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Ground Level Phosphine Application Systems——Towards a Safer Workplace

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Abstract: Phosphine generating metal phosphide products have been in use in grain storage around the world for nearly 50 years. Early label recommendations suggested admixture into the grain stream as the most convenient method of application. A recent label change in Australia reflects the need to prevent admixture of spent phosphide residues with grain. This requires tablets or pellets applied in the headspace of the storage be placed onto a tray or similar device to capture the powder residue. This application method requires the fumigator to work at the top of some very tall silos and often in a confined or restricted area.

Techniques have been developed in Western Australia that enables sealed steel silos to be dosed at ground level, removing the need to climb the silo. The systems include: (i) a thermosiphon (temperature driven) distribution system in small farm silos, (ii) a fan operated recirculation system with an external phosphine generating system attached to larger sealed silos, and (iii) in unsealed silos, using a top up technique to maintain phosphine concentration at the required levels.

The results from trials with these techniques demonstrated the thermosiphon distributed phosphine gas safely and effectively throughout the grain bulk. All fumigations in the sealed silos reached the Department of Agriculture and Food Western Australia recommended protocol for elimination of all life stages of stored grain insects. In the unsealed silos, fumigation success was directly related to ambient wind conditions.

Key words: thermosiphon, phosphine, distribution, ground level application

Introduction

Recent changes to the phosphine label do not permit direct admixture (Pratt & Desmarchelier 1998 [9]) of phosphine generating products with grain, requiring the application of aluminium phosphide (AlP) formulation to the headspace of the storage. To retain the use of aluminium phosphide it must be applied in a manner that prevents contamination of grain. This may be onto a tray or similar device designed to contain the powder residue or by using a blanket or bagchain formulation. This means the fumigator must climb at least six metres and often work in a small or difficult area to apply a toxic product.

This paper reports on ground level generation and application systems using: (i) thermosiphon and (ii) an electric fan to distribute the phosphine in the grain bulk and avoid the need to climb the silo to insert AlP.

i) In 2005 Bird's Silos (Popanyinning, Western Australia) developed the first commercial thermosiphon (Cook, J. S. 1980[5], Boland 1984[3], Banks 1985[2], Cooper and Marszal 2000[4]) designed specifically to deliver phosphine generated in a reaction chamber' at the base of a sealed farm silo into the headspace. This system allows the fumigator to load the required AlP dose at ground level providing a safer, open air working environment.

Trials using a thermosiphon demonstrated phosphine gas can be safely and effectively distributed using a thermosiphon throughout the grain bulk in small farm silos up to 91mcapacity (Newman2006[7]). The trials were conducted with prototype equipment which demonstrated its efficacy but was vulnerable to damage and produced gas concentrations up to 7000 ppm in the phosphine chamber. A second prototype produced lower concentrations up to 4000 ppm and was of a more robust design. Further testing of the thermosiphon system was suggested.

ii) Electric fan powered recirculation systems to move other fumigant gases into a product had been in use in the grain storage industry for many years. In 1980 a low flow/low pressure centrifugal fan recirculatory system was patented by Cook[5] to move phosphine gas through a grain bulk. The system has been emulated in many grain stores around the world with all relying on the insertion of tablets or pellets

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of AlP to the headspace. To achieve this many devices have been created to insert the formulation and capture the spent residue. The development of the aluminium phosphide blanket formulation removed some of the difficulty of applying loose tablets but still requires the fumigator to climb to the top of some very tall silos.

Powered ground level application systems have been in operation for many years, for example Siroflo and more recently Diluphos using gaseous formulation of phosphine. Other phosphine generating devices use metal phosphides activated in water to create phosphine and then move it into a grain bulk using a centrifugal fan. These systems provide rapid generation of phosphine to reduce fumigation time but are relatively high cost and require technical knowledge to maintain them.

Banks (1985 [2]) predicted that gas could be generated outside the grain store and delivered into the grain. A fan able to move a high concentration of phosphine gas very quickly to all parts of the silo without creating an explosion is outlined in AFHB/ACIAR (1989[1]). This states that fans should not exceed 10k Pa differential pressure or have a tip speed greater than 40 m/s.

A large amount of grain is stored in unsealed silos on farms in Australia, presenting difficult conditions to control grain insects. An external ground level application system will provide safer AlP application and also install a low cost recirculation system with the ability to maintain gas values by topping up low concentrations throughout the fumigation. Fumigation success in unsealed storage is highly dependant on the number of leak points and external wind conditions. Label recommendations in Australia now require application of phosphine to the headspace and prohibit the application of phosphine to a grain stream but surface applied phosphine gas concentrations will not persist in a leaky headspace.

