect to the enclosure across all leaks at all times. This can be done either by adding sufficient gas continuously, as in the Siroflo system (Winks 1986), or on demand, as in some CA systems (Tranchino et al. 1980).



**Fig. 5.** Sorption of phosphine by a typical Australian wheat sample ( $\Delta$ ) and an exceptionally sorptive one ( $\circ$ ). Both samples at 25°C and 12% moisture content (H.J. Banks, unpublished data).

No models have been published to predict the extent of dilution of internal gases by air leakage. Detailed field data on gas concentration distributions close to leaks are meagre, though reports of concentration data from treatments often give some unusually low readings in particular areas. These low readings will often occur close to the boundaries of an enclosure, a particularly important region, as invading pests are first likely to establish there and conditions may be particularly favourable to pests through moisture accumulation and segregation of chaff and other matter. The region is likely to be less accessible to introduced gases because of the very factors favouring the pests.

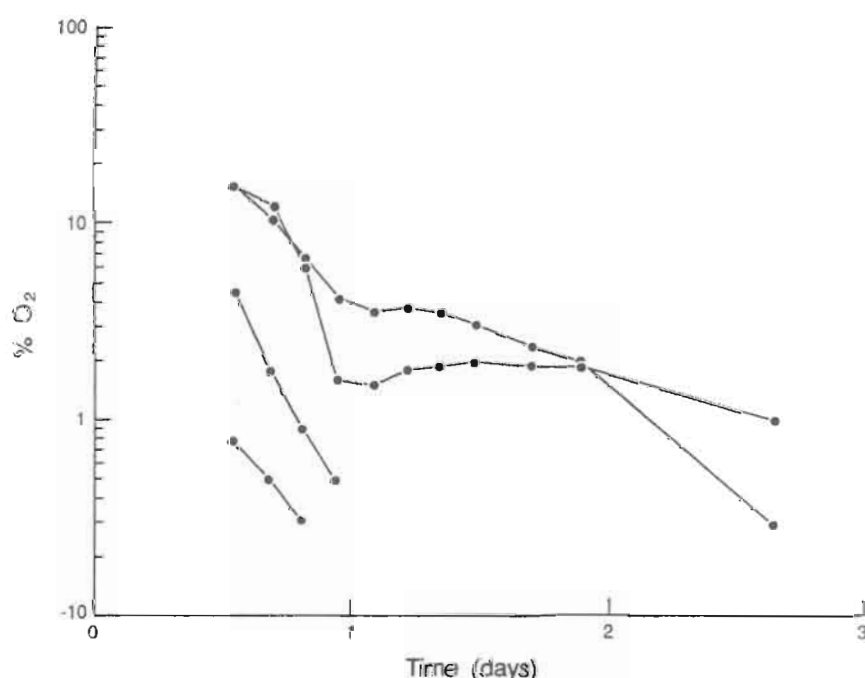
### Store Scale

Gas interchange occurs between the storage atmosphere and the outside environment, usually typified as leakage, and there is gas transfer within the store controlled by natural convection and forced distribution. While these phenomena are well recognised, the magnitude of

their influence on concentrations within a store is often unknown to those practicing CA and fumigation. Full-scale practical observations have been very limited, but modelling has helped illustrate their effects. These large-scale phenomena, leakage and convection, interact, although mathematical modelling has so far treated them separately.

### Gas Interchange with the External Environment

Leakage from an enclosure under CA or fumigation is affected by a number of factors, summarised in Table 4. Mathematical analyses of these effects and how they influence average gas concentrations within an enclosure has been given by Banks and Annis (1984a) and Barker (1974). The analyses indicate the magnitude of leakage expected from each factor in isolation. However, because distribution of leakage points is important, and there is as yet no suitable method for defining this distribution, or of treating combined effects, its predictions are approximate only. In poorly sealed enclosures, wind and the chimney effect are



**Fig. 6.** Oxygen concentration history of some points close to the wall in a bin of barley purged with nitrogen, showing very slow displacement of oxygen. All other points measured in this experiment purged rapidly (< 24 hours) to below 1.0% O<sub>2</sub> (H.J. Banks and P.C. Annis, unpublished data).

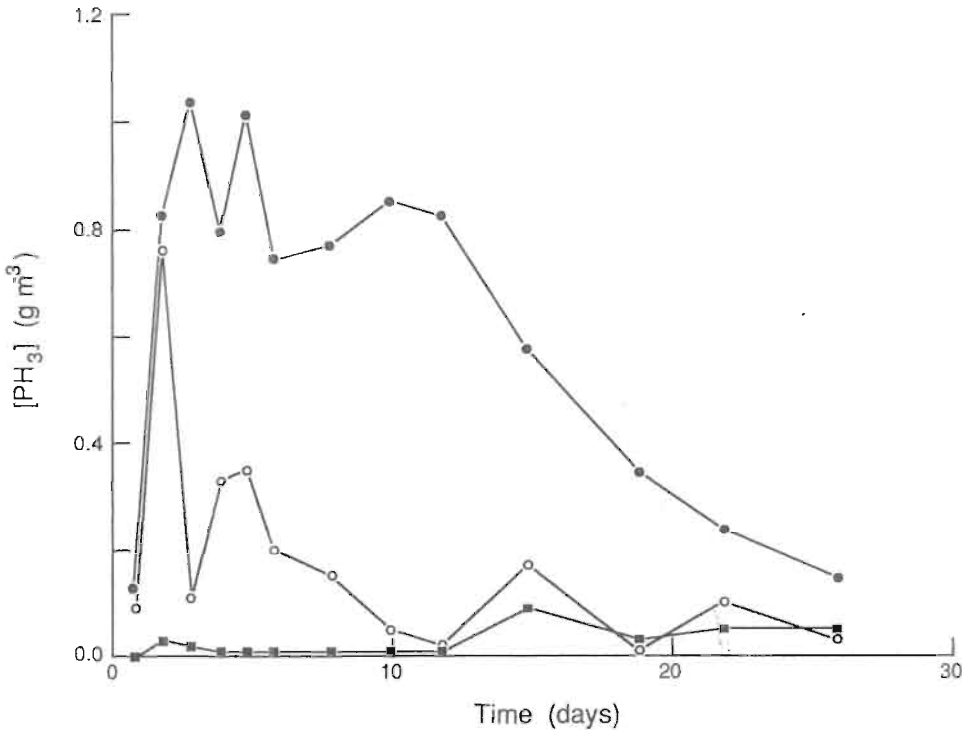
**Table 4.** Environmental factors causing leakage from an enclosure. In approximate order of importance for a poorly sealed storage (after Banks and Annis 1984a).

- Wind
- Chimney effect
- Temperature variation in the headspace
- Barometric pressure variation
- Temperature variation in the bulk
- Permeation (plastic film enclosures only)
- Diffusion

expected to be the main causes of gas loss, with temperature variation and sometimes barometric pressure effects predominating in well-sealed enclosures. In the limited published information available (see Banks and Annis 1984a), this appears to have generally been found to be so in practice.

### Internal Distribution

The internal distribution of gases in an enclosure is largely determined by natural convection currents, unless some form of forced distribution is used. Diffusion can play only a minor role except over short distances (< 1 m). These convection currents result from differences in gas density at different points caused either by temperature or composition. For circulation to occur, the less-dense gas must be directly or indirectly below the more dense. If this is not so, the system is stable and no convection results. The surface-application technique for phosphine fumigation relies on convection to distribute the gas. Phosphine concentrations become even throughout the grain and headspace within large, well-sealed, shed-type stores in a few days (Banks and Annis 1984b). Structures that are tall and narrow tend to have less effective convection currents than squat structures, and adequate distribution may take weeks. In extreme cases, the gas is lost by sorption and leakage before adequate distribution can be achieved. Where internal convection



**Fig. 7.** Average concentrations of phosphine achieved in a bunker of wheat (●) dosed at 0.78 g/t compared with observations from the two windward corners (○, ■) where air ingress occurred (data from Banks and Sticka 1981).

currents are linked with leakage caused by the chimney effect, there may be no dispersion of phosphine in a particular direction. Conway and Mohiuddin (1984) and Banks (1977) demonstrated the chimney effect by creating a band of phosphine in the centre of a wheat bulk in a silo bin. In the former case, where the grain was cooler than the environment, the gas descended and was lost by leakage. In the latter case, with warmer grain, it rose. No significant internal movement occurred in the opposite direction in either case.

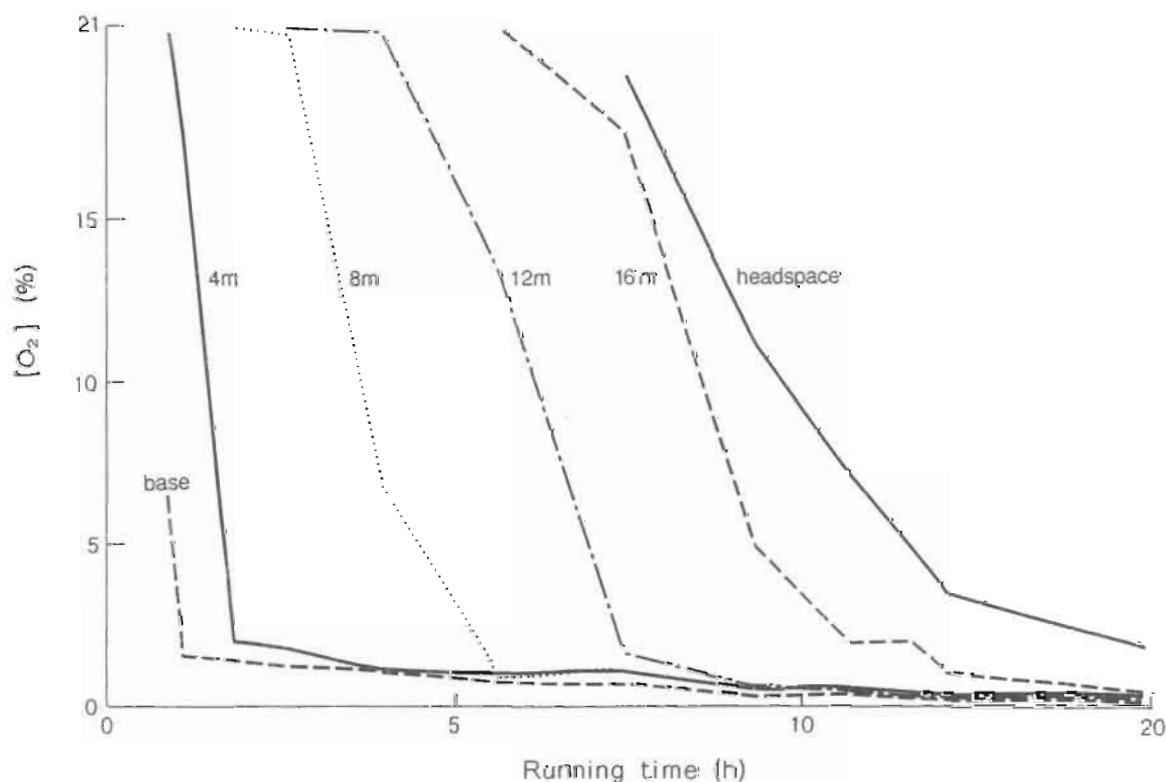
Ships' holds are especially difficult to fumigate effectively by a surface-application method without forced distribution (Leesch et al. 1986) as the convection currents that might otherwise distribute gas are weak; the colder gases are below the warmer ones in holds and so there is little driving force for convection. It should soon be possible to predict this type of behaviour in detail, given temperature data on the grain bulk and surroundings.

The mathematical treatment of natural convection in grain is complex and has been

restricted to description of movement of unadsorbed fumigants in two-dimensional, regularly shaped enclosures with constant temperature walls or ones undergoing a step change in temperature (Nguyen 1986). Leakage was not included. The models have not yet reached the level of development where predictions of behaviour of fumigants can be made for real three-dimensional systems with fumigants affected by sorption.

### Forced distribution

Aeration systems that force air through grain are well known. The rate of air flow under pressure through particular grains is described by the Hückill coefficients as outlined by Hunter (1983). This equation underlies the various mathematical models that are available to calculate air flows for various arrangements of duct work and storage design. These models deal with discrete air fronts without dispersion, and do not include fumigant sorption/desorption phenomena. However, there is a



**Fig. 8.** Fall in oxygen content in a flat-bottomed 2000 t bin of wheat, diameter 13.9 m, at various points in the bin when purged from the base at 100 m<sup>3</sup>/hour with < 0.5% O<sub>2</sub> in 12% CO<sub>2</sub>, balance inert gases (H.J. Banks, unpublished data). Position of sampling points; on bin centre line at heights above base as marked.

numerical model of the coupled heat and moisture transfer occurring during aeration that includes dispersive effects (Wilson 1988). Inclusion, at least theoretically, of fumigant effects into this model should be possible, though the relevant controlling parameter values may not yet be available.

In practice, gases under forced flow, such as during addition of controlled atmospheres, traverse a grain bulk in the mode known as 'disperse plug flow', with the initially sharp boundary between the existing interstitial atmosphere and introduced gas becoming more diffuse as the front proceeds. Fig. 8 shows the sigmoid concentration profile typical of such a front. Presumably, similar effects occur when fumigants are force distributed and mathematical models of the process should include a description of this dispersion.

## Conclusion

This paper has given a brief overview of where we stand as regards understanding of gas behaviour in fumigation and CA and an indication of where we ought to be. The size and complexity of problems that need to be overcome, and the difficulty of their analysis, should not deter investigation, as the objective is worthwhile: rational and optimal use of CA and fumigation. However, a good strategy is required to attack it successfully. I believe that careful coordination is required between researchers involved in measurement and model development and persons who can gather data from full-scale treatments. Without this, models will be produced that do not reflect reality and much effort will be expended in unnecessary measurement.

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# Specification and Design of Enclosures for Gas Treatment

C.J.E. Newman\*

## *Abstract*

The paper draws on experience within the Australian grain industry to review the state-of-the art in relation to the design and specification of gastight storages, concentrating principally on its application to the storage of grain in bulk.

Problems associated with sealing different types of storages are discussed and commonly used sealing materials and methods are reviewed. The paper also covers in some detail points which should be considered when preparing specifications for sealing work, including types of contract and the selection and specification of sealing materials. The paper draws attention to current deficiencies in test standards and acceptance criteria for many commonly used coatings.

The paper also reviews current gastightness testing procedures and commonly used methods of air leak detection.

SINCE the inception of gastight storages for fumigation treatment of grain in the 1960s, the art of gas-sealing has evolved into a well controlled 'science', and it is now almost standard practice in Australia for new storages to be built to gastightness specifications. Significant efforts have also been made to seal numerous older storages in order to gain the benefits, both financial and operational, that sealed storages can offer.

The cost of gas-sealing new storages need not be high if the design is detailed to facilitate sealing. In fact, for some types of structures the cost can be negligible. The cost of retro-sealing older structures not designed for gas-sealing can, however, be significant. In both cases, the cost of sealing will be largely dependent on the detailed design of the storage structure while the success of the sealing will be dependent to a large extent on the appropriateness of the specification relating to its application.

This paper concentrates on design details for new structures that facilitate sealing, and on

appropriate materials and specifications for achieving satisfactory sealing of both new and old structures.

## **Sealable Storage Types**

Virtually any type of grain storage can be made gastight. As noted in other papers in these proceedings, bag stacks are routinely gas-sealed in China and some Southeast Asian countries by fully enveloping them in polythene sheets which are carefully sealed at all joints either by heat welding or by mechanical fastening (Fig. 1).

Bulk storages can be similarly sealed; for instance as is commonly practiced in Australia where bulk grain in bunker storages is encapsulated within reinforced PVC or polyethylene covers which are mechanically sealed together at joints and around the periphery.

With permanent bulk storages it is necessary to seal the storage structure itself. Almost any storage structure can be sealed, the cost depending to a large extent on the type of structure and its design detail.

\*Bulk Grains Queensland, PO Box 136, Toowoomba, Qld 4350, Australia.



**Fig. 1.** Sealed bag stack (China 1986).

In Australia, grain storages are normally constructed from either concrete or steel. Vertical silos and horizontal sheds built from these materials are routinely sealed for fumigation. There has been little work done in the sealing of timber or masonry storages which are rarely found in Australia. There is, however, little doubt that the materials and methods that have been developed for sealing steel and concrete structures could equally well be used for sealing timber and masonry storages.

### **Design of New Storages for Ease of Sealing**

This section covers design aspects for new storage structures to facilitate sealing. Section 4 looks at the design of doors and other apertures to facilitate routine sealing for fumigation.

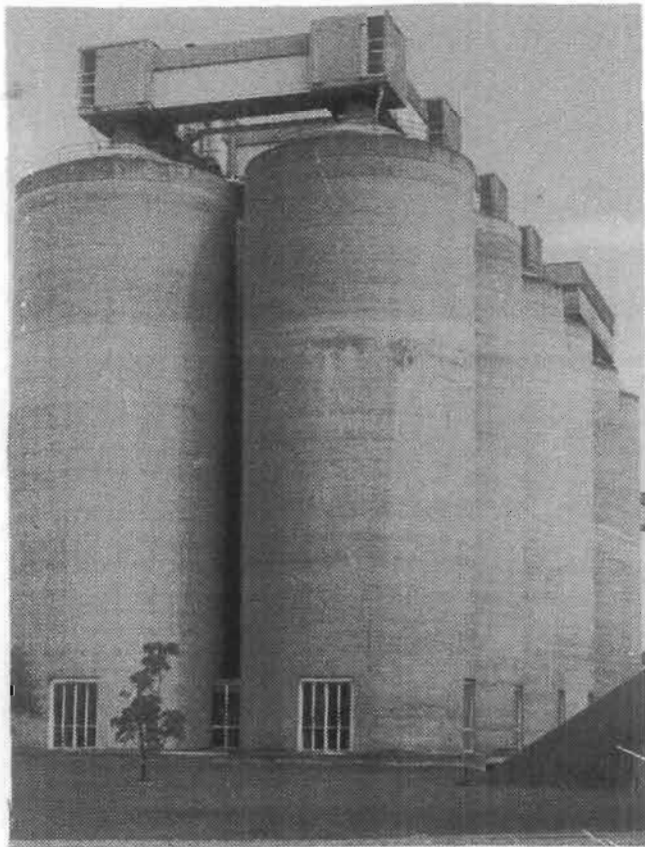
#### **Reinforced Concrete Silos**

Gastight concrete silos (Fig. 2) have been routinely constructed in Australia over the last

20 years and most have retained their gastightness throughout prolonged usage. A good example is a group of twelve 2600-tonne bins built in Brisbane, Queensland in 1968 which have been filled and emptied on average around 25 times per year or, say, a total of 500 times to date. The bins are of reinforced concrete slip form construction, with cast-in-place conical concrete floors and roofs. They have retained a high standard of gastightness without the need for any surface coating or treatment. Indeed, this applies to all of the 150 or so concrete silos, varying from 1000–7000 tonnes capacity, that have been built in Queensland over the last 20 years (Newman 1987).

The following basic principles were established in Queensland for the achievement of gastightness in reinforced concrete silos:

- Bins should be independent rather than interconnected (Fig. 3). Interconnection of bins results in nonuniform expansion of the walls which can cause vertical cracking. Fitting of gastight roofs to interconnected bins is also much more difficult. It can be added that independent bins are easier and generally less costly to build than interconnected ones.



**Fig. 2.** Gastight concrete silos at Pinkenba, Queensland, Australia.

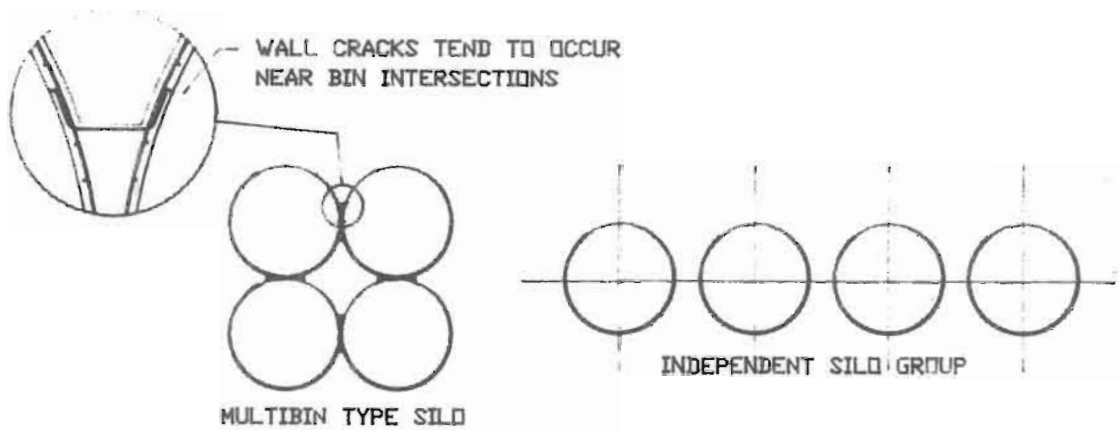


Fig. 3. Independent silos are easier to make gastight than interconnected bins.

- Sufficient reinforcing steel must be incorporated into the bin walls. Tensile stresses in the horizontal reinforcement should not exceed 135 MPa under peak pressures (normally during outloading). Higher stresses should not be permitted even if high strength steels are used, since cracks will become unacceptably wide. Single reinforcement (i.e. a single mat of horizontal and vertical reinforcement) centrally placed has proven satisfactory in bins of up to 3000 tonnes capacity. Nevertheless, double reinforcement (separate mats adjacent to each face) results in a very significant increase in wall stiffness, ensuring greater resilience against uneven loading. Double reinforcement is to be strongly recommended in new constructions, especially in silos of over 3000 tonnes capacity or in silos which are to be eccentrically loaded or unloaded. Typical features of gastight concrete silos are illustrated in Figure 4.

- High standards of quality control and supervision during construction are essential to ensure that:

- placement of reinforcing steel is correct;
- the specified cement content is used in the concrete;
- maximum water:cement ratio is not exceeded (0.55 recommended for most environments);
- 'cold' joints do not occur during construction or, if they do, that they are properly cleaned and treated to ensure a good bond;
- concrete temperature is controlled before and after pouring;
- curing of the concrete surfaces is properly carried out; and

- good construction practices are rigorously followed.

- The effects of eccentric filling and emptying of a silo should not be under-estimated. Off-centre emptying in particular can create major grain pressure differentials around the bin circumference (Fig. 5). These can result in distortion of the bin wall and thus a risk of vertical cracking (Gorenc et al. 1986).

A detailed discussion of eccentric loadings is beyond the scope of this paper. There are, however, a few matters that should be attended to in order to minimise loss of gastightness when eccentric loading and unloading is liable to occur.

- Use double reinforcement in the bin wall as outlined earlier, to increase resistance to distortion and cracking (Wood 1983).

- The bin wall should be rigidly connected to the foundation or bottom ring-beam by reinforcing steel (Fig. 6). This will substantially increase the stiffness of the wall and also simplify sealing of the joint. The sealing of such joints is most readily achieved by a PVC water-stop cast into the concrete.

- Use of the bin roof as a stiffening member will also add significantly to the rigidity of the bin walls. A stiffening member has itself to be very rigid, and a concrete roof cast in place is likely to be the most appropriate form of construction to give adequate stiffness. While there are many circumstances in which it is cheaper to construct steel or precast concrete roofs for concrete wall silos, a stiffening action is harder to achieve by this course and consequent movement of the wall below the roof can occur making a gas seal difficult to maintain (Fig. 7).

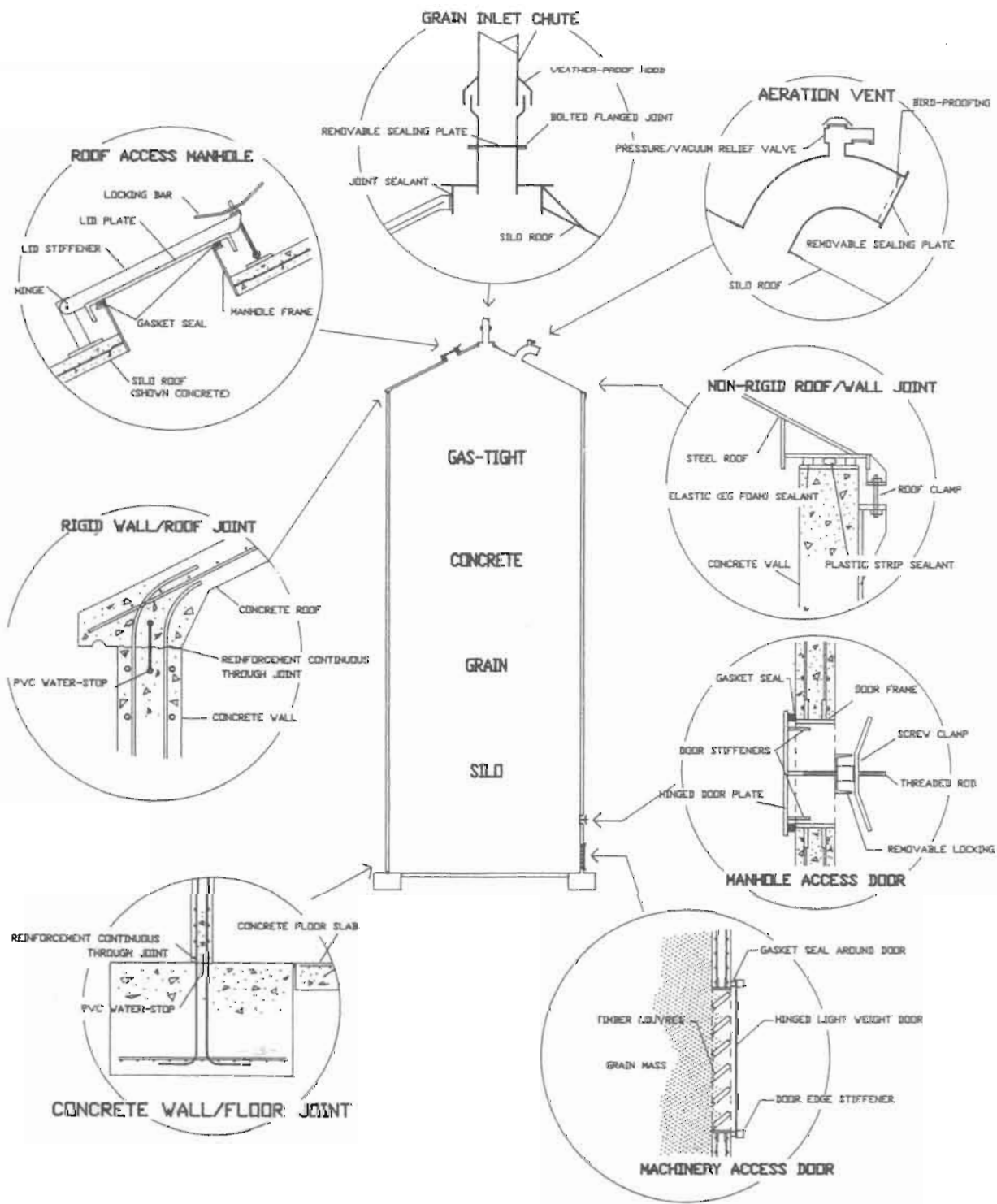
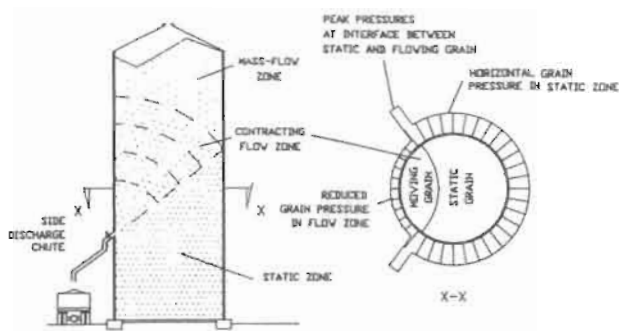


Fig. 4. Typical features of a gas-tight concrete silo.

In considering sealed concrete silos, the potential use of carbon dioxide for grain disinfection needs to be considered: the chemical reactivity between this gas and concrete can pose both short- and longer term problems. Through the process of 'carbonation',  $\text{CO}_2$  converts calcium hydroxide in the cement matrix to calcium carbonate. This results in a

potential long-term reduction in corrosion protection to reinforcing steel, caused by the neutralisation of the alkaline component of the concrete. A very rapid rate of gas 'loss' can also occur in a new concrete structure which is exposed to  $\text{CO}_2$ , due to the rapid uptake of gas that can take place. Extra  $\text{CO}_2$  must be added to make up for this loss and adequate pressure



**Fig. 5.** Grain pressure differentials resulting from eccentric discharge of a vertical silo.

relief needs to be provided to guard against structural damage resulting from the high negative pressures that can occur inside the storage as the reaction takes place (Banks and McCabe 1988).

### Welded Steel Silos

Welded steel silos are inherently gastight and require no special design considerations in relation to gas sealing. An exception applies to silos with concrete floors, where the joint between wall and floor has to be made gastight (Fig. 8). Such joints usually occur between the steel wall and concrete foundation or stub wall and can be sealed with a wide variety of sealant types. The choice of sealant may depend on whether or not movement between the steel wall and concrete foundation is to be permitted, but either way it is unlikely that an adequate seal would prove difficult to achieve.

### Bolted Light Gauge Steel Silos

While heavy gauge bolted steel silos should not present difficulties in sealing, light gauge bolted bins have generally not been easy to

seal and, indeed, until recent times were often considered unsealable due to the amount of movement that occurs in the wall joints and at bolt fixings during filling and emptying.

Recent development work in Australia has resulted in designs for light gauge steel silos that can be sealed to a high level of gastightness. One design uses adhesive cellular foam sealing strips as gaskets between the corrugated steel sheets forming the walls. Also, special fabric-reinforced washers that remain stable under high compressive forces are used under all bolt heads thereby sealing the bolt holes.

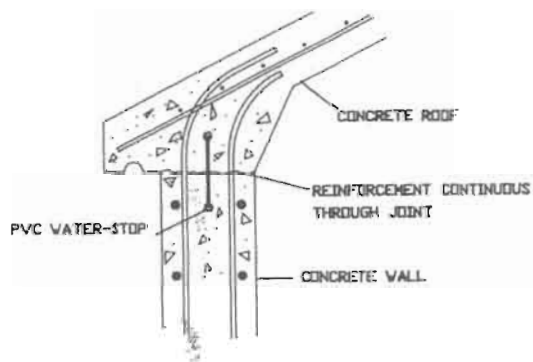
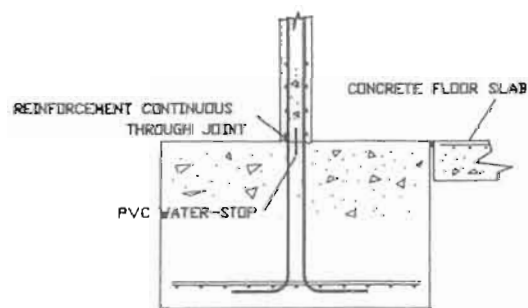
The conical roof of this type of structure also differs from most standard light gauge bins; a rigid framework of radial beams (rafters) supports light gauge steel roofing segments. Excessive movement of the roof sheeting is thus prevented, allowing joint sealants to remain intact and effective.

Another form of light gauge bolted steel silo that has been successfully gas sealed incorporates a light-weight skeletal frame onto which the internal walls and external roof sheeting are attached (Fig. 9). Despite the large number of laps, joints, fastenings, and complex interfaces, silos such as these can be made gastight provided care and attention is given to detail during design and construction.

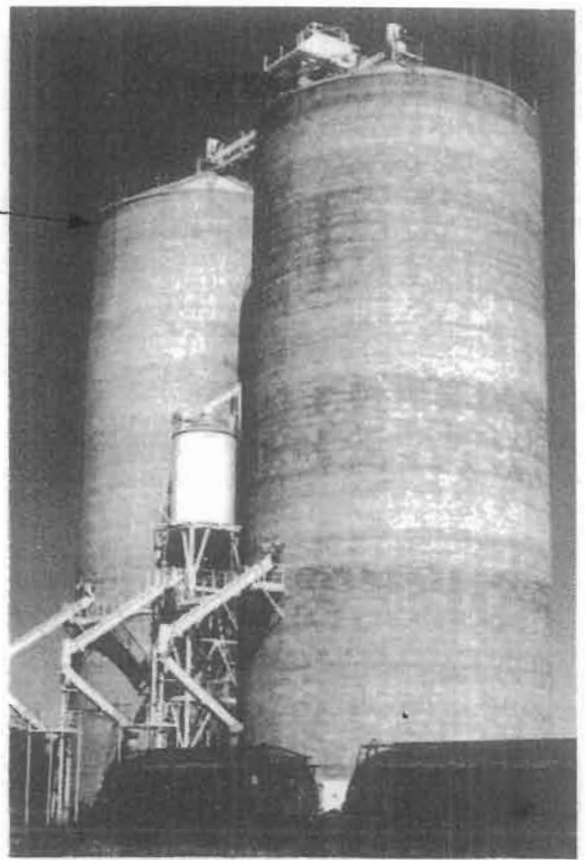
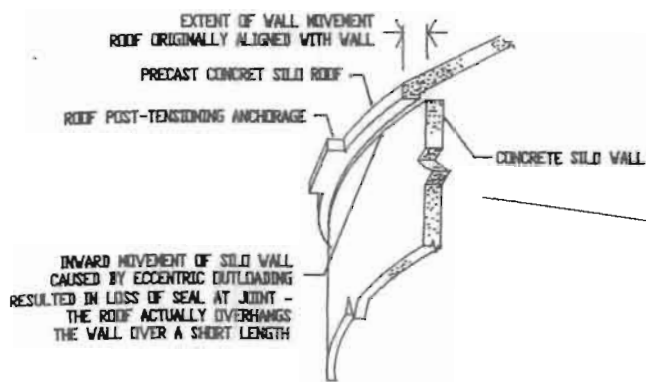
### Horizontal Sheds and Similar Structures

Horizontal bulk-storage sheds in Australia are usually steel-framed with corrugated steel sheeting forming the walls and roof, although the load-bearing walls are sometimes made of concrete.

Sealing of such structures is made easier if the design is carefully detailed to facilitate the application of sealants.



**Fig. 6.** Detail of typical rigid connections at the top and bottom of a concrete silo wall. Note PVC water stop in gas sealing joint.



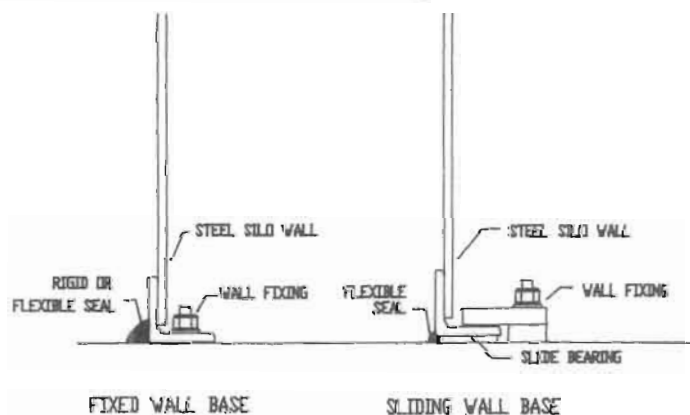
**Fig. 7.** Example of loss of seal caused by eccentric discharge through side chutes in concrete silos.

Principle design requirements are as follows:

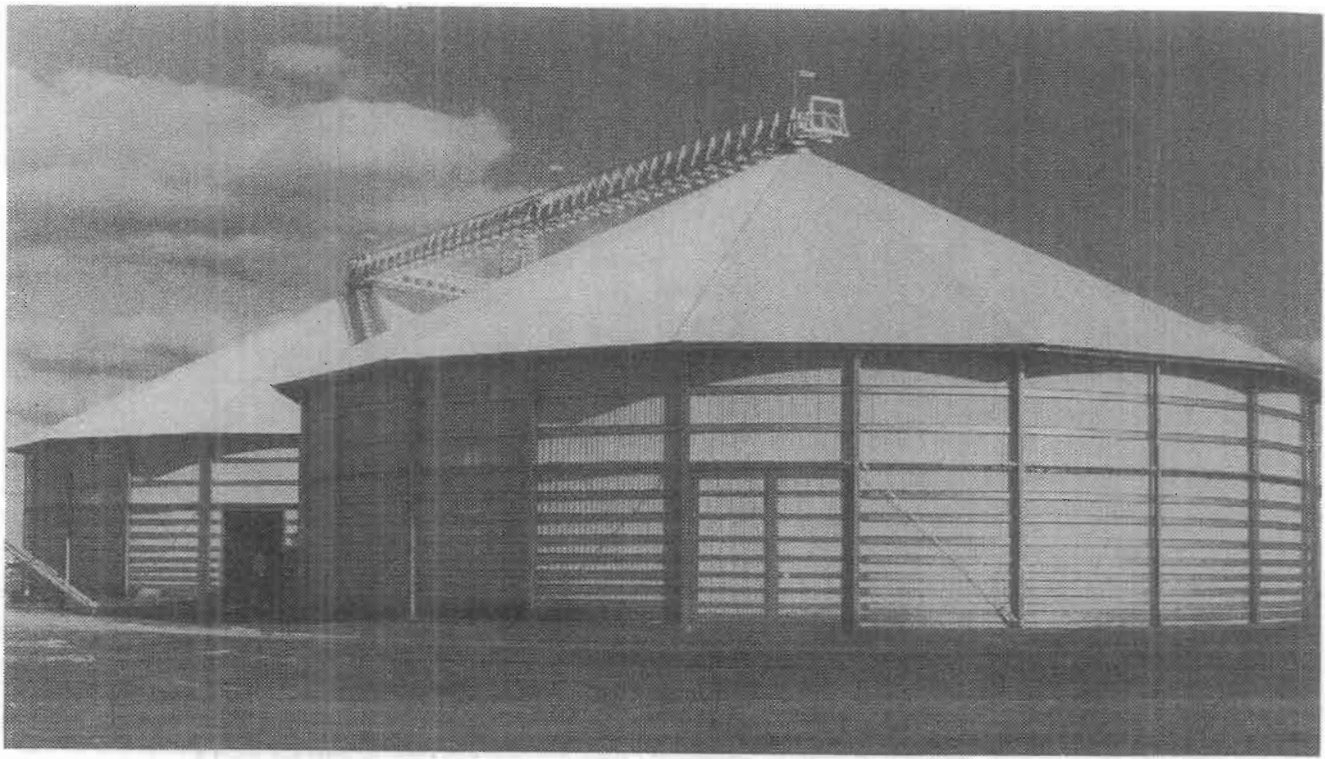
- Gaps between sections of sheeting (e.g. between roof and wall sheeting) should be kept to a minimum and bridged with steel flashings.
- Deflections under load (either from grain load, wind-load, or static air pressure differentials) should be kept to a minimum by good structural design and by use of adequate fastenings for attaching and joining the wall or roof sheeting to the structural framework. The number of fastenings may exceed that required to resist normal wind loads.

Regardless of the care a designer takes, many of the joints in such structures will need sealing. In particular, joints will occur between corrugated sheets where they overlap either at their sides or ends. Gaps will also occur wherever corrugated sheets are attached to flat (uncorrugated) structural members or flashings. However, sealing of such joints or gaps is not difficult, though the work has to be done with great thoroughness.

Preformed foam 'corrugation closures' are available for most standard corrugation profiles, though an application of sealant coating over



**Fig. 8.** Typical connections between walls and footings of steel silos.



**Fig. 9.** Gastight bolted light gauge steel silo.

them is still necessary to ensure gastightness. Alternatively, sprayed polyurethane foam (Fig. 10) is often applied to bridge over corrugation gaps, though once again a sealant coating is normally applied over the top.

Sealing of laps between corrugated sheets can be done in a number of ways. These include:

- Applying silicone sealant inside each joint as the sheets are set in place and fixed together. Since silicone 'sets' relatively quickly, successful implementation of this method requires conscientious roof sheeters working under close supervision.
- Injecting acrylic sealant paint into the joints after placement of the sheets. To be effective, this method requires releasing the fixings to inject the sealant into the joints and refixing again immediately afterwards.
- Applying silicone sealant or sealant coating externally over the joints.
- Applying a preformed cellular foam sealing strip between sheets before they are fixed. To be effective this requires extra fastenings to ensure that the foam gasket is maintained in compression along the full length of the joint.

It is not uncommon for a combination of these treatments to be applied; for instance, lap joints may be externally coated with acrylic sealant after being pre-sealed with silicone or foam sealing strips.

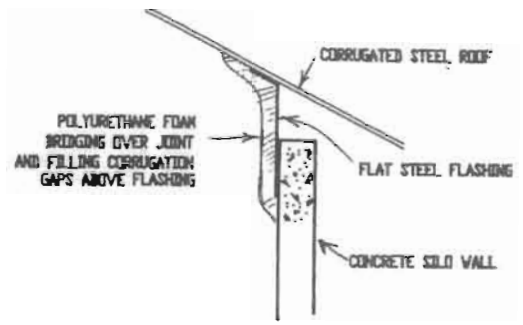
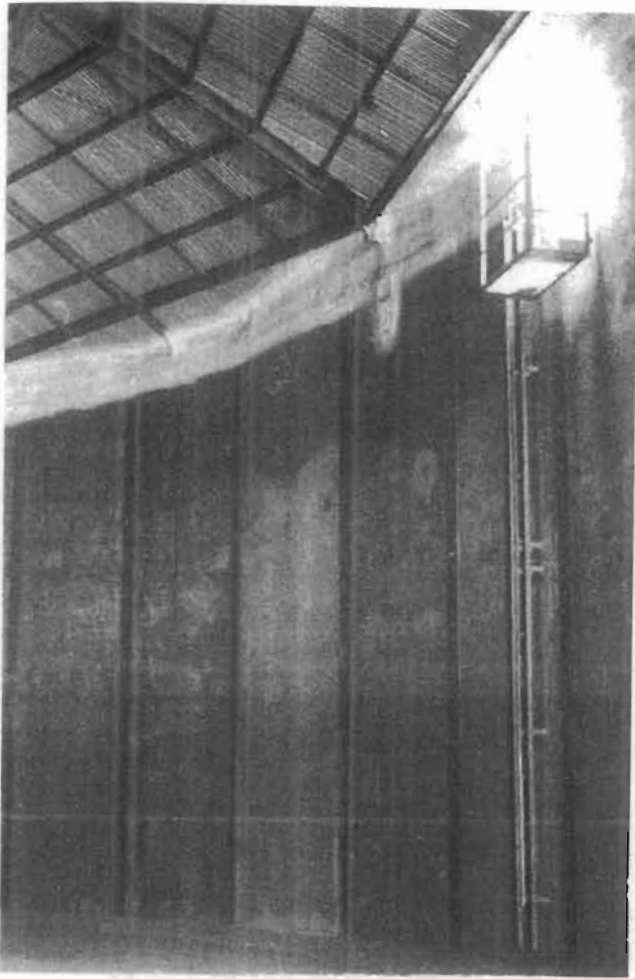
Particular care needs to be taken at the interface between roof and walls of such structures. Whilst side laps between sheets may be sealed to prevent gas passing through them, the sealant will not normally prevent gas passing along them. If this leakage path is not interrupted at the wall/roof interface, such joints will form 'tunnels' for gas to leak from (Fig. 11(a)). It is thus important to seal across the full width of all lap joints at roof/wall interfaces and to provide continuity between these seals and the seal between the roof and wall. A similar situation occurs at ridge cappings which require blocking off at their ends (Fig. 11(b)).

### **Pressure Venting**

It is important to recognise that a gastight structure will be subject to internal variations in pressure relative to that of the external atmosphere. Pressure differentials can arise from a number of causes; for instance, variations in atmospheric pressure, wind effects, and air displacement during filling or emptying of the storage.

Adequate pressure-relief venting of a sealed storage is essential to avoid excessive pressure differentials that might cause structural damage. Vents must be large enough to allow air to pass into or out of the structure at a rapid enough





**Fig. 10.** This figure illustrates the application of polyurethane foam for sealing the joint between the concrete wall and corrugated steel roof of a squat silo.

rate to control internal pressures. They must be designed (or adjusted) to operate at positive and negative pressure differentials below the critical values which could cause structural damage (specifications for ventilators are discussed later in this paper).

### White Painting

While pressure venting is essential for structural safety, it conflicts with gastightness requirements. It is thus important to take steps to minimise the amount of air movement into and out of the storage enclosure. White painting of the outer surfaces of steel clad structures has a dramatic effect in reducing temperature changes inside. In sunny conditions, the internal temperature of a white painted steel clad structure can be some 10°C lower than inside an unpainted galvanised steel structure, while the surface temperature of the steel may be 30°–40°C lower. Such a

temperature reduction will significantly reduce the amount of air displaced through thermal expansion. Similarly, radiation losses during darkness will be reduced from a white painted structure, minimising air intake from contraction of the internal atmosphere.

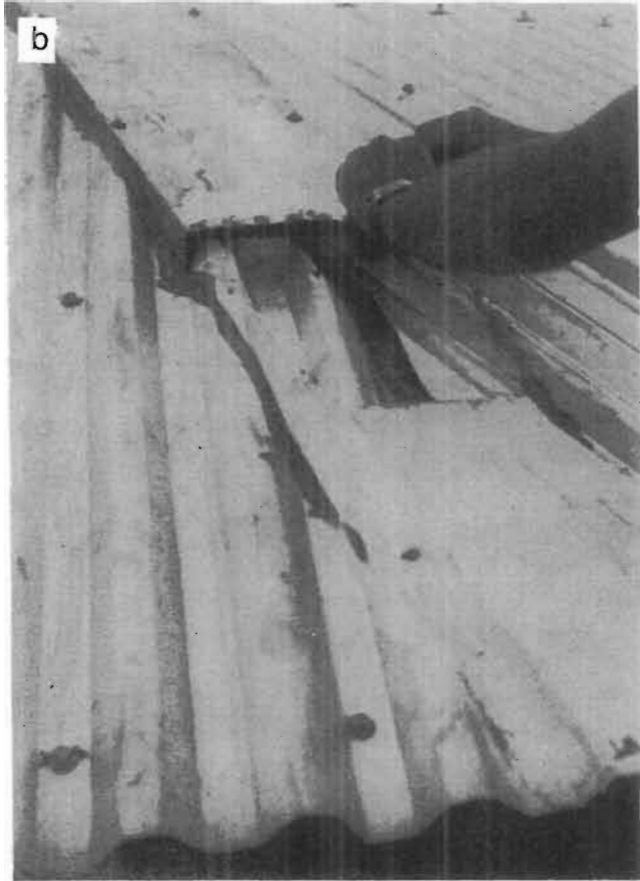
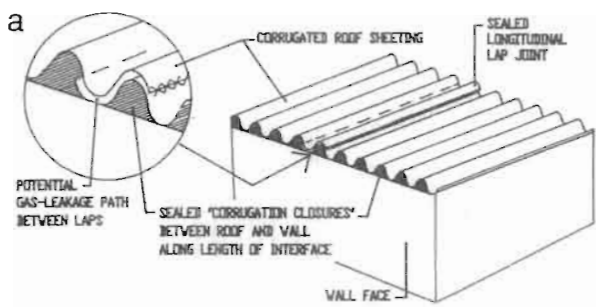
Because of the thickness of concrete sections used and their relatively low thermal conductivity, white painting of concrete structures is not normally necessary

### Detail Design of Openings

It is important that the various openings fitted to grain storage structures be designed to facilitate sealing to specified levels of gastightness.

### Openings for Personnel Access

For ease of access, manholes should be hinged openings with doors that are both rigid



**Fig. 11.** (a) Location of a potential gas leakage path along sheeting laps. (b) Sealing under ridge capping. Note that sides of capping are sealed with silicone.

and light (Fig. 12). Rigidity is desirable since it minimises the number of fixings required to seal the closed door against a gasket.

Access doors that are not subject to grain pressure normally open outwards, while those that should open inwards so that they cannot be opened accidentally when the storage contains grain. The grain pressure will also assist in holding the door against the sealing gasket.

A combination of lightness and rigidity can usually be achieved by use of relatively light plate to form the door itself and stiffening its perimeter by attaching flanges or stiffeners. The gaskets used should be capable of sealing the

door without further application of silicone type sealant. Appropriate gasket materials are discussed later, under specifications for gastight sealing.

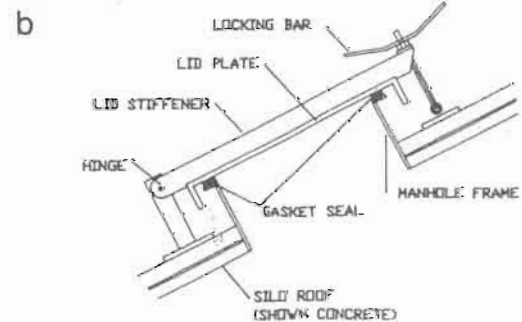
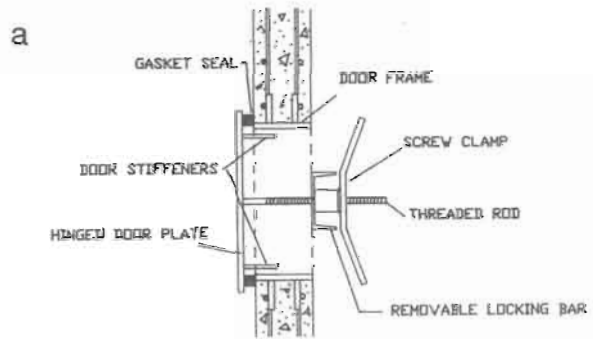
### Machinery Access Doors

Access may be required for machinery or equipment, particularly into flat-bottom silos. Such openings are generally larger than those for personnel and may have to accommodate large machinery such as front-end loaders (Fig. 13). The doors normally open outwards since it is often necessary to drain residual grain from inside before gaining entry.

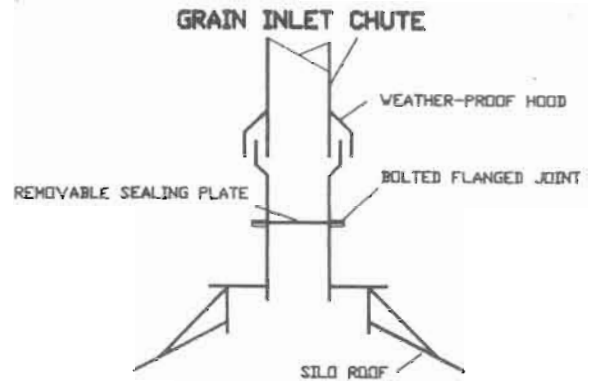
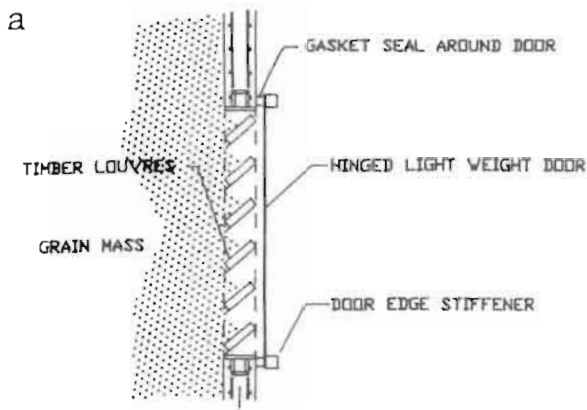
Sealing of machinery access doors can usually be achieved with an appropriate gasket. Clamping forces will need to be high if the door is subjected to grain pressures, multiple bolt fastenings around the perimeter usually being needed. Sealing effort can be reduced (as can the weight of the door) if grain pressure is carried by either an internal load bearing door or removable louvres.

### Grain Inlet Chutes

It is normal practice for gas-sealing of inlets and discharge chutes to be carried out



**Fig. 12.** (a) Typical inward-opening manhole subject to grain pressure when the silo is loaded. (b) Silo roof manhole with outward opening door.



**Fig. 14.** Sealable silo inlet chute.

effective and offers an additional benefit (in some applications) of providing for relative movement between the chute and the storage structure.

### Grain Discharge Openings

Gas sealing of gravity-fed discharge chutes usually entails use of slide gate to make the seal (Fig. 15). This can be done either by jacking the valve plate upwards until it seals against the discharge chute (the plate being lined with rubber to form a gasket), or by jacking a sealing ring down around the outer edge of the valve plate. The latter is probably simpler since jacking of the valve plate means that it has to be moved against the grain pressure.

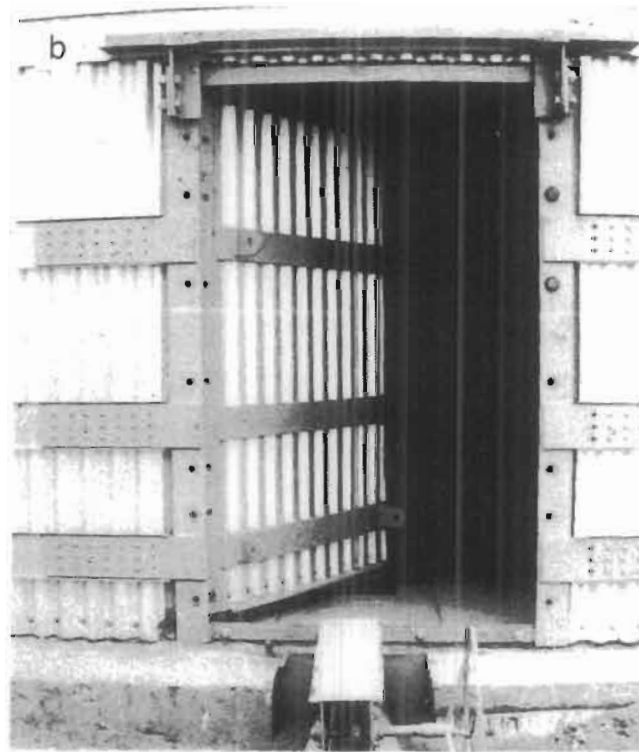
An alternative arrangement is to enclose the valve in a gastight enclosure and to fit a separate sealing plate below it when required.

Another type of valve which has reportedly been used with success is a simple knife gate valve as used for controlling liquid flows. These are manufactured as proprietary items and come in a range of sizes, being commonly available up to 600 mm diameter. Manufactured with stainless steel components and internal seals, they require no secondary sealing mechanisms since the automatically seal when closed.

Non-gravity discharge by means of a conveying device may require either gas-sealing of the conveyor itself (Fig. 16(a)) or removal of the conveyor to allow sealing to be carried out (Fig. 16(b)).

### Fans, Ventilators, and Associated Equipment

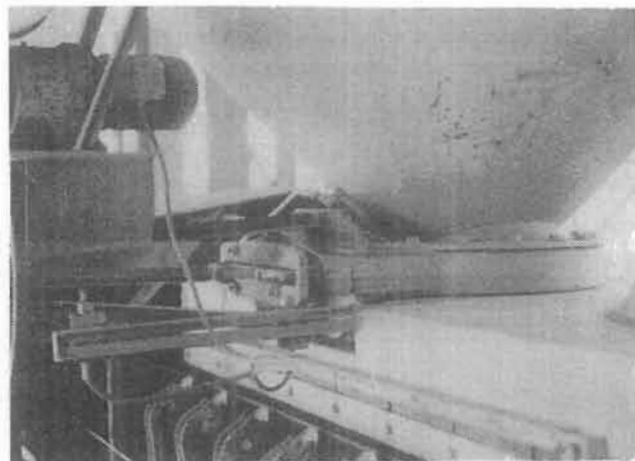
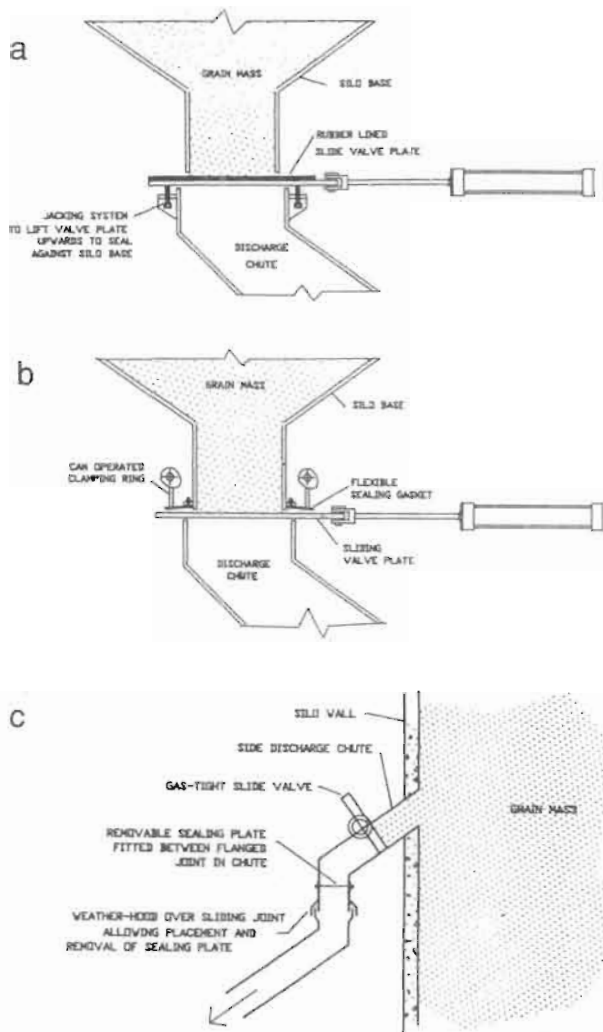
There is no contradiction in the concept of a gastight aerated storage. Aerated storages can



**Fig. 13.** Machinery access doors: (a) light door with internal louvres; (b) heavy door able to cope with grain pressures and wall stresses.

manually. Not only is it generally safer, in that the fumigator has to physically check valve settings and seals before fumigating, but it is also much less costly than automating.

Where a grain path is to be sealed, it is normal to use a retractable or removable plate, which can be withdrawn from the grain stream when the chute is in use. A commonly used sealing method provides a means of manually inserting a sealing plate (or diaphragm) into the chute and compressing it, either with bolts or clamps, to render it gastight. The system illustrated in Fig. 14 is extremely cheap and



**Fig. 15.** (a) Gas sealing of discharge valves. (b) Downward clamping of sealing ring around valve plate. (c) Sealing plate in chute below valve. (d) Knife gate valve.

readily be made gastight, and gastight storages can also be aerated provided care is taken in the design of fans and air vents.

Axial fans (commonly used on horizontal sheds) normally incorporate direct-drive motors

mounted within the air-stream. Such fans can be readily gas-sealed by fitting a sealing plate over the inlet opening (Fig. 17(a)). However, where phosphine fumigation is proposed it is advisable to remove the fan and seal the aeration inlet duct, so as to avoid damage to the motor windings.

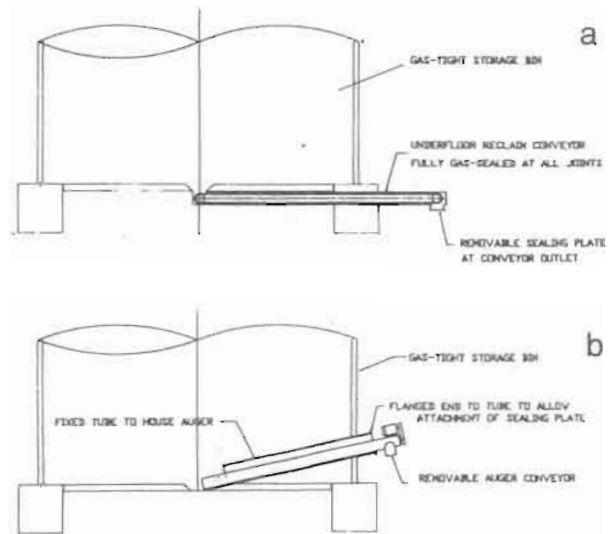
Centrifugal fans (usually used for aerating vertical silos) should be fitted with a stuffing-box seal where the drive shaft passes through the outer casing (Fig. 17(b)). A removable blanking plate can be fitted to the fan inlet, which should be flanged to facilitate attachment of the plate.

Aeration ventilator openings should be specifically designed for ease of sealing with flanged ends for attachment of blanking plates (Fig. 17(c)).

### Pressure Relief Valves

Oil bath and weighted diaphragm types of pressure relief valve are in common use. Both remain gastight below their release pressure.

An oil bath valve consists of a steel chamber partly filled with oil and divided by a partitioning plate, the bottom of which is immersed in the oil (Fig. 18). One side of the chamber is vented to atmosphere, the other to the storage. Air entering or leaving the storage must pass below the partition and through the oil; the pressure at which the passage of air will begin in either direction is controlled by the depth that the partition is immersed in oil: the



**Fig. 16.** Gas sealing of discharge conveyors: (a) sealing of the conveyor; (b) removable conveyor with sealable access tube.

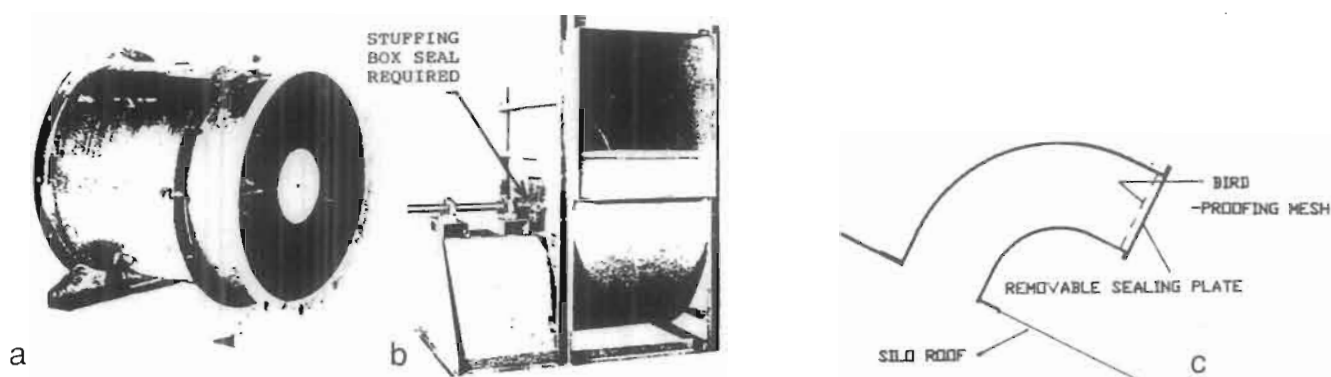


Fig. 17. Sealing fans and ventilators: (a) axial fan; (b) centrifugal fan; (c) ventilator.

deeper the oil, the greater the pressure differential that the valve will sustain. The wider the oil bath the greater the airflow rate which can be passed.

A diaphragm valve consists of a counterweighted sealed diaphragm which is lifted off its seating at a predetermined pressure differential that is adjustable by the mass of counterweight (Fig. 19). Proprietary valves are available with separate diaphragms for relieving positive and negative pressures. Such devices are relatively simple and could be fabricated to suit individual needs when proprietary valves are unavailable or unsuitable.

There appear to be no guidelines in common use for sizing pressure relief valves; however, it is suggested that a vent area of approximately 0.1 square millimetre for each cubic metre of storage volume should be sufficient to relieve pressure differentials resulting from internal air temperature changes of 1°C per hour (0.1 mm<sup>2</sup>/m<sup>3</sup>/°C/hour). A good design guide is 1 square millimetre of area per cubic metre of storage volume.

### Electrical Fittings

It is important to seal or otherwise protect electrical equipment inside or communicating with any storage where phosphine fumigation is to be carried out. Phosphine reacts aggressively with copper and will quickly destroy electrical components which it comes into contact with.

### Retro Sealing of Older Storages

The previous sections have discussed the design and construction of new storages in order to achieve gastightness.

Older storages were seldom built with gas-sealing in mind and hence they usually present much greater difficulties in sealing. While it may be technically possible to seal any type of storage, costs may become prohibitive in some instances.

Methods and materials used to seal older storages are similar to those used for sealing new ones. However, the amount of sealing effort is likely to be greater and structural modifications may be needed; for instance, modifications to doors and other openings to facilitate sealing, closing up of gaps and openings, strengthening structural members, and extra fixing of cladding. Once the structure is modified, the actual sealing work is generally carried out as for a new structure (Woodcock 1983).

A method of sealing large door openings commonly used in Western Australia involves special light-weight 'sandwich panel' sealing doors specially made up to fit the opening. The sandwich panels consist of polystyrene foam sheeting reinforced with a fibreglass skin. They have been found in some situations to be more economical than modifying the original door to render it gastight. The panels are clipped into place on the outside of the load-bearing door and the edges sealed using a bandage-type seal (see subsequent section on **Bandage Seals**).

A very important consideration when sealing old structures is to establish the positive and negative internal pressures which it is capable of safely supporting, and to provide pressure relief valves accordingly (Ripp 1985).

There have been a number of publications giving detailed descriptions of sealing work on individual storages.

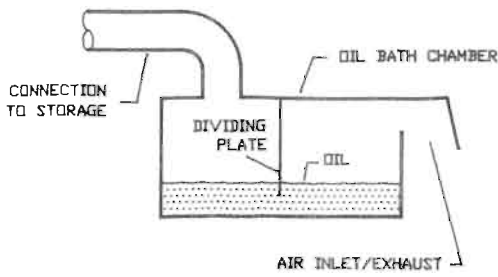


Fig. 18. Oil bath type pressure relief valve.

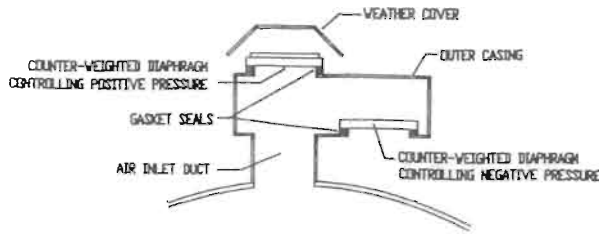


Fig. 19. Diaphragm type pressure relief valve.

## Sealing Materials

Such a wide variety of sealing materials are available that a full coverage of them is beyond the scope of this paper. This paper will discuss those material types commonly used for storage sealing. It should not be assumed that other materials not covered in this paper are unsuited to the purpose.

### Plastic (Non Elastic) Joint Sealants

Sealants in this category include bitumen and butyl type mastics. They can be useful as 'pre-formed' strips but have been largely superseded by other sealant types in recent years.

Such sealants can be useful in high compression joints where uneven surfaces are brought together. High compressive stress will force the sealant to flow into gaps and surface blemishes to form a seal. A typical application is where pre-cast concrete roof panels or a prefabricated steel roof is placed on top of a concrete silo wall (Fig. 20). The surface at the top of the wall will often be uneven and a plastic sealant will 'flow' into the voids under the weight of the roof. The sealant may, however, need to be retained with, for example, elastic foam strips, to prevent it flowing out of the joint.

Since the plastic sealant is resistant to rupture, seals of this type will tolerate a high degree of shearing movement. Plastic sealants are not, however, recommended for non-compressive joints since they cannot accommodate tensile stresses. Also, they often have a tendency to become brittle, particularly when exposed to sunlight.

### Elastic Adhesive Joint Sealants

Polysulphide and silicone type sealants fall under this heading. They are particularly useful for sealing non-compression joints and, since they are applied after the joint is formed, for 'retro-sealing' compression joints. Such sealants are usually applied by caulking gun and need to 'cure' for a period of time to develop their elastic properties. They need to develop a good adhesive bond to the surfaces to which they are applied so that they will maintain intimate contact with them if tensile or shear stresses occur.

Silicone and polysulphide sealants are used principally for sealing abutting surfaces (concrete to concrete, steel to steel, or steel to concrete) and will tolerate some tensile and shearing stresses before rupturing. The sealant cross-section needs to be carefully controlled to maximise the amount of deformation it will tolerate, general principles being that the depth of sealant should be about half its width and that a bond-breaking strip be incorporated under the seal to ensure that it is bonded only at its sides (Figs 21 and 22).

