STORABILITY OF CEREAL GRAINS AND OIL SEEDS IN NITROGEN.

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ABSTRACT

The experimental facilities and the research methodology applied in the studies on grain storability in nitrogen with various residual oxygen concentrations are described.

A summary of the results, showing that nitrogen storage offers a large number of advantages over traditional storage techniques, are presented, and the limiting factors for the successful storage of different grains in completely and partially bio-inert atmospheres, especially in regard to moisture content, are described.

INTRODUCTION

The preservation of quality during long-term storage of grains is a severe problem in many parts of the world. High temperatures and excessive moisture in the stored products or high humidity in the storage ambient permit the proliferation of insects and moulds which cause large losses of qualitative, nutritional and sanitary nature.

Hermetic storage has been used in many countries for a very long time. It permits to exclude exogenous factors which cause grain spoilage and the technique has been extended even to large-scale storage facilities (Hyde et al., 1973).

In order to overcome difficulties linked to the slow natural depletion of oxygen in the interstitial atmosphere in gas-tight stores and to rationalize the technique for industrial storage facilities by excluding excessive carbon dioxide build up and initial spoilage of high moisture grains by fungi, long-term experiments were carried out on the effects of nitrogen on various stored commodities.

In small storage facilities and in simulation experiments the beneficial effect of nitrogen on stored grains was shown (Shejbal, 1978) and a nitrogen fumigation and storage technique was developed which has been successfully operating since several years in large scale storage facilities in Italy (Shejbal, 1979a).

The aim of this paper is to summarize the research approach, the experimental data and the main features of the nitrogen storage technique, indicating its possibilities and limits.

MATERIALS AND METHODS

Laboratory storage facilities, micro- and mini-silos, were used for storability tests of soft and durum wheat, barley, maize, rice paddy, peas, oil seeds, nuts etc. In all experiments the evolution of quality changes throughout the storage period was studied, since only in this way it is possible to establish storability limits. This approach necessitates sampling at regular time intervals without disturbing excessively the gas composition in the silos.

The micro-silos (volume 12 l) (Fig. 1) were set up in series in the laboratory and the single silos were unloaded at given storage times, in order to allow the complete analysis of the stored product without disturbing the material to be stored for longer periods of time. This arrangement permits to study especially high moisture grains in which even a short change in the interstitial atmosphere composition, due to sampling, may be detrimental.

Mini-silos were equiped with three sampling points at different heights of the stored product column and were installed either in the laboratory at a constant temperature (Fig. 2) or under an open shed (Fig. 3), thus permitting storage experiments with and without fast temperature fluctuations.

It should be noted that in no case does storage in small containers permit a true simulation of the conditions of a large grain bulk, since heat dissipation from the structure does not allow heating phenomena to occur. Such phenomena are of particular importance in products in which insect or mould proliferation is active or oxidation of fat in oil-seeds may take place. Mini-silos placed at outdoors