The system described in this paper draws air from the headspace, passes it through the phosphine gas release chamber and into the base of the grain store and is suitable for sealed and unsealed stores. It is simple, can be manufactured with local materials and uses the most readily available aluminium phosphide formulation. Gas evolution is controlled by the moisture content of the recirculating air and is more suited to long term storage. The trials described in this paper were conducted under the previous label conditions that allowed the use of phosphine in unsealed silos.

1 Thermosiphon Powered Ground Level Phosphine Application Systems

1.1 Trial 1

1.1.1 Materials and Methods

This trial was conducted on a property near Kojonup, WA, February 14 – 22, 2006. A sealed silo with a pressure test (P) >180 seconds halving time and a capacity of 91m , was loaded to 98% fill with oats at a moisture content of 10.2%, and a temperature of 28℃. A thermosiphon made of black 90 mm internal diameter PVC pipe extending from the silo roof (close to the peak) down to the base of the sidewall where a water trap was built into it to collect any condensate that might accumulate inside the pipe.

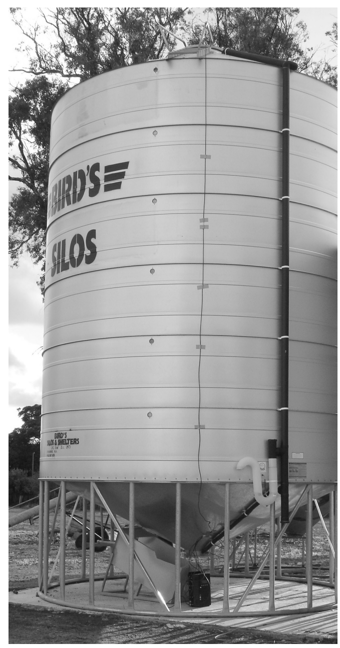

Fig. 1 Black thermosiphon pipe connected to reaction chamber at base

The thermosiphon was connected to a 'reaction chamber' at the base of the silo using 32 mm internal diameter (id) flexible pipe attached to the underside of the cone base. (Figure 2) In this silo the 100 mm deep space between the lower seal plate and the butterfly valve' grain control device (flat steel disk swivelling on its axis in the outloading port) was used as the reaction chamber.

The grain in the silo was treated at $1.5 g/m^3$ using 130 aluminium phosphide tablets placed on the lower seal plate.

A Spectros Instruments Non Dispersible Infrared (NDIR) fixed filter phosphine monitor with the ability to measure phosphine concentr-

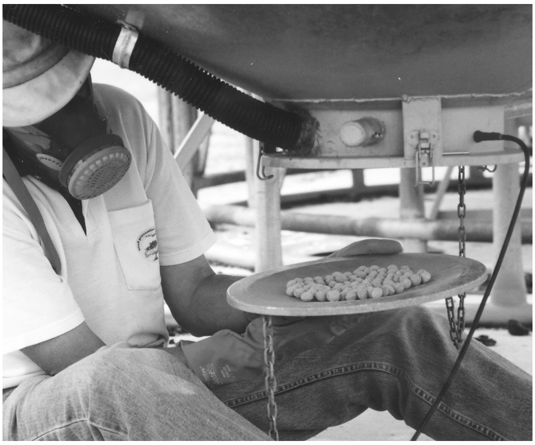

Fig. 2 Loading AlP tablets into reaction chamber at base of silo and showing pipe that carries the gas to the thermosiphon tube.

ations > 3 000 ppm was used: (i) to ensure the safe operation of the system during the trials, and (ii) for automatic recording of gas concentrations at four points in the silo, sampling every 15 minutes in sequence for eight days. Sample tubes for this instrument were connected to the phosphine chamber, headspace, NE wall and the cone base using 5 mm id tubing attached to plastic fittings inserted through drilled holes.

1.1.2 Results

The first eight days of the fumigation period were monitored when gas values are most likely to peak in the phosphine chamber. (Fig. 3) The daily maximum and minimum temperatures were obtained from a weather station on the property.

