Destruction of toxic and environmental harmful gases

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DOI: 10.5073/jka.2010.425.262

Abstract

Environmental and Occupational Health and Safety or OH&S issues have influenced the focus to capture / destroy toxic and environmental harmful gases expelled from fumigated storage. These storages are aerated to Threshold Limit Value (TLV) levels at the completion of fumigation to ensure it is safe for human re-entry. Most fumigants by design are toxic and some have additional environmental hazards. The once universal fumigant, methyl bromide (CH_3Br), while restricted by the Montreal Protocol because it is an ozone depletor, is still used commercially in tonnage quantities. The use of CH_3Br is now mostly restricted to Quarantine Pre-Shipment (QPS) fumigations. The CH_3Br dose level is approximately 10.000 ppm and the recommended maximum respiratory level is 5 ppm. The universal fumigant gas, phosphine (PH_3), a very toxic gas, has a recommended TLV of 0.3 ppm. The sterilant, ethylene oxide (EtO), a known carcinogen, could have niche fumigation-sterilisation applications if the aerated gas could be destroyed. The use of heat to decompose toxic gases can involve the extracted contaminated air being fed into a burner where the hot zone destroys and decomposes the vulnerable fumigant gas. While flame burning at high temperature pyrolysis is 100% effective with EtO, most fumigants will form acidic by-product. Other issues include the need to re-locate capture and destruction equipment to service multiple locations and the large dilution required to reach TLV levels. A current alternative consists of adsorbing fumigants on activated charcoal. The spent activated charcoal requires chemical processing and or burial. There are cost issues with the initial purchase of the activated charcoal and post-treatment chemical processing of the adsorbed fumigant. Another disposal option is the burial of the spent charcoal in landfill sites. The ongoing safe use of fumigants is critical to important export industries especially the large volume bulk grain and export timber market.

Keywords: Fumigants, Capture, Destruction, Incineration, Acidic reactants.

1. Introduction

International border protection requires elimination of the introduction of quarantined pests and pathogens. As an aid in this endeavour, imports and exports are subjected to mandatory quarantine and pre-shipment fumigations using toxic gases.

The Australian Quarantine and Inspection Service (AQIS) manage quarantine controls at Australian borders to minimise the risk of exotic pests and diseases entering the country. AQIS also provides import and export inspection and certification to help retain Australia's highly favourable animal, plant and human health status and wide access to overseas export markets. In addition to quarantine requirements, high volume fumigations are carried out by bulk grain and food manufactures for stored-product insects in grain and processed foods.

Fumigants by their nature and properties are toxic gases and vapours. Imports and exports are subjected to mandatory quarantine and pre-shipment fumigations using toxic gases (methyl bromide, phosphine, sulfuryl fluoride and ethylene oxide).

Occupational Health and Safety (OH&S) and Environmental requirements are an issue and are best achieved by removal of fumigants at the completion of the fumigation. The removal of fumigant is usually carried out by the fumigators who take positions up-wind and vent the fumigant to atmosphere by lifting the tarpaulin sheets. The use of forced air from electric fans are sometimes used. With grain silos, aeration fans if available, can be used to speed up the venting of fumigants. Earlier industry practice of fume extraction allowed toxic gas concentration of four hundred times (400x) the Threshold Limit Value (TLV) to be vented, which in the case of CH_3Br is 2000 ppm. This high level was justified when using a stack vent and relying on dilution in the atmosphere. Today, when approval is sought, the concentration required by Australian authorites, is usually the TLV, ie 5 ppm with CH_3Br.

Capture and removal of the toxic fumigants ensure safe working conditions and avoid contamination of the environment. The fumigant gas recapture system requires the aeration of the fumigated commodity and subsequent capture of the diluted fumigant from the contaminated air to reduce the risk of human exposure to employees, bystanders, transporter and un-packers.

In addition to OH&S concerns there is the environmental issue of ozone depletion with the fumigant, methyl bromide. A number of countries have regulated the mandatory capture of methyl bromide and other fumigants. The current "degassing" method consists of adsorbing fumigants on activated charcoal. The spent activated charcoal requires chemical processing and or burial. There are cost issues with the initial purchase of the activated charcoal, post-treatment chemical processing of the adsorbed fumigant or burial of the spent charcoal in landfill sites. The ongoing safe use of fumigants is critical to important export industries especially the large volume bulk grain and export timber market.

The innovation described in this paper is a thermal oxidizer system fitted with a solid-state-acidic reactor to eliminate any acidic gases formed in the burning process.

