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TRIALS OF TWO PHOSPHINE GENERATORS BASED ON A NEW FORMULATION OF ALUMINIUM PHOSPHIDE

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ABSTRACT

Trial results are presented of two types of phosphine (PH₃) generator designed to use a new formulation of aluminium phosphide. A quick release generator, designed to deliver up to 600g of PH₃ over five hours to rapidly establish an effective concentration in sealed storage, was tested in three trials in which 3 kg of PH₃ was generated. A slow release generator, designed to provide controlled rates of PH₃ production, was tested at 4 g h⁻¹ and 8 g h⁻¹. These rates can be maintained for sixteen days to service active fumigation techniques, which supply a relatively constant flow of fumigant in air at an effective concentration and small positive pressure to the fumigated store. This is sufficient to prevent dilution to ineffective fumigant concentrations by wind and temperature effects that can cause air ingress and gas loss. Maintenance applications could also use this type of generator to offset gas loss due to leaks, wind and diurnal temperature effects. Recirculation techniques could use a combination of the two types of generator, the quick release to rapidly establish and distribute the fumigant throughout the storage and the slow release to maintain this concentration for the remainder of the fumigation.

INTRODUCTION

Phosphine PH₃ is the main insect control measure used in stored products in Australia and is used widely in many parts of the world for insect control. With insects developing increasing levels of PH₃ resistance, some applications which were successful previously, now fail to control some strains of insects. Methods designed to ensure efficacy were developed over the more than forty years of PH₃ use, including sealed storage technology to more effectively contain the fumigant, and label rates that balance time of exposure against PH₃ concentration to take advantage of the increased toxicity of PH₃ at lower concentrations. Positive application methods such as SIROFLO[®] (Winks and Russell 1994) and recirculation systems for PH₃ (Noyes and Kenkel 1994) were developed to ensure effective gas distribution within the fumigated storage. Improved monitoring and measurement systems for PH₃, now available, provide a capacity to ensure target exposures are met.

Controlled on-site generation of PH_3 gas for fumigation has long been desired by the storage industry in Australia. The ability to manage controlled delivery of gas for fumigation can provide many advantages and is currently provided by 2% mixture of PH_3 in carbon dioxide (CO_2) in cylinders. Phosphine from cylinders has allowed the development of active application methods, which permit less than well-sealed structures to be fumigated successfully (Winks and Russell 1994). In spite of the convenience presented by cylinders, they do have some drawbacks: the requirement for a high-pressure delivery system; the weight of the cylinder and CO_2 solvent is up to 70 kg; and the greater cost compared to PH_3 from tablets.

Generators that use available phosphine-generating formulations as a source of PH_3 do exist, with a number reported as being used in China (Li *et al.*, 1999, Wu, 1999, Yuan and Liu, 1999). The Stored Grain Research Laboratory (SGRL) within CSIRO Entomology Australia has also worked on a prototype generator using phosphide tablets as the PH_3 source. These formulations were designed to react slowly with humid air and because they are highly reactive in water, controlled generation over long periods remains complex and difficult. Also, rapid generation of PH_3 in water can present significant hazards from the exothermic reaction and the possible generation of flammable headspace concentrations. The design difficulties for generators to use current phosphide formulations essentially come from the need to first keep the formulation dry in the storage hopper for extended periods and second to then pass the formulation into a wet reactor. Maintaining this dry/wet interface requires complex solutions to prevent powdered formulation reacting and blocking the delivery pathway. For these reasons, SGRL and the grain storage industry in Australia have abandoned this approach.

Phosphine generators now being considered for use in Australia are based on a new phosphide formulation, which was invented by CSIRO Australia (Waterford *et al.*, 1994). United Phosphorus Ltd., India is carrying out commercial development in conjunction with the Australian grains industry and CSIRO.