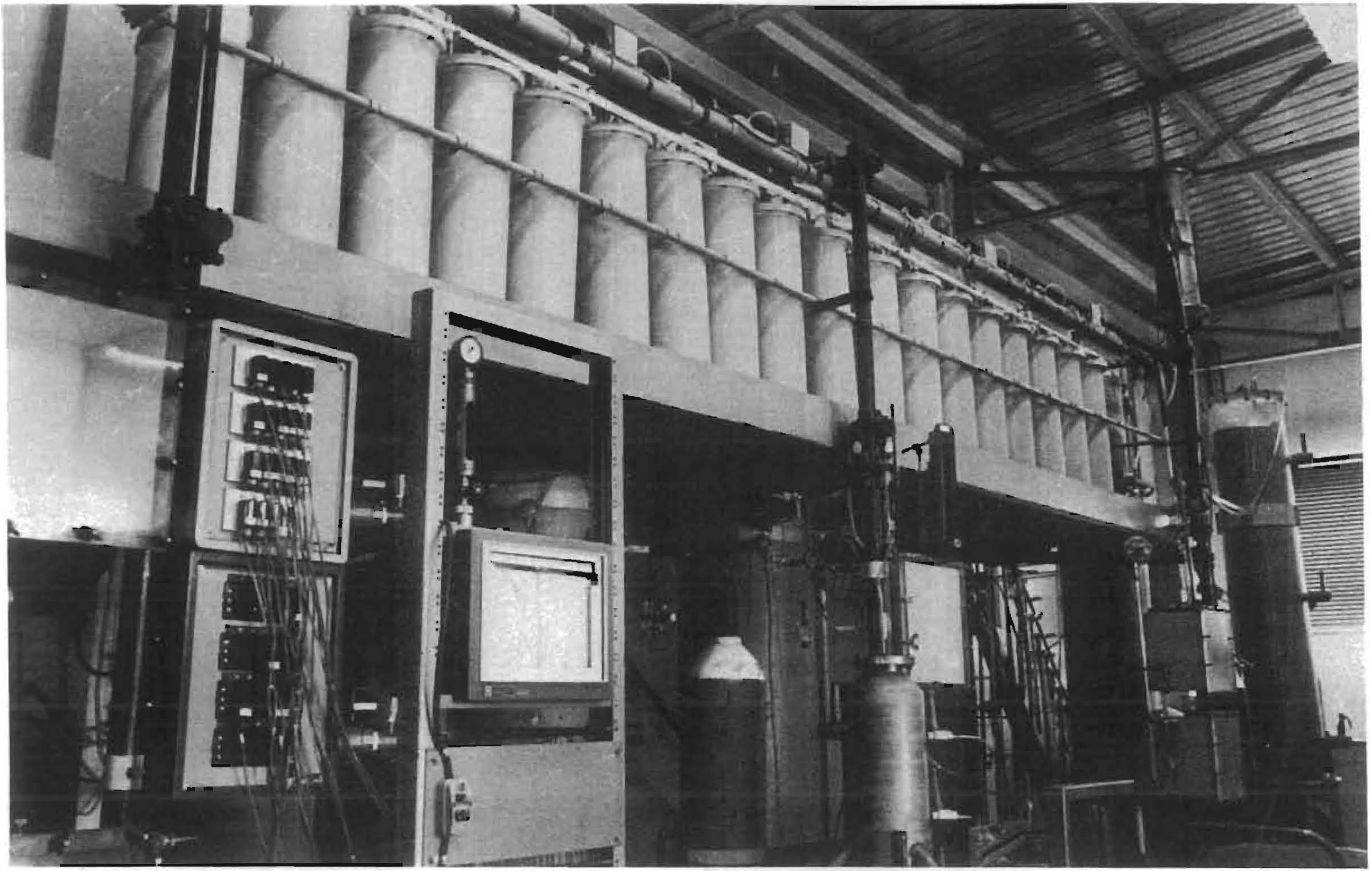

Fig.1. Gas-tight micro-silos (12 l volume, PVC) in laboratory. In foreground temperature and gas flow monitoring equipment.

ambient temperature permit a satisfactory simulation of phenomena occurring in the head-space and upper layers of large storage facilities.

Thermostated mini-silos (Fig. 2) were used for storability tests on dry cereal grains, especially in regard to viability preservation.

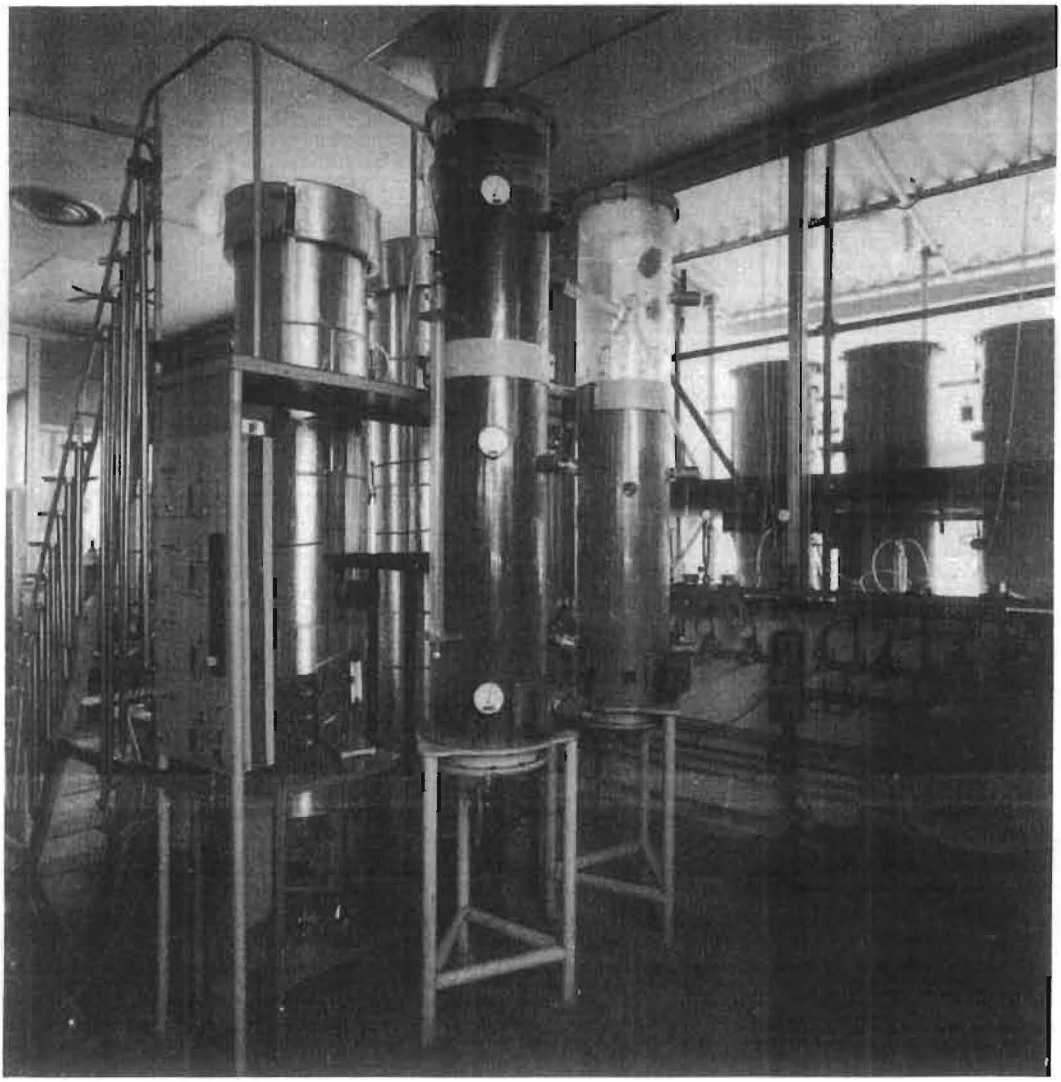

Fig.2. Plexiglass and thermostated steel mini-silos in laboratory. Under the window the automatic pressurization equipment.

