Generation of phosphine gas for the control of grain storage pests

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Abstract

The phosphine generator is a device for rapid production of phosphine (PH_3) gas to be introduced into grain storage. The aluminum phosphide (ALP) tablets are used as raw material and its effective constituent is 56%. When the aluminum phosphide and water are brought into contact a hydrolyzation reaction takes place to produce the phosphine gas. Controlling the reaction temperature, reaction pressure and the dosage of aluminum phosphide immersed in the water, the hydrolyzation reaction can be controlled or the output speed of phosphine generated can be controlled. If phosphine concentration exceeds the explosive limit, the phosphine easy catches fire and causes explosion. The carbon dioxide is an inert gas. Before the high concentration phosphine is released into air, using carbon dioxide dilute it to make the phosphine concentration diminution, until phosphine concentration is very low than the phosphine explosion limit. According to the amount of phosphine generated in unit time, mixing an amount of carbon dioxide with it at the same time, controlling both proportion between phosphine and carbon dioxide can be realized. weight ratio between phosphine and carbon dioxide has been proved to be safe by practice. This ratio is 2% phosphine to 98% carbon dioxide. If the generation of phosphine gas can be controlled, the phosphine generator can be used for phosphine recirculation fumigation at low or high concentrations. The generator is operated outside of the storage structure and the phosphine gas is introduced into the structure, either directly through the gas distributor or through recirculation system which has a recirculation fan.

Keyword: Phosphine, Generator, Fumigation, Grain, Storage, Pests

1. Introduction

Phosphine has been used widely in grain storage globally because it is effective, easy to use, has strong penetration and is inexpensive. In China for the national grain reserves, annually 2500 t of aluminum phosphide are applied, of which 1000 t are applied using phosphine generators. Although the phosphine resistance of pests has been increasing, the following combinations have been applied: phosphine generators in combination of recirculation fumigation in improved gas tightness storages; phosphine generators in combination of recirculation fumigation, under plastic film; phosphine generators in combination of gas distributor for fumigating multiple stacks or containers.

The phosphine generators technology is based on the combination of carbon dioxide and phosphine for fumigation. After mixing phosphine produced by phosphine generator with carbon dioxide in a steel cylinder, the gas is conveyed into the treated premises. This technology has several advantages, such as reducing the potential combustion, increasing gas penetration, improving uniform distribution in grain bulks, reducing the fumigation time, and reducing polluting residues.

2. Phosphine recirculation fumigation technology

Phosphine recirculation fumigation technology has been regarded as an effective and feasible way for pests control in silos and warehouses. It could make phosphine uniform distribution by recirculation fan and recirculation pipe. From its effect for pest's control, people usually took this as a simple, safety, economic and effective way.

Before fumigation, we should be familiar with the air tightness of the grain storage to be fumigated. This is the key factor in the success of the recirculation fumigation. An accepted standard of the air tightness of grain storage consists of pressure decay half life time from 500 Pa to 250 Pa should be 200 sec in large empty silos, and over 60 sec in empty warehouses.

The first part of the equipment is the phosphine recirculation system that is composed of the following five parts: A. Phosphine generator; B. Recirculation fan; C. Aeration pipe on the bottom of the granary;

D. Recirculation pipe on the surface of grain and under plastic sheeting; E. Recirculation pipe on the outside wall of granary. (Fig. 1)

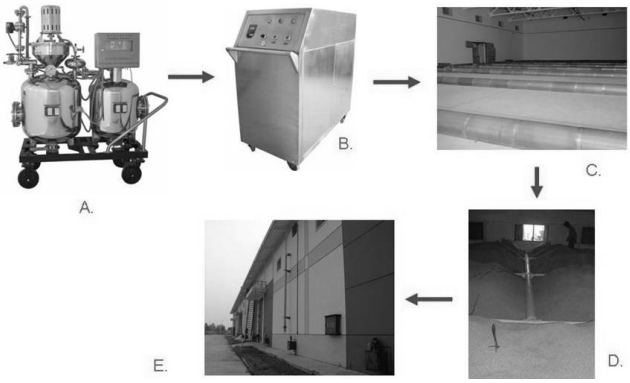

Figure 1 Phosphine recirculation fumigation system. The red arrows show the direction of phosphine movement in the recirculation fumigation system.