Modern silicone sealants are generally more easily applied than polysulphides. Silicone sealant is a 'one-part' pre-packaged material

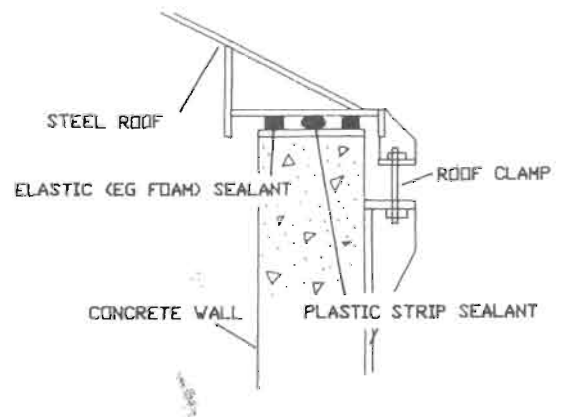


Fig. 20. Typical use of plastic sealant in a compressive joint between a silo roof and wall.

## Acrylic-Based Sealant Paints

Of all the various forms of sealants used in gas-sealing of storages, acrylic-based sealant paints are by far the most important. They can be used on virtually any substrate and adapted to seal most types of joints, cracks, or other potential routes of gas-leakage. In fact, it should be possible to seal most storages using only this type of sealant.

Sealant paints are generally acrylic-based emulsions with a high solids content. They are easy to apply, bond well to most surfaces, bridge over small cracks, dry and cure quickly, retain flexibility and elasticity in the event of subsequent joint movement, and are easy to recoat.

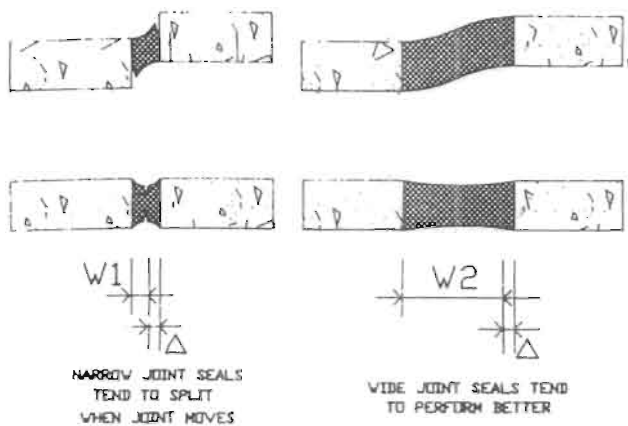
Acrylic sealant 'coatings' generally contain at least 50% solids, either as pure acrylics (plus pigments) or mixtures of acrylics and other plastics such as styrenes (referred to as copolymers). Higher solids content coatings yield thicker films, while the addition of thixotropes can produce mastic-type sealants suitable for caulking wide gaps.

Acrylic and copolymer sealant coatings can be used in a wide range of sealing applications including:

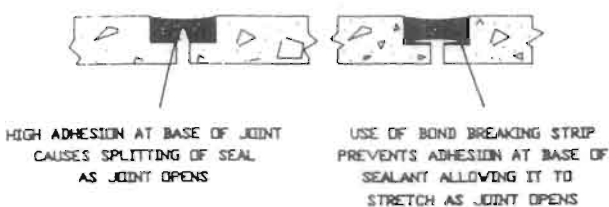
- sealing porous surfaces (e.g. concrete, masonry, timber, fabric);
- sealing cracks in concrete;
- sealing lap joints in steel cladding; and
- as bandage seals.

Acrylic sealant coatings are easy to apply and are relatively forgiving of poor application procedures. Good adhesion can be achieved on most surfaces without the use of primers. Nevertheless, as with all paints, surface preparation is critical to good performance, removal of oils, dirt, and loose particles being essential before application of the sealant.

Since they are relatively inert and unaffected by ultraviolet light, acrylics can be expected to give excellent durability in external applications. They are also flexible and extensible, although some loss of flexibility is likely to occur due to changes in temperature (Lloyd 1985). Finally, they are non-toxic and therefore can be used in contact with foodstuffs. A later section of this paper—**Materials Specifications for Sealants**—provides further information on acrylic sealant membrane application.



**Fig. 21.** Sealants perform better if they are applied so that the seal formed is wider than its depth.



**Fig. 22.** Sealants perform better if not bonded underneath.

usually applied from a cartridge inside a caulking gun. Curing is by chemical reaction with atmospheric moisture.

Polysulphides are supplied in two parts which have to be thoroughly mixed together on site immediately before application. Curing is by chemical reaction between the two components. Sealant failures resulting from inadequate mixing are not uncommon.

While both silicones and polysulphides types have very good bonding properties, very careful surface preparation and priming is usually necessary for good bonding to be achieved, particularly in the case of polysulphides. The latter may also deteriorate and become brittle when exposed to the sun for extended periods, a defect not generally shared by the silicones.

Silicones are available only in 'caulking' grade—i.e. they must be 'gun applied'—whereas 'pourable' grade polysulphides are available for filling horizontal joints. Nevertheless, polysulphides have been largely superseded by silicones in recent years. Generally, silicones are much easier to work with (requiring no mixing) and cure more quickly and reliably. Silicone sealant specifications receive further mention in the next section.

## Polyurethane Sealant Membranes

Flexible polyurethane is another material with potential for storage sealing, although it is much more expensive than acrylic compounds and may include toxic components that render it unsuitable for applications which place it in contact with foodstuffs.

Flexible polyurethanes do, however, offer excellent adhesion and flexibility in external applications, and may outperform acrylics in terms of bond strength and elongation. This type of membrane sealant may therefore find a use in critical sealing situations where its good adhesion and excellent strength and elongation warrant the high cost.

## Bandage Seals

'Bandages' are used for bridging gaps too wide for a sealant coating. They are especially useful for sealing joints where a great deal of movement can occur (Fig. 23). The edges of the joint are coated with sealant (e.g. acrylic) and a cloth or fabric 'bandage' is then placed across the joint while the sealant coating is still wet. The bandage is then painted over with sealant to make it gastight. Since the fabric acts mainly as a support (or bridge) for the sealant coating, its composition is, to some extent, not critical. However, a coarsely woven material is preferable to ensure good penetration and adhesion of the paint. Strength can also be advantageous in some situations where there is a risk of mechanical damage. In such cases, glass-fibre or polyester fabrics are commonly used. Where joint movement is expected, it should be accommodated by placing a concertina-type fold in the part of the bandage over the joint.

Acrylic sealant coatings are usually employed to coat bandage seals of this type, but an alternative is to use a preformed PVC membrane bonded to each side of the joint with an epoxy type adhesive. Such a seal will give excellent and reliable results but is relatively difficult to apply, often requiring specialist applicators.

## Sprayed Rigid Polyurethane Foam

Where very large apertures require sealing, it is usual to close them with some form of bridging before sealing. Timber, galvanised iron, and mortar are often used for this purpose, as are bandages as described above.

Polyurethane foam is a very useful material for bridging gaps, particularly where access is difficult or where the joint is irregular and difficult to close. The material is formed from two liquid components which, when mixed together, expand to 20–30 times their original volume by the rapid development of the cellular foam structure. The foam then hardens to become a relatively strong and rigid structure. It also bonds extremely well to most surfaces provided they are properly cleaned and dried. Porous surfaces may need priming or pre-sealing (Anon. 1987).

Application is usually by spray (the two components being mixed together in the spray nozzle), but it is not uncommon for the liquid mixture (suitably retarded) to be poured into joints or cavities where access is difficult. These then become filled as the foam expands.

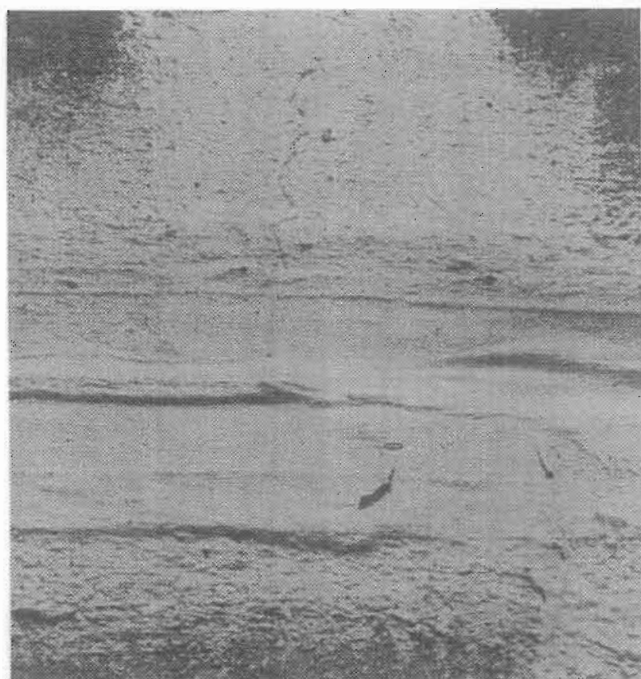
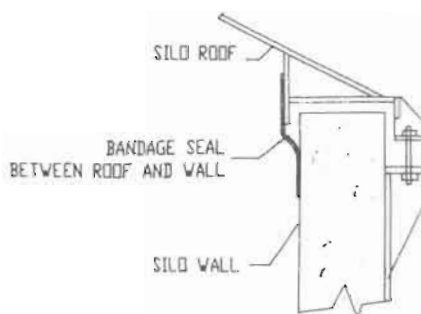


Fig. 23. Joint sealing (upper) and crack sealing (lower), typical applications of bandage seals.



Polyurethane foam is widely used as a heat insulation material; for instance on steel roofs. It can also be used to seal and strengthen badly corroded roofs. Its principal role in grain storage sealing is however, not as insulation, but as a 'bridging' medium. Further information on its use is given under **Specifications for Gastight Sealing**.

### **Gasket Materials**

Gasket seals are required to perform so great a range of functions that it is not possible to describe all suitable materials. Generally, they need to combine good elasticity with sufficient rigidity to accommodate unevenness in the surfaces being joined. Gasket material specifications are discussed briefly under **Specifications for Gastight Sealing**.

### **Specifications for Gastight Sealing**

Whether gas-sealing is to be undertaken by a contractor or on-site labour, and whether it is to be carried out on a new or old structure, the level of gastightness to be achieved needs to be specified. This section looks primarily at the specifications applicable to gas-sealing work by contract. Material specifications are also discussed.

### **Specification for Sealing Contracts**

In drawing up a sealing contract the first choice to be made is whether to seek a performance specification or to specify the precise sealing methods to be adopted. Current practice in Australia is almost universally to use performance specifications, since the onus is then clearly placed on the contractor to achieve the required degree of gastightness. Such a specification normally states the criteria for acceptance of the degree of seal achieved (usually by means of a 'pressure-decay test') and the contractor is allowed to undertake the work in any way he chooses. The onus is thus transferred almost wholly to the contractor to achieve the desired result and the 'risk' is carried by him.

The alternative—specification of materials and sealing methods to be used—leaves a high level of uncertainty as to which party carries the risk. If the specified seal is not achieved, it may be either the contractor's responsibility

because of poor workmanship or the client's as a result of inappropriate specification. Uncertainty and dispute is then almost inevitable in the event of failure to meet the specified performance.

A performance specification does not, however, assign all risks to the contractor. Some risks will always remain with the client, including the following:

- The contractor may fail to achieve the specified standard and back down on the contract. This is best avoided by engaging a reputable contractor with proven competence.
- The contractor may use poor quality materials or poor sealing methods. While these may achieve the specified test standards, they may also have poor durability and subsequently fail in service.
- The storage enclosure may have defects affecting its ability to be sealed. If the storage sealing is part of a 'design and construct' contract package, the responsibility will be with the contractor to overcome such difficulties. If the sealing contractor is not responsible for structural adequacy of the enclosure, then contractual complications will arise if structural problems (e.g. excessive deflections under test pressure differentials) make sealing difficult.

Contractual difficulties are best avoided by unequivocal definition in the contract documents of where responsibilities for risk are to lie. Clients should recognise that they should not expect to get something for nothing, and that they should expect to pay for what they get. Quality seldom comes cheap and the lowest price is not necessarily the best. If the client wants the contractor to carry risk, then this should be reflected in the contractor's price. If not, then the client must be prepared to pay for problems beyond the control of the contractor. Documentation should be drafted so as to anticipate, where possible, the problems that may arise, and to define cost responsibility as clearly as possible for every situation.

In essence, the most appropriate specification for most storage sealing contracts should incorporate a performance-based objective for the contractor, where the degree of seal that must be achieved is clearly defined, as are the acceptance criteria.

A performance-based specification automati-

cally precludes the use of a method based specification. A client cannot tell a contractor precisely how to do the work and then hold the contractor responsible for the outcome. A performance-based specification thus removes some of the client's opportunity to control the quality of the work as it is progressed.

There are various means of overcoming this problem:

- Quality standards for materials that can be used on the job (allowing the contractor to select conforming materials of his choice) can be specified.
- Alternatively, the contractor may be required to submit for approval, at the tender stage, full details of all materials he proposes to use.
- In addition, the contractor should be required to submit for approval at the tender stage full details of the sealing methods and procedures that he proposes to use.

In this way, the contractor chooses his own materials and methods and thus retains full responsibility for performance. At the same time he makes a commitment at the time of tendering as to the materials, procedures, and methods which he intends to adopt, thus giving the client the opportunity to assess the quality of the proposal before awarding the contract, and to monitor (and to some extent control) the quality of the work as it is undertaken.

A warranty period should also be clearly defined, spelling out the guarantees as to performance that are to be provided by the contractor. Often a 5-year warranty is specified which requires an annual gastightness test by the contractor and repair of any leaks that are found.

A properly drafted (and preferably a standardised) set of General Conditions of Contract should be used, clearly defining how the contract is to be administered and where contractual responsibilities lie. Standard Conditions of Contract are often available from national 'Standards' organisations and government departments [e.g. Australian Standard AS 2124 (Anon. 1986) or the (Australian) National Public Works Committee's (NPWC) Conditions of Contract].

Finally, it should be emphasised most strongly that the choice of contractor is of paramount importance in achieving successful results. It is strongly recommended that the past performance of a prospective contractor be

thoroughly investigated, and client references carefully followed up.

## **Material Specifications for Sealants**

As discussed earlier, minimum quality standards should be specified for sealing materials and methods of application. The following sections look at specifications for some of the commonly used sealants.

### *Acrylic Sealant Coatings*

As noted previously, acrylic sealant coatings are by far the most widely used materials for grain storage sealing. It is thus important that the most appropriate materials be selected for the purpose.

Desirable properties of sealants to be applied externally include:

- non toxicity
- ease of application in a single coat.
- durability
- gap-bridging ability
- good adhesion to a variety of surfaces
- relative impermeability
- flexibility over a wide temperature range
- extensibility over a wide temperature range
- high tensile strength
- low shrinkage

For internal application, the following additional properties are important:

- abrasion resistance if in contact with moving grain
- surface hardness
- suitability for contact with foodstuffs
- non-reactivity with fumigants such as methyl bromide, phosphine and CO<sub>2</sub>

In Australia, at least, there are no clearly definable test standards for sealants and there does appear to be a clear need for the formulation of more precise testing procedures, and performance criteria based on these tests, to allow comparative testing of sealant coating materials to be systematically undertaken. It is beyond the scope of this paper to discuss in detail what might be appropriate test methods and performance criteria. However, the following brief comments are included to highlight the needs and problems.

**Toxicity.** In Australia, most commonly used paint coatings have a 'GPC' approval issued by the Government Paint Committee. Such approvals imply that a Material Safety Data Sheet (MSDS) for the paint product has been checked for currently known harmful chemicals as listed by the U.S. Food and Drug Administration (FDA) and other regulatory and testing agencies. Thus, in general, approved paints do not contain toxic compounds and all acrylic coatings with GPC approvals can be assumed to contain no known harmful chemicals.

When specifying coatings, it is strongly recommended that a Material Safety Data Sheet or similar information be checked for any sealant which is to come into contact with grain.

**Durability.** It is inappropriate to specify a level of durability since it is always difficult to determine and must ultimately be assessed by field performance. Accelerated UV testing could provide an indication of UV susceptibility. The Western Australian grain handling authority's test procedure, for example, involves 2000 hours exposure to mercury discharge. Condensation testing (AS1580 452.1) (Anon. 1981a) and salt spray testing (AS1580 452.2) (Anon. 1981b) could give comparative indications of susceptibility to moisture etc. It should be noted that most acrylic type sealant coatings have no corrosion inhibitors and seldom offer good corrosion protection on their own (without primer).

**Gap-bridging Ability.** This is an important property from an applicator's point of view and one which can affect the cost of applying sealant coatings. An implied requirement of the existing 'standards' in Australia is that coatings should be able to bridge 1.5 mm gaps. Since most coatings will meet this requirement a need exists for 'comparative' testing of coatings. While no standard test is currently in use, it may be possible to assess performance in this respect by coating a sheet of etched galvanised steel punched with holes of varying diameters. Bridging ability could be measured by the maximum diameter hole which will be covered over by a film of specified thickness.

**Elongation or Strain.** Strain is defined as the ratio between the change in length and the original length, i.e.

$$\text{Strain} = \frac{\text{Stretched Length} - \text{Unstretched Length}}{\text{Unstretched Length}}$$

This is a very important property for an elastic sealant. Values of 300, 500, and even 700% are often quoted by manufacturers, but it should be recognised that such figures are obtained using narrow test strips that are free to contract laterally as they are stretched. Were this contraction to be inhibited, the ultimate strain figures would reduce significantly.

When applied to a sealed joint, the coating is usually equivalent to a very wide and short test sample that is incapable of significant change in width as a result of elongation. It is suggested that a standardised test should reflect this fact, utilising perhaps a 50 mm wide test sample clamped 5 mm apart. The results should give a more factual interpretation of the ability of a material to accommodate joint movements.

**Tensile Strength and Adhesion.** The test suggested above to measure elongation should also yield a realistic figure for tensile strength (Fig. 24). Strength, however, is not in itself a particularly important property and is relevant only in relation to adhesion or bond-strength.

The relationship is important in situations where unexpected movement occurs as, for instance, where a new crack occurs in a concrete surface underneath a sealant coating. If the coating bond is very high, such that adhesion is maintained almost to the edges of the new crack, then the unstretched length is close to the initial crack width which is zero. Thus the strain tends towards 'infinity' and tensile failure is inevitable (Fig. 25).

Where adhesion is weaker in relation to tensile strength, progressive bond failure will occur at the edges of the crack thus increasing the effective unstretched length. Strain in the coating is thus reduced and tensile failure less likely to occur.

Coating adhesion is highly dependent on the nature of the surface being coated. It is also of particular relevance to coating performance when applied to brittle substrates such as concrete, which itself is a highly variable material not least in terms of its surface qualities. It is thus hard to envisage a standardised test which will reliably indicate the performance of a coating in all circumstances.

Nevertheless, it is suggested that a simple test providing good comparative indications of

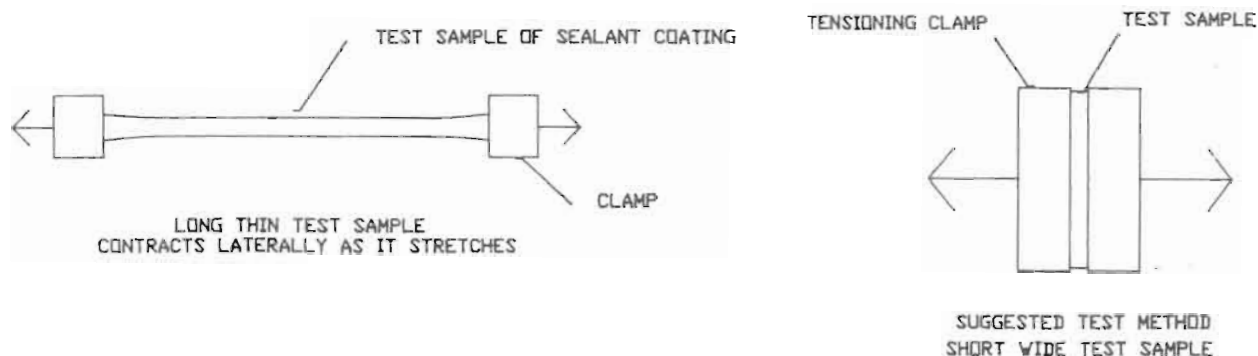


Fig. 24. Methods of testing tensile strength of sealant coatings.

performance could be devised by using a 50 mm wide strip of standard grade glass paper to represent a standard surface texture (Fig. 26). This could be pre-cut before being coated with a nominated thickness of the sealant coating. Tensile testing of the cured sample would provide a relationship between stress and strain and, in particular, should give guidance as to loss of adhesion that takes place prior to failure. It should indicate the coating's potential performance when used for sealing concrete surfaces subject to cracking and movement. The current criterion for this property set by CSIRO in Australia stipulates that a '100% extension of a 0.3 mm wide crack should be withstood without failure'.

*Abrasion Resistance and Adhesion.* While good adhesion is potentially a negative attribute in the circumstances just dealt with, it is, on the other hand, essential in the context of ensuring that the coating will not fall off or becoming detached as a result, for example, of air pressure differentials across it. In abrasive situations, such as the internal surfaces of bins, good adhesion becomes of even greater importance.

Some acrylic based sealants are specifically formulated to improve abrasion resistance, but there appear to be no established test

procedures to assess performance. There are, however, a number of procedures which could be developed into a standard test method; for instance, the loss of coating (by weight) from a disc of prepared substrate (e.g. graded sandpaper or etched galvanised steel) could be measured after it has rotated a certain number of times in contact with grain. Alternatively, a 'tumbler' type of apparatus could be used to compare abrasion resistance.

No quantitative standards have yet been set.

*Surface Friction.* Surface friction is an important property in circumstances where the internal wall surface of a silo is to be coated, as may be the case when interconnected concrete silos are to be sealed. The forces exerted by the grain mass on the walls of a silo are directly related to the wall surface roughness and, in general, reducing the friction between the grain and the wall will result in higher horizontal grain pressures and higher wall tension stresses.

If a coating is to be applied to the internal walls of a silo, it is important to know what effects it will have on grain pressures (Banks 1984). The Western Australian grain handling authority assesses this coating property using a standard 'pencil hardness' test (AS 1580-405.1) (Anon. 1978). It is questionable, however, whether such a test is reliable in determining

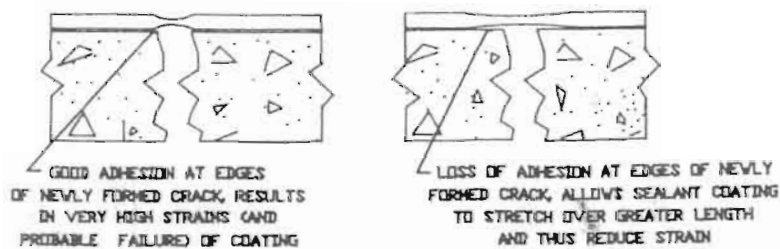


Fig. 25. Diagrams showing how sealant coatings bridge cracks better if their adhesion fails.

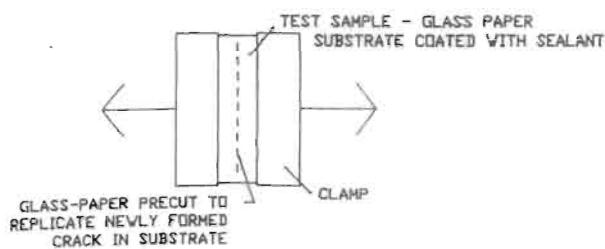


Fig. 26. Suggested method for testing tensile strength/adhesion of surface coatings.

the effects of a coating on the friction angle between grain and a silo wall and it is strongly recommended that an accurate determination of the kinematic angle of friction between grain and the coating surface be undertaken before a coating is selected.

**Flexibility.** The Western Australian grain handling authority specifies a bend test (as per AS 1580-402.1) (Anon. 1981c) requiring checking for cracking or detachment of the coating as applied to galvanised steel, when bent over a 6 mm diameter mandrel at 25°C. No evidence of cracking in the coating is permitted.

**Permeability.** The Western Australian grain handling authority's test standards specify permeability testing in accordance with American Society for Testing of Materials' E96 Procedure B. The acceptance criteria are not defined.

While it appears to be the case that specifications and acceptance criteria need to be better defined for sealant coatings, it should be recognised that a number of coating types have been successfully used for sealing a variety of storages. The Western Australian grain handling authority has had more experience with these coatings than any other grain industry group, and has conducted its own comparative testing of numerous products. It has also developed an extensive weathering and exposure testing site on the roof of one of its large horizontal grain storages, where several coating suppliers have applied their coatings side-by-side with those of their competitors.

#### Specifications for Gaskets

A gasket material needs to be:

- rigid enough to withstand the compressive forces applied to it;

- elastic enough to deform and conform to any unevenness in the surfaces being joined;
- resilient, i.e. reverts to its original shape when released from a deforming force;
- durable and chemically resistant; and
- gastight under moderate compressive stress.

Solid materials (e.g. rubber) will usually best suit situations where contact pressures are high. Rubber hardness should be specified by Shore-A or 'Duro' hardness, 40 or less indicating a soft rubber suited to forming gaskets.

Where contact pressures are low, cellular or foam gaskets are more appropriate. A number of types are available, including rubber, polyurethane, PVC, and polyethylene. Unlike polyurethane flexible foams, which are usually open-cell, polyethylene and PVC foams have the advantage of being quite inert and having a closed-cell structure, making them inherently gastight and non-absorbent. They are also available in a wide range of hardness. PVC foams are generally softer and more resilient than polyethylenes and may offer better sealing performance on lighter weight doors and closures.

Trial and error may sometimes be the best approach to selecting the most suitable material for a particular application.

#### Silicone Sealant Specifications

The term 'silicone sealant' defines a range of products that are very widely used throughout the building industry. It is surprising therefore that there are few industry 'standards' against which material qualities can be assessed.

It is important to recognise that there are different type of silicone sealants. Some, for example, bond better to steel and others to concrete, and some have better elongation properties than others and are more suited to sealing joints that accommodate movement. Importantly, some silicones release acids as they cure rendering them unsuited for use in contact with steel or concrete; 'neutral-cure' sealants should be specified for such purposes.

In view of the absence of general industry standards for silicone sealants, and the relatively small usage of the material in the grain industry, it is common practice to specify a suitable product from a recognised manufacturer and to permit the use of 'approved equivalents'.

Good quality spray polyurethane foam is not easy to produce and specifications should call for the engagement of an experienced applicator using high quality materials and good application equipment.

The most easily specified and verified measure of quality is the foam density, which should not be less than  $32 \text{ kg/m}^3$  for non traffic areas, and  $48 \text{ kg/m}^3$  where extra rigidity is required.

The specification should require that density be routinely checked during the spraying operation to ensure that quality is being maintained. Samples are cut from the workface with a sharp knife or sprayed onto a separate test panel, and visually inspected before density testing. A sample should be taken for at least every 200 square metres of coating. Coating thickness should also be checked regularly using a needle probe.

The formation of the foam is dependent upon the expansion of a refrigerant 'blowing agent', the rate of expansion being dependent upon the heat of the chemical reaction which forms the polyurethane material. Ambient humidity and temperature, and surface temperatures, are important factors which can affect the quality of the finished product. Special chemical formulations should be specified for high and low ambient temperatures.

Polyurethane foams are not weatherproof, and they are subject to U/V degradation. When applied externally, it is essential to overcoat them with an appropriate material to provide protection. An acrylic sealant coating (as previously described) is commonly used.

## **Gastightness Testing**

### **General**

In defining a performance specification for gas-sealing work, the test procedure and acceptance criteria must be clearly specified. Appropriate procedures and acceptance criteria have long been established by the CSIRO in Australia and have gained widespread industry acceptance (Banks and Annis 1980).

The test involves applying a pressure differential between the inside and outside of the storage enclosure by the development of a positive or negative internal pressure, and then

measuring the 'half-life decay', i.e. the time taken for the pressure differential to reduce to half its starting value.

The acceptance criterion is for a half-life decay of not less than 8 minutes for a full structure or 15 minutes for an empty structure. The decay time for partially filled structures can be estimated on a pro-rata basis.

Because pressure differentials are affected by external factors such as temperature changes, wind, and barometric pressure changes, it is important that accurate testing be carried out under stable atmospheric conditions—ideally shortly before sunrise. This applies particularly to steel structures, which are subject to rapid temperature change from insolation.

### **Test Equipment**

Equipment needed for pressure testing includes the following:

- A blower or suction unit to generate a pressure differential. For structures up to around  $3000 \text{ m}^3$  capacity, a small hand-held blower, or vacuum cleaner, will normally suffice. For very large structures (or very leaky ones) a small axial fan is usually necessary to generate a pressure differential sufficient to conduct a test.
- A quick acting valve to isolate the storage from the air supply or, where an axial fan is used, it is usual to flange-mount the fan to the structure and to clamp a sealing plate over the outside of the fan when the specified starting pressure is reached.
- A manometer attached to the structure to measure the internal air pressure. For low pressure differentials, such as may be applied to a horizontal shed structure (say, less than 250 pa), an 'inclined' manometer is desirable for accurate measurements. For higher pressures, such as may be applied to a silo structure, a simple U-tube manometer is normally sufficient.

### **Test Procedure**

The test procedure is simple.

1. Atmospheric conditions are checked for stability—usually intuitively for routine tests, but by measurement for experimental or other critical tests.

2. The blower device is connected to the structure by suitable means (e.g. flexible hose) and then switched on.
3. The pressure differential is monitored and once it reaches a value slightly in excess of the nominated test pressure, the cut-off valve is closed and the blower switched off.
4. A timer is started when the pressure differential drops to the nominated test pressure and stopped when the pressure reaches half this value. The decay time is recorded.

### Detecting Gas Leaks

In preparing a specification for pressure testing of a storage some points to be followed are:

- Specify who is responsible for conducting the tests. Usually the sealing contractor will undertake the initial tests on the empty storage but the client may elect to conduct the tests when the storage is full and at the end of the warranty period specified in the sealing contract.
- Specify that all detectable leaks are to be sealed, even when the pressure standard is achieved.
- Specify methods of leak detection. To some extent, leak detection methods are chosen to suit the storage and the type of fumigant that will be used.

For independent, above-ground storages with no interconnecting galleries, it should suffice to use leak detection methods based on sound and a 'soapy water' test. In the latter, a mixture of detergent and water is sprayed over the storage surface, and leaks are revealed by bubbling.

In some cases (e.g. when testing for leaks through the floor of the enclosure, or listening for leaks in the roof) it is often more appropriate to apply negative pressure and to search for leaks on the inside the structure.

Leaks often become evident by inspection from inside the structure when application of a positive pressure opens gaps through which daylight can be seen.

When a storage structure interconnects with conveyor galleries or adjacent enclosed workspaces, the existence of leaks should be much more closely investigated even after the pressure decay test is successful: a serious

hazard would be created if any gas leakage paths vented into such areas. It is thus essential in such circumstances to employ appropriate gas monitoring equipment to thoroughly test for the presence of gas during the first fumigation of the storage.

### Conclusion

Fumigation is one of the most important weapons available in the ongoing war against insects causing grain losses. At the same time, ineffective fumigation practice represents a long-term threat to the usefulness of available fumigants because of the risk of insect resistance developing. The key to effective fumigation practice is the availability of an adequately sealed storage.

There can be few circumstances where the cost of sealing new storages to an adequate standard of gastightness cannot be justified, and there are few circumstances where adequate gastightness cannot be achieved if appropriate design detailing has been adopted. The technology is simple and straightforward and requires little more than common sense and careful attention to detail to ensure that satisfactory results are achieved.

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## Report on Session 3: Physical Processes in Fumigation and CA Storage

Chairman: Dr S.H. Ho, National University of Singapore  
Rapporteur: Mrs F. Caliboso, NAPHIRE, Philippines

Two invited papers were presented in this session.

A paper by Dr H.J. Banks of CSIRO, Australia, reviewed the state of the art in knowledge of the behaviour of various gases relevant to CA and fumigation. He described different gas processes and phenomena at three scales: molecular; store; and intermediate. Some estimates of diffusion coefficients for the materials in air, the apparent values within grain, and the values for permeation through a plastic film were also presented.

Following a recent study, Dr Banks reported that methyl **chloride** is released over a considerable period following methyl **bromide** treatment of grain. This could lead to incorrect estimations of methyl bromide residues and reaction rate constants. The finding that the sustained production of methyl chloride from methyl bromide-treated materials can be substantially prolonged, merits practical consideration of current ventilation periods after fumigation and perhaps their redefinition.

Another significant finding is that phosphine is strongly sorbed by paddy, so that adequate fumigation may not be attained by employing normal dosages, even in a perfectly sealed enclosure. Likewise, high moisture grain absorbs phosphine rapidly.

Finally, Dr Banks noted gaps in the current knowledge on the various processes involved in gas behaviour and suggested areas along which research could productively proceed.

Design specifications for gastight enclosures were the subject of discussion by Mr C. Newman of Bulk Grains Queensland, Australia. Drawing on engineering experience within the Australian grain industry, the speaker described the requirements for gastight grain storages. Mr Newman's paper details points which should be considered when preparing specifications for sealing work, as well as specifications for, and selection of commonly used sealants. Careful choice of contractor and close supervision of the sealing work were emphasised. Also covered were procedures for testing gastightness and methods of detecting leaks. Attention was drawn to the problems associated with sealing different types of storages as well as deficiencies in test standards and acceptance criteria for commonly used coatings.

General discussion in the session focussed on the following major concerns or issues:

1. There is a need for the costs involved in sealing storages to be indicated.
2. A full understanding of phosphine sorption in paddy is required in order to provide guidance on appropriate dosages.
3. In the light of the finding that the liberation of methyl chloride from methyl bromide fumigation could be prolonged, serious concern was expressed on the hazards involved in venting methyl chloride to the environment.
4. Guidelines on the labelling of fumigants must be incorporated in the fumigation recommendations presented at the conference.

5. Feedback from relevant agencies is needed to guide the future directions of research in the region.

6. Acknowledging that a serious gap exists in the flow of information between researchers and extension workers and target beneficiaries, a system of coordinating research on fumigation and CA on a global level was recommended. The importance of convening seminars or workshops on fumigation and CA on an annual or biennial basis was stressed. In this regard, in-country seminars should be encouraged. It was also recommended that international conferences on fumigation/CA topics be conducted at reasonably frequent intervals.

# Application Methodology

# Recent Developments in Controlled Atmosphere Technology

E. G. Jay\*, H.J. Banks†, and D. W. Keever§

## Abstract

Laboratory studies have shown that controlled atmospheres, applied in combination with elevated temperatures, can reduce the exposure time needed for control of stored-product insects. This relationship is demonstrated by the presentation of recently developed data on all life stages of *Lasioderma serricornis* (F.).

Field studies conducted in the United States (U.S.) on the use of carbon dioxide to control stored product insects are described. These range from the treatment of herbs and spices in a 45m<sup>3</sup> chamber to the application of carbon dioxide into a bunker containing 27,680 tonnes of maize, and include an account of the use of carbon dioxide in a tobacco warehouse, a bolted metal bin, and a river barge. The future of controlled atmospheres in the U.S. is discussed.

LITERATURE on the use of controlled or modified atmospheres (CAs, MAs) to control pests of raw and processed agricultural products is extremely abundant. The large amount of literature is caused by serious interest in the subject, interest which has come to a peak twice over the last decade when two symposia on the subject were held and their proceedings published (Ripp et al. 1984; Shejbal 1980).

Most of the work reported, however, has been of laboratory studies on the effects of various combinations of carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), and oxygen (O<sub>2</sub>) on one or more species of insects. These studies have usually been conducted with adults only, and the gas mixtures used when the effects of CO<sub>2</sub> were being studied are generally not those found when a storage container is actually treated with this gas in the field.

\* U.S. Department of Agriculture, Agricultural Research Service, P.O. Box 22909, Savannah, GA 31403 USA

† CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

§ U.S. Department of Agriculture, Agricultural Research Service, P.O. Box 1555, Oxford, NC 27565 USA

Large gaps therefore exist in our knowledge on the effects of actual field concentrations of O<sub>2</sub> on all life stages of several of the more important stored-product insects. Jay (1986) reported on the time × elevated temperature × CA concentration effects on all life stages of *Tribolium castaneum* (Herbst). Although this work was conducted at from 32 to 43°C and some exposure times to produce 100% mortality of larvae and adults were not included it did show, for example, that at a CO<sub>2</sub> concentration of 90% (balance air) it took 40 hours to achieve complete mortality of eggs of this species, while at 43°C it took only 16 hours to obtain this level of control.

Future laboratory studies should include all life stages of the test insects involved and be conducted at several realistic temperatures and over the range of CA concentrations that can be attained and maintained in the field. We cannot be confident of achieving high levels of control in field situations under less than perfect circumstances until such data are available for the economically important species of stored-product insects.

An important requirement for use of CAs is that the storage to be treated is sealed to a high standard of gastightness. A remarkable sealing program has been carried out in Western Aus-

tralia to render most of that State's large bulk storages gastight and suitable for CA and treatment with phosphine (Ripp 1984). This program showed what a potent combination of money, talent, research, and manpower can do toward making CAs a viable insect management tool. The rest of the world, however, is not so fortunate. Although research is funded in developed countries such as the Canada, France, Israel, Italy, the United Kingdom, and U.S., most countries still rely on residue-producing conventional fumigants or protectants to control insect pests in storage facilities.

Several reasons were outlined by Jay (1986) for the apparent lack of involvement in the use of CAs in the U.S. These are still generally applicable and include the general lack of commitment to spend the funds needed to seal storage structures and the extreme competition in the phosphine business, leading to greatly reduced prices for this fumigant. Another reason for the lack of commitment is the general reluctance of the producers of CO<sub>2</sub> and N<sub>2</sub> to make a clear decision as to whether or not a large market exists for their products and, subsequently, to attempt to enter this market in a dedicated manner. In the U.S., five large CO<sub>2</sub> producers have labels from the Environmental Protection Agency (EPA) permitting them to use their product as pesticides on all raw and processed agricultural products. Three of these five companies have recently seriously studied the use of CO<sub>2</sub> for health foods, including herbs and spices, for large quantities of maize and sorghum stored in bunkers or temporary storages, and for use in tobacco warehouses. However, this is only a small portion of the potential market.

Carbon dioxide can be competitive in cost with conventional fumigants in the U.S. if the source of supply or plant is close (< 80 km) to the treatment site. Bulk carbon dioxide can, in a situation such as this, cost as little as \$66 U.S./tonne (541m<sup>3</sup>), rising to \$143 U.S./tonne when transported about 400 km. Treatment costs can therefore be more than doubled if the treatment site is far from the production site.

There has been little or no interest in the use of N<sub>2</sub>, except in laboratory studies, in the U.S. in the 20 years of sporadic field testing with CO<sub>2</sub>. The reason for this is that private corporations involved in the raw and processed agricultural food industry are reluctant to expend the funds to bring their storage vessels

up to a high degree of gastightness. This sealing is necessary when N<sub>2</sub> is used for treatment but is not so critical when CO<sub>2</sub> is used and supply is cheap. When CO<sub>2</sub> is purchased at or near \$66 U.S./tonne some leaks can be tolerated and the use of CO<sub>2</sub> can be economically feasible when compared with conventional fumigants. However, this is not true when the cost for CO<sub>2</sub> approaches \$100 U.S./tonne.

There has been some recent interest in the U.S. on the use of CA or inert atmosphere generators and some government and commercial research has been conducted in this area. The information produced from these studies has not been published and is not available, so this paper will not consider this method of CA application.

This paper will present data on laboratory studies involving all life stages of *Lasioderma serricorne* (F.) at temperatures >27°C. and using several different CAs. It will also present data from field studies involving the use of CO<sub>2</sub> in treating: tobacco in a warehouse; barley in a river barge; herbs and spices in a small container; rice in a sealed bolted metal bin; and maize in a large bunker or temporary storage.

### Laboratory Studies on *Lasioderma serricorne* (F.)

Eggs (0–3 days old), larvae (25–26 days old), pupae (2–4 days old as pupae), and adults (0–6 days old as adults) of *L. serricorne* were individually exposed to four CO<sub>2</sub> concentrations and to one N<sub>2</sub> concentration at either 32, 38, or 43°C at 55–60% relative humidity (RH) using laboratory equipment described by Jay and Cuff (1981).

Table 1 shows the results of this study. Eggs exposed at 32°C to 65 or 78% CO<sub>2</sub> were completely controlled in 72 hours while 120 hours were required to obtain this level of control at 90 or 98% CO<sub>2</sub>. At 38°C, 72 hours were required to obtain 100% mortality at CO<sub>2</sub> levels of 65 or 90% while those exposed to 78 or 98% CO<sub>2</sub> or to 99% N<sub>2</sub> were completely controlled in 48 hours. Eggs exposed at 43°C were completely controlled in 6–48 hours depending on the CA composition and concentration. Larvae of this species were totally controlled in from 24–96 hours at 32°C with

98% CO<sub>2</sub> giving the fastest kill. At 38°C the time for 100% control ranged from 24–72 hours while at 43°C it ranged from 6–48 hours with the higher CO<sub>2</sub> atmosphere and the N<sub>2</sub> atmosphere generally giving more rapid control.

All pupae of *L. serricornis* were killed at 32°C in 48–96 hours, in 48–72 hours at 38°C, and in 6–24 hours at 43°C when exposed to the five different CAs. Adults of this species were completely controlled in 24–72 hours at 32°C with 65% CO<sub>2</sub> giving the fastest control. The time for 100% mortality was reduced to 16–24 hours at 38°C and to 6–16 hours at 43°C, with the CAs containing 90 and 98% CO<sub>2</sub> giving total control of adults after six hours of exposure.

When the data for all life stages are pooled, the longest exposure time required to produce 100% mortality of these stages at 32°C was 120 hours, at 38°C 72 hours, and at 43°C 48 hours. The CA containing 99% N<sub>2</sub> produced 100% mortality of all life stages at 32°C in 96 hours or less. At 38°C the N<sub>2</sub> atmosphere produced 100% mortality of eggs, larvae, and pupae in 48 hours or less, i.e. as fast as, or faster than any CA containing CO<sub>2</sub>. At 43°C the N<sub>2</sub> atmosphere produced 100% mortality in 24 hours which was faster than all the CAs containing CO<sub>2</sub> except for the atmosphere containing 98% CO<sub>2</sub> which controlled all life stages in six hours at this temperature and the CA containing 90% CO<sub>2</sub> which controlled adults in six hours.

## Carbon Dioxide Treatment of a Tobacco Warehouse

L. Ryan, D.L. Faustini, and R.M. Lehman of Philip Morris, Inc., U.S., were the first to successfully treat bulk (> 28 000 m<sup>3</sup>) tobacco

storages with CO<sub>2</sub> in 1987 (L. Ryan, pers. comm. 1988). They found that maintaining a 40% CO<sub>2</sub> concentration for 8 days killed all stages of *L. serricornis* at a commodity temperature of 26.7°C. Brown and Williamson, Lorillard, and American Tobacco Companies, U.S., have also investigated CO<sub>2</sub> as a means of disinfesting warehouses, small chambers and shipping containers.

Keever (1989) treated with CO<sub>2</sub> a 12 700 m<sup>3</sup> warehouse located in North Carolina, U.S., which contained 1005 tonnes (3320 m<sup>3</sup>) of tobacco. All life stages of *L. serricornis* were used for bio-assay. They were placed at the centres of the two types of tobacco containers (hogsheads: 1.42 m<sup>3</sup>; cases: 0.66 m<sup>3</sup>) and in the warehouse free air space. Nine gas sampling lines were installed in the warehouse: four within the bulk of the tobacco containers adjacent to the caged insects and five in the free air space inside the building.

Liquid CO<sub>2</sub> from a road tanker was injected into the bottom of the building through 1.3 cm i.d. copper tubing and a liquid injection nozzle which converts liquid CO<sub>2</sub> to a powdery form of dry ice. The dry ice was changed to gas by the elevated temperature of the warehouse and the turbulence of injection. Pressure was relieved in this and subsequent applications by opening a door on the opposite end of the building.

The initial purge of the building required 3.75 hours and 18 tonnes of CO<sub>2</sub> were used to bring the concentration to about 60% throughout the warehouse. After the initial purge, daily applications were made in the late morning hours for the remainder of the test to bring the concentration back to about 60% CO<sub>2</sub>. About 9 tonnes were used in the first five daily

**Table 1.** Time (h) required to obtain 100% mortality of *Lasioderma serricornis* when exposed to five controlled atmospheres at three elevated temperatures and 55 to 60% RH.

Atmosphere (%) <sup>a</sup>		Eggs			Larvae			Pupae			Adults		
CO <sub>2</sub>	N <sub>2</sub>	32°C	38°C	43°C	32°C	38°C	43°C	32°C	38°C	43°C	32°C	38°C	43°C
65	28	72	72	48	96	72	48	72	48	24	24	24	16
78	18	72	48	48	72	48	24	48	48	16	48	16	16
90	8	120	72	30	72	48	16	96	72	16	48	16	6
98	1	120	48	6	24	24	6	96	48	6	72	24	6
0.03	99	96	48	24	48	24	16	96	48	16	72	24	16

<sup>a</sup> Balance of concentration is O<sub>2</sub>, argon and rare gases

applications which required about 1.5 to 2.0 hours to complete. About 7 tonnes were used on the day before aeration of the warehouse. A total of 71 tonnes CO<sub>2</sub> was used during the test, which lasted seven days. Two fans were placed on the floor of the warehouse to distribute the CO<sub>2</sub> and were run continuously during the test. The temperature of the tobacco was 23.3°C during the test, while free air temperature ranged from 22.2–26.7°C (maximum) and from 11.7–16.7°C (minimum). The mean free air temperature was 22.9°C. The RH in the free air space ranged from 59–96% with a mean of 65.4%.

Table 2 presents the mean pre- and post-purge CO<sub>2</sub> concentrations in the free air space of the warehouse. The prepurge CO<sub>2</sub> concentrations ranged from 34–39% while the postpurge concentrations ranged from 60–62%.

Table 3 shows the CO<sub>2</sub> concentration in the cases and hogsheads prior to the daily purge. The mean CO<sub>2</sub> concentration from day 2 to 7 was 38–42% in the cases and 42–45% in the hogsheads. The hogsheads were retaining more CO<sub>2</sub> because of their larger size.

One-half of the cages containing *L. serricornis* were removed from the warehouse after 5 days of treatment and the remainder at the end of the test. All insects from both the 5- and 7-day exposures were killed and mortality of control eggs, larvae, and adults was very low. Mortality of control pupae reached 36%, possibly because of handling injury.

The test showed that CO<sub>2</sub> will control *L. serricornis* in field situations. However, it is obvious that the warehouse was very leaky and a large amount of CO<sub>2</sub> was required to obtain

**Table 2.** Mean pre- and post-purge CO<sub>2</sub> concentrations in the free air space of a warehouse containing tobacco

Day	CO <sub>2</sub> (%)	
	Prepurge	Postpurge
1	0 <sup>a</sup>	60
2	36	62
3	34	61
4	34	60
5	36	61
6	38	62
7	37	62
8	39	60 <sup>b</sup>

<sup>a</sup>Prior to treatment

**Table 3.** Mean CO<sub>2</sub> concentrations in cases or hogsheads containing tobacco prior to daily addition of this gas to warehouse or about 24 hours after previous application.

Day	CO <sub>2</sub> (%) in	
	Cases	Hogsheads
1 <sup>a</sup>	32	15
2	41	42
3	39	44
4	38	45
5	42	45
6	41	45
7	42	45
8 <sup>b</sup>	52	54

<sup>a</sup> Readings taken after initial purge

<sup>b</sup> Readings taken about 12 hours after previous application

this result. At a CO<sub>2</sub> cost of U.S.\$77/tonne, the cost for this treatment was \$5.44/U.S. tonne of tobacco. This heavy use could probably have been reduced by using 0.3–0.4 mm polyvinyl chloride (PVC) sheeting to seal doors, windows, and vents as a substitute for the 0.15 mm polyethylene sheeting that was used in the test. Also, the practice of rapid addition of CO<sub>2</sub> to bring the concentration up to about 60% each day could have been replaced by a slow continuous addition of this gas into the upper regions of the warehouse to compensate for the leaks. This technique would have probably greatly reduced the amount of CO<sub>2</sub> applied daily after the initial purge.

### Treatment of a River Barge Containing Barley

A river barge with two grain holds about 9 m wide, 15 m long, and 12 m deep was filled with 1415 tonnes of barley. During the 4-hour loading period 4.8 tonnes of CO<sub>2</sub> were applied from a road tanker through a hose and a liquid injection nozzle. After loading, an additional 4.5 tonnes of CO<sub>2</sub> was injected below the surface of the grain along the longitudinal axis of the barge during a 2.5 hour period. The barge was shipped the following day from its loading point, Clarkston, ID, U.S., to a terminal elevator at Portland, WA, U.S.

Before loading, gas sample lines and caged insects were suspended in the barge. Four cables, each having 9 cages of insects in groups of three each and three gas sampling lines attached to them at different depths were

used in the study. The gas sampling lines were located next to the cages and two cables held sampling lines and cages at depths of about 0, 5, and 10 m from the bottom of the holds. The second pair of cables was positioned so that the sampling lines and cages were located 0, 3, and 7 m from the bottom of the holds. Bioassay was conducted using a mixture of from 1–5-week-old *Rhyzopertha dominica* (F.). About 5 g of wheat containing these immatures was placed in each cage.

Table 4 shows that the initial concentration in the barge immediately after application ranged from 61–100%, with the higher concentrations located at the middle and bottom sample sites. Gas samples taken after the barge had been in transit for 2.8 days showed that there was little or no CO<sub>2</sub> at the top sampling points, from 22–70% CO<sub>2</sub> at the middle sites, and from 75–90% CO<sub>2</sub> at the bottom sampling points. The barge arrived in Portland about 4.7 days after the CO<sub>2</sub> application. At that time there was little or no CO<sub>2</sub> in the top of the barley from 0–41% in the middle of the bulk, and from 57–86% CO<sub>2</sub> in the bottom of the grain bulk. The grain temperature dropped from 38°C at the start of the test to 35°C after 2.8 days and to 23°C at the time the grain reached the terminal elevator.

Determination of the effectiveness of the treatment was made by comparing the number of live insects that had emerged from the treated grain to those that emerged from untreated grain and converting this to a percent reduction in emergence (PRE) after the 30-day post exposure examination. Table 5 shows that from a + 9.1 (increase over control emergence) to a 77.4 PRE occurred in those insects treated in the top layer of barley in the barge. A 92 to 100 PRE was observed in the insects in the middle of the grain bulk and a 100 PRE was recorded for the insects in the bottom of the barge. The mean number of control insects that emerged per cage from 10 cages was 20.8.

**Table 4.** Percent CO<sub>2</sub> at 3 depths/4 locations in a river barge containing barley

Sample	Days after CO <sub>2</sub> application		
	0	2.8	4.7
Top	64–68	0–2	0–1
Middle	75–100	10–22	0–41
Bottom	61–97	75–90	57–86

The loss of CO<sub>2</sub> in the upper level of the barley and the consequent inadequate control of the insects in this area was initially attributed to poor sealing of the hatch covers. However, during a safety inspection prior to unloading, CO<sub>2</sub> concentrations of 40–50% were found in the access areas outside the holds and adjacent to the bearings for the unloading augers which were built in on this barge. This was possibly the major reason for the drop in concentration although the loose hatch covers were believed to be partially responsible.

### Carbon Dioxide Treatment of a Chamber Containing Herbs and Spices

A 45.3m<sup>3</sup> truck body was used as a chamber for the CO<sub>2</sub> treatment of seven different herbs or spices in their original shipping containers. Descriptions of the commodities and their containers are given in Table 6. The truck body was 7.6 m long, 2.4 m wide, and 2.4 m high, and was supposedly well sealed for methyl bromide fumigation of herbs and spices. Five cages, each containing about 30 larvae of either *Tribolium confusum* (J. duVal), *Trogoderma glabrum* (Herbst), *Attagenus megatoma* (F.), *L. serricornis*, or *Plodia interpunctella* (Hübner) were placed within the bulk of the commodity at each of 10 locations within the chamber. Gas sampling lines and thermistors for temperature measurement were placed next to the cages in the bulk of the commodity and an additional set of 5 cages, a gas sampling line, and thermistor were placed in the free air space above the commodity.

A supply vessel containing 340 kg of liquid CO<sub>2</sub> was used to treat the chamber. The CO<sub>2</sub> was injected using a plastic pipe which ran from the vaporiser to the floor at the front of the chamber. A sheet of PVC was placed in front of the rear doors to prevent leaks in that

**Table 5.** Percent reduction in emergence (PRE) of *Rhyzopertha dominica* resulting from the CO<sub>2</sub> treatment of a river barge containing barley<sup>a</sup>.

Depth	PRE at insect cage location			
	1	2	3	4
Top	76	75	77	+9.1
Middle	92	100	100	98
Bottom	100	100	100	100

<sup>a</sup> Locations 1 to 4 were forward to aft in the barge



area, which was partially opened when the chamber was being initially purged with CO<sub>2</sub>. It was sealed during the remainder of the test and a small flow of CO<sub>2</sub> maintained to compensate for leaks.

Two large electric heaters were placed in the chamber to raise the temperature of the commodity and reduce the exposure time. These heaters maintained the temperature in the free air space from 32°–48°C and caused a gradual rise in temperature in the commodities (Table 7). The initial purge of CO<sub>2</sub> lasted 7.5 hours and brought the concentration in the free air space to ca. 96%. The CO<sub>2</sub> concentration was maintained for an additional 111.5 hours and during this period ranged from 68–100% with most readings showing a mean free air space concentration of over 90%. A total of 1134 kg of CO<sub>2</sub> was used for this treatment, or about 3 to 4 times the amount that would have been needed in a tightly sealed container of this size.

Table 8 shows the CO<sub>2</sub> concentrations in representative herbs and spices and in the free air space. The CO<sub>2</sub> readily penetrated through the container walls into all the commodities, except for the sealed cardboard drum containing lemon peel where the concentration slowly rose to resemble that of the free air space.

Only 5 of the 1608 larvae that were exposed in the chamber survived the CO<sub>2</sub> treatment. One *L. serricornis* larva in a cage in a box of chamomile flowers was alive at the end of the test, while four *T. glabrum* larvae survived in the cage placed in a cardboard box with a plastic liner containing parsley flakes. Control mortality was 20% for *P. interpunctella* larvae, 6% for *T. glabrum* larvae, and 0% for *T. confusum*, *L. serricornis* and *A. megatoma* larvae.

**Table 6.** Herbs and spices treated with carbon dioxide in a 45.3 m<sup>3</sup> chamber

Commodity	Package	Weight (kg)
Chamomile flowers	Cardboard box	11.3
Peppercorn	Burlap	63.5
Sage leaf	Woven poly, heat sealed	11.3
Poppy seed	Multiwall paper	22.7
Parsley flakes	Cardboard box, plastic liner	6.4
Basil	Burlap	25.0
Lemon peel	Cardboard drum	45.4

**Table 7.** Temperature in representative herbs or spices or in free air space during CO<sub>2</sub> treatment of herbs and spices

Commodity	°C at hours after initiation of purge			
	24	48	72	101 h
Free air	42	40	44	38
Chamomile	28	30	31	31
Peppercorn	19	23	25	28
Lemon peel	27	29	31	32 (cracked lid)
Lemon peel	26	29	31	32 (sealed lid)

**Table 8** Carbon dioxide concentrations in representative herbs or spices or in free air space during chamber treatment.

Commodity	CO <sub>2</sub> (%) at hours after start of purge <sup>a</sup>			
	24 <sup>b</sup>	48	72	101 h
Free air	68	94	88	97
Chamomile	71	94	88	98
Peppercorn	69	95	88	99
Lemon peel	80	90	89	100 (cracked lid)
Lemon peel	48	69	72	94 (sealed lid)

<sup>a</sup> Balance of concentration is air

<sup>b</sup> CO<sub>2</sub> flow off for 4 hrs prior to this reading

The doors to the container were opened at the end of the treatment and the sheet of PVC removed. A large box-type window fan was placed at the rear of the container and run for about three hours. Carbon dioxide was not detected in the free air space after this aeration and no more than 1% was detected in the containers having sample lines in them.

## Treatment of Rice in a Bolted Metal Bin

A bolted metal bin was sealed by spraying with a PVC formulation on the joints of the overlapping sheet metal to reduce gas loss. An attempt was made to seal the wall to cap joint with polyurethane foam. The bin was then filled with 544 tonnes of rough rice and all ventilators, access ports, and the shaft to the aeration fan were covered with plywood which was sealed to the metal with silicon rubber adhesive. Sealing costs for the bin were (all U.S.\$): labour \$1344; materials \$900; and equipment \$1200. Assuming that the equipment would be used to seal 20 bins at the facility, the costs for sealing this bin was about \$4.00/tonne. An effort was made to pressure

test the bin before CO<sub>2</sub> application, but some regions were apparently not properly sealed and the attempt failed.

Seven gas sample lines were placed from the top to the bottom of the bin at intervals of 1.8 m. A thermistor was placed in the bin 1 m below the surface of the grain in the area where insects were exposed for bioassay. Immature *R. dominica* were used for bioassay as this is the main pest of rice in the South Florida, U.S. location where this trial took place. Laboratory cultures 1, 2, 3, 4, or 5 weeks old were blended and about 5 g of the grain containing the immatures was placed in each of 50 cages. These cages were put into groups of 5. Eight of these groups were placed about a metre below the surface of the rice to be treated. The other two groups were not treated but held in an adjacent building in a large bag of rice from the treated bin.

The bin was purged from the bottom, with the pressure relieved by opening an access port at the top. A 4-hour purge at a rate of 408 kg/hour produced a 94–97% CO<sub>2</sub> concentration throughout the bin. Flow was reduced at this time and was adjusted to compensate for leaks. The access port was closed and sealed. A mean of 35.9 kg/hour of CO<sub>2</sub> was applied into the bin headspace to compensate for leaks for an additional 4 days, making the total used 5760 kg. The total cost for CO<sub>2</sub> at U.S.\$134 per tonne was U.S.\$762, making the treatment cost per tonne of rice U.S.\$1.40. During the four days the CO<sub>2</sub> was slowly introduced into the bin the concentration at the bottom of the bin ranged from 57–98%; in the middle of the bin it ranged from 52–86%; and in the top at the same depth as the caged insects it ranged from 49–90% with a mean of 66.2%. The mean temperature of the grain 1 m below the surface was 31.6°C during the test.

Bioassay was successful in that no *R. dominica* adults emerged from the grain that was treated with CO<sub>2</sub>, while a mean of 20.5 adults per cage emerged from the controls held in untreated grain.

### **Carbon Dioxide for Control of a Natural Infestation in a Bunker Containing Maize**

A well-sealed PVC-covered bunker containing 27 600 tonnes of shelled yellow maize was

treated with CO<sub>2</sub>. Before treatment it had become naturally infested with a wide range of insect pests. The bunker was approximately 137 m long, 46 m wide, and 12 m high at the peak. It was constructed on an asphalt base with reinforced concrete walls and had a 0.3 mm thick cover which was tightly attached to the walls. Grain temperatures, as recorded from 38 thermocouple cables installed in the bunker, ranged from -5 to 40°C. However, the temperature of most of the grain ranged from about 2–15°C. The high temperatures were caused by insect and mould activity, and associated heating and moisture migration. The mean moisture content of the grain was 14.7% and ranged from 12.2–28.7%.

Sixteen gas sampling lines were probed into the maize. Three sets of four lines were placed at depths of 3, 5.5, and 8.5 m at the northern and southern ends and at the center of the bunker. An additional line was placed about 1 m deep in the maize at each of the four corners. Before CO<sub>2</sub> application, 87 maize samples, each of about 0.7 L, were taken by vacuum sampler at depths of either 0.3 and 1.5 m, or 0.3, 1.5 and 3 m, or 0.3, 1.5, 3, and 6 m at 5 locations across the width of the bunker. This pattern was repeated 5 times down the length of the bunker. Similar samples were taken at 0.3 and 1.5 m or 0.3, 1.5, and 3 m at the northern and southern ends of the bunker. Ninety-five samples were taken from the same sites in the same manner at the end of the test.

Before treatment, the bunker was pressure tested using a large vacuum cleaner. An initial vacuum of 0.62 cm of water was obtained. This dropped to 0.46 cm after five minutes and to 0.33 cm of water after 10 minutes, indicating that the bunker was well sealed.

Carbon dioxide was applied from a mobile vessel which was filled, from three road tankers, with 54.5 tonnes of liquid. The liquid was converted into gas by a vaporiser and then led into the aeration shaft running the entire length of the bunker. The purge took 66.25 hours and 39.9 tonnes were applied in this period. An additional 1.6 tonnes of CO<sub>2</sub> was applied four days after the initial purge was stopped, over a period of about four hours. A small aeration fan was modified for use as a recirculation fan and this was attached to a hole cut in the end of a piece of plywood which sealed off a second longitudinal aeration shaft. A 10-cm i.d. hose was attached to the fan and

the hose was run to the top of the bunker and under the fabric. The system was designed to gently recirculate CO<sub>2</sub>, carrying it from the bottom of the bunker to the top to ensure that no areas of low CO<sub>2</sub> concentration formed. The fan was generally run for about 10 hours each day for the 15 days the test was in progress.

Table 9 presents the mean and range of CO<sub>2</sub> concentrations in the bin following the purge. The mean CO<sub>2</sub> concentration was 79.7% one day after application stopped and 72.2% after three days, indicating a 3.3% per day loss of CO<sub>2</sub>. A cold front came through the area during this period, with winds of 40–50 km/hour. Two small aeration fans were placed in the grain bulk on top of the bin to pull the cover down tight over the maize as there was some possibility of it blowing loose. These fans were operated intermittently throughout the test whenever it was windy and it is believed that this contributed to the loss of CO<sub>2</sub> and also to the variability of this loss. The daily CO<sub>2</sub> loss rate varied from 6.6 to 7.3% during the third through the seventh day of the test; from 6.6 to 5.5% between the seventh and tenth days of the test; and from 4.5 to 5.5% between the tenth and

**Table 9.** Mean and range of CO<sub>2</sub> concentrations in a bunker containing maize

Days after start of test	CO <sub>2</sub> (%)	
	Mean	Range
1	79.7	58-90
3	72.2	43-78
7	65.1	16-82
10	54.7	37-69
12	44.5	15-60
15	43.1	24-50

twelfth days. Daily percentage losses were 4.6% from the twelfth to the fifteenth days. A total of 41.5 tonnes of CO<sub>2</sub> was used in the test and the total cost for treatment was U.S.\$3206 or U.S.\$0.116 per tonne when the delivered price for CO<sub>2</sub> was \$77 U.S. per tonne.

The following insects were collected from the bunker: *Oryzaephilus surinamensis* (L.), *Cryptolestes pusillus* (Schoenherr), *Abasverus advena* (Waltl), *Tribolium castaneum* (Herbst), *Sitophilus oryzae* (L.), *Sitophilus zeamais* Motschulsky, *Typhaea stercorea* (L.) and Pteromalidae.

The presence of *T. stercorea* (fungal-feeding beetles) and parasitic wasps indicate that the maize was in poor condition with mouldy regions and was heating. Table 10 shows that, of the original 87 samples collected before the treatment, 28 were infested with live insects and these 28 samples contained a mean number of 31.7 insects at the seven-day examination. Ten of these pretreatment samples could not be examined because of heavy levels of fungus growth in them after a 30 or 60 day holding period. At the 30 day examination, 41 of the examined 77 pretreatment samples had a mean infestation rate of 78.2 insects per sample while at the 60 day examination the 40 samples contained a mean of 110.8 live insects per sample. The increase in the number of samples infested after 7 days (28 out of 87) to the number of samples infested after 30 days (41 out of 77) is due to the presence of undetected immatures or eggs in the maize at the 7 day examination.

Table 10 also presents data from the examination of the 95 posttreatment samples. Only one live insect was found at the 7 day examination while three live insects were found in two samples at the 30 day examination. A total of five live insects was in 3 samples at the 60 day examination. The number of insects per sample

**Table 10** Number of samples infested out of 87 pretreatment or 95 posttreatment samples collected; total number of live insects, and percent reduction in emergence (PRE) resulting from a carbon dioxide treatment of a bunker containing 27,680 tonnes of maize<sup>a</sup>

Days after sampling	Samples taken					PRE (%)
	Pretreatment		Posttreatment			
	Infested	Insects	Infested	Insects		
7	28	856	1	1	>99.99	
30	41	3,207	2	3	>99.99	
60	40	4,430	3	5	>99.99	

<sup>a</sup> 10 pretreatment samples were heavily infested with fungus and were not examined after 30 and 60 days

in the pre-treatment samples (either 77 or 88) was raised to the equivalent of the 95 posttreatment samples and the number of insects in the pretreatment samples was divided into the number in the posttreatment samples. The result was converted to percent reduction in emergence (PRE) for the test. The PREs presented in Table 10 are all well over 99.99% for all three examinations for the samples indicating a very high level of control of the insects in the bunker. About two months after the test was complete the bunker was opened and 450 tonnes of grain damaged by moisture and fungus were removed. Live insects were not found during this operation.

## Discussion

The laboratory study reported here on *L. serricornis*, together with the information provided by Childs and Overby (1983), provides some guidance for attempts to control this insect in the field. This is substantiated by results of the bioassay in the field study in a tobacco warehouse. If someone has not already done so, perhaps a computer program could be developed to analyse the vast amount of available data on CAs. Such a program would include time  $\times$  temperature  $\times$  CA concentration  $\times$  insect species and life stage information which could be correlated into readily usable parameters for field use of these atmospheres.

Five field tests were reported on in this paper and only one, the use of CO<sub>2</sub> in a bunker containing maize, can be considered successful from an economic point of view since the CO<sub>2</sub> cost per tonne of maize in this study was \$0.116/U.S. tonne. Three of the other four studies had costs for CO<sub>2</sub> ranging from \$0.58 U.S./tonne in the barge study to \$1.40 U.S./tonne in the rice study (plus sealing costs), and went up to \$5.44/U.S. tonne in the tobacco study. These costs are not acceptable even by U.S. standards. Jay and D'Orazio (1984) reported CO<sub>2</sub> costs of from \$0.23 to \$0.39 U.S./tonne for the treatment of wheat, sorghum, rice, or maize in upright concrete, fiberglass-lined steel, or welded steel bins.

These tests, with the exception of the barge test, were highly successful in that they all produced insect mortality approaching or attaining 100% of the caged or natural infestations and, in two cases (tobacco, herbs

and spices), provided new user groups the opportunity to witness this alternative, residue-free method of control.

Industry has acted on these studies. One small pest control company treated over 750,000 tonnes of maize and sorghum in bunkers in 1988 and has had no subsequent reports of insect activity in this grain. Similarly, in 1988 a large CO<sub>2</sub> processor successfully treated tobacco warehouses with a volume of over 285,000 m<sup>3</sup>. The rice processor is continuing to use CO<sub>2</sub> because his product is for health food stores whose customers see residues as undesirable. Similarly, U.S. herb and spice trade organisations are very interested in CAs because a large portion of their product is destined for the health food market.

Perhaps this trend represents the direction CA use will take in the near future in the U.S. Several commodities studied in the tests described in this paper have a high unit (tonne, kg, etc.) value and their end users often object to pesticide residues. The trend may carry through into commodities such as tree nuts, dried fruit, and groundnuts—which have a high value per unit—and from there to general grain.

Economics is generally the driving force in any decision to change from conventional pesticides or fumigants to CAs. The economics is not necessarily directly related to costs of treatment and/or sealing but can be concerned with worker safety, residues, the emission of conventional fumigants into the atmosphere, the time needed for treatment, the regulatory removal of a pesticide or fumigant from use, or other factors. We are observing a gradual change to CAs in some areas of the raw and processed agricultural food industries in the U.S. Time and regulatory pressure will possibly be the main factors bringing about changes in this area.

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Division, Dallas, TX 75233, U.S. in the bunker study and J. Manner of this company in the river barge study. G. Baskin, T. Lane, and C. Briceland of Liquid Carbonic Corp., Chicago, IL 60629, U.S. were closely involved in the studies on the herbs and spices, and rice.