Controlled release of PH_3 in generators is an easier and safer task because the new formulation is less reactive than tablets and blankets both in air and when water is added. Extensive laboratory trials of the new formulation have been completed. These focused on different methods to generate PH_3 in order to select the best method for controlled reaction. The results of these laboratory trials are not reported here but have provided a clear understanding of the limits within which the new formulation can be used safely. Development of the generators has so far focused on two types: a rapid release generator, where the PH_3 is delivered over 5 to 8 h or during a single work shift to service gas tight storage and recirculation systems; and a slow release generator, where the release of PH_3 is controlled over 16 d to service active application techniques such as SIROFLO. Both of these generators rely on the controlled way in which the formulation and water are brought together to react and produce PH_3 and the management of reactor headspace concentration, which is kept well below the flammability limit for PH_3 in air. Trials of the rapid release generator were carried out at a storage godown (warehouse) in Ahmadabad, India in December 1999. Trials of a commercial version of the slow release generator were completed in Australia at Yongala, South Australia in August 2000 and Shepherds Siding, New South Wales in October 2000.

MATERIALS AND METHODS

Rapid release generator

A stainless steel reaction vessel was the major component of this type of generator. A supply of water sufficient to complete the reaction of the formulation and a controlled method to bring the water and formulation together comprise the rest of the generator. Three trials produced up to 9.5 kg of PH_3 equivalent from the new formulation. Displacement of the generated PH_3 from the reaction vessel into the fumigation was achieved by a flow of approximately 26 L m^{-1} of CO_2 from a compressed gas source. The aluminium phosphide reaction was achieved by the controlled addition of water to the formulation contained in the reaction vessel. The water addition was such that the reaction was completed over approximately 5 h. Two reactor designs were available for these trials. The first did not have an integral system to support the formulation within the reactor during generation. For this trial, blocks of the formulation were suspended in calico bags from a rail at the top of the reactor. The second generator had a system of mesh cages designed to contain the blocks of formulation within the reactor.

Blocks of formulation, adding up to about 6 kg, were loaded into the reaction vessel. This was equivalent to about 3 kg of PH_3 . The top was sealed and the outlet connected by a flexible line to the gas distribution line installed in the godown. Once the CO_2 flow was started, water was added manually at a predetermined rate. The temperature rise within the generator was monitored. At the completion of the reaction, the residues were recovered from the vessel and disposed of.

Slow release generator

The slow release generator consists of three major components: reaction vessel; control panel; and associated water storage, delivery and control equipment. Each component weighed less than 25 kg for portability. The PH_3 output from the generator was connected to the inlet of the silo *via* a flexible line. The formulation, sized for a production rate of 4 g h^{-1} over 12 d, was placed into the reaction vessel the top sealed and the controlled reaction commenced. The phosphine concentration within the reaction vessel was monitored manually. A gas sampling system and gas chromatograph fitted with a phosphorus-specific flame photometric detector was used to automatically measure and record concentrations at other points around the fumigation. When the reaction of the formulation was completed, as indicated by a rapidly falling PH_3 concentration, the reactor was flooded with water to complete the deactivation of the formulation prior to disposal of the reaction residue that is essentially aluminium hydroxide.

RESULTS

Rapid release generator

Concentrations within the godown during the trials are shown in Fig. 1. The first trial was stopped after 1.75 h when it became clear, by the rise in temperature within the reactor to 68°C , that the calico bags used to support the formulation had allowed the reaction to proceed at a faster rate than planned. The water was drained and the CO_2 flow continued as a safety precaution. The rapid rise in concentration within parts of the godown during the first few hours is the result