The second part of the equipment is the fumigant generator and distribution system (Fig. 2): A. Phosphine generator; B. Gas distributor.

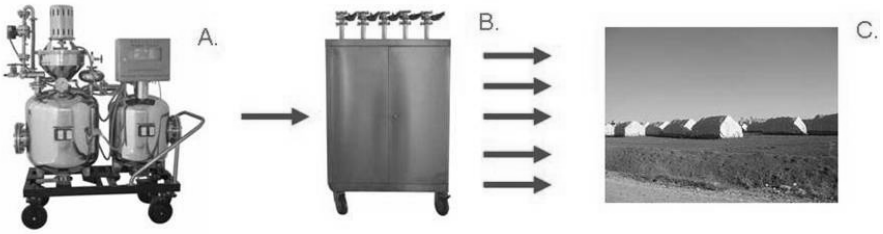

Figure 2 Regulating distributes fumigation system. The red arrows show the direction of phosphine movement in the regulating distributes fumigation system.

3. Operation principle the phosphine generator

The phosphine generator is a device for rapid production of phosphine gas to be introduced into grain storage. The aluminum phosphide is used as raw material. The generator is operated outside of the storage structure and when the recirculation fan is activated, the gas mixture of phosphine and carbon dioxide from phosphine generator is conveyed to the outlet of recirculation fan. The air flow carries the mixture gas into the ventilation system on the bottom of grain storage. By using the recirculation fan the phosphine gas is introduced into the stored grain. Through the ventilation pipeline the phosphine gas can be uniformly distributed.

The recirculation fan that is used in recirculation fumigation system should conform the following parameters: fan power ≤1kW; air pressure ≤1kPa; air flow rate ≤1000 m^3/h; linear velocity of lamina brim ≤ 40m/s. For granaries with improved gas tightness, the exchange air flow rate of the granary should be at least two times per day.

4. Phosphine recirculation fumigation technology under plastic film

It is possible to apply phosphine recirculation fumigation in grain bulks under plastic film after grain surface is covered by plastic film, and recirculation pipes are installed in the grain surface and connected to ventilation pipes. Sealing by plastic film, could prevent phosphine leaking and keep effective concentration for a long time.

5. Phosphine generators in combination of gas distribution system

This system is composed by A. Phosphine generator and B. Gas distributor (Fig. 2) The gas distributor is mainly composed of 5 unit gas flow meters which are specially used for regulating the gas flow of carbon dioxide. Adjusting the 5 unit gas flow meters, the mixture of phosphine and carbon dioxide can be divided into proportional 5 pipes. This set up enables fumigation of several warehouses or several stacks or several containers at the same time.

6. Operation of the phosphine generator

One fumigation process needs 8 kg aluminum phosphide (tablets or pellets), 180kg water, 8 cylinders of carbon dioxide each of 20 kg gas, and 110V or 220V electric source.

The phosphine generator can produce about 2.66 kg of phosphine in 2 h. Before the generator begins to work, air from its internal chamber should be removed by flushing with carbon dioxide. The tablets or pellets of aluminum phosphide are automatically supplied through a timing motor device to a reaction chamber that contains water. The phosphine gas is produced and then carried by carbon dioxide into the storage. Since the phosphine concentration is maintained below 2% in air, there is no fire hazard.

The generator is controlled by a computer. Once programmed, the generator will operate automatically, until the 8 kg aluminum phosphide is processed.

During the generator operation, the aluminum phosphide and water are brought into contact to produce the phosphine gas. Controlling the reaction temperature, reaction pressure, and the dosage of aluminum phosphide immersed in the water, the hydrolyze reaction and the amount of phosphine generated in per unit time can be controlled. Aluminum phosphide is automatically supplied (through a timing motor device) into a reaction chamber that contains water. In this reaction the gas phosphine is generated immediately, and then it is carried by carbon dioxide into the grain storage (Fig. 3).