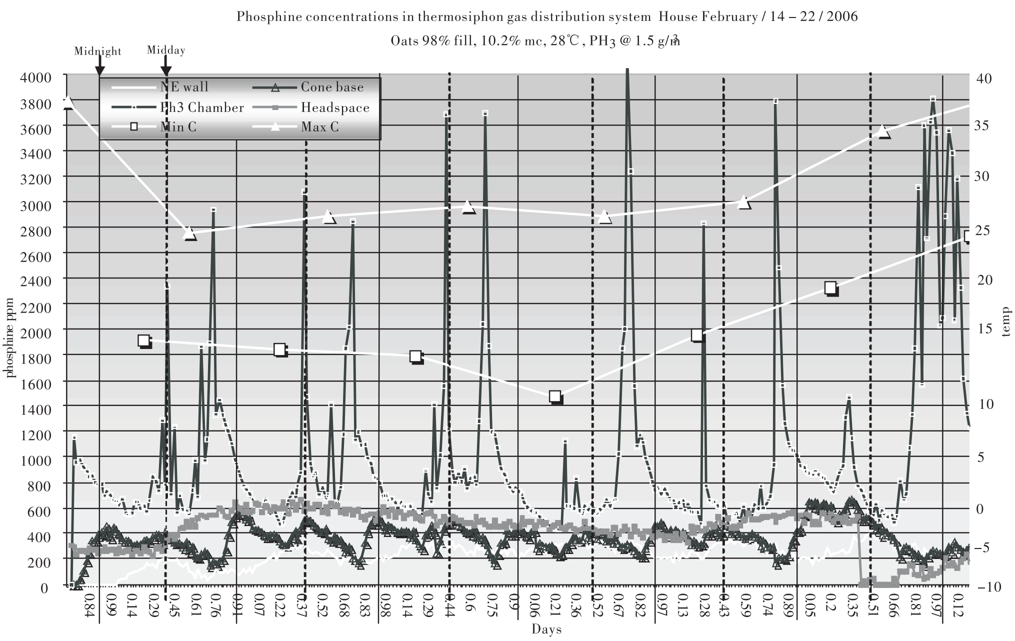

Fig. 3 Gas value record for 7 day fumigation on a thermosiphon powered silo.

The NE wall, the Cone base and the Headspace showed good distribution of the gas with all points above 100 ppm after 20 hours and reaching 200 ppm shortly afterwards. The concentrations were nearly consistent during the 7 day recorded period, which is in contrast to a top loaded non-recirculated fumigation which has high initial peaks and gradually falling concentrations. The sudden drop in concentrations on day six in the headspace and slow rise over 12 hours cannot be explained apart from possible equipment malfunction.

The marked rise and fall of the concentrations in the reaction chamber is characteristic of thermosiphon fumigation. This happens when air flow is halted in the thermosiphon and occurs when the commodity temperature is approximately equal to the ambient temperature. This situation has been observed to continue for up to 4 h (Newman 2006 [7]).

Some interesting changes of concentrations in Figure 3 demonstrate the influence ambient temperatures can have on the movement of air in the thermosiphon pipes.

For example the comparatively low morning peak on the fifth day is most likely Vthe result of cool air moving more rapidly down the thermosiphon under the influence of 8℃ overnight and early morning, pushing gas out of the phosphine chamber and into the cone of the silo.

On the seventh night the ambient conditions were warm from late evening until the early morning, close to the internal temperature of the grain bulk. It appears the air in the thermosiphon has stalled or was moving very slowly through the phosphine reaction chamber giving rise to peak gas values of almost 4 000 ppm. These gas readings oscillated between 2 000 and 3 500 ppm until early morning which could be attributed to slight air movement or partial vapour pressure moving gas past the butterfly valve into the cone base of the silo.

1.2 Trial 2

1.2.1 Materials and Methods

A second trial was carried out at Balaklava in South Australia 27 May to 10 June 2008 under cool winter conditions on an elevated cone based sealed silo ($P^{1/2}$ = 60s) with a capacity of 149m^3 loaded to 60% fill with oats at a temperature of 19.5℃ (moisture content unknown). A thermosiphon constructed of 90 mm id PVC pipe painted black was attached to the west side entering the roof near the peak and terminating in a water trap at the base of the wall. A 50 mm id PVC pipe was attached from the thermosiphon to the reaction chamber at the base of the silo.

Monitoring points using 1.5 mm id tube were inserted at the base of the silo wall at North, South, East and West sides, through the cone just above the butterfly valve and close to the reaction chamber and inserted into the roof near the peak with the tube running down the outside of the wall to the ground. A stainless tube carrying a monitoring line was inserted into the centre of the silo through the wall two days after fumigation commenced. A deeper reaction chamber 100 mm deep fitted to the bottom outlet grain control butterfly valve was trialled to hold the tablets. The reaction chamber contains a mesh platform which allows the powder to fall away as the gas evolves and prevents delay in gas release. (Fig. 4 & 5)

Fig. 4 Deep phosphine chamber – tablets loaded onto mesh tray.

