Phosphine generator trial using external air dilution

Ryan, R.F.*#1, Shore, W.P.2, Newman, C.J.E.3
1 VAPORFAZE, PO Box 4, Sans Souci NSW 2219, Australia. Email: robert.ryan.consultant@gmail.com
2 GasApps Australia Pty Ltd, 6/20 Valediction Rd, Kings Park NSW 2148, Australia
3 Grain Tech Systems, China, 8 Shun An Road South, Shun Yi District, Beijing, China

* Corresponding author
# Presenting author
DOI: 10.5073/jka.2010.425.263

Abstract

A commercial phosphine (PH₃) generator manufactured by Beijing Liangmao Technology Development Company Limited, China was used in a fumigation trial on 5000 tonne bunker storage. The generator’s production of PH₃ is controlled by the rate of dosing conventional aluminum phosphide (AlP) tablets into 100 kg water in the reaction chamber.

Because PH₃ is flammable and explosive if certain a concentration is reached in air, it is usually mixed with carbon dioxide (CO₂) in the weight ratio of 50:1. This trial’s objective was to minimise the amount of CO₂ and dilute the generated PH₃ with air. The PH₃ generated is purged from the reaction chamber by a continuous low flow of regulated CO₂ gas. The PH₃-rich CO₂ purge stream was fed into the suction inlet of an external venturi. A high pressure fan was used to produce the air flow through the venturi to create the vacuum to suck in and dilute the PH₃ rich stream from the generator. The PH₃ was diluted in the air-flow to ensure a non-flammable concentration of less than 1% (10,000 ppm) and thence fed directly into the bunker storage. The trial successfully demonstrated the viability of generating phosphine in this manner, and excellent results in PH₃ concentration and distribution was achieved in very short time periods. The capacity of the generator was limited to 8 kg of AlP tablets, equivalent to 2.667 kg of PH₃, or sufficient to fumigate 2667 m³ of grain at a dosage rate of 1 g/m³. A much larger version of the machine would be required to fumigate medium size bunker storages in the 10,000 to 15,000 tonne range. Notwithstanding, the generator offers an attractive package combining the speed and convenience associated with the use of gaseous PH₃ with the low cost of AlP formulations.

Keywords: Phosphine fumigant, On-site generator, Metallic phosphide, Non-flammable

1. Introduction

The preferred fumigant for stored product insect in bulk grain is phosphine because it is the lowest cost fumigant when generated from solid metallic phosphide products (usually aluminium phosphide: AlP). The major hazard concern with phosphine is its wide range of flammability with a lower flammability limit of 1.8% in air. Another issue with PH₃ is its approximate 5 day exposure time which is extended by the 1-2 days required to generate PH₃ gas from AlP tablets reaction with atmospheric moisture.

PH₃ was mostly generated in-situ from AlP tablets until the commercial availability of PH₃ as a compressed gas [either as 100% or non-flammable mixtures of PH₃ in CO₂ (2.6 vol%) or nitrogen: N₂ (2.0%)].

On-site PH₃ generators allow the quick release of PH₃ from AlP tablets by dropping the tablets into water; however this exacerbates the flammability issue. One solution is to purge with large volumes of CO₂, however the additional number of cylinders required adds cost and complications in remote locations (N₂ cylinders can be substituted for CO₂ however this required three times the number of gas cylinders). While some CO₂ cylinders are required for pre-purging and post-purging the reactor, the required number is significantly reduced by mixing the generated PH₃ with air prior to release into the storage to be fumigated. While related techniques can be used, this trial used a venturi which allowed the intimate mixing of PH₃ and air to a non-flammable level of less than 10,000 ppm prior to discharge into the grain storage.
2. Materials and methods

A commercial PH₃ generator manufactured by Beijing Liangma Technology Development Company, China was used in the fumigation of 5000 tonnes of wheat. The generator’s production of PH₃ is controlled by the rate of dosing conventional Aluminum phosphide (AlP) tablets into 100 kg water in the reaction chamber. The maximum rate of dosing is 24 tablets/minute (24 g of PH₃/minute = 72 g of AlP/minute). The recommended capacity of the generator was 8 kg of AlP tablets, equivalent to 2.667 kg of PH₃, or sufficient to fumigate 2667 m³ of grain at a dosage rate of 1 g/m³.