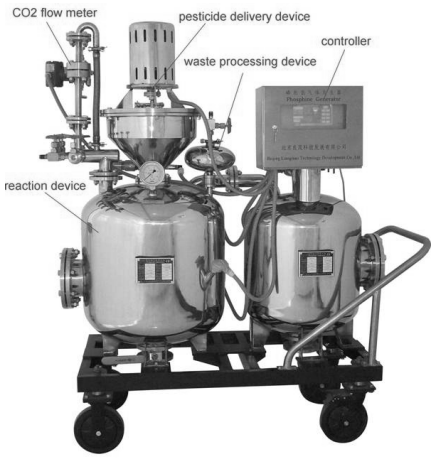

Figure 3 Configuration of the phosphine generator. The configuration of the phosphine generator. It includes: aluminum phosphide delivery device, container, reaction device, container, filtration container, controller, carbon dioxide supply valve, carbon dioxide (CO_2) flow meter and waste processing device, reagent container.

Because the phosphine is flammable and explosive, it should be mixed with carbon dioxide by weight ratio of 98% carbon dioxide and 2% phosphine before the phosphine is released into air.

The cone-shaped container can hold 8 kg aluminum phosphide (tablets or pellets). A timing motor is located on the top of the container and its spiral device rotation speed can be controlled by the phosphine generator. The spiral device supplies aluminum phosphide into the reaction container that can hold 100 kg water User can adjust the carry speed by touch screen on the controller of phosphine generator. The adjustable range is 12~72 g/min. One gram of aluminum phosphide (tablets or pellets) can produce about 0.33 g phosphine, so the capacity of pure phosphine is 4 ~24 g/min. If the immersed speed of the aluminum phosphide into water in reaction container is 72 g/min, after 111 minutes 8 kg aluminum

phosphide is consumed, and the total capacity of phosphine generated in one cycle of fumigation is 2.66 kg.

The aluminum phosphide tablets contain some wax that causes delay in its hydrolyzation reaction. After the total aluminum phosphide is immersed into the water the function of the reaction container is terminated, but carbon dioxide is blown for at least 60 minutes, until the hydrolyzation reaction can be nearly completed.

7. Reaction and filtration container

Before fumigation, water is added into the reaction and the respective filtration container. During the whole process in one cycle of fumigation, the capacity of the reaction container is 100 kg water for reaction reagent, and the capacity of the filtration container is 80 kg water. The water of the filtration container is used for filtration of the foam generated in reaction container; and also for cooling the phosphine and carbon dioxide mixture gas.

When the aluminum phosphide is added into reaction container, it reacts with water at once and generates the gas phosphine immediately. A certain amount of carbon dioxide gas is supplied to mix with the gas phosphine in the reaction container, and then the mixture of the two gases is conveyed into the filtration container. After cooling and filtration, the cool and pure mixed gas can be released into the site to be fumigated or into the gas recirculation pipe.

The other function of carbon dioxide gas is agitating the aluminum phosphide in the reaction container, so that the aluminum phosphide hydrolysis reaction can be accelerated.

The pressure gauge on the reaction container indicates working pressure of the mixture of phosphine gas and carbon dioxide. The pressure transducer is a sensor that can detect the pressure inside the reaction container. If the pressure inside reaction container exceeds the set pressure, the controller sends an alarm signal. The working pressure of the reaction container is 2~5 kPa, that is depending on the gas resistance from the outlet of phosphine generator to fumigation sites. In case of excessive pressure in reaction container, the safety valve is automatically activated for releasing the excessive pressure.

The temperature sensor can detect the temperature inside the reaction container. If the temperature inside reaction container is exceeded, the controller of phosphine generator can give an alarm. The working temperature is 35 to 60°C, depending on the gas generation rate and environment temperature. If the gas generation rate and environment temperature are both higher, the working temperature is also higher and vice versa. The electric heater is controlled by the controller of the generator to heat the water inside reaction container.

8. Controllers

The work of the phosphine generator is controlled by a microcomputer inside the controller of phosphine generator. The working parameters can be set and displayed on a touch screen.