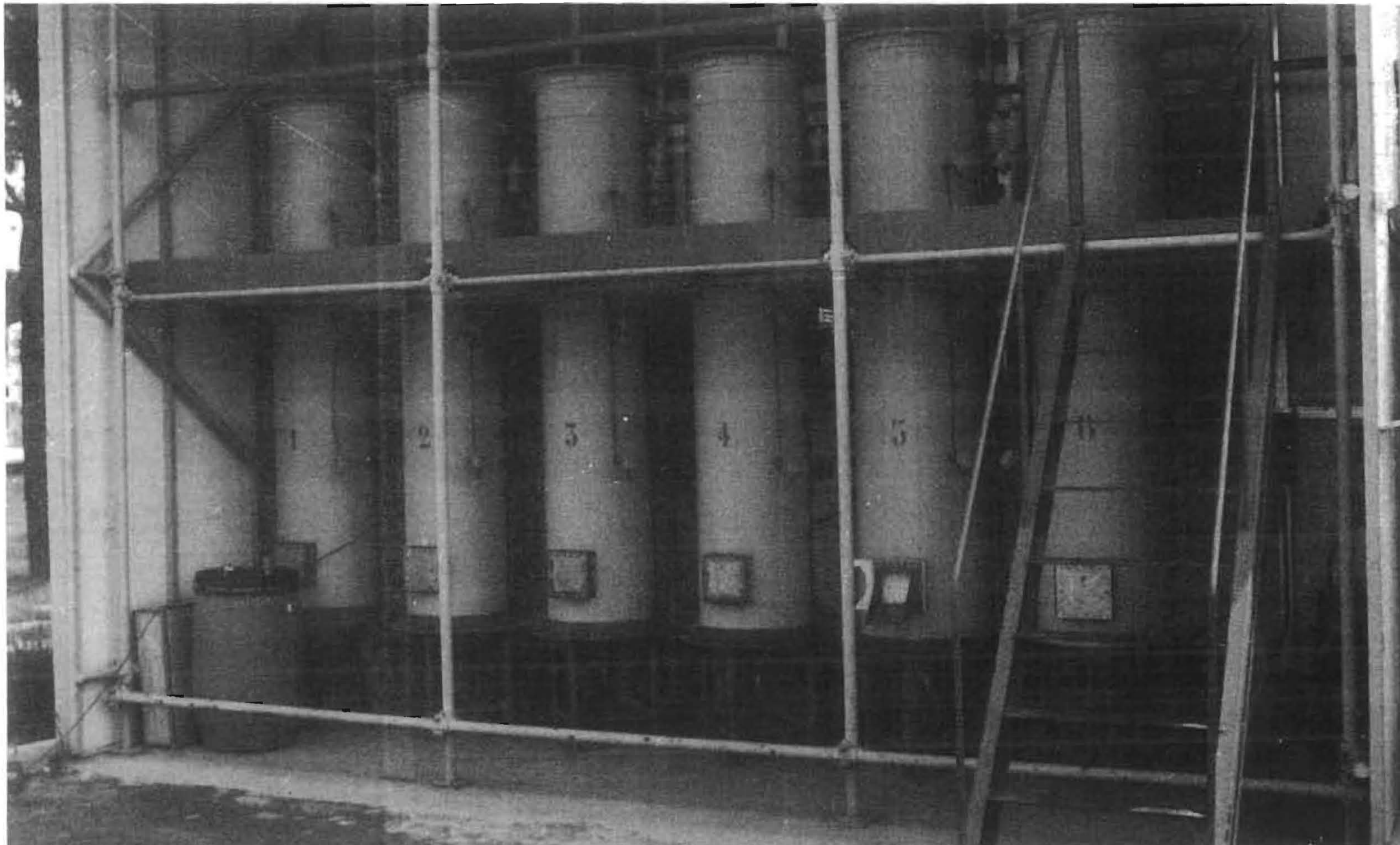

Fig.3. Eternit mini-silos at external ambient temperature. Gas-tightness achieved by epoxy-paints.

For laboratory scale simulation of conditions persisting inside a huge granular stored product bulk, which are nearly adiabatic, an experimental apparatus was designed (Fig. 4), which permits to measure heat production rate of very low intensity in the stored product (Tranchino et al., 1980a). Autocatalytic phenomena taking place in oil seeds were measured in this apparatus.

Fig.4. Adiabatic apparatus for simulation of storage conditions inside a large grain bulk.

Laboratory scale storage experiments were repeated at pilot scale in 27 m^3-fiber-glass bins (Fig. 5), permitting the assessment of quality changes during storage in various controlled atmospheres also by industrial milling and other processing by the food industry. Scaling up from these bins presents no difficulty.

Gas flows, monitoring of storage conditions, analyses of the interstitial atmosphere composition, as well as biological, chemical, mycological, rheological and nutritional analyses carried out on all tested stored products were described in detail before (Shejbal et al., 1973; Lombardi et al., 1976; Shejbal, 1976; Shejbal, 1979b). The principles of nitrogen preservation of grains developed in the experimental facilities were applied to large-scale gas-tight bins for barley, wheat and sunflower seed storage.