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# Recent Developments in Fumigation Technology, with Emphasis on Phosphine

R.G. Winks\*

## Abstract

With the increasing use of phosphine as a grain fumigant and the spread of phosphine resistance, it is vital that phosphine toxicity be understood and that steps be taken to use the gas effectively. This paper outlines some of the components of phosphine toxicity and describes some of the characteristics of phosphine resistance. The paper also describes some new methods of application as well as recent developments in old methods.

FUMIGATION remains one of the more effective methods available for the disinfestation of stored products. Although it is now quite an old technique, there are a number of new developments that may have a significant impact on the way it is used in the future.

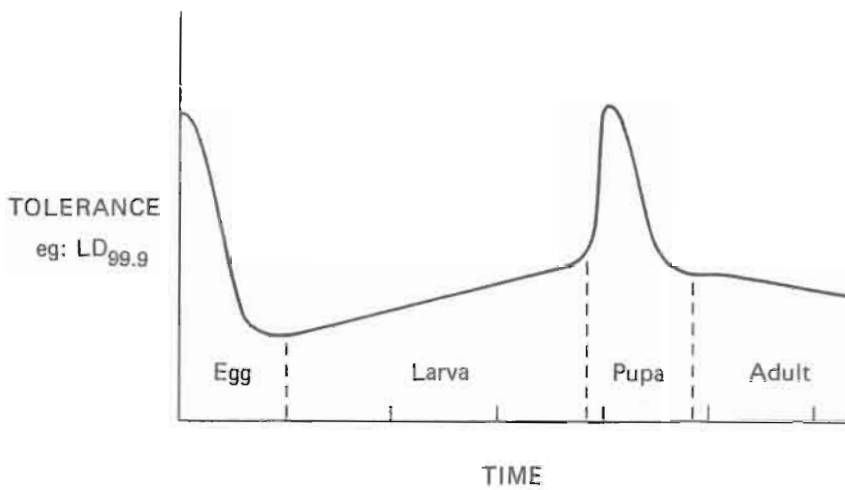
## Phosphine Toxicity

For many years, the approach to setting dosage rates for fumigants and other agricultural chemicals has been to choose a level that will kill the most tolerant stage of the most tolerant species likely to occur in the fumigation enclosure. The use of methyl bromide, for example, has been based on this philosophy (Brown 1959). It is therefore not surprising that early uses of phosphine were similarly based, although users knew that the gas evolved slowly and that the fumigation consequently took longer. While studies on the toxicity of methyl bromide to insects showed that, for the most part, the toxicity followed the relationship in which the product of concentration (C) and time (t) was a constant for a particular level of response, e.g. the LD<sub>99</sub>, the toxicity of phos-

phine displayed a significant departure from this relationship (Howe 1973). In a number of studies it was shown that exposure time was the more important variable of dosage (Winks 1984).

Although early studies of phosphine toxicity on particular stages of insects showed that exposure time was the more important variable of dosage, the magnitude of the deviation from the relationship  $C \times t = k$ , generally obtained for adults, did not account for the importance of exposure time in practical fumigations. The importance of exposure time in practice lies in the variation in tolerance of immature stages. Indeed, the key to successful fumigation with phosphine lies in understanding the large variation in tolerance of the immature stages and that this tolerance changes with time of development (Fig. 1). With the dosages commonly used in practice, an adequate concentration must be maintained for long enough for eggs to approach or reach the larval stage, and pupae must approach or reach the adult moult. It follows from this that, if the rate of decay of concentration is greater than the rate of decay of tolerance of the most tolerant stages (eggs and pupae), there is a probability of survival. Thus, if the dose of phosphine (the amount absorbed) does not reach a toxic level before the phos-

\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

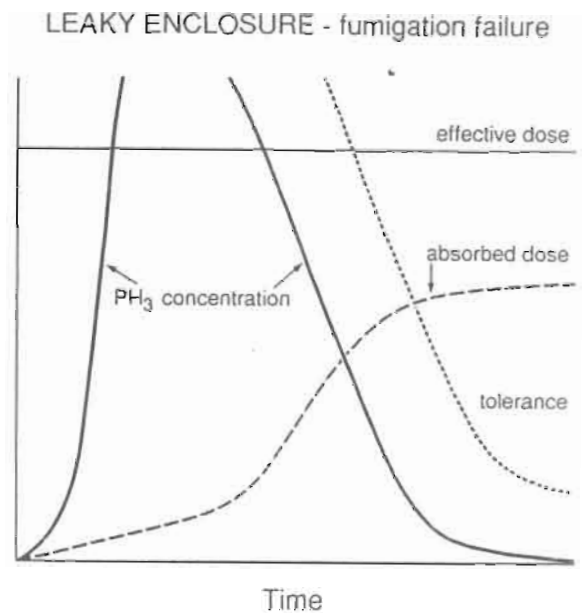


**Fig. 1.** Schematic representation of the change in tolerance to phosphine of the different stages of stored product insects with time.

phine concentration decays to zero, the insect will survive. This can be represented schematically as in Figure 2, which describes the response of pupae. The effective dose is that necessary to kill, and may describe an individual or a population. The time scale, in terms of tolerance or absorbed dose, will vary with species and with temperature.

Sealing the fumigation enclosure will lower the loss rate of phosphine and thus retain sufficient gas for long enough for an effective dose to be absorbed (Fig. 3). Because of the low application rates that are commonly used, it is necessary for the tolerant stage to develop to a less tolerant stage, whereupon it either succumbs to the dose absorbed from a more or less constant uptake rate, or that the uptake rate increases as development towards the next stage proceeds. Thus, to achieve a high probability of success, the minimum exposure period should be approximately equal to the maximum development period of the most tolerant stage. It is essential, of course, that at the minimum exposure period there is still sufficient gas left in the enclosure for the insects to absorb. It follows from this that the critical concentration is that at the minimum exposure period. If we take, for example, a maximum pupal development time of 10 days, then if there is sufficient gas left after 10 days to kill young adults, the probability of success will be high.

From this it can be argued that the critical concentration is that needed to kill the most tolerant adult, while the critical exposure time is the maximum development time of the slowest-developing tolerant insect stage within the

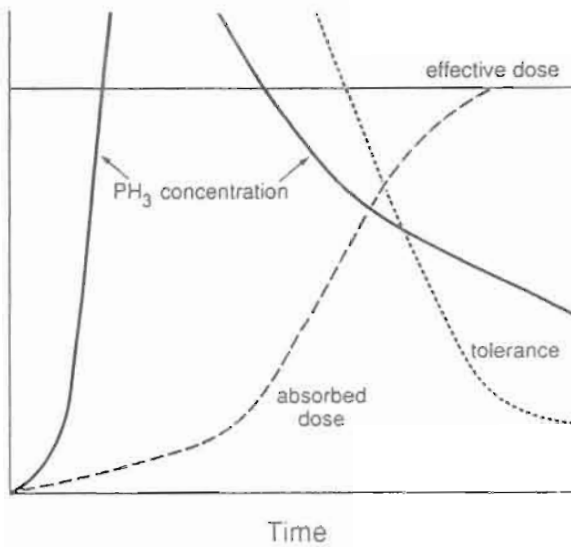


**Fig. 2.** Schematic representation showing that in a leaky fumigation enclosure the absorbed dose does not reach a lethal level when the concentration decreases faster than the tolerance of stages like eggs and pupae.

enclosure. This is true, of course, whether we are talking about susceptible or resistant insects. Since the rate of development of the tolerant stages cannot be increased readily, the key to successful fumigation lies in reducing the rate of decay of the concentration. This may be achieved either by improving the level of sealing of storages, or by using different methods of application that will allow continuous input of gas.

With a constant concentration, one would expect that, as the tolerance of, for example,

### SEALED ENCLOSURE - successful fumigation

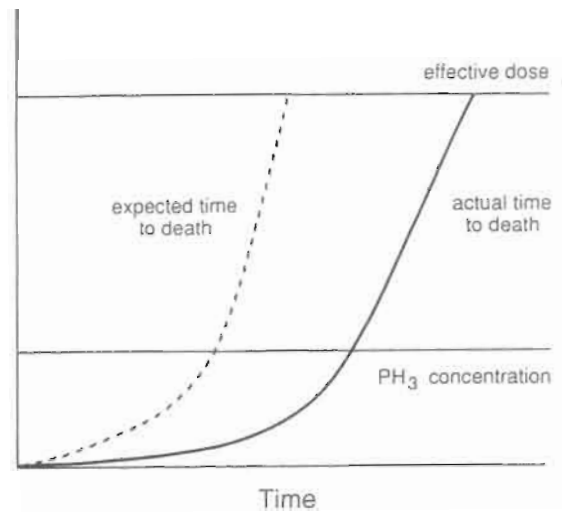


**Fig. 3.** Schematic representation showing that, in a well-sealed enclosure, the absorbed dose reaches a lethal level because the rate of decrease of the concentration is less than that of the tolerance of eggs and pupae.

the pupal stage decreased, the amount absorbed would increase more or less exponentially (Fig. 4); i.e., it is influenced only by the rate of change of tolerance. Thus, it could be expected that the time to death of an individual or a population would be governed simply by the time of development of the most tolerant stage and would be more or less predictable from the biology of the species. The data we have, in contrast to those of Reynolds et al. (1967), suggest that phosphine delays the rate of development, and that a prediction of time to death derived from the biology of the species would be too short to achieve complete kill of the population. If there is delay of development when insects are exposed to a constant concentration in the laboratory, it is reasonable to expect that there will be similar delays in the field which would further exacerbate the problem of short exposure times because of poor sealing or because the fumigation is terminated early for operational reasons.

It is sometimes suggested that if the level of sealing is not adequate then all that is required is a higher dose. In a leaky store that is about half full, a typical situation for many sheds or godowns, even with high application rates the likelihood of success is quite low (Fig 5.). It should be noted that the concentrations shown in this Figure 5 are calculated average concen-

### APPLICATION OF CONSTANT CONCENTRATION



**Fig. 4.** Schematic representation showing that the absorbed dose can be expected to reach a lethal level after a period of exposure to a constant concentration. Studies show, however, that the actual time to death is greater than expected from the development times of a species.

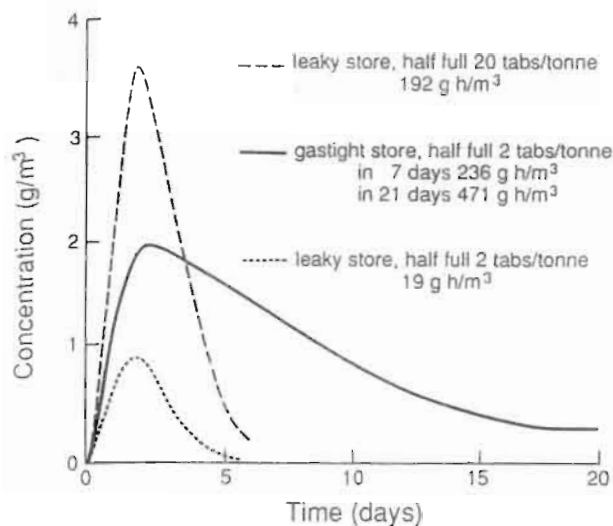
trations and grossly underestimate the problem. While the high application rate would succeed if the calculated concentrations were achieved throughout the storage, with the leakage rate involved, there would be many large pockets of much lower concentrations in which the fumigation would fail. On the other hand, the  $C \times t$  product calculated for a well-sealed storage with a leakage rate of 5% per day, suggests that, providing the temperature is at least above 15°C, the application rate could be reduced quite significantly.

## Resistance to Phosphine

Insects would seem to have a greater propensity to become resistant to phosphine than to many, if not most, other toxicants. In the laboratory, we have produced resistance in every strain of every species that we have attempted to select, including standard reference strains that have been in culture for over 20 years. Moreover, with a limited number of selections we have, in many cases, produced stable levels of resistance; i.e., there has been no regression of the resistance for over 10 or more years. One cannot help but wonder about selection programs that appear to be so efficient that we



### SEALING vs LARGE INCREASE IN APPLICATION RATE



**Fig. 5.** Calculated concentration profiles showing the dosage achieved by adding additional fumigant to a leaky fumigation enclosure compared with the dosages achieved by sealing the same enclosure.

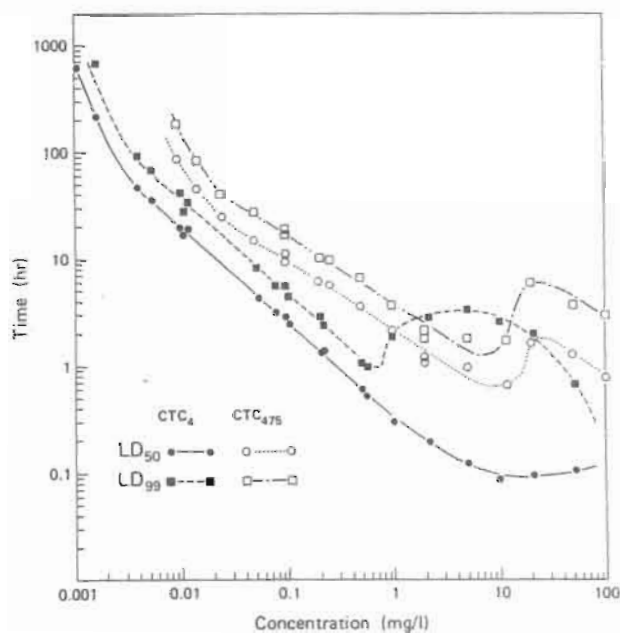
achieve apparent homogeneity so quickly. It is difficult to believe that we are dealing with a low-frequency resistance gene that has occurred as a result of random mutations. A further fact that has emerged is that we seem to reach an upper limit of resistance quite quickly. Under normal circumstances these facts would not augur well for the future of a chemical as a control agent. However, there are mitigating facts that put phosphine into a different category to contact insecticides such as organophosphates:

- the levels of resistance are not so high as to preclude the continued use of phosphine; and
- the magnitude of resistance varies with concentration (Fig. 6) (Winks and Waterford 1986).

The magnitude of resistance is calculated as the ratio of an appropriate lethal dose for the strains being compared, e.g. the LD<sub>99</sub>, and may be expressed as a ratio of lethal concentrations for fixed exposure periods or a ratio of times to absorb a lethal dose at a fixed concentration. An examination of the curves of Figure 6 shows that the level of resistance varies with concentration, and indeed this should be expected with any combination of poison and target organism where dosage is comprised of more than one variable. It should also be noted that if

one were to measure resistance using traditional approaches, such as a range of concentrations at a fixed exposure period, the measure of resistance or 'resistance factor' would be greater than if a range of exposure times were chosen at a fixed concentration. This characteristic of phosphine is due to the fact that the exponent  $n$ , the toxicity index, for phosphine in the relationship  $C^n t = k$  is less than 1. As the magnitude of this exponent decreases, the difference between measurements at fixed concentrations and fixed times increases so that there can be a perception of quite high levels of resistance. This is so for adults of strains of *Sitophilus* spp. and *Rhyzopertha dominica*, with their much lower exponents than those for *Tribolium* spp., when tested following the guidelines of the FAO Resistance Test Method, i.e., with a range of concentrations at a fixed exposure period.

Although changing tolerance confounds traditional analysis of  $Ct$  relationships in immature stages, the limited data available suggest that the changing tolerance has the effect of a very low exponent of toxicity, which again would have the effect of producing a high level of resistance or relative tolerance if fixed exposure tests of, for example, 20 hours were used. Pupae of *Sitophilus granarius* provide a good example of this.



**Fig. 6.** The relationship between the time required for an LD<sub>50</sub> and LD<sub>99</sub> at each of a range of fixed concentrations of phosphine to which adults of a resistant strain of *Tribolium castaneum*, CTC<sub>475</sub>, and a susceptible strain, CTC<sub>4</sub>, were exposed (from Winks and Waterford 1986).

Complete control of phosphine-resistant strains can be achieved with phosphine by choosing the dosage parameters carefully. On the basis of our present knowledge, this will mean choosing concentrations to minimise resistance and retaining the concentration for longer periods. Following the more traditional approaches of adding more chemical will only exacerbate phosphine resistance.

Clearly, there are only two options for using phosphine that will minimise selection for resistance on the one hand and permit the control of resistant strains on the other:

- use of gastight enclosures; or
- use of methods of application that will provide a constant concentration throughout the enclosure even if it is not gastight.

The continued use of phosphine other than in either of these two ways is courting disaster, particularly as the usage of this fumigant increases. Even in conditions of severe economic constraint it would seem more sensible to pay the cost of implementing one of the two alternative options than to pay the cost of no longer being able to use the fumigant.

## New Methods of Application of Phosphine

*Multiple dosing.* In an attempt to increase the time of exposure in godowns, TDRI (now ODNRI) developed a method of adding a second batch of fumigant to the enclosure when the concentration dropped below a certain level (Friendship et al. 1986). This method is based on adding strings of aluminium phosphide sachets to the headspace of the enclosure through a port in the side of the godown. While the objectives are in keeping with our understanding of phosphine toxicity, the method should be used only in sheds or godowns that achieve a reasonable standard of gastightness. In structures that are not gastight, there will be pockets of low concentration around, for example, doors and windows, especially under windy conditions, that will decrease the probability of success. Although this method of application has some novel features, it does nothing to ensure that there will be a uniform concentration throughout the grain mass and relies for success on a random-

ness of factors that contribute to gas loss. Where there is some uniformity of gas loss factors, e.g., wind direction, the probability of success decreases. In addition, prolonged exposure periods, that may be necessary for resistant strains, may render the method uneconomical.

*SIROFLO.* SIROFLO is a method of applying phosphine for which patents are pending and thus only limited information can be presented. The method is based on the dilution of a low concentration of phosphine into an air stream that is introduced into a storage, thus producing a small positive pressure (Fig. 7) (Winks 1986). The pressure thus produced assists distribution and offsets factors that contribute to gas loss from the storage. The method currently relies on the use of a 2% gas mixture of phosphine in carbon dioxide available from Commonwealth Industrial Gases, but we are also developing a controllable on-site generator in conjunction with Wellcome Australia and Detia. The details of the generator are also covered by patent. The fact that with both sources of gas the process becomes completely controllable is one of the key attributes of SIROFLO. Both the concentration and the exposure time can be varied easily before and during a fumigation to cope with the many factors that influence the outcome. In the absence of well-sealed enclosures, it is currently the only method of using phosphine that could

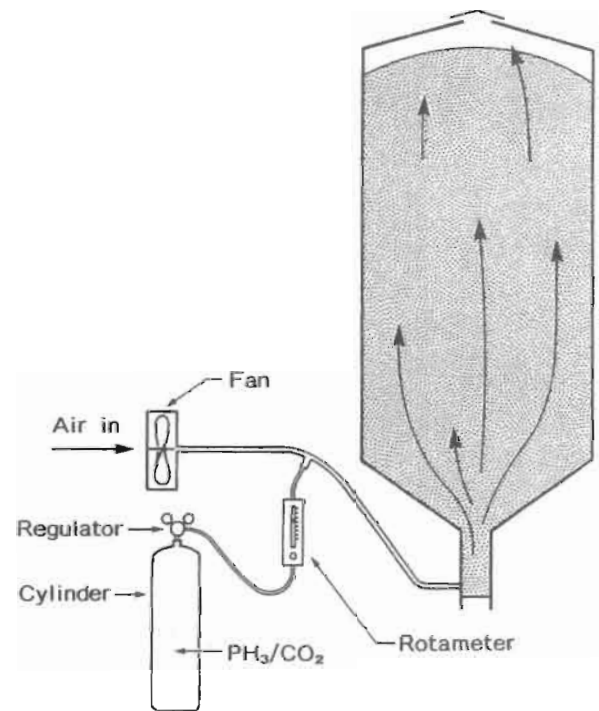


Fig. 7. Schematic diagram of the SIROFLO method for applying phosphine to vertical silos.

be relied upon to control phosphine-resistant strains, i.e., to have adequate control over the exposure time. Indeed, much of the laboratory development of SIROFLO has been with phosphine-resistant strains, and it has successfully controlled two infestations of resistant *Rhyzopertha dominica* in the field.

Unlike recirculation systems, which have both positive and negative pressures and thus require high standards of gastightness, SIROFLO is a flow-through process and in this way a positive pressure is maintained throughout the enclosure. Although it offsets most of the factors that give rise to gas loss, there are still certain minimum requirements. The method is currently being implemented in vertical silos in Australia and in some horizontal storages, although the latter are still in the development phase. These trials are primarily aimed at optimising distribution systems and flow rates.

In Australia, the greatest interest in the SIROFLO process is as a grain protection method. Grain can be stored for long periods using the process without using normal protectants. Moreover, the costs of protection are substantially less than the costs that are associated with the current grain protectants. The method is also more acceptable than conventional fumigation methods in terms of both worker safety and environmental considerations.

Licensing Agreements for SIROFLO with Wellcome Australia, Detia Freyberg and Commonwealth Industrial Gases (a member of the British Oxygen group) are expected to be finalised during 1990, whereupon the method will become available progressively in countries outside Australia.

*Cylinders and on-site generators.* While both cylinders and on-site generators of the type mentioned in the previous section have obvious advantages in the context of a method such as SIROFLO, they are also advantageous as a source of gas in methods of fumigation where there is a benefit associated with developing the full concentration rapidly. Such methods have advantages in recirculatory fumigation systems. In such systems, the most effective approach to introducing gas is to be able to meter its input in accordance with the flow rate of the fan so that the full dosage is introduced in the time equivalent to one air change of the enclosure. This should achieve uniform distribution of the fumigant in the shortest possible time.

On the subject of recirculatory fumigation, there is a perception that phosphine fumigation in silos equipped with recirculation can be done in a shorter time. Times as low as a few days have been suggested. This is totally inconsistent with our knowledge of phosphine toxicity and while short exposure times might achieve an illusion of success by killing adults and larvae they will not kill eggs and pupae. Such practices are, in fact, an effective way to select for phosphine resistance. The only reduction in exposure time that is possible in the context of effective fumigation is associated with the time required to introduce the full dosage of gas. Thus, cylinders and, in due course, on-site generators, will provide the added advantage of reducing the fumigation time by about a day over blankets for example. It is, of course, essential to understand that the exposure times required for phosphine fumigation are not from when the fumigation is started but from when uniform distribution of gas can be expected. While the two times may have been similar for methods using admixture of tablets they are vastly different for methods based on surface application followed by convective distribution.

## 'Old' Methods Revisited

*In-transit shipboard fumigation.* The use of fumigants, particularly phosphine, in ships holds during a voyage has been under evaluation by scientists of the U.S. Department of Agriculture Laboratory at Savannah, Georgia for some years now. The results of the earlier trials were not particularly successful, and in some cases the trials failed to achieve even a cosmetic fumigation (Zettler et al. 1984). Recently, this group conducted trials in which a recirculation system was installed before the grain was loaded. Flexible perforated ducting was laid around the floor of the hold and on the grain surface. By comparison, the recirculation system achieved complete distribution in about 5 days of a 25-day voyage whereas the earlier method, which they refer to as the 'tubing-probe method', took 20 to 21 days to achieve distribution in the same 25-day voyage (Robinson 1988). This use of ducting was an attempt to improve the poor distribution obtained in earlier trials.

Clearly, in-transit ship fumigation should be considered only when all else has failed and

should be contemplated only in vessels with gastight holds, i.e., no access to other parts of the ship, and when some provision has been made to recirculate the gas.

*Fumigation under gas-proof sheets.* Although gastightness has been recommended or implied in all such methods for a very long time (Brown 1959), it is only recently that methods have been developed that will achieve such standards reliably in sheeted bag stacks and enable them to be tested. Details of these developments are given elsewhere in these proceedings.

## **Worker Safety and the Environment**

During recent years, greater attention has been directed towards the safety of workers when fumigants are used, and in many countries, greater attention has been focused on the release of fumigants into the atmosphere. These concerns are not directed exclusively at fumigants but reflect greater concern for industrial chemicals, worker safety and environmental pollution generally.

In the context of worker safety, there remains a need for more efficient monitoring systems. Since health authorities do not generally recommend static sampling of workspace atmospheres it imposes a requirement to develop efficient personal monitors that are also relatively inexpensive. Ideally, a personal monitor that is activated when some level is exceeded is needed. However, such a device should accommodate the concept of a time-weighted average exposure and upper limits of concentration. Currently, such sophistication is available only in intelligent instruments incorporating a range of detectors suitably driven with black boxes filled with electronic components a long way removed from the concept of a cheap personal monitor. Until a suitable personal monitor is available, there will be a tendency for people responsible for operational procedures to treat time-weighted averages of threshold limit values (TLVs) as ceiling limits, with consequent additional operational constraints.

In a number of countries around the world, environmental considerations are becoming more acute. Discharging fumigants like methyl bromide into the atmosphere is causing con-

cern. Environmental agencies are raising questions about the dispersal and fate of fumigants. Moreover, they are invoking levels that are considerably below the TLVs applicable to workspace environments. It is argued that such TLVs are set with normal healthy members of the workforce in mind, not young children or the elderly, and a lower environmental level would therefore seem to be more appropriate. Thus, when grain storages are close to houses there is a possibility that these lower levels might be found in and around these houses. There is therefore a need to understand more precisely the factors that influence the dispersal of fumigants in the atmosphere. Secondly, there is a need to consider the development of suitable scrubbers that will remove fumigant from silo exhausts and destroy it. In densely populated areas, this approach may be the only way that we will be able to continue to use fumigants in the future.

## **The Future of Fumigants**

Fumigation will remain one of the more valuable control strategies for the preservation of grain and other stored commodities for many years to come. It is still the cheapest method available for disinfesting grain. Phosphine, I believe, will remain one of the more important fumigants available for this purpose. However, unless steps are taken to employ it effectively, resistance will spread and it will remain of use to only those countries that have the capacity to employ longer exposure periods. It is important to realise that where the capacity does not exist to prolong exposure periods the only hope is alternative and less convenient or effective fumigants. Other methods of disinfestation will be more costly.

It is to be hoped that, by the time of the next Conference on Controlled Atmospheres and Fumigation, methods of usage of phosphine will have improved dramatically. It is vital that, in some of the developing countries where such a method is most needed, efforts be made to use the fumigant properly. The argument that these countries cannot afford the costs of sealing or alternative methods of application is untenable. These are the very countries that cannot afford to lose a fumigant like phosphine, for to do so is to risk losing more grain to insects. I wonder what the cheaper cost is?

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# Generation and Application of Modified Atmospheres and Fumigants for the Control of Storage Insects

S. Navarro and E. Donahaye\*

## *Abstract*

Modified atmosphere (MA) and fumigation treatments are carried out to create an environment lethal to insects in stored commodities. The sole alternative to fumigation for in-storage insect control which also offers a diversity of applications and toxic-residue-free treatment is the MA method. This paper reviews what are currently the most frequently used methods for generation and application of MAs and fumigants. MAs can be generated from liquefied gas, bulk transported in road tankers, or delivered from cylinders for small-scale treatments. The alternative approach is on-site generation of MAs. This includes the use of exothermic gas generators based on combustion of hydrocarbon fuel, and the use of air compressors and molecular sieves to produce nitrogen from air. Possibilities for on-site generation of MAs from biological sources, including assisted hermetic storage by external biogenesis of MAs, as well as conventional hermetic storage, are also discussed. The effects of MAs on most common insects have been studied in relation to concentration and exposure time in order to establish dosage schedules. These show that carbon dioxide-air atmospheres are usually more toxic than oxygen-deficient ones. The methods of application and their gas supply requirements are reviewed in relation to the constructional limitations of the existing enclosures to be treated.

Fumigants are produced and marketed in containers convenient for application, either in liquid state in pressurized cylinders, or in solid-state formulations. Methods of generation for the most commonly used fumigants, namely methyl bromide and phosphine, and for various fumigant mixtures are discussed. Fumigant application using gravity penetration, grain stream admixture, assistance from recirculation, and vacuum and space techniques, all of which continue to be widely used, are critically reviewed.

INCREASED public concern over the adverse effects of fumigant residues in food and the environment has led to the partial substitution of fumigation by alternative control methods. Among these methods the only one that retains the special capacity of fumigation for in-situ treatment of stored commodities, as well as offering a similar diversity of application technologies, is the modified atmosphere (MA) method. Although this method has become well established for control of storage pests, its commercial use is still limited to a few countries (Banks and Ripp 1984; Fleurat

Lessard and Le Torc'h 1987; Jay and d'Orazio 1984; Navarro et al. 1979; Shejbal 1980).

Assessing several possible reasons for the lack of commercial acceptance of the MA method, Annis (1987) emphasised two in particular: its high cost; and the lack of sufficient information on its reliability. However, in our opinion both these limitations are temporary. Clearly, cost comparisons between fumigation and alternative methods must be weighted against consumer acceptance. As for the reliability of the method, the considerable research that has been done on the effects of MA on insects has provided a firm basis for the technology, and the potential to largely replace conventional fumigation (Banks and Ripp 1984).

\*Department of Stored Products, ARO, The Volcani Center, Bet Dagan, Israel. Contribution from the Agricultural Research Organization. No. 2600-E, 1989 series.

The application of MAs and fumigants is most appropriate for bulk storage of grain either on-farm or at central storage installations, in structures that are sealed to an acceptable level of gastightness. Commodities such as dried fruits, flour, and spices requiring treatment in relatively small lots may be treated in specially designed fumigation chambers. Chambers for fumigation at atmospheric pressure have been described by Bond (1984) and these may be adapted for MA application.

Methods of generating and applying MAs and fumigants will be discussed, with emphasis on the main differences between them.

## Methods for Generating Modified Atmospheres and Fumigants

### Generation of Modified Atmospheres

The objective of MA treatment is to attain a composition of atmospheric gases rich in  $\text{CO}_2$  and low in  $\text{O}_2$  within the storage enclosure or treatment chamber for long enough to control the storage pests. At present, the most widely used source for production of such atmospheric gas compositions is tanker-delivered liquefied  $\text{CO}_2$  or  $\text{N}_2$ . Availability and suitability of this means of gas supply must be questioned when the gases are transported over long distances from an industrial production area to the storage site. Therefore, potential alternative methods of generating MAs should also be considered.

#### *Supply of Gases from Tankers*

When the target MA gas composition is  $<1\%$   $\text{O}_2$  or high  $\text{CO}_2$  concentration, a commonly used method is to supply  $\text{N}_2$  or  $\text{CO}_2$  from pressurised tankers. The practical aspects of purging grain storages have been described by Guiffre and Segal (1984) for  $\text{CO}_2$ , and by Banks et al. (1980) for  $\text{N}_2$  and  $\text{CO}_2$ . A significant portion of the cost of applying MAs generated from tankers is for transportation and on-site purging. Bulk liquid gas is transported in conventionally insulated road tankers.

For large-scale application of  $\text{N}_2$  or  $\text{CO}_2$ , vapourisers are essential. These devices consist of a suitably designed receptacle with a heating medium (electricity, steam, diesel fuel, or propane), a hot-water-jacketed super-heated coil, and forced or natural draught. A forced-

draught-type vapourizer with electrical super-heating has been found to be convenient (Guiffre and Segal 1984).

#### *Exothermic Gas Generators*

For on-site generation of MAs by combustion of hydrocarbon fuel to produce a low  $\text{O}_2$  atmosphere containing some  $\text{CO}_2$ , commercial installations—termed exothermic gas generators or gas burners—are available. Such equipment was originally designed for MA storage of fresh fruits. Their MA composition is designed to allow the presence of some 2–3%  $\text{O}_2$  and to remove  $\text{CO}_2$  through scrubbers. Therefore, their use in the grain industry requires several adaptations, such as: tuning the equipment to obtain an  $\text{O}_2$  level of  $<1\%$ ; utilisation to full advantage of the  $\text{CO}_2$  generated; and removal of excessive humidity from the atmosphere generated.

Combustion of propane yields about 13%  $\text{CO}_2$ , and of butane about 15%. The MA generated is more toxic than a  $\text{N}_2$  atmosphere deficient in  $\text{O}_2$ . This is due to the presence of  $\text{CO}_2$  in the MA causing hypercarbia which synergises hypoxia leading to enhanced insect mortality (Bell 1984; Calderon and Navarro 1979, 1980; Navarro and Jay 1987). Equipment has been designed to operate with open-flame burners, catalytic burners, and as internal combustion systems. Full-scale field trials using open flame burners (exothermic MA generators) (Storey 1973; Fleurat Lessard and Le Torc'h 1987), and catalytic burners (Navarro et al. 1979) to provide a low  $\text{O}_2$  gas mixture, have proved successful. Open-flame burners are capable of producing high gas flow rates at low  $\text{O}_2$  tension. Consequently, the generated MA can be applied directly to purge the treated enclosure. On the other hand, catalytic systems reduce the  $\text{O}_2$  concentration in the atmosphere by a fixed fraction during passage through the catalyst, and therefore should preferably be used in a recirculation system. The development of a modified internal combustion engine for MA generation has been reported (Banks 1984a). In spite of its advantages over the open-flame and catalytic burners as an easily operated, transportable, and independent system, information on field application of such combustion systems is lacking.

#### *On-site $\text{N}_2$ Generators*

Commercial equipment which uses the

process of  $O_2$  adsorption from compressed air passed through a molecular sieve bed—sometimes called 'pressure-swing adsorption' systems—is available (Zanon 1980). For continuous operation a set of two adsorbers is provided, which operate sequentially for  $O_2$  adsorption and regeneration.  $N_2$  at a purity of 99.9% can be obtained through regulation of inlet airflow. This method of  $N_2$  generation is a relatively new approach in MA generation technology. Equipment is now being manufactured that is rated to supply an outlet flow rate of  $120\text{ m}^3/\text{hour}$  at an outlet purity of 98%  $N_2$ . However, in view of the high capital cost involved, it would seem wise to undertake a long-term cost-benefit analysis to explore the financial viability of such installations.

### *Biogeneration of MAs*

Two principal forms of biogeneration of MAs are considered, namely, 'Hermetic storage' and 'Assisted hermetic storage'.

#### Hermetic storage:

A high level of gastightness is required for a structure to be suitable for hermetic storage of dry grain. The effect of restricted air supply on storage insects was studied by Oxley and Wickenden (1963) who suggested that in leaky structures it is necessary to increase the rate of  $O_2$  consumption to a level at which insect infestation cannot persist. Burrell (1980) concluded that sealing infested grain using hermetic storage to kill the insects can be satisfactory for a heavy infestation in warm grain. However, because of the long storage period required before complete kill is obtained, it is likely to prove uneconomical for light infestations or when grain is cool.

To obtain complete control of all insects and so eliminate the danger of renewed infestation of grain removed from the hermetic container, Banks (1984a) proposed a possible solution of increasing consumption of  $O_2$  by artificially infesting the grain with insects. Similarly, Burrell (1980) intentionally wetted a small region of the stored commodity. Because part of the commodity is sacrificed for the generation of the MA, Banks (1984a) has termed this type of storage 'hermetic storage with sacrificial areas'. Nevertheless, the authors' experience suggests that hermetic storage of grain in flexible plastic storage systems, under subtropical climatic conditions, is an excellent

approach, provided there is a certain degree of tolerance to the presence of insects at critical areas in the storage structure (e.g. at the grain surface, where moisture condensation is likely to occur). At the end of long-term hermetic storage, when unloaded grain was destined for immediate consumption, the risk of spreading insect infestation was found to be negligible. Insect control success due to the hermetic storage treatments was comparable to conventional fumigants (over 99.9% kill), and losses due to insect activity were minimal (0.15% loss in weight for a storage period of 15 months) (Navarro et al. 1984).

#### Assisted hermetic storage:

The term 'assisted hermetic storage' was introduced by Banks (1984a) in order to define a process in which MA generation is assisted by a biogenerator source without sacrificing the commodity. Using a similar approach, Calderon et al. (1981) examined the possibility of generating a MA by inoculating wet rice bran. The best known working example of assisted hermetic storage is that in use in China (Lu 1984). With this method, removal of  $O_2$  is achieved by recirculating storage gases through a closed system containing racks of moist grain and bran infected with a particular mould culture. This MA generation system merits further attention to explore the potential for its use at locations where a regular supply of industrial gases is nonexistent or cannot be economically justified.

### *Potential Systems for the Generation of MA*

Newer methods for the generation of MAs have been discussed by Banks (1984a). They include extraction of  $N_2$  from the low  $O_2$  exhaust stream produced by the combustion of hydrocarbons in air (Zanon 1980), catalytic oxidation of ammonia, hydrogen combustion, direct electrolytic or catalytic removal of  $O_2$ , removal of  $O_2$  by chemical reaction, producer gas combustion systems to generate  $CO_2$ , combustion of methane derived from fermentation, burning carbon-containing materials in air, burning coal or charcoal in  $O_2$ , and production of  $CO_2$  from fermentation.

### **Generation of Fumigants**

Contrary to the MAs, the list of chemicals that fall within the definition of fumigants is long.



However, due to diverse unfavourable properties, including the fact that many can produce long-term hazardous effects, the number of fumigants approved for use has declined, and at present only a few remain in service. In the light of environmental protection awareness and a general trend in agriculture towards integrated pest management, there has been a tendency in developed countries to reduce dependence on fumigation for insect control. However, since fumigation is one of the most efficient means of insect control, it continues to play an important role in the protection of stored commodities. This is especially so in less-developed countries, mainly because of the difficulties involved in application of integrated techniques, where developments to date have been directed mainly to bulk storage, either on-farm or at central storage level. In a GASGA seminar on Fumigation Technology in Developing Countries (Anon. 1986), it was emphasised that the use of phosphine has greatly simplified application procedures for fumigation. At the same seminar the danger of relying on only two widely used fumigants, namely phosphine ( $\text{PH}_3$ ) and methyl bromide (MB), was also recognised. In this section, we address methods of generation of fumigants, with major emphasis on  $\text{PH}_3$  and MB.

#### *Generation of Fumigants Applied in the Gaseous State*

The most commonly used fumigant gases are hydrogen cyanide (HCN) and MB. HCN boils at  $26^\circ\text{C}$ . It is generated by the action of an acid on sodium or potassium cyanide, from the reaction of calcium cyanide with moisture in the air, by volatilising liquid HCN from cylinders, or from HCN absorbed in inert materials formulated on highly porous cardboard discs. HCN was once used extensively for fumigation of stored products but because of several unfavourable properties it has been almost completely superseded by MB and  $\text{PH}_3$ .

MB continues to be one of the most commonly used fumigants for stored-product treatment. Its boiling point is  $3.6^\circ\text{C}$ . It is marketed as liquid under pressure and is generated from steel cylinders (with capacities of 2.25 to 816 kg), from cans containing 0.45 or 0.68 kg, or from glass ampoules usually containing 20 mL MB. The cylinders are equipped with siphons and in warm climates MB vapour pressure above the liquid is sufficient to

produce self-discharge. To assist discharge from cylinders, some manufacturers inject  $\text{N}_2$  into the space above the liquid MB. At temperatures below  $15^\circ\text{C}$ , or for large-scale applications where latent heat of evaporation cools the remaining MB below its boiling point, a vapouriser consisting of a coil of copper tubing immersed in a water bath heated to  $65^\circ\text{C}$  is advisable (Bond 1984).

#### *Generation of Fumigants Applied in the Liquid State*

Well known liquid fumigants are ethylene dibromide, ethylene dichloride, carbon tetrachloride, and carbon disulphide. They have been used for fumigation of small quantities of grain, spot fumigation in large bulks, and the localised fumigation of milling equipment. Ethylene dibromide, ethylene dichloride, and carbon tetrachloride are suspected as being carcinogenic in addition to possessing other toxic effects, while the flammability of carbon disulphide presents a hazard (Navarro 1986). Although they continue to offer practical solutions for the fumigation of small quantities of commodities in less-developed countries, their application in general has not been encouraged, and legislation in some countries has banned the use of several liquid fumigants. This group of fumigants, with boiling points above room or moderate outdoor temperatures ( $20$ – $25^\circ\text{C}$ ), are usually described as liquid fumigants. When used in a fumigation chamber, it may be necessary to volatilise the liquid by heating. During gas evaporation, even distribution should be ensured by circulation with fans or blowers.

#### *Generation of Fumigants Applied in the Solid State*

Phosphine ( $\text{PH}_3$ ) is a low boiling point fumigant ( $-87.4^\circ\text{C}$ ). To regulate its release and suppress its flammability, it is formulated as 3.0 g aluminium or magnesium phosphide tablets or 0.6 g pellets, which yield approximately 1 g and 0.2 g of  $\text{PH}_3$ , respectively. In addition, aluminium or magnesium phosphide powder is marketed in permeable paper bags (sachets), or in blankets, and magnesium phosphide is also marketed in the form of flat plates (206 g in weight). These plates are individually sealed in gastight foil pouches. Upon exposure of the aluminium or magnesium phosphide to

atmospheric moisture, phosphine starts to evolve. In general, magnesium phosphide formulations release the phosphine more rapidly than aluminium phosphide products (Bond 1984).

## Methods for Applying Modified Atmospheres and Fumigants

### Application of Modified Atmospheres

The prerequisites for application of MA are described below:

#### Choice of Atmospheric Gas Composition

A simple and descriptive graphical presentation to illustrate the relationship between exposure period, O<sub>2</sub>, and CO<sub>2</sub> concentration, and mortality of different insects' life stages, was compiled from the literature by Annis (1987). In his review, he proposed provisional dosage regimes at grain temperatures of 20–29°C.

A summary of these dosage regimes is given in Table 1, which shows that the use of an atmosphere with less than 1% O<sub>2</sub> requires considerably longer exposure times than 80% CO<sub>2</sub> atmospheres to kill insect populations other than *Trogoderma granarium*. The basis for preparing these regimes was the time response of the most tolerant developmental stage of the most tolerant insect species. In the absence of *T. granarium*, a low O<sub>2</sub> regime should be based on the response of *S. oryzae* pupae, while the CO<sub>2</sub> regimes should be based

on *Tribolium castaneum* adults and larvae (Annis 1987; Navarro and Jay 1987).

Dosage regimes presented in Table 1 should be viewed as very generalised recommendations. More recently published information (Navarro and Jay 1987; Reichmuth 1987) indicates that further work is needed to enable precise dosage recommendations to be established for the application of MAs for the major stored-product insects under the wide range of intrinsic and extrinsic factors involved. Thus, recommended dosage regimes should be based on temperature ranges appropriate to specific climatic conditions and also to the dominant insect species found in the commodities involved. Aspects of commodity moisture content (Bell 1987; Navarro 1978), socioeconomically acceptable control levels, the time-frame within which control must be accomplished, and the expected leak-rate standard in which the MA treatment will be performed will probably all play an important role in future recommendations.

#### Rate of Supply

Due to the relatively long exposure time involved, one basic concept with MA application methods is the combination of two separate phases: an initial 'purge' for the establishment of the desired atmospheric gas composition, and a subsequent 'maintenance' phase in which the desired gas composition is maintained during the exposure period (Banks and Annis 1977). This concept differs from the 'single-shot' treatment suggested by Banks et al.

**Table 1** Suggested provisional dosage regimes for control of all stages of the 12 most common insect species of stored grain, using modified atmospheres at temperatures between 20 and 29°C\*.

Atmospheric gas concentration (%)	Controls most common grain insects including <i>Trogoderma granarium</i> (yes/no)	Exposure period (days)
<1 O <sub>2</sub> (in nitrogen)	yes	20
Constant CO <sub>2</sub> in air		
40	no	17
60	no	11
80	no	8.5
80	yes	16
CO <sub>2</sub> decay in air from >70 to 35	no	15

\*Compiled from Annis (1987).

(1980). This latter-type treatment is suitable basically for CO<sub>2</sub>, when an initial concentration of higher than 70% is established and the gastightness of the structure is sufficient to allow maintenance of a concentration at above 35% for at least 10 days.

With MA treatment a large volume of the intergranular free space plus the headspace of the silo needs to be displaced. The rate of gas supply is purely an economic aspect of the application of MAs, since a substantial portion of the expense involved consists of the cost of transporting the liquid CO<sub>2</sub> or N<sub>2</sub> and of the on-site purging, which is a time-consuming process (Guiffre and Segal 1984). If on-site bulk gas tanks are not installed, truck demurrage charges must be added. With gas burners the aspect of transportation is less critical, since the quantities of hydrocarbon gas used are considerably less.

The gas supply rates required for the application of selected MAs are listed in Table 2. The proposed supply time at 'purge' phase for a MA of <1% O<sub>2</sub> is considerably shorter than for the other MAs. This shorter 'purge' time derives from the physical characteristics of N<sub>2</sub> (Banks and Annis 1977). A method (not included in Table 2) that has been used by the present authors in small bins of 50-tonne capacity consists of direct gas supply to the bin in a liquid state, thereby reducing the supply time considerably. This method is discussed in the section on gas supply in a liquid state.

### Structural Requirements

Storage structures designed specifically for the application of MAs are practically non-existent, apart from those in Australia (Ripp et al. 1984). According to Banks and Ripp (1984) there is in Australia an increasing trend toward the use of sealed storage for dry grain, accompanied by the conversion of existing structures to sealed storage rather than construction of new installations. Large-scale operations of this type have not yet been reported from other parts of the world. Therefore, before deciding on the method of MA application, careful examination should be made of sealing requirements to obtain a standard acceptable for maintaining the gas composition over the designed exposure period (Banks 1984b).

### Application of MA in a Gaseous State

For application of N<sub>2</sub> or CO<sub>2</sub> into upright storages, simple inlet systems fitted into the bin wall can be used for gas introduction. The design of the system should be such as to prevent excessive pressure buildup over weak areas of the silo bin wall, especially around the inlet pipe. For purge rates of 6 m<sup>3</sup>/min, an inlet pipe of 8 cm diameter has proven convenient (Banks and Annis 1980). However, in bins equipped with a grain aeration system, it is advantageous to use the inlet duct system as the gas introduction point in order to obtain improved purging efficiency.

**Table 2.** Rates of gas supply requirements for modified atmosphere application.

Selected atmospheric gas concentration	Application phase	Amount of gas per tonne commodity	Supply time (h)
<1% O <sub>2</sub> in N <sub>2</sub>	Purge	1-2 m <sup>3</sup> N <sub>2</sub>	<12
	Maintenance	0.01-0.06 m <sup>3</sup> N <sub>2</sub>	**
>70% CO <sub>2</sub> in air	Purge	0.5-1.0 m <sup>3</sup> CO <sub>2</sub>	<48
	Maintenance	0.02-0.04 m <sup>3</sup> CO <sub>2</sub>	**
Gas burner <1% O <sub>2</sub> with >14% CO <sub>2</sub>	Purge	47-66 g C <sub>3</sub> H <sub>8</sub>	<48
	Maintenance	0.6-1.2 g C <sub>3</sub> H <sub>8</sub>	**
>70% CO <sub>2</sub> in air	Single-shot	0.5-1.0 m <sup>3</sup> CO <sub>2</sub>	<48

\* Compiled from Banks (1984a). Only gas composition supported by field experience are presented in this table. Basic assumptions for above requirements are; that storage is filled with grain (minimum headspace) and pressure decay time is <5 mins for decay from 500 to 250 Pa.

\*\* According to the dosage regime, see also Table 1.

When purging upwards, high CO<sub>2</sub> levels tend to remain in the lower layers of large bins and this may result in uneven and sometimes inadequate CO<sub>2</sub> concentrations for insect control, especially in the upper layers of bins (Wilson et al. 1980). To overcome this, especially in the 'single-shot' CO<sub>2</sub> application method where no maintenance phase is used, it is important to introduce an air injector into the CO<sub>2</sub> stream so as to produce a CO<sub>2</sub>-air pre-mix at the designed concentration, or to recirculate the CO<sub>2</sub>-air mixture until the desired CO<sub>2</sub> concentration is attained in all regions of the bin.

For the application of CO<sub>2</sub>, Jay (1971, 1980) has proposed three methods. These, together with the recirculation and blending method (Navarro et al. 1979; Wilson et al. 1984) comprise the five basic application methods

suitable for MAs. They are summarised in Table 3 and presented schematically in Figure 1. Recirculation gives the most uniform concentration and it can be applied by moving the gases inside the bins upwards or downwards (Navarro et al. 1986). The main gain in using downwards flow is with application by burner gas. It permits advantage to be taken of the long path of the external gas delivery pipe to cool and thereby dehumidify the hot gases after the burner.

#### *Application of MA in Liquid or Solid State*

For small silos and MA treatment chambers of up to 100 m<sup>3</sup>, a direct supply of CO<sub>2</sub> from cylinders equipped with a siphon was tested by the authors. By this means, CO<sub>2</sub> is released in a liquid state from the pressurised cylinder (Fig. 2).

**Table 3** Methods of application of modified atmospheres

Method of application	Applicable MA	Main advantages	Main disadvantages	Reference
1. Purge a full silo from the top.	CO <sub>2</sub>	Requires only one application. Labour requirements are minimal.	Purging time is long. Some CO <sub>2</sub> is lost in outflow with air mix.	(3) (4)
2. Lift the atmosphere out (air displacement method). Continuous purge from bottom.	CO <sub>2</sub> N <sub>2</sub> GB*	Labour requirements are low. No loss of gas in mixing. Works best with N <sub>2</sub>	Gas purging region of silo should be leak-free. With CO <sub>2</sub> it creates high localised concentration, so blending may be necessary.	(1) (2) (3) (6)
3. Apply CO <sub>2</sub> in the grain stream (snow, dry ice).	CO <sub>2</sub>	Method is fast. No vaporisation equipment is needed.	Danger of explosion. Constant supervision during application.	(3)
4. Recirculation.	CO <sub>2</sub> GB	Homogenous concentration is obtained. No loss of gas in mixing.	Recirculation equipment is necessary.	(5) (7)
5. Blending and purging.	CO <sub>2</sub>	Homogenous concentration is obtained. No loss of gas in mixing.	Air CO <sub>2</sub> mixing equipment is necessary	(7)

\* GB, gas burner atmosphere, consisting of <1% O<sub>2</sub>, 15% CO<sub>2</sub>, and 84% N<sub>2</sub>.

\*\* [1] = Banks and Annis (1977).

[2] = Fleurat Lessard and Le Torc'h (1987).

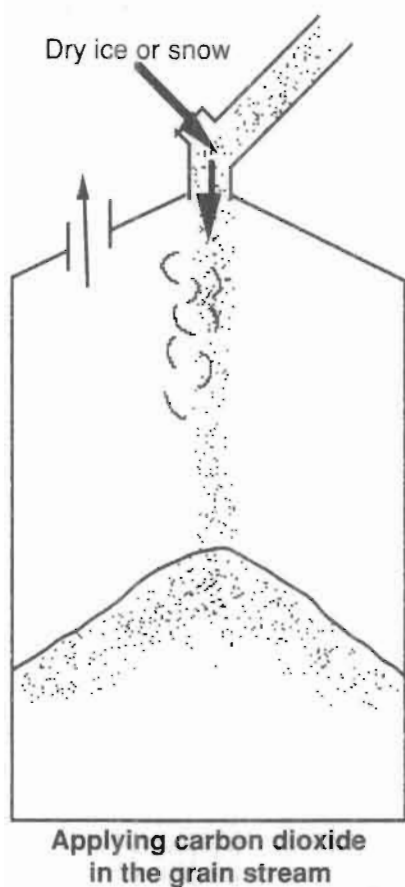
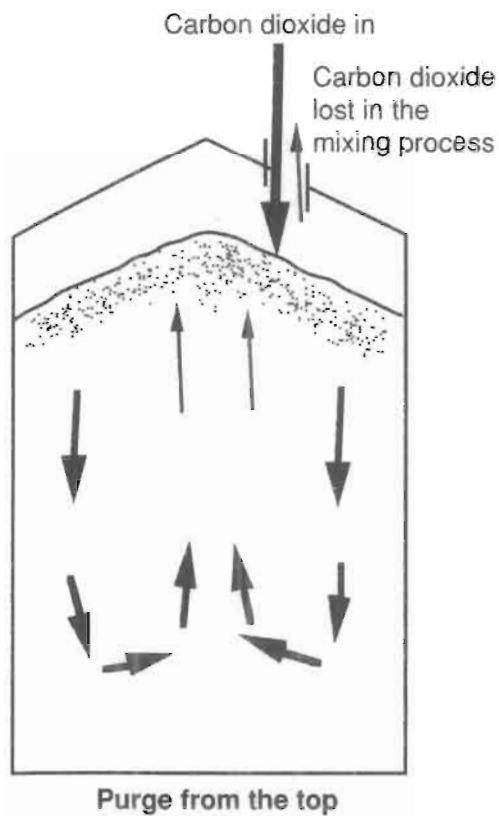
[3] = Jay (1980).

[4] = Jay and Pearman (1973).

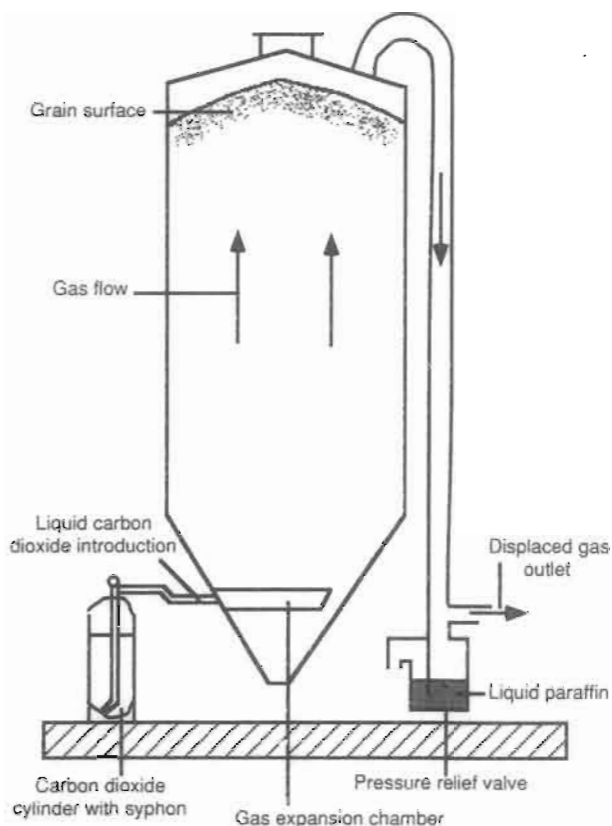
[5] = Navarro et al. (1979).

[6] = Storey (1973).

[7] = Wilson et al. (1984).



**Fig. 1.** Different modified atmosphere application methods



**Fig. 2.** Liquid application of CO<sub>2</sub> suitable for small silos and modified fumigation chambers.

A large volume of CO<sub>2</sub> can thus be introduced into the treated enclosure in a relatively short time, thereby causing displacement by lift-out of a substantial portion of the atmosphere from the free space of the treated structure. Great care should therefore be taken to install a large enough vent pipe and to ensure that the structure can withstand the pressure build-up at the initial purging phase. In addition, it is strongly recommended that the pressure of the treated structure be monitored. Our experience with this method of gas supply has been that at a rate of 4 m<sup>3</sup> CO<sub>2</sub>/min, pressure build-up within a chamber of 110 m<sup>3</sup> was less than 60 Pa when the vent pipe's internal diameter was 75 mm.

Application of CO<sub>2</sub> in the form of dry ice to control insects infesting flour in hopper cars (Ronai and Jay 1982) and in freight containers (Sharp and Banks 1980) was investigated. The results indicate that further field trials are needed before recommending this method of application under commercial conditions.

### Application of Fumigants

#### Structural Requirements:

A fundamental requirement rarely met in

practice is that fumigable structures be gastight. The major factors which determine the level of gastightness are the porosity of the structural fabric and the structural defects which cause leakage. On the other hand, even when large structures are rendered virtually gastight, external factors—including diurnal ambient temperature fluctuations, changes in barometric pressure, and wind velocities—should be recognised as influencing gas loss after application (Winks 1979). For fumigable silo bins which meet the demand for high standards of gastightness, it is therefore also necessary to provide an adequate pressure-relief valve similar to that recommended for MA treatments. Insect control by fumigant applications is achieved by maintaining a certain concentration over a predetermined exposure period. After a fumigant has been applied, its concentration within the interstitial air space rises and then progressively declines at a rate depending on the gastightness of the structure. Several factors contribute to the formation of this typical concentration decay curve, in addition to the external factors mentioned above: diffusion through leaks; permeation through the structural fabric; and sorption of the fumigant by the commodity. Banks (1985b) and Winks (1986) have reported on current work to overcome these factors: a flow-through method which is capable of maintaining a constant concentration for the entire length of the required exposure time.

#### *Dosage Schedules for the Application of Fumigants:*

In practice, fumigant concentrations exhibit a characteristic decay which differs from that of the typically constant concentrations under which their toxicity to insects has been determined in the laboratory. Very little work has been done to demonstrate the differences between the effects of constant and changing concentrations of fumigants on their toxicity to insects (Reichmuth 1986).

Dosage schedules for the application of fumigants have been recommended both by professional bodies and commercial companies. Research on dosage recommendations is usually based on the response of pests to fumigants directed toward complete control, in order to avoid selection for resistance. Recent critical evaluation of the concept of concentration time product (Ct-product), especially when  $\text{PH}_3$  is

applied at high concentrations, has led to revision of previously established dosage and exposure recommendations.

Methyl bromide continues to provide an effective solution for fumigations of short duration and has been used effectively where exposure time poses serious limitations, as in cases where throughput of fumigation chambers requires rapid turnover, or for quarantine applications. For example, a recommended 24 hour dosage for fumigation of bulk grain in flat storages is  $32.0 \text{ g/m}^3$  for MB applied under gastight sheets within a temperature range  $21\text{--}25^\circ\text{C}$  (Bond 1984).

Laboratory results on MB Ct-products that produce 99.9% kill of a wide range of insects (except *T. granarium* and certain species of mites) continue to serve as a basis for calculation of initial dosages and exposure times for a wide range of commodities (Anon. 1970). To calculate the desired Ct-product in practical fumigation, allowances must be made for possible losses of fumigant through leaks, and for sorption by the commodity. Information on the intensity and speed of sorption of the fumigant by the commodity is essential for determination of the effective concentration in the interstitial space. However, test results on fumigant-commodity interaction are lacking (Banks 1985a). Recommended dosages, especially for MB, therefore differ markedly from those calculated in the laboratory (Anon. 1970).

Recent information on dosages of  $\text{PH}_3$  has pointed to two characteristics of this material which differ basically from those of other fumigants and which pose problems in the establishment of dosage schedules: (i) the large variation in susceptibility of different species and stages of the same species; and (ii) the relatively long initial exposure time necessary to achieve a toxic effect (Bell 1986). A summary of some recommended dosage rates and exposure periods for  $\text{PH}_3$  is given in Table 4.

There has been a noticeable trend towards lowering the concentrations while extending the exposure period. This is the outcome of the fact that for short exposures at high concentrations there is a protective stupefaction effect that renders the more tolerant stages, especially eggs and young pupae, even less susceptible (Winks 1986, 1987). Conversely, prolonged exposure at low  $\text{PH}_3$  concentrations allows insect development to continue, so that tolerant stages develop into susceptible ones and are thus controlled. However, for the adoption of this approach the

gastightness level of the fumigated structure must be high enough to allow retention of the fumigant for a sufficient time to achieve complete kill.

Control of  $\text{PH}_3$ -resistant strains certainly requires further attention, and would justify revision of current recommended dosage schedules shown in Table 4. However, to avoid spread of  $\text{PH}_3$  resistance (Mills 1986) at this stage, and until new methods of application are proven feasible, it would be prudent to fumigate with  $\text{PH}_3$  only in structures with a high standard of gastightness (Winks 1986). The following discussion on methods of application, although adaptable to other fumigants, is directed mainly to the use of MB and  $\text{PH}_3$ .

#### Gravity Penetration (Surface Application)

For large-scale fumigation of bulk grain,

liquid-type fumigants are best applied to the surface of the grain by means of sprayers. Although MB and  $\text{PH}_3$  are both heavier than air in the gaseous phase, they have been considered inappropriate for deep penetration of the grain mass by surface application. However, for flat storage, in gastight systems where the grain pile is either longer or wider than high, then fumigation by simple surface-application relying on natural convection currents assisted by diffusion, should be sufficient to provide an even distribution.

The presence of high dockage concentrations within the grain bulk may create pockets which act as barriers to fumigant penetration (Viljoen et al. 1981). Convection currents induced by temperature gradients, depending on their direction, may also impede dispersal of the fumigant applied to the surface of the grain bulk. This aspect, usually neglected in relation

**Table 4** Recommended dosage regimes for the control by phosphine of stored product insects in grain, in well sealed storages, at different temperatures.

Temperature range °C	Dosage (g/m <sup>3</sup> )	Controls most common stored grain insects including			Exposure period (days)	Recommending body @	Reference***
		S.o.*	T.c.*	T.g.*			
10-20	1.0	yes	yes	yes	16	P	[2]
	1.0	no	yes	no	10	P	[2]
>15	4	CK**	CK	CK	14	C	[6]
	7.5	CK	CK	CK	8	C	[6]
	12.5	CK	CK	CK	14	C	[6]
	16.5	CK	CK	CK	8	C	[6]
	18.5	CK	CK	CK	4	C	[6]
	21	CK	CK	CK	5	C	[6]
	1.1-2.75	CK	CK	CK	4	C	[1]
2.4	CK	CK	no	4	P	[4]	
20-30	1.0	yes	yes	yes	12	P	[2]
	1.0	no	yes	yes	8	P	[2]
	1.0	no	yes	no	5	P	[2]
15-25	1.5	yes	yes	yes(?)	10	P	[5]
	2.5	yes	yes	yes	7	P	[5]
>25	0.3	CK	CK	CK	28	C	[3]
	0.4	CK	CK	CK	28	C	[3]
	1.5	yes	yes	yes	7	P	[5]
	2.5	yes	yes	no	5	P	[5]

@C = commercial

P = professional

\*S.o. = *Sitophilus oryzae* or *S. granarius*

\*T.c. = *Tribolium castaneum* or *T. confusum*

\*T.g. = *Trogoderma granarium*

\*\* CK = assumes complete kill

\*\*\* [1] = Anon. (1981)

[2] = Anon. (1984)

[3] = Banks (1986)

[4] = Bry et al. (1980)

[5] = Winks et al. (1980)

[6] = Wohlgemuth (1986)

to fumigant distribution in grain bulks, has recently been considered by Nguyen (1985), who proposed a mathematical model to conduct numerical experiments. Experimental work is needed to elucidate the influence of convection on retention of fumigant concentrations in certain locations of the bulk or to assist in their distribution.

Application of MB assisted by CO<sub>2</sub> in vertical grain bins (Calderon and Carmi 1973; Cohen et al. 1980; Viljoen et al. 1981), and its use as a space fumigant (Wainman et al. 1983), has been reported. With this method of application CO<sub>2</sub> apparently acts as a carrier and conveys the MB through the grain mass to the lower layers, thereby achieving adequate distribution. It is noteworthy that no detailed experimental work has yet been reported on the distribution of PH<sub>3</sub> assisted by CO<sub>2</sub>.

#### *Direct Mixing of Fumigant into the Grain Stream*

Only solid or liquid-type fumigants should be used for this method of application. In direct mixing, the fumigant is applied to the grain stream during loading of the bin. Granular calcium cyanide evolving HCN, and aluminium phosphide tablets or pellets evolving PH<sub>3</sub>, are the most common solid-type fumigants used (Bond 1984; Wohlgemuth 1986). The principal disadvantages of the method are: an empty silo bin is required; the movement of material from one bin to another involves expenditure of energy; the amount of broken kernels is increased; the application time is longer; and, if sachets of aluminium phosphide are applied, manual addition into the grain stream is necessary.

#### *Recirculated Fumigation*

For recirculation using permanent or temporary installations, a silo structure should be sufficiently gastight to prevent the fumigant-air mixture from being forced out under the pressure exerted by the recirculation fan. This method has been recommended for MB and HCN (Bond 1984) and consideration of the results of an investigation of the flammability properties of PH<sub>3</sub> (Green et al. 1984) leads to the conclusion that phosphine could be recirculated using the systems described by Cook (1984) and Boland (1984). Recirculation ensures adequate distribution of the fumigant within a shorter time

than with natural convection. A further improvement to application of CO<sub>2</sub>/MB mixtures into the bases of bins was developed by Williams et al. (1984), under whose system the CO<sub>2</sub>/MB mixture displaces the air in the storage evenly, thereby resulting in a shorter fumigation time and lower MB residues than those for MB alone.

#### *Vacuum Fumigation*

Vacuum fumigation has been used mainly in plant quarantine work, and for fumigating commodities which are difficult to penetrate at atmospheric pressure (Bond 1984). Methyl bromide has been used as a general-purpose fumigant in vacuum fumigation. Sensitivity of two *Carpophilus* species to MB at reduced pressure was found to be greater when individuals were exposed to a MB-CO<sub>2</sub> mixture, rather than MB alone (Navarro and Donahaye 1987). Since penetration of MB into coarse granular products such as wheat is very rapid at atmospheric pressure, there seems to be no advantage in using vacuum methods for the control of stored grain pests (Burns-Brown and Heuser 1953).

#### *Stack Fumigation*

Cereals and other grain products stored in bags, dried fruits stored in boxes, and tobacco, are the commodities most often fumigated under sheets. An important aspect of this method of fumigation has been the development of new plastic materials, leading to the introduction of types of sheeting satisfactory for fumigation (Bond 1984; Winks 1979). PVC sheets have been used to cover stacks of bagged grain for fumigation (Annis et al. 1984). The method consists of two PVC sheets; one to cover the floor and the other to cover the stack, both chemically bonded to provide a sealed enclosure. This improved method of fumigation of stacks has proven satisfactory for the application of PH<sub>3</sub> or CO<sub>2</sub> (Annis et al. 1984). This method of fumigation differs in principle from the general concept of fumigation under 'gas-proof sheets' (Anon, 1974), where the cover sheets are 'sealed' to the untreated floor using 'sand snakes.'

#### *Fumigant Mixtures*

The application of fumigant mixtures has long



been recognised as a means of overcoming the disadvantages of using a single fumigant. This practice, particularly with mixtures of CO<sub>2</sub> with PH<sub>3</sub> or MB, was reviewed by Navarro (1986). The use of some fumigants with inconvenient properties has been discontinued, leaving the field of stored products protection with two common fumigants, MB and PH<sub>3</sub>. The use of these fumigants in conjunction with CO<sub>2</sub> appears to offer a possible solution for the improvement of their application.

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# The Current Status of Fumigation and Controlled Atmosphere Storage Technologies in China

Liang Quan\*

## Abstract

This paper provides a brief outline of the current status of fumigation and controlled atmosphere technologies in China.

Phosphine is the most important fumigant for the control of stored grain insects. More than 90% of the fumigations undertaken in national storages are done with phosphine. In order to produce moderate concentrations and long exposure periods phosphine is generated from zinc phosphide and, in some cases, applied intermittently. Phosphine fumigation combined with controlled atmosphere is widely practiced. Research work had confirmed that it is economic and practical to synergise phosphine with appropriate concentrations of oxygen and carbon dioxide.

Controlled atmosphere storage by purging with nitrogen or carbon dioxide is restricted by cost and shortage of materials. It is used only in some large cities for long-term storage of milled rice. Most stored paddy and wheat is treated by the method of natural deoxidation (hermetic storage). The effectiveness of different oxygen and carbon dioxide concentrations was determined in laboratory simulations of natural deoxidation. The influence of relative humidity, the effect of controlled atmospheres on the quality of stored rice, and the temperature range over which safe storage is possible were also determined.

Suggestions are made as to priorities for future research.

THE use of fumigation and controlled atmospheres (CA) for grain storage in China has come some way since 1980. Improvements in fumigation technology have focussed on the very widely used phosphine, though chloropicrin and methyl bromide are still applied in certain circumstances. Controlled atmosphere storage was first put into practice in 1979. Because of the restricted availability of materials, it is basically natural airtight storage (also called 'deoxidated storage' in China). However, some papers dealing with other measures have been published.

In this paper, the author does not intend to present the result of research without practical significance. Rather, technologies in general use are covered. Also, some existing problems and the views of the author are expressed.