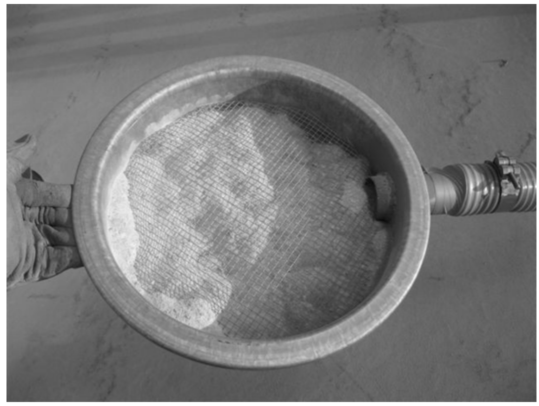

Fig. 5 Deep phosphine chamber – tablets spent and powder under mesh.

The oats in the silo were treated at 1.5g/m^3 using 228 aluminium phosphide tablets which were placed in the reaction chamber. The gas concentration was measured with a Draeger Miniwarn that has a value limit of 1000 ppm.

1.2.2 Results

Phosphine concentrations passed the 100 ppm threshold two days after dosing and reached 200 ppm in all parts of the silo two days later (day 4). They remained above 200 ppm for nine days at which point monitoring was terminated. (Fig. 6)

The cooler ambient conditions compared to Trial 1 created a different pattern of gas concentrations. The concentrations were highest at the base monitored point indicating the air is travelling mainly down the thermosiphon and pushing the gas up into the cone. This is caused by an ambient temperature lower than the commodity temperature. Maximum concentrations of 1 000 ppm were recorded in the base point two days after fumigation commenced. An ambient temperature spike of 21℃ after noon on the fourth day demonstrates the air flow reversing in the thermosiphon pipe when the base values drop to 550 ppm and the top values rise to 550 ppm. The base value rose back to 1 000 ppm as the ambient temperature cooled overnight. The sudden fall and rise of all points on day 12 and 13 are unexplained and it is speculated the gas was moving to other parts of the silo. This could only be fully examined with more intensive monitoring in future trials.

1.2.3 Discussion

1. It has been demonstrated in these trials that a thermosiphon system effectively delivers phosphine gas into the grain bulk from the phosphine reaction chamber and produces rapid equalisation throughout the profile. The system has the advantage of not needing expensive ele-

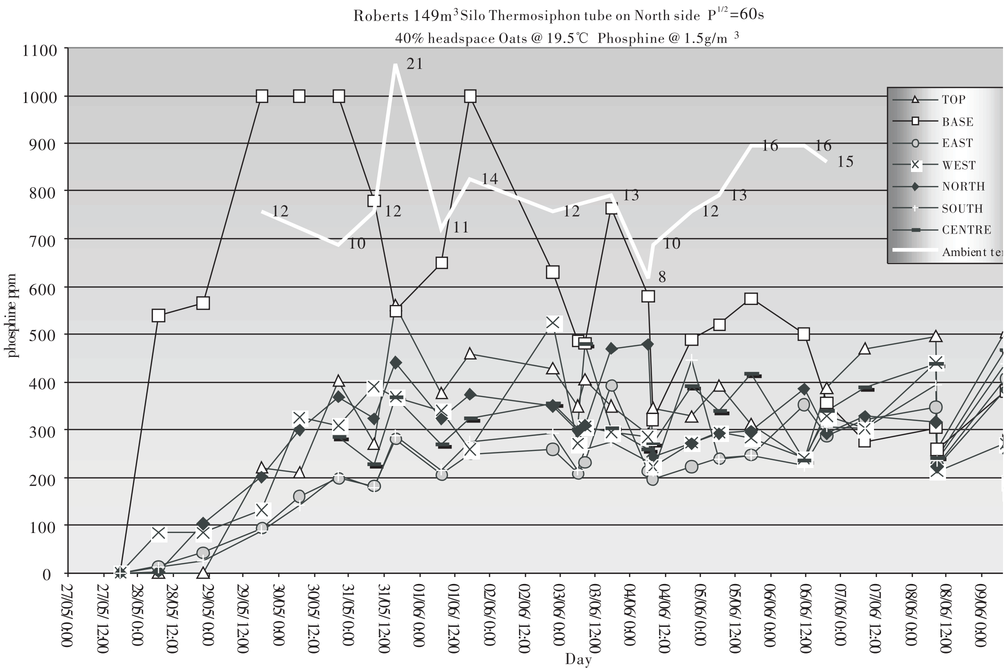

Fig. 6 Thermosiphon fumigation dataBalaklava South Australia℃

ctricity connection but it will only be effective in a well sealed silo. Application of phosphine tablets under the silo ensures there can be no admixture of the residue with the grain. In these trials despite the air stall within the thermosiphon and subsequent rapid escalation of gas concentrations in the phosphine reaction chamber, the phosphine concentrations remained well below the lower flammability threshold.