While in the experimental bins purging with nitrogen was always carried out from the top towards the bottom in order to take advantage of the gas density differences, in the large-scale facilities the initial purge is carried out from the bottom towards the top (Fig. 6) in order to avoid excessive pressure in the head-space which might be dangerous for the bin roof. Maintenance of a slight constant positive pressure in the storage facilities ensures the automatic substitution of gas (Fig. 7) lost by leaks or operation of the safety valve when high temperatures in the head space gas are reached due to insolation. The over pressure in the bins also counteracts convective fluxes and diffusion from outside.

The gas-tight bins for malting barley (2200 m^3 each) were built in galvanized steel (Fig. 6) while the silos for wheat (Fig. 8) and sunflower seeds are constituted of a number of medium-sized monolithic fiber glass bins. More details on the large scale facilities are presented elsewhere (Tranchino et al., 1980b).

RESULTS AND DISCUSSION

The overall picture, obtained in experimental storage trials with cereal grains shows that long term preservation in nitrogen is advantageous at all temperature and moisture content levels (up to 30°C and 19% respectively) as compared to storage in air.

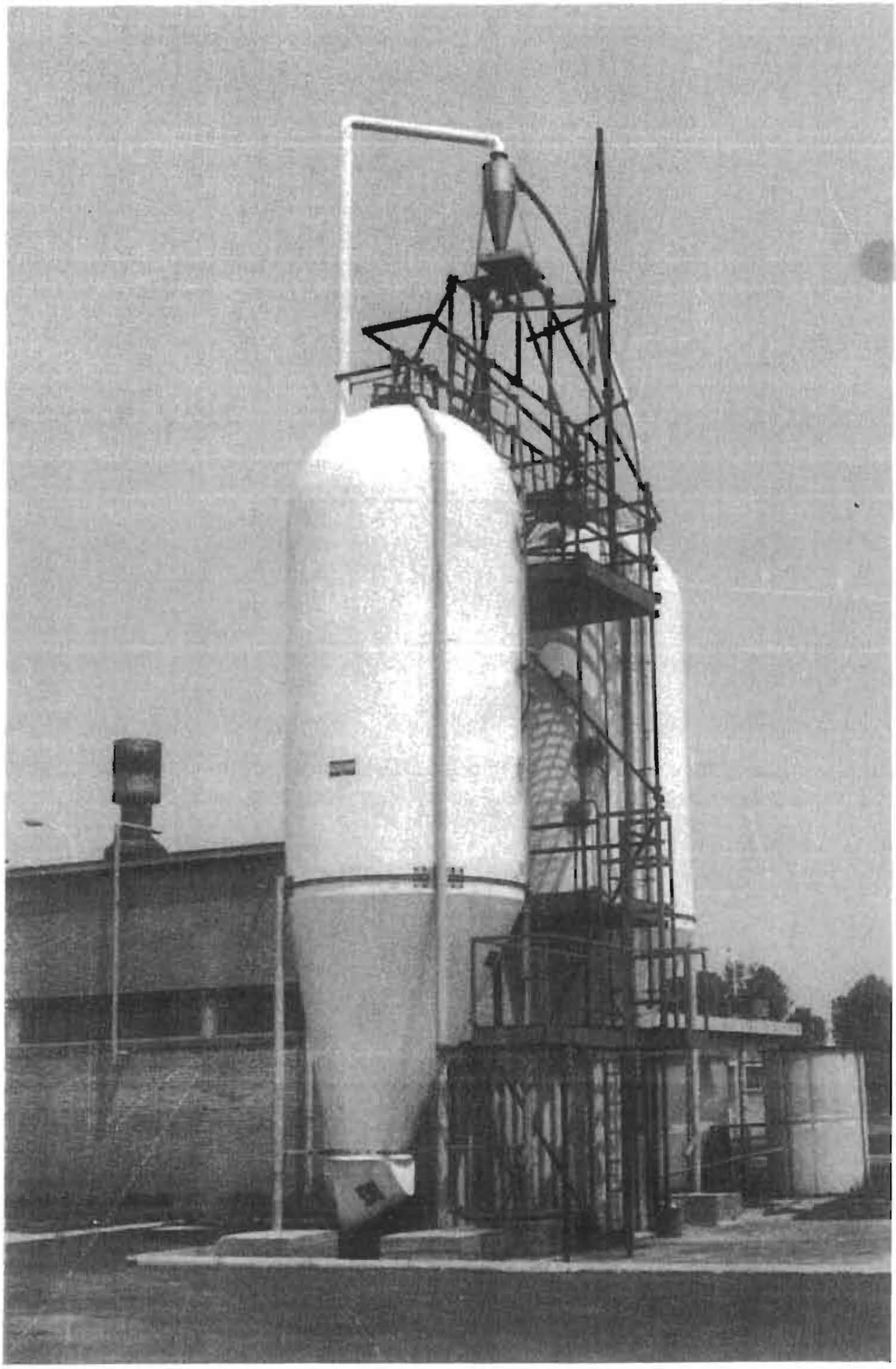

Fig.5. Fiber-glass midi-silos for controlled atmosphere storage trials at pilot scale.