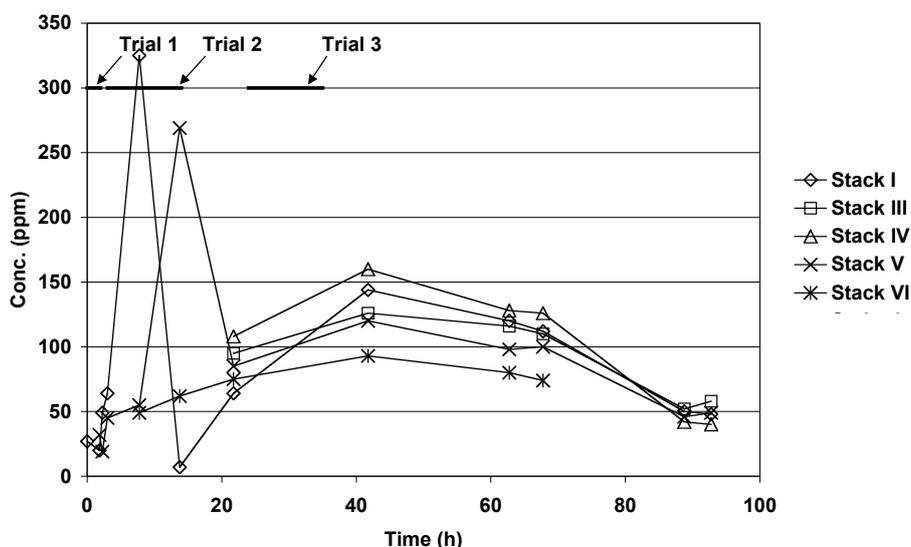


Fig.1. Concentration of phosphine measured at several points within a godown during three trials of a rapid release fumigator using a novel aluminium phosphide formulation.

of the PH_3 delivered from this trial. Subsequent inspection of this generator showed that nearly all the aluminium phosphide had reacted and been transferred into the godown as PH_3 . The second reactor was then started. Here the formulation was not contained in calico bags and the reaction proceeded as expected. However, because of the experience with the first trial the rate for water addition was reduced and so the longer time of 10.75 h was taken to initiate and complete the reaction. When the second trial was complete, the third trial was started at the designed rate for water addition and the PH_3 was generated over about 7 h. Average PH_3 concentrations within the godown rose to between 100-150 ppm throughout the period of gas addition. However, once the gas addition was stopped, the godown was not sufficiently gastight to hold the gas and the concentrations declined steadily to around 50 ppm when the fumigation was terminated at 92 h.

Slow release generator.

Two trials were completed using the slow release generator. Figure 2 shows the concentration achieved in the inlet at the base of the bin and at the peak of the bin during the first trial. The delay between inlet and peak concentration reflects the time it takes fumigant to be driven to the top of the bin by the airflow. The inlet concentration results from dilution of the PH_3 generated with the application airflow and the flow through the generator designed to carry the generated PH_3 into the inlet airstream. The average generation rate calculated from the measured total airflow going into the bin for the duration of the trial was 4.1 g h^{-1} .

A second trial was run over four days at the higher rate of 8 g h^{-1} . The purpose of this trial was to evaluate the feasibility of the increased rate using the same equipment as the first trial.