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\*Guangdong Institute of Cereal Science Research, 313 Dongfeng Central Road, Guangzhou City, People's Republic of China.

## Fumigation Technology

Fumigation is an important measure for the control of stored grain insects in China. It occupies a critical position in the system of integrated pest management (IPM), especially for pest control in national storages.

Owing to the cost of treatment and the demand for simplicity and convenience of application, almost 90% of fumigation treatments are conducted using phosphine. In some cases phosphine is generated by reacting zinc phosphide with sulphuric acid. Chloropicrin is used occasionally as a component part of combined fumigation with phosphine or as an alternative for the control of phosphine-resistant insects. There have been no developments in application technology in recent years. Methyl bromide has, for many years, been used for quarantine treatment only.

Research and development has been

concentrated on the technology of phosphine fumigation, especially since the 'Report of the FAO Global Survey of Pesticide Susceptibility of Stored Grain Pests' published in 1976 (Champ and Dyte 1976) and the appearance of phosphine-resistant insects in China.

### Generally Recognised Principles of Phosphine Fumigation

The generally recognised concepts and principles of phosphine fumigation in China are based on long-term practice and the results of overseas research.

The following are judged as essential criteria for phosphine fumigations even in the absence of formal regulations:

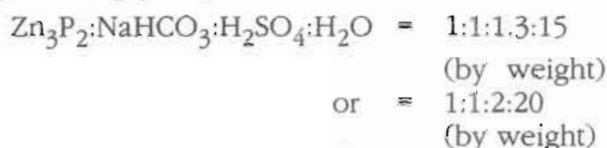
- Efforts must be made to accomplish good sealing conditions.
- Both bagged and bulk grain should be covered with plastic sheeting for fumigation.
- The outer surface of the fumigated grain must be disinfested.
- Slow-release methods are better for relatively poor conditions and long-exposure times.
- Exposure time should never be less than 120 hours.
- In routine phosphine fumigations for control of normal insect populations, the Ct product should exceed 150 mg.hr/l.
- If fumigation failure recurs continuously, reasons must be sought and live insects collected for resistance discrimination.
- A fumigation is judged as successful if no live insects appear within three months.
- Contact insecticides should be used to prevent reinfestation.
- The fumigant used should be varied from time to time if possible.

### Use of Zinc Phosphide for Phosphine Generation

Sulphuric acid reacts with zinc phosphide to produce phosphine. Though the reaction is flammable, if the acid is diluted with water to a concentration less than 10% (w/w) and the zinc phosphide is wrapped in strong, water permeable paper, combustion may be prevented and phosphine generated slowly. In order to give added assurance of safety, the zinc phosphide may also be mixed with sodium bicarbonate. If

this is done, phosphine and carbon dioxide are generated simultaneously, and the carbon dioxide produced can not only prevent flame and explosion but also synergise the effectiveness of phosphine. However, the rate of phosphine generation by this method is much faster than from Phostoxin, so it is not suitable for long exposure periods unless the total dosage is divided in two or three portions applied intermittently.

The best formulation for this method of generating phosphine is:



### Supplementary Method for Retarding the Rate of Phosphine Release by Phostoxin

Phosphine toxicology decrees that the gas must be used at moderate concentrations over long exposure periods for stored grain insect control. In some circumstances, for the purpose of keeping moderate phosphine concentrations in treating high moisture content grains, the rate of generation remains too rapid. An experiment to retard the rate of phosphine release by using small polyethylene bags for longer exposure periods was successful. The thickness of polyethylene film was 0.03–0.06 mm. Fewer than five tablets of Phostoxin were put into each bag and applied separately in and around bagged milled rice stacks. By this method, phosphine concentration could be maintained within the range of 0.01–0.05 mg/L for nearly three months. This range of phosphine concentration is ineffective against developing insects, but any adults emerging will be killed during the long exposure period (Guangzhou Institute of Cereal Science Research 1985).

Although this method is successful in long-term milled rice storage, the author believes that it would be better to improve Phostoxin formulations to meet the need for slower release rather than improving the method of application by users. The production of further varieties of Phostoxin is warranted.

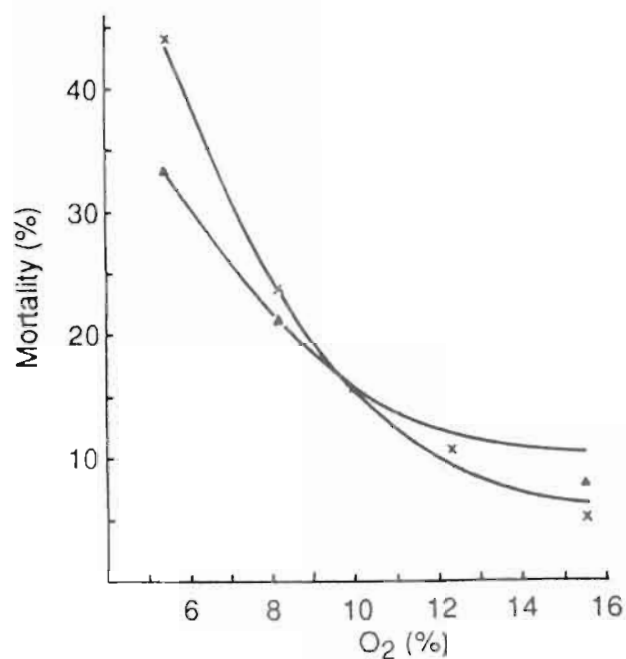
### Combined Use with Controlled Atmosphere

It is well known that the atmosphere within stored grain may be changed by the respiration of insects, microorganisms, and the grain itself.

Indeed, this modification of the storage atmosphere has also played a role in fumigation. However, it was not until the 1970s that research to exploit this phenomenon to enhance the effectiveness of fumigation was undertaken. The results of research carried out in China (Liang Quan et al. 1980) confirmed that both low oxygen and carbon dioxide rich atmospheres can increase the effectiveness of phosphine against common stored grain beetles. The results of a series of biological determinations showed that when oxygen is lowered to 12%, the toxicity of phosphine begins to rise and this tendency continues progressively as oxygen concentration is further lowered to 5% (Figs 1 and 2).

It was also shown that the starting synergistic concentration of raised carbon dioxide is 4%. Above 8%, however, the synergistic effect remains unchanged (Fig. 3).

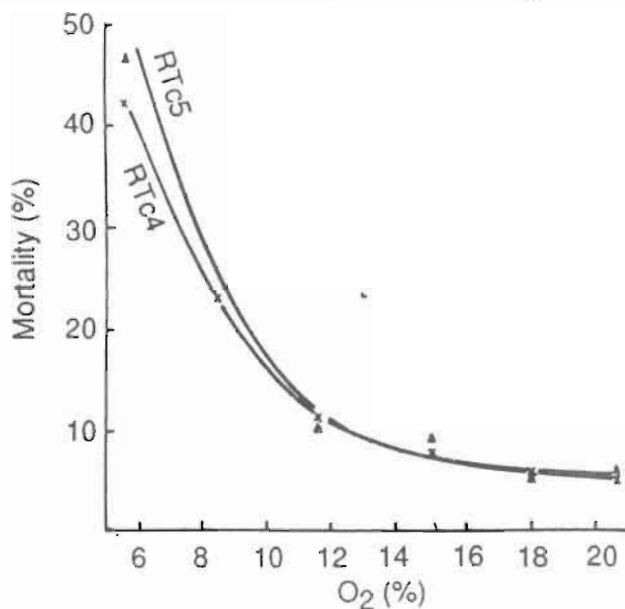
Therefore, the synergistic range of concentrations was recommended as oxygen lower than 12% and carbon dioxide 4%–8%. Very low oxygen or very high carbon dioxide atmospheres are impractical in China at present because it is not possible to attain them under general conditions of natural deoxidation. On the other hand, lower than 5% oxygen in phosphine fumigation is unnecessary, because insects can be killed by low oxygen only over long exposure periods.



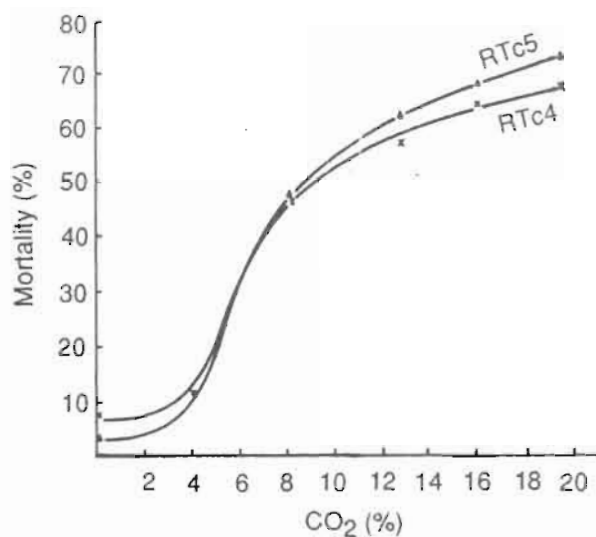
**Fig. 1.** Synergism of phosphine activity by lowered oxygen concentration (*Tribolium castaneum*: CO<sub>2</sub> 4%; PH<sub>3</sub> 0.006 mg/L; 28°C; 20 hours) (Liang Quan 1981).

## Intermittent Application of Phosphine

As noted earlier, most of the existing storages in China are not gastight. Although some remedial measures to improve the level of sealing are undertaken, the concentration of phosphine cannot be maintained, and the required Ct product is usually not attained. The principles of permeability and the toxicity characteristics of phosphine, mean that it is essential to generate the gas uniformly and to maintain effective concentrations for longer.



**Fig. 2.** Synergism of phosphine activity by lowered oxygen concentration (*Tribolium castaneum*: CO<sub>2</sub> 0%; PH<sub>3</sub> 0.007 mg/L; 28°C; 20 hours) (Liang Quan 1981).



**Fig. 3.** Synergism of phosphine activity by increased carbon dioxide concentration (*Tribolium castaneum*: O<sub>2</sub> 21%; PH<sub>3</sub> 0.007 mg/L; 28°C; 20 hours) (Liang Quan 1981).

Some reports have suggested that when the total phosphine dosage is applied in batches at one- or two-day intervals, the Ct product attained—over the same exposure period—is higher than when it is all applied at the one time (Liu Bao-kui 1982; Nanyuan Research Groups 1985).

This method is especially suited to zinc phosphide generation of phosphine. It has been to some extent commercialised.

### **Use of Convection Currents for Phosphine Fumigation**

Research work on convection currents in stored grain was carried out in China in the mid-1970s (Guzhuang Storage 1976). Although the results were obtained from field experiments, they are basically identical to the later theoretical findings of Nguyen in Australia (see, for example, Nguyen 1986).

The research demonstrated that the direction of flow in bulk grain varies with position in the grain mass. The flow is driven by temperature differences, with the rate of flow determined by the degree of these differences. In addition, it was shown that the direction of the current may also be influenced by insolation and wind. So that an effective application position for fumigant can be selected, it is essential that variations in current direction be known.

The Guzhuang Storage later reported (Guzhuang Storage 1985) that about 130,000 yuan (renminbi) had been saved in its own facilities by using this method over the previous fifteen years.

### **The Problem of Phosphine Resistant Insects**

Phosphine resistant strains of stored grain insect species were first found in China in 1979 (Liang Quan 1979), and resulting failures of routine phosphine fumigations appeared shortly afterwards. The first report of a local survey (Liang Quan 1975) verified that resistant strains occurred among all the major grain beetles except *S. zeamais*, and were widely distributed in Guangdong Province. However, the resistance ratios were limited (1.3–7.4). A strain of *S. oryzae* with a pronounced resistance ratio (63.7) was found in the eastern part of Guangdong. In the meantime, a nationwide survey had begun to reveal the overall situation. The results of this survey were published in 1983 (Research

Institute of Grain Storage, Ministry of Commerce 1983). They showed that phosphine resistant strains were widely distributed but mainly in southern areas of the country. The most noticeable species was again *S. oryzae* in which resistant strains amounted to 18% of total samples.

Although the resistance levels do not reach the degree at which phosphine is generally ineffective, they are a warning signal to develop long-term strategy as there is no foreseeable alternative to phosphine in the immediate future. The occurrence of phosphine resistance is therefore seen as a latent crisis in the control of stored grain insects.

As elsewhere in the world, much research has been carried out to delay the development of phosphine resistance and to eliminate resistant populations. Nevertheless, the situation could be further improved. The above-mentioned tactical viewpoint has been neither recognised nor accepted widely in practice. Rules and regulations have still not been drawn up and neither has a monitoring system for resistance been established. Much work on dissemination and in organisation therefore remains to be done.

## **Controlled Atmosphere Technology**

As is well known, controlled atmosphere storage is one of two components of modified atmosphere storage, the other component being natural airtight storage i.e. natural deoxidation storage. In China, the current situation is that almost 90% of airtight storage relies on natural deoxidation. The technique of purging with nitrogen or carbon dioxide has been adopted in some large cities for the storage of bagged rice, but is too expensive for rural use. In order to meet the needs of rural storage, since the late 1970s much work had been done to investigate measures for supplementing deoxidation, such as by using micro-organisms, nitrogen-producing machines, and molecular sieves and deoxidants. The results suggest that most of these measures have no widespread viability and that natural deoxidation will remain as the most practicable approach.

### **Sealing Materials and Methods**

There are no fully sealed storages used for CA

storage in China, basically because problems with the materials and technology have not yet been solved. CA storage is therefore always undertaken with the aid of plastic sheeting, most usually polyethylene or PVC. Laminated films are used for packing small quantities of high quality rice or other foods.

In the larger cities, if the storage period is more than three months, the stacks of bagged rice or flour are usually covered with 0.2 or 0.4 mm thick polyethylene or PVC sheets on all sides for natural deoxidation. If the moisture content is 13–14%, the concentration of oxygen will fall to 5% or so and carbon dioxide will increase to 8–10%.

In bulk-stored grain, only the surface can be covered with plastic sheeting. In many cases, the operator links up the sheets and the wall with the aid of a wooden trough and rubber piping. The wooden trough is fixed on the wall around the surface of bulk grain. The hem of the sheet can be placed into the wooden

trough by the use of rubber pipe. It is a simple and convenient method.

Given the conditions just described, it is easy to predict that most of the 'airtight' storage in China is leaky, so it is difficult to control insect pests using CA alone. In many cases it needs to be combined with phosphine fumigation.

The need to improve the gastightness of existing storages in China has a high priority, together with the development of sealing materials and methods.

### Monitoring of Airtightness

Technology for monitoring airtightness has lagged behind in China. At present the most widely used method is to measure the changes in oxygen or carbon dioxide concentration during the process of deoxidation. The pressure attenuation method is used only in some experimental situations.

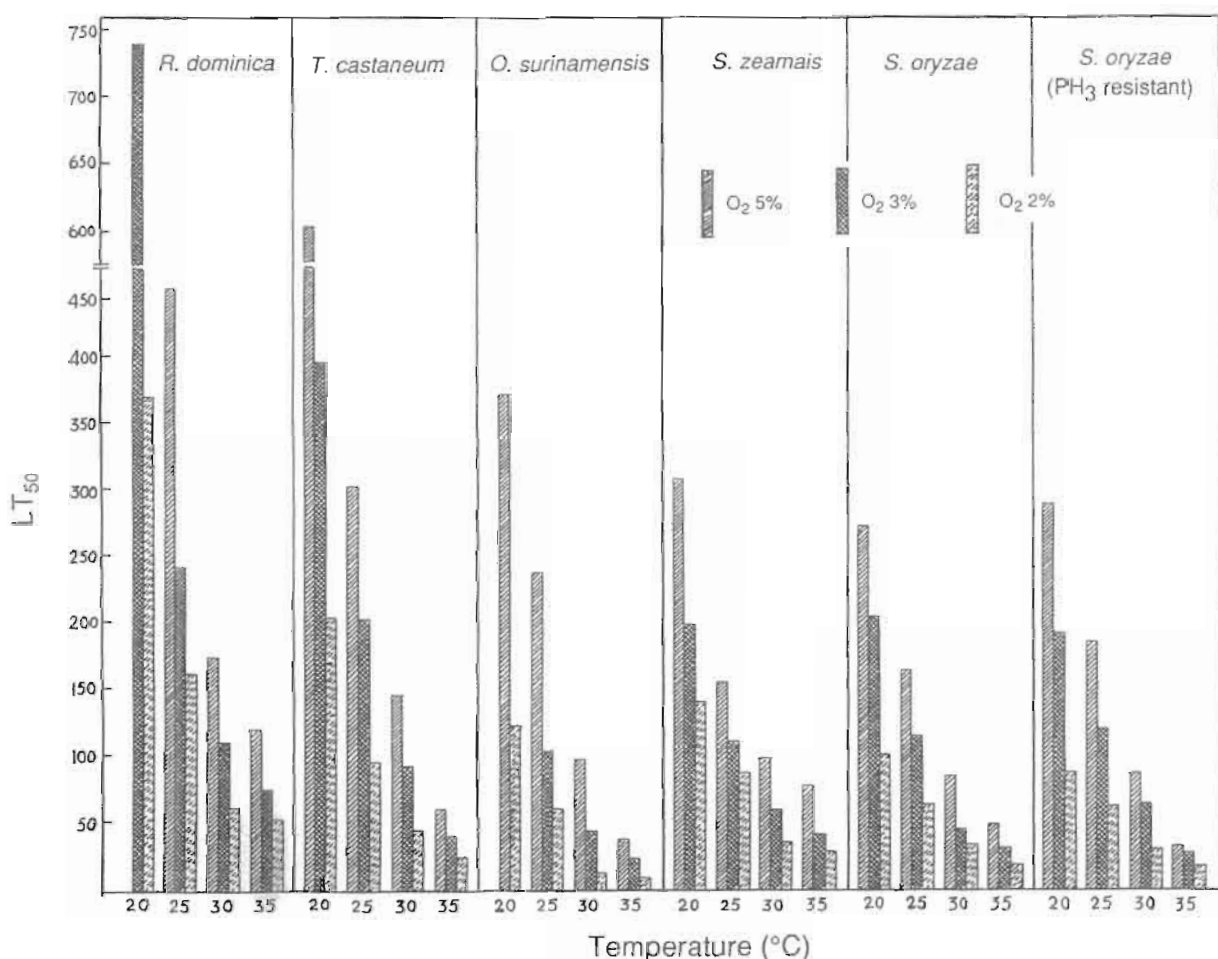


Fig. 4. Tolerance of stored grain beetles to low oxygen concentration at various temperatures (Liang Quan 1981).



## Effect of Controlled Atmosphere on the Quality of Milled Rice

A cooperative study (Research Institute of Grain Storage, Ministry of Commerce et al. 1981) of the effects of normal periods of CA application on the quality of milled rice was carried out. The conditions of CA and temperature required for safe storage were defined by a series of determinations of peroxidase, fatty acid, water soluble acid, and reducing sugar as well as taste evaluation. The conclusions were:

- Oxygen concentration has no effect on the quality of milled rice at moisture contents lower than 13.5%.
- At an oxygen concentration of 5% and moisture content of 14–14.5%, milled rice can be stored safely for 6 months.
- At moisture contents of 15–15.5% or 16%, if milled rice is stored in lower than 0.5% oxygen concentrations the temperature must be lowered to 25°C or 20°C, respectively, for safe storage.

• The viscosity of milled rice following storage is correlated with oxygen concentration during storage rather than temperature.

## Susceptibility of Stored Grain Insects to Controlled Atmospheres

A series of laboratory tests was carried out to evaluate effectiveness of different CA conditions (Liang Quan 1981). The susceptibilities of adults of common stored grain beetles were found to be as follows.

- The  $LT_{50}$  under 2%, 3%, and 5% oxygen conditions is *R. dominica* > *T. castaneum* > *S. zeamais* > *S. oryzae* = PH<sub>3</sub> resistant *S. oryzae* and *O. surinamensis* (Figs 4 and 5).
- Lowered temperature can increase the efficacy of a fixed low oxygen concentration. For *T. castaneum* in 2% oxygen at temperatures of 20°C, 25°C, 30°C, and 35°C, the  $LT_{50}$  are 204, 94, 46, 22 hours, respectively. It seems that the susceptibility of insects may increase 100% as the

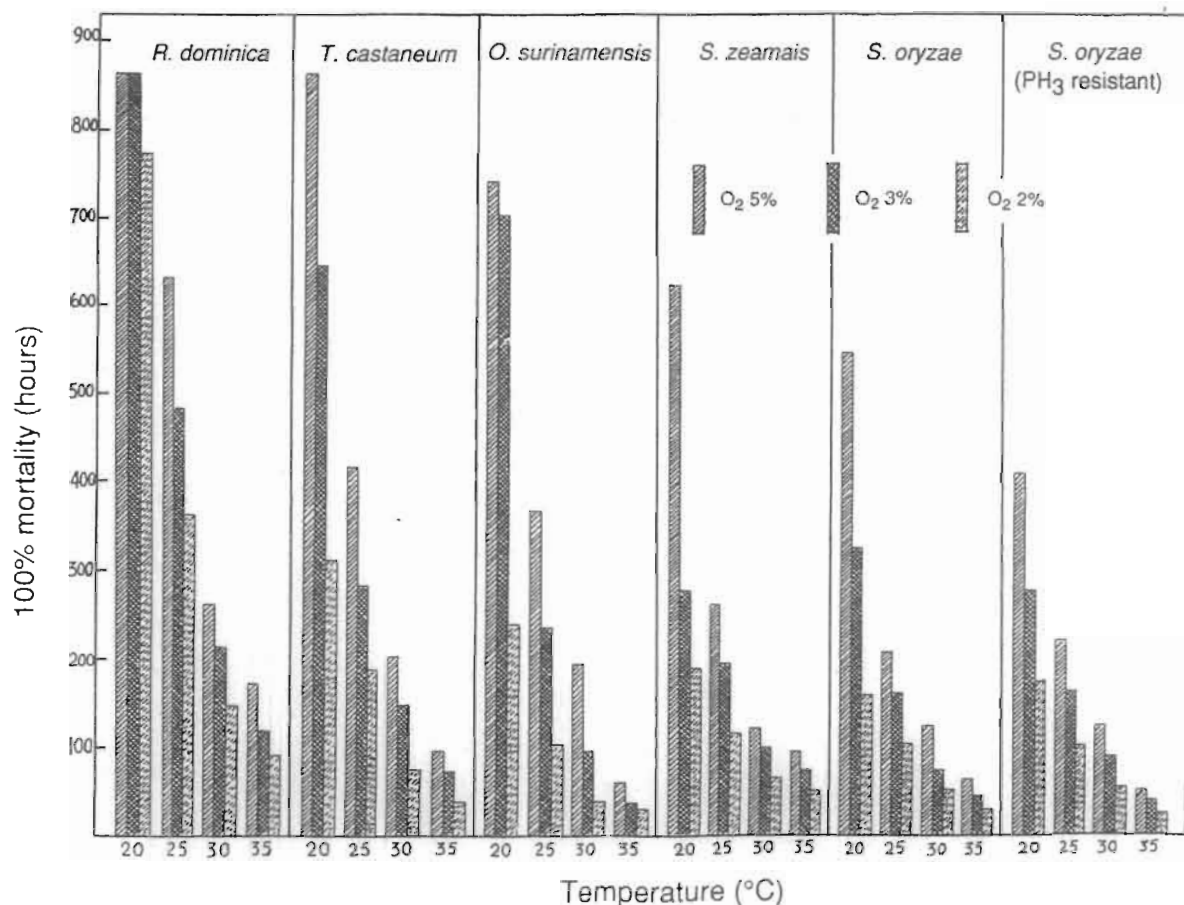


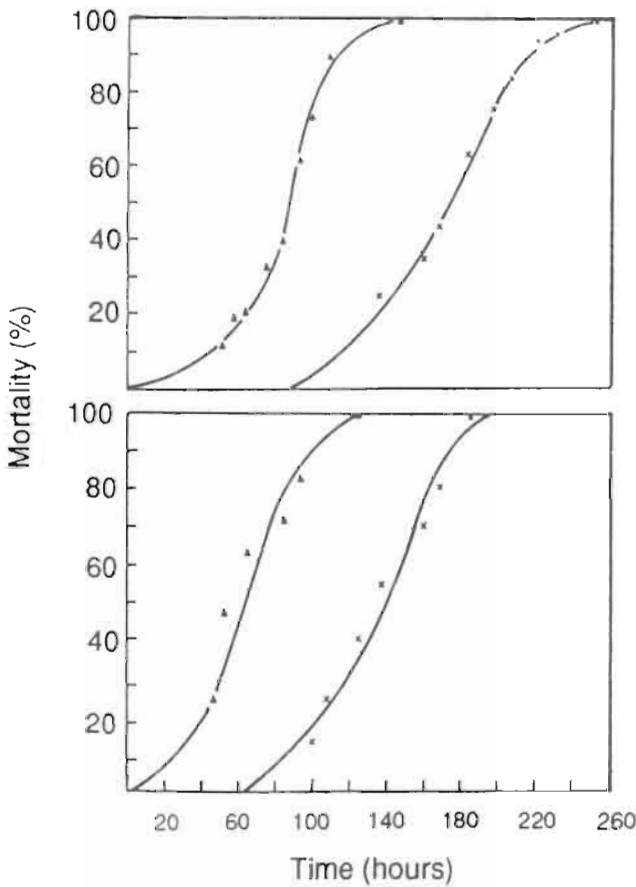
Fig. 5. Time to 100% mortality of stored grain beetles at various temperatures in different low oxygen atmospheres (Liang Quan 1981).

temperature is raised by 5°C steps in fixed low oxygen concentrations.

- Increasing the concentration of carbon dioxide in CA can increase the effectiveness against insects (Fig. 6).
- Relative humidity is an important factor in CA control of insects (Fig. 3) especially in the control of *S. zeamais* and *R. dominica*. The mortality of insects under low RH conditions is much higher than under high RH conditions in CA (Fig. 7).
- Once CA-treated insects are exposed to normal atmospheres their death may be accelerated.

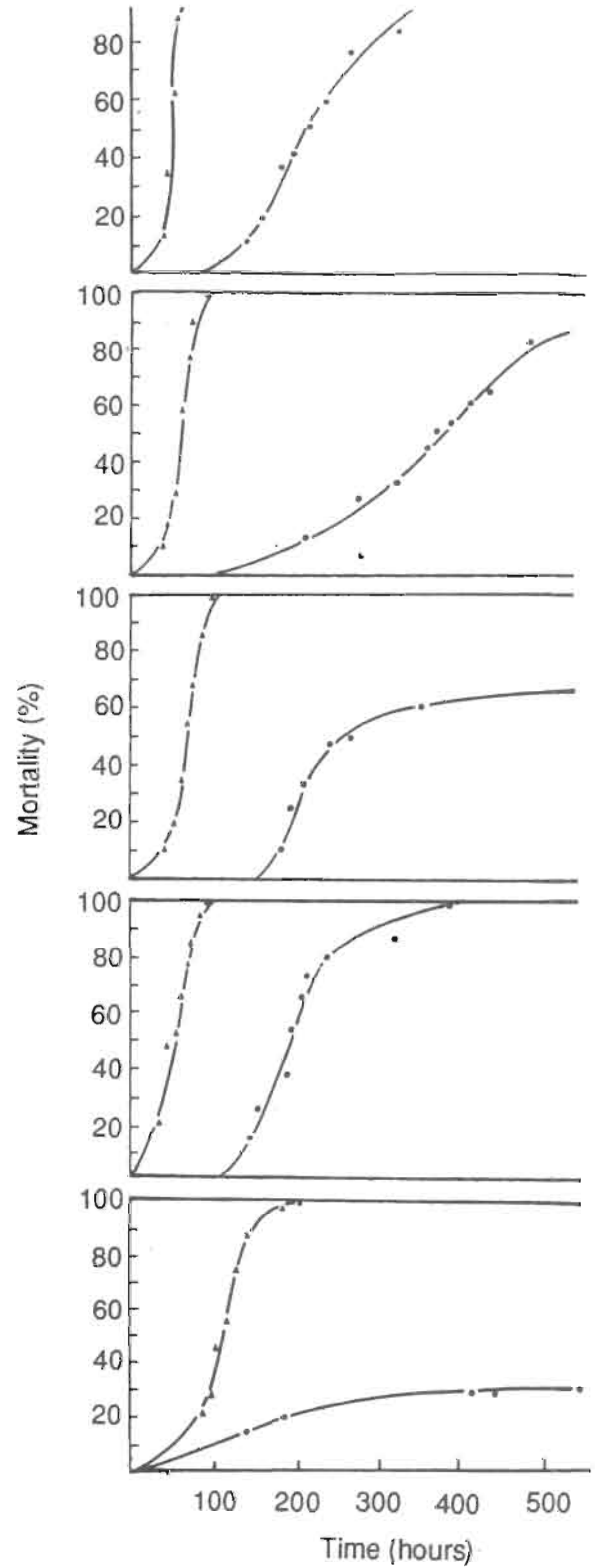
### Future Requirements

The use of fumigation and controlled atmospheres for the control of stored grain insects in China is advancing steadily. While many international and national achievements have played an important role in increasing the social and economic benefits of the technologies, much basic work remains to be done.



**Fig. 6.** Synergism of the effect of low oxygen atmospheres on stored grain beetles by carbon dioxide (30°C, O<sub>2</sub> 5%) (Liang Quan 1981). Δ, CO<sub>2</sub> 10%; ×, CO<sub>2</sub> 0%.

- A practical and effective method suited to rural stored grain insect control is needed.
- Effort should be made to improve the gastightness of existing storages.



**Fig. 7.** The influence of relative humidity on the effectiveness of low oxygen atmospheres against grain beetles. (O<sub>2</sub> 3%, N<sub>2</sub> 97%, 30°C). Δ, RH 50-70%; ×, RH 80-90%.

- The international flow of scientific information needs to be promoted, as does increased international research cooperation.
- Rules and regulations concerning the management of fumigant application need to be developed, promulgated, and enforced.
- Monitoring of phosphine resistance and the development of counter-measures to phosphine resistance are high priority activities.

## Acknowledgment

The author expresses appreciation to Dr B.R. Champ, ACIAR, Australia for inviting and supporting the production of this paper.

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## Report on Session 4: Application Methodology

Chairman: Mr Loo Kau Fa, LPN, Malaysia  
Rapporteur: Mr E. Ripp, CAFCO, Australia

THE first paper in this session, covering recent developments in controlled atmosphere technology, was prepared by E. Jay, H.J. Banks, and D.W. Keever, and presented by Dr Jay. Coverage was restricted to developments in the United States since the last international conference on controlled atmosphere storage, held in Perth, Western Australia, in 1983.

The paper related the results of field studies on the use of carbon dioxide, focussing on the influence of higher temperatures, as well as the results of laboratory studies involving the application of various CAs to all stages of *Lasioderma serricorne* at 27°C.

Field studies reported included the use of carbon dioxide (CO<sub>2</sub>) to treat:

- 1000 tonnes of tobacco in a warehouse of 13000 m<sup>3</sup> capacity;
- 1400 tonnes of barley held on a river barge;
- a quantity of herbs and spices in a 45 m<sup>3</sup> chamber;
- 550 tonnes of rice in a bolted metal bin; and
- 27 600 tonnes of maize in a plastic-sheeted bunker.

All trials were considered successful, that involving the bunker, for example, yielding 99.99% mortality for a CO<sub>2</sub> cost of 11.6 cents per tonne. Other field trials, while not producing economic results, were known to be influenced by other factors.

Laboratory studies indicated that higher temperatures enhanced the results of CO<sub>2</sub> treatments. This was supported in practice by the results of the warehouse trials involving tobacco.

Future use of CA is indicated by the interest shown for commodities of high unit value. One small company has successfully treated 750 000 tonnes of maize. Economics, time, and regulatory pressure will possibly be the most important factors influencing increased use.

The second paper in this session was prepared and presented by Dr R.G. Winks. It described recent developments in fumigation technology, with particular reference to phosphine, and Dr Winks also qualified 'recent' as covering progress since the 1983 conference in Perth.

Particular progress has been made in refining the concentration by time (Ct) relationship. This has reinforced the need to maintain minimum concentration levels for long enough for the most tolerant stages of insect development (eggs and pupae) to succumb.

An extension of the time at which a given concentration is maintained can be achieved by improving the level of sealing of a storage or by using methods of gas application that allow continuous input to compensate for leakiness. The paper stressed that increased single dosage rates will not extend the exposure time in a

leaky storage, and suggests that sealing storages to adequate levels provides scope for significant reductions of dosages.

Dr Winks provided information on resistance factors relating to phosphine that give hope for control over the effects of this phenomenon. Such control is achievable with an appropriate Ct product.

Clearly, there are two components to the Ct equation. As noted above, the concentration obtained from a specific dosage can be maximised by improving the level of sealing. It is also possible, however, to compensate for leakiness by altering the method of application of the fumigant.

The intermittent addition of fumigant to a leaky structure during a treatment (the purge method) tends to lead to fumigation failures because of the effects of external factors such as wind.

Dr Winks described a method of continuous application of the fumigant under a small positive pressure (the 'Siroflo' method) presently under development, noting that it was the only method of phosphine application that could be relied upon to control resistant strains or give adequate control over time in the Ct equation.

While the paper cautioned that the new method has some minimum requirements, these were not described. Also, Dr Winks' statement that costs of Siroflo protection are substantially less than those associated with grain protectants currently in use and that the method is more acceptable in terms of worker safety than conventional fumigation methods were not substantiated and must therefore remain in doubt until more information is available. It is understood that, because there is a patent pending on the method, much information on it is commercially confidential.

The paper discusses the use of phosphine discharged from cylinders or generated on site and the perceived advantages of the various methods of generating the fumigant.

The paper concludes with strong recommendations to all users of phosphine to improve fumigation methods so that the material will continue to be available. All are agreed on this.

The third paper of this session, prepared by Dr S. Navarro and Dr E.J. Donahaye, and entitled 'Generation and application of modified atmospheres and fumigants for the control of storage insects', provided a review of methods of generation and application of modified atmospheres and fumigants. The paper was presented by Dr Navarro.

In dealing with generation of modified atmospheres and fumigants, Dr Navarro covered:

- supply from tankers
- exothermic generator
- on-site nitrogen generators
- biogeneration of modified atmospheres
- potential systems for future use
- generation of fumigants, including gaseous, liquid and solid materials.

As regards application of gases, the following issues were discussed:

- choice of modified atmosphere composition
  - the rate of supply of a modified atmosphere
  - structural requirements
  - application of gaseous, liquid and solid materials;
- as well as the following matters relating to the application of fumigants
- structural requirements e.g. sealing, pressure relief vents
  - dosage schedules

- gravity penetration
- recirculation of fumigant
- admixture
- vacuum fumigation
- stack fumigation
- fumigation mixtures.

The paper provided a useful overview of the field.

The final paper in this session, prepared by Liang Quan of the Guangdong Provincial Cereal Science Research Institute, People's Republic of China, was presented, in Mr Liang's absence, by Dr B. Champ. The paper was entitled 'The current situation and principal technologies used in fumigation and controlled atmosphere storage of grain in China'.

Phosphine is the major fumigant used in stored produce insect control in China. Some 90% of grain in national stores is fumigated with this material. In most cases, bagged and bulk grains are covered with plastic sheeting for fumigation and controlled atmosphere and hermetic storage.

Since conditions for fumigation are relatively poor, a slow release method and extended exposure times are preferred. Minimum exposure times of 120 hours are quoted. The development of slow release methods and extended exposure periods has led to concentration regimes of 0.01 mg/L-0.05 mg/L and exposure times approaching 3 months.

Liang Quan has found that a reduction of oxygen concentration to 12% or 5% improved the effect of phosphine and that CO<sub>2</sub> concentrations of 4-8% also had a synergistic effect.

Attention to intermittent application, the use of convection in distribution, and the problem of resistance in insects in China, as related in Mr Liang's paper, closely paralleled comments made by other speakers during the conference, indicating that the situation in that country is very similar to that pertaining elsewhere. In relation to resistance control, a set of regulations is being drawn up to minimise the spread of the phenomenon.

Controlled atmosphere technology is well understood in China but has not been applied to total storages. Sheeting stacks of bags or bulk is in general use, although in the main, respiratory reduction of O<sub>2</sub> and increase of CO<sub>2</sub>, is relied upon in conjunction with phosphine fumigations.

In the discussion session following presentation of the four papers, Dr Jay stressed that future laboratory studies must include all life stages of the test insects, must be conducted at several realistic temperatures, and over the range of controlled atmosphere concentrations that can be attained and maintained in the field. Such data will assist in achieving high levels of control in actual field situations for economically important species of stored product insects under less than perfect circumstances.

Dr Winks said that research was urgently needed first to determine the extent of any residues in grain arising from reaction with phosphine and second to develop personal monitors for phosphine to be carried by fumigation personnel.

Dr Navarro made the following comments:

- More research is needed on the effects of humidity on mortality of insects held under modified atmospheres.
- Methods for biogenesis of modified atmospheres need to be developed for situations where other means of gas application are uneconomic.
- Application of modified atmospheres and phosphine to storages with poor levels of gastightness should be discouraged unless an additional maintenance phase proves to be effective.

- To avoid the build-up of resistance in storages with low levels of gastightness and in cases where a gaseous treatment needs to be carried out in a limited exposure time, the use of methyl bromide is recommended.
- More research is needed to clarify details of the retention or distribution of fumigants under the influence of convection currents and other physical forces within grain bulks.
- To reduce toxic residues and improve application methods, further research is needed on the use of fumigant mixtures in conjunction with modified atmospheres.

## **Sealed Storage of Bag Stacks**



# Storage of Bagged Maize Sealed in Plastic Enclosures in the Philippines

G.C. Sabio, D. Alvindia, D.D. Julian, R. Murillo Jr., and M.S. Sambrano\*

## Abstract

This paper reports on trials of the efficacy of a long-term sealed storage technique based on carbon dioxide or phosphine atmospheres as alternative means of controlling pest infestation and related quality losses in large stacks of maize in the Philippines. Fourteen 230 tonne bag-stacks of white maize were observed for storage periods ranging from 61–283 days. Eleven stacks were sealed. Nine of the sealed stacks were treated with carbon dioxide and 2 with phosphine. The other 3 stacks remained unsealed and were surface treated with protectant insecticides to serve as controls reflecting standard storage practice.

Both gases provided satisfactory insect control. In the sealed stacks, significantly lower counts of primary and two secondary insect pests were observed. Insect-damaged grain and weight losses were also reduced. Likewise, there were decreases in mould growth and mould-infected grains as compared with the insecticide-treated control stacks.

The significance of the results, in terms of the reliability and acceptability of the sealed plastic enclosure technique, is discussed.

In the Philippines, large quantities of maize (corn) are stored. White maize is the second most important staple food, while yellow maize is used as a stock food ingredient.

Large quantities of maize are usually stored in warehouses by private traders/millers and by the government through the National Food Authority (NFA). The grain is commonly packed and handled in 50 kg polypropylene bags, and stored in large stacks for varying periods. Normally, the private sector holds grain for shorter times averaging just over 2 months, while the NFA stores maize for an average of 6 months as buffer stocks to provide food and feed security for the country.

Stored maize has always been subject to problems of pest infestation, especially insect

pests, and the problems become greater during long-term storage. In these circumstances, the NFA uses chemical control measures consisting of repeated surface application of grain protectants and fumigation. Nevertheless, the problem remains, as evidenced by the large losses (11% over an 8-month period) incurred (Sabio et al. 1984).

A possible solution to the problem is seen in the sealed plastic enclosure technique for storing of stacks of bagged grain and treating them with carbon dioxide (CO<sub>2</sub>) or phosphine (PH<sub>3</sub>). This technology, which was initially developed in Australia, has been reported as providing not only initial disinfection, but also a barrier against reinfestation, thereby offering long-term grain protection (Annis et al. 1984). The technique has been successfully applied in Australia, Indonesia, and Papua New Guinea on rice and coffee (Annis and Graver 1986), but not on maize.

\* National Post Harvest Institute for Research and Extension, CLSU Compound, Muñoz, Nueva Ecija, Philippines

An assessment of the sealed enclosure storage technique for storage of bagged maize stacks was therefore undertaken, with the primary objective of evaluating and providing information on its technical suitability, economic feasibility, and social acceptability, using CO<sub>2</sub> and phosphine gases as fumigants. Specifically, the study aimed to assess the reliability of the technique in terms of protection from reinfestation by insects and maintenance of maize quality during long-term storage.

## Materials and Methods

The field trials were conducted in two private warehouses leased by the NFA in Cebu City, Philippines from November 1985 to June 1988. The warehouses were of concrete construction and roofed with green-painted corrugated iron sheeting interspersed with translucent fibreglass sheeting to provide natural lighting. Heavy infestation by rodents and birds was observed in these warehouses. Heavily insect infested stocks of maize and rice were also present in the warehouse at the time of the study. The test commodity (white maize) was drawn from the stocks procured by NFA in General Santos City and South Cotabato on Mindanao island.

Fourteen 228–249 tonne stacks measuring 11 m long × 7.3 m wide × 4.6 m high were constructed. Eleven of these stacks were sealed, and nine treated with CO<sub>2</sub> and two with phosphine. Details of the stacks used in the five trials are given in Table 1.

The main objective of the early trials was to evaluate the efficacy of the technique using CO<sub>2</sub> in terms of all the parameters set out for this study. The last trial aimed to investigate the

efficacy of phosphine as an alternative fumigant to CO<sub>2</sub>. Three stacks were left uncovered and used as controls. They were subject to the usual NFA pest control program, which mainly involved stack spraying, fogging, and fumigation with phosphine.

All stacks were built according to the 'Chinese stacking system', except that an aisle was provided to facilitate collection of samples from marked bags at the middle of the stacks. These were constructed 1.5 metres away from the wall and 1 metre apart from each other. The experimental layout of each trial is illustrated in Fig. 1 (a–d).

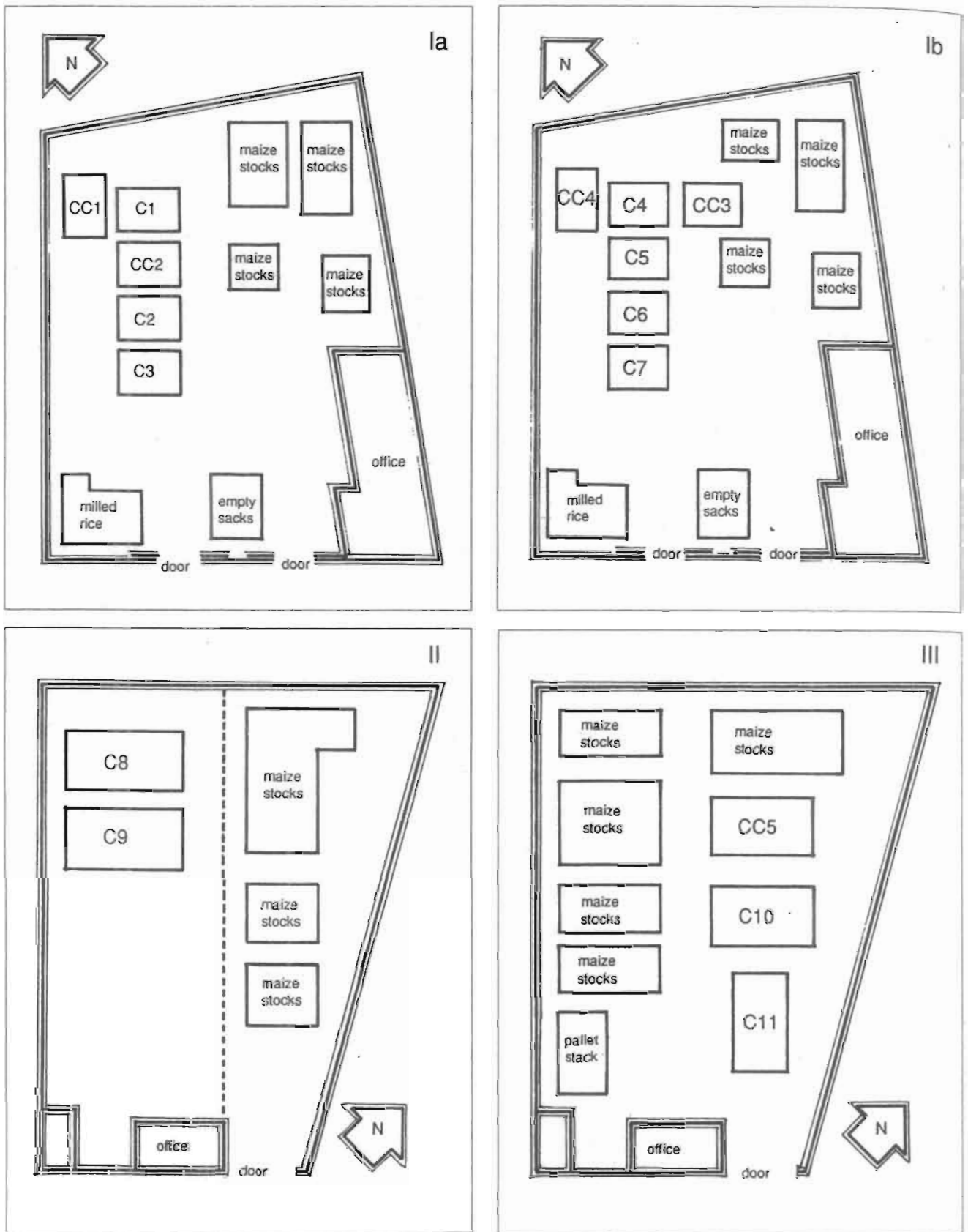
The stacks used for CO<sub>2</sub> and phosphine treatments were sealed in flexible plastic enclosures, tested for gastightness (Annis and Graver 1986). The top, or cover, sheets were made of nylon fibre reinforced PVC of approximately 350 g/m<sup>2</sup>, and the floor sheets of 0.8 mm unsupported PVC sheeting. When the standard pressure test had been achieved, the sealed stacks were fumigated.

The CO<sub>2</sub> was applied in the manner described by Annis and Greve (1984). Liquid CO<sub>2</sub> was obtained from inverted cylinders of compressed gas (food grade quality, nominal capacity 22 kg) which were fastened in a specially devised discharging rack (Fig. 2).

Fumigation of stacks with phosphine-generating tablets was undertaken according to the conventional procedure. The total number of tablets needed for fumigation was appropriately distributed around the stack. Tablets were introduced through slits about 25 cm long, cut along the folded 'skirt' of the covers on all sides (Fig. 3) after pressure testing had been successfully completed. These slits were immediately resealed.

**Table 1.** History of maize stocks used

Treatment	No. of stacks	Mass (tonne)	Initial condition	Duration of trial (days)
CO <sub>2</sub>	9	228–247	3 months old, slightly infested 9 months old, heavily infested	155–239
PH <sub>3</sub>	2	231–240	1 month old, with few insects alive	136–142
Control	3	228–249	1 month old with few insects alive; 3 months old, lightly infested	135–283



**Fig. 1.** Configuration of warehouse and stacks for field trials Ia and Ib, II, and III on stored maize. C = treated maize; CC = control stacks.

Details of pressure test results and dosages of CO<sub>2</sub> and phosphine are given in Table 2.

**Table 2.** Summary of CO<sub>2</sub> and PH<sub>3</sub> dosage rates and gastightness of enclosures

Stack code	CO <sub>2</sub> dosage (kg CO <sub>2</sub> /tonne)	Pressure test result
C1	2.08	31 min 15 sec
C2	2.08	35 min 8 sec
C3	1.84	36 min 28 sec
C4	1.83	25 min 37 sec
C5	1.11	25 min 17 sec
C6	1.69	22 min 37 sec
C7	1.61	20 min 5 sec
C8	1.5	10 min
C9	1.5	12 min
	PH <sub>3</sub> dosage	
C10	1 tablet/tonne	5 min
C11	1 tablet/tonne	8 min

Grain sampling was carried out at the start and end of the trial. Composite samples (2 kg), made up from samples speared from all bags in the stack, were gathered. Additionally, 1 kg samples were collected with spears from the 24 individually marked bags.

Moisture content determinations were carried out by drying grain samples for one hour in a vented oven at 130°C (Anon. 1982). Total insect

numbers were obtained by counting all adult insects, both live and dead, sieved from the samples. The numbers of insect-damaged grain kernels needed for estimation of weight loss were determined by hand counting the number of damaged kernels in a 1000-grain sample. The magnitude of losses incurred was assessed through the count and weigh method (Harris and Lindblad 1979). The insect species responsible for damaging the grains were classified as primary pests and others as secondary pests for the purpose of this study.

The presence of fungi on grains and the extent of microbial infection were determined by plating sterilised grains in potato dextrose agar.

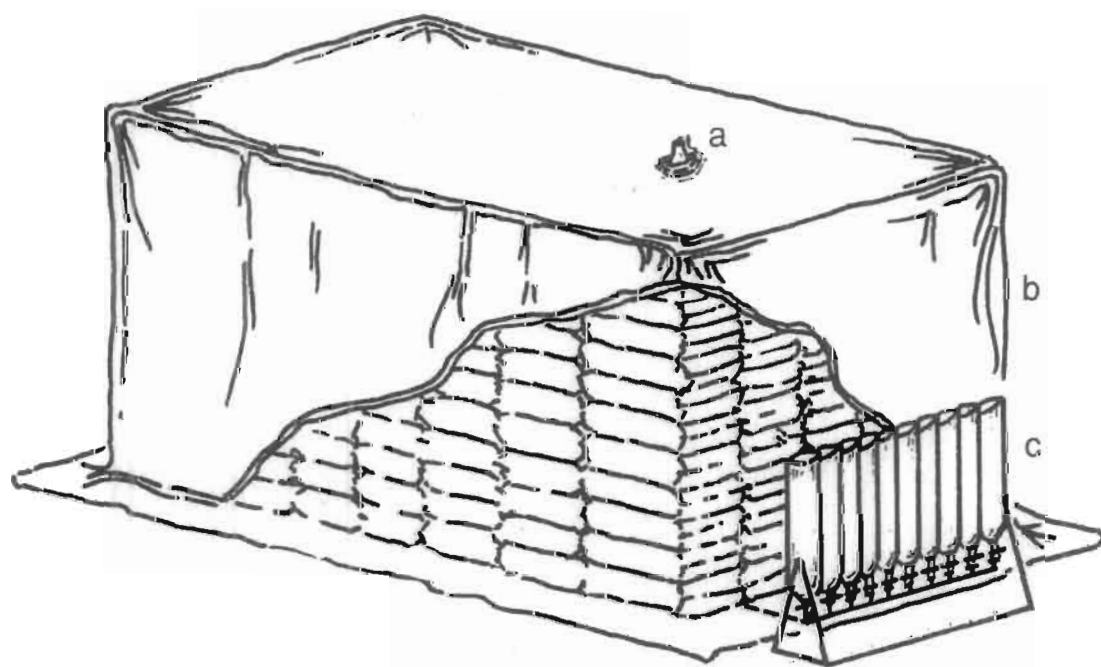
Gas concentrations were monitored by drawing samples out of the stacks through semi-rigid nylon gas sampling lines (2 mm i.d.) and Draeger detector tubes with a Draeger pump (Fig. 4).

Assessment has also been made of the operational convenience and cost of keeping bagged maize stacks in sealed plastic enclosures under CO<sub>2</sub> and phosphine atmospheres (Annis 1990).

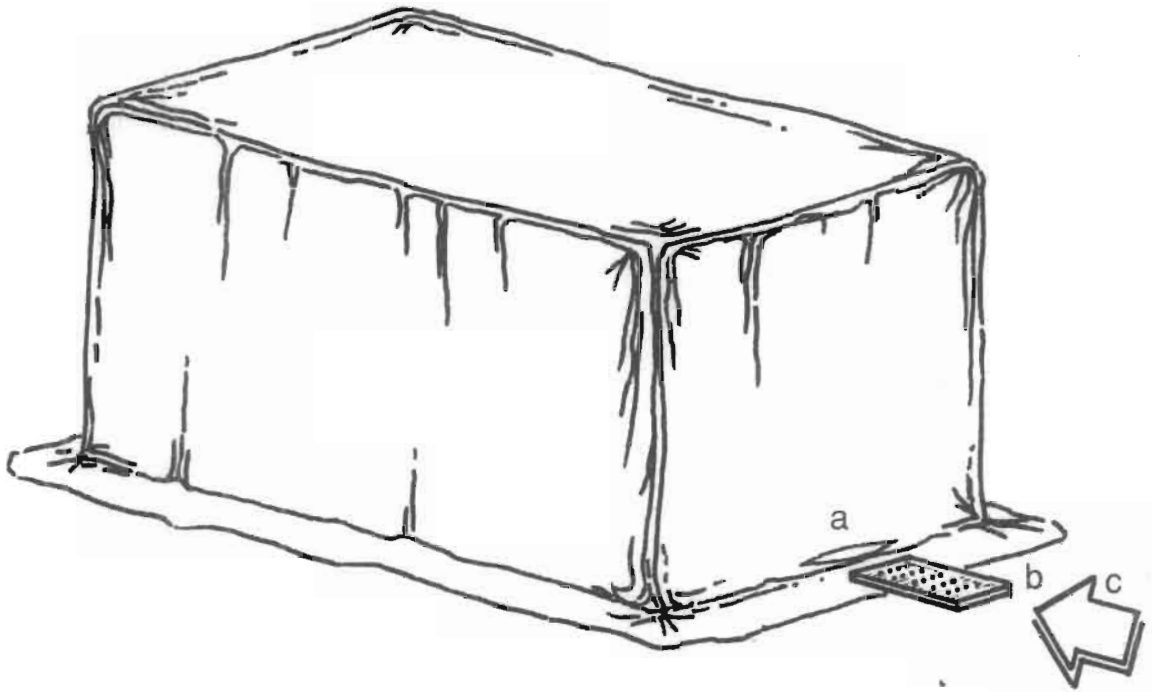
## Results

### Percentage Moisture Content

The moisture content of maize in stacks sealed for an average period of 4.6–7.8 months did not significantly change, whereas in the



**Fig. 2.** Diagram of inside of sealed stack showing: (a) gas escape vent; (b) bagged commodity; and (c) CO<sub>2</sub> introduction system with inverted cylinders.

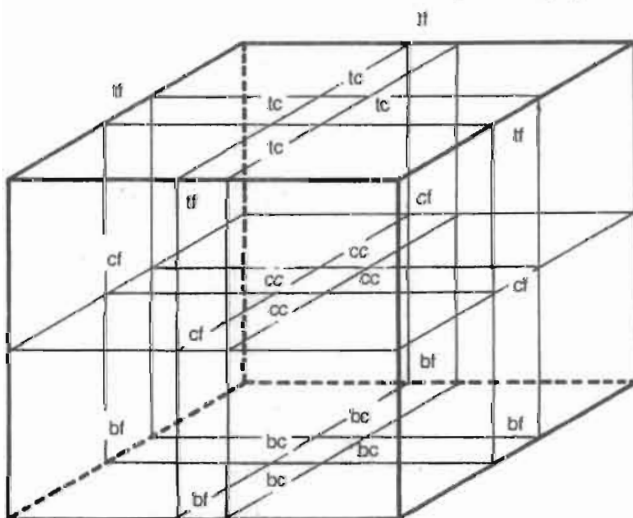


**Fig. 3.** Diagram of enclosed stack showing: (a) open slit on the lateral 'skirt' of cover sheet; (b)  $\text{PH}_3$  tablets in a corrugated cardboard box; and (c) entry direction.

control stacks the moisture content in one stack fell by 1.6% after 4.5 months and by 0.7–1.0% in the other two after 9.3 months of storage. Other sealed stacks stored for a year or more have shown a significant decrease in moisture content ranging between 0.4 and 1.3%. (A very low moisture content of 10.2% has been recorded in two stacks after 13 months storage.)

### Insect Infestation

Initial and final counts of the primary pests,



**Fig. 4.** Predetermined sampling points (24) within the stacks: tf = top face; tc = top core; cf = centre face; cc = centre core; bf = bottom face; bc = bottom core.

*Rhyzopertha dominica* and *Sitophilus zeamais* and of the secondary pests *Cryptolestes* spp. and *Tribolium castaneum* revealed no significant increases in most sealed stacks (Tables 3–4). However, in the control stacks large increases in the number of these pests were observed (Table 5).

### Percentage Insect-Damaged Grain

The percentage of insect-damaged grain did not significantly change (Table 6) in the two phosphine-treated stacks and in most of the seven  $\text{CO}_2$  treated stacks after 4.6 and 7.8 months of storage, respectively. On the other hand, in the control stacks for both trials there were significant levels of damaged kernels, reaching 1.9% over 4.5 months storage and 2.5–5.7% over 9.3 months.

### Percentage Weight Loss

No significant increases (Table 7) in percentage weight loss were observed in the phosphine-treated stacks after 4.6 months of storage, while in the control a 6.6% increase was observed. In the  $\text{CO}_2$ -treated stacks, there was no significant change in two stacks but a significant increase was recorded in one stack at the end of 7.8 months. The magnitude of loss observed did not significantly differ from that recorded in the two control stacks observed.

**Table 3.** Increase in density of major insect pests in CO<sub>2</sub> treated stacks.

Stack code	Insect species				No. of observations
	<i>Rhyzopertha dominica</i>	<i>Sitophilus zeamais</i>	<i>Tribolium castaneum</i>	<i>Cryptolestes</i> spp.	
C2	NS (0)	*** (0,3)	*** (1,15)	*** (1,13)	48
C3	NS (1)	NS (0)	*** (2,14)	*** (2,15)	48
C6	NS (1)	NS (1)	NS (1)	NS (33)	48
C7	NS (1)	NS (4)	NS (2)	NS (7)	48
C8	NS (1)	NS (3)	NS (3)	NS (2)	48
C9	NS (0)	NS (0)	NS (0)	NS (2)	48

NS P &gt; 0.050; initial count in brackets (insects/kg)

\* P &lt; 0.050

\*\* P &lt; 0.025 initial and final counts in brackets (insects/kg)

\*\*\* P &lt; 0.010

**Table 4.** Increase in density of major insect pests in phosphine-treated stacks

Stack code	Insect species				No. of observations
	<i>Rhyzopertha dominica</i>	<i>Sitophilus zeamais</i>	<i>Tribolium castaneum</i>	<i>Cryptolestes</i> spp.	
C10	** (2,3)	NS (5)	*** (3,5)	NS (3)	54
C11	NS (2)	NS (6)	NS (5)	NS (10)	54

NS P &gt; 0.050; initial count in brackets (insects/kg)

\* P &lt; 0.050

\*\* P &lt; 0.025 initial and final counts in brackets (insects/kg)

\*\*\* P &lt; 0.010

**Table 5.** Increase in density of major insect pests in control stacks

Stack code	Insect species				No. of observations
	<i>Rhyzopertha dominica</i>	<i>Sitophilus zeamais</i>	<i>Tribolium castaneum</i>	<i>Cryptolestes</i> spp.	
CC1	*** (0,71)	*** (0,17)	*** (0,48)	*** (2,46)	48
CC2	*** (0,18)	*** (0,5)	*** (1,34)	*** (0,46)	48
CC3	*** (2,8)	** (4,8)	*** (5,15)	NS (9)	54

NS P &gt; 0.050; initial count in brackets (insects/kg)

\* P &lt; 0.050

\*\* P &lt; 0.025 initial and final counts in brackets (insects/kg)

\*\*\* P &lt; 0.010

### Microbial Infection

Stacks of newly procured maize were initially found to heavily infected with *Aspergillus flavus* (93–100%) and *A. niger* (27–93%). Infections with *Penicillium* sp., *Rhizopus* sp., and *Diplodia* sp. were also noted but at a much lower level. Other stacks of older and drier grains were found to be infected with all these fungal species except *Diplodia* sp., but to a lesser extent overall. Final results (Table 8) indicate that infection with *A. flavus* in sealed stacks of newly procured grains fell by 55–57% to after 4.6 months storage and 83–90% after 7.8 months. Infection with *A. niger* fell to zero after 4.6 months and by 85–

100% after 7.8 months. The percentage of infected grains in sealed stacks of older grains fell slightly. Levels of infection by *Penicillium* in control stacks increased 4.5 times after 4.6 months storage, but decreased by 38.9% and 9.5% for *A. flavus* and *A. niger*, respectively.

### Discussion

To show that a proposed pest control method is reliable and acceptable it is necessary to demonstrate:

- that it will kill all the target pests;
- that it will not harm the commodity; and

- that it can be carried out within the resources (human and material) available.

The observations reported in this paper address two of these requirements: insect control and damage to the commodity.

If a disinfestation is not complete in a sealed insect-infested commodity there are two likely consequences: as insect damage increases dry matter loss rises and the metabolic activity of the insects may cause heating. This, in turn, will lead to moisture migration, with the attendant possibility of moulding.

On the simple basis of numbers of live insects, all treatments in the trials reported were successful, there never being more than a few live insects at the end of the storage period no matter how long it was. There was, however, occasionally a significant increase in the number of dead insects during the storage period, suggesting that population death had taken some time to occur or, as is more likely, that the more tolerant and less obvious immature stages continued to develop to the less tolerant and more obvious adults before dying. Neither of these possibilities is excluded by the observations of percent insect-damaged grains which showed increases in damage in three of the six CO<sub>2</sub>-treated stacks. This was matched by a corresponding percentage weight loss in only one stack, suggesting the damage was caused by emerging rather than feeding insects.

In the control stacks there was virtually always a significant increase in numbers of in-

**Table 8.** Percentage reduction of infected kernels with major storage fungi

Species	Treatments			Control New Grain
	CO <sub>2</sub>		PH <sub>3</sub>	
	New grain	Old grain	New grain	
<i>Aspergillus flavus</i>	86.8%	25.2%	56.2%	38.9%
<i>A. niger</i>	92.8%	23.3%	100.0%	9.5%
<i>Penicillium</i> sp.	-	26.0%	100.0%	increased (4.5x)

sects, many of which were alive at the end of the storage period.

There was no significant moisture build up or localisation in either the treatments or in the controls. There was moisture loss from the control stacks and there appeared to be a moisture reduction in the sealed stacks stored for a year or more. There was no increase in percent of kernels infested with storage fungi in the tests, an observation consistent with the grain moisture observations. Phosphine treatments appeared to give rise to a significant reduction in the three fungi isolated, as also did CO<sub>2</sub>, but to a lesser extent. These findings were unexpected and, while promising, will need investigating under more carefully controlled conditions before any reliance can be placed on them.

**Table 6.** Number of stacks showing different levels of significance of increase in percentage insect damaged kernels

Treatments	Levels of significance				
	NS	0.05-0.025	0.025-0.01	0.01-0.005	<0.005
CO <sub>2</sub>	3	1	1	1	1
PH <sub>3</sub>	2	-	-	-	-
Control	-	-	-	-	3

**Table 7.** Number of stacks showing different levels of significance of increase in percentage weight loss

Treatments	Levels of significance				
	NS	0.05-0.025	0.025-0.01	0.01-0.005	<0.005
CO <sub>2</sub>	0	-	1	-	-
PH <sub>3</sub>	2	-	-	-	-
Control	-	1	-	-	1

## Conclusion

Safe long-term storage of dry bag-stacked maize is possible in sealed plastic enclosures. If disinfestation is complete then there appears to be a significant advantage to this kind of storage. The initial disinfestation can be carried out using either phosphine or carbon dioxide. Whichever treatment is used, there is some reduction in the number of insect-damaged kernels and a significant reduction in percentage weight loss.

## Acknowledgments

These field trials were carried out by NAPHIRE with the support of ACIAR. The National Food Authority of the Philippines provided the test commodity, warehouse facilities, and other logistic support.

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# Carbon Dioxide Treatment for Sealed Storage of Bag Stacks of Rice in Thailand

**Chuwit Sukprakarn, Krauawan Attaviriyasook,  
Lamaimaat Khowchaimaha, Kanjana Bhudhasamai, and  
Boodsara Promsatit\***

## *Abstract*

An evaluation was made of the use of carbon dioxide (CO<sub>2</sub>) for controlling insects during long-term storage of rice. The first trial was carried out between 6 June and 3 December 1985. Three 72-tonne stacks of the rice varieties Na-sai, wet season rice, and Hom Mali were used. They were treated with CO<sub>2</sub> at 1.98, 2.03, and 1.97 kg/tonne of rice and opened for inspection after 2, 4, and 6 months, respectively. During the storage period, changes in temperature and relative humidity within the stacks were monitored. The moisture content, quality, and insect infestation of grain were investigated before and after storage. The treatment gave total insect control: no live insects were found in any of the treated stacks. There was no increase in percentage of fungal infection, except in the stack stored for 6 months. Aflatoxin was not detected and grain quality fell slightly at longer storage periods. In order to prove the effectiveness of CO<sub>2</sub> for control of insects during long-term storage, a second trial was conducted from 6 March 1986 to 6 March 1987. Three 63-tonne stacks of milled Na-sai rice were used. The stacks were treated with CO<sub>2</sub> at rates of 1.81, 2.11, and 2.41 kg/tonne of rice and were opened at 4, 8, and 12 months, respectively, after treatment. The results of this trial showed total protection from insects for up to 8 months, while some live insects were found in the third stack, opened at 12 months. There was no increase in the percentage of fungal infection, rather it decreased and aflatoxin was not detected in any stack. Rice quality was slightly changed, but all samples were acceptable.

This paper presents the results of both trials.

In Thailand milled rice is stored in warehouses in variable-sized stacks of jute bags. The warehouses are usually of the horizontal type ventilated to permit cooling of the grain through natural convection.

In this type of storage the grain is prone to insect attack and losses due to insect infestation are one of the basic problems of storing bagged rice. The main insect control procedure for bag storage in Thailand is fumigation. At present, only methyl bromide and phosphine are in use to fumigate bag stacks. However, if grain remains in storage for a substantial period after fumigation, it will be reinfested by insects sometime after removal of the fumigation sheets. There is therefore a need to develop a

storage technique to guard against reinfestation. Apart from preventing losses during storage, there is also a need to develop a method to preserve the quality of grain for longer storage periods so as to meet the nutritional requirement of the consumers. The introduction of carbon dioxide to control insects and prolong safe storage of grain is a new technology that can achieve these aims.

Carbon dioxide (CO<sub>2</sub>) is a fumigant that produces no harmful residues and is relatively safe to use (Annis and Graver 1985). It is effective in killing insects in all stages of their life cycles and could be used for long-term storage of milled rice (Annis et al. 1984; Suharno et al. 1984).

This paper describes the results of two trials on the use of carbon dioxide in the sealed storage of bag stacks of rice in Thailand.

\*Department of Agriculture, Ministry of Agriculture and Cooperatives, Bangkok, Bangkok 10900, Thailand.

## Materials and Methods

### Trial I

The first trial was carried out at Mah Boonkrong Rice Mill Co. Ltd, Pathumthani Province, between 6 June and 3 December 1985. Three 72-tonne stacks of bagged milled rice of three different varieties—Na-sai, wet season, and Hom Mali—were used. After CO<sub>2</sub> had been added, the stacks were then uncovered sequentially at 2, 4, and 6 months for stacks 1, 2, and 3 respectively. The rice was then sampled for insect and fungal infestation, and for rice quality assessment. Further details of the trial stacks are given in Table 1.

### Enclosure construction and testing

For each stack, a floor sheet (5 × 7 m) of PVC film with thickness 0.76 mm was laid on the concrete floor. The stack was then built on wooden pallets over the floor sheet. An enclosure (4.2 × 6.0 × 5.9 m) of 0.24 mm thickness plastic sheeting was fitted over the stack and the inner edge of the enclosure bonded to the floor sheet with sealant (Barrier adhesive). A domestic vacuum cleaner was used to create a small negative differential

pressure within the enclosure. Leaks and imperfections in the seal were then detected by visual inspection and by the sound they made. After the leaks had been sealed, the degree of gastightness was determined by the steady-state pressure test method.