2. These initial trials were conducted with limited resources and further testing is needed to investigate fumigations under a greater range of commodity and environmental conditions. For example the effect of higher moisture grain on the speed of evolution of the gas, fumigation under cool conditions, placement of the thermosiphon pipe in relation to sun movement and use on larger silos.

3. While thermosiphon application addresses the safety concerns for climbing and working at heights with a dangerous product, it also places the worker in close proximity to the AlP tablets under the silo. Care must be taken when opening the reaction chamber that the spent powder is not blown over the worker. Full protective clothing and full face mask is recommended for these situations.

2 Electrically Powered Ground Level Application System in Sealed and Unsealed Steel Silos

2.1 Trial 1 Sealed silos

2.1.1 Materials and Methods

The first trial of a powered ground level application system in WA was at the Quaker Oats storage complex in Forrestfield from 1226 July 2006 on a 3 200m sealed steel silo with a below ground concrete cone, which exhibited $P^{1/2}$ = 180 seconds (500 Pa to 250 Pa). The silo was filled to 95% capacity with oats at 8.8% moisture content. A ground level pressure relief valve was connected to the headspace by a 200 mm steel pipe. The pipe was fitted with Camlock couplings to accept 100 mm i. d. flexible food quality PVC reinforced hose to move gas between the headspace, the reaction chamber and the base of the silo. A 3.2m × 0.8m × 0.47m phosphine reaction chamber was constructed with Camlock fittings on each end to receive the flexible pipes and sliding mesh trays inside the chamber to allow the rollout of three 3 metre AlP blankets.

Gas values were recorded using a Canary Company, Silo Chek' gas monitor through 1.5 mm i. d. nylon tubing inserted through the silo wall at four points around the base and one in the headspace and at the gas point of entry and exit from the silo.

2.1.2 Gas blown into headspace

The fumigation commenced by loading the reaction chamber with three AlP blankets providing 3 000g of phosphine gas in the silo, at a dosage rate of 0.95g/m. (Fig. 7) The released gas was blown into the headspace and the air/gas mixture drawn from the bottom of the silo.

Fluctuating gas values in the headspace after day 8 and no detectable gas in the below gr

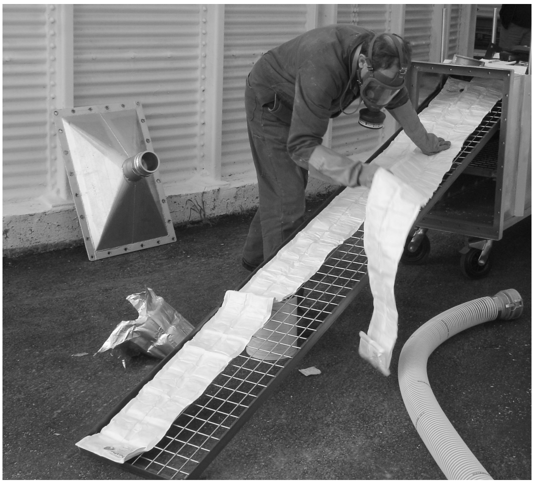

Fig. 7 Loading AlP blankets into the reaction chamber

ound cone compromised the fumigation and it was decided to reverse the air flow to try to increase the gas concentration in the cone. (Fig. 8) An additional monitoring point was inserted in the unloading auger.

2.1.3 Gas blown into the base

A trial in an adjacent silo of the same capacity and with the same pipe work fitted was commenced with the AlP reaction chamber reversed and the hoses connected to draw gas from the headspace and blow it into the base. This fumigation demonstrated lethal gas values for seven days in the cone auger but recorded variable concentrations in the headspace. (Fig. 9)