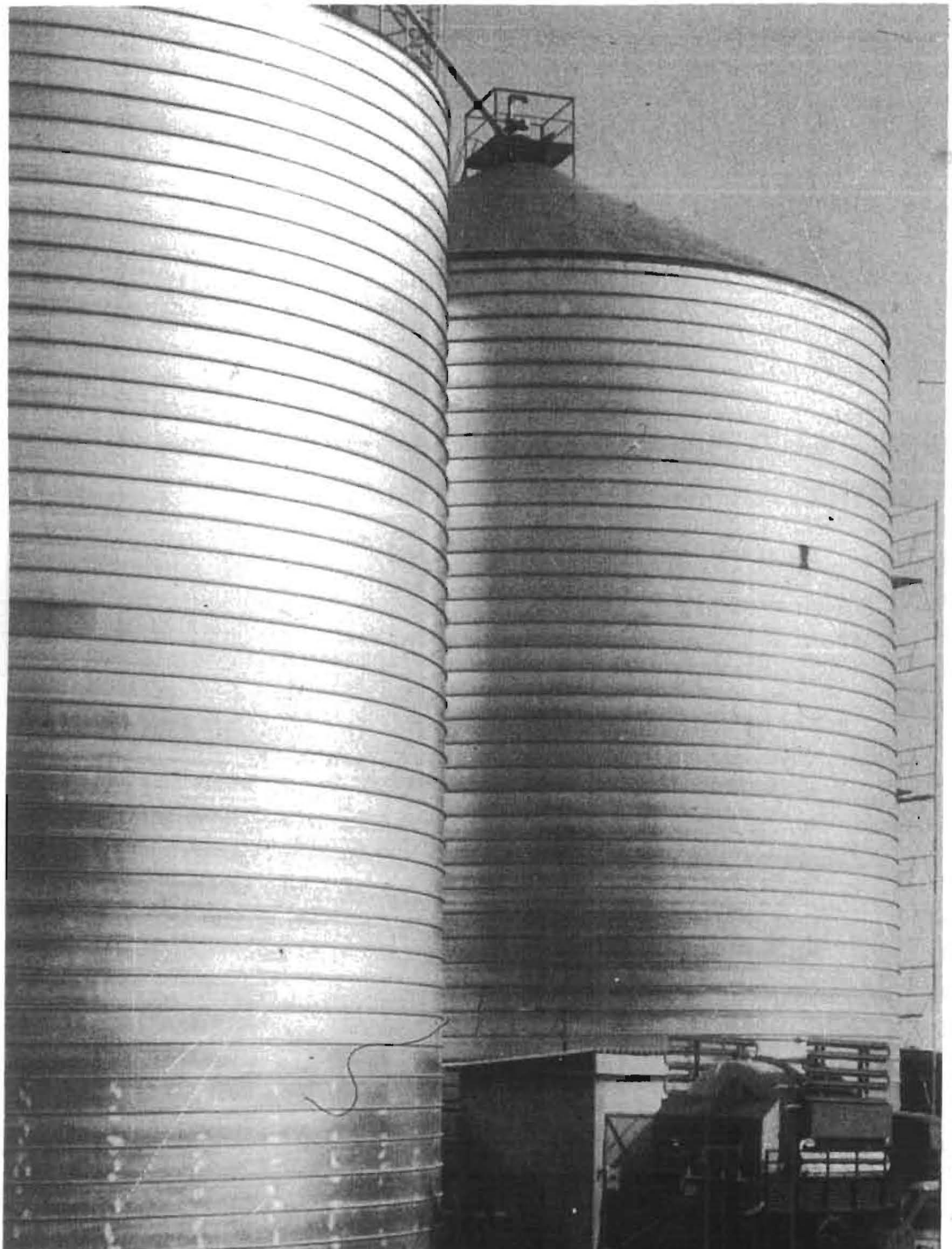

Fig.6. Steel barley storage bins (IVO, Tuscania) during initial purge with gaseous nitrogen from mobile regasification unit.