Because PH₃ is flammable and explosive over 1.8% [18000ppm] PH₃ it is usually mixed with CO₂ in the weight ratio of 50:1 (2% by weight PH₃ in CO₂ is non-flammable). This trial’s objective was to minimise the amount of CO₂ and dilute the generated PH₃ with air. The PH₃ generated is purged from the reaction chamber by a continuous low flow of regulated CO₂ gas. The PH₃-rich CO₂ purge stream is fed into the suction inlet of an external venturi. A high pressure fan was used to produce the air flow through the venturi to create the vacuum (1 kPa) to suck in and dilute the PH₃ rich stream from the generator. The PH₃ was diluted in air flow to a non-flammable concentration of less than 1% (10,000 ppm) prior to delivering this air to the bunker storage.

The measurement of the PH₃ was achieved with commercial instruments used by field fumigators [MiniWarn – Draeger; Silo Chek – Canary Co]. Dilution equipment was prepared which was capable of ten times dilution in air of any PH₃ samples greater than 1000 ppm to keep within the range of the electrochemical instruments used.

3. Results

The trial successfully demonstrated the viability of generating phosphine in this manner, with excellent results in PH₃ concentration and distribution of non-flammable PH₃ gas was achieved in very short time periods (~4 hours, Figures 1 and 2). The generator was operated at its maximum dispensing rate of 24 tablets/minute (24 g of PH₃/minute = 72 g of AlP/minute). In excess of 50 samples were taken to monitor the PH₃ level in the air flow into the bunker grain storage. The cumulative PH₃ produced is graphically presented in Figure 1, and shows 80% is obtained within 3 h and 100% after 6 h. The PH₃ concentration (ppm) profile over a seven 7 h period is shown in Figure 2. The peak PH₃ concentration measured was 4400 ppm and the irregular peak (at 2 h) was the result of temporary blockage in the tablet dispenser. The “blip” at the end of the 7 h period was the result of a mineral acid addition to determine residual PH₃.

![Figure 1](image_url)  
*Figure 1  \(PH₃\) generator Trial (PH₃ Production - % of total).*
The CO₂ purge was ~3 kg/h and PH₃ generation was ~0.6 kg/h i.e. a ratio of CO₂ to PH₃ of 5:1 which is a tenfold reduction in CO₂ consumption.

4. Discussion

The time required to generate PH₃, while an order of magnitude improvement on generation from AlP exposure to atmosphere moisture, needs to be further reduced. The capacity of the PH₃ generator was 8 kg of AlP tablets, is limited and required “time-out” to prepare additional batches where required.

The field trial demonstrated the need for a larger PH₃ generator (5x times the capacity of the unit tested) and reduction of the PH₃ generating time.

The purge ratio of CO₂ to PH₃ of 5:1, a ten-fold reduction in CO₂ consumption required for a non-flammable mixture, will need to be maintained but preferably reduced using the proposed larger generator (15 kg PH₃).

The much larger version of the PH₃ generator is required to fumigate medium size bunker storages in the 10,000 to 15,000 tonne range. Preference is for the re-design unit to incorporate “real time” removal of spent tablet residues with addition of a filter to minimise the scale up required for the reaction chamber.

Notwithstanding, the existing generator offers an attractive package combining the speed and convenience associated with the use of gaseous PH₃ with the low cost of AlP formulations.

Acknowledgements

Special thanks to Zhao Baoxing, Beijing Liangmao Technology Development Company Limited, China for the loan of their portable PH₃ Generator to conduct this trial in Australia. We are indebted to William Shore and Reji Peruvilil of GasApps Australia Pty Ltd for assistance with modifications allowing this trial to proceed.