### CO<sub>2</sub> introduction

Liquid CO<sub>2</sub> from 20 kg cylinders was introduced into the enclosure through a copper pipe (5 mm i.d.) connected to a PVC pipe (3 cm i.d.) and placed under the pallets. The amount delivered was determined from the loss of weight of the cylinders. An outlet vent of 30 cm diameter was made on the top of the enclosure to allow escape of displaced gases during CO<sub>2</sub> application. CO<sub>2</sub> was added until the concentration at the top was approximately 15% and that at the bottom over 60% (Table 2). The three stacks were thus treated with 1.98, 2.03, and 1.97 kg of CO<sub>2</sub> per tonne of rice. The introduction pipe was then removed and the outlet vent and introduction region sealed.

### CO<sub>2</sub> temperature, and relative humidity measurement

Drager gas tubes were used to measure the

**Table 1.** Details of stack dimensions and loads in trial I.

	Stack 1 (2 months)	Stack 2 (4 months)	Stack 3 (6 months)
Height (m)	4.4	4.4	4.4
Width (m)	3.9	3.9	3.9
Length (m)	5.9	5.9	5.9
Mass of rice (tonnes)	72.0	72.0	72.0
Rice moisture content before treatment (%)	10.3	10.8	10.5
Rice moisture content after treatment (%)	11.8	11.7	10.7
Rice temperature (°C)	33.0(29.8–37.6)	32.4(29.8–40.4)	32.2(26.8–40.5)
Ambient temperature (°C)	29.5(27.7–31.1)	29.8(28.4–32.3)	29.8(27.7–31.1)
Relative humidity in stack (%)	65.4	65.0	62.6
Ambient relative humidity (%)	67.6	67.3	67.3

**Table 2.** Summary of CO<sub>2</sub> exposures for each test stack in trial I

Stack no.	CO <sub>2</sub> at end of gas addition		Average CO <sub>2</sub> after 24 hrs	CO <sub>2</sub> remaining after 10 days	Exposure time at > 35% CO <sub>2</sub> (days)	Time under cover after CO <sub>2</sub> treatment until opening stack (days)	CO <sub>2</sub> present on uncovering stack			
	%	%					%	%	Top	Middle
1	>15	>60	>60	60	31	60	17	18	15.5	16.8
2	>15	>60	>60	60	25	120	3	5	4.5	4.2
3	>15	>60	>60	60	40	180	-	-	-	-

relative humidity (RH) and CO<sub>2</sub> concentration within the stacks compared with the surrounding area. Temperatures within and outside the stacks were measured by hand held thermocouples and read from a LCD thermometer. CO<sub>2</sub> and water vapour concentrations were sampled from within each stack through semi-rigid nylon gas sampling lines (2 mm i.d.) placed in the stack during construction at three levels—top, middle, and bottom. Water vapour values were converted to relative humidities using the psychrometric chart. These measurements were recorded each day for the first 7 days and then once a week until the stack was uncovered.

Sampling for grain quality, fungal infection, and insect infestation was then carried out.

During construction of the stacks, 6 kg subsamples of 15 kg of rice per stack were taken to assess quality changes, mould damage, and insect infestation. When the stacks were uncovered, the grain was again sampled to determine any effects of CO<sub>2</sub> treatment. For this investigation, the rice was divided into three parts for assessment of grain quality, fungal infection, and insect infestation.

- Rice quality was assessed from physical, palatability, and chemical characteristics (Anon. 1975).
- Fungal infection was assessed by the blotter method (Anon. 1966).
- Insect infestation was determined by sampling for adults or free-living larvae from each stack before and after CO<sub>2</sub> treatment and by holding samples in the laboratory for 6 weeks to allow any hidden infestations to develop.

## Trial II

A second trial (Table 3) was carried out between 6 March 1986 and 6 March 1987, in order to store rice up to 12 months.

Three stacks, each of 63 tonnes of milled rice, were treated with CO<sub>2</sub> at rates of 1.81, 2.11, and 2.41 kg/tonne of rice (Table 3) and the stacks opened at 4, 8, and 12 months after treatment (Table 4).

In this trial, milled rice was packed in 'jumbo' bags weighing 700 kg rather than 100 kg gunny sacks. Otherwise procedures were as for the first trial.

**Table 3.** Details of stack dimensions and loads in trial II.

	Stack 1 (4 months)	Stack 2 (8 months)	Stack 3 (12 months)
Height (m)	5.0	5.0	5.0
Width (m)	3.5	3.5	3.5
Length (m)	6.0	6.0	6.0
Mass of rice (tonne)	63.0	63.0	63.0
Rice moisture content before treatment (%)	10.3	10.1	10.2
Rice moisture content after treatment (%)	10.4	10.3	10.3
Rice temperature (°C)	30.5 (29.0–33.8)	31.2 (28.8–35.4)	31.7 (27.9–36.5)
Ambient temperature (°C)	31.9 (29.4–35.0)	32.0 (29.4–35.0)	31.9 (29.0–35.0)
Relative humidity in stack (%)	66.2	59.3	63.9
Ambient relative humidity (%)	62.2	62.0	62.4

**Table 4.** Summary of CO<sub>2</sub> exposures for each test stack in trial II.

Stack no.	CO <sub>2</sub> at end of gas addition		Average CO <sub>2</sub> after 24 hrs	CO <sub>2</sub> remaining after 10 days	Exposure time at > 35%	Time under cover after CO <sub>2</sub> treatment until opening stack	CO <sub>2</sub> present on uncovering stack			
	%	%	%	%	(days)	(days)	%	%	%	%
	Top	Bottom					Top	Middle	Bottom	Mean
1	>15	>60	48.0	50	26	120	5	5	5	5
2	>15	>60	50.3	50	23	240	0	0	0	0
3	>15	>60	49.3	60	36	360	0	0	0	0

## Results and Discussion

The results of the two trials were as follows:

### Insect infestation

In both trials, insects were observed damaging bagged milled rice before and after treatment. Rice samples from all stacks contained a number of live and dead insects before treatment. Species represented included *Tribolium castaneum*, *Oryzaephilus surinamensis*, *Cryptolestes pusillus*, *Corcyra cephalonica*, and *Sitophilus* spp. The populations of

some species increased after the 45 days of incubation undertaken to assess hidden infestation. No live insects were detected after uncovering the stacks in trial I, (maximum 6 months storage), but some dead insects were found. In trial II, no live insects were found in the stacks opened at 4 and 8 months. However, the third stack, opened after 12 months storage, contained live *Tribolium castaneum*, and *Oryzaephilus surinamensis* feeding on and damaging the milled rice (see Tables 5, 6, 7, and 8).

It was not clear why CO<sub>2</sub> had no effect on the populations of *Tribolium castaneum* and

**Table 5.** Insects present (numbers per 3 kg sample) in samples taken before and after treatment in trial I.

Species	Before treatment						After treatment					
	Stack 1		Stack 2		Stack 3		Stack 1 (2 months)		Stack 2 (4 months)		Stack 3 (6 months)	
	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead
<i>Tribolium castaneum</i>	2	0	2	1	4	2	0	3	0	6	0	3
<i>Corcyra cephalonica</i>	3	0	5	0	0	0	0	1	0	0	0	0
<i>Oryzaephilus surinamensis</i>	3	0	0	4	3	0	0	5	0	1	0	4
<i>Sitophilus</i> spp.	0	0	4	0	0	0	0	0	0	3	0	3

**Table 6.** Insects present (numbers per 3 kg sample) in samples taken before and after treatment in trial II.

Species	Before treatment						After treatment					
	Stack 1		Stack 2		Stack 3		Stack 1 (4 months)		Stack 2 (8 months)		Stack 3 (12 months)	
	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead
<i>Tribolium castaneum</i>	1	2	3	1	4	1	0	4	0	3	96	18
<i>Oryzaephilus surinamensis</i>	0	1	3	0	2	0	0	3	0	2	45	6
<i>Sitophilus</i> spp.	3	0	1	1	0	2	0	1	0	0	0	2

**Table 7.** Hidden infestation (numbers per 3 kg sample) in samples taken before and after treatment in trial I.

Species	Before treatment						After treatment					
	Stack 1		Stack 2		Stack 3		Stack 1 (2 months)		Stack 2 (4 months)		Stack 3 (6 months)	
	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead
<i>Tribolium castaneum</i>	14	0	8	0	11	0	0	0	0	0	0	0
<i>Corcyra cephalonica</i>	0	0	2	5	0	0	0	0	0	0	0	0
<i>Oryzaephilus surinamensis</i>	9	0	15	0	8	0	0	0	0	0	0	0
<i>Sitophilus</i> spp.	3	0	4	2	0	0	0	0	0	0	0	0
<i>C. cephalonica</i> (larvae)	0	0	46	0	0	0	0	0	0	0	0	0

*Oryzaephilus surinamensis* found after 12 months storage. The CO<sub>2</sub> had been added at a dosage of 2.4 kg/tonne of rice, which has been determined (Annis et al. 1984; Sukardi and Martono 1983) to be an optimal dosage. The enclosure was inspected regularly and no holes or tears were found in the sheeting. It may be that the 700 kg polypropylene woven jumbo bags used in the trial are less penetrable to the gas than are jute bags.

### Fungal infection

Fungal species contaminating the grain were detected by collecting 400 grain samples and plating 25 grains per petri dish. The plated samples were then incubated on moist blotter at 23±2°C for 7 days, under alternating cycles of 12 hours Near Ultra Violet (NUV) light and 12 hours darkness. The results in trial I showed that the numbers and percentages of fungal species in the first two stacks had not increased as compared to pretreatment levels. However, in

the third stack the percentage of fungal infection was slightly increased. Genera such as *Fusarium* and *Penicillium* were subsequently observed to be contaminating the grain (Table 9). It was found later that the sheet covering this stack had been torn during the last month of the trial, thereby permitting entry of outside air.

In trial II, during which the enclosures were completely sealed, the percentage of *Aspergillus* spp. and *Fusarium moniliforme* contaminating the grain before treatment decreased significantly after treatment. Only *Curvularia lunata* was found infecting the grain in the stack treated for 12 months (Table 10).

Aflatoxin analysis by thin layer chromatography (TLC) determined that the in both trials was completely free from aflatoxin contamination.

### Rice quality

Na-sai and wet season rice are classified as intermediate amylose content (20–25%), having soft gel consistency (over 60 mm) with low and

**Table 8.** Hidden infestation (numbers per 3 kg sample) in samples taken before and after treatment in trial II.

Species	Before treatment						After treatment					
	Stack 1		Stack 2		Stack 3		Stack 1 (4 months)		Stack 2 (8 months)		Stack 3 (12 months)	
	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead	Alive	Dead
<i>Tribolium castaneum</i>	3	0	3	2	2	0	0	7	0	4	23	7
<i>T. castaneum</i> (larvae)	0	0	0	0	11	0	0	0	0	0	12	0
<i>Oryzaephilus surinamensis</i>	4	1	37	0	5	0	0	86	0	6	6	3
<i>O. surinamensis</i> (larvae)	0	0	20	0	0	0	0	0	0	0	0	0
<i>Sitophilus</i> spp.	2	0	0	0	0	1	0	0	0	0	0	0
<i>Cryptolestes pusillus</i>	0	0	0	0	0	1	0	0	0	1	0	0

**Table 9.** Fungal infection (percentage per 1 kg sample) in trial I.

Species	Before treatment			After treatment		
	Stack 1	Stack 2	Stack 3	Stack 1 (2 months)	Stack 2 (4 months)	Stack 3 (6 months)
	(%)	(%)	(%)	(%)	(%)	(%)
<i>Aspergillus flavus</i>	11	38	10	3	29	14
<i>A. niger</i>	0	3	1	0	0.5	6
<i>A. glaucus</i>	6	11	7	0	0	0
<i>Penicillium citrinum</i>	0	0	1	0	2	3
<i>P. islandicum</i>	0	0	0	0	0	3
<i>Fusarium moniliforme</i>	0	0	0	0	0	6

intermediate-to-low gelatinisation temperatures, respectively. They need about 17–18 minutes cooking to produce moderately tender rice. Hom Mali variety has a low amylose content (below 19%), soft gel consistency, and low gelatinisation temperature. All three varieties are aromatic and the aroma of all samples was detectable.

In trial I, the cooking and eating qualities before and after treatment were investigated.

Amylose content, soluble amylose, elongation ratio, elongation index, cooking time, total solid suspended in excess cooking water, and water uptake ratio were not significantly different. The gel consistency was slightly decreased, however, and fat acidity and volume expansion tended to increase with storage period. Hom Mali (before treatment) had higher fat acidity than Na-sai and wet season rice. The fat acidity of Hom Mali after

**Table 10.** Fungal infection (percentage per 1 kg sample) in trial II.

Species	Before treatment			After treatment		
	Stack 1	Stack 2	Stack 3	Stack 1 (4 months)	Stack 2 (8 months)	Stack 3 (12 months)
	(%)	(%)	(%)	(%)	(%)	(%)
<i>Fusarium moniliforme</i>	5.5	0	0	2.5	0	0
<i>Aspergillus flavus</i>	5.0	3.0	0	5.0	1.0	0
<i>A. niger</i>	0.5	8.0	0	0	7.0	0
<i>A. terreus</i>	4.0	0	0	2.5	0	0
<i>A. fumigatus</i>	0	10.0	0	0	5.0	0
<i>Cladosporium</i> sp.	0	0	2.0	0	0	1.0
<i>Curvularia lunata</i>	0	0	0	0	0	3.0

**Table 11.** Rice chemical and cooking quality analysis in trial I.

Characteristics	Before treatment			After treatment		
	Stack 1	Stack 2	Stack 3	Stack 1 (2 months)	Stack 2 (4 months)	Stack 3 (6 months)
Amylose (%)	24.31	22.87	13.71	23.70	23.0	15.20
Soluble amylose(%)	13.10	12.60	7.10	13.00	12.40	7.40
Alkali test						
spreading value	5.90	5.20	7.00	5.90	5.50	6.90
gelatinisation temp.	L	I/L	L	L	I/L	L
Elongation ratio	1.93	2.01	2.11	2.13	1.98	2.30
Gel consistency (mm)	89	95	93	69	93	66
Cooking time (min)	18	18	15	17	17	16
Total solids (g/8 g raw rice)	0.59	0.52	0.24	0.57	0.46	0.36
Volume expansion	3.60	3.72	3.46	4.00	4.20	5.01
Water uptake ratio	3.06	2.94	2.90	3.06	3.04	3.17
Fat acidity (mg %)	12.10	10.75	22.66	13.11	14.95	30.87
Brabender viscogram						
Gelatinisation temp. °C	70.5	72	58	71	72	70
Peak viscosity(B.U.)	750	740	880	800	700	880
Set back (B.U.)	+140	+160	-70	+260	+180	20
Consistency (B.U.)	350	420	310	500	400	340
Breakdown (B.U.)	200	260	380	240	220	320
Palatability						
Aroma	5.14	5.40	5.50	5.32	4.93	4.86
Tenderness	5.50	5.59	5.95	4.61	5.07	5.77
Cohesiveness	5.27	5.54	6.09	4.96	5.57	6.05
Whiteness	6.95	6.82	6.40	6.61	6.75	6.11
Glossiness	5.68	5.68	5.95	4.68	5.61	5.46

6 months storage increased by up to about 31% resulting in a distinguishable off-smell of the cooked rice.

Rheological changes in a viscous paste of 10% rice flour were assayed using a Brabender Visco/Amylograph. Results of the peak viscosity consistency and breakdown value showed no differences. The setback value showed an obvious increase in viscosity after treatment. Similarly, the cohesiveness of cooked rice and the palatability test score were decreased after treatment.

Investigation of the palatability of cooked rice showed that the score of all characters tended to decline after treatment. This indicated that the cooked rice had reduced aroma, tenderness, cohesiveness, whiteness, and glossiness as storage period increased. Moreover, the higher

fat acidity after treatment resulted in a lower aroma score because the off odour of cooked rice could be distinguished (Table 11).

As regards physical quality, Na-sai variety showed a slight increase (from 10.29 to 11.48%) in moisture content after storage under CO<sub>2</sub> for 2 months. There were no yellow grains in either initial or stored samples, and the degree of whiteness of the milled rice was quite stable at between 47–48. In wet season rice held under CO<sub>2</sub> for 4 months, the grain moisture content and yellow grains were slightly increased, but the whiteness was unchanged. The Hom Mali variety showed a slight increase in grain moisture content, yellow grains, and degree of whiteness (Table 13).

In trial II, amylose content, elongation ratio,

**Table 12** Rice chemical and cooking quality analysis in trial II

Characteristics	Storage period						
	Before treatment	4 months control	4 months treated	8 months control	8 months treated	12 months control	12 months treated
Amylose (%)	25.76	26.53	26.24	27.17	26.38	26.70	27.06
Gel consistency (mm)	83	37	48	35	38	38	36
Elongation ratio	1.58	1.60	1.59	1.76	1.63	1.74	1.80
Free fatty acid (mg %)	11.62	29.69	25.88	46.63	35.63	51.00	49.00
Alkali test							
spreading value	6.2	5.5	5.6	5.4	5.7	5.2	5.2
gelatinisation temp.	L	I/L	I/L	I/L	I/L	I/L	I/L
Aroma of raw rice	0	0	0	0	0	0	0
Small scale cooking test							
volume expansion	3.92	3.66	3.83	3.50	3.67	3.84	4.08
total solids, (g/g raw rice)	0.79	0.74	0.81	0.66	0.63	0.51	0.53
water absorption	2.86	2.44	2.50	2.44	2.59	2.97	2.85
Brabender viscogram							
gelatinisation temp. °C	69.4	69	69.5	70	70	70.5	70
peak viscosity (B.U.)	570	565	630	960	930	920	920
setback (B.U.)	+145	+150	+130	+110	+140	+100	+140
consistency (B.U.)	370	410	410	520	545	500	540
breakdown (B.U.)	230	160	280	440	405	440	400
Palatability							
aroma	5.1	5.2	5.2	5.2	5.1	4.0	4.7
tenderness	5.2	5.3	5.0	5.0	4.8	4.5	4.9
cohesiveness	5.7	5.8	5.6	5.9	5.8	5.2	5.2
whiteness	7.2	7.0	7.0	6.9	6.9	6.4	6.2
glossiness	6.1	5.7	5.5	6.2	6.1	5.4	5.2

Gelatinisation temperature: L = Low, I/L = Intermediate-Low

Aroma (raw rice): 0 = none, + = scented, ++ = strongly scented

Palatability

aroma	tenderness	cohesiveness	whiteness	glossiness
9 = scented	9 = soft	9 = sticky	9 = white	9 = glossy
1 = off-aroma	1 = hard	1 = fluffy	1 = light brown	1 = dull

and free fatty acid (FFA) levels were increased in both control and treated samples as storage period increased. Compared with the control, the amylose content of treated samples did not markedly change during storage, though it tended to increase slightly as storage period lengthened. The same pattern occurred with elongation ratio.

FFA levels increased noticeably as the storage period lengthened. The control showed higher FFAs than the treated samples, particularly for the 8 months storage period. However, as the storage period extended to 12 months, the difference in FFA levels between control and treated samples became insignificant. This suggested that the reduction of CO<sub>2</sub> concentration might cause the rapid increase of FFA levels in treated samples. On the other hand, the increased FFA at 12 months storage was accompanied by off-odours in the cooked rice. However, no off odour could be detected from raw rice soaking in 10% sodium chloride solution. Also, as the storage period extended, the alkali spreading value gradually decreased. Na-sai needed a somewhat longer cooking time after than before treatment. The gel consistency of the starch slurry rapidly decreased after storage, indicating an increase in hardness of rice following storage.

In small scale cooking tests, total solids suspended in excess cooking water appeared to decrease. Volume expansion and water absorption also appeared to fall during 8 months storage, and showed no recovery in the rest period. Although the elongation ratio of the grain increased during cooking, the volume

expansion of cooked rice did not show the same effect.

Determination of rheological properties of the viscous paste showed changes in gelatinisation temperature, peak viscosity, setback, consistency, and breakdown value. The gelatinisation temperature, peak viscosity, consistency and breakdown value clearly increased during storage. The setback value of treated samples remained unchanged, but appeared to fall in untreated stored samples. Increasing infestation of the controls was observed during storage, possibly contributing to the decrease in setback value. Although the setback value of the control samples was decreased, gel consistency measurements indicated that the rice was harder following storage.

As regards the palatability of cooked rice, the score of all characters tended to decrease as storage period increased. Storage tended to cause reduction in aroma, tenderness, cohesiveness, whiteness, and glossiness, as has been reported before. Eight months storage under carbon dioxide did not affect aroma and cohesiveness. However, lower scores were obtained following longer storage periods. The cooked rice became less sticky and had an unpleasant smell when cooked. The tenderness, whiteness, and glossiness all gradually decreased during storage. Nevertheless, although these changes in palatability occurred, the product was still acceptable to consumers after 8 months storage (Table 12).

Rice moisture content increased slightly in all stacks. There was no significant change in the degree of whiteness and no yellow grain was

**Table 13.** Rice physical analysis in trial I

	Before treatment			After treatment		
	Stack 1	Stack 2	Stack 3	Stack 1 (2 months)	Stack 2 (4 months)	Stack 3 (6 months)
Yellow grain (g)	0.0	0.02	0.06	0.0	0.11	0.60
Degree of whiteness	47.0	46.5	40.0	48.0	47.0	42.3

**Table 14.** Rice physical analysis in trial II

	Before treatment			After treatment		
	Stack 1	Stack 2	Stack 3 (4 months)	Stack 1 (8 months)	Stack 2 (12 months)	Stack 3
Yellow grain (g)	0.03	0.0	0.02	0.0	0.0	0.0
Degree of whiteness	50.1	50.6	50.8	48.0	50.0	49.3



found in the treated stacks (Table 14). This suggests that sealed storage following CO<sub>2</sub> treatment can preserve rice quality for up to 12 months.

### Conclusion

The results of trial I, in which milled rice was stored for up to 6 months in sealed plastic enclosures following CO<sub>2</sub> treatment, were satisfactory in terms of control of insect infestation and prevention of reinfestation. No live insects were observed in any treatments. Aflatoxin was not detected, despite the fact that the percentage and numbers of some fungal species increased, particularly in the stack stored for 6 months. Although rice quality changed little during storage, it did tend to decrease with increase in storage period.

In trial II, rice quality assessments gave results similar to those from trial I. However, the percentage incidence of most fungal species decreased, with an increase in only one minor species. CO<sub>2</sub> was effective in controlling insects in the stacks opened at 4 and 8 months, but not in the stack sealed for 12 months.

It is concluded that the CO<sub>2</sub> treatment method is effective in controlling insect pests and mould growth, and will preserve milled rice during long-term storage, provided the enclosure remains sealed.

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# Commercial Experience of Sealed Storage of Bag Stacks in Indonesia

Yun C. Nataredja\* and R.J. Hodges†

## Abstract

BULOG has adopted the use of sealed plastic enclosures purged with CO<sub>2</sub> as one option for the long-term storage of bagged, milled rice. This system has been successfully implemented in two phases beginning in 1984 and since then some 90,000 tonnes of milled rice have been stored for periods up to 2.5 years. Although the technique has been an operational success, in that the outturn quality has met with considerable approval, technical and managerial improvements are possible.

Technically, there is a need for further developments to reduce costs, by increasing the potential for reuse of sheets and by lowering the rate of failure in gas retention. It is believed that the failure rate could be much reduced by further technical refinement.

On the management side, there remains considerable scope for the full integration of the CO<sub>2</sub> method into BULOG's operational system. This could be achieved through a more comprehensive cost-benefit analysis, better forecasting of requirements for long-term storage, and more accurate identification of the best locations for long-term stocks. It appears that the CO<sub>2</sub> system may become a permanent feature of the BULOG rice storage system, its extent being governed by the need for longer term storage.

THE long term storage of bagged, milled rice under carbon dioxide (CO<sub>2</sub>) in fully sealed plastic enclosures offers an alternative to the regular use of fumigation and insecticide spraying for grain preservation. The initial development of the technique was undertaken by CSIRO in Australia, and the technology transferred to the humid tropics through a collaborative small-scale project with BULOG, at Tambun, West Java (Annis et al. 1984). The technique was successfully used to store about 700 tonnes of rice, with a 12% moisture content, for periods of up to 4 months. The practicalities of implementing the technique were considered and it was found that the enclosures could be built by two men in just over an hour.

As the method was clearly practicable, BULOG undertook a larger scale trial using

6400 tonnes of rice at 13-14 % moisture content (Sukardi & Martono 1984; Suharno et al. 1984). This trial compared the use of CO<sub>2</sub> and phosphine in sealed enclosures for periods of up to 16 months. From the results, it was concluded that CO<sub>2</sub> treatment was more effective than phosphine in controlling both insect pests and mould growth and would be ideal for use in long-term storage, provided the enclosures remained undamaged. Some consideration was also given to the economics of the method. An analysis was performed on costs and anticipated rice losses. This gave the minimum break-even period with normal pest control methods as about 9 months. Later analysis based on costs alone put the break-even period at about 12 months (Suharno 1986).

Against this background of successful experimental trials, it was with some confidence that BULOG embarked upon operational CO<sub>2</sub> storage in 1984. To date, some 90,000 tonnes of milled rice have been stored at various locations in Indonesia (Table 1). The

\* National Logistics Agency (BULOG), Jl Gatot Subroto 49, Jakarta, Indonesia.

† Pest and Quality Control Advisor, BULOG-ODNRI Project, Dolog Jatim, Jl Jend. A Yani 146-148, Surabaya, Indonesia.

techniques employed are summarised in the Appendix. This short paper describes the operational methods used by BULOG, gives summaries of some of the data collected by the operational teams, and considers technical and management aspects that might be improved.

## Operational Considerations

### CO<sub>2</sub> Concentration

Stocks in the BULOG system are purged with CO<sub>2</sub> to give an initial concentration of the gas of 80%, declining to a minimum of 50% after 10 days and not less than 10% after 6 months. This dosage schedule is somewhat higher than the latest recommendations for the technique, which are for 70% CO<sub>2</sub> initially, declining to 35% after 15 days or longer (Annis 1986). At the time the technique was developed in Indonesia, an initial concentration of 60% was required. However, this was increased when live, but moribund, specimens of *Sitophilus oryzae* were

discovered some weeks after treatment. It is well established that this species is particularly tolerant of CO<sub>2</sub> (Annis 1986).

The gas levels achieved in 57 rice stacks in East Java during the 1987-88 program are shown in Figure 1. (Data from stacks with substantial leaks have not been included.) The profile of decline in gas concentration matches that recorded during experimental studies by Sukardi and Martono (1983). The concentration regime has been successful in destroying existing infestations and preserving rice quality.

Two practical questions concerning the gas concentration are worthy of consideration:

- Is it necessary to insist on so high an initial gas concentration?*
- What should be done if the gas concentration drops below 10%, as it invariably does after about 8 months, and continued long-term storage is envisaged?*

Currently, BULOG regulations would stipulate regassing, but there is no conclusive evidence that this is necessary. If regassing is performed, it is not known what extent of regassing would be cost effective for any given additional storage period.

**Table 1.** Tonnages of milled rice preserved at various locations in Indonesia using the CO<sub>2</sub> method

Region	Phase1	Phase2	Total
Jakarta Raya	28200	14116	42316
West Java	4750	0	4750
Central Java	2700	1500	4200
East Java	11578	19730	31308
South Sulawesi	4900	0	4900
North Sumatra	4500	0	4500
Total	56628	35346	91974

### Failures in Gas Retention

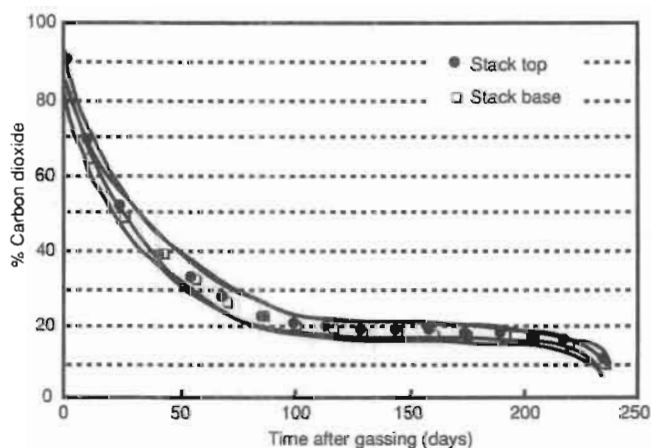
Gas retention failure in stacks can take three forms:

- large gas leaks in the first 10 days, resulting in the initial fumigation by CO<sub>2</sub> being ineffective;
- subsequent failures due to large holes made in the sheets by, for example, rodents; and
- failures due to small leaks that result in a gradual fall in the CO<sub>2</sub> concentration to below 10% during the first 6 months after gassing.

The frequency of failure has been found to

**Table 2.** Records of failures in gas retention at various locations in Indonesia (incomplete data).

Location	No. of stacks	No. of failures	% Failure
Jakarta	109	32	29
West Java	12	7	58
Central Java	16	0	0
East Java	70	13	17
South Sulawesi	6	3	50
North Sumatra	12	2	17



**Figure 1.** Mean CO<sub>2</sub> concentration in rice stacks.

vary between locations (Table 2) averaging around 25%. Much higher failure rates were encountered in those stores suffering from heavy rodent infestation, e.g. in West Java, South Sulawesi, and Jakarta (Table 2). In East Java, about 17% of stack treatments failed. In the first 10 ten days after purging, 3 of 70 stacks required regassing. These failures all occurred at a particular site and, together with the somewhat higher than specified gas dosages needed to achieve an 80% initial concentration, resulted in use of an average of 3.2 rather than 2.4 kg of CO<sub>2</sub>/tonne. In the most recent phase of CO<sub>2</sub> storage in East Java, failures to retain more than 10% gas were remedied without financial loss as the stocks concerned were distributed soon after the enclosure atmosphere had fallen below 10% CO<sub>2</sub>. While this management option may frequently present itself, in a well planned CO<sub>2</sub> program where all stacks are stored for the minimum period required to break-even with normal stock protection methods, such failures would necessarily represent an undesirable loss.

Recorded causes of failures are rodent damage, inadequate sealing, manufacturing defects in the plastic sheets, and holes caused by contact with the wooden pallets. Birds and insects (e.g. *Rhyzopertha dominica*) made holes in sheets on only two occasions. It seems probable that the failure rate could be much reduced if (a) an effective anti-rodent strategy involving rodent barriers and poison baits were developed for those godowns used in the CO<sub>2</sub>

program, (b) better quality sheets were used, and (c) pallets were abandoned and the bags stacked directly on the base sheet.

### Rice Quality and Value

Quality changes in rice stored for 70–250 days under CO<sub>2</sub> in East Java are given in Table 3. Samples were taken from marked bags on the stack surface at the start of the storage period and again from the same bags at the end. All the sampling and analyses were undertaken by Pest and Quality Control staff as part of their normal routine.

Overall, there seems to be a general trend towards a small increase in the numbers of brokens and yellow grains, and in the moisture content. Small increases in moisture content and yellowed grains in the outer bags of stacks have been observed previously (Sukardi and Martono 1983; Suharno et al. 1984). In contrast, observations on rice stored in Jakarta for 2.5 years showed a very slight decrease in moisture in the outer layers, but agreed in other respects. In Table 3 a comparison is also made of quality factors for stacks which had a period of storage at below 10% CO<sub>2</sub> concentration for an average of 34 days (range 15–66 days), with those from stacks maintained at a higher concentration throughout the storage period. It would appear that storage at the lower concentration had, on average, no detrimental effects. In fact, the rice quality from these stacks appeared somewhat better. Even those stacks held for the longest

**Table 3.** Quality analysis of rice from the East Java CO<sub>2</sub> program (Mean %  $\pm$ sd)

Storage period (days)	Number of stacks	M.C.			Brokens			Yellow\Damaged grains		
		Start	Finish	Change	Start	Finish	Change	Start	Finish	Change
70–100	17	13.41	13.83	0.43	22.82	24.44	1.62	2.30	2.28	-0.03
		0.36	0.11	0.37	3.38	2.50	2.81	0.58	0.57	0.40
101–200	24	13.42	13.38	-0.04	26.29	28.25	1.96	2.22	1.98	-0.24
		0.32	0.48	0.38	2.43	3.06	3.19	0.61	0.78	0.66
201–250	21	13.44	13.74	0.32	5.37	25.42	0.05	1.62	2.19	0.57
		0.26	0.23	0.15	4.79	5.57	2.42	0.41	0.38	0.40
Overall mean $\pm$ sd		13.42	13.63	0.21	25.03	26.24	1.22	2.04	2.13	0.09
		0.31	0.39	0.38	3.89	4.30	2.96	0.62	0.62	0.62
Stacks*	47	13.40	13.64	0.24	23.88	25.51	1.64	1.92	2.01	0.10
>10% CO <sub>2</sub>		0.30	0.39	0.41	3.59	4.40	3.11	0.54	0.54	0.63
Stacks**	15	13.48	13.60	0.11	28.33	28.35	0.02	2.40	2.47	0.07
<10% CO <sub>2</sub>		0.35	0.38	0.25	2.64	3.18	2.05	0.68	0.73	0.60

\* Mean %  $\pm$ sd for stacks always maintained above 10% CO<sub>2</sub>

\*\* Mean %  $\pm$ sd for stacks stored part time below 10% CO<sub>2</sub>

periods at below 10% CO<sub>2</sub> all showed levels of deterioration comparable with those where higher levels of CO<sub>2</sub> had been maintained.

Throughout the period in which rice was stored under CO<sub>2</sub> in well-sealed plastic enclosures no mould growth was observed on stocks. This was achieved with routine inspection of incoming rice, which is accepted for conventional BULOG storage if its moisture content falls within the range of 12–14%. Thus, earlier fears that moisture related problems would hamper storage under CO<sub>2</sub> in sealed enclosures have been unfounded.

Laboratory analysis for quality does not necessarily confirm consumer acceptability of a stock. Information was therefore collected from the Godown Chiefs in East Java who were responsible for the distribution of rice from both the CO<sub>2</sub> and normal storage programs. Godown Chiefs are well placed to judge consumer reactions to the stocks they hold. Consumers choose their rice carefully and will complain at poor quality. All four Godown Chiefs were enthusiastic about the quality of rice from the CO<sub>2</sub> program, saying that although it may sometimes have rather less taste, it was preferred by the consumer because of its noticeably better odour, visual appearance, and the cleanliness of the jute bags in which it is provided.

Previous studies and the present observations all lead to the conclusion that the CO<sub>2</sub> technique provides an excellent method of quality preservation, to the extent that rice preserved under this method may be sold at a premium over similar rice stored under a conventional regime. As an example, rice stored in Jakarta for 2.5 years received an almost 8% higher price than similar stock stored by more conventional means (Table 4).

### Plastic Sheets

Initial experience with plastic sheets manufactured in Australia showed that such

sheets rarely had problems with gas retention as they were made of durable plastic with low permeability to CO<sub>2</sub>, and had strong seams and a relatively high resistance to rodents. Financial constraints and government policy have forced BULOG to rely on locally manufactured sheets. Unfortunately, these are of lower quality and consequently retain gas less well. This situation might be improved if BULOG provided manufacturers with clear specifications on permeability, ageing qualities, and resistance to physical damage.

From the start of this work it was clear that the most expensive element in the use of CO<sub>2</sub> was the provision of plastic sheets. For this reason the ability to reuse sheets at least once is very important (this is further emphasised in another paper later in this conference). Some reuse has been achieved in the two programs but it has been observed that, especially in East Java, the sheets are stored after use in godowns that also contain rice. As a result, they are sometimes severely damaged by rodents. To improve the potential for reuse of sheets it may be worth while providing them with durable carrying cases in which they can be stored safe from rodent attack and other means of physical damage.

Problems with sheets might be further reduced if it was found possible to replace the base sheet by coating the floor beneath CO<sub>2</sub> stacks with a gas proof paint.

## Managerial/Planning Considerations

The management and planning for the CO<sub>2</sub> programs has been relatively trouble-free, although it cannot yet be said that the system is used to full operational efficiency. There seem to be no problems in obtaining supplies of local plastic sheeting, glue, or gas. The pest control teams have found the technique easy to apply. Local management of CO<sub>2</sub>-stored stocks

**Table 4.** Prices at sale of CO<sub>2</sub> stored rice and rice stored by conventional means

Wholesaler group	Price of CO <sub>2</sub> rice (Rp/Kg)	Price of conventional rice (Rp/Kg)	Price difference
1	225	210	15
2	230	210	20
3	230	215	15

has proven considerably easier than for conventional stocks. Apart from rodent eradication, there has been no need for routine pest and quality control activities or store cleaning and the stores can be kept locked for most of the time. However, the CO<sub>2</sub> technique does include some extra duties for godown staff, in particular monitoring CO<sub>2</sub> concentrations, checking for holes in the sheets, and quality analysis of samples taken from the stocks before and after storage. All Godown Chiefs questioned considered that their responsibilities were much less onerous with the CO<sub>2</sub> program and they considered that losses, especially those through pilfering, were much reduced. All the Godown Chiefs were keen for the continuation of the program.

There have been some problems arising from the following aspects of central management:

(a) planning and scheduling of the distribution of materials for the preparation of the plastic enclosures has not always been done in sequence with rice procurement; and

(b) information on which stocks are likely to be required for longer term storage and their locations has not always been available. The difficulties of accurate forecasting in the most recent program resulted in many stocks not being maintained long enough for the costs of CO<sub>2</sub> storage to break-even with insecticide spraying and fumigation.

## Conclusions

The successful application of the CO<sub>2</sub> technique to about 90,000 tonnes of rice since 1984 has led to the establishment of the method as one of BULOG's main options for the long-term storage of milled rice. The extent of its use in the future will be determined by actual requirements for long-term storage. The technique needs further development in both technical and managerial areas. Special priority should be given to:

(1) reducing the failure rate in gas retention by implementing rodent control programs, developing better specifications for locally made plastic sheets, and eliminating wooden pallets;

(2) increasing the potential for reuse of sheets through better specification of sheet quality and more careful storage of sheets between uses;

(3) precise determination of the break-even storage period between CO<sub>2</sub> storage and conventional techniques, based on both costs and benefits (recent progress on this is reported in another paper in these proceedings);

(4) determination of the most efficient balance between conventional pest control and CO<sub>2</sub> storage on the basis of sound forecasting of grain procurement and distribution; and

(5) prediction of the ideal geographical locations for long-term storage based on sound operational planning.

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## Appendix

### A SUMMARY OF BULOG INSTRUCTIONS FOR THE APPLICATION OF THE CO<sub>2</sub> TECHNIQUE

#### Preparation of the Stack and Enclosure

1. A PVC sheet (0.76 mm thick) is placed on the floor where the stack is to be built.
2. Wooden pallets, in good condition, are positioned on top of the sheet to leave a sheet margin of 50 cm.
3. A stack of milled rice is built on the pallets, using stock with a moisture content of about 13%. The upper surface of the stack should be level before a tailored plastic sheet is fitted over the stack.
4. The margin of the plastic base sheet, which will be glued to the plastic cover, is cleaned with detergent.
5. The edges of the base and cover are glued together using Rakol Ultra DX glue.
6. For the sampling of CO<sub>2</sub> gas, a plastic pipe (25 mm i.d.) is inserted through the cover at the base of the stack. The same pipe is also used testing the gastightness the stack and allows the insertion of the copper CO<sub>2</sub> filler pipe. A paralon pipe (12.5 mm i.d.) is inserted into a hole at the top of the stack. The paralon pipe is then connected to a plastic pipe (7.7 mm i.d.), using putty, which trails to the ground. This pipe is used for sampling CO<sub>2</sub> gas from the top of the stack and for air pressure measurements.

#### Checking for Leaks

1. A domestic vacuum cleaner is connected to the CO<sub>2</sub> filler pipe at the base of the stack. To monitor the vacuum, a manometer is attached to the pipe leading from the top of the stack. When the air pressure difference between the inside and outside of the stack reaches 40 cm on the manometer the vacuum cleaner is turned off. The stack is then checked for leaks and any found are repaired.
2. The vacuuming and repair are repeated until the plastic enclosure can hold a differential in air pressure of 50% for about 15 minutes.

#### Adding CO<sub>2</sub>

1. The vacuum is released and a hole cut at the top of the stack to allow the escape of air when CO<sub>2</sub> is added below. The air pressure/CO<sub>2</sub> measuring pipe is closed.
2. Liquid CO<sub>2</sub> from cylinders, or more usually a tanker, is delivered to the stack through a copper pipe (17 mm i.d.) inserted at its base. The CO<sub>2</sub> will run in below the pallets. A dose of about 2.4 kg/tonne is administered, at which time the concentration of CO<sub>2</sub> is measured, via the CO<sub>2</sub> measuring pipe inserted at the top of the stack, using a 'Cosmotector'. When a concentration of 80% CO<sub>2</sub> is

reached gassing is complete and the vent hole and CO<sub>2</sub> delivery pipe are sealed.

#### Monitoring

After gassing regular checks are made for the following:-

##### 1. Gas Concentration

The concentration of gas is checked every day for the first 10 days by measurement at the base and top of the stack using a 'Cosmotector'. A minimum concentration of 50% is required for the first 10 days. Thereafter, measurements are made every 15 days or earlier if a leak is suspected. If the CO<sub>2</sub> level reaches less than 10% in the first 6 months regassing is required after a vacuum test.

##### 2. Damage to the System

Daily inspections are made for

- the presence of holes in the plastic sheeting caused by rats, birds, or insects
- any loosening of the putty used to join the plastic pipe work
- any condensation under the covers
- the presence of living insects and/or micro-organisms on the surface of the stack

##### 3. Rice Quality

The quality of rice coming from the CO<sub>2</sub> program is checked by sampling at the beginning and end of the storage period. Samples are taken from five marked bags on each side of a stack before the covers are put on. This procedure is repeated at the end of the storage period and the results compared.

# Sealed Storage of Bag Stacks: Status of the Technology

P.C. Annis\*

## *Abstract*

The potential of permanent sheeting for long-term storage of bag-stacks has been suggested for many years, but practical experience with the technique has not always matched expectation. A simple and reliable system of bag-stack sealing previously reported was tested for reliability at several locations in Southeast Asia. These tests have demonstrated that the technique makes it possible to reliably store dry grains for long periods after a single initial treatment with either carbon dioxide or phosphine. Grain quality was never any worse and normally better than that stored using conventional bag-stack methods. Data from these trials have provided the basis for implementing the method with carbon dioxide, and a set of preliminary recommendations for its use with phosphine. The enclosure must be sealed to give a pressure halving time of >10 min and ideally >15 min. A single dose of 1.5 kg CO<sub>2</sub> per tonne will then give a concentration >35% CO<sub>2</sub> for >15 days, the concentration regime needed to kill all insects. With phosphine, the dosage requirements are harder to define. However, in weakly sorptive grains such as milled rice and maize, a dosage of about 1 g PH<sub>3</sub> per tonne appears to be adequate for a complete disinfestation. The phosphine dosage required to disinfest potentially sorptive commodities, such as paddy, may have to be determined on the basis of the observed phosphine concentration and redosing if necessary. Using the recommendations on sealing and dosing it is possible to routinely and reliably maintain dry bagged grains for long periods in a good condition.

THIS paper gives a brief review of the development of sealed bag-stack technology from its early use to its current form, and discusses the current status of the technique. The review highlights recent developments and experience with the technique, and shows how it has changed in status from being somewhat unreliable, to a standard pest and quality control procedure ready for routine use.

The first extensive use of sealed bag-stack technology in Australia, and possibly in the world, was in the period 1917–1919. By modern standards the technique was cumbersome. The enclosures were made of wooden sheeting and sealed with bituminous materials. Low oxygen atmospheres were piped into the

enclosures from a coke-fired producer gas plant (Winterbottom 1922). While these treatments were at least partly successful, they were in no way reliable (Ratcliffe et al 1940).

It was not until the second world war that further extensive sealed stack treatments were again carried out. These treatments, in enclosures of soldered flat iron, were with carbon bisulphide, ethylene chloride/trichloroethylene and, experimentally, with methyl bromide (Wilson and Gay 1946). They reported success in reducing the number of insects but not in eliminating infestations. In these early studies the level of sealing was not tested and it is likely that there were still many leaks in the 'gastight' enclosures. Neither a perfect disinfestation nor insect-proof storage was possible because of these leaks.

\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia



A new impetus was given to sealed stack technology when the gaseous fumigants methyl bromide and phosphine became widely used with advent of more convenient plastic gas-proof sheeting. Initially, the sole reason for sheeting was to retain gas for long enough to kill insects, not to form an insect proof barrier. In fact, immediately after fumigation the sheets were removed, either to minimise the number of sheets needed or due to concern that sheeting would lead to excessive moisture migration. The process became widely used and known as 'fumigation under gas-proof sheets'. In this process, a more-or-less defined procedure could be followed to give a high-degree of insect kill (e.g. Brown (1954) and, more recently, Anon. (1974)).

Later, it was realised that, because of the high level of kill achieved, if the sheets were left in place, the commodity should remain free from infestation for a long period without further treatment. Several workers (Anon. 1959; Prevett 1962; Hyde and Kockum 1963; Halliday et al. 1968; McFarlane 1980) tried to make use of this. The practical results, however, did not match the theoretical expectation. Generally, these workers found that the procedure was not reliable; reinfestation occasionally occurred and moisture migration to the stack surface appeared to be encouraged. The reasons for these problems were hard to identify, but the four most likely causes were:

1. inadequate gas retention, thereby allowing some insect survival
2. incomplete barrier to reinfestation
3. excessive moisture migration caused by localised heating due to the metabolic heat of insects that are progeny from 1 or 2 above
4. excessive initial moisture content.

The first three of these possibilities could be eliminated if the enclosures were totally sealed.

Development of controlled atmosphere (CA) technology for bulk grain led to systematic studies on the causes of gas loss from large sealed structures. The increased knowledge of gas processes from these studies was used in the formulation of recommendations for the use of CA for the storage of bulk grains (Banks and Annis 1977) and for recommendations concerned with upgrading the practice of phosphine fumigation in Australia (Winks et al. 1980; Williams et al. 1980). An important aspect of these sets of recommendations is that a high standard of gas-tightness is essential to ensure reliable treatment.

This was true also for phosphine, a fumigant formerly considered suitable for use in unsealed or partially sealed systems.

It has since been shown that treatments based on these recommendations work reliably when: sealing had passed a pressure test; correct dosage had been applied; and problems with distribution of gas had been overcome (e.g. Banks and Annis 1984). In many commercial treatments it became clear that the high level of gastightness also conferred a substantial degree of 'insect-proofness' on the enclosure (Banks et al. 1980).

Initial attempts to reproduce this in sealed bag-stacks failed, because the enclosure used for 'fumigation under gas-proof sheeting' (see Anon. 1959) produced neither a reliable nor a testable seal. The method of sealing to the floor, using sand-snakes or similar means, could not survive pressure testing. It was therefore impossible to assess the level of sealing objectively before gas addition. The only methods of assessing sealing were by measuring gas concentration during the treatment period or indirectly by observing the level of mortality in bioassay of naturally occurring insects. Concentration measuring was rarely carried out and it is extremely difficult to interpret insect mortality as a quantitative measure of sealing. In the few papers where there were adequate concentration data to be able to calculate a gas-loss rate, the rates calculated would have been too high for carbon dioxide treatment (Annis et al. 1984), and were often too high for effective phosphine fumigation (e.g. Cogburn and Tilton 1963). A plastic floor-sheet used in conjunction with various ad hoc sealing methods, such as self adhesive tapes and rolling sheets together, was also unsatisfactory (Annis and Graver 1986).

The problem of overcoming the unreliability of sealing and producing a sealed bag-stack enclosure that could be pressure tested was overcome by fabricating a PVC cover sheet tailored to fit closely to the stack and sealing this to a PVC floor-sheet with a PVC cement. This type of enclosure was used as the basis for assessing the feasibility of using carbon dioxide treatment as a preliminary to long-term sealed storage of bag-stacks in sealed enclosures. These trials, carried out in Australia, Indonesia and Papua New Guinea (Annis and Graver 1986), along with independent work in China using polyethylene sheeting (reported by Rännfelt 1980), showed that the method was techni-

cally feasible and could be economical over a range of conditions. The Indonesian workers proceeded with further trials and subsequent commercial treatments with milled rice, and their experiences have been reported previously (Anon. 1984) and elsewhere in these proceedings (Nataredja and Hodges 1990).

Australian workers, in collaboration with others in Malaysia, Thailand and the Philippines, further investigated the technique to test its reliability and range of applicability. These trials form the basis for the rest of this paper. Several specific aspects of this work have been reported previously elsewhere.

## Method

Bag-stacks of milled rice, paddy and maize were treated with carbon dioxide in sealed plastic enclosures using the method of Annis et al. (1984). Some stacks were treated with phosphine using a modification of this method, by the technique described by Sabio et al. (1990). Treatments were carried out in a range of sites in Malaysia, the Philippines, and Thailand. The treatments are summarised in Table 1. During these trials, specific attention was directed at pressure testing, gas concentration, insect numbers, and changes in quality. Specific methodologies for measurement of quality and insect infestation are given elsewhere (Annis et al. 1987; Esteves et al. 1988; Gras et al., in press). The results of quality and insect data will be reported in only general terms. The main discussion here will be on the pressure test and gas concentration results.

Pressure testing was carried by observing the time for a negative pressure difference, with respect to atmospheric, to decay from approx. 200 Pa to half the initial value. In several cases this was much longer than an hour. On these occasions, an extrapolation of a logarithmic pressure decay curve was used to approximate the halving time. Applied CO<sub>2</sub> doses were measured by difference weighing of the gas supply cylinders. On most occasions, gas was added until the carbon dioxide concentration at the top of the stack was at least 70%. However, a few stacks were dosed at a predetermined low dosage rate of about 1.0 kg per tonne. The phosphine treated stacks were dosed with 1-4 g PH<sub>3</sub> per tonne.

Gas concentration measurements were made from at least two parts of the stack; one near

**Table 1.** Sources of data from sealed bag-stack treatments referred to in this paper.

Country/ commodity	Treatment	Stack size	Number of treatments	Storage period
<i>Malaysia</i>				
Milled rice	CO <sub>2</sub>	215 t	15	3-13 months
	PH <sub>3</sub>		3	
<i>Philippines</i>				
Milled rice	CO <sub>2</sub>	290 t	5	3-12 months
	PH <sub>3</sub>		2	
Paddy	CO <sub>2</sub>	190 t	17	3-12 months
	PH <sub>3</sub>		6	
Maize	CO <sub>2</sub>	240 t	10	3-12 months
	PH <sub>3</sub>		2	
<i>Thailand</i>				
Milled rice	CO <sub>2</sub>	70 t	9	3-6 months
	PH <sub>3</sub>		4	
Previously reported comparable trials:				
<i>Indonesia</i>				
Milled rice	CO <sub>2</sub>	177 t	4	1-4 months
<i>Australia</i>				
Milled rice	CO <sub>2</sub>	108 t	1	1 month
Totals	CO <sub>2</sub>		61	
	PH <sub>3</sub>		17	
<b>Grand total</b>			78	

the top and the other near the bottom. These were taken at appropriate intervals; daily at the start of the treatment and reducing to weekly towards the end. Carbon dioxide concentration was estimated using Dräger carbon dioxide detector tubes. A diluting chamber was used when concentrations were above 60%. Phosphine concentrations were measured directly with Dräger phosphine detector tubes.

Regression analysis of concentration with time was carried out on both logarithmic and reciprocal transformed average carbon dioxide concentration (Annis et al. 1984, Appendix 2) give the rationale for these transformations]. The regression equation for the transformation of best fit was used to calculate the concentration at 15 days. The concentration at 15 days was then fitted as a function of pressure test and dose using a generalised linear model computer package GLIM.

In the case of phosphine concentrations, only two statistics were calculated: the regression analysis of the decay curve and calculation of the concentration at 10 days.

## Results

### Quality and Insect Infestation

Results from these trials are very extensive and will be presented in detail elsewhere when full statistical analysis is complete. Results from the work on maize stored in the Philippines have been presented both for carbon dioxide (Gras et al., in press) and for phosphine (Sabio et al. 1990), as have results for milled rice in Thailand (Sukprakarn et al. 1990). The most detailed analysis has been completed on the results of the carbon dioxide treated stacks.

In summary, the quality results indicated that, over a wide range of quality parameters, long-term storage in sealed bag-stacks produced a better commodity at out-turn than conventional storage for the same period. However, quality deterioration was not totally arrested by this form of storage and some 'ageing' of the product occurred. Some moulding was found in one stack in Malaysia, in which there was also some degradation of quality. The data so far analysed from the phosphine treatments indicate that quality preservation of the commodity is equivalent to that obtained from carbon dioxide treatment.

Insect control was always good: in no case was a stack more than very lightly infested at the end of the storage period. Ten stacks in the Philippines contained very low numbers of *Sitophilus zeamais*, *S. oryzae*, and *Rhyzopertha dominica*, almost certainly the result of insects seen boring into the stacks (Sabio and Graver 1986). One stack in Thailand contained a few psocids close to a small hole in the seal at ground level. One stack in Malaysia had a single bag infested with *Sitophilus* spp. This bag was next to a known leak at the top of the stack. All the phosphine-treated stacks have so far demonstrated excellent insect control, i.e. there were no apparent survivors and there has been no reinfestation.

### Pressure Tests

A wide range of pre-treatment pressure-test results were observed. These varied between

pressure halving times of 6 and 270 minutes. A minimum of 10 minutes was the target. This was easily exceeded with new sheets, but as sheets were re-used, greater sealing and inspection efforts were required to achieve this target.

### Concentration Decay Rates

*Carbon dioxide.* The logarithm and the reciprocal of concentration were always well correlated with time ( $r^2 > 0.8$ ) and it was usual for one of the correlations to be better than the other, sometimes very much so. The best correlation, based on the highest  $r^2$ , was used to calculate the carbon dioxide concentration at 15 days.

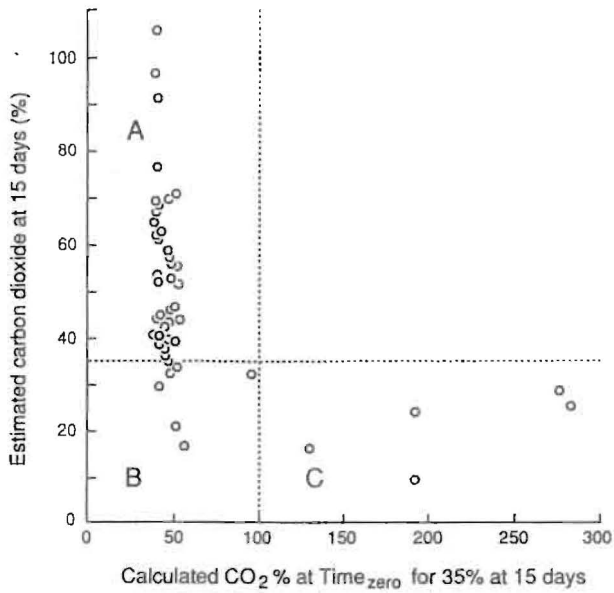
Of the treatments so far analysed, 42 retained concentrations of 35% or more at 15 days and 12 less than 35% at 15 days. A calculation of the concentration axis intercept needed to give a concentration of 35% carbon dioxide at 15 days gave an intercept of close to or above 100% for 6 of the treatments not meeting the 15 day > 35% target.

*Phosphine.* The course of phosphine concentration decay with time was very much like that of carbon dioxide, except the loss rates were both higher and much more variable between types of commodities (see Table 2) and, in the case of paddy, with either time after harvest or the number of fumigations.

**Table 2.** Loss rate of phosphine from sealed stack fumigations.

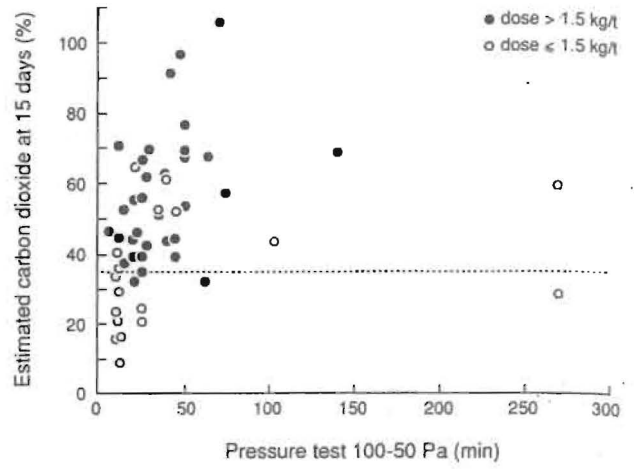
Commodity	Date treated	Loss rate per day	S.D.
Paddy	Dec 1987	0.538	0.074
	Mar 1988	0.254	0.039
	Jun 1988	0.178	0.023
Milled rice	Feb 1988	0.037	0.002
	Jun 1988	0.072	0.021
Maize	Jun 1988	0.125	0.062

The concentration target for phosphine fumigation for commodity above 25°C is 7 days > 100 mg/m<sup>3</sup> (Annis 1990). A concentration of > 100 mg/m<sup>3</sup> at 10 days was used to assess these trials to allow for the release rate of phosphine from the phosphide preparation and to ensure distribution throughout the enclosure. Calculation of the concentration at 10 days gave values of less than 100 mg/m<sup>3</sup> for 7 stacks of more recently



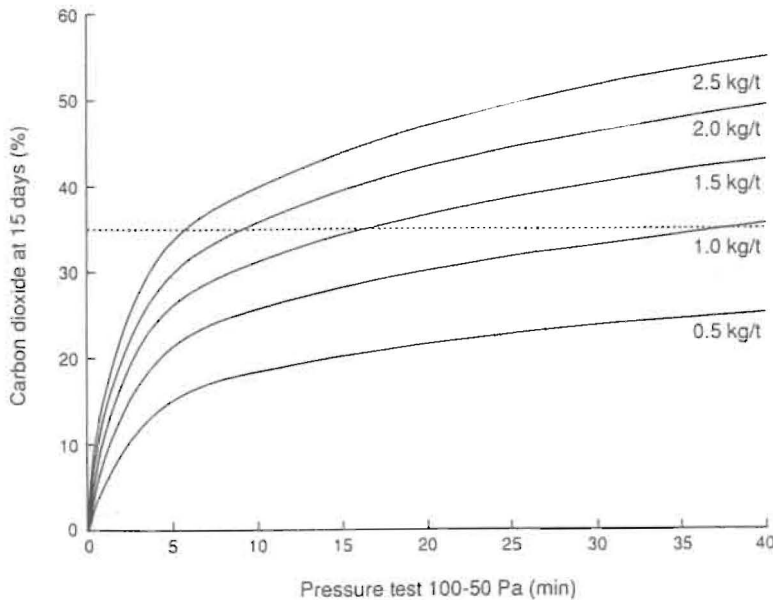
**Fig. 3.** Estimated CO<sub>2</sub> concentration at 15 days compared with the calculated concentration required at the start of treatment to give a concentration of 35% CO<sub>2</sub> at 15 days. Data from the CO<sub>2</sub> treatments referred to in Table 1.

where  $C_{15}$  is the carbon dioxide concentration at 15 days,  $P$  is the pressure test halving time, in minutes, for 200–100 Pa, and  $D$  is the applied dose in kg per tonne. A plot of this equation (Fig. 5) shows this relationship over a range of useful values. It is clear that doses below 1.0 kg per tonne are not useful and it is only over 1.5 kg per tonne that the required pressure test is reasonably easy to obtain (aver-



**Fig. 4.** Estimated CO<sub>2</sub> concentration at 15 days compared with pressure tests showing the influence of high and low dose rates. Data from the CO<sub>2</sub> treatments referred to in Table 1.

age pressure test in this study 40.9 min). The data of Annis et al. (1984) imply a value of 1.48 m<sup>3</sup> per tonne for the ratio of gaseous volume to mass in a sealed sheeted bag-stack of milled rice (this includes the billowed volume of the newly purged enclosure). At 30°C this is the equivalent of 2.56 kg of pure carbon dioxide per tonne of commodity at the start of the treatment. On the basis of the average concentration decay observed in these trials, an average initial concentration of  $45.96 \pm 4.83\%$  CO<sub>2</sub> was required to give an average concentration of 35% in 15 days. This is the equivalent of 1.18



**Fig. 5.** CO<sub>2</sub> concentration at 15 days calculated using equation (1) to show the combinations of pressure tests and dosages needed to give the required concentration of 35% CO<sub>2</sub>.

kg per tonne, a value very close to that derived from Figure 1 for a pressure test of 40 min.

The practical implications of these results are that, in the case of treatments with carbon dioxide, there can be some trade-off between the amount of gas added and pressure test achieved, but this is only true within small limits. Equation 1 is based on tonnes of commodity. Dosage rates based on an enclosed volume are sometimes preferred. However, it is very difficult to estimate the true gas volume within a sheeted stack that changes its volume with gas addition, whereas the mass of grain in a stack is almost always known. Calculations based on mass are both easy to make and useful for economic evaluation of the method.

Equation 1 gives only a best estimate of the dosage rate required and is useful for planning and analysis of results. The actual dosage of carbon dioxide in any treatment has to be established during that treatment by observing the concentration at the top of the stack during gas addition. Carbon dioxide addition is continued until the concentration at that point exceeds approximately 70% CO<sub>2</sub>.

Dosage levels with phosphine are not nearly as well established and there are no simple initial concentration criteria. It is clear that, with weakly sorptive commodities (milled rice, and to a lesser extent maize), a dosage of 1 g PH<sub>3</sub> per tonne is more than adequate for sealed stack fumigation. In the case of paddy, there is no easy answer. From the data, paddy appears to be both highly and variably sorptive, particularly when first fumigated or recently harvested (see also Banks 1990). On the basis of the observed concentrations dosages of up to 10 g PH<sub>3</sub> per tonne may be required. It appears that at present the only way of ensuring a sound phosphine fumigation of paddy is an a posteriori method: that is, treat the paddy, measure the concentration, then if necessary treat again with the dosage appropriately adjusted.

## Conclusions

After an initial disinfestation with either carbon dioxide or phosphine, sealed bag-stacks can provide safe insect-proof storage for long periods. This can be carried out in a plastic sheet enclosure sealed to an achievable pressure test (goal > 15 min, minimum 10 min halving time). Paddy, milled rice, and maize require a dose in the range 1.5 to 2.0 kg of carbon

dioxide per tonne. To some extent, lower levels of sealing can be tolerated but at the expense of higher dosages. It is not possible to establish a unique phosphine dosage, as it appears that this is determined by both the commodity type and its provenance. However, a dose of 1.0 g per tonne should be enough for non-sorptive materials, although this may well eventually be found to be excessive in some cases.

There appears to be no quality, technical, or scientific reason to prevent sealed-stack storage now being considered a routine treatment option when used with carbon dioxide, dry commodities and indoor storage. Outside these three restrictions, its use must be still considered a developmental technique. While not enough is known about phosphine dosage requirement to give the same status to this kind of treatment, its use is bound to be a great improvement on current practice and further development of the technique should be encouraged.

There is nothing magical about sealed stack storage. It will be subject to failures, but if adequate care is taken these should be few and far between. In order to operate sealed-stack storage to its maximum advantage, good house-keeping, hygiene and rodent control remain important. Indeed, they become more important but perhaps easier to carry out.

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## Report on Session 5: Sealed Storage of Bag Stacks

Chairman: Mr P.C. Annis, CSIRO, Australia  
Rapporteur: Mr A. Rahim Muda, MARDI, Malaysia

THIS session was concerned with the late stages of development and the early stages of commercial implementation of a new technology: that of treating bag-stacks with gaseous fumigants in enclosures that are much more gastight than those that have previously been in general use. Theoretically, good sealing should not only ensure a reliable disinfestation but should also provide a long period of protection from reinfestation. The papers presented at this session put this hypothesis and the technology under intense scrutiny.

In their paper, Sabio and co-workers showed firstly that sealed storage did not harm stored rice or maize. This is an unusual approach but one that was important in the case of sealed storage, where a fear of moisture migration and consequent commodity damage has been expressed. Other findings of interest were that sealed stack storage, in general, produced a better quality commodity at out-turn than conventional bag-stack storage. There seems to be a reduction in fungal infection in grain treated with phosphine and an observation was made that requires more explanation, namely, that while insect control was excellent, a significant increase in the number of dead insect sometimes occurred during the storage period. The paper by Chuwit Sukprakarn and others confirmed the overall findings of Sabio et al. applied not only to maize but also to milled rice, and thereby added to the evidence concerning the overall efficacy and reliability of the technique.

Yun and Hodges reported on some of the operational and management concerns which became apparent during large-scale commercial experience with the technique. While its use has been an operational success there remains room for technical and managerial improvement. The need to further reduce cost and decrease the rate of gas retention failure was indicated. Managerially there remain problems of integrating sealed storage under CO<sub>2</sub> into an existing operational system but it was felt that its role was for stocks of rice identified for long-term storage (9 months or longer).

Annis summarised the coordinated experiments carried out before and during the course of an ACIAR project on the use of sealed plastic enclosures. His paper showed that this form of storage was reliable, caused no damage to the stored commodity, that disinfestation and protection from infestation were excellent, and that there was a satisfactory out-turn of commodity after long storage periods. The paper also presented estimates of the sealing and carbon dioxide dose required for successful treatments. These estimates should be useful for planning and for economic evaluation of the method.

The four papers presented during this session very carefully examined a relatively new storage system. The studies they report were designed to reveal problems with the system and to determine its limitations. That some treatments failed partially in this process is not surprising. The papers together report the treatment of approximately 10 500 tonnes of commodity stored in about 400 stacks. It is interesting to speculate on the number of failures that would have been observed in the same number of routine conventional treatments.

The the work reported here almost certainly marks the end of the research phase for this storage technique as it has been shown to now be ready for commercial use. There is undoubtedly room for further development, but this will best take place consequent upon routine use in commercial environments .



# **Issues Relating to the Application of Fumigation and CA**

# Regulatory Policies, Technology, and Related Factors Affecting the Use of Fumigants and Controlled Atmospheres

C.L. Storey\*

## *Abstract*

Pesticides used for the disinfection of stored grain are receiving increased scrutiny and challenge by regulatory agencies throughout the world. In the US, several fumigant materials whose use has spanned more than 50 years (methyl bromide, chloropicrin, and aluminium/magnesium phosphide) are under intense review by the nation's Environmental Protection Agency. This paper discusses the interactions of policy, technology, and related factors which impact on fumigant use and identifies specific data requirements for their continued registration. The regulatory status of controlled atmospheres in the US is also discussed.

CHEMICAL grain fumigants have provided the principal remedial procedure used to control insect infestations in bulk stored grain for more than 50 years. Their use became an essential control measure when no other pesticide treatment could reach an infestation deep within the grain mass. Today, controlled atmosphere treatments of grain involving alteration of the proportions of the normal gaseous constituents of air (oxygen, nitrogen, carbon dioxide) to provide an insecticidal atmosphere represents the most likely direct substitute for chemical fumigation of grain. The two methods of pest control appear, however, to be following divergent paths of development.

The availability of chemical fumigants for the control of pests affecting agricultural commodities has significantly diminished over the past few years, especially in the United States. Specifically, the compound ethylene dibromide (EDB) was suspended by the U.S. Environmental Protection Agency (EPA) from all further sale, distribution, or use in February 1984 and the distribution of liquid fumigants containing admixtures of carbon tetrachloride (CCl<sub>4</sub>), carbon disulphide (CS<sub>2</sub>), or ethylene dichloride (EDC) was ended on 31 December

1985 (EPA 1985). These fumigant mixtures dominated the U.S. fumigant market for nearly 30 years reaching a peak annual use estimated at 5 million gallons (ca 19 million litres) in the late 1950s (Storey et al. 1986). In contrast to the cancellation of liquid fumigant mixtures, EPA established an exemption from the requirement of a residue tolerance for controlled atmospheres on all raw, dried, or processed agriculture commodities (EPA 1980, 1981) and listed the atmospheres as an alternative to chemical fumigants for insect control in harvested grains (EPA 1985).

While it is not our purpose here to explicitly document the demise of liquid grain fumigants, it may be useful to re-examine some of the factors that resulted in action against these materials in order to better understand the events now affecting the future of the three remaining fumigants—methyl bromide, chloropicrin, and aluminium/magnesium phosphide—still approved for use in the United States.