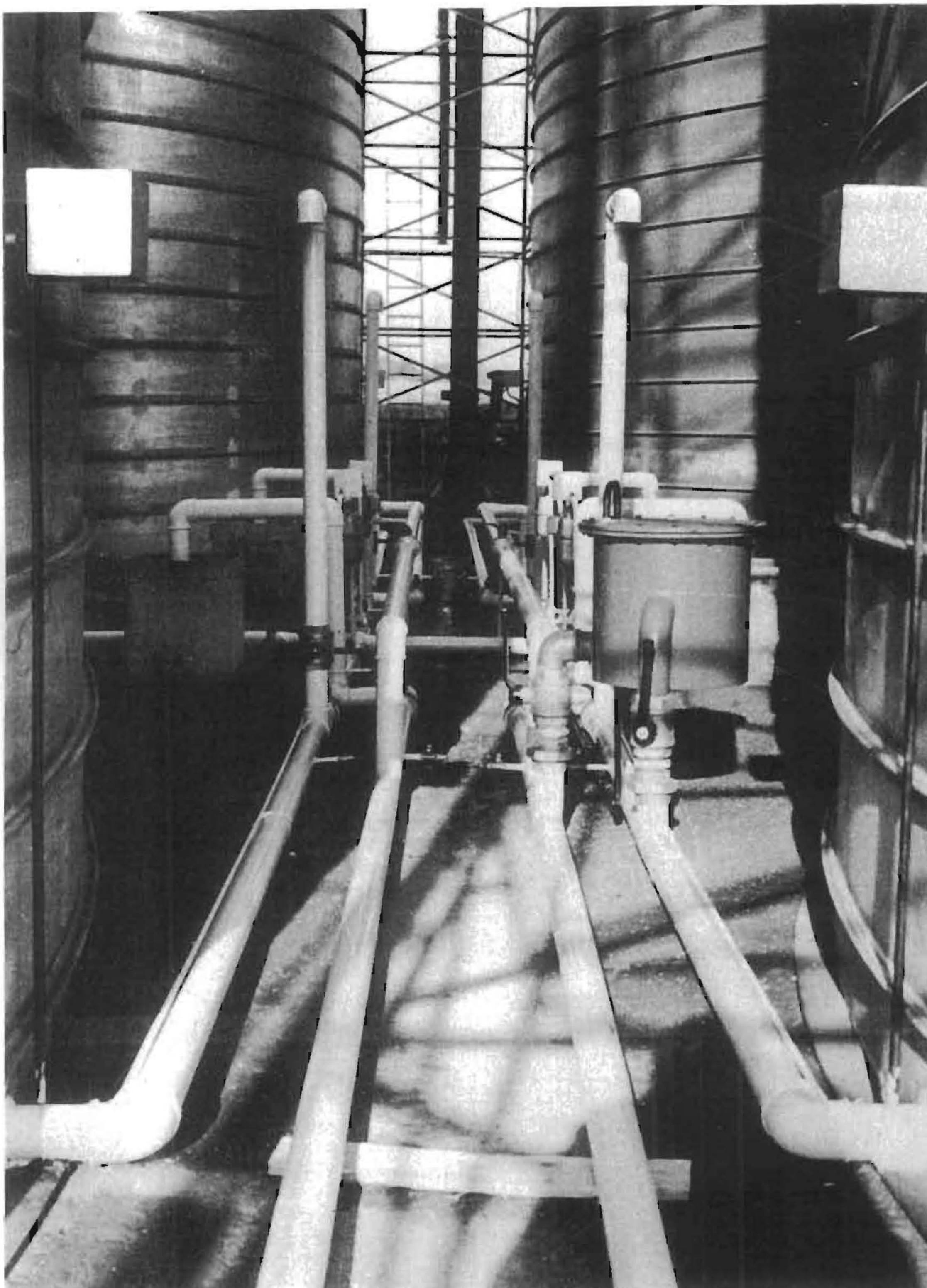

Fig.7. Nitrogen distribution system for initial purge (from bottom) and maintenance of the inert interstitial atmosphere (from the top) of large-scale steel storage bins.

Fig.8. Silo of Società Romana di Macinazione, Rome, for the storage of wheat. The fiber-glass bins (600 m^3 each) are equipped for nitrogen fumigation and storage of grain.

At moisture contents up to 14.5%, the better storability of the grains in technical nitrogen (0.2-0.5% residual oxygen) is evident especially over long periods of time, since mould attack is absent also in the oxygen rich normal atmosphere. Grain quality, i.e. germination energy and capacity, rheological and baking characteristics, as well as the content of nutritional components, is maintained significantly longer than in air at all temperatures studies (10° to 30°C). Germination energy is the most sensitive indicator of grain deterioration (Shejbal and Di Maggio, 1976).

In pure nitrogen (residual oxygen content less than 0.01%) all characteristics, except cereal grain viability, are maintained as well as in technical nitrogen. However, also in this atmosphere, germination energy and capacity are preserved significantly longer than in air.

In Fig. 9 the storage periods are shown in which 90% of the initial viability of soft wheat seeds is preserved, as a function of moisture content and temperature, in pure nitrogen. Such a graphic representation, though correct and easy to understand, has however only a limited value. It may be misleading in practice, since the initial quality and the history of the grains to be preserved under nitrogen are of cardinal importance for successful maintenance of quality in general and viability in particular. Products in which deterioration has already started cannot be safely stored in anoxia. Thus the data in Fig. 9 refer to grain which, at the start of storage in nitrogen, had a germination energy not lower than 90% and a mould count not higher than 10^4 germs/g, with storage fungi virtually absent (less than 5% of the total fungal count).

It seems more adequate to indicate the limiting factors of grain storage in nitrogen atmospheres and the rough limits of storability of the various features (Table 1).

At moisture contents between 14.5 and 19%, the beneficial effect of storage in nitrogen is evident also in short periods of time, since mould attack is the main cause of fast deterioration in aerated storage.