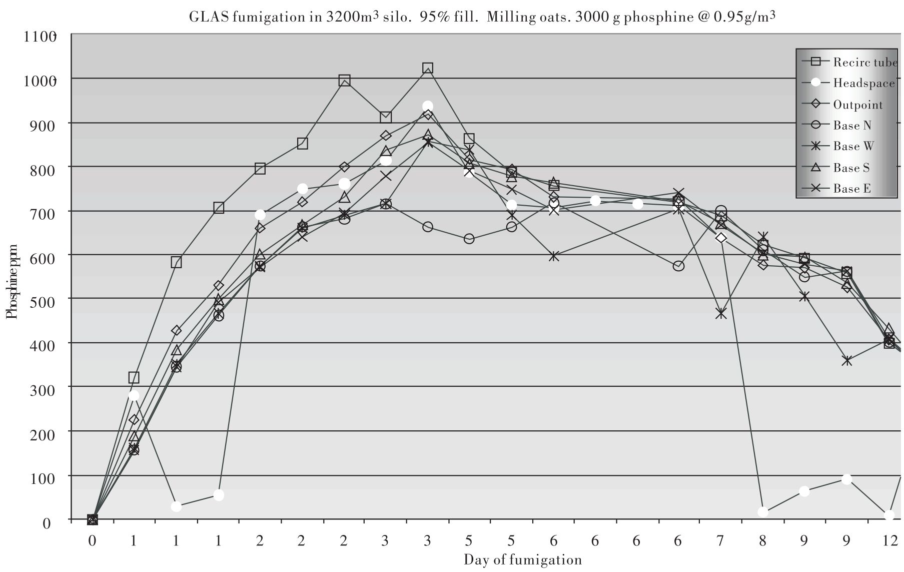

Fig. 8 Chart data from initial 3000g fumigation

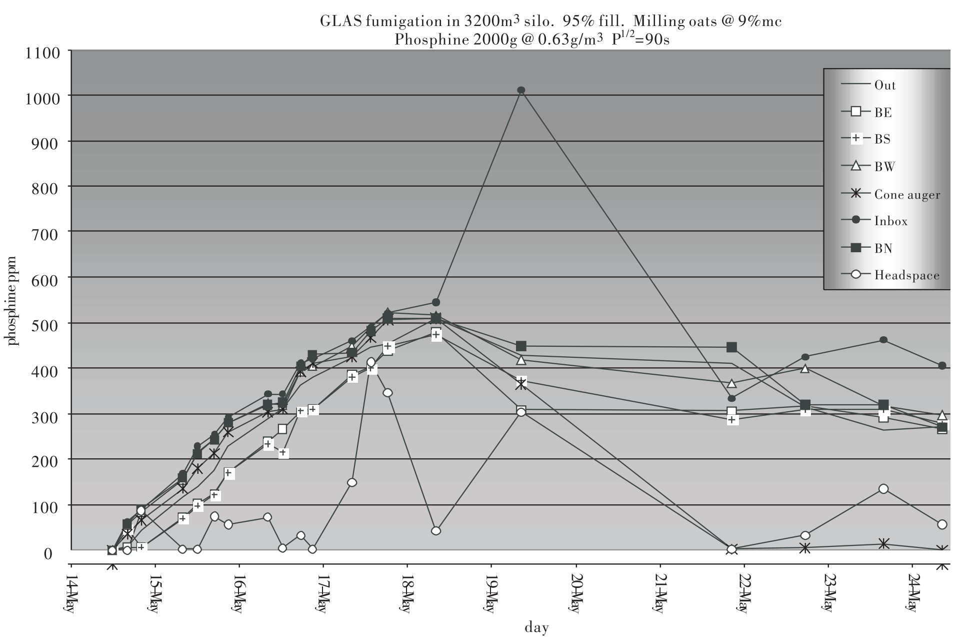

Fig. 9 Reversed flow fumigation

2.1.4 Discussion

Fluctuations in gas values in the head-space of these silos are most likely caused by strong winds creating a chimney or venturi effect' on the silo drawing gas out through any leak points. The slide valve under the top drag chain was a suspect leak point because it has to be sealed by applying mastic and dust makes it difficult to seal effectively.

From this trial and complimentary work on Closed Loop Fumigation (Newman 2008[8]) it is suggested that blowing the gas into the base of the storage is more likely to result in an effective fumigation than pressurising the head-space with a greater risk of gas loss through leak points.

In a sealed silo the outcome is more predictable and monitoring may be conducted once a day, however two readings per day will provide a better indication of the success of the fumigation and in particular give more accurate start and finish times of the protocol period.

This powered recirculation system contributes to a safer workplace, reduces the physical stress on employees, decreases the time to reach threshold gas concentration in all parts of the silo and reaches equalisation of the gas more rapidly than a top loaded fumigation relying on thermal currents and partial vapour pressure to distribute the gas.

2.2 Trial 2 Unsealed silos

2.2.1 Materials and Method

A trial was commenced at Cunderdin WA in March 2008 to control *Tribolium castaneum* (Herbst) on a farm in four 1 171m unsealed silos. The safe option to apply 1 900 AlP tablets into the silo was to construct a phosphine reaction chamber at ground level to hold the tablets on trays and blow the gas into the base of the silo. Loading the tablets onto trays in the headspace though a 500 mm entry hatch 13 metres above ground level and afterwards retrieve the spent powder is much more hazardous.