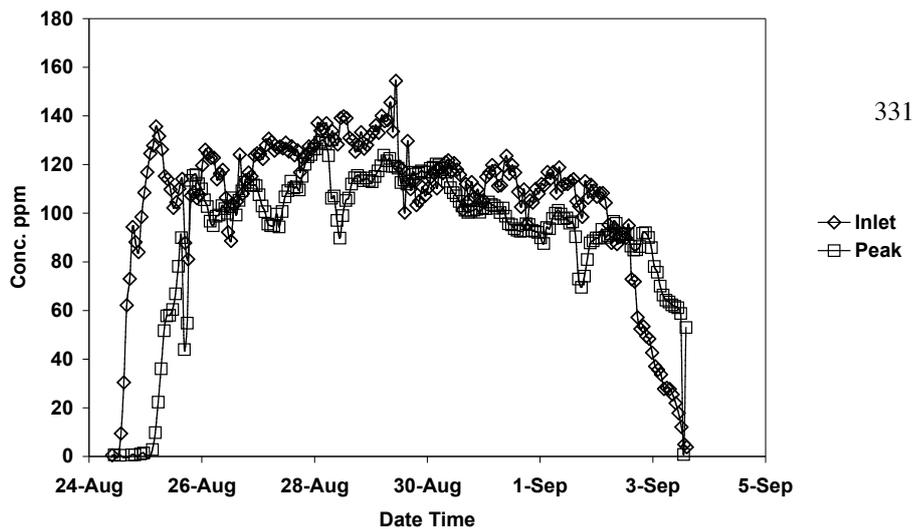


Fig. 2. Concentration within a SIROFLO treated bin where the phosphine was supplied by a slow release generator using a new aluminium phosphide formulation.

DISCUSSION

Rapid release

The CO₂ gas flow used to drive the generated PH₃ into the godown was a precautionary measure for these trials. A commercial version of the rapid release generator will use a blower to provide air to displace the gas into the fumigation site. Laboratory trials show that a suitably sized airflow that maintains the headspace concentration well below the flammable limit for PH₃ in air is an efficient and safe approach to move the PH₃ out of the generator and into the fumigation site. The reaction rate of the formulation in the rapid release generator is designed to complete the reaction during a single work shift and to match recirculation rates in the storage to allow for even distribution of the gas through the commodity being fumigated. Because the effective concentration can be established much more quickly than with current formulations, the fumigator can either shorten the fumigation period by a day or gain an extra day of PH₃ exposure within a conventional fumigation period. The latter is an important advantage as longer exposure times are being advocated to offset increased tolerance of insects to PH₃.

Slow release generator

These trials were conducted to evaluate a commercial prototype and to determine whether the generator would provide a satisfactory fumigation when exposed to the weather conditions in remote South Australia during winter. The weather during the trial included winds up to 50 km h⁻¹, sleet and lashing rain and temperatures below 0°C during which the generator performed as expected, delivering PH₃ gas at the design rate for the complete fumigation period. The second trial proved that a higher rate was feasible with the existing prototype and provided data for the design of larger generators that will supply up to 150 g h⁻¹ PH₃ over 16 days needed to fumigate the larger unsealed horizontal sheds using SIROFLO. Two generators would service this application in large flat grain bulks within the Australian storage system, one at either end of the storage.

CONCLUSIONS

This technology provides several advantages over phosphine from cylinders: it provides a controlled source of phosphine that is less expensive, and a delivery system at ambient pressure that reduces the risk of high-pressure leaks of fumigant. Furthermore, it provides an incremental production of PH_3 , which means that only part of the total PH_3 to be produced is present in the generator at any time. This reduces the overall hazard associated with failure of the generator.

This technology provides several occupational health and safety advantages: ground level application and retrieval obviates any requirement for carrying formulation to the top of the store, entering a confined space and then re-entering that space to retrieve spent material after ventilation. The technology provides portability, with no component of the generating equipment exceeding 25 kg, hence easing the task of installation and removal. A further benefit relates to deactivated residue. The system is designed to complete the reaction of phosphide within the reaction vessel, in a controlled way, in every situation before removing any residue, including interrupted or aborted fumigation. This reduces PH_3 content of the residue at disposal from the up to 5% present in standard formulations to <50 ppm in the new formulation (Waterford *et al.* 1994). Storage before disposal will further reduce this level.

Reduced hazards associated with storage, handling and transport because the new formulation is much less reactive in air: this new way to generate and apply phosphine to stored-products, either quickly to establish concentrations in sealed storage, or in a slow controlled release for active applications, is nearly ready for adoption. Trials of commercial versions of the generator to be undertaken in 2001 will provide information so that specification of the formulation, such as size of block, and delivery rates can be finalised. These trials will also provide data for registration and labelling, and test occupational health and safety design features of both types of generator. Like all new products, success will be tested in the market place. Once the Australian large-scale bulk storage market is established, other uses and markets will then be developed including simple inexpensive generators for on-farm use and international markets.

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