In nitrogen containing up to 0.2% oxygen, moulds develop slower

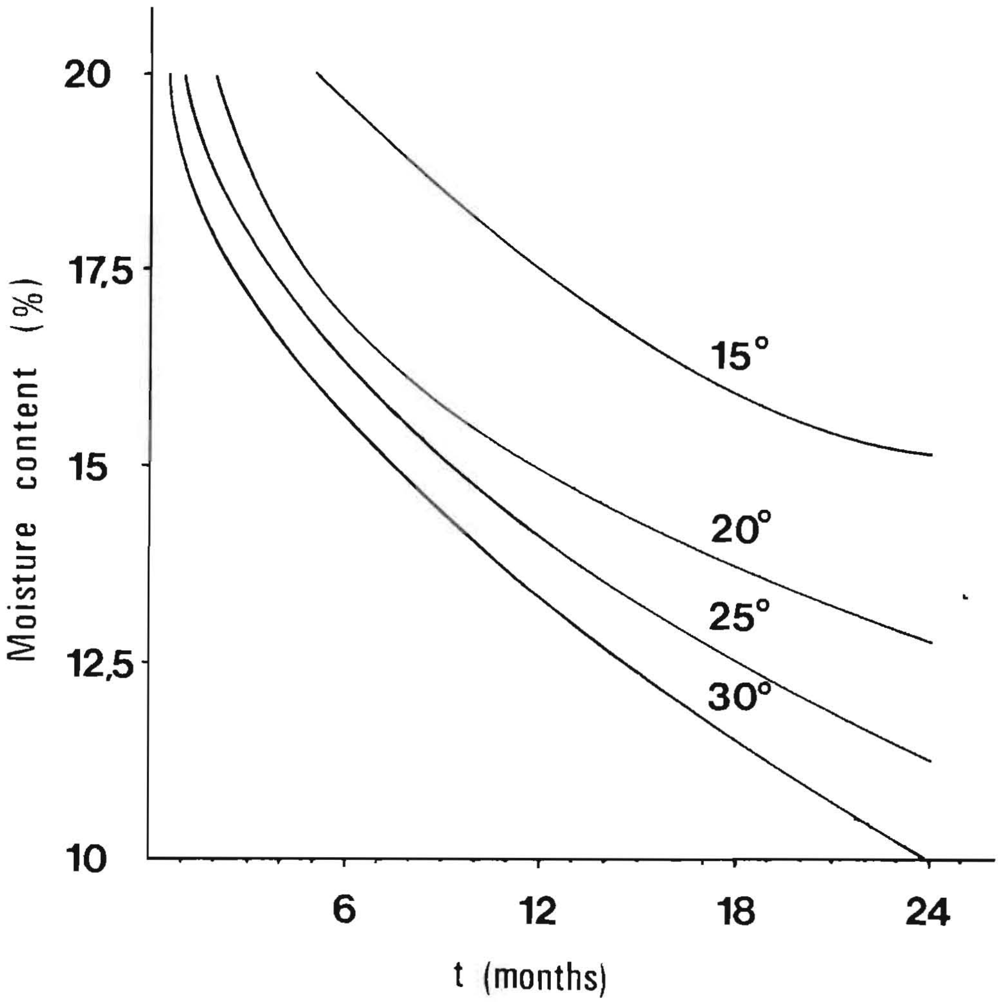

Fig.9. Storage periods in which viability of soft wheat decreases by 10% when preserved in pure nitrogen.

than in air, but are not inhibited. Cereal grains may thus be preserved for significantly longer periods of time than in air, but after the initial lag-phase of fungal development, deterioration cannot be avoided at these residual oxygen concentrations (Di Maggio et al., 1976).

In pure nitrogen, fungal proliferation is completely inhibited and total germ counts tend to diminish in time (Di Maggio 1980). Progressive deterioration of the cereal grains, due to endogenous enzymes, takes place in total anoxia at a slow rate. Thus safe storage of cereal grains at moisture contents, at which, in Mediterranean climatic conditions, it is not possible to maintain grain for more

TABLE 1 CEREAL GRAIN PRESERVATION IN NITROGEN ATMOSPHERES

Moisture content (%)	Temperature (°C)	Residual oxygen concentration (%)	Technol. & nutr. quality preservation (time)	Germination energy preservation (time)	Limiting factor
$m.c. \leq 14.5$	$T \leq 30$	$0 < O_2 \leq 0.5$	years	years	germinability
$m.c. \leq 14.5$	$T \leq 30$	$O_2 = 0$	years	year	germinability
$14.5 < m.c. \leq 16$	$T \leq 25$	$0.2 \leq O_2 \leq 0.5$	year-months	months	mould growth
$14.5 < m.c. \leq 16$	$T \leq 25$	$O_2 = 0$	year-months	months	germinability
$16 < m.c. < 19$	$T < 25$	$0.1 < O_2 < 0.2$	months-weeks	month-weeks	mould growth
$16 < m.c. < 19$	$T < 25$	$O_2 = 0$	months	month-weeks	technological quality

than a few days in the presence of air, can be carried out for several months, depending on the initial quality of the grains and on the actual moisture content. The viability of the grains decreases significantly slower in anoxia than in the presence of air but cannot be arrested (Quaglia et al., 1977). Endogenous degradation of saccharides, resulting in a progressive increase in reducing sugars and a decrease in non-reducing sugars, seems to be independent of the composition of the interstitial atmosphere; it proceeds slower than the loss of viability. The increase of reducing sugars parallels the loss in technological quality of the stored moist grains (Lombardi et al., 1976).

There is an important exception to the behaviour of cereal grains in anoxia (Table 1). In fact, it is not convenient to preserve high moisture paddy (m.c. higher than 16.5%) in anoxic conditions for long periods of time, since anaerobic respiration takes place, causing the development of odours, which may make the product unsuitable for human consumption.

Oil-seed storability is higher in nitrogen atmospheres than in air (Table 2). The quality of the seeds at the start of storage is of fundamental importance, especially as far as fat acidity is concerned. For example, sunflower seeds with fat acidity values not higher than 2 (expressed as mg KOH required to nutralize 1g of oil) may be preserved for long periods of time also at critical moisture content levels but at FAV values of 3 or more, deterioration of the lipids cannot be controlled by anoxia.