The technique used includes the use of a blower sucking air and fumigant from the fumigation space. The make-up air is controlled to maintain a negative pressure in the fumigation space, which has the beneficial properties of assisting desorption of the fumigant and maintaining a weather-proof seal when using tarpaulins in stack fumigations. The blower discharges the fumigant/air mixture into a burner that will heat the air, burn and decompose the fumigant. At elevated temperature the fumigants will break down into products of decomposition and combustion, some of which will be acid gases. The burner discharges the hot gas (surplus air, nitrogen, products of decomposition and products of combustion) into a hot solid alkaline aggregate which will react with acid gases.

2. Materials and methods

Field trials were carried out on FCL (full container load) shipping containers undergoing stack quarantine fumigations. The following equipment was fitted onto fumigated containers requiring aeration: high pressure blower: - GAST Model # R5325A-2 (static pressure = 14.9 kPa; airflow rate = 8 m^3/h), incinerator: - 0.3 m x 1.5 m steel, burner: propane flare, absorbent: 130 mm deep aggregate bed on steel wire mesh support. Special attention was required to keep combustible materials (tarpaulin, rubber hose tyres and plastic pipe) away from the incinerator; and to reseal the system after opening for the lighting of the burner. A length of copper tubing was used to sample the hot gas emitting from the top of the incinerator and to deliver a cool gas sample to the analyser instrument. High methyl bromide readings were analysed using an Interferometer and a Photo Ionisation Detector (PID) used for methyl bromide levels less than 1000 ppm.

Up to nine containers are the norm but for this field trial a stack of four containers (72 m^3 x 4 = 288 m^3) were used. The containers were sealed by a tarpaulin and made gastight using "sand snakes" at the point where the tarpaulin touches the concrete pad. The fumigation space needs to be "gastight storage" to ensure the minimum Concentration x time (Ct) product required for a successful fumigation. This helped in producing a negative pressure during the trial.

The concentration of the methyl bromide fumigant initially was approximately 10.000 ppm (1.0 vol%) which decreases over the fumigation exposure time (in some situations the concentration may be maintained at a constant level). At the completion of the fumigation the methyl bromide fumigant level needs to be cleared to be below the TLV of 5 ppm.

Usually forced air draft is used to aerate the fumigated containers. For the field trials the high pressure blower was used to create a partial vacuum. This resulted in a more controlled flow which had the additional benefits of more uniform extraction of the fumigant and shrink-fitting of the fumigation tarpaulin sheets. The flow was approximately 3 air changes/hour and the dilute fumigant / air mixture was passed into a flame and then into a heated aggregate bed.

The flame and bed act as a "thermal oxidiser" converting the methyl bromide to hydrobromic acid (HBr) which can be removed using alkaline absorbers. Because of the high temperature, solid aggregates absorbers are preferred. The flame can produce temperatures up to 2000°C but would normally be regulated to the decomposition or auto ignition temperature of the fumigant (methyl bromide auto ignition temperature is 537°C).

3. Results

As the early prototype was not capable of being pressurized, the initial trials were conducted with a shallow 130 mm deep solid adsorbent bed to allow gas flow through the bed.

The level of methyl bromide dropped from 3000 ppm to 25 ppm in less than one hour which was satisfactory as it included the warm-up time for the bed.

The heating of the bed was not uniform as indicated by variations in colour indicating channelling in such a shallow bed. The maximum heating was concentrated above the flare burner. The burner test was limited to one hour and the aeration was completed by standard fumigation practice.

4. Discussion

The innovation of using a blower to create a partial vacuum assisting the aeration of fumigated shipping containers was of interest to quarantine fumigators. The blower would allow fumigators to run aeration unattended overnight without concern of wind driven rain causing water damage to FCL contents. The partial vacuum ensured a stretched and water proof seal on the containers being aerated.

The use of a blower allows the attachment of a burner and absorber to capture and destroy the fumigant emissions. The initial test quickly reduced the methyl bromide emission from 3000 ppm to 25 ppm and it is expected that further tests will reduce methyl bromide levels to 5 ppm and fix any acid gas.

Future testing will include improved temperature control of the mixed gases, uniform flow through deeper adsorbent beds and the selection of effective aggregate absorbents.

The current aeration of containers after fumigation is very open and makes no effort to capture the residual fumigant. The proposed system is a closed one with the capture of the fumigant, and by-products within the system. Because of the high temperature involved in the thermal oxidation, some care is required in the sealing and operation of the system.

Acknowledgements

Special thanks to William Shore and Reji Peruvelil of GasApps Australia for assistance with high pressure blowers and prototype thermal oxidiser.