## **Fumigants and the Media**

Although it is generally recognised that chemical fumigation will continue to play a critical role in future pest management strategies (Bond 1984; Storey et al. 1986), pesticides in general and fumigants in particular

\* Consultant: Stored Grain Pest Management, 3022 Sunnyside Drive, Manhattan, Kansas 66502, USA.

are receiving increased scrutiny and challenge, especially in the U.S. After decades of relative obscurity, fumigant 'incidents' have become front-page news filled with sensationalism and, in many instances, gross misinformation. An improper dockside disposal of aluminium phosphide material in a 55-gallon drum, which resulted in a minor fire, was equated to the Bhopal, India, disaster and the manufacturer of the phosphide material was misidentified as Union Carbide of India ('Dockside toxic leak controlled', Savannah News 1 March 1987). A project to treat imported wood stumps with methyl bromide was not too subtly captioned ...'Brunswick company will use a carcinogen to fumigate shipments' (Atlanta Journal /Constitution 7 July 1986). Following EPA's cancellation of EDB, a major newspaper in the central states ran a three-day series of articles examining the use, hazards, and long-term health risks associated with fumigant use and criticised the Agency's 'bogging down' in not following through with programs to adequately regulate grain fumigants ('Toxic harvest', Minneapolis Star & Tribune 2, 3, and 4 September 1984). These articles were later followed by an open advertisement in the same newspaper placed by a law firm offering to represent anyone who suspected themselves of suffering injury related to liquid fumigant exposure (Minneapolis Star & Tribune, 3 April 1985).

## **EPA: Lineage and Policies Affecting Fumigants**

Because EPA is currently inundated with a broad range of environmental concerns encompassing such diverse problems as air pollution, water quality, acid rain, and toxic waste dumps, it is easy to lose sight of the fact that this important government agency was essentially created out of an amendment (U.S. Federal Environmental Pesticide Control Act of 1972) to the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) for the primary purpose of regulating the use of pesticides. This amendment to FIFRA required that all pesticides be classified for either 'general' or 'restricted' use and that individuals who use or supervise the use of restricted pesticides would require training in application as well as certification through a responsible state agency. The Federal Environmental Pesticide Control Act (FECPCA)

marked the first attempt to create a national pesticide policy that would identify the potential hazards of pesticides and also provide a measure of accountability on the part of individuals using pesticides.

By the mid-1970s, EPA began issuing a series of Pesticide Policy Enforcement Statements (PEPS) to inform users and the general public of policies being adopted by the Agency involving specific aspects of pesticide use. One of these policies established a new registration guideline entitled 'Rebuttable Presumption Against Continued Registration of a Pesticide' (RPAR). This Special Pesticide Review Process was initiated against a pesticide if EPA determined that use of the pesticide exceeded or 'triggered' risk criteria in the following areas:

### **RPAR Triggers**

1. Acute toxicity
2. Chronic toxicity (oncogenic or mutagenic effects)
3. Reproductive effects
4. Wildlife (endangered species, non-target species)
5. Non available emergency treatment or antidote

As the title of the process implies, a chemical which triggered one or more of the risk areas was prejudged unregistrable unless the registrant(s) of the chemical could provide data acceptable to the Agency which would prove the risks were within acceptable limits or were unfounded. In due course, RPARs were issued against ethylene dibromide, carbon tetrachloride, chloroform, and ethylene oxide. In most instances, the risk criteria exceeded by these fumigant materials was in the area of chronic toxicity, specifically tumor formation in test animals. To some, EPA's RPAR registration policy was a classic example of a 'Catch 22' situation in which a 'no response' resulted in cancellation of registration, or the cost of data development for response was greater than market returns, or the data submitted might be judged inconclusive or, worse still, self-incriminatory. To others, the RPAR process was a bureaucratic 'black-hole' into which data flowed, but out of which no decisions ever emerged; yet, marketing of the suspect chemical continued while the issue was debated.

The RPAR actions against the liquid fumigant components were taken nearly 20 years after

passage of the Miller Law in the 1950s which made illegal the use of any chemical which left harmful residues in the grain. Joint industry/government residue studies (Lynn and Vorhes Jr. 1957) during that period had concluded that the common fumigant chemicals would 'not carry through into finished ready-to-eat foods and that residues present in the grain immediately following treatment bore little relationship to levels which would exist at milling or feeding'. What changed with time was not the policy of 'no harmful residues', but the analytical skill in detecting residues. Today, the limits of quantitative analysis in chemistry have improved a million-fold due to advances in instrumentation and methodology. As a result, fumigant residues previously judged as not present became readily detectable at the part per billion (ppb) and part per trillion (ppt) levels.

### **Deregistration of EDB**

Following discovery of EDB residues in groundwater associated with soil fumigations and the reporting of EDB per se, rather than as inorganic bromide residues in milled cereal grain products (Rains and Holder 1981), pressures mounted on EPA to cancel registration of the chemical compound. In fact, most of the manufactured EDB was used primarily as an additive in leaded gasoline with less than 10% of production (ca 20 million pounds or 9.1 million kilograms) used for agriculture purposes. Furthermore, about 90% of agriculture use of EDB was as a pre-plant treatment injected into the soil to protect crops from attack by nematodes. The remaining EDB was used in programs to fumigate citrus and other fruits and vegetables under quarantine programs and in admixture with other fumigant compounds for the treatment of stored grain and milling equipment. Only about one-fourth of the liquid fumigants marketed contained any EDB. When present, it generally constituted 1.2 to 7.4% by weight of the liquid mixture. The total amount of EDB formulated fumigants marketed was sufficient to treat only about 2% of the grain volume handled annually through the US grain marketing system (Storey 1983).

Although the justification for the 'emergency' nature of the action which suspended all uses of EDB is still open to question, the aftermath of the decision became all too readily visible. Nightly pesticide accounts on the evening news

from each major network, TV pictures of grain-based milled products being removed from grocery shelves, and the characterisation of products as 'contaminated' following analyses of questionable reliability took a heavy toll in consumer confidence in food safety. It also placed much of the cereal food industry in a defensive position and was likely a major factor in speeding up EPA's subsequent review of the remaining fumigant materials. After decades of relative obscurity, the act of fumigation and the chemicals used in the process were suddenly thrust into public attention. Although the media blitz soon waned, the public perception of pesticide use on food was clearly affected. A survey conducted by the Food Marketing Institute on consumer attitudes toward foods revealed that concerns about pesticide residues had largely replaced previous concerns about food additives in general or such traditional food concerns as cholesterol, sugar, and salt.

### **EPA Fumigant Registration Requirements**

Following suspension of EDB, the Agency supplemented the RPAR process with a 'Data Call-in Notice' which reviewed existing scientific data concerning fumigants and identified essential but missing information which may not have been available or required when individual fumigant materials were initially registered. The Data Call-in Notices essentially told fumigant registrants what new information would be required for continued registration of their product and of the need to establish a specific timetable for submitting the data.

EPA also developed a 'Label Improvement Program for Fumigants' designed to help minimise occupational exposure to fumigants. The program stipulated changes in fumigant label information and in fumigant use that would require two trained persons be present during the principal fumigant operation, required the use of approved respiratory devices when concentrations of fumigant exceeded a prescribed level or were unknown, and required specified direct-reading detector devices to monitor fumigant concentrations to prescribed levels as a condition of reentry into fumigated areas or following transfers of treated grain.

Data required under the Data Call-in Notice for the three major liquid fumigant components

(carbon tetrachloride, carbon disulphide, and ethylene dichloride) included product chemistry, analytical methodology and residue, teratogenicity, and reproduction and oncogenicity studies. The general reaction of most registrants of these fumigant materials was that the costs of developing the data to satisfy the registration requirements far exceeded the total profit that could reasonably be expected from these products for the subsequent 5–10 years. As a result, none of the registrants agreed to supply the necessary information and instead requested voluntary cancellation in lieu of complying with the additional data requirements. Not a shot was fired or a prisoner taken—the battle was over before it began.

When the end came for these materials their loss was not nearly as critical as it appeared. In part, because liquid fumigants had already lost a substantial share of the fumigant market to aluminium phosphide fumigants and, in part, because the ongoing EPA questions about their continued registration were being translated into rumours and a pervasive feeling of uncertainty about 'what's next on the list'. As a result, there was abandonment of pest management strategies featuring liquid fumigants well before they were 'officially' cancelled.

### **Guidance for Reregistration of Fumigants**

Following cancellation of liquid fumigants, EPA combined information developed in the various registration programs for each of the three remaining fumigants (methyl bromide, chloropicrin, and aluminium/magnesium phosphide) into a single reregistration document for each material: 'Guidance for the Reregistration of Pesticide Products Containing Chloropicrin as the Active Ingredient, Sept. 1982; Guidance for the Reregistration of Pesticide Products Containing Methyl Bromide as the Active Ingredient, Aug. 1986; and Guidance for the Reregistration of Pesticide Products containing Aluminium or Magnesium Phosphide as the Active Ingredient, Oct. 1986.' The documents provide a step-by-step outline of EPA's assessment of the scientific database for each fumigant, evaluate the potential hazards associated with registered uses of the material, determine what additional data are required on health and environmental effects, and review the adequacy of label information.

### **Chloropicrin**

The guidance document for chloropicrin requires that residue chemistry data resulting from postharvest use in stored grain be developed. Specific toxicology data may also be required if significant residues are detected and a residue tolerance will have to be established. Industry support for chloropicrin's use as a soil fumigant is being developed, but only one registrant has indicated a commitment to develop the necessary data for grain use. The present deadline for submitting the required residue data is 1 July 1989

Until the question of reregistration is settled, users of chloropicrin are subject to the limitations and conditions inherent in its 'restricted' classification. Furthermore, if the concentration of chloropicrin in work areas, as measured by an approved detection device, exceeds 0.1 ppm (0.7 mg/m<sup>3</sup>) an approved air purifying respirator for organic vapours or a self-contained breathing apparatus (SCUBA) or combination air supplied/SCUBA respirator must be worn. No treatments are to be permitted when commodity temperatures are below 40°F (5°C). Finally, when treated commodities are transferred to another site without adequate aeration, warning notices must be erected at the new site until the commodity is aerated below the prescribed threshold concentration. Degassing chloropicrin fumigated commodities is a monumental task and problems have repeatedly surfaced involving rail cars of grain containing high gas concentrations but no warning notices. Demurrage costs resulting from having to set the cars aside and fines for transporting cars with no warning notices displayed may well curtail the future use of chloropicrin irrespective of EPA's eventual reregistration decision.

### **Methyl Bromide**

A summary of the data requirements for reregistration of methyl bromide is as follows:

Methyl bromide major data 'gaps'

#### *1. Toxicology database*

- subchronic inhalation studies in rat and rabbit
- chronic feeding trials in rat and dog
- mutagenicity (bone marrow, DNA synthesis)
- teratogenicity in rabbits

- worker exposure monitoring (dermal and inhalation)

## 2. Tolerances (*residue chemistry*)

- residue data on methyl bromide, per se
- metabolism in plants
- acceptable daily intake (ADI) for methyl bromide, per se

## 3. Efficacy

- minimum application rate under high and low pest severity.

In response to these extensive requirements, the Methyl Bromide Industry Panel began negotiations with EPA for the development of alternative data and for substitution of some toxicology data already completed. Tests by the panel are also in progress to establish worker exposure information specific to bulk grain fumigation. Additionally, the panel petitioned EPA for the establishment of tolerances for methyl bromide per se in or on several commodities, including cereal grains (except maize) at 0.3 ppm (2.1 mg/m<sup>3</sup>) and maize at 2.0 ppm (14 mg/m<sup>3</sup>) (EPA 1986). In an effort to gain support for reregistration, the Methyl Bromide Industry Panel told user groups that the postharvest market was relatively small (ca 2 million pounds or 908 000 kg) and that limited money was available to develop the required data. Recent statements by the Methyl Bromide Industry Panel indicate that methyl bromide users are cooperating to help supply data to satisfy the 'gaps' still existing.

Interim use requirements for methyl bromide designate it a 'restricted' use pesticide and establish a guideline for respiratory protection and applicator/worker safety requiring a self-contained breathing apparatus or combination air supplied/SCUBA respirator when methyl bromide concentrations exceed 5 ppm (35 mg/m<sup>3</sup>) or are unknown. Applications of methyl bromide require the presence of two trained persons during fumigant introduction and no treatments are allowed when commodity temperatures are below 40°F (5°C). Transfers of treated commodities require warning signs to be erected at the new site until it is established that methyl bromide concentrations have been aerated below the threshold limit.

## Aluminium/Magnesium Phosphide

Aluminium/magnesium phosphide major data 'gaps' identified are:

### 1. Toxicology database

- subchronic inhalation studies in rats
- teratogenicity test in (1) animal species
- mutagenicity battery
- worker exposure information (monitoring of all work activities where exposure is possible)

### 2. Generic product chemistry

- physical and chemical characteristics (bulk density, oxidising-reduction information, flammability, storage stability).

An organisation of 'metal' phosphide registrants in the US has agreed to jointly support development of the required data and partial requirements submitted under the reregistration process are now under review by EPA.

The present operational requirements for aluminium/magnesium phosphide use establish the 'restricted' classification and require that an approved respiratory device be worn if exposure is likely to exceed the eight hour time-weighted average (TWA) of 0.3 ppm (2.1 mg/m<sup>3</sup>) during application, or a 0.3 ppm ceiling at any time during fumigation or upon reentry into fumigated areas after they have been aerated. It is also recommended that hydrogen phosphide concentrations should be documented for each type of routine fumigation performed where worker exposure could occur. The agency originally set the exposure limit at 0.1 ppm (0.7 mg/m<sup>3</sup>), but decided to leave the exposure at the previously established 0.3 ppm limit until a review of the required toxicology data is completed. For concentration levels up to 15 ppm (105 mg/m<sup>3</sup>) a full-face gas mask/hydrogen phosphide canister combination may be used. Above this level or in situations where the hydrogen phosphide concentration is unknown, an approved self-contained breathing apparatus or its equivalent must be worn.

## Future of Fumigant Use

The future of fumigant use may be characterised as being composed of three basic components:

- technical factors;
- regulatory policies; and
- cost/benefit/risk relationships.

*Technical factors* include developments in fumigant formulation and application/distribution methodology (such as presented in the conference) that provide for more effective and efficient, and safer methods of utilising fumigant chemicals. Developmental progress in these areas is absolutely essential to retaining fumigation as a primary management tool, but such technical factors alone are not the 'tail that wags the dog'.

*Regulatory policies* are both a bureaucratic minefield and an environmental necessity. Fumigant chemicals are indeed highly toxic and hazardous to use. And, whether out of ignorance or indifference, fumigant misuse has occurred. EPA's regulatory policies are now establishing the ground rules of what chemicals may be used, what commodities may be treated, the conditions of treatment that must be met, and the training requirements necessary for licensing individuals who apply or supervise application of fumigants. Above all else, these regulatory policies and guidelines are establishing accountability, which in many respects has been lacking in the past. EPA's fumigant regulation is also an open-ended process. Revelations in fumigant residue chemistry or toxicological links to cellular dysfunction, irrespective of its actual medical significance, can quickly escalate the 'cost' of retaining fumigant registration in terms of both monetary expenditures for data development and in public/user confidence in the safety of the fumigant material. Despite its precarious existence, fumigation is still authorised and extensively used in the U.S. We expect it to continue to be a mainstay for pest management in stored grain in the years to come. Still, nothing is forever—especially fumigant registration by the Environmental Protection Agency.

The third component of fumigant use—*Cost/Benefit/Risk Relationships*,—is perhaps the most important interacting combination of factors affecting the likely future use of fumigants. Tighter control on fumigant application procedures requiring additional investment in monitoring devices and safety equipment, together with expanded formats for training, record keeping, and misuse penalties will

clearly influence both commercial and private fumigators. However, the dominant factor affecting fumigation costs and decisions on fumigant use may well be the rapidly escalating liability insurance costs for fumigant applicators and marketers. Rate increases reportedly as high as 500% have occurred in recent years and many in the fumigant industry question whether fumigation services, particularly in rural areas, will be available in the future. The attendant expenses in travel, labour, materials, safety equipment, and liability coverage involved in servicing grain storage accounts presents a situation where the 'costs' of fumigation are being pushed well beyond the current discount penalties assessed by grain buyers for the presence of insects in grain deliveries. Under marketing practices where the benefits derived from reducing insect losses and improving grain marketability are not easily recognised or tabulated in monetary terms, rationalising the increased cost of treatment may be difficult. Furthermore, the nearly exclusive emphasis on the negative risk aspects of fumigant use has justifiably raised questions of whether fumigation benefits are worth the personal and corporate 'risks' involved. It is likely a valid observation today, to suggest that fumigation decisions in the cereal food processing industry that were once the prerogative of the sanitation departments are now being made in the boardrooms and legal departments of the companies. The ghost of EDB lingers on!

### **Controlled Atmospheres: EPA Registration Policies**

Because of the nonproprietary nature of controlled atmospheres, the Pesticide Petitions requesting exemption for carbon dioxide, nitrogen, and combustion-product gas from the requirement of a tolerance on raw, dried, and processed agricultural commodities (EPA 1980, 1981) were submitted by the U.S. Department of Agriculture rather than by individual gas companies or equipment manufactures. In response to the petitions, EPA concluded that the usual data requirements (toxicology studies, metabolism studies, analytical methods, residue data) for pesticide petitions were not applicable to the three atmospheres and would therefore be waived. Following establishment of the exempt status, gas suppliers were furnished with registration guidelines and directions for

developing labels for their specific gases. Several carbon dioxide suppliers have now registered and labelled their gases, but no nitrogen labels have been registered to date.

The original plan for registering combustion product gases was to label the use of the inert gas generator as a 'device' since generation of the atmosphere was 'on site' rather than transported to the site as with carbon dioxide or nitrogen gases. EPA concurred that the generator was indeed a device, but then further declared that, as a device, it was not subject to registration under the Federal Insecticide, Fungicide and Rodenticide Act (Miller 1982). At present, the generators and their use locations are being recorded as pesticide production sites. As the list of 'devices' (gas diffusion membranes, pressure swing adsorption units, internal combustion engines, etc.) proliferates in the future, it is likely that EPA will have to further revise its registration guideline for controlled atmospheres.

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# Use of Controlled Atmosphere and Fumigation as a Management Tool for Grain Stocks: the Problems and Prospects

R.J. Delmenico\*

## Abstract

Co-operative Bulk Handling Limited, the grain Bulk Handling Authority for Western Australia, has a total grain storage capacity of 10.4 million tonnes. Since 1980 the company has initiated a policy of progressively sealing grain storages to maintain stocks free of insect infestation at substantially reduced levels of pesticide residues, by the use of controlled atmospheres and fumigants. Fumigation is also extensively used in PVC covered storages. It is acknowledged that the quality and condition of grain currently received in Western Australia is compatible with CA storage and that any future changes in receival standards, such as higher grain moisture tolerance, may influence pest control strategy. The paper discusses the operational advantages, problems and strategy associated with the reliance on the use of controlled atmospheres and fumigants on a large scale and the prospects of such a system for the future.

Approximately 90% of Western Australia's grain production is received into the central storage system as it is harvested over the months of November and December. Grain temperature is within the range 28°–32°C when the commodity is put into storage. With a typical Mediterranean-type climate, the storage of large volumes of bulk grain over substantial periods of time offers a favourable environment for development of populations of a range of stored product insects.

Before 1980 Co-operative Bulk Handling Limited relied almost entirely on the wide-scale use of organophosphorous grain protectants, with a limited use of fumigants at export terminals, to maintain grain stocks free of infestation. It was from 1980 that the company initiated a policy of progressively sealing existing storages to allow the use of controlled atmospheres or fumigants and started to augment capacity with PVC covered storages suitable for fumigation. This fundamental change in stored product pest control was prompted by the following circumstances:

- An increase in the level of insect resistance to broad-spectrum and relatively inexpensive protectants.
- The high cost of alternative, second generation protectants, such as the pyrethroids.
- An increased reluctance by domestic and international markets to accept grain containing pesticide residues.

To date, of a total storage capacity of 10.4 million tonnes, Co-operative Bulk Handling has approximately 6.8 million tonnes (Table 1), or 65%, that exclusively uses either controlled atmosphere or fumigation as the control measure.

Changes to control strategy introduced since 1980 have significantly altered the management of grain stocks.

## Storage Hygiene

Before intake of new season's grain, unsealed storages are thoroughly washed to remove accumulated grain residues and dust. A residual insecticide is then applied to the storage fabric. While necessary, this procedure is expensive in terms of labour and resources, and may not always be possible where there is insufficient time between emptying the storage and receival of new season's grain.

\*Co-operative Bulk Handling Limited, 22 Delhi Street, West Perth, Western Australia 6005.

An advantage with CA storages is that all background insect populations are eradicated during treatment. Pre-harvest hygiene in these storages is now confined to ancillary handling equipment and the removal of grain dust only where there is sufficient quantity to produce a potential fire or explosion hazard.

The physical barrier these storages provide (once sealed) against external reinfestation offers the added advantage of not having to implement comprehensive and expensive herbicide treatments around them to eliminate potential harbours for insects.

The physical barrier is also effective against rodents. Consequently, control programs and the quantity of rodenticides used have both declined in recent years.

CA storage, by total exclusion of birds, has completely eliminated contamination of bulk stacks from this source, although flocks of one of the native parrot species have occasionally caused considerable and expensive damage to external sealing membranes. As a consequence, changes have been made to sealing techniques to reduce shielding urethane foams where they have been utilised externally.

A recent survey indicated that the use of CA storages had, since 1980, realised some \$2 million savings in the company's expenditure towards storage hygiene

## Grain Protectants

Previously, all grain received into the central storage system was treated with a grain protectant. Detailed storage planning and staff training were required to ensure uniform treatment, with different maximum residue limits (application rates) and protectants to meet market requirements.

With CA storages there is no need for protectant application equipment (pumps, vats, solenoids, nozzles, etc), or for additional trained staff to ensure correct application. The costs associated with purchase, storing, stock-taking, and distribution of protectants, and the provision and maintenance of application equipment, have dramatically decreased as the proportion of CA storages has increased.

An indication of the decrease in the usage of grain protectants can be demonstrated (Fig. 1),

**Table 1.** Storages exclusively using controlled atmosphere or fumigation: 1979–1988 (capacities shown in tonnes).

		Vertical	Horizontal	Sub-totals	Totals
1979	Seaboard	2 200		2 200	2 200
1980	Country		69 000	69 000	69 000
1982	Country	95 000	453 900	548 900	548 900
1983	Seaboard		285 800	285 800	
	Country		394 600	394 600	680 400
1984	Seaboard	106 600	182 400	289 000	
	Country		530 900	530 900	819 900
1985	Seaboard	238 350	100 000	338 350	
	Country		360 500	360 500	698 850
1986	Seaboard	50 600	365 800	416 400	
	Country		415 400	415 400	831 800
1987	Seaboard	28 600		28 600	
	Country		191 200	191 200	219 800
1988	Seaboard	22 000		22 000	22 000
	<b>Total</b>	<b>543 350</b>	<b>3 350 400</b>		<b>3 893 750</b>

To the end of 1988 figures show:-

1. Country ('Inland') storage capacity sealed	= 2 511 400
2. Seaboard installations total capacity sealed	= 1 382 350
Total sealed storage capacity	= 3 893 750
Total PVC covered storage capacity	= 2 963 300
Grand total	= 6 857 050

with usage for 1988–89 expected to be only 20% of that in 1985–86.

The advent of CA storages has also enabled the continued use, in non-CA storages, of less expensive protectants such as fenitrothion. There is no doubt that, with a system relying solely on grain protectants, Co-operative Bulk Handling Limited would, through increased levels of insect resistance, have had to utilise more expensive alternative protectants.

## Resistance

While each grower's load continues to be sampled for grain insect infestation when delivered to storage, the consequences of undiscovered infestations are greatly diminished if the grain is allocated to CA storages.

Furthermore, the level of 'on-farm' insect resistance to grain protectants has less impact on grain protection strategy as the number of CA storages increases.

An increase in the level of on-farm resistance to phosphine is of some concern in Western Australia. The State Department of Agriculture is conducting an on-going survey of on-farm phosphine resistance. Preliminary results show an increase from 4.5% (71 of 1581 farms surveyed) in 1982, to 20.5% (92 of 448 farms surveyed) in 1986. The extent and significance of this increase is difficult to determine in the absence of comprehensive survey data. There is, however, evidence to suggest that recent

sampling has been biased toward farms with a poor hygiene record, or where it is known inadequate on-farm fumigations have been conducted.

At this stage phosphine resistance levels are low and infrequent and can be readily controlled with the existing phosphine dosage and exposure regime.

Versatility and economics lead to the extensive use of phosphine as the preferred material. Nevertheless, at additional cost, existing CA storages can utilise other gases. Extensive field trials have been conducted using methyl bromide, carbon dioxide, and nitrogen. Comparative costs per tonne of each treatment are: phosphine \$A0.02; methyl bromide \$A0.22; carbon dioxide \$A0.10; nitrogen \$A0.60.

## Storage

Grain stored in bulk or bags is prone to moisture migration and subsequent spoilage. Primary factors influencing the rate of moisture migration are the grain moisture content at harvest and the temperature gradients experienced during storage. Storages in Western Australia are predominantly horizontal and up to 300,000 tonnes in capacity. With 'surface-only' techniques being used, and thermal convection relied upon for uniform distribution of gas, minimum exposure periods prevail for four weeks and frequently much longer if the grain is not required for out-loading.

Fortunately, Western Australian grain is relatively dry when harvested (less than 12% moisture content) and storage losses resulting from moisture migration are rare. Therefore, grain can be stored for prolonged periods while under fumigation with the confidence that quality will be maintained.

Typically, a Western Australian country CA storage will be fumigated in January and the grain inspected or sampled in April or May. Should the grain not be required for outturn in the immediate future, the storage will then be refumigated and held, in a sealed condition, pending movement. It is unusual for such storages to be fumigated more than once in 4–5 months, or more than twice over 8–10 months.

Similar strategies are adopted in horizontal storages at export terminals where this need for prolonged exposure periods requires careful planning and placement of grain stocks. However, vertical cells at terminals are

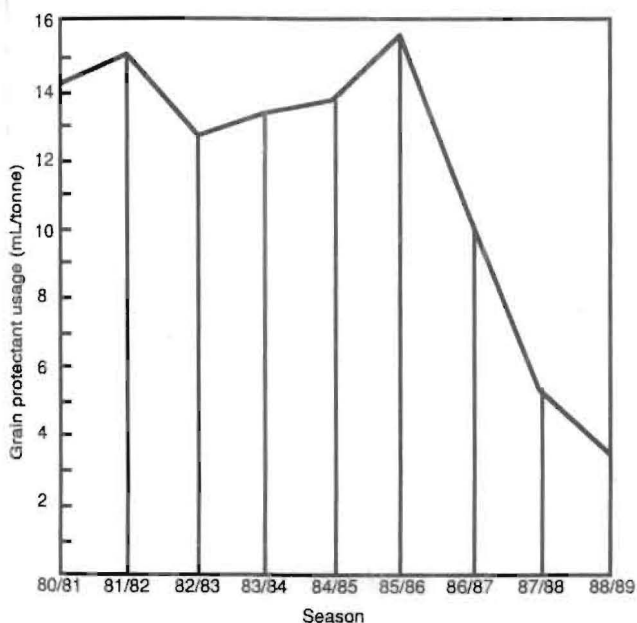


Fig. 1. Grain protectant usage in Western Australia over the period 1980–81 to 1988–89.

equipped for recirculation allowing for shorter minimum exposure periods of 7–10 days with phosphine, and 14–20 days with carbon dioxide.

Difficulties in the use of CA and fumigation occasionally arise in large horizontal storages, particularly those at export terminals. Until these storages are full—and this can take from several weeks to several months—the grain is subject to insect infestation. Coupled with the prolonged exposure periods required, grain may not be available immediately after harvest from country installations; or to meet unexpected shipping commitments from export terminals.

Similarly, the length of time it takes to outload, particularly if outloading is intermittent, can require a refumigation due to infestation from external sources.

Front-end loaders are normally used for outloading horizontal storages. The resultant atmosphere of grain dust and exhaust gases make mechanical ventilation of storages and respiratory protection for drivers essential.

Productivity and efficiency are markedly affected by 'down-time' resulting from mechanical or electrical failures. Co-operative Bulk Handling runs a comprehensive routine preventative maintenance program. The long exposure periods of CA storage mean that for much of the year equipment is unavailable for

maintenance. Accordingly, maintenance programs must now be scheduled and coordinated to coincide with times when it is safe to enter these storages.

It should be emphasised that the advent of CA storage has necessitated a fundamental change to storage strategy. Grain in these storages is now fumigated as a matter of routine and as an integrated quality control measure. Previously, fumigation was used as a last resort where infestation could not be controlled by other methods. Frequently, it was the end result of constant turning of grain prior to export, a strategy that is now largely obsolete with consequent savings in resources and an increase in productivity.

## Sampling

In the past, grain in Western Australian country storages was physically inspected on a weekly basis. Additionally, representative samples were drawn bi-monthly for residue analysis and, in the event of insect infestation, further samples were required for insect resistance testing. Following the introduction of CA storage, the need for intensive sampling has been much reduced, with consequent better utilisation of labour and laboratory resources, and a reduction in costs.

Nevertheless, problems can occasionally occur

**Table 2.** Number of pesticide residue tests undertaken in Western Australia, 1978–88.

Season	Organo-phosphates	Biores-methrin	Organo-chlorines	Carbaryl	Pyre-thrins	Misc.	Year total
78–79	9 490	628	99	262	–	–	10 479
79–80	12 538	2007	62	231	12	17	14 867
80–81	6 104	587	69	115	28	65	6 968
81–82	8 222	405	10	10	110	52	809
82–83	5 935	131	27	–	25	8	6 126
83–84	8 147	269	112	–	73	154	8 755
84–85	8 114	350	70	2	5	75	8 616
85–86	8 844	785	20	–	–	40	9 689
86–87	7 847	162	71	–	45	130	8 255
87–88	7 792	65	212	2	7	32	8 110
Grand total	83 033	5389	752	622	305	573	90 674

**Organophosphates** include fenitrothion, malathion, chlorpyrifos-methyl (Reldan), dichlorvos (DDVP), pirimiphos-methyl (Actellic), and etrimfos.

**Miscellaneous** includes deltamethrin, s-methoprene, piperonyl butoxide, carboxin, fenvalerate, and 2,4,5-T.

where samples of grain are required and cannot be readily obtained because the storage is being fumigated. Fortunately, such samples are seldom required as accurate data are kept on quality characteristics of the grain in each storage.

## Pesticide Residues

The CA and fumigation regime has permitted flexibility in preparing cargoes to meet stringent and diverse overseas and domestic market requirements as regards levels of pesticide residues.

Depending on destination, these requirements can range from total acceptance of CODEX Maximum Residue Limits (MRLs) to a virtual 'nil tolerance' for any level of pesticide residue.

The volume of nil residue grain now resulting from CA storages provides sufficient stocks to supply markets requiring nil residues. Additional flexibility is provided through blending of treated and untreated grain to meet any outturn standards. The Co-operative Bulk Handling has no problem in complying with CODEX MRLs.

The number of pesticide residue tests conducted by the company (Table 2) has remained fairly constant, with a slight trend downward, over recent years. This is despite increasing consumer concern over pesticide residues in food commodities (reflected in market specifications) and a significant increase in crop production over the last decade. The downward trend is expected to continue as more storages are modified for CA and fumigation.

## Handling and Transport

Rail transport is used to take some 70% of grain from inland receival points to seaboard export terminals. The remaining 30% is conveyed by road.

There are 321 CA storages and 186 PVC covered storages in the system and, consequently, more than 50% of all grain is not treated with a residual grain protectant. To prevent this grain from becoming infested during transport, particular emphasis is placed on the design and hygiene of all rail rolling stock and road transport vehicles.

In order to make best use of existing resources and improve efficiency, all of one type of grain is now loaded to each train (Block or Unit train) where possible. CA storages complement this system, as grain can confidently be outloaded

knowing it is free of infestation. The concept of total outloading means more effective use of CA and fumigation, rather than frequent treatment of progressively smaller stacks in a storage. The Block train concept, due to higher daily loading rates, also reduces the possibility of grain becoming infested during outloading.

In non-CA (unsealed) storages, outloading programs may be frequently interrupted due to previously undiscovered infestation and the need to implement remedial retreatment or fumigation. The sensitivity of some markets to specific pesticide residues also affects out-loading programs from non-CA storages.

All major Western Australian export terminals have a combination of integrated vertical and horizontal storages, with a significant proportion adapted for CA or fumigation. The success of this strategy is reflected in the decline, in recent years, in the number of shipping rejections due to insects (Table 3).

The years 1976-77 to 1978-79 indicate the high rejection levels associated with the use of malathion only. The slight reduction in 1978-79 arose from the introduction of fenitrothion to treat approximately 50% of that year's crop.

The dramatic decline in rejection levels between 1978-80 and 1982-83 was the result of the total move to fenitrothion and the influence of inland CA storages.

The equally dramatic increases over 1983-84 and 1984-85 primarily arose from a lack of fumigation capacity at export terminals due to the unavailability of hydrogen cyanide and the unsuitability of storages at that time for controlled atmospheres or phosphine fumigation.

**Table 3.** Shipping rejections (insects) at export terminals.

Year	Tonnes exported	Insect rejections
Nov 76 - Oct 77	3 444 317	68
Nov 77 - Oct 78	3 884 222	64
Nov 78 - Oct 79	3 557 750	51
Nov 79 - Oct 80	4 350 094	22
Nov 80 - Oct 81	3 271 549	13
Nov 81 - Oct 82	4 798 618	8
Nov 82 - Oct 83	5 372 932	7
Nov 83 - Oct 84	5 012 538	27
Nov 84 - Oct 85	6 205 570	27
Oct 85 - Oct 86	5 829 644	7
Nov 86 - Oct 87	6 290 477	5
Nov 87 - Oct 88	4 043 760	6

The impact of the introduction of CA and fumigation capacity at export terminals is evident from 1985–86 onwards.

## Safety

The broadscale use of grain protectants requires hundreds of employees, both permanent and casual, to become involved in some aspect of the storage, distribution, mixing, and application of pesticides. At each and every stage, despite intensive training and close supervision, there is a risk of exposure to toxic chemicals.

CA storages have significantly reduced the number of sites where grain protectants are now applied, and the occupational hazards involved in their use have correspondingly declined.

Fumigations are conducted at country installations after the receival staff have left the site. At export terminals, CA storages are totally enclosed ensuring a safe working environment.

More than five million tonnes of grain are now fumigated annually in Western Australia by fewer than 50 fully qualified, experienced, and licensed specialists.

## Future

From the results of a study of the period 1980–81 to 1986–87, it was estimated that CA storage had saved Western Australian grain growers some \$30 million in additional expenditure. This was principally because there was no need to introduce more expensive, alternative protectants.

In the absence of further dramatic 'breakthroughs' in stored product pest control, it is Co-operative Bulk Handling's intention to continue, as finances allow, to modify all remaining 'sealable' storages to suit CA and fumigation.

While initial establishment costs are higher than current alternatives, they are quickly offset by considerably lower operating costs.

The confident ability to provide national and international trade with insect and pesticide-free grain is an added advantage in markets placing an emphasis on quality.

As previously stated, the company relies primarily on the use of phosphine and, to a lesser extent, carbon dioxide. Nevertheless, the industry is well aware that pesticides are under constant toxicological review, and many that

were previously considered suitable are now no longer available.

Similarly, as environmental concerns develop into major social issues, even the long-term future use of carbon dioxide cannot be assured.

Fortunately, Western Australian CA storages have been designed for other atmospheres (such as low-oxygen), although at this stage phosphine will continue to be used as the preferred material.

## Summary

This section of the paper provides a brief outline of the strategies applied at country in-stallations, in transport, and at export terminals.

### Country CA Storage

#### *September–October*

- Storage plans and allocation finalised according to estimated quantity of grain to be delivered; anticipated quality; anticipated term of storage (liaison with marketers).

- Storages prepared for forthcoming receivals. Maintenance completed; ancillary equipment cleaned (no use of pesticides).

#### *November–December*

- Grain received from growers—no grain protectants applied.

- Grain exceeding storage capacity is transported (rail or road) to export terminal.

#### *January*

- Grain receivals completed

- Ancillary equipment cleaned and accessible grain dust and residues 'blown-down' with compressed air.

- Storage entry points sealed and pressure test conducted.

- Storage fumigated

#### *February–May*

- Storage remains under fumigation with gas concentrations monitored weekly.

- In the event of grain being required for outloading, one weeks ventilation is necessary.

#### *May*

- At this stage gas concentrations have declined to very low levels or are 'nil'.

- Storage is ventilated followed by a thorough check of grain quality.
- Should grain have been partly outloaded previously, and program is complete, storage will be refumigated.
- Should grain be required for outloading within four weeks, storage will be resealed and checked weekly, but not refumigated.

#### *June–September*

- Gas concentrations continue to be monitored on a weekly basis until grain is required for outloading.

### **Transport**

On outload from country receival points, each rail wagon or road truck is clearly marked to indicate the grain type and quality, and whether it is untreated or treated (including the treatment rate).

When inloaded at an export terminal, the grain—through computer inventory control—maintains its identity until it is loaded to ship.

### **Export Terminal**

With the exception of Kwinana, all Western Australian export terminals receive untreated grain direct from growers. The proportion of this grain that is treated with a protectant depends primarily on:

- the CA storage capacity at each terminal and;
- market requirements for specific residue limits.

Grain received direct from growers and allocated to CA storage is fumigated as a routine procedure. Grain that is received following fumigation in a country CA storage, is not re-fumigated if it is scheduled for export within a period of 4–6 weeks.

After fumigation at a terminal, the grain is seldom ever refumigated and may remain in a sealed environment for up to six months, or until consigned to ship.

## **Conclusion**

No attempt has been made in this paper to describe all the circumstances that have varied following the introduction of CA storage on a large scale. Rather, the objective has been, by way of comparison, to give a broad outline of some of the major changes that have influenced operational management practices.

Under existing storage and handling strategies, the advantages of CA storage far outweigh the disadvantages. Nevertheless, should circumstances change (such as, for example, the need to store grain with high moisture content), then the current CA storage program could radically alter.

CA storages have provided an economic and versatile method of meeting increasingly stringent market requirements. However, the nature of the gases utilised, and the circumstances under which they are used, necessitate thorough co-ordination of all facets associated with the storage, transport, and outturn of bulk grain.

# Cost-Benefit Analysis of Stock Preservation Systems. A Comparison of Controlled Atmosphere and the Use of Conventional Pesticides under Operational Conditions in Indonesia

J.A. Conway\*, M.K. Mitchell\*, M. Gunawan\*, and Yusuf Faishal†

## *Abstract*

In attempting to adapt the cost-benefit technique as a management tool for general application to stock preservation systems, the data derived from the three-year operational experience of Badan Urusan Logistik (Bulog) with controlled atmosphere (CA) storage in Indonesia are used.

A financial cost-benefit approach is adopted in order to derive the Break-Even Month (BEM) for CA and conventional fumigation-based preservation systems for milled rice. The sensitivity of the results to a range of assumptions is determined for those factors considered to be of primary cost significance on the basis of operational experience of the two techniques. The limited actual data on valued benefits is placed in the context of the sensitivity of the BEM to benefit assumptions. The relevance of these results to other foodgrain marketing systems in the ASEAN region and the use of the BEM concept in evaluating CA for bagged storage systems elsewhere are discussed.

Development work in Australia in 1979 and on a larger scale in Indonesia in 1980 explored the technical feasibility of using controlled atmospheres containing introduced carbon dioxide for disinfecting sheeted stacks of bagged milled rice (Annis et al. 1984).

This work showed that the presence of the plastic sheets, or the levels of CO<sub>2</sub> retained, or a combination of the two factors, prevented reinfestation by insect pests for up to four months when the stacks were left sealed after the initial gassing. It was further demonstrated that initial rice quality was maintained without detectable deterioration for the 4-month trial period.

Operational scale work by BULOG in 1982 evaluated the possibility of maintaining initial

rice quality, in addition to disinfecting the stock and preventing reinfestation, for up to 16 months following sealing and gassing with CO<sub>2</sub> (Suharno et al. 1984). This initiative to explore the longer-term possibilities of the technique was stimulated by BULOG's desire to identify appropriate, longer-term, stock preservation systems. The agency was faced with a growing stock inventory, leading to slower turnover and increased risk of quality deterioration. The results of this later work indicated that the objectives could be achieved with the CO<sub>2</sub> technique, provided that the integrity of the sealed system was maintained throughout the storage period.

Still faced with heavy stocking pressure, BULOG placed 65,000 tonnes of milled rice under CO<sub>2</sub> at various locations in 1985 and maintained this stock successfully for 18-24 months. A program for 145,000 tonnes of stock under CO<sub>2</sub> for 1987-88 was subsequently scaled down to roughly 50,000 tonnes due to shortage of rice stock for long-term storage.

\*BULOG/ODNRI Development Project, c/- British Embassy, Jl. M.H. Thamrin, Jakarta, Indonesia.

†Integrated Planning Unit, Badan Urusan Logistik (Bulog), Jl. Gatot Subroto, Jakarta, Indonesia.



Annis and van Graver (1987), in proposing an Integrated Commodity Management Strategy for the ASEAN region, advocated a short-term (less than 9 months) approach based on admixture of chemical protectants with commodities. For periods of more than 9 months, the use of CO<sub>2</sub> in sealed stacks was recommended, although it was suggested that the definition of short or long term would be reduced as familiarity with sealed storage procedure increased. In Indonesia, although there are Pesticide Committee clearances for admixture of insecticides with commodities at the BULOG level, the bag handling system does not lend itself to cost-efficient admixture, therefore this technique is not adopted by BULOG.

BULOG's 'conventional' stock preservation system is based on quarterly fumigation of stock under gasproof sheets and a regime of routine application of contact insecticides to stack surfaces and warehouse structure. This system has been described as part of BULOG's Integrated Storage Pest Management (ISPM) program by Sidik et al. (1985). Under this regime, certain types of qualitative deterioration are inevitable if storage is prolonged, and ancillary problems such as physical losses, insecticidal residues, adulteration of stock, etc. assume significance.

## Comparison of Techniques

In terms of relative costs, the CO<sub>2</sub> technique is characterised by heavy initial expenditure followed by low maintenance costs for the remainder of the storage period. Conversely, the conventional regime requires a modest initial investment but involves higher maintenance costs reflecting the expensive pesticides required on a routine basis.

It was suggested in the earlier developmental work with CO<sub>2</sub> that costs for a one-year storage period were roughly equal to those of the conventional regime. This assumed that physical losses with the CO<sub>2</sub> system would be 50% of those estimated to occur with the conventional system. Later examinations of relative costs by BULOG suggested that, for storage periods in the 12-15 months range and beyond, CO<sub>2</sub> became economically viable. However, no assessment of the effect of benefits, if any, was made.

There is a wide range of possible benefits for the CO<sub>2</sub> technique. These can be

categorised into three groups:

(a) *Reduction in quantitative losses (actual weight losses) caused by:*

- shrinkage
- spillage
- pest attack
- pilferage etc.

(b) *Reduction in qualitative losses (loss of market value) due to changes in:*

- colour
- head rice yield
- texture
- moisture etc.

(c) *Difference in operational/environmental factors between the two systems:*

- working conditions
- exposure to pesticides
- labour demand
- pesticide residues etc.

This study concentrated on those benefits for which data were available and which were of primary significance to BULOG. These were comparative figures on quantitative and qualitative losses as just listed under (a) and (b).

Although it is clear that use of the CO<sub>2</sub> system confers considerable positive operational and environmental benefits such as those in (c), they are not at all easy to quantify in monetary terms. This is partly because within the BULOG storage system one or more storage units at a typical complex will be used for CO<sub>2</sub> and other units will continue to be used for conventional storage. After a period of use for CO<sub>2</sub> stock, a unit will revert to conventional use. Full equipment and staff inventories are therefore maintained even if, for the period of CO<sub>2</sub> usage, they are not required in a particular unit or group of units.

## Analysis and Results

The two categories of storage preservation system, conventional and CO<sub>2</sub>, involve different patterns of cost (expenditure) and benefit over time. However, in the BULOG context many of the costs of grain storage such as warehousing, or the interest charges on the capital embodied in grain stocks, are common to both systems. Under these circumstances, a discounting approach based solely on those items of cost or

benefit which are not common to both systems seemed appropriate. Also, from the perspective of BULOG management, a financial rather than an economic assessment was more relevant. Thus questions of shadow exchange rates and shadow wage rates are not addressed here. The methodology adopted is precisely that of financial cost-benefit analysis as described, for example, in Gittinger (1982) and numerous other texts.

**Costs**

The comparison of techniques is focused at the warehouse level. Overheads, management costs, etc. are assumed to be common to the two systems. Also, the costs associated with the procurement and storage of 3500 tonnes of bagged milled rice (corresponding to a standard BULOG warehouse), meeting BULOG's standard intake quality requirements, are assumed to be identical and are excluded.

Appendices 1 and 2 show examples of typical model outputs for an initial six-month storage period and illustrate cost components assembled.

As mentioned earlier, the essential difference between the two systems from a financial perspective is that the conventional approach involves relatively low initial costs, but relatively high operating costs, whereas the CO<sub>2</sub> system is just the reverse. Hence, for very short

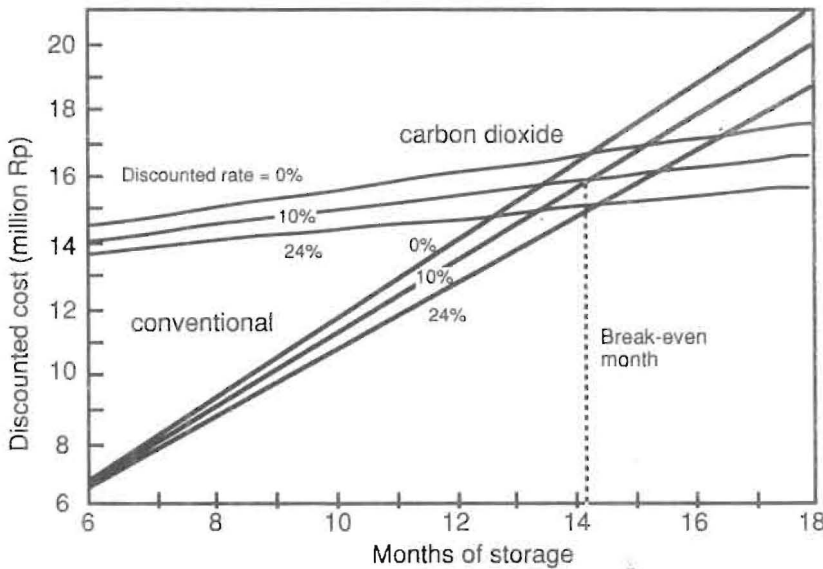
periods of storage the conventional approach is certain to be cheaper whereas, even if both systems were to provide equal benefits in terms of the quantity and quality of grain preserved, there will be a point of time in store beyond which the CO<sub>2</sub> technique will show a cost advantage. This point of time is referred to as the Break-Even Month (BEM). Figure 1 sets out the storage costs over time for the two systems under three assumptions concerning the discount rate. The costs were actually calculated for 6, 12, and 18 months of storage with intermediate values interpolated on a straight-line basis.

The three discount rate assumptions correspond to:

- (1) A non-discounted solution (0%)
- (2) A rate corresponding to BULOG's current financial situation (see below) (10%)
- (3) A realistic commercial rate in Indonesia (24%).

The main conclusion to be drawn from Figure 1 is that for the purposes of comparing conventional and CO<sub>2</sub> rice preservation systems in the BULOG context the discount rate adopted is not a critical factor. Even taking the difference between the two extreme cases (i.e. 0 and 24%) the impact on the BEM is minimal, corresponding to less than two weeks of storage.

From BULOG's financial perspective the inter-



**Fig. 1.** Comparative costs of BULOG stock preservation systems. Assumes 3500 tonnes in one warehouse, 50% RV for CO<sub>2</sub> plastic cover and base, and 5% probability of CO<sub>2</sub> failure.

est charged on government loans, specifically for rice, is 6%. Allowing for non-interest discounting of the future by BULOG management, 10% would seem a reasonable rate to use for internal management purposes and is adopted for the remainder of this paper.

Figure 1 could be interpreted as implying that, given the cost assumptions made, and in the absence of benefits, the CO<sub>2</sub> system would be appropriate only for rice for which the expected period in store exceeds 14 months. However, of the necessary assumptions, two were deemed both controversial and (probably) important enough to seriously affect the BEM. These were:

- (1) The residual value (RV) ascribed to the plastic cover and base (which will be termed the 'plastic enclosure') needed for CO<sub>2</sub> storage.
- (2) The probability that a given application of CO<sub>2</sub> would fail to maintain the necessary concentration of gas (e.g. due to leaks) and have to be repeated.

### The Residual Value of CO<sub>2</sub> Enclosure

The term residual value (RV) is used here to represent not the likely sale value of the CO<sub>2</sub> enclosure, but rather the reuse value to BULOG itself. Hence, an RV of 50% implies that, on average, all plastic enclosures would be used twice, 25% that, again on average, only half would be used twice, and zero percent that none would be reused or sold. In practice, the scrap value was assessed at 10%, and 67% taken

as the upper limit for RV (corresponding to use three times). Figure 2 indicates that the impact of the RV assumption on the BEM in the absence of CO<sub>2</sub> failure is substantial. For example, an assumption that only half the sheets could be used twice (RV = 25%) as against the assumption that, on average, all sheets would be used twice (RV = 50%) increases the BEM by 3.75 months.

This result demonstrates the high proportion of costs embodied in the purchase of the plastic enclosure.

Operational experience indicates that a figure of 50% RV is a reasonable working assumption and this has been adopted for the remainder of this paper.

### The CO<sub>2</sub> Failure Rate

The term 'failure' is used to describe the situation where some time after the introduction of CO<sub>2</sub>, monitoring procedures reveal an inadequate concentration of gas. It is assumed that a complete resealing and regassing will be required together with their associated costs.

Although the expected number of 'failures' might be assumed to decline as staff become more familiar with the sealing and gassing techniques, a proportion of failures is still possible, due to damage to the plastic enclosure either at time of gas application or during the storage period. Figure 3 sets out the effect of failure rate assumptions between 0 and 40%. Since the latter corresponds to two out of five sealing and gassing attempts resulting in failure, an even higher level would imply serious and

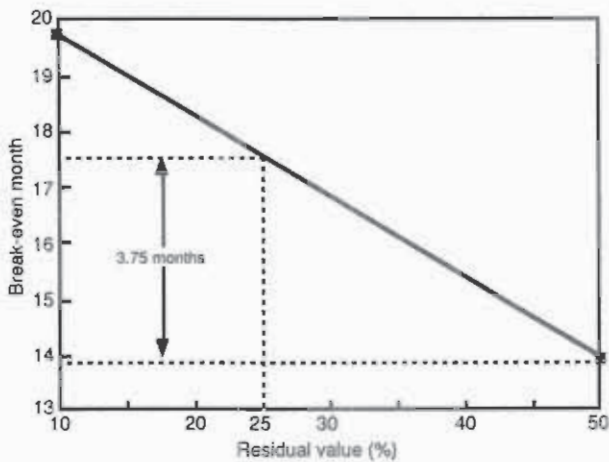


Fig. 2. Break-even month and CO<sub>2</sub> cover and base residual value. (Assumes 0% probability of CO<sub>2</sub> failure.)

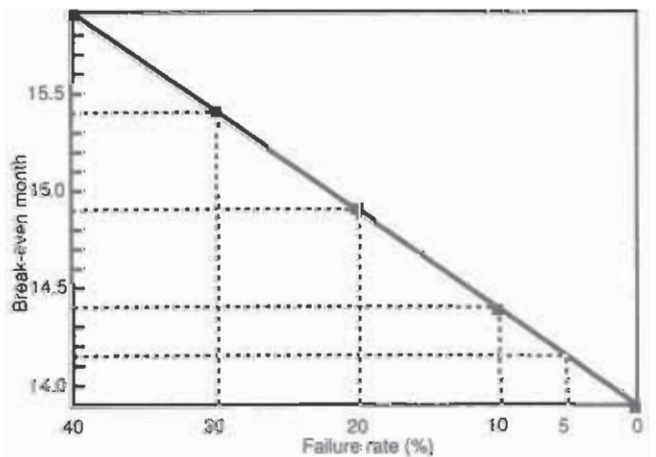


Fig. 3. Break-even month and CO<sub>2</sub> failure rate at 50% RV of CO<sub>2</sub> cover and base.

unacceptable management or technical deficiencies with the CO<sub>2</sub> technique.

From Figure 3 it can be seen that even this very wide range of failure rates corresponds to a variation in the BEM of just two months. Experience in BULOG operations would indicate that failure rates of 5–10% are realistic. This narrower range corresponds to less than 0.5 months differences in BEM. Hence, in situations where a fairly high level of technical and managerial control is achievable, the precise level of CO<sub>2</sub> failures is unlikely to critically affect the choice of preservation technique.

## Benefits

In approaching the benefits issue attempts were made to quantify, in monetary terms, differences in quantitative and qualitative losses. Other benefits, or indeed disadvantages, of CO<sub>2</sub> as against conventional systems could well be included in a full social cost–benefit analysis but that was beyond the scope of the work presented here.

As a first stage in assessing the impact of benefits certain assumptions were made to simplify the analytical procedure. These were that:

- (1) rice stored for periods of four months or less would be treated as 'fresh' by consumers and both weight and quality losses would be identical under the two systems; and
- 2) after four months, benefits (of one system over the other) would accrue equally for each additional month of storage.

Both these assumptions are arbitrary, but operational experience and the data collected to date do not provide evidence pointing to alternatives. On a priori grounds one might expect qualitative and quantitative losses to accelerate under conventional storage if fumigations were not 100% successful. Hence, interpreting losses recorded after substantial periods of storage as if they had occurred evenly over the period, probably exaggerates early period losses and understates those in the later period.

It may also be noted that while conventional storage might, in theory, demonstrate benefits over CO<sub>2</sub>, in fact, none has been observed to date. Hence, the term 'benefits' is used to refer

to qualitative or quantitative advantages of CO<sub>2</sub> over conventional storage expressed in monetary terms.

With these assumptions, the benefits of CO<sub>2</sub> storage can be expressed as a revenue stream, zero for months 1–4 and constant thereafter. The curve in Figure 4 describes the BEM for a range of benefit values expressed in rupiah per kilogram of rice stored per month.

As would be expected from algebraic considerations, benefits reduce the BEM but at a diminishing rate as the level of benefit rises<sup>1</sup>. As can be seen, even at very low levels of benefit, e.g. 0.2 Rph/kg/month, the impact on the BEM is considerable. This represents approximately 0.044% of the value of the rice per month or 0.53% per year, yet results in a reduction in the BEM of almost 4 months.

Figures were obtained on actual weights of intake and outturn, on an individual stack basis, in three storage complexes in East Java where stocks were held for comparable periods under both preservation systems. The results were used to derive a 95% confidence interval for the reduction in actual weight losses accruing to the CO<sub>2</sub> system.

Recorded losses under both concentration regimes were extremely low. The mean weight loss per month in store was only 0.0125% for 33 stacks under the conventional system and 0.0038% for 37 stacks under CO<sub>2</sub>. Although the means were significantly different at the 95% confidence level, the size of that difference (0.0088% of weight loss per month) is very small. At prevailing Indonesian prices of around Rph450/kg, this difference corresponds to a benefit of 0.039 Rph/kg/month.

A test-marketing was carried out at a major Jakarta wholesale market utilising stock from

<sup>1</sup> Consider the simple case where the discount rate is zero, and for conventional and CO<sub>2</sub> storage respectively, 'A' and 'B' are the initial costs and 'x' and 'y' the operational costs per month. Then if 'n' is the Break-Even Month, and 'a' the number of months after which CO<sub>2</sub> storage yields (equal monthly) benefits of value 'z'  
 $A + nx = B + ny - (n-a)z$   
 $n(x-y+z) = B - A + az$   
if  $k_1 = B - A$ ,  $k_2 = x - y$  and  $k_1, k_2 \geq 0$   
then  $n = (k_1 + az)/(k_2 + z)$   
and  $dn/dz = (ak_2 - k_1)/(k_2 + z)^2$   
hence assuming  $k_1 \geq ak_2^2$  (i.e. benefits start before the BEM) then  $dn/dz \geq 0$  and as  $z \rightarrow \infty$ ,  $dn/dz \rightarrow 0$  and  $n \rightarrow a$ .

both preservation systems, originating from an identical consignment and stored for 18 months in Jakarta storage complexes. In the test-marketing used for this study, it was considered that the two factors which contributed most to the higher retained value of the CO<sub>2</sub> stock were (a) whiteness and (b) hardness/texture of the milled rice. In some rice marketing systems, the quality factors conferring enhanced value will differ but a similar approach to their quantification may be adopted. The results indicate that benefits could be as high as 1.0 Rph/kg/month, i.e. approximately 0.22 per cent of the value of the rice, per month.

Figure 4 places these rather sparse data in the context of the potential impact of benefits on the BEM.

From these results it would appear that the cost-effective use of the CO<sub>2</sub> technique as an alternative to conventional storage depends heavily on the value ascribed to benefits.

## Discussion

It should be reemphasised that the results presented here are based on assumptions which were held to be valid for the public sector storage system in Indonesia. The results reflect the costs and benefits of the two preservation strategies compared under the prevailing cost structure and storage management practices within that system.

Management practices, as well as costs and benefits, may differ markedly in other countries.

These results must therefore be regarded as specific to Indonesia.

The results show that, without quantified benefits, the point at which costs for both CO<sub>2</sub> and conventional preservation systems are broadly equal (BEM) is at 14 months of storage, assuming a 50% RV and 5% CO<sub>2</sub> failure rate.

The BEM is shown to be very sensitive to the residual value placed upon the plastic cover and base used to form the gastight enclosure for the CO<sub>2</sub> technique. Therefore, the likelihood of damage to, or degradation of, this plastic enclosure is a critical factor in an assessment of the financial viability of the technique.

The opposite is true regarding the requirement to reseal and regas enclosures following failure to maintain a gas-tight seal. However, the minimal impact of this factor on the BEM reflects the wide availability and relatively low price of CO<sub>2</sub> in Indonesia.

Ascribing even relatively small monetary values to the benefits of the CO<sub>2</sub> system has a considerable impact on the BEM and hence on the choice of storage technique. The evidence currently available seems to indicate that if the value of benefits could be realised the BEM would be reduced dramatically, perhaps to around six months. This being the case, the quantification of benefits, especially in relation to rice quality, is critical if the organisation involved is in a position to realise such benefits in monetary terms. Where this is not the case, as for example in Indonesia where that portion of the national rice stock distributed to civil servants is sold to the government at a fixed

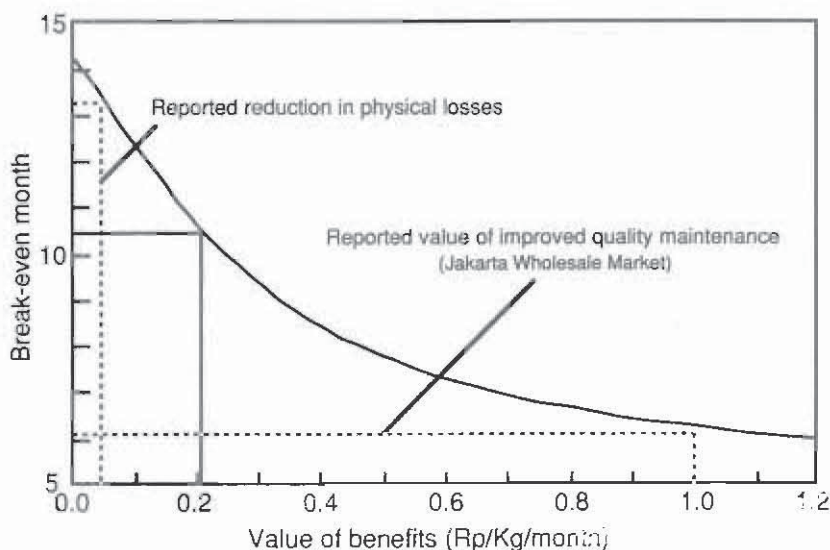


Fig. 4. Break-even month and the value of benefits.

price, the quality issue relates more to the potential benefit to consumers than to finance.

The physical losses incurred in both systems were very low and so therefore was the effect on BEM. Again, there will be many bagged storage systems where physical losses assume a much greater significance than in the BULOG system and where the combined effects of efficient pest elimination with the CO<sub>2</sub> coupled with a physical barrier, could produce substantial loss reductions.

The methodological framework developed here would seem to have wide applicability to public grain storage systems where a choice of preservation technique is available. The adoption of the cost-benefit framework helps to identify data requirements and indicates the relative importance of difference costs and benefits. This in turn points to the areas where further research is most needed from the management perspective.

### Acknowledgments

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Appendix 1. Costs—CA System. Example of typical model output for a six month storage period.

Assumptions

1 Tonnage treated	3500
2 Storage period (months)	6
3 Discount rate/year	10%

Costs (Rph)

Item		Item		Residual Value
		10	Plastic cover	10,319,400 50%
4 Cost of labour (Rph/day)	1,000	11	Plastic base	4,620,000 50%
5 Skilled labour (Rph/day)	5,000	12	Sealing material	250,000 15%
6 Cost of supervisor (Rph/day)	2,000	13	Vacuum cleaner	750,000 90%
7 Electricity tariff (Rph/KWH)	750	14	Rodent proofing	250,000 90%
8 Interest rate/annum	6.00%	15	CO <sub>2</sub> meter	800,000 90%
9 Bank admin. charge(InitialLoan)	0.50%	16	Sundry cleaning	10,000
		17	Rodenticides	2,000
		18	CO <sub>2</sub> gas Rph/Kg	569

No. Description Initial cost (Rph)

1	Plastic cover	10,319,400
2	Plastic base	4,620,000
3	Sealing material	250,000
4	Vacuum cleaner	750,000
5	Rodent proofing	250,000
6	CO <sub>2</sub> meter	800,000
7	Sundry cleaning	10,000
8	Cleaning godown	70,000
9	Sheeting stacks	200,000
10	Sealing & pressure testing	7,000

Operational cost and residual value (Rph)

		Jan 88	Feb 88	Mar 88	Apr 88	May 8	Jun 88
1	Application CO <sub>2</sub>	0	4,183,988	0	0	0	0
2	Checking concentration and damage	0	50,000	5,000	5,000	5,000	5,000
3	Resealing	0	0	12,500	0	0	0
4	Regassing	0	0	209,199	0	0	0
5	Electricity	0	36,000	0	0	0	0
6	Rodenticides	0	98,250	0	98,250	0	0
7	Training	0	30,000	0	0	0	0
8	Removal plastic cover & base	0	0	0	0	0	50,000
9	RV Plastic cover	0	0	0	0	0	(5,159,700)
10	RV Plastic base	0	0	0	0	0	(2,310,000)
11	RV Sealing material	0	0	0	0	0	(37,500)
12	RV Vacuum cleaner	0	0	0	0	0	(675,000)
13	RV Rodent proofing	0	0	0	0	0	(225,000)
14	RV CO <sub>2</sub> meter	0	0	0	0	0	(720,000)
15	Interest on initial loan	0	86,814	86,814	86,814	86,814	86,814
16	Bank admin. charge on initial loan	86,382	0	0	0	0	0
17	Interest on working capital	0	21,991	1,133	516	25	275
	Total outflow	17,362,782	4,507,043	314,647	190,580	91,839	(8,985,111)
	Present value of cost		13,940,213				
	Benefit (Rph/kg/month) 0.1	0	0	0	0	350,000	350,000
	Net Outflow	17,362,782	4,507,043	314,647	190,580	91,839	(258,161)
	Net present cost		13,270,128				(9,335,111)

Appendix 2. Costs—Conventional System. Example of typical model output for a six month storage period.

Assumptions Conventional by contractor & BULOG

1 Tonnage treated	3500
2 Storage period (months)	6
3 Discount rate/year	10%

Costs

Item		Item	Rph
4 Cost of labour (Rph/day)	1,000	10 Fumigation Eq./Set	912,400*
5 Skilled labour (Rph/day)	5,000	11 Power Sprayer	1,500,000
6 Cost of supervisor (Rph/day)	10,000	12 Fumigant/kg.	77,850
7 Electricity tariff (Rph/KWH)	750	13 Insecticide/litre	79,860
8 Interest rate/annum	6.00%	14 Fumigation fee Contractor/Ton	399
9 Bank admin. charge(Initial loan)	0.50%	15 Spraying fee Contractor/m <sup>2</sup>	25
		16 Spraying fee Dolog/m <sup>2</sup>	2

No Description	Initial cost (Rph)	Jan 88	Feb 88	Mar 88	Apr 88	May 88	Jun 88
1 Fumigation equipment	0	91,200	0	0	91,200	0	0
2 Sprayer	1,500,000	0	0	0	0	0	0

Operational cost and residual value (Rph)

1 Fumigation cost by contractor	0	1396500	0	0	1396500	0	0
2 Spraying by contractor	0	208250	0	0	208250	0	0
3 Spraying—Damfin by Dolog	0	452359	452359	452359	452359	452359	452359
4 Spraying Fee by Dolog	0	11107	11107	11107	11107	11107	11107
5 Cleaning godown	0	20000	20000	20000	20000	20000	20000
6 Incidentals	0	10000	10000	10000	10000	10000	10000
7 RV Sprayer (95%)	0	0	0	0	0	0	(1425000)
8 Interest on initial loan	0	7500	7500	7500	7500	7500	7500
9 Interest on working capital	0	10947	2467	2467	10947	2467	2467
10 Bank admin. charge	7500	0	0	0	0	0	0
Total outflow	1507500	2207863	503433	503433	2207863	503433	(921567)
Sum of nominal cost	6511957						
Present value of cost (Discounted Cost)	6428948						

\* Including plastic sheet, sand-snakes and protective equipment.



# Needs for R & D in Fumigation and Controlled Atmospheres for Grain Storage

H.J. Banks\*

## *Abstract*

The main limitations for fumigation, at present, concern public health and environmental laws, and length of treatment time, and, for CA, cost and speed of action. Research needs to be aimed at overcoming these limitations if the technology is to progress. Controlled atmospheres are being considered as one of the alternatives to fumigation. With increasing concern over the possible effects of many chemicals, including fumigants, there is pressure to provide data to justify and improve existing fumigation practices, and to reduce the perceived and real potential hazards of use of highly toxic fumigants. There is a need to coordinate effort on environmental and public health aspects of fumigants internationally so appropriate data can be gathered quickly and avoid precipitate restriction or removal of these valuable materials from use. It is likely that there will be introduced, in the near future, a requirement for both personal monitors for workers close to fumigations and for scrubbers to remove fumigant from exhaust gases after treatments. The need for more rapid turn-around will force a reevaluation of fumigant regimes, perhaps leading to shorter treatments at higher dosages, particularly with methyl bromide. Reevaluation of currently permitted but nevertheless neglected fumigants—hydrogen cyanide and the formates—is overdue. CA research needs to provide means of creating and maintaining atmospheres cheaply and increasing their speed of action, particularly at low temperatures. The use of membranes, propane burners, and chemical absorbers for making low-cost, oxygen-deficient atmospheres on-site all show promise. There is a need for further research to define the limits of action of various atmospheres against specific pests and to develop systems for storage of intermediate moisture content (14-18%) grain.

FUMIGATION and controlled atmospheres (CA) are mature technologies. Both have been subject to much research and development (R & D) and are at a stage where application is largely routine. Opportunities for further development appear limited. Yet even now both techniques face some challenges. Fumigation in particular is under pressure from increasing restriction driven by concerns over public health and the environment, and the reaction of both markets

and workers to the use of highly toxic chemicals.