The results of the laboratory and pilot-scale trials have been confirmed for wheat and malting barley in the Italian large scale facilities (Tranchino et ál., 1980b) and general characteristics of the nitrogen storage method of grain have been determined. In Table 3, the features both of short-term fumigation applications of nitrogen for insect control (see also Banks et al., 1980) and of long-term preservation are summarized.

As can be seen, the substitution of the interstitial atmosphere by inert gas influences positively all the main exogenous product quality deteriorating agents and thus contributes to the stability

TABLE 2 OIL SEED PRESERVATION IN NITROGEN ATMOSPHERES

Moisture content (%)	Temperature (°C)	Residual oxygen concentration (%)	Technol. & nutr. quality preservation (time)	Germination energy preservation (time)	Limiting factor
m.c. ≤ 6	T ≤ 25	$0 < O_2 \leq 0.5$	years	years	germinability
m.c. ≤ 6	T ≤ 25	$O_2 = 0$	years	year	germinability
6 < m.c. ≤ 8	T ≤ 20	$0.2 \leq O_2 \leq 0.5$	year	year	germinability
6 < m.c. ≤ 8	T ≤ 20	$O_2 = 0$	year	year	germinability
8 < m.c. < 10	T ≤ 20	$0.2 \leq O_2 \leq 0.5$	months	months	mould growth
8 < m.c. < 10	T ≤ 20	$O_2 = 0$	year	months	technological quality

of the simplified ecosystem in the confined storage environment.

The main advantages and disadvantages of the technique are summarized in Table 4. They refer to highly gas-tight storage structures, mostly of new construction. It is possible to use inert gas for the reduction of oxygen contents in the interstitial atmosphere of grains in less airtight structures when only disinfestation is required. The cost of the gas necessary to maintain an atmosphere lethal to insects will determine, after the initial fast purge, the economic feasibility of such an operation. Biologically non-inert gases, such as carbon dioxide in various mixtures with oxygen and nitrogen, may be more advantageous for short term disinfestations of leaky structures. According to results obtained in parallel experiments to those mentioned above, carbon dioxide can however not be recommended for long term preservation of grains in large bulks for human consumption, since it causes organoleptic changes which may result in an unacceptable depreciation of the stored products, although they may be of a reversible nature. Negative effects of carbon dioxide at high concentrations (above 60%) on quality were observed in all tested grains within weeks or months. Twelve percent moisture content wheat from pilot scale bins was found to be unacceptable at milling after 1 year storage in a mixture of carbon dioxide, nitrogen and oxygen (8: 91.5:0.5 v/v)(Shejbal,1979a).

As can be seen in Table 4, the apparent disadvantages of the nitrogen fumigation and storage technique are strictly related to the management of the storage facilities. The very fact that the structures have to be gas-tight and filled with inert gas, excludes their use in those places where very frequent grain movement is envisaged and where also the slower disinfestation by anoxia, as compared to chemical pesticides and fumigants, is not acceptable. Where medium and long-term storage is envisaged, the slightly increased investment costs of gas-tight structures are easily outweighed by the advantages and savings achieved by the technique (Tranchino, 1980) and correct management and planning can substancially reduce problems related to partial unloading of storage bins.

TABLE 3 FEATURES OF NITROGEN FUMIGATION AND STORAGE METHOD

Chemical protectants and additives

- excluded both for storage facilities and stored products
  : toxic residues excluded

Insects and mites

- Perfect penetration of gas through commodity
  : Immediate inhibition of biological activity
    = hot spot formation and moisture increase excluded
    = loss of stored product excluded
    = infestation excluded
  : Full kill of all stages of development by 15-20 days treatments
- Development of resistance to long term anoxia exposure excluded
- Simple and safe fumigation treatment

Rodents and birds

- infestation excluded
  : no loss of stored product

Fungi and yeasts

- proliferation significantly retarded in technical nitrogen, inhibited in pure nitrogen
  : Storability of grains at critical and medium moisture contents significantly
    extended due to
    exclusion of temperature and moisture increase
    exclusion of off-odours
    retarded loss of viability
    retarded loss of technological and nutritional quality
- Contamination by mycotoxins during storage excluded
- Drying may be delayed or avoided
  : savings on investment costs
  : savings on operating costs

Oxidative reactions

- significantly reduced
  : fats protected
  : weight loss reduced
  : secondary explosions and auto-ignition excluded

Viability of caryopses

- Germinative energy and capacity maintained significantly longer than in air
  : storage of seeds and cereal grains for malt production possible in large storage facilities
- Damaging effect of high temperatures reduced

Technological and nutritional parameters of stored products

- preserved for long periods of time without need of additional measures
  : particularly convenient for medium and long term storage
  : convenient for safe large-scale buffer and strategic stocks

Operating costs

- Storage cost for a one year preservation is in the order of a single fumigation by chemical products or lower
- Operating costs decrease with increase of storage facility capacity

Investment costs

- not significantly increased when gas-tightness foreseen at silo construction

TABLE 4 Advantages (+) and disadvantages (-) of nitrogen fumigation and storage technique

+	use of chemical protectants and additives excluded
+	primary and secondary toxic residues excluded
+	full kill of insects at all stages of their development achieved
+	fungi controlled by pure nitrogen
+	quality of grains preserved for longer periods even above critical moisture contents
+	secondary explosions and fire hazards are prevented
+	operating costs are reduced or not increased
-	gas-tight storage facilities with slightly increased investment costs needed
-	disinfestation operation slower than with toxic chemicals
-	partial unloading may increase operating costs and moisture migration

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