A sealed phosphine reaction chamber was constructed from 3 m × 0.45 m × 0.45 m steel plate and fitted with wheels to enable it to be moved easily to all silos on site. The fan bolted to the chamber had a differential pressure of 500Pa and fan tip speed of 25.4 m/s and was measured to draw 41.8 litres per second of air from the headspace providing three air changes in the silo per day.

A 90mm diam PVC pipe was inserted into the roof of the silo, continuing to ground level and connected to the reaction chamber by a flexible 80mm reinforced hose. The gas from the reaction chamber was injected into the base of the silo via a 10 cm × 90 cm perforated steel pipe inserted into the grain.

In this case the silo wall sheets were partially sealed during construction but it was technically unsealed. Some effort was made to reduce the number of gaps prior to the fumigation in the roof to wall joint and the peak loading point. (Fig. 10)

Fig. 10 Sealing the roof to wall joint

The roof lap joints were not sealed and the chain conveyor housing in the base remained a leak point.

2.2.2 Results

2.2.2.1 High wind fumigation

The fumigation commenced by loading 1900 AlP tablets into eight trays made from 20 litre plastic containers sawn in half and with a plastic mesh support for the tablets. (Fig. 11 & 12)

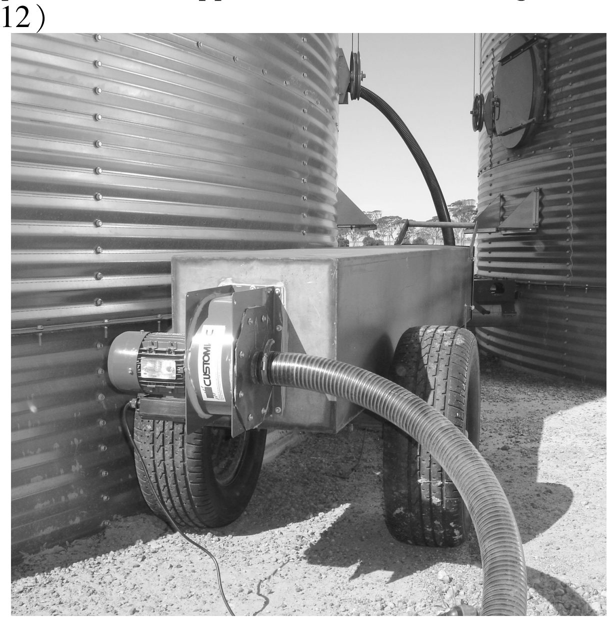

Fig. 11 Farm constructed ground level application system

Fig. 12 **Internal view showing AlP trays with plastic mesh**

The fan on the fumigation chamber was turned on and left running for most of the fumigation period.

This period was characterised by strong easterly winds with a mean ranging from 12 to30 kph prevented the gas values on the windward side from rising above 16 ppm except for a brief period.

This finding coincides with earlier work by Newman [8] on the gas loss caused by strong ambient winds.

The fan was turned off at day three and the gas values at the sampling points fell rapidly, demonstrating the need to keep the fans running in unsealed silos to hold the gas within the grain. The fan was re-started 21 hours later.

This fumigation did not achieve the fumigation protocol outlined by DAFWA of > 100ppm for 7 days and was deemed to have failed.

2.2.2.2 Moderate wind fumigation

The same silo was fumigated the following month with a new load of grain during a period of more moderate wind conditions. (Fig. 13)

All monitored points of the silo rose above 100 ppm after 36 hrs and stayed >100ppm for a further 60 h under very low ambient wind conditions. On day five a 25 kph southerly wind demonstrated the vulnerability of unsealed fumigation when values dropped rapidly at the south monitored point. An additional 1 000g of AlP was added 24 hrs later raising the gas concentrations at three points while two points on the south and east remained below the 100 ppm target value coinciding with a rise in wind speed from the south.

Even though two points in the silo failed to reach the protocol gas values, and the warm grain remained in the silo for a further three weeks before outloading commenced, the grain was outloaded and sold over a period of seven weeks with no live insects detected.

(Harris, E. 2008 pers comm. [6])

2.2.3 Discussion

Moving the gas into the base of an unsealed silo places it directly into a more protected zone in the grain bulk and as the gas exits from the surface of the grain it is drawn quickly back to the base reducing the gas loss caused by external winds.

The grain in the test silos ranged between 8.5% and 11% and observations show peak gas values usually occur after 36 – 48 h which is comparable to the most common top loaded' farm fumigations. Equalisation throughout the bulk is more uniform and occurs much faster than in standard fumigations. Peak values in the headspace tend to be lower because the gas is drawn back into the return pipe soon after it emerges from the grain bulk.