In some countries, e.g. West Germany, fumigations are so constrained by regulation as to be difficult to carry out, while in others, notably USA, the threat of litigation over possible effects of fumigants has led some industries to discontinue their use. Controlled atmospheres are now being considered as alternatives to fumigation. However, they are less convenient and familiar, and need some further development, particularly to reduce associated capital costs, before they can be regarded as competitive in most sit-

\* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

uations. This paper summarises the R & D needs for both fumigation and CA as applied to grain and, perhaps just as importantly, gives topics on which effort no longer seems required. A related analysis, focusing particularly on the needs for R & D for fumigation in the humid tropics, was given recently by Banks (1987). Note that there are many background data and development results available on CA and fumigation, though this may not always be recognised or easily accessible, with consequent wasteful duplication of effort. There is often more to be gained from efficient information retrieval and assimilation than from carrying out new trials or experiments. There is a continuing need for topical and thorough reviews to collect the widely dispersed data on particular aspects of fumigation and CA.

Research on gas processes as a means of grain preservation should be kept in perspective. Usually the objective is better pest control in stored grain rather than better fumigation. Gas processes are but one of many approaches that can be used to help achieve the basic aims of grain storage, providing a system that keeps grain adequately, given the economic and strategic constraints of the situation. The categories of grain preservation and disinfection techniques available are summarised in Table 1. Gas processes are unique in that they can achieve complete disinfection from pests in a short time and without moving the grain. Nevertheless, other techniques or combinations thereof, may give adequate protection and possibly at a lower cost. On the other hand, use of fumigation or CA may often be the optimum way of dealing with a particular situation.

Despite the foregoing considerations, there are several avenues of research related to CA and fumigation that appear worth pursuing. Some, notably those concerned with environmental and public health aspects, must be urgently addressed if sudden restrictions on the use of fumigants in particular are to be avoided. The research areas needing attention can be summarised thus:

Enabling technologies for both CA and fumigation	<ul style="list-style-type: none"> <li>- sealing and storage design</li> <li>- flow through techniques</li> <li>- action levels</li> </ul>
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#### Fumigation-specific problems

- basic parameter estimation
- rates of formation and definition of residues
- biological activity, including ways of enhancement
- effect on processing and end use parameters
- monitoring, public health and environmental concerns
- quarantine
- replacement fumigants

#### Controlled atmospheres problems

- gas supply systems
- effect on processing and end use parameters
- enhancement of action

### Enabling Technologies and Common Problems

Both CA and fumigation rely on containment of gases within an enclosure for sufficient time to effect the desired action, be it pest control, mould control, or grain quality preservation. Both have similar basic needs in terms of structures and are subject to the same set of constraints in terms of gas behaviour. The main differences are associated with the toxicity of fumigant chemicals to humans and the possibilities for quality protection. Common problems are discussed first in this section, followed by a consideration of problems specific to either fumigation or CA.

#### Sealing of Enclosures; Flow-through Techniques

It is well recognised that treatment enclosures must be sealed to some extent. Permanent sealing of many storage types is now routine (Ripp et al. 1984) and well-sealed enclosures for bag stacks are easily made (Annis and Graver 1986; Annis et al. 1984). Some development work is needed to determine optimum sealing pro-

**Table 1.** Processes for insect control in stored grain

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Biological control
Chemical protectants and growth regulators
Drying and use of aridity
Exclusion
Gas processes — fumigation and CA
Heating and cooling
Insect-resistant varieties
Irradiation (ionising)
Physical removal and hygiene
Shock and impact
Trapping

---

cesses, including consideration of availability of materials and skills for particular local conditions. The level of sealing required to guarantee a high probability of successful treatment, given otherwise adequate dosing and distribution, lies in the range given by pressure decay times (pressure halving) of 3–15 minutes (Banks and Annis 1984; Annis 1990), with 5 minutes a typical specification. Many structures that do not achieve this level are treated, with the inevitable risk of control failure. Data are needed on the balance between sealing effort and cost to achieve a satisfactory standard, and on the costs incurred in failures (retreatment costs, resistance selection, commodity damage, safety risks, etc.). Without this background, statements such as 'sealing is expensive' are meaningless.

Two approaches have been made towards reducing the level of sealing required, the 'flow-through' technique (Winks 1986) and the multiple dosing technique (Friendship et al. 1986). The flow-through technique relies on continuous addition of gas to counteract the tendency of air to enter leaks and to replace any lost fumigant. In theory it should be possible to add gas at such a rate that pressures across leaks are always positive with respect to the external environment and so no leakage in occurs. Except in well-sealed systems the costs of this are prohibitive and 'flow-through' systems depend on a fluctuating concentration of active agent close to the leaks. Flow-through systems, common in CA (Banks and Annis 1977; Jay 1980), have recently been applied to phosphine fumigation (Winks 1986). Multiple dosing, a compromise between 'one-shot' and 'flow-through', attempts—by repeated addition of

new fumigant—to maintain concentration in the face of leakage. The known physics of gas leakage into stores (Banks and Annis 1984) leave no doubt that, at some level of leakiness, failures using these techniques are very probable. Research is required to quantify the expected failure rate for given situations and levels of sealing, thus providing a basis for standards for these methods.

### Action Levels

A problem common to both CA and fumigation is the definition of action levels—levels of infestation at which a control treatment should be undertaken. In warm climates, there is a very high likelihood that grain taken into store from the producer and most handlers will carry infestation. Where the market operates on the basis of a nil tolerance, i.e. no detectable pest infestation, there is little doubt that control measures should be applied when the grain is taken into store. Thus, in Australia, almost all grain taken into large bulk storage is treated within two months of receipt.

Where some infestation and damage are acceptable to the end user, the problem is more complex. As yet, there is no recognised standard that gives a guide to when fumigation or CA disinfestation should be applied, though this is clearly required. However, it will need to combine considerations of cost, the potential risk, pest numbers, the favourability of the environment for pest proliferation, and end-user requirements.

An action level of 20 insects per tonne for storage periods of less than six weeks in tropical situations has been recommended (AFHB-ACIAR 1989). However, it may well be that the correct approach, in most cases, will be to apply a treatment regardless of whether infestation is detected or not, rather than adopt a complex decision-making process.

## Fumigation — Problems Requiring R & D

### Basic Parameter Definition, Value Estimation, and Modelling

The processes underlying the interaction of fumigants and grain are discussed in another

paper in these proceedings (Banks 1990). There is a need to define and quantify these processes to provide a better understanding and give well-based input into mathematical models of fumigation processes. Properly developed models should allow design predictions of the likely course of events in untried situations (e.g. residue formation at untested temperatures; different grain types; moisture or fumigant distribution in unfamiliar structures) without the need for much full-scale trial work.

A major problem outstanding in fumigation is the elucidation of the chemical pathways leading to residue formation in grains for even the most common fumigants, methyl bromide and phosphine. Residue studies for methyl bromide have largely concentrated on observing the fate of the easily observed bromide moiety, ignoring the fate of the methyl group. The research underpinning the current perception of where the methyl group goes relates almost entirely to one study on wheaten flour (Winteringham et al. 1955). There are very few data on whole grains (but see Shiroishi et al. 1961). Opinions on the fate of phosphine (Anon. 1988) rely largely on studies on artificial substrates and the erroneous belief that either no residues are formed or, if they are, they consist of phosphorus oxyacids only. However, there are indications that the situation may not be so simple. Phosphine, despite its volatility, can be retained for long periods on grain (Dumas 1980), suggesting some reversible chemisorption, possibly leading to further reaction, and there are indications that at least part of the phosphine taken up becomes bound to protein in some form (Tkachuk 1972). There are no data on the alteration products made when phosphine reacts with grain constituents. Without knowledge of the pathways involved in chemisorption, and reaction measurements of some fundamental features, understanding of fumigant behaviour towards grain must remain empirical, with the danger that conclusions drawn may not apply to new situations, such as unfamiliar conditions, grains, or even grain varieties.

There is much work to be done on measurement of the kinetics of fumigant interaction with grains and similar commodities. In particular, the rates of diffusion and reaction of fumigants in grain, and sorption isotherms on grains should be determined. However, there

is always the chance that, given our imperfect knowledge of the controlling mechanisms, effort will be misdirected and measurements will need to be repeated in the light of new information. It is to be hoped that some unifying principles will be discovered that will avoid the need to study, in detail, each grain and set of conditions. Some examples of this approach have already been reviewed by Banks (1986a). The processes underlying sorption and desorption must be properly defined. They can then presumably be incorporated into models that are likely to reliably predict real fumigant behaviour in real situations. At present, construction of complex models to predict gas behaviour, such as during venting or convective transfer, seems both premature and dangerous. They may result in conclusions that are limited at best, but may even be misleading.

### **Biological Response to Fumigants and Increasing Speed of Action**

The biological response of at least the common grain pests to the common fumigants at fixed concentrations is now known (Hole et al. 1976; Bond 1984; Price and Mills 1988). However, some further work may be required to determine the response of minor pests and to monitor resistance development. The main problem is how to fit the known laboratory-determined generalities into practice. Close investigation of the response of insect pests to phosphine has come up with some unpalatable results, notably that phosphine may be ineffective when applied for short periods (Winks 1986), and this problem becomes more acute at lower temperatures. A way of enhancing the toxicity so exposure periods could be reduced would certainly be useful.

There is often an economic advantage in being able to carry out a disinfestation rapidly. With the current pressures to optimise throughput and utilisation of facilities, it is likely that fumigant schedules will need to be reevaluated. There appears to be no way that exposure times for phosphine can be reduced from the quite long periods required for complete disinfestation (7 days at 25°C), apart from preheating the grain mass as suggested by Jay (1986). Claims that some phosphine-producing formulations can give shorter effective exposure periods appear to be unfounded. However, with methyl bromide, short exposure periods do

appear to be feasible because, for the same Ct-product, concentrations for short exposures are more effective than low concentrations for long times. The main constraints to carrying out methyl bromide fumigation rapidly thus appear to be distribution and removal of the gas after a treatment rather than toxicology, and research should concentrate on optimising the former factors.

There is a need for data on the response of pests to varying concentrations of fumigant, particularly phosphine, so as to be able to relate laboratory data with the normal concentration-time variation found in practice. When a fumigation is carried out in a partially sealed system, regions close to leaks may be subjected to fluctuating concentrations. In most treatments the concentration of fumigant falls with time as a result of sorption and leakage after the initial charge has become distributed. It has yet to be fully demonstrated how effective such concentrations are and what effect they have on behaviour and development. It may be that some pests can avoid the action of the fumigant either by movement, or alteration of development so that a tolerant phase or state is prolonged. Fluctuating concentrations may or may not have advantages over the normal fixed or falling concentrations. There are indications that the rapid rise and then slow fall of concentration, typical of a good phosphine treatment, may be less effective than a constant concentration (Reichmuth 1986). However, this has as yet to be shown for the pupal and egg stages, the developmental stages most tolerant of phosphine and thus most likely to survive treatments.

### End-Use Parameters

The effect of fumigants on end-use parameters is a strangely neglected field of research. With the exception of data for the effects of fumigants on the milling and bread-making quality of wheat, there is little information available (but see Taylor 1975; Banks 1981). Data are particularly scarce for tropical grains and cultural practices, and where grain is stored hot and possibly close to or above normal safe moisture limits. Systematic studies are required on the effect of fumigants on end-use qualities such as germination, yield from treated seed, and texture and acceptability of cooked products such as grits, boiled rice, and many oil-seeds. Current indications suggest that neither phosphine nor methyl bromide cause unaccept-

able changes in processing and organoleptic qualities of products derived from treated grains, but methyl bromide may often affect germination. Some cultivars may even be sensitive to phosphine (Joubert and du Toit 1969; Kamel et al. 1974).

### Quarantine Treatments

Quarantine treatments must be highly reliable. At present, methyl bromide is almost always specified as the fumigant for such treatments. This is despite data suggesting particular target organisms would be better controlled by other agents (e.g. *Trogoderma granarium* with phosphine (Bell et al. 1984)) and the need for exceptional dosage rates (e.g. 120 g/m<sup>3</sup> against the snail *Achatina fulica* (Bond 1984)) with the likelihood that a single treatment may give bromide residues exceeding normally permitted tolerances. There is an urgent need to undertake the tests necessary to substantiate alternative fumigants (or other processes) as acceptable quarantine treatments.

### Environmental and Worker Safety Considerations

Increasing public and worker awareness and concern over use of chemicals in almost all forms makes it inevitable that highly toxic fumigants will be scrutinised finely, and there will be increasing regulatory pressure and accountability in their application. In particular, there may well be a need for personal monitors to record and quantify exposure or prove non-exposure of persons in the vicinity of fumigation, and for stationary process monitors to record and control emissions of fumigant. Devices must be both specific and cheap. At present there are no machines available that will provide a dosimeter-type record of exposure for either methyl bromide or phosphine that are sensitive enough to record below current hygienic standards. Generally, the apparatus available for measuring fumigant concentrations is inadequate, and improved systems are urgently needed. Of the machines available for methyl bromide monitoring, only indicator tubes distinguish between methyl bromide and methyl chloride. The others (e.g. infrared detector, simple gas chromatograph) record a composite of the two gases. Devices recently described for phosphine monitoring are either not continuous (Harris 1986) or

apparently unavailable commercially (Ducom and Bourges 1986).

A possible solution to the concern over emission of fumigants directly into the atmosphere is to conduct treatments only in enclosures that are very well sealed and thus reliably contain the fumigant. At the end of the fumigation period, the atmosphere in the enclosure would be vented through some system that absorbs or decomposes the fumigant in the exhaust gas. To my knowledge, no such device that could be fitted to grain storages at an acceptable cost has yet been developed for either phosphine or methyl bromide.

There is an urgent need to provide well-substantiated information on the fate of fumigants in the atmosphere. It is said that both methyl bromide and phosphine break down quickly in free air. However, the studies on which these conclusions are based (Castro and Belser 1981; Fritz et al. 1982) were conducted using ultraviolet radiation of wavelengths shorter than present naturally in the lower atmosphere, and much longer half-lives than the few hours suggested may be expected around fumigation areas.

### **New and Old Fumigants**

The choice of fumigants for grain is very restricted. In practice usually only two—methyl bromide and phosphine—are considered. Research is needed to broaden this choice so that, should one or both of these no longer be available for some reason (e.g. supply, consumer preference, insect resistance, regulatory restriction, etc.), others may immediately be available. The choice may be widened either by development of new fumigants or resurrection of discarded materials. It is often said that there can be no new fumigants, as a fumigant must be highly volatile and simple chemistry restricts the choice to small molecules composed of light elements only. Most of the possible volatile compounds have already been tested and found inappropriate for some reason. While the perceived need for high volatility may not be correct—a case can be made for highly toxic but rapidly degradable materials of low volatility as fumigants (Banks and Desmarchelier 1979)—it is undoubtedly true that the choice is very limited. Even if an alternative fumigant were selected, the required testing and registration procedures would present a formidable

barrier to its adoption and use. Materials formerly used as fumigants, and currently discontinued or overlooked—notably the formates and hydrogen cyanide—appear to have more promise. Such materials need reassessment in the light of modern techniques of application and use, and residue requirements. Their biological activity may also need reinvestigation to a standard where it is comparable with that for methyl bromide and phosphine. Their spectra of action against immature stages, for instance, are not well defined.

## **Controlled Atmospheres**

There are three main outstanding problems in CA technology:

- atmosphere generation technology;
- definition and enhancement of biological action; and
- effect on end use parameters

General CA technology has been developed to a level where it is ready for commercial use requiring little adaptation to meet local requirements. Its use is largely constrained by cost, the need to adapt storages, and unfamiliarity with the technique. The slow speed of action can also restrict use.

### **Atmosphere Generation Technology**

Significant progress has been made recently towards replacing the use of tanker gases, often both inconvenient and expensive at remote sites, with systems of on-site generation of CA. There is now a choice of processes available for on-site production of gas for CA (Banks 1984), including membrane separation systems, pressure-swing absorption systems and burners. All of these are capital intensive, and complex pieces of equipment and further development is required to reduce costs or provide cheaper alternatives. Some alternatives have already been suggested (Banks 1984). The biological systems relying on metabolism to remove oxygen seem attractive in their simplicity but have yet to be demonstrated on a large scale. Chemical absorbers such as the iron-based 'Ageless' also show promise (Ohguchi et al. 1983). It may be that a combination of oxygen removers and metabolic action of the grain could give a modern form of hermetic storage.

## Biological Activity

The overall picture of the response of coleopterous pests of grain to various CAs is now reasonably well known (Annis 1987; Reichmuth 1987), though there is still some uncertainty as to the role of CO<sub>2</sub> in low oxygen atmospheres, and the temperature dependency of many CAs could be better defined. Data on the action of CAs on mites and other invertebrate grain pests, e.g. psocids, indicate that CAs can affect them (Bailey and Banks 1980; Navarro et al. 1985; Leong and Ho 1990) but systematic studies are not available. The effects on moulds vary widely with the target species and strain and particular atmosphere used, and further detail is required on mould control and associated toxins at both the laboratory and field scale.

The slow action of CAs at low storage temperatures (< 20°C) is a major hindrance to use of the technique. Methods to enhance the speed of action at low temperatures would be most welcome.

## Quality Effects

The effects of CAs on various quality and end-use parameters are reviewed in another paper in these proceedings (Gras 1990). In general, under relative humidities of less than about 70% and storage temperatures below 35°C, little or no effect is observed. However, at intermediate moisture contents (14–18% for wheat) there can be some beneficial effects on quality retention compared with grain stored in air. The effects are usually small in comparison with benefits obtained by reducing moisture content or temperature, but may nevertheless be useful in specialised situations. The application of CAs in otherwise marginal storage conditions seems to merit further research and development. CO<sub>2</sub>-air mixtures and atmospheres with very low oxygen content (< 0.3%) show particular promise for inhibiting spoilage.

## Combination

Study of the effect of combinations of fumigation and CA and other processes continues to hold promise as a means of enhancing action against pests, despite lack of positive effect of phosphine with methyl bromide (Bond and Morse 1982), and only partial success with

phosphine with CO<sub>2</sub> (Desmarchelier 1984). Use of CO<sub>2</sub> as a carrier gas for fumigant is now well demonstrated (Navarro 1986; Hah et al. 1981; Banks 1986b) and application of CA with heat seems to be a good alternative to fumigation for some insect control (Jay 1986). The observation by Buscarlet et al. (1987) that nitrogen CA rapidly kills insects after irradiation is most interesting and worthy of further investigation, as it may solve one of the main drawbacks to the use of radiation, namely the presence of live, but sterile, insects after treatment. The combination of disinfestation by gases with use of a permanently sealed insect-resistant enclosure is well known (Banks and Ripp 1984; Annis and Graver 1986). There is a need for extension of this technique with provision of cooling in some way to enhance the storability of sensitive commodities such as moist grains, or where retention of very high levels of germination is required.

## Conclusion

This paper has attempted to highlight particular areas of concern and ignorance with regard to fumigation and CA. The most urgent problems for fumigants are associated with the understanding of environmental effects, public health implications and residue problems. For CA, there is a particular need to develop and prove systems that generate and maintain the required gas mixture at low cost.

New demands for information on the effects of fumigants are likely driven by the general trend to scrutinise closely the use of chemical control methods, and the public perception that use of chemicals on foodstuffs is to be avoided. Obviously, it will be important for research workers to anticipate and gather appropriate data to meet such demands. Some conflicting requirements are already present and more are likely to arise. In particular, there is a problem that a material may become banned for use in some industrialised countries for what may seem minor defects when viewed in the context of its use in poorer areas. In the latter, food supply is a critical priority and the recorded adverse effects may not be regarded as significant. However, the decisions in the sophisticated markets will certainly influence use elsewhere via requirements for treatment of commodities in international trade. It follows that researchers everywhere should at least take

note of trends in regulations and usage in regions such as Europe and North America when planning research work on fumigants.

With efficiently applied effort, particularly in the areas of environmental and public health concern, it should be possible to anticipate the demands of regulatory authorities with regard to fumigants. This should avoid the sudden loss of either of our two remaining widely-used fumigants, phosphine and methyl bromide, as a result of lack of appropriate data, rather than from a demonstration of unforeseen adverse effects. At present, research work on fumigants is conducted at a national level though, in view of the breadth and complexity of the task, it seems appropriate that there be some international coordination of this effort to ensure that both critical problems are addressed and that scarce resources are well employed.

Controlled atmosphere techniques appear to be in a much less vulnerable position than fumigants. However, it must be remembered that, as used against insect pests, the atmospheres are lethal to humans and doubtless there will be increasing regulation of CA. Nevertheless, even now CA appears to present a reasonable alternative to fumigation, at least at high storage temperatures.

It is to be hoped that further research in fumigation and CA will provide no unpleasant surprises and that use of gases will continue to provide efficient pest control in stored grain.

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## **Report on Session 6: Issues Relating to the Application of Fumigation/CA**

Chairman: Mr José B. Santos, NAPHIRE, Philippines

Rapporteur: Professor Toshiharu Yoshida, Okayama University, Japan

THE first paper in this session was entitled 'Regulatory policies, technology, and related factors affecting the use of fumigants and controlled atmospheres'. It was written and presented by Mr C.L. Storey, who outlined the serious environmental problems posed by several fumigant materials used in the United States over the past few years. Mr Storey cited the incidents, in most cases exaggerated or sensationalised, that have resulted in the suspension from further sale, distribution, or use of some of these chemicals, and have also led to stricter measures being imposed by the US Environmental Protection Agency (EPA) on the use of the remaining fumigants. Because of this development, the speaker suggested reexamination of some of the factors that resulted in action against these materials in order to understand better the events that might affect the future use of the three remaining fumigants (methyl bromide, chloropicrin and aluminium-magnesium phosphide) in use in the United States.

The paper also discusses the interaction of policy, technology, and related factors which impact on fumigant use and identifies specific data requirements for continued registration of fumigant materials. The author also discussed briefly the regulatory status of controlled atmospheres in the United States.

The second paper—'Use of Controlled Atmosphere and Fumigation as a Management Tool for Grain Stocks: the Problems and Prospects'—presented by Mr R.J. Delmenico of Co-operative Bulk Handling Ltd (Western Australia) touched on the use of Controlled Atmosphere (CA) systems and fumigation in Western Australia, giving a historical review of CA storage practices there.

The author also discussed the operational advantages, problems, and strategies associated with the reliance on the use of CA and fumigants on a large scale and the prospects for such systems in the future in the advanced grain producing countries.

Mr Delmenico emphasised that, under existing storage and handling strategies, the advantages of CA storage far outweigh the disadvantages. Moreover, should circumstances warrant (such as the storage of grain with high moisture content) then the current CA storage provided an economic and versatile method of meeting market requirements. However, the nature of gases utilised, and the circumstances under which they are used, necessitate a thorough coordination of all factors associated with the storage, transport, and outturn of bulk grain.

The third paper in the session, 'Cost-Benefit Analysis of Stock Preservation Systems: a Comparison of CA and the Use of Conventional Pesticides Under Operational Conditions in Indonesia', was prepared by Mr J.A. Conway and Mr M. K. Mitchell of ODNRI, U.K. and Mr M. Gunawan and Mr Yusuf Faishal of Bulog, Indonesia. The paper, presented by Mr Mitchell, gave a financial cost-benefit analysis of CA and fumigation-based preservation systems for milled rice, based on mathematical models. He used the Break-Even Month (BEM) as reference point in evaluating the cost advantage of the CA technique. He also discussed the relevance

of these results to other food grain marketing systems in the Asian region and the use of the BEM concept in evaluating CA for bagged storage systems.

Mr Mitchell emphasised that the results of the study were based on assumptions which were held to be valid for government-sector storage in Indonesia. Management practices, as well as costs and benefits, may differ markedly in other countries.

The final paper in this session, 'Fumigation and CA R & D Activities and Needs Around the World' presented by Dr H.J. Banks of CSIRO, Australia gave a comprehensive overview of current practices and likely future developments in fumigation and CA techniques. He emphasised the limitations on fumigation imposed by health and environmental laws and length of treatment time and, for CA, cost and speed of action. He suggested that research work needs to be done in order to overcome these limitations for the technology to progress. He recommended the reevaluation of the currently permitted but neglected fumigants—hydrogen cyanide and the formates—for fumigation and the use of membranes, propane burners, and chemical absorbers for making low-cost oxygen-deficient atmospheres. He also recommended that further research be done to define the limits of action of various atmospheres against specific pests and to develop systems for storage of intermediate moisture content grain. The paper also summarised the R & D needs for both fumigation and CA as applied to grain.

Dr Banks suggested that systematic studies are needed on the effect of fumigants on end-use qualities such as germination and yield from treated seed, and texture and acceptability of cooked products such as maize grits and polished rice.

In the evening parallel workshop for this session, two recommendations were agreed upon:

1. Since there are very few fumigants registered and available for use—and these might become fewer in the future because their registration is cancelled or manufacturers stop their production due to the high cost involved—it is suggested that an ongoing Conference/Workshop should address the problem of developing substitute technologies to augment the existing chemical fumigants.
2. Outside the U.S. EPA, governments of advanced countries should support research work in the development of these substitutes.

# **Poster Papers and Commercial Presentations**

# **Long-term storage of bag stacks in plastic enclosures: an operations manual for carbon dioxide fumigation**

**P.C. Annis and J. van S. Graver**

Stored Grain Research Laboratory, CSIRO Division of Entomology,  
GPO Box 1700, Canberra, ACT 2601, Australia

This poster presentation launched a prepublication draft of a manual directed at fumigators-in-charge and others who are closely involved with 'hands on' aspects of fumigation. The publication is presented as a step-by-step 'how to' manual of operations for those involved in planning and undertaking fumigations of bag stacks with carbon dioxide. It is based on extensive experience gained by use of the technique in Southeast Asia, and is the first in a series concerned with the fumigation of specific storage types using specific fumigants and will be Part 2 of 'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region'. A prepublication draft of Part 1 of the recommendations, covering general principles and practice, was also available to conference participants.

# Current Strategies for the use of Controlled Atmospheres for the Disinfestation of Grain under UK Conditions

C.H. Bell, E.C. Spratt, and B.E. Llewellyn

Ministry of Agriculture, Fisheries and Food, ADAS Central Science Laboratory, London Road, Slough, Berks SL3 7HJ, U.K.

## Introduction

Two aspects critical for the use of controlled atmospheres for disinfestation of grain under U.K. conditions are their efficacy at low temperatures and their cost. Of a total U.K. grain storage capacity of about 26 million tonnes, some 8 million tonnes are provided by bins. Grain coming into store is usually dried to below 16% moisture content (m.c.) soon after arrival, and then cooled by forced aeration to below 10°C. However, residues left from the previous harvest often give rise to infestation. Cooling of the bins below 10°C effectively prevents further breeding or development but substantial numbers of adults may be found wandering in the new grain. Eventually these will start to breed in any area of localised heating originating from microbiological or mechanical activity. The control of adult pests is thus often the primary objective at low temperatures.

The performances of modified atmospheres based on carbon dioxide (CO<sub>2</sub>) and on the exhaust from burning propane were compared in laboratory and farm-scale trials.

## Tests on Storage Pests in the Laboratory

Atmospheres were produced by passing gas fed from cylinders through a 'Signal' gas blender and conditioning the stream to 70% relative humidity at the experimental temperature. With CO<sub>2</sub> concentrations down to 40% in air, 2 weeks exposure at 10° or 15°C was sufficient to kill all stages of the psocids *Liposcelis bostrychophilus* and *Lepinotus patruelis*, and adult beetles of *Cryptolestes ferrugineus*, *Rhyzopertha dominica*, *Oryzaephilus surinamensis*, *Sitophilus granarius*, *S. oryzae*, and *Tribolium castaneum* (Table 1). A similar exposure to the burner atmosphere (10–15% CO<sub>2</sub>, 1% oxygen, and 84–89% nitrogen) killed the last four species at both temperatures but 3–4 weeks exposure was required for *C. ferrugineus* and *R. dominica*. Mortality of the batches of 100 insects was assessed 7 days after return to air.

## Purging of Grain Bins

The 19 m<sup>3</sup> welded steel bins sealed to give an applied pressure half-life of 2–20 minutes were set up with wheat at 14.4%, 15.1%, and 16.0% m.c. at 15 ± 2°C. Each was purged with simulated burner gas at the rate of 5 L/minute for up to 3 days (two atmosphere changes), by which time oxygen levels had fallen to 1%. The 16% m.c. bin maintained the atmosphere without further supply of gas for seven days (Table 2), during which time oxygen levels were held below 1%, probably as a re-

**Table 1.** Time (days) for control of adult beetles and all stages of psocids with CO<sub>2</sub> at 10° and 15°C

Species	CO <sub>2</sub> range (% in air)	10°C	5°C
<i>Sitophilus granarius</i>	40-95 100	10 >10	8 14
<i>S. oryzae</i>	40-95	7	4
<i>Cryptolestes ferrugineus</i>	40 60-100	>8 10	12 7
<i>Rhyzopertha dominica</i>	40-100	11	8
<i>Oryzaephilus surinamensis</i>	40-100	7	5
<i>Tribolium castaneum</i>	40-100	7	6
<i>Liposcelis bostrychophilus</i>	40 80-100	>8 10	12 >7
<i>Lepinotus patruelis</i>	40 80-100	>8 9	6 8

**Table 2.** Maintenance of a typical exhaust gas atmosphere in 19 m<sup>3</sup> bins (pressure 50% decay time 2.5 min) loaded with wheat of different moisture contents.

Purge time (days)	Flow rate (L/min)	CO <sub>2</sub> /O <sub>2</sub> levels at wheat surface		
		14.4% mc	15.1% mc	16.0% mc
0	5	0/21	0/21	5/14
1	5	4/12	4/11	10/4
2	5 → 1	11/2.3	11/2.4	15/0.2
3	1 → 0.5	11/1.5	11/1.5	15/0.1*
4	0.5	-	12/1.3	15/0.2*
6	0.5	13/1.3	12/1.1	14/0.9*
7	0.5	13/1.2	13/1.1	14/0.7*
9	0.5 → 0.25	13/1.0	13/1.1	15/0.8*
10	0.25 → 0.5	13/1.3	13/1.6	15/0.8*
14	0.5	13/1.1	13/1.1	15/0.8*

\*Gas flow stopped at 72 hours.

sult of micro-biological activity. The atmosphere in the other bins was successfully maintained by a reduced gas flow of 0.5 L/minute (one atmosphere change every 2 weeks).

Similar tests were conducted with CO<sub>2</sub> on wheat at 14% m.c. in three free-standing galvanised metal plate bins sealed to give pressure half-lives of 5, 30, and 60 seconds. The last standard was achieved only by dismantling and rebuilding the bin. To maintain nearly 100% CO<sub>2</sub> throughout the 5 sec. bin in wind speeds up to 2 m/sec, an atmosphere change was required every 18 hours. CO<sub>2</sub> was supplied from new 'minitanks', each producing 70 m<sup>3</sup> of gas. When the flow was shut off, CO<sub>2</sub> in the 5 sec. bin dropped to below 50% in somewhat less than 24 hours, while the 30 and 60 sec. bins required 4 and 10 days, respectively, for a similar fall.



## Conclusions

The gas produced by burning propane kills adult beetles within four weeks at 10°–15°C, while CO<sub>2</sub> requires only 2 weeks and remains fully effective down to less than 50% in air. Despite these advantages, burner gas is still a considerably cheaper method of achieving control, provided that a burner is available. Farm bins are not sufficiently gastight for one-shot CO<sub>2</sub> treatments, a pressure half-life of at least 1 minute being required for a 10-day exposure, together with calm weather. For both CO<sub>2</sub> and burner gas, continuous flow systems offer the only practical method to achieve control. Any measures which can increase the gastightness of bins towards a 30 second half-life pressure test result are likely to be cost effective but achieving a higher standard may not be practicable for existing storages.

# Problems and New Approaches for the Use of Phosphine as a Grain Fumigant in the U.K.

**C.H. Bell, B. Chakrabarti, and K.A. Mills**

Ministry of Agriculture, Fisheries and Food, ADAS Central Science Laboratory, London Road, Slough, Berks SL3 7HJ, U.K.

## Introduction

Grain is stored in the U.K. in diverse structures, including galvanised steel bins and concrete silos, and on the floor in purpose-built stores, converted aircraft hangars, and other buildings. This diversity, coupled with the prevailing cool, damp weather conditions, creates difficulty in devising a general set of recommendations for the use of phosphine. From a biological viewpoint, further complexities arise because of the very wide differences in tolerance between stages of the same species of stored product pests, between different strains and species, and because of the effect of temperature on the concentration and exposure time ranges over which phosphine acts efficiently.

After harvest, grain is dried by flat-bed aeration or by use of grain dryers, and is then cooled, usually down to 4°–10°C. Nevertheless, localised problems often occur within large bulks, and infestations may reach noticeable proportions. Fumigation by phosphine is the only control method that is currently available for treating the whole bulk in situ. Use of liquid fumigant mixtures is now precluded with the lowering of the permitted maximum residue level (MRL) for carbon tetrachloride in the U.K. to 0.1 ppm from 1 January 1989. This paper describes some new results relating to the toxicity of phosphine under marginal conditions and some developments leading to increased fumigation efficacy.

## The Effect of Temperature on the Minimum of Exposure for Control

Recent tests on diapausing larvae of *Ephestia elutella* show that, for concentrations over 2 mg/L, the time required to achieve 99% kill at 25°C stabilises around 30 hours. This compares with about 23 hours for 99% kill at similar concentrations at 15°C (Table 1). Thus, the minimum time for achieving 99% kill increases with increasing temperature, indicating an active defence mechanism at work.

Experiments involving larvae in diapause demonstrate the toxic effect of phosphine in the absence of development. For many species, the minimum exposure period required for control is governed by the developmental rate of eggs or pupae. Phases of high natural tolerance are bridged by longer exposures as development continues in the presence of phosphine. Where such developmental effects control fumigation efficacy, lowering the temperature increases the exposure period required for kill, until cold itself becomes lethal.

**Table 1.** Effect of temperature on the minimum effective exposure period of phosphine at high concentration against diapausing larvae of *Ephestia elutella*.

Concn (mg/L)	15°C			25°C			
	LD <sub>99</sub> (mg hours/L)	b±SE	Lt <sub>99</sub> (hours)	Concn (mg/L)	LD <sub>99</sub> (mg hours/L)	b±SE (hours)	Lt <sub>99</sub>
—	—	—	—	0.18	12.5	6.90±1.41	70.2
0.60	31.1	3.44±0.43	51.8	0.5	23.0	4.45±0.80	46.0
1.02	37.2	3.46±0.42	36.5	1.2	65.4	2.98±0.5	52.7
1.48	49.7	3.51±0.43	33.6	—	—	—	—
1.95	43.3	3.25±0.47	22.2	2.22	68.9	3.58±0.66	31.0
3.04	74.8	3.84±0.68	24.3	2.70	70.7	3.52±0.4	26.2
4.10	92.3	2.64±0.51	22.5	3.71	121.9	3.15±0.70	32.9

Mean Lt<sub>99</sub> for 1.95 – 4.10 mg/L : 23 hours

Mean Lt<sub>99</sub> for 2.22 – 3.71 mg/L : 30 hours

## Effect of Changing Concentration Levels on the Toxicity of Phosphine

In tests on all stages of a resistant strain of *Cryptolestes ferrugineus*, the level of kill obtained was related to the concentration remaining at the end of the exposure period rather than the total Ct product. A 10-day exposure with Ct product 65±10 mg hours/L was chosen (Table 2). Also evident was the advantage of concentration levels falling later rather than earlier in the exposure period in terms of enhancing the level of kill obtained. In most cases survival was attributable to pupae or prepupae. Kills of other stages of this resistant strain exceeded 99% in all tests.

### Dosing Methods for the Use of Phosphine

Results at low and changing concentration levels of phosphine highlight the need to delay the fall of concentrations to as late as possible in the exposure period. In practical terms this implies either a high degree of sealing, which can be expensive,

**Table 2.** Effect of different concentration profiles of phosphine on the toxicity of a 10-day exposure to pupae of *Cryptolestes ferrugineus*

Concentration profile	Ct product (mg hour/L)	% mortality	Concentration at end of 10-day exposure (mg/L)
Rising to 1.7 mg/L then 75% leakage per day	66.5	75.7	0.001
Rising to 0.94 mg/L then 50% leakage per day	58.4	96.6	0.01
Rising to 0.39 mg/L then 10% leakage per day	61.5	96.7	0.12
Level concentration (<2% leakage per day)	55.9	97.1	0.23
Rising to 1.4 mg/L in first day then falling to 0.11 mg/L after 4 days	73.6	82.0	0.10
Rising to 1.4 mg/L in first day then falling to 0.09 mg/L after 7 days	74.1	96.9	0.08

or a system of repeated or continuous introduction of gas. Formulations containing aluminium phosphide supply phosphine gas over a 1–3 day period, depending on temperature and availability of moisture. Under leaky conditions these generation times are too short to provide an effective exposure and insufficient to distribute gas throughout the bulk. Repeated application is unlikely to solve the problem of excessive leakage unless performed almost daily.

Promising results have been obtained in wheat-filled bins up to 175 tonnes capacity using a 2–3% mixture of phosphine in carbon dioxide, supplied from gas cylinders. After sheeting the grain surface, 5 g phosphine per tonne was applied within half an hour to the base of each bin via a copper pipe inserted into the aeration system. The gas was evenly distributed within 12 hours. Twenty-four hours later, concentrations in the bins had fallen to below 0.2 mg/L. Thereafter, concentrations above 0.3 mg/L could be maintained at most points by a very low top-up rate of 30 litres of 3% (by volume) phosphine in carbon dioxide per hour. This method of dosing has considerable potential for wider use in the U.K.

# Eating Qualities of Milled Rice under Carbon Dioxide Storage

**Ab. Rahim Muda and Faridah Mat Elah**

Food Technology Division, MARDI, GPO Box 12301, Kuala Lumpur, Malaysia.

## Introduction

The eating quality of rice is one of the most important factors in determining overall rice quality. It is defined by various characteristics of the cooked rice including appearance, cohesiveness, tenderness, glossiness, odour, and colour. All these characteristics undergo significant changes during storage.

Rice ages during storage, the process involving changes in physicochemical characteristics, such as development of off-odour, harder texture, reduced stickiness and glossiness, which influence its cooking, eating, and nutritional qualities.

As part of ACIAR Project 8307 on 'Long term storage of grain under plastic covers', cooking and eating qualities of rice were evaluated following long term storage under CO<sub>2</sub>, with a view to assessing any effects of the gas.

## Materials and Method

Milled rice samples stored under either CO<sub>2</sub> or ambient air were collected and cooked for sensory evaluation after 4 and 8 months storage. The rice stored under CO<sub>2</sub> was tightly sealed in a PVC enclosure and purged with CO<sub>2</sub> gas at a dosage of 2 kg/t rice for insect disinfestation. Thirty samples taken from a 200t stack were bulked into a single working sample and used for sensory evaluation for each storage method and sampling period.

The rice was washed twice with tap water and cooked in an electric cooker with a rice-to-water ratio of 1:2. One sample from each storage method was served for evaluation. The quality of cooked rice was evaluated on the basis of its palatability. Fifteen trained panelists judged the odour, tenderness, cohesiveness, colour, glossiness, and overall acceptability of the cooked rice using a rating scale of 1-9 (Fig. 1). The eating qualities of the rice stored under CO<sub>2</sub> and the untreated control rice were statistically compared by t-test.

## Results

After 4 months storage the rice stored by both methods showed similar eating qualities (Table 2). The odour, tenderness, and glossiness of the rice scored moderately (mean score 5), implying normal acceptance or no indication of deterioration. The creamy-white colour (score of 7), though indicative of initial signs of aging associated with storage, did not adversely affect local preference as indicated by good overall acceptance (score of 6). However, as regards cohesiveness, the rice from both treatments showed an decrease in stickiness, a change at variance with the preference of a large section of the local population.

**Fig. 1.** Form used for scoring quality characteristic of cooked rice following storage.

**Sensory Evaluation of Cooked Rice**

Name:

Date:

Sample:

Characteristics			
A	Odour	9	- none
		7	- weak
		5	- moderately strong
		3	- strong
		1	- very strong
B	Tenderness	9	- very tender
		7	- tender
		5	- moderately tender
		3	- slightly hard
		1	- hard
C	Cohesiveness	9	- well separated
		7	- partially separated
		5	- sticky
		3	- very sticky
		1	- pasty
D	Colour	9	- white
		7	- creamish white
		5	- greyish white
		3	- light brown
		1	- brown
E	Glossiness	9	- very glossy
		7	- glossy
		5	- moderately glossy
		3	- dull
		1	- very dull
F	Overall acceptability	9	- very good
		7	- good
		5	- fair
		3	- poor
		1	- very poor

After 8 months storage, the control stack began to show initial deteriorative changes (score 5) indicated by the off-odour, a less glossy appearance, and stickiness. Changes in the odour and overall palatability of the control rice were significantly greater than those of rice stored under CO<sub>2</sub> whose overall level of acceptability remained good. Nevertheless, the colour of rice from both treatments was creamy-white, which is a notch below the 'full-white' appearance associated with rice fresh from the mill.

**Discussion**

The odour of milled rice changes very readily during storage due to accumulation of volatile off-odour compounds in the intergranular air (Barber 1972). As compared with the results of previous investigations (Kongseree et al. 1985; Primo et al. 1970;

**Table 2.** Comparison of mean score of eating qualities between milled rice stored under CO<sub>2</sub> and ambient environments at different storage period.

Storage period (months)	Mean Score of CO <sub>2</sub> -Treated vs Ambient					
	Odour	Tender -ness	Cohesive-ness	Colour	Glossiness	Overall Acceptability
4 (Treated -Ambient)	5.3 - 5.2	5.7 - 5.6	3.9 - 4.3	7.6 - 7.0	5.5 - 5.8	6.8 - 6.1
8 (Treated -Ambient)	8.1 - 4.6*	6.1 - 5.8	5.0 - 4.8	8.5 - 8.0	4.2 - 4.8	6.7 - 4.4
4 vs 8 (Treated -Ambient)	5.3 - 8.1*	5.7 - 6.1	3.9 - 5.0*	7.6 - 8.5	5.5 - 4.2*	6.8 - 6.7

\*Significant at 5%

Yasumatsu et al. 1965), which reported off-odour within 2 weeks to 4 months of storage, the scoring standard used in this study indicated a very slow development of off-odour in rice stored under ambient conditions for 8 months. The apparently stronger odour from rice stored under CO<sub>2</sub> after longer storage (mean score of 8 after 8 months compared with 5 at 4 months) might have been due to aroma induced by the presence of CO<sub>2</sub> gas, though variations due to the preferences of the panelists themselves are also a possibility.

Colour is the most stable among the eating qualities evaluated. This finding is similar with observations from other investigations (Pelshenke and Hampel 1967; Yasumatsu and Morita 1964) which reported no significant changes in colour after 6 months storage for white rice under ordinary conditions. In the present study, both CO<sub>2</sub> treatment and ambient storage showed no effect on colour.

The cohesiveness of the rice is known to decrease with storage (Barber 1969; Irwin 1959; Yasumatsu 1968). In this study the rice from both storage treatments showed reduced stickiness following as little as 4 months storage.

The tenderness of rice was expected to decrease, resulting in firmer texture, as observed in the investigations already cited. However, our studies revealed stabilisation in texture following both treatments.

The significantly better overall palatability of milled rice stored under CO<sub>2</sub> as compared with rapidly deteriorating qualities observed in rice stored under ambient conditions as shown in this study indicates a need for in-depth studies with regard to the interaction between the rice and the CO<sub>2</sub> gas during storage.

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# Relating Sensory Evaluation to Other Quality Factors in Stored Rice

**P.W. Gras and M.L. Bason**

CSIRO Division of Plant Industry, Wheat Research Unit, P.O. Box 7,  
North Ryde, NSW 2113, Australia

**L.A. Esteves**

NAPHIRE, CLSU Compound, Muñoz, Nueva Ecija, Philippines

**A.M. del Mundo**

University of the Philippines, Department of Foods and Nutrition, College of Human Ecology,  
UPLB, College, Laguna 3720, Philippines

## Introduction

Storage of rice affects its quality as judged by the consumer. Many tests have been developed which purport to categorise rice quality in terms of its acceptability to consumers. There are, however, few data that relate consumer judged quality with other tests for quality change occurring in stored rice. Storage time and conditions have been related to change in yellowness in rice (Gras et al. 1989) as measured by the CIE  $b^*$  value (Anon. 1986). This value is objective and simple to measure, whereas sensory evaluation is subjective, labour intensive, and time consuming. The relationship between change in yellowness resulting from storage to the changes in sensory quality of the stored rice is therefore of particular interest. The aim of this study was to relate the results of several standard quality tests with consumer rating of cooked and raw rice for samples of grain stored under a range of controlled conditions.

## Materials and Methods

Paddy rice cv. Pelde (1985 and 1986 harvests) was exposed to a range of storage gas atmospheres, humidities, temperatures, and exposure times (Gras et al. 1989). Samples were taken from conditioned grain immediately before exposure and after intermediate and long storage periods. Samples were de-husked using a Satake rice huller (THU-35A), and polished using a Satake grain testing mill (TM-05). Established methods were used to determine alkali spreading value (Little et al. 1958), chalky kernels, milling recovery, head rice yield (Cristobal 1983), fat acidity values (AACC 1965), gel consistency (Cagampang et al. 1973), cooking time, optimum cooking water, percent height increase, and percent weight increase (del Mundo 1979). Yellowness was measured using the  $b^*$  coordinate (Anon. 1986) of the Minolta Chroma Meter model CR-110 (Anon. 1984). Volume expansion was determined by cooking 40 g of rice in a wire basket (100 mm high  $\times$  40 mm diameter, gauge 1 mm) for 20 minutes and calculating the ratio of the heights before and after cooking. The proportion of discoloured (yellowed) kernels was determined by hand sorting 50 g subsamples.

Sensory evaluation (del Mundo 1979) of samples was carried out in Barangay Lamot II, Laguna, Philippines, using a panel of 33 untrained consumers to determine the acceptability and ranked preference of both raw and cooked rice. Each

presentation consisted of four samples, of which one was a control (cv. Sinandomeng). Non-sensory quality tests were performed in duplicate, and the means used for comparisons with each other and with the data from sensory evaluations. The raw preference data were adjusted by subtracting the control value in each presentation to make values from different presentations comparable. The percentage acceptability values were normalised by converting to a percentage of the within-presentation control. All of the quality parameters were compared using pairwise correlation. Multiple regression was used to compare sensory data (as the dependent variables) to the other quality data (independent variables), with terms not contributing significantly to the fit progressively removed.

## Results and Discussion

There was a positive relation between the cooked and raw sensory qualities, which were in turn negatively related to the yellowness of the grain (Figs 1 and 2). Preliminary analyses indicated that the natural logarithm of the yellowness was well correlated with the sensory scores and was used in all subsequent analyses.

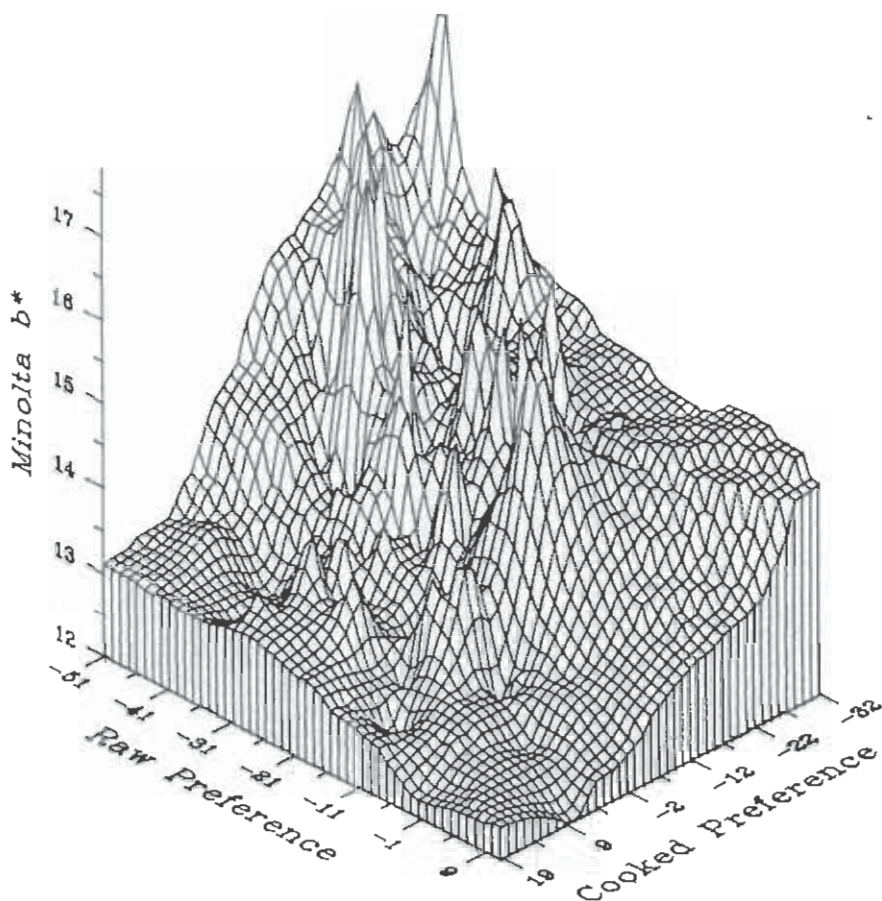


Fig. 1. Relationship of raw preference, cooked preference, and Minolta  $b^*$  value for stored rice cv. Pelde.

The highest correlations observed were between the four sensory measures (cooked rice preference, raw rice preference, cooked rice acceptability, and raw rice acceptability), between the yellowness and the four sensory measures, and between the percent chalky grains and head rice yield. There was a strongly negative correlation between the yellowness and all four sensory measures; that is, yellowness increased during storage but acceptability and preference decreased. Consequently, significant change in the yellowness during storage appears to

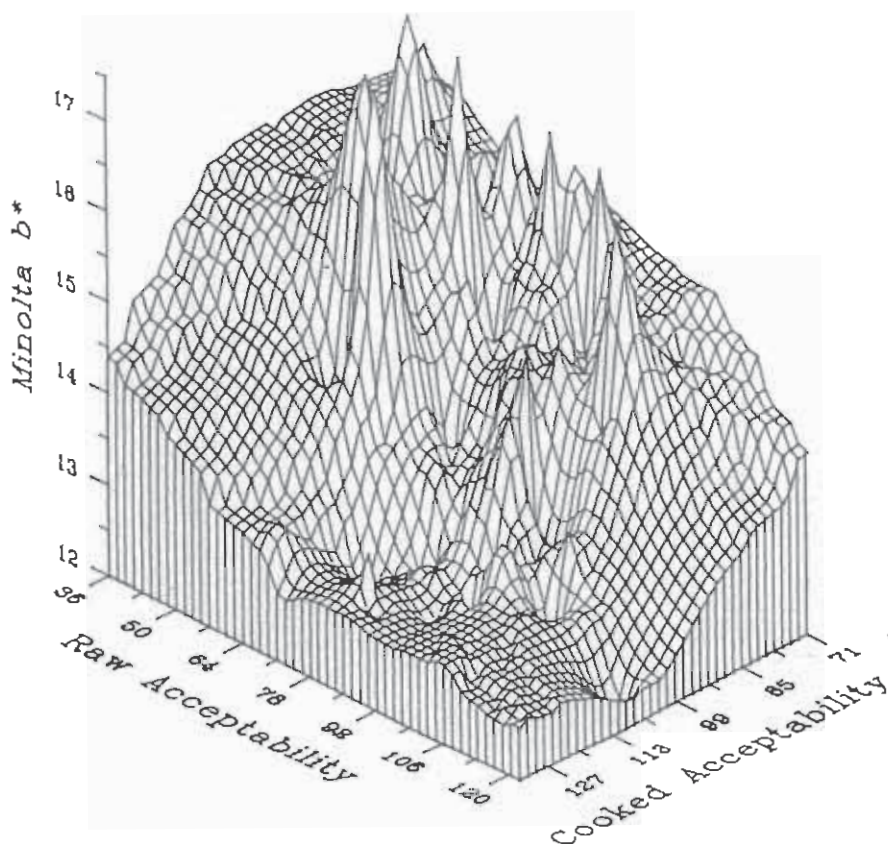


Fig. 2. Relationship of raw acceptability, cooked acceptability, and Minolta b\* value for stored rice cv. Pelde.

provide an objective and simple test to assess change in sensory acceptance of rice during storage.

There were smaller but still significant correlations between the sensory measures and the other quality parameters tested. In particular, cooked rice sensory quality was negatively correlated with alkali spreading value, fat acidity, head rice yield, milled rice yield, volume expansion, and percent yellows. Most of these parameters are known to increase during storage (Juliano 1985), whereas preference and acceptability decrease. Therefore, these correlations may also be attributable to storage changes within the rice.

Multiple regressions of all the non-sensory quality parameters against each of the four sensory parameters showed that the largest part of the explained regression variance could, in every case, be attributed to the yellowness. Other factors that significantly contributed to the fit were the percent chalky grains and fat acidity in the cooked rice evaluation, and the alkali spreading value, cooking time, fat acidity, milling recovery and percent weight increase in the raw rice evaluation. The overall fit of the regressions for cooked rice acceptability and preference ( $r^2 = 0.589$  and  $0.465$ , respectively) was not much less than that obtained by regressing the two sensory parameters for cooked rice against each other ( $r^2 = 0.608$ ). The limited degree of correlation between the two measures of cooked rice sensory quality illustrates the subjective nature of these evaluations. This indicates that the overall fit of the cooked rice sensory quality with the non-sensory parameters was reasonably close to the best that could be expected.

Consumer preference of rice varies between countries and even between regions in some places (Juliano 1985). Nonetheless storage usually has an effect on

consumer preference. Therefore, the change in yellowness resulting from storage will probably provide a measure of sensory quality in most places, but the magnitude of the relationship will vary from place to place. Further work is required to quantify this relationship in other areas.

## Conclusions

Sensory evaluation of the stored rice was most closely related to the yellowness, percent chalky kernels, alkali spreading value, cooking time, milling recovery, percent weight increase, and fat acidity value. The most discriminating of these was the yellowness. Changes in this value therefore provide a simple and objective means of monitoring changes in consumer acceptance of stored rice.

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# Seed Viability under Different Storage Conditions

**Darka Hamel\***

Institute for Plant Protection,  
Zagreb, Yugoslavia

## Introduction

The aim of this study was to compare the effects of various types of storage conditions on the viability of seeds, with a specific objective of determining the effect of long-term storage under carbon dioxide (CO<sub>2</sub>) on germination.

## Materials and Methods

### Storage Conditions

The following storage conditions applied:

- normal warehouse storage;
- storage in an air-conditioned chamber (T = 9°C, relative humidity 65 ± 10%); and
- chamber storage under constant (35 ± 5%) carbon dioxide.

### Seeds

The following types of seeds were tested:

- maize (*Zea mays* L.) — BC388
- winter wheat (*Triticum* sp.) — Sivka: untreated seeds; Baranjka: treated seeds
- spring wheat (*Triticum* sp.) — Anka: untreated seeds
- soybean (*Glycine max* (L.))
- green pea (*Pisum sativum*) — Provansalac mali
- onion (*Allium cepa* L.) — Srebrenac skopski majski
- paprika (*Capsicum annuum* L.) — Rotund zuta
- kale (*Brassica oleracea* var. *sabauda* L.) — Zeljezna glava
- parsley (*Petroselinum hortense* Hoffm) — Berlinski
- lettuce (*Lactuca sativa* L.) — Majska kraljica
- grass seed (*Festuca rubra* L.) — Chewings fescue
- rapeseed (*Brassica napus* var. *oleifera* L.) — Jet neuf

### Method of Packing

Seeds were stored in small lots in jute and laminated plastic bags, as well as in their original paper packages. The laminated plastic bags used for seed storage were purged with CO<sub>2</sub> then sealed.

\* Paper presented at the conference by Dr P.W. Gras, CSIRO Division of Plant Industry, Sydney, Australia.

## Storage Period and Seed Testing

The total storage period was 12 months. Viability was tested by the standard (JUS) method on samples of 200 seeds at the beginning of the experiment and after 6 and 12 months.

## Results and Discussion

Determinations of seed viability at the beginning of the experiment and after 6 and 12 months are given in Table 1.

**Table 1.** Viability of seeds (%) after 6 and 12 months in a warehouse, an air-conditioned chamber, or in a carbon dioxide atmosphere

Seeds	Time of testing (months)	Warehouse storage			Air-conditioned chamber			CO <sub>2</sub> chamber		
		Paper bag	Jute bag	Plastic bag	Paper bag	Jute bag	Plastic bag	Paper bag	Jute bag	Plastic bag
Wheat (Baranjka)	Initial	98								
	6	91	93	83	92	85	93	55	73	81
	12	87	85	89	86	90	92	25	69	79
Wheat (Sivka)	Initial	93								
	6	92	91	79	91	91	89	47	25	83
	12	85	86	89	96	86	86	24	65	71
Wheat (Anka)	Initial	73								
	6	83	81	78	76	83	80	–	–	83
	12	77	72	76	76	79	85	–	–	73
Rapeseed	Initial	90								
	6	75	68	66	43	60	69	32	37	53
	12	83	79	86	63	85	84	44	21	78
Maize	Initial	97								
	6	94	92	95	94	94	92	95	93	95
	12	96	96	95	96	97	96	94	96	96
Soybean	Initial	76								
	6	67	76	70	82	75	75	56	54	60
	12	80	77	70	78	85	80	25	40	66
Green pea	Initial	93								
	6	93	91	92	94	95	92	90	89	91
	12	86	94	93	87	92	92	90	87	86
Parsley	Initial	79								
	6	66	68	51	69	71	63	34	34	62
	12	27	44	41	25	14	17	6	15	5
Paprika	Initial	85								
	6	33	46	51	68	78	71	1	6	16
	12	2	2	–	18	18	66	0	0	0
Lettuce	Initial	78								
	6	76	50	38	75	70	79	20	86	37
	12	76	73	65	75	78	79	0	89	53
Kale	Initial	90								
	6	88	97	97	95	96	94	95	95	94
	12	64	57	48	73	70	71	58	90	54
Onion	Initial	91								
	6	89	77	95	88	91	89	69	85	95
	12	91	93	82	99	83	91	67	66	98
Grass seed	Initial	82								
	6	89	77	95	88	91	89	35	64	54
	12	52	32	15	27	56	59	38	–	–

It can be seen from the results that the viability of maize, green pea, and, to a lesser extent, onion seeds remained constant for all package types and storage conditions. For the most part, however, all other seed displayed lower germination after storage under CO<sub>2</sub>.

### **Warehouse Storage**

For 6 of the 13 types of seed tested, the samples held in laminated plastic bags filled with CO<sub>2</sub> displayed lowered germination following 6 months storage than did seeds held in paper or jute bags. The greatest reductions in germination occurred with parsley, paprika, kale, and grass seed following 12 months storage.

### **Air-conditioned Chamber**

After 6 and 12 months, almost all seeds stored in laminated plastic bags had viabilities equal to or better than those stored in the other types of packages. The exceptions were grass and parsley (6 months) and grass, parsley, and paprika (12 months).

### **CO<sub>2</sub> Chamber**

Wheat and rapeseed stored in laminated plastic bags displayed higher germination than the seeds of those two species held in the other types of packages. In general, the laminated plastic bags appeared to afford the greatest protection, though paprika, parsley, and lettuce seeds were clearly sensitive to the CO<sub>2</sub> used to purge the bags.

Note that any insects present in laminated plastic bags will be killed following purging with CO<sub>2</sub> and the seeds will be protected during storage as long as the bag remains intact. Also, all insect stages will be controlled by the constant CO<sub>2</sub> atmosphere of the chamber.

## **Conclusion**

This study suggested that, with the exception of maize and green peas, CO<sub>2</sub> atmospheres can reduce the viability of stored seeds. Care must therefore be taken in using CA strategies based on CO<sub>2</sub> for long-term protection of seed from insect infestation.

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## Susceptibility of *Liposcelis entomophilus* (Enderlain) to Carbon Dioxide

Edmund C.W. Leong and S.H. Ho

Department of Zoology, National University of Singapore,  
Lower Kent Ridge Road, Singapore 0511

*Liposcelis entomophilus* (Enderlain) is common in food stores in the tropics where the prevailing hot and humid conditions provide an ideal environment for its proliferation. *L. entomophilus* has been reported in rice warehouses in Indonesia and Malaysia (Semple 1985), Thailand (J. van S. Graver, personal communication), and in Singapore. Densities as high as 1500 live insects per kilogram of rice have been encountered in Singapore (S.H. Ho, unpublished data), while even higher densities (up to 4000 live psocids per kilogram) were recorded from Indonesia (C.P. Haines, unpublished data). The occurrence of these psocids in large numbers would pose both a cosmetic problem in stored grain and a nuisance to workers.

In a recent review (Annis 1986), the absence of information on the response of stored product psocids to controlled atmospheres was obvious. The work reported here was therefore undertaken to establish the time-to-100% kill of *L. entomophilus* exposed to various concentrations of carbon dioxide (CO<sub>2</sub>).

Mixed-age samples of *L. entomophilus* (>150 individuals per cage) were exposed to various concentrations of CO<sub>2</sub> and the time-to-100% kill determined. Five cages were placed in each exposure chamber. Chambers were constructed from vacuum desiccators, which were placed in incubators. All tests were carried out at 30°±1°C and 75±3% relative humidity. There were three replicates of each treatment. The CO<sub>2</sub> concentrations were monitored daily with a Riken interferometer (Model 18) calibrated for CO<sub>2</sub>.

The results, incorporating additional data obtained after the conference, suggest an inverse relationship between concentration and time required for 100% kill (Table 1). Increasing the concentration of CO<sub>2</sub> from 30 to 90% decreased the time-to-100% kill from 5 days to 1 day. Observations on the susceptibility of the different life stages suggests that the egg stage is the most tolerant to CO<sub>2</sub>. Further work is presently in progress to ascertain the order of susceptibility of the other life stages.

**Table 1.** Time-to-100% kill of mixed-age sample of *Liposcelis entomophilus* exposed to various concentrations of CO<sub>2</sub> at 30°±1°C and 75±3% RH.

%CO <sub>2</sub> concentration (mean±S.D.)	Time-to-100% kill (days)
20.9±0.7	>1 week
30.7±1.5	5
41.0±1.1	4
51.4±1.2	3
60.8±1.5	3
70.7±1.4	3
80.8±1.3	2
92.8±1.3	1



Currently suggested dosage regimes (Annis 1986) for constant as well as declining CO<sub>2</sub> concentration would be adequate for the control of *L. entomophilus* in well sealed enclosures.

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## Use of Phosphine to Control Storage Insects in Rice

**Pitoon Urairong, Kitiya Kitkuandee, Prasoot Sittisuang,  
and Nipon Makatan**

Department of Agriculture, Bangkok, Bangkok 10900, Thailand

Three different treatments of phosphine were applied to RD23 rice seed and, following treatment, weight loss, number of infested seeds, germination, and vigour of the seed were measured. The first treatment applied one fumigation at 2.0 g of active ingredient per cubic metre 7 days before storage, the second applied fumigation at monthly intervals for 6 months, and the third a single fumigation and covering of the sacks with plastic sheeting for a period of 6 months. In addition, a control of untreated seed was used. In general, phosphine gave better results in terms of minimal weight loss and the number of infested seeds, with fumigation and covering with plastic sheeting. There was no difference between the treatments and the control as far as seed germination and vigour were concerned.

# Flexible PVC Liners for Hermetic or Modified Atmosphere Storage of Stacked Commodities

**E. Donahaye and S. Navarro**

Department of Stored Products, Agricultural Research Organization,  
The Volcani Center, Bet Dagan, Israel

Flexible PVC liners have been developed to completely envelop stacks of bagged grain or other durable food commodities, so as to enable outdoor storage to be carried out in situations where no storage structures are available. They are weather resistant, waterproof, have low permeability to gases, are resistant to rodent penetration, and are made in various sizes to hold from 5 to 50 tonnes of grain. They have no rigid structural parts and can be quickly and easily erected or dismantled.

Two versions of these liners have been developed:

- **Storage cubes for hermetic storage**

These provide farmers with appropriate storage technology for protecting grain from insects and rodents for prolonged periods without need for chemical treatments.

They also provide storage facilities in disaster situations when food is transported to areas where no warehouses exist, or where blockages in the food pipeline necessitate emergency storage.

- **Small scale modified atmosphere (MA) treatments**

These are storage cubes equipped with inlet and outlet ports to enable application of MAs or conventional fumigants by gravity displacement.

Potential applications are:

- insect control in organically grown commodities
- insect disinfestation of dried fruits
- wax moth control in honey combs.

Advantages of these liners for MA treatments are simplicity and efficiency of application with no head-space and no need for pressure release valves. They can also be used for prolonged storage after treatment to prevent reinfestation of the commodities.

# **On-farm Sealed Storage in Western Australia: a Progress Report**

**C.R. Newman**

APB Centre, Bougainvillea Avenue, Forest Field, Western Australia 6058

On-farm sealed grain storage was introduced into Western Australia in 1982. This method of grain storage and insect control was new to farmers and associated industry. Mistakes were made and corrected, and designs were altered to accommodate more effective sealing methods. From personal observations and field reports it was clear that many farmers did not understand or correctly apply fumigation technology.

A study of a discrete area of the Western Australian central wheat belt was conducted to discover the extent of the problem and establish the requirements for an extension campaign. Fifty-six per cent of silos examined did not achieve the gastightness standard required and all silos that had been in use for more than three years failed the test. The reasons for failure are discussed.

# The Toxic Action of Phosphine, Methyl Bromide, Methyl Chloroform, and Carbon Dioxide, Alone and as Mixtures, Against the Pupae of *Tribolium castaneum* Herbst (Coleoptera: Tenebrionidae)

**S. Rajendran**

Infestation Control and Protectants, Central Food Technological Research Institute,  
Mysore 570 013, India

The toxicity of phosphine, methyl bromide, methyl chloroform, and carbon dioxide, and mixtures of phosphine/methyl bromide, methyl bromide/methyl chloroform, phosphine/carbon dioxide, and methyl bromide/carbon dioxide to 1–2 day old pupae of *Tribolium castaneum* Herbst was studied. Joint action ratios estimated at LD50 and LD90 for a 24 hour exposure indicated antagonism in the effect on the pupae of phosphine and methyl bromide (except at LD50 in a mixture of 0.01 mg/L concentration of phosphine and methyl bromide), and of methyl chloroform and methyl bromide (Table 1). Carbon dioxide up to 40% concentration enhanced the toxic action of phosphine as well as methyl bromide; when increased further, carbon dioxide failed to increase their toxicity proportionately. Carbon dioxide alone produced a maximum of 11% mortality of the pupae exposed to 20–80% concentrations for 24 hours. The order of toxicity of the fumigants at both LD50 and LD90 on a weight (mg/L) basis or molar per volume (moles/L) basis was phosphine > methyl bromide > methyl chloroform.

**Table 1.** Toxicity data on phosphine, methyl bromide, and methyl chloroform and joint action ratios of their mixtures in tests against 1-2 day old *Tribolium castaneum* pupae exposed for 24 hours at 26±1°C and 60-70% relative humidity.