Fumigations on farms in Australia are usually not monitored and rely on the label rate to reach the recommended c × t product. This will work effectively in a sealed silo up to 200t, but above this size there is a need to recirculate, and ideally the silo should be sealed. In reality a small percentage of large grain silos on farms in Australia are sealed to a fumigation standard or have a recirculation system installed. The cost of sealing can be significant, up to 20% of the initial construction cost. If there is an unwillingness to commit funds, poor fumigations will continue.

A ground level application system attached to these silos enables the concentration to be manipulated by topping up the AlP charge in the chamber as needed during the fumigation to maintain the designated gas concentration × time protocol.

Using a ground level application system in these types of silos provides a level of control over the fumigation and with selection of appropriate calm weather conditions by referring to the meteorological forecasts, good monitoring, and management of the AlP recharge in the reaction chamber, it has the potential to eliminate all stages of insects that are strongly resistant to phosphine.

To enable fumigation in the many unsealed silos in Australia there is a need to develop a phosphine label that gives instruction on main-

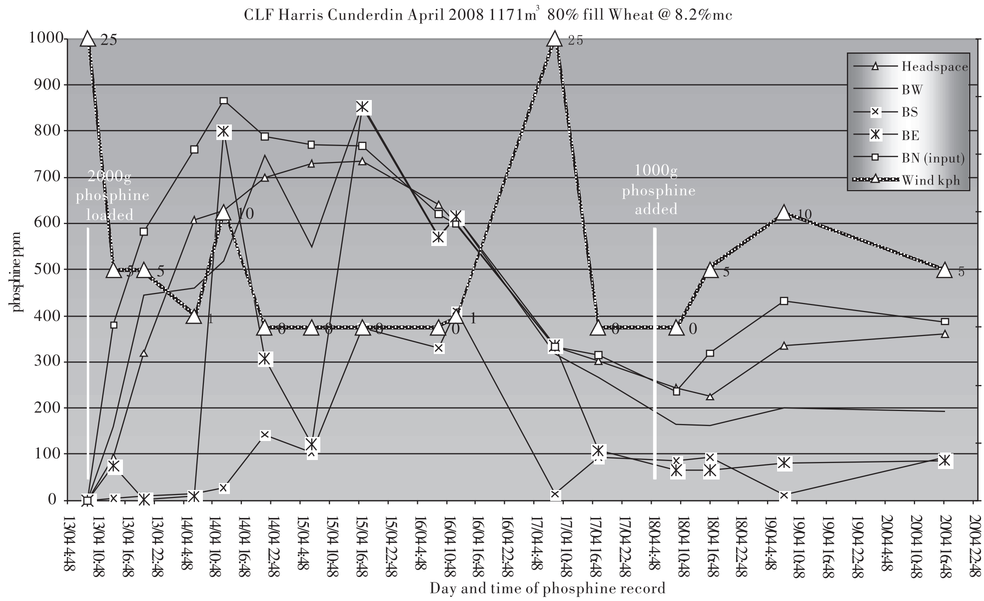

Fig. 13 **Influence of low wind conditions on internal gas values**

taining a protocol above a minimum concentration. The most recent phosphine label provides for fumigation only in sealed silos and for application of AlP to the headspace. This type of fumigation is highly susceptible to fumigant loss in unsealed silos and will result in selection for resistance in the insects present. A formal trial to assess techniques to distribute gas evenly throughout the silo is needed to provide data for a label stating required gas concentrations.

Conclusion

The trials reported in this paper have demonstrated the success of thermosiphon attached to sealed silos and an external ground level fan powered phosphine generating and recirculating device attached to large sealed silos. Both systems produced lethal phosphine concentrations to eliminate all life stages of the insects present.

Using an external phosphine generating device on large unsealed silos is subject to external weather conditions with the risk of fumigation failure and requires a much higher level of management for success.

The new Australian Standard that requires silos that are constructed as sealed, regardless of size, to conform to a pressure test of three minutes or longer from 500 Pa to 250 Pa will impact on the quality of the construction of farm silos in the long term. However there are large numbers of existing grain silos constructed many years ago that remain structurally sound but the cost of retro sealing is not economical for the remaining life of the silo.

Fumigation using an external generating and recirculation device is an attractive short term option to continue to use the silo. This system offers the chance to eliminate all grain insects in unsealed storages at a lower cost than complete retro sealing the grain store to the current grain industry standards.

Future trials should aim toward producing recommendations that will enable effective management of this system.

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