Fumigant/ fumigant mixture	LD50 (mg/L)	Fiducial limits	LD90 (mg/L)	Fiducial limits	Slope±SE	$\chi^2$ (d.f.)	LD90 /LD50	Joint action ratio at LD50	Joint action ratio at LD90
Phosphine (PH <sub>3</sub> )	0.017	0.01 0.02	0.085	0.06 0.14	1.81±0.04	28.1(6)	5.1	-	-
Methyl bromide	2.852	2.77 2.93	3.708	3.61 3.83	11.23±0.06	6.8(6)	1.3	-	-
Methyl chloroform	208.400	175.50 240.70	391.500	324.80 546.70	4.68±0.07	12.4(5)	1.9	-	-
0.0025 mg/L PH <sub>3</sub> + methyl bromide	2.984	2.89 3.07	3.978	3.80 4.25	10.25±0.07	1.0(3)	1.3	0.81	0.82
0.01 mg/L PH <sub>3</sub> + methyl bromide	1.022	0.79 1.14	4.670	3.23 10.06	1.94±0.05	9.7(4)	4.6	1.06	0.82
2.5 mg/L methyl bromide + methyl chloroform	83.010	68.90 97.81	496.000	362.30 789.80	1.65±0.06	2.8(4)	6.0	0.76	0.65
3.0 mg/L methyl bromide + methyl chloroform	51.220	42.06 60.95	239.000	195.00 313.00	1.91±0.06	4.5(4)	4.7	0.76	0.65

## Post-fumigation Productivity of Some Stored Products Insects

S. Rajendran

Infestation Control and Protectants, Central Food Technological Research Institute,  
Mysore 570 013, India

The effect of fumigants and atmospheric gases on the rate of multiplication or productivity of insects varies between species. Studies were made of the multiplicative potential of the survivors of populations exposed either at LD50 or to a range of fumigant concentrations as larvae (*Trogoderma granarium* Everts), pupae (*Callosobruchus chinensis* L. and *Sitophilus oryzae* L.), and adults (*S. oryzae*, *Tribolium castaneum* Herbst, *Oryzaephilus surinamensis* L., *Rhyzopertha dominica* F.).

Reduced productivity was noted in *S. oryzae* and *T. castaneum* exposed as adults to LD50 doses of ethylene oxide, chloropicrin, and ethylene dibromide (Table 1). Phosphine had an adverse effect on *S. oryzae* at LD50, on *T. granarium* at a dose causing 52% kill, on *R. dominica* (Table 2), and on a phosphine-resistant strain of *O. surinamensis* at higher lethal concentrations (Table 3). A significant reduction in multiplication of *T. castaneum* and *S. oryzae* was observed following exposure to dichlorvos vapour causing more than 86% kill (Table 4). Trichloroethylene and a mixture of trichloroethylene and acrylonitrile caused an increase in productivity of *T. castaneum* (Table 5).

A nitrogen atmosphere causing 90% mortality of *R. dominica* in 72 hours affected its productivity, and enriched carbon dioxide atmospheres had a similar effect in *T. castaneum* but not in *S. oryzae*, *R. dominica*, or *T. granarium*.

**Table 1.** Doses of fumigants inhibiting the multiplicative potential of some stored product insects when exposed for 24 hr at 25°–30°C.

Fumigant/mixture	Species and life stage exposed			
	<i>T. castaneum</i> adult	<i>S. oryzae</i> adult	<i>R. dominica</i> adult	<i>T. granarium</i> larva
Ethylene dibromide	0.72(40.3)	1.49(31.9)	1.40(95.5) 1.60(98.2)	1.00(83.7) 1.25(81.0)
Ethylene oxide	3.39(49.8)	1.06(38.8)	1.00(11.1) 1.25(59.0) 1.50(76.6)	N.E.
Chloropicrin	1.08(70.0)	0.57(57.7)	–	–
Acrylonitrile	N.E.	0.40(68.1)	–	–
Carbon tetrachloride	N.E.	N.E.	–	50.00 (90.8) 60.00 (97.2) N.E.
Methyl iodide	N.E.	N.E.	–	–
Methyl bromide– Ethylene dibromide 1:1 w/w	1.00–3.00 (26.4–98.1)	–	–	–
Acrylonitrile– Carbon tetrachloride 36:65 w/w	N.E.	N.E.	–	–
Acrylonitrile– 8% carbon dioxide	0.46(67.5)	0.19(54.4)	–	–
Nitrogen	–	–	99.9%/72 hr (89.7)	–

Doses in mg/L with % kill achieved in parenthesis.  
N.E. No effect on the productivity.

**Table 3.** Mean±SD productivity of phosphine-resistant\* *Oryzaephilus surinamensis* adults exposed to phosphine for 24 hr at 26 ±1°C.

Dose (mg/L)	No. of replicates	Corrected final mortality (%)	Productivity (progeny produced/adult-day) during	
			first 12 days	later 22 days
Control	6	(20.7)	0.50±0.07	0.51±0.05
0.01	6	5.0	0.49±0.11	0.54±0.02
0.02	6	6.7	0.44±0.08	0.52±0.03
0.04	6	45.4	0.49±0.17	0.57±0.16
0.06	12	79.3	0.38±0.19	0.58±0.17
0.08	12	78.3	0.34±0.19	0.53±0.23
0.20	12	97.1	0.14±0.20†	0.55±0.60
0.40	12	100.0	–	–

\* × 94 at LD99.9

†Significant from control after Duncan's new multiple range test (P<0.05).



**Table 2.** Effect of phosphine, methyl bromide, and carbon dioxide on the productivity of some stored product insects exposed for 24 hr 25–30°C.

Species	Life stage exposed	Phosphine			Methyl bromide			Carbon dioxide		
		No effect*	Inhibitory*	Percent inhibition	No effect*	Inhibitory*	Percent inhibition	No effect*	Inhibitory*	Percent inhibition
<i>T. granarium</i>	larva	0.002–0.008 (0.7–22.7)	0.016 (40.4)	39	1.0–2.0 (16.0–43.5) 3.0 (98.6)	0.5 (10.9) 100	18	8–64 (5.0–44.)	–	–
<i>R. dominica</i>	adult	0.002–0.016 (2.2–79.4)	–	–	0.6–0.9 (6.3–77.3)	1.0 (95.2)	68	40–80 (8.6–95.7)	–	–
<i>S. oryzae</i>	adult	–	0.006 (35.7)	50	–	1.14 (60.5)	14	–	23.2 (38.3)	16
<i>T. castaneum</i>	adult	0.008 (71.0)	–	–	–	2.65 (65.5)	22	–	49.7 (32.0)	23

\* Doses in mg/L or % CO<sub>2</sub> with per cent mortality achieved in parenthesis. Values are means of three replicates in *S. oryzae* and six in others.

**Table 4.** The productivity of *S. oryzae* and *T. castaneum* adults surviving exposure to dichlorvos vapour for 24 hr at 26±1°C.

Insect	Dose	Corrected final mortality (%)	Productivity*
	(mg/m <sup>3</sup> )		(mean±SD)
<i>S. oryzae</i>	2.8	0	1.25±0.31 <sup>a</sup>
	5.7	0	1.29±0.25 <sup>ab</sup>
	8.5	34.7	1.30±0.35 <sup>ab</sup>
	14.2	86.9	0.67±0.66 <sup>b</sup>
	19.8	92.4	0.46±0.80 <sup>c</sup>
	25.6	99.5	0
	Control	(12.5)	1.40±0.24 <sup>a</sup>
<i>T. castaneum</i>	3.5	18.3	1.89±0.66 <sup>ab</sup>
	7.1	62.8	2.52±0.82 <sup>a</sup>
	14.2	78.1	2.36±1.90 <sup>ab</sup>
	21.2	87.9	1.21±1.39 <sup>b</sup>
	28.2	93.0	0.57±0.99 <sup>c</sup>
	35.3	100	0
	Control	(3.4)	1.71±0.45 <sup>ab</sup>

\* Progeny produced/adult-day during the post-fumigation holding period of 14 days.

Each value is mean of eight replicates.

Means followed by different letters differ significantly at 1% (*S. oryzae*) and 5% (*T. castaneum*) levels by Duncan's new multiple range test.

**Table 5.** Increased productivity of *T. castaneum* adults surviving exposure to the LD<sub>50</sub>s of trichloroethylene and 35:65 w/w acrylonitrile-trichloroethylene mixture for 24 hr at 25°–30°C.

Fumigant	LD <sub>50</sub> (mg/L)	Actual mortality recorded (%)	Productivity (Mean* and range of progeny)	
			Control	Fumigant
Trichloroethylene	30.2	47.2	3914 (3743–4200)	5230 (4800–5501)
Acrylonitrile-Trichloroethylene	3.3	36.0	3914 (3743–4200)	5105 (4520–5500)

\* Each value is mean of three replicates.

## Management of Stored Product Pests by Controlled Atmosphere using Biogas

**B.D. Shukla and A. Dakshinamurthy**

Post Harvest Engineering Division, Central Institute of Agricultural Engineering,  
GTB Complex, TT Nagar, Bhopal-462 003, India.

Seed of blackgram *Vigna mungo* Linn. with a moisture content of  $10.5 \pm 1\%$  were used for studies of controlled atmosphere storage using biogas with composition 61% methane and 38% carbon dioxide in various storage structures at ambient conditions of  $26^{\circ}$ – $32^{\circ}$ C and 50–60% relative humidity. Narrow mouth glass containers of 2 kg capacity with provision for inlet of the gas and for making them airtight with rubber corks were used. Twenty-five adults of one-day-old *Callosobruchus maculatus* Fab. were placed into each of the containers and biogas introduced at a rate of 10 L/kg of grain. The containers were left undisturbed for one month. In another treatment, biogas was introduced and the containers were kept closed for only 24 hours. These treatments were compared with phosphine fumigation and an untreated control. All treatments were replicated five times. Observations were made on the effect on adult insects at hourly intervals after treatment, mortality and recovery of adults after 24 hours, development of successive generations at monthly intervals, consumer acceptability of the treated product, and germination of seeds after two months.

To assess the potential of biogas controlled atmospheres for management of insect pests in field situations, wheat stored in metal and solid polyethylene structures of 100 kg capacity and flexible polyethylene structures of 50 kg capacity were tested under ambient conditions using the test insect *Sitophilus oryzae* Linn. The mortality of weevils was recorded as previously. Further, the repeated use of biogas at weekly, 10 and 15 day, and monthly intervals was tested in metal containers to observe the effect on the development of subsequent generations of insects.

Mortality of *Callosobruchus maculatus* adults exposed to biogas was 100% (Table 1) when the gas was applied and left undisturbed for a month, and 97.6% when the gas was vented after 24 hours. The mortality was 98.4% following phosphine fumigation, while mortality in the untreated control was nil.

Data on the development of successive generations following various treatments (Table 1) indicated that treating with biogas and keeping the enclosure closed for one or two months had a marked influence on the immature stages of the insects. The number of adults emerging from 1 kg of pulse after one month was highest (79 per kg) in the control, followed by aluminium phosphide treatment (22 per kg), biogas treated and kept intact for 24 hours (3 per kg), and zero in the biogas treatment kept closed for a month. Similarly, after two months, there was no emergence of adults where the biogas was maintained without leakage. This was followed by the 24 hour treatment, the aluminium phosphide and the untreated control where adult emergence increased to a maximum of 152 per kg of pulse.

Consumer acceptability of the grain was not impaired by biogas treatment as there was no discernable difference between the treated and untreated grains in either appearance or colour. None of the fifty consumers tested could identify any variation between the biogas treated and untreated pulses.

When the use of biogas controlled atmospheres for insect pest management in large-scale storage of wheat was tested with various structures, it was found that in metal containers prevention of leakage was difficult and the mortality of weevils thus reduced. The data (Table 2) revealed that in metal containers the mortality of weevils was only 44% after 24 hours, while it was 90% or more in solid and flexible polyethylene structures. Similarly, due to the variation in leakage of introduced biogas, the development of successive generations was higher in metal containers than in the other two structures. In the untreated control, mortality was zero and development more rapid.

Attempts to use the biogas as single and multiple doses at different intervals proved (Table 3) that a single dose had no greater influence in reducing the development of *S. oryzae*. The population of 25 adults initially introduced could multiply to 34 in a period of one month. However, repeated use of biogas as multiple doses could dramatically reduce the initial population of 25 to 12, 8, and

**Table 1.** Effect of controlled atmosphere using biogas on *C. maculatus* and seeds of Blackgram.

Treatment	Mortality of adults	Recovery of adults	Development of generation		Germination after two months
	%	%	1 month after	2 months after	%
Exposed to Biogas for 1 month	100	0	0	0	92.2
Exposed to Biogas for 24 hours	97.6	2.4	3.2	7.0	82.6
Phosphine fumigation	98.4	1.6	21.6	66.2	69.4
Control	0	100	78.6	151.6	37.2
SED	3.70	-	9.53	2.93	5.27
C.D.(P=0.05)	7.98	-	20.56	6.32	11.37

**Table 2.** Effect of biogas on *S. oryzae* in different storage structures.

Structures	Mortality	Development of generations	
	%	I	II
Metal bin	44	32	74
Solid polyethylene	90	Nil	Nil
Flexible polyethylene	98	Nil	Nil
Control	Nil	86	193

**Table 3.** Effect of single and multiple doses of biogas on development of *S. oryzae*

Doses	Initial population	After 1 month
Single dose	25	34
Weekly intervals	25	Nil
10-day intervals	25	8
15-day intervals	25	12

zero in a period of one month, when used at 15 days, 10 days, and weekly intervals, respectively. It can therefore be concluded that even in relatively poorly sealed storage structures, biogas can be effectively used for the management of stored product pests.

# Fumigation of Dried Cocoa Beans Against Insect Pests of Storage

**A. Sivapragasam**

Cocoa/Coconut Division, Mardi, PO Box 25, 36307, Sungai Sumun, Perak, Malaysia

**Mohd. Azmi**

ASEAN-Planti, PO Box 209, UPM Post 43400, Serdang, Selangor, Malaysia

One of the problems during the storage of dried cocoa beans in Malaysia is that due to insect pests. Cocoa beans for export are rejected if there are 10 or more live insects per gunny sack (nett weight 62.5 kg) in a random sample of 16 sacks examined during preliminary inspection at grading centres. Such rejected beans need to be fumigated using methyl bromide (98% w/w methyl bromide + 2% w/w choropicrin), before a certificate for export will be issued.

Despite the extensive and continued use of methyl bromide in cocoa beans, quantitative information on its efficacy against the common insect pests of cocoa beans is lacking. To remedy this, two experiments were conducted: (a) a small-scale experiment at ASEAN-Planti (hereafter called experiment 1; and (b) a commercial scale experiment at the Federal Agricultural Marketing Authority (FAMA) grading centre in Port Kelang (hereafter called experiment 2. In both experiments, the changes in concentration of the fumigant with time were also monitored.

In experiment 1, fumigation was carried out under a wooden structure (2 m × 2 m × 2 m) inside which 20 gunny sacks, arranged in a cross-stack manner, were placed. Four insect species were tested, viz, adults and larvae of *Tribolium castaneum*, adults of *Oryzaephilus mercator*, adults and larvae of *Lasioderma serricorne*, and eggs and larvae of the moth *Corcyra cephalonica*. For each insect species, twenty adults or immatures were used. The insects were confined in plastic cups (8.5 cm high × 4.5 cm diameter, top covered with 18 mesh steel gauze) which was half filled with broken cocoa beans. The cups were randomly placed at various points within the structure and at each point all the above stages and species were represented. To monitor the gas, sampling tubes were inserted at the top, bottom, and middle of the stack. In the last case, separate sampling lines were placed outside (middle 1) and inside (middle 2) the gunny sacks. A thermal conductivity meter (Fumiscope®) was used for recording gas concentration. The structure was then covered with a tarpaulin which was sealed at the base using sandsnakes and soil. Methyl bromide was applied at a dosage of 0.45 kg from the top of the stack. A control (no fumigation) experiment was also set up similar to the one for the fumigant treated stack to evaluate natural mortality of insects.

In experiment 2, two lots of gunny sacks which had been rejected due to high insect counts were used. Each lot contained about 160 sacks weighing a total of 10 tons. The size of the stack was 4.2 m × 4.8 m × 3.5 m. After the introduction of test insects and gas sampling tubes, the stack was covered with a tarpaulin. Methyl bromide was applied from the top of the stack at a dosage of 0.14 kg per tonne of beans.

In experiments 1 and 2, complete mortality was obtained for all test insects in cups

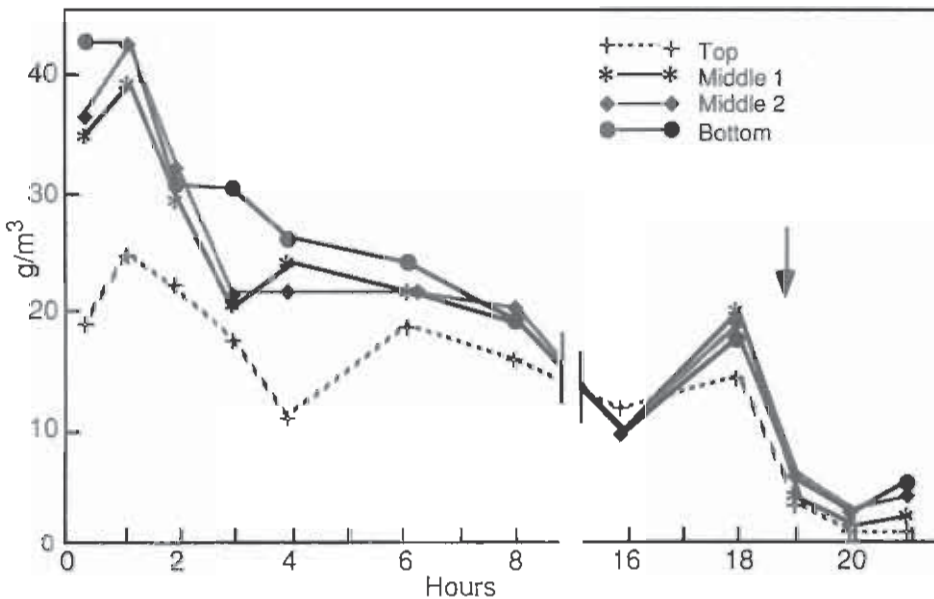
except eggs of *C. cephalonica*, regardless of position within the stack. Thus, in experiment 1, about 40% egg survival of *C. cephalonica* was obtained in the treated sacks, compared with the control where 50% survival was obtained. Insect counts from samples of beans taken after fumigation revealed complete mortality of all insects in fumigated samples in experiment 1 where the mean number of insects before fumigation was 5.0. In experiment 2, however, a few living immature individuals were found in the fumigated sacks (Table 1).

**Table 1.** Number of live insects in samples of cocoa beans before and after fumigation with methyl bromide at a dosage of 0.14 kg per tonne.

Sack number	No. of insects	
	Prefumigation <sup>1</sup>	Post-fumigation <sup>2</sup>
1	5	0
2	2	0
3	7	0
4	3	1
5	2	2
6	13	0
7	4	0
8	6	0
9	8	0
10	7	0
11	5	0
12	6	1
13	3	0
14	9	0
15	8	0
16	7	0

<sup>1</sup> From sacks examined during preliminary inspection

<sup>2</sup> Immatures only from another batch of 16 bags excluding those sampled during preliminary inspection.



**Fig. 1.** Changes in methyl bromide concentration at various positions within a stack of cocoa beans fumigated at a dosage of 0.14 kg per tonne. Arrow shows time of start of aeration after removal of tarpaulin. Middle 1 — outside gunny sack; Middle 2 — inside gunny sack.

In both experiments, there were variations in fumigant concentrations between the top and bottom of the stack until about 16 hours after fumigation, with the bottom having a higher concentration than the top. There was little difference in fumigant levels between the Middle 1 and Middle 2 positions. In experiment 2, gas concentrations in all positions dropped rapidly on aeration to a mean level of about 2 g/m<sup>3</sup> from a mean level of 15 g/m<sup>3</sup> before aeration (Fig. 1).



# Fumigation of Wheat in a High Vertical Bin with a Mixture of Methyl Bromide and Carbon Dioxide

**Y. Carmi**

Agricultural Research Organisation Stored Products Division, Volcani Center,  
Bet-Dagan, Israel

**L. Klein and S. Cohen**

Bromine Compounds Ltd, P.O. Box 180, Beer-Sheva, Israel

The efficacy of a fumigant mixture of methyl bromide and carbon dioxide was tested by fumigation of a 30 m high concrete bin with a capacity of 1200 m<sup>3</sup> of wheat. Methyl bromide dosage was 80 g/m<sup>3</sup> and that of carbon dioxide 125 g/m<sup>3</sup>. The two gases were sprayed simultaneously into the headspace of the bin from pressurised cylinders.

Measurement of methyl bromide concentrations was done with the assistance of plastic tubes placed at various locations inside the bin before it was filled.

Good distribution of methyl bromide was obtained, producing lethal concentrations in all parts of the bin, including the bottom, after 24 hours. A slightly better and more rapid penetration was noted along the walls of the bin. The fumigation killed all insects present.

Methyl bromide/carbon dioxide mixtures are currently in commercial use in Israel. Dosages employed are 50 g/m<sup>3</sup> methyl bromide and 200 g/m<sup>3</sup> carbon dioxide in the form of dry ice.

# 'Wise Joseph Sacks': a Hermetic Storage System for Small-scale Use

**A. Murray\***

Grain Security Foundation Ltd, PO Box 886, Bondi Junction, NSW 2022, Australia

The 'Wise Joseph Sack' (Fig. 1) is a sack of 50 kg nominal capacity made from a specialised, heat-sealable, plastic laminate. The laminate incorporates a metal foil component to reduce oxygen permeability.



**Fig. 1.** Sealing Wise Joseph Sacks in the field

Trials carried out in collaboration with Silliman University in the Philippines have shown that dry grain may be stored in Wise Joseph Sacks for long periods under humid tropical conditions, without need for pesticides or fumigation. Storage periods of at least 12 months are possible for white maize and paddy, without loss of germination or other qualities. Furthermore, insect infestation present at the time of packing is eliminated by the hermetic system and the bags themselves are resistant to reinvasion by pests. Unprotected grain in woven polypropylene sacks stored together with grain in Wise Joseph Sacks was extensively damaged by insect pests. In an extreme case, pesticide-free yellow maize (12% moisture content) lost 23%

\* Paper presented at the conference by Dr H.J. Banks, CSIRO Division of Entomology, Canberra, Australia.

dry matter after 9 months storage in normal woven sacks, but samples from the same stock stored beside the normal sacks in Wise Joseph sacks lost not more than 0.5 %.

The upper moisture limit for safe storage has not been determined and, until proven otherwise, it would be prudent to use Wise Joseph Sacks to store only grain at below normally accepted safe moisture levels. However, storage trials under humid tropical conditions at 75% equilibrium relative humidity in Wise Joseph Sacks have shown no increase in aflatoxin content over 6 months storage and mould proliferation was apparently inhibited by the modified storage environment in the sacks.

The Wise Joseph Sacks are undergoing further tests to determine acceptability and further define limitations to their use. They appear to offer a system where the householders and small-scale farmers can store their own grain for consumption or seed, avoiding the need to sell during the harvest glut and buy again later at higher prices.

## 'Bubble' Fumigation: a New Concept

**C.P. Smith**

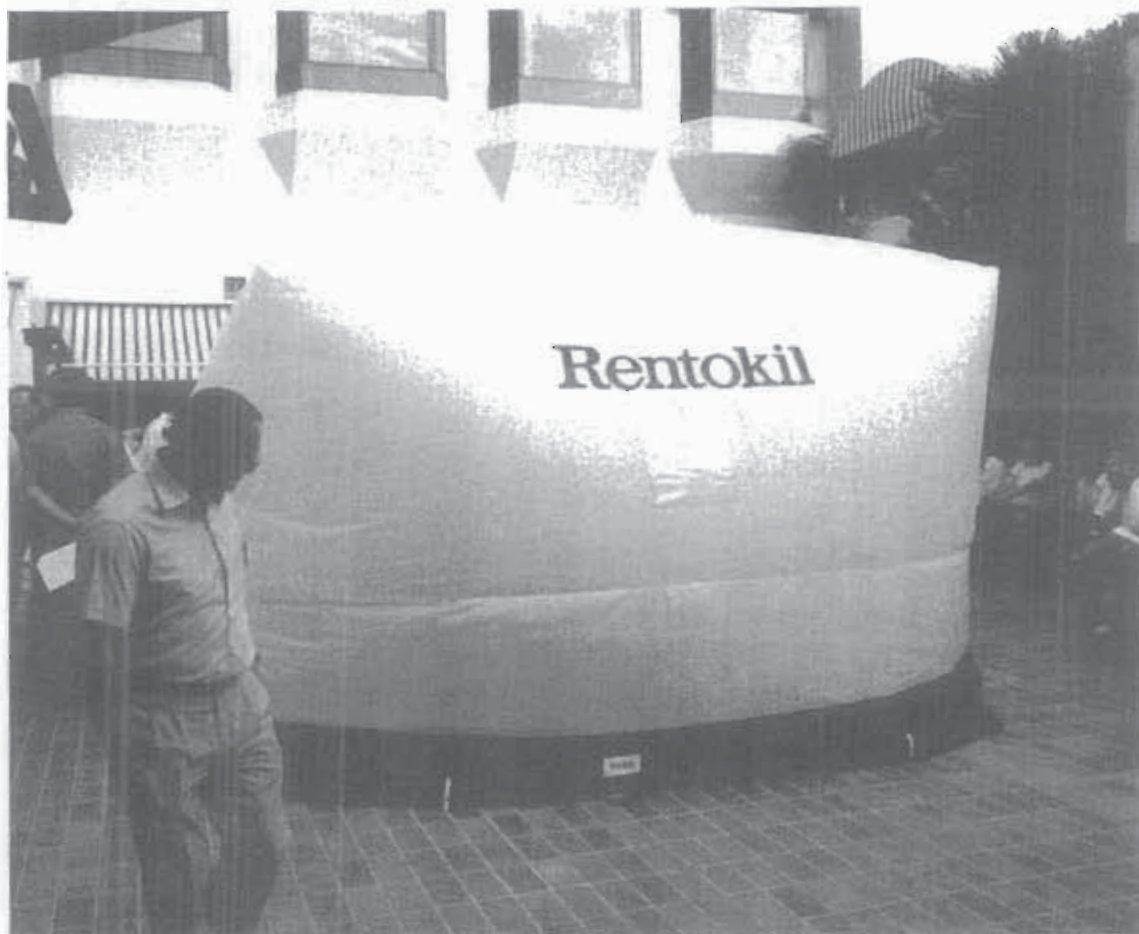
Rentokil PLC, Felcourt, West Sussex RH19 2JY, U.K.

Traditional methods of fumigation have a number of limitations. Chief among these for small stack fumigations are inefficient sealing and, when using methyl bromide which is 3.5 times heavier than air, the phenomenon of layering.

These limitations can be overcome by the use of fumigation chambers, but such devices are expensive and for the most part their installation is feasible only for the regular treatment of high-value commodities.

Another major problem of traditional methods of fumigation is, of course, that of the likely occurrence of residues in food and the environment, a situation to which there is increasing resistance among consumers and regulatory authorities.

Against this background, Rentokil set about developing a new, portable fumigation system to overcome current limitations. The result is the so-called 'Bubble' fumigation system, the 'bubble' being a sealed plastic enclosure as described in subsequent paragraphs and shown in Fig. 1.



**Fig. 1.** Sealed enclosure of Rentokil Fumigation System

The key to the system is a unique, purpose-made, gastight zip for sealing the enclosure. The zip is made from a mixture of hard-wearing durable plastics. One half of the zip is welded to the leading edge of a purpose-made top cover, made from a PVC, polyester-net-reinforced fumigation sheet. The other half is welded to a base sheet made from a hard-wearing chloro-sulphonated polyethylene.

When the top cover and base sheet are zipped together they form a bubble that is, for all practical purposes, gastight and has the ability to safely receive, hold, and be purged of fumigants. The enclosure also allows fumigations to be carried out in locations where they would not normally be permitted.

The standard fumigation bubble has a capacity of 30 m<sup>3</sup>, but virtually any shape or size between 1 and 90 m<sup>3</sup> could be made. The 30 m<sup>3</sup> enclosure will hold up to 12 loaded pallets, but as few as one pallet can be fumigated, or even a single object such as a table. There is virtually no restriction on the type of commodity, or item, that can be treated. Moreover, the enclosure, attached to a dehumidifier, can be used as a pesticide-free dehumidification chamber for mite and booklouse control.

For methyl bromide fumigations a purpose-built dispenser unit is used (Fig. 2). This first creates a partial vacuum within the enclosure, so aiding the subsequent penetration of fumigant into tightly packed commodities and permitting some reduction in fumigation times.

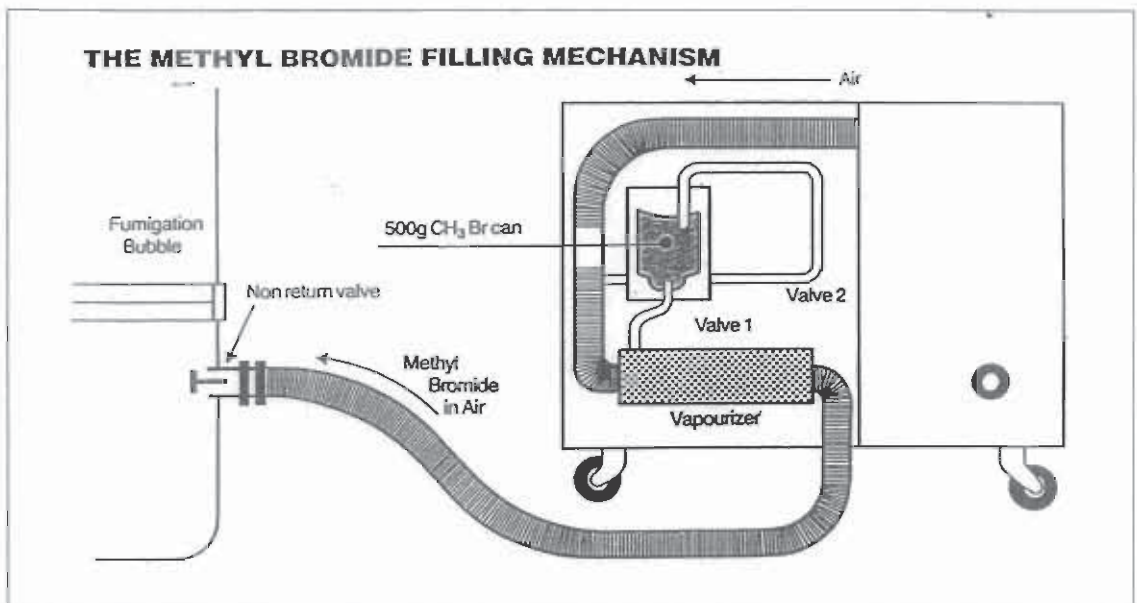


Fig. 2. Rentokil Fumigation System methyl bromide filling mechanism

If phosphine is used, standard phosphine-generating tablets are simply placed in the enclosure before it is zipped up.

At the end of a fumigation the gas contents of the enclosure are force ventilated to a suitable discharge point, or can be vented through a gas scrubber of, for example, activated carbon, so ensuring the release into the atmosphere of clean air only (Fig. 3).

The chamber is also suitable for fumigations using carbon dioxide or nitrogen.

As regards gas retention and Ct products, the bubble fumigation system behaves as a fumigation chamber. Trials conducted with empty bubbles and methyl bromide (Fig. 4) demonstrate the gastightness of the system. Fig. 5 shows the performance of the system for a methyl bromide fumigation of 8 tonnes of bagged cocoa beans. A Ct product of more than 300 g hours/m<sup>3</sup> was achieved.

In summary, the Rentokil Fumigation System overcomes many of the disadvantages

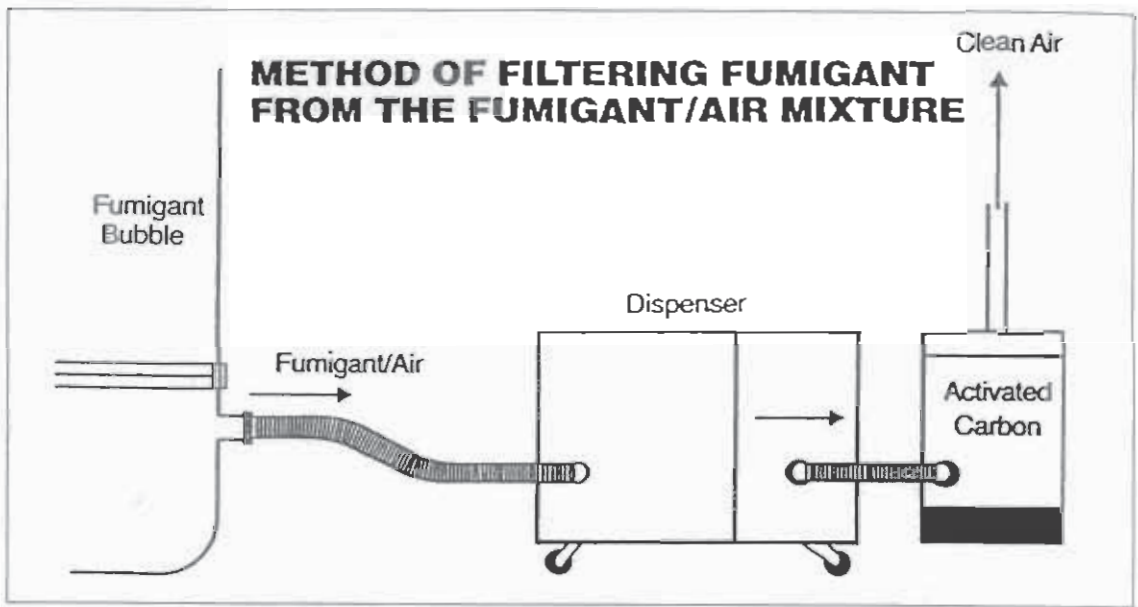


Fig. 3. Rentokil Fumigation System: method of scrubbing fumigant from ventilated enclosure.

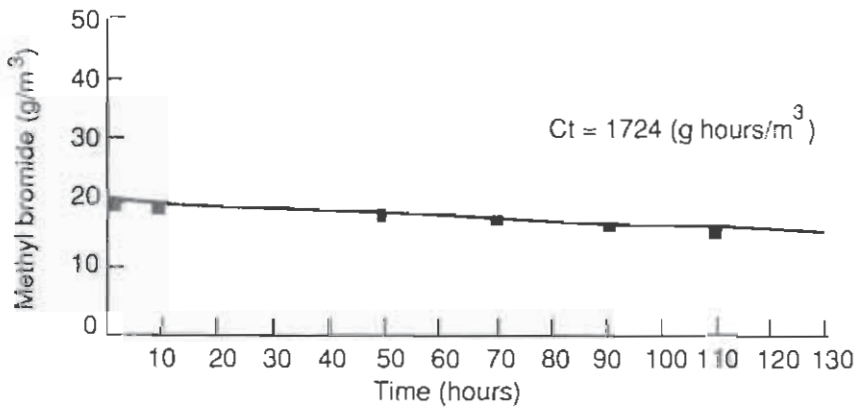


Fig. 4. Retention of methyl bromide in an empty fumigation 'bubble'.

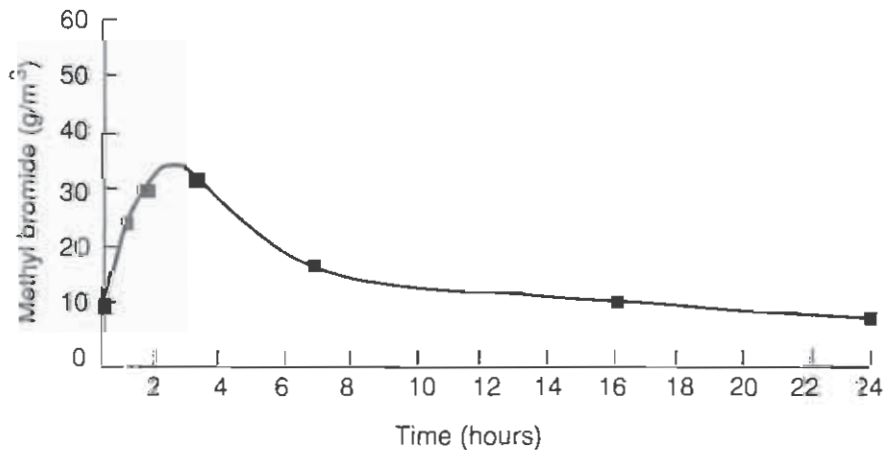


Fig. 5. Methyl bromide concentration in a 30 m<sup>3</sup> fumigation 'bubble' during fumigation of 8 tonnes of bagged cocoa.

es associated with traditional stack and chamber methods of fumigation. It enables fumigations to be safely undertaken in locations previously deemed unsuitable, and may enable the wider use of alternative fumigants such as carbon dioxide.

## Report on Session 7: Poster Papers and Commercial Presentations

Mr J. van S. Graver, CSIRO Division of Entomology, Australia  
Rapporteur: Ms G.C. Sabio, NAPHIRE, Philippines

This was the first ACIAR grain storage conference at which a session was devoted to submitted (as against commissioned) papers. It was decided that these should be presented as poster papers that would be on display for the duration of the conference, and that their authors would make short presentations during the penultimate session of the meeting. The papers complemented those presented during earlier sessions, and generally covered practical applications of fumigation and CA technology.

Aspects of the biological responses to treatments with gases were reported in a number of poster papers.

Dr P.W. Gras described the relationship between sensory evaluation of rice stored under controlled atmospheres and other quality factors. He indicated that as yellowness increased during storage, acceptability and consumer preference decreased. Thus, changes in yellowness can provide a simple and objective means of monitoring changes in consumer acceptance of stored rice.

Ms D. Hamel (in a paper presented on her behalf by Dr Gras) reported on the viability of a range of seeds after storage under various conditions. Seeds of paprika, parsley, and lettuce were found to be most sensitive to carbon dioxide, with viability reduced to zero in paprika.

Mr E.C.W. Leong spoke about laboratory trials on the toxicological response of psocids to various concentrations of carbon dioxide. His results indicated that the egg is the most tolerant stage and that current recommendations for infestation control with this gas appear to be adequate. During the discussion following this paper, the observation was made that regular, calendar-based fumigations of polished rice appeared to enhance psocid numbers—possibly due to the suppression of natural enemies.

Dr B. Shukla reported on the potential of biogas-based controlled atmospheres to manage insect pests in grain stored in rural situations, where fumigant usage is limited. In laboratory studies, biogas consisting of 31% methane and 38% carbon dioxide gave high mortality rates in a number of pest species and consumer acceptance of grain stored under these conditions remained unaffected.

Dr S. Rajendran presented two papers. He first reported on the results of a study of the post-fumigation productivity of some stored product insect species. He measured the effects on multiplicative potential of survivors of insect populations exposed to either a  $LD_{50}$  or to a range of fumigant concentrations as larvae. In his second paper, he discussed the toxic action of methyl bromide, methyl chloroform, and carbon dioxide, alone or as mixtures, against pupae of *Tribolium castaneum*.

Application methodology was the subject of five papers.

Speaking to two papers, Dr C.H. Bell gave an account of the problems involved in the application of phosphine and controlled atmospheres in farm bins in the U.K. He emphasised the need for effective sealing for the successful implementation of gaseous control methods. In farm-scale trials with carbon dioxide-based atmospheres, he reported that continuous-flow systems offer the only practical method for achieving insect control in existing, unsealed structures. In the second paper, he reported some new results relating to the toxicity of phosphine applied under margi-

nal conditions. He also described a continuous-flow, top-up method of dosing using a 2–3% mixture of phosphine in carbon dioxide supplied from gas cylinders. The system, which was reported to have considerable potential for wider use in the U.K., appeared to be similar to that described by Dr R.G. Winks earlier in the meeting.

Reporting on the presents status of on-ram sealed storages in Western Australia, where 65% of properties now have one or more sealed silos, Mr C.R. Newman indicated that grain infestation had dropped from 22% to 3% in all farm stores over the past 10 years. However, a survey of silos that had been in use for more than 3 years suggested that lack of maintenance has become a problem that can lead to failure to control infestations.

Mr I. Klein described the use of methyl bromide/carbon dioxide mixtures to improve fumigant distribution in sealed steel silos having no provision for recirculation. In trials using this mixture, good fumigant penetration, distribution, and total insect control had been achieved within 24 hours.

In another presentation concerning methyl bromide fumigation, Mr A. Sivapragasam reported on the control of insects infesting cocoa in Malaysia.

A newly developed portable and sealable fumigation enclosure—the Rentokil Bubble—was demonstrated and described by Mr C.P. Smith. This well sealed system can be used for both fumigation and CA applications. It is well suited to quarantine fumigation of small consignments, and could have application in bag storages where there is always a need to fumigate empty bags and unused dunnage, a role that the Volcani Cube (see below) is also able to fulfill.

There were four papers relating to sealed storage of bag stacks.

Mr P.C. Annis circulated a pre-publication draft of an operations manual for carbon dioxide fumigation of bag stacks sealed in plastic enclosures. The final publication will be presented as a step-by-step 'how to' manual. Conference participants were invited to comment to the authors on the format and presentation of the contents.

The results of a comparative sensory evaluation of polished rice held in carbon dioxide-treated bag stacks and in conventional storage over an 8 month period were presented by Mr Rahim Muda. It was found that rice stored on the carbon dioxide-treated, sealed enclosures was significantly more palatable than rice held in conventional storage.

Mr Pitoon Urairong reported that effective insect control was obtained in rice seed fumigated with phosphine and subsequently held under permanently sheeted, but unsealed, stacks.

The Volcani Cube, a system for outdoor storage of bagged commodities was described by Dr E. Donahaye. Based on flexible PVC membranes that can be sealed to provide hermetic or modified-atmosphere storage, the system can provide storage for 5–50 tonnes of bagged commodities. As with the Rentokil Bubble, the Volcani Cube could find immediate application as an adjunct to storage hygiene by providing the means to fumigate empty bags, spillage, and dunnage.

In other presentations in this session:

- Mr E. Highley outlined the scope of the draft 'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region: Part 1. Principles and General Practice', being produced under the auspices of the ASEAN Food Handling Bureau and ACIAR. Comments and suggestions on the draft were solicited for incorporation in the final copy;
- Mr J. van S. Graver discoursed on the accomplishments and current activities of the Stored Grain Research Laboratory of CSIRO Australia;
- Safeway Silos described its product range and current clients; and
- on behalf of the Grain Security Foundation, Dr H.J. Banks outlined the benefits of its 'Wise Joseph Sacks'.



# Conference Summary

## Conference Summary

WE now come to the final part of the closing session of the conference. It is my lot to try to summarise what has transpired in what I believe has been a very successful gathering of people interested in fumigation and controlled atmosphere technology. The linkages established in the organisation of the conference have undoubtedly contributed to this. ACIAR certainly had a vested interest in the conference as we had just concluded a successful project on long-term storage of grain using controlled atmospheres as the protective treatment of quality, and we were looking to extend the information obtained as widely as possible. Association with the Steering Committee of the International Symposia on Controlled Atmosphere Grain Storage was therefore timely and the support of the Committee has been a major factor contributing to the success of our gathering.

It is very appropriate that our local partner has been the National University of Singapore. Singapore, as the commercial centre of this part of the world, is an ideal venue, and the NUS, as the centre of learning, the appropriate sponsor—for we all came here to learn.

In my summary of the proceedings of the conference, I do not propose to reiterate what our Chairmen have so capably said already. Rather, I would like to highlight the most relevant issues that I feel have emerged from the various papers and the discussions that they provoked.

It was evident to me from listening to the presentations, that the conference has been opportune in coinciding with times of major change in perceptions of preserving grain quality by use of fumigation and controlled atmosphere storage. Indeed, it is with quality itself that the issues of prime importance lie. The recognition of quality as a genuinely marketable commodity has particular significance. The first element of this is the matter of chemical residues in grain. Attitudes to these are hardening and there is a definite swing towards controlled atmospheres. Our industry colleagues from Australia, in responding to market pressures, have demonstrated that such a course is commercially viable. It has been economic to construct appropriately gastight structures or to take steps to seal many existing structures. Methods for this have been developed and thus CA is now available as an option for preservation of quality. Nevertheless, the conventional fumigants, particularly phosphine, will be with us for the foreseeable future. The world needs them and the fine-tuning of their use as described in many papers during the conference and as exemplified by the CSIRO development of flow-through techniques with phosphine, will ensure that they continue to play a useful role.

This leads me logically to refer to the timely production of the set of 'Suggested Recommendations for the Fumigation of Grain in the ASEAN Region' which has been discussed during this meeting. The consensus that had been reached in recognising the need for this document and the appreciation of the benefits that will accrue from its availability have been endorsed at this meeting. There can be no losers, as these benefits will apply equally to fumigation operators and users of their services. The document is multipurpose. It provides a complete text for those responsible for fumigation, with definitive sections that outline the processes and procedures of fumigation in a format appropriate and with sufficient technical details for inclusion

in official regulations. It also provides a basis for contractual arrangements for fumigation and the operational detail necessary for the actual conduct of the fumigation. But the task is only half done. Part 1 is virtually complete but the subsequent parts must follow quickly if the document is to be of practical use. The first of the supplements covering fumigation of bag stacks with carbon dioxide has been available in draft form for discussion at this meeting. It is hoped to finalise this operations manual and similar manuals covering other types of fumigation with phosphine and with methyl bromide in the near future.

Let me return to considerations of quality. It is very encouraging to note the attention that is now being given to quality studies paralleling the development of the different technologies, whether they involve the conventional fumigants or CA. The appreciation of quality as an adjunct to treatment of grain is becoming mandatory as markets and consumers become more discriminating and price differentials become significant. Quality has certainly been a common thread running through our conference and has been the subject of recommendations for further attention.

A critical element in the wide range of quality studies now in progress has been the application of simulation modelling. This has enabled all relevant parameters to be taken into account in quantitatively defining quality and so optimising technology, without making often unacceptable assumptions. This has been brought about by the availability of fast, high capacity computers in compact form at generally affordable prices. I believe simulation modelling has not realised its full potential but we are already seeing the benefits from optimisation studies with their integral economic considerations. Similarly, there have been exciting developments in process control whereby manual operations are increasingly being replaced by microprocessor control with its attendant reliability and precision. The level of competence of supervision of operations is thus that of the designer of the software and not that of the often unskilled worker.

A very important point was raised concerning the appropriateness of research and development work with fumigation and CA technology. It is vital today, with resources as limited as they are and a pressing need for accountability in all activities, that technology be cost-effective and that if developed, it is used. For this to happen the studies must be appropriately targetted right from the beginning. The need for the work must be adequately defined and the problem evaluated before resources are expended. Today there can be limited scope for developing technology and then looking for a use for it. It has always been difficult to create needs in industry when industry has not already perceived these needs.

This leads of course to consideration of sociological and economic inputs to research and development studies. These disciplines provide the quantification and objective justification for any piece of work in a form that is understandable by and acceptable to administrators who are really only concerned with the bottom line—that the work is economically viable and appropriate. Fortunately, engineers and biologists have come to realise that they can no longer work in isolation and, as we have seen in this meeting, they are working side by side with economists. The benefits are immense. The technology that is developed has a better chance of introduction into industry with benefits to all. The basic problem, as I indicated earlier, is that resources for research and development activities are limited—and by limited I mean that the total resources available are less than those in aggregate that are required to fully address specific problems. Economic assessments can be made of proposed interventions at different points where problems occur in the chain from production to final disposal to consumers. These assessments provide the objective comparison of the potential benefits to be derived, so that priorities can be established to maximise the return from the resources available. I trust we all agree that the collaborative approach between technologists, economists, and of course

sociologists is now mandatory in all our activities. We surely cannot beat them, so let's join them.

The perennial but vital question of dissemination of information has been raised on many occasions throughout the conference. There are networks available internationally, regionally—as exemplified by AFHB's information network, and of course to varying degrees within countries. The strength and effectiveness of these networks are dependent on support and positive inputs from users. Users must not look only for outputs—they must also contribute to the basic data pool, including assistance to the organisers in expanding mailing lists to ensure that all target groups are reached. One cannot expect too much unilateral activity from the networks—somebody has to pay for it and resources are limited. Thus, I reiterate that networks improve with use but that users should contribute in kind to networks as well as deriving services from them.

I must now finalise my summary and as this is my last opportunity to do so, I wish to make some acknowledgements. Firstly, on behalf of the National University of Singapore and ACIAR, I would like to express our appreciation for the efforts of our local colleagues in the Ministry of Trade and Industry, particularly Mr Chan Ban Leong and Mr Chai Soon. I would also like to single out Ms Irene Villapando of the AFHB whose dedicated and professional organisational skills have contributed enormously to the smooth conduct of the conference.

I would also like to express the thanks of the organisers to the speakers, the Chairpersons, and their rapporteurs and to all participants for their valuable contributions and the manner in which they have interacted to make this conference, I repeat, so successful.

*Dr B.R. Champ*  
ACIAR

## Participants

### Australia

**Mr P.C. Annis**

Stored Grain Research Laboratory  
CSIRO Division of Entomology  
GPO Box 1700  
Canberra, ACT 2601

**Dr H.J. Banks**

Stored Grain Research Laboratory  
CSIRO Division of Entomology  
GPO Box 1700  
Canberra, ACT 2601

**Dr B.R. Champ**

ACIAR Postharvest Research  
Program  
c/- CSIRO Division of Entomology  
GPO Box 1700  
Canberra, ACT 2601

**Mr G.J. DGLISH**

Entomology Branch  
Queensland Department of Primary  
Industries  
Meiers Road  
Indooroopilly, Qld 4068

**Mr R. Delmenico**

Co-operative Bulk Handling  
GPO Box L886  
Perth, WA 6001

**Mr J. Freebairn**

South Australian Co-operative  
Bulk Handling Ltd  
GPO Box 1568  
Adelaide, SA 5001

**Mr H.W. Gayfer**

Co-operative Bulk Handling  
GPO Box L886  
Perth WA 6001

**Dr P.W. Gras**

CSIRO Wheat Research Unit  
Private Bag, P.O.  
North Ryde, NSW 2113

**Mr J. van S. Graver**

Stored Grain Research Laboratory  
CSIRO Division of Entomology  
GPO Box 1700  
Canberra, ACT 2601

**Mr G.R. Helgeson**

South Australian Co-operative  
Bulk Handling Ltd  
GPO Box 1568  
Adelaide, SA 5001

**Mr E. Highley**

ACIAR  
GPO Box 1571  
Canberra, ACT 2601

**Dr A. Hocking**

CSIRO Division of Food Research  
PO Box 52  
North Ryde NSW 2113

**Mr B.A. Kelly**

South Australian Co-operative  
Bulk Handling Ltd  
GPO Box 1568  
Adelaide, SA 5001

**Mr J.V. Moore**

Safeway Silos  
29 Bide Street  
Taringa, Qld 4068

**Mr C.J.E. Newman**

Bulk Grains Queensland  
PO Box 136  
Toowoomba, Qld 4350

**Mr C.R. Newman**

APB Centre  
Bougainvillea Avenue  
Forest Field, WA 6058

**Mr E. Ripp**

CAFCO  
19 Amethyst Crescent  
Armadale, WA 6112

**Dr G.J. Ryland**

G.J. Ryland and Co.  
78 Hutt Street  
Adelaide, SA 5000

**Ms S.M. Salinders**

CAFCO  
19 Amethyst Street  
Armadale, WA 6112.

**Mr C.D.T. Thurlow**

Centre Secretary  
ACIAR  
GPO Box 1571  
Canberra, ACT 2601

**Dr D. Webley**

Australian Wheat Board  
GPO Box 4562  
Melbourne, Vic. 3001

**Ms K.A. Wheeler**

CSIRO Division of Food Processing  
PO Box 52  
North Ryde, NSW 2113

**Dr G. White**

Entomology Branch  
Queensland Department of Primary  
Industries  
Meiers Road  
Indooroopilly, Qld 4068

**Dr R.G. Winks**

Stored Grain Research Laboratory  
CSIRO Division of Entomology  
GPO Box 1700  
Canberra, ACT 2601

### Canada

**Dr E.J. Bond**

Canada Agriculture Research Centre  
1400 Western Road  
London  
Ontario N6G 2V4

### France

**Dr P. Ducom**

Ministere Agriculture  
Laboratoire Denrees Stockees  
Service Protection Vegetaux  
Chemin Diartigues  
33152 Cenon Cedex

### Federal Republic of Germany

**Mr Lothar Kraemer**

Prosanitas GmbH  
PO Box 1256  
D-6947 Laudenbach

**Dr A. Moog**  
Detia Export GmbH  
PO Box  
D-6947  
Laudenbach

**Dr C. Reichmuth**  
Biologische Bundesanstalt für  
Land- und Forstwirtschaft  
Institut für Vorratsschutz  
Königin-Luise Strasse 19  
D-1000 Berlin 33

## Hong Kong

**Mr Peter Fung**  
Permea Asia Pacific  
Room 2807-08 Windsor House  
311 Gloucester Road  
Hong Kong

## India

**Dr S. Rajendran**  
Infestation Control &  
Protectants Area  
Central Food Technology Institute  
Mysore 570 013

**Mr Mallikarjuna Rao**  
National Dairy Development Board  
P&E Group  
Anand-88001  
Gujarat State

**Mr R.D. Shroff**  
United Phosphorus Limited  
167 Dr Annie Besant Road  
Worli, Bombay 400018

**Dr Banshi D. Shukla**  
Project Coordinator  
AICRP on Post Harvest Technology  
Central Institute of Agricultural  
Engineering  
GTB Complex  
T.T. Nagar  
Bhopal 462003

**Mr K. Subramanian**  
United Phosphorus Limited  
167 Dr Annie Besant Road  
Worli, Bombay 400018

## Indonesia

**Mr J.A. Conway**  
Project Manager  
Bulog-ODNRI Development Project  
C/- British Embassy  
Jl. M.H. Thamrin 75  
Menteng  
Jakarta

**Mr Fatchurrahman**  
Pt. Sucofindo Surabaya Branch  
Jalan Kedung Sari No. 1  
Surabaya

**Mr R.J. Hodges**  
Bulog/ODNRI Project  
Kav 819, Bintang  
Diponggo  
Dukuh Kupang  
Surabaya

**Mr M.K. Mitchell**  
Bulog-ODNRI Development Project  
C/- British Embassy  
Jalan M.H. Thamrin 75  
Menteng  
Jakarta

**Mr Nataredja Yun Cahyana**  
National Logistics Agency (Bulog)  
49 Jalan Gatot Subroto  
Jakarta

**Dr Okky Setyawati**  
SEAMEO-BIOTROP  
PO Box 17  
Bogor

**Dr Mulyo Sidik**  
Research Co-ordinator  
National Logistics Agency (Bulog)  
49 Jalan Gatot Subroto  
Jakarta

**Mr S. Sudarsana**  
M.H. Thamrin No. 11  
Jakarta

**Professor Dr Sitti Soetarmi  
Tjitrosomo**  
SEAMEO-BIOTROP  
PO Box 17  
Bogor

**Mr Yusof Faishal**  
National Logistic Agency (Bulog)  
49 Jalan Gatot Subroto  
Jakarta

## Israel

**Dr E.J. Donahaye**  
Department of Stored Products  
Agricultural Research Organization  
The Volcani Centre  
PO Box 6  
Bet Dagan 50250

**Mr Levi Klein**  
Bromine Compounds Ltd  
PO Box 180  
Beer-Sheva

**Dr S. Navarro**  
Department of Stored Products  
Agricultural Research Organization  
The Volcani Centre  
PO Box 6  
Bet Dagan 50250

## Japan

**Mr Masamichi Hino**  
Kubota Ltd  
2-35 Jin Mucho  
Yao City 581

**Mr Yoshihiro Inoue**  
Kubota Ltd  
2-35 Jin Mucho  
Yao City 581

**Professor Toshiharu Yoshida**  
Laboratory of Applied Entomology  
Faculty of Agriculture  
Okayama University  
Tsushima, Okayama 1700

## Korea

**Mr Cheong Han Seuk**  
Do Nam Pest Control Co. Ltd  
2-18 Mansuk-Dong Dong-Gu  
Inchon

**Mr Ho Bong Lee**  
Korea Pest Control Co. Ltd  
57 Seonrin-Dong Chung-Ku  
Inchon

**Mr Lee Ghab Woo**  
Korea Pest Control Co. Ltd  
Busan B2  
271-18 Hakjang-Dong, Buk Ku  
Busan

**Mr Tae Suk Lee**  
Do Nam Pest Control Co. Ltd  
2-18 Mansuk-Dong Dong-Gu  
Inchon

## Malaysia

**Mr Mohd. Azmi Abdul Rahim**  
ASEAN Planti  
Bag Berkunci 209  
PO Universiti Pertanian Malaysia  
43400 Serdang  
Selangor

**Mr Dhiauddin bin Mohd Nour**  
Food Technology Division  
MARDI  
GPO Box 12301  
Kuala Lumpur 50774

**Ms Faridah Bt. Mat Elah**  
Food Technology Division  
MARDI  
GPO Box 12301  
Kuala Lumpur 50774

**Mr Kamarozaman bin Bujang**  
Lembaga Padi dan Beras Negara  
1st Floor, Bangunan Umno  
Jalan Hang Tuah  
Melaka

**Mr Terry Kong Kim Wah**  
Rentokil Malaysia Sdn Bhd  
36 Lorong Rahim Kajai 14  
Taman Tun Dr Ismail  
Kuala Lumpur

**Mr Lee Chin Hin**  
Lembaga Padi dan Beras Negara  
Tingkat 13-17  
Bangunan Perkim 250-D  
Jalan Ipoh  
51200 Kuala Lumpur

**Dr Lee Nai Pin**  
Wellcome Malaysia Sdn Bhd  
7 Lorong SS 13/3F  
Subang Jaya  
47500 Petaling Jaya  
Selangor

**Mr Loo Kau Fa**  
Lembaga Padi dan Beras Negara  
Tingkat 13-17  
Bangunan Perkim 250-D  
Jalan Ipoh  
51200 Kuala Lumpur

**Mr Abdul Rahim B. Muda**  
Food Technology Division  
MARDI  
GPO Box 12301  
Kuala Lumpur 50774

**Ms Ruslima binti Abdullah**  
MARDI  
GPO Box 12301  
Kuala Lumpur 50774

**Mr A. Sivapragasam**  
Cocoa/Coconut Division  
MARDI  
PO Box 25  
36307 Sungai Sumun  
Hilir Perak  
Perak

**Ms Irene Villapando**  
Project Officer  
ASEAN Food Handling Bureau  
Level 3, G14 and 15  
Damansara Town Centre  
50490 Kuala Lumpur

**Mr Wang Yung Shyan**  
Lembaga Padi dan Beras Negara  
Tingkat 20  
Bangunan Perkim 250-D  
Jalan Ipoh  
51200 Kuala Lumpur

**Mr Yusof bin Othman**  
Agriculture Department  
Jalan Gallagher  
50632  
Kuala Lumpur

## Nepal

**Mr Servi van den Akker**  
FAO/Nepal Food Corporation  
UNDP  
PO Box 25  
Kathmandu

## Philippines

**Ms Miriam A. Acda**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Dr Marietta Adriano**  
National Economic Development  
Authority  
Amber Avenue, Pasig  
Metro Manila

**Mr Narciso L. Alano**  
Regional Director  
Region II  
National Food Authority  
Santiago  
Isabella

**Mr Dionisio Alwindia**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Manolito C. Bulaong**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Mrs Filipinas Caliboso**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Mr Ricardo T. Deang**  
Fertiliser and Pesticide Authority  
6th Floor, Raha Sulayman Building  
Benavidez, Makati  
Metro Manila

**Ms L.A. Esteves**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Dr Rosalinda P. Garcia**  
National Crop Protection Centre  
University of the Philippines at Los  
Baños  
College, Laguna 4031

**Mr Rolando B. Gomez**  
Quality Assurance Division  
Technical Services Directorate  
National Food Authority  
101 E. Rodriguez Sr. Avenue  
Quezon City

**Mr Alfredo T. Gonzalez**  
Pest Control Association  
of the Philippines Inc.  
41 AT Gener  
Comer Kamuning Road  
Quezon City

**Mr D.D.T. Julien**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Ms G Sabio**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Dr Jose B. Santos**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

**Ms Perlina D. Sayaboc**  
NAPHIRE  
CLSU Compound  
Muñoz, Nueva Ecija

## Singapore

**Mr K.S. Boon**  
Department of Zoology  
National University of Singapore  
33A Chancery Lane  
Singapore 1130

**Mr Chai Soon**  
Ministry of Trade and Industry  
Rice Control Unit  
102 Pasir Panjang Road  
Singapore 0511

**Mr Chan Ban Leong**  
Ministry of Trade and Industry  
3 Shenton Way  
Treasury Building No. 48-00  
Singapore 0106

**Mr Chung Keng Meng**

Wellcome Singapore Pte Ltd  
33 Quality Road  
Singapore 2261

**Mr T. Fernandez**

Quicksilver & Co. Pte Ltd  
126 Joo Seng Road  
No. 08-08 Gold Pine Industrial  
Building  
Singapore 1336.

**Mr R.A. Flinn**

Wellcome Singapore Pte Ltd  
33 Quality Road  
Singapore 2261

**Miss Goh Poh Moi**

Department of Zoology  
National University of Singapore  
Lower Kent Ridge Road  
Singapore 0511

**Mr J. Heppoletie**

Sita Pest Control  
450-452 Alexandra Road  
Singapore 0511

**Mr John Ho Hwa Hiong**

Rentokil Singapore Pty Ltd  
4 Chang Charn Road  
Singapore 0315

**Dr S.H. Ho**

Department of Zoology  
National University of Singapore  
Lower Kent Ridge Road  
Singapore 0511

**Mr Jan de Jong**

Eastreco (Pte.) Ltd  
29 Quality Road  
Singapore 2261

**Miss Lau Woei Yuen**

Department of Zoology  
National University of Singapore  
Lower Kent Ridge Road  
Singapore 0511

**Mr R. Lee Teck Poh**

SGS All-Pest Management Pte Ltd  
5 Sixth Lokyang Road  
Singapore 2262

**Mr Lee Thap Hin**

Singapore Storage and Warehouse  
Pte Ltd  
102 Pasir Panjang Road  
Singapore 0511

**Mr E.C.W. Leong**

Department of Zoology  
National University of Singapore  
Lower Kent Ridge Road  
Singapore 0511

**Mr F.H.T. Lim**

Knockout Pest Control Pty Ltd  
450-452 Alexandra Road  
Intrans Warehousing Complex  
Singapore 0511

**Mr J.L.H. Lee**

Knockout Pest Control Pte Ltd  
450-452 Alexandra Road  
Intrans Warehousing Complex  
Singapore 0511

**Mr Loh Fang Tong**

Ridpest Private Limited  
7 Ruby Lane  
Singapore 1232

**Mr J. Low Hong Kuan**

S.G.S. Singapore (PTE) Ltd  
Blk 71, Ayer Rajah Crescent No. 07  
-18  
Ayer Rajah Industrial Estate  
Singapore 0513

**Mr Lum Kwong Toh**

Department of Zoology  
National University of Singapore  
Lower Kent Ridge Road  
Singapore 0511

**Dr I. Madan**

Eastreco (Pte.) Ltd  
29 Quality Road  
Singapore 2261

**Mr Ng Say Kiat**

Rentokil Singapore Pty Ltd  
4 Chang Charn Road  
Singapore 0315

**Mr Ong Keng Ho**

Agriculture Division PPD  
17 km Sembawang Road  
Singapore 2776

**Dr Dante de Padua**

Program Officer  
IDRC  
Tanglin PO Box 101  
Singapore 9124

**Mr F. Pius**

Quicksilver Pest Control Co. Pte Ltd  
126 Joo Seng Road  
No. 08-08 Gold Pine Industrial  
Building  
Singapore 1336

**Mr Poh Cheng Sui**

Ridpest Private Limited  
7 Ruby Lane  
Singapore 1232

**Mr Rafael L. Pranata**

c/- Department of Zoology  
National University of Singapore  
14A Clementi Road  
Singapore 0512

**Mr G. Surajan**

Sita Pest Control and Fumigation  
Services  
450-452 Alexandra Road  
Inchcape House  
Singapore 0511

**Mr M. Susaretnam**

Knockout Pest Control Pte Ltd  
450-452 Alexandra Road  
Singapore 0511

**Mr A.M. Sutton**

Wellcome Singapore Pte Ltd  
33 Quality Road  
Singapore 2261

**Mr K.C. Tan**

Bayer Singapore  
4 Penjuru Lane  
Singapore 2260

**Mr Tan Khoon Seng**

Singapore Storage & Warehouse  
Pty Ltd  
102 Pasir Panjang Road  
Singapore 0511

**Mr R. Tan Yong Kwang**

Singapore Storage & Warehouse  
Pty Ltd  
102 Pasir Pajang Road  
Singapore 0511

**Mr J. Tan Wey Ing**

Singapore Storage & Warehouse  
Pty Ltd  
102 Pasir Panjang Road  
Singapore 0511

**Mr Tay Teng Soo**

SGS All-Pest Management Pty Ltd  
5 Sixth Lokyang Road  
Singapore 2262

**Mr J-P. Tzack**

Quicksilver Pest Control Co. Pte Ltd  
126 Joo Seng Road  
No. 08-08 Gold Pine Industrial  
Building  
Singapore 1336



**Mr G.S. Vijaya Kumaran**  
Sita Fumigation Services Pte Ltd  
450-452 Alexandra Road  
Singapore 0315

**Mr Jolly Wee**  
SGS All Pest Management Pty Ltd  
5, Sixth Lok Yang Road  
Singapore 2262

**Mr A. Whipp**  
Agroveterinary Division  
Roussel Uclaf  
541 Orchard Road  
#19-01 Liat Towers  
Singapore 0923

**Mr Andrew Yap**  
Wellcome Singapore Pte Ltd  
33 Quality Road  
Singapore 2261

## South Africa

**Mr E.J. Jordan**  
Southern Associated Maltsters Pty  
Ltd  
PO Box 27  
Caledon 7230

## Thailand

**Mr Chuwit Sukprakarn**  
Entomology and Zoology Division  
Department of Agriculture  
Bangkhen, Bangkok 10900

**Mr J. Howard**  
Siam Control Company Ltd  
994 Soi Thonglor  
Sukhumvit Road (55)  
Prakanong  
Bangkok 10110

**Ms Kanjana Bhudhasamai**  
Seed & Postharvest Pathology  
Branch  
Plant Pathology & Microbiology  
Division  
Department of Agriculture  
Bangkhen, Bangkok 10900

**Mrs Manthana Khumlekhasing**  
Agricultural Toxic Substances  
Division  
Department of Agriculture  
Bangkhen, Bangkok 10900

**Mr Pinit Nilpanit**  
Entomology and Zoology Division  
Department of Agriculture  
Bangkhen, Bangkok 10900

**Dr Vichian Hengsawad**  
Department of Entomology  
Faculty of Agriculture  
Chiang Mai University  
Chiang Mai 5002

**Mr Wichai Chivakanit**  
Wellcome Thailand Ltd  
64/1-4 Pan Road  
Silom  
Bangkok 10500

**Mr Winai Hansasiripot**  
Wellcome Thailand Ltd  
64/1-4 Pan Road  
Silom  
Bangkok 10500

## United Kingdom

**Dr C. Bell**  
ADAS Slough Laboratory  
Ministry of Agriculture, Fisheries  
and Food  
London Road  
Slough, Berkshire SL3 7HJ

**Mr J.R. Cox**  
ODNRI  
Storage Department  
London Road  
Slough, Berkshire SL3 7HL

**Mr C.P. Smith**  
Rentokil PLC  
Felcourt  
West Sussex RH19 2JY

## United States of America

**Mr H.E. Arkens**  
Great Lakes Chemical Corporation  
PO Box 2200  
U.S. Highway 52 North West  
West Lafayette, Indiana 47906

**Dr E. Jay**  
c/- USDA-ARS South Atlantic Area  
Stored-Product Insects Research and  
Development Laboratory  
PO Box 22909  
Savannah  
Georgia 31403

**Dr Edwin L. Soderstrom**  
USDA-ARS Horticultural Crops  
Research Laboratory  
2021 South Peach Avenue  
Fresno, California 93727

**Mr C.L. Storey**  
Consultant  
3022 Sunnyside Drive  
Manhattan, Kansas 66502

**Mr Ahmed Syed**  
B&G International  
Rte 611 Plumsteadville  
Renneygranic 18949

## Zimbabwe

**Mr Noah Kutukwa**  
Grain Marketing Board  
PO Box 8014, Causeway  
Harare

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