The phosphine generator can be used at low phosphine concentration and long exposure time, or at high phosphine concentration and short exposure time. User can increase or decrease the gas generation rate from 12 to 72 g/min. According to the working speed, the microcomputer calculates the required quantity of carbon dioxide, to ensure the proportion of 2% phosphine to 98% carbon dioxide. The flow rate of carbon dioxide is also showed on the touch screen from 100 to 600 L/min (about 200 to 1200 g/min), equivalent to rate of gas generation from12 to 72 g/min. According the requirement quantity of carbon dioxide, user needs to adjust the carbon dioxide supply valve on steel cylinder by manual for supplying the gas of carbon dioxide to phosphine generator.

The pressure transducer can detect the pressure inside reaction container, which is from 2 to 5 kPa. The temperature sensor can detect the temperature inside reaction container, which is from 35°C to 60°C. If the normal values of these parameters are exceeded, the controller of phosphine generator can send an audible alarm. User can set the rate of aluminum phosphide to be immersed into the water inside reaction container, and the required carbon dioxide gas flow displayed on touch screen.

9. Carbon dioxide supply valve and flow meter

Providing enough carbon dioxide is the key to ensure the safety of fumigation process. The gas flow for the carbon dioxide supply valve should be adjusted 120 L/min (240 g/min), the total gas flow of five units carbon dioxide supply valve should be 1200 g/min. When they are mixed, their weight proportion is 98.04% carbon dioxide and 1.96% phosphine in the gas mixture. The carbon dioxide loaded in steel cylinder is the gas source for the phosphine generator. The carbon dioxide supply valves are set on the steel cylinder. The maximum capacity of one carbon dioxide supply valve is 120 L/min (240 g/min). According to the phosphine generator rate and the quantity of carbon dioxide, the user can decide how many carbon dioxide steel cylinders should be used. For example, if the phosphine generator rate is 72 g/min, the output speed of pure phosphine is 24 g/min, each carbon dioxide cylinder can supply 120 L/min (240 g/min) carbon dioxide gas, user should be using five carbon dioxide cylinder, which can supply 600 L/min (1200 g/min) carbon dioxide, so that the weight proportion between phosphine and carbon dioxide is 2:98.

Frost and ice is usually formed when carbon dioxide is released from carbon dioxide cylinder through a supply valve. Therefore, electric heating is applied on carbon dioxide supply valve to avoid such a phenomenon.

The carbon dioxide gas has two more functions. One is agitation in the reaction container to ensure aluminum phosphide hydrolyzing reaction is complete in the water. The other is in adjusting the temperature of the mixed gas at the outlet of phosphine generator.

10. Reagent container

After the hydrolyzation reaction of aluminum phosphide in water, two kinds of materials are produced: aluminum hydroxide and phosphine. The chemical formula is: AlP+3H2O=Al (OH) 3+PH3. So the waste liquid includes aluminum hydroxide [Al (OH) 3] and the residual water that looks like a watery mud in the reaction container.

Because aluminum phosphide includes a little wax, sometimes the hydrolyzation reaction is not complete, so the waste liquid includes an amount of phosphine. Before releasing the waste liquid from the reaction container, the phosphine gas in the waste liquid must be cleared.

To eliminate the presence of residual phosphine, the waste liquid is treated using a special reagent composed of nitric acid (HNO3), perchloric acid (HClO4) and copper sulphate (CuSO4), at a ratio of 1000 mL, 500 mL, and 70 to 100 g, respectively.

d. After processing, the waste liquid can be changed into a non-poisonous liquid which is safe and can be disposed of by the normal route for industrial waste.

Nitric acid is mainly used to neutralize ammonia in the waste liquid. The oxidant, nitric acid can oxidize low valence phosphorus. Perchloric acid is mainly used as the oxidant which can oxidize low valence phosphorus. Also used to neutralize ammonia in the waste liquid. As the catalyst, copper sulphate (CuSO4) is used to catalyze the reaction between perchloric acid and low valence phosphorus. After adding perchloric acid into copper sulphate (CuSO4), the reaction between perchloric acid and low valence phosphorus can be accelerated.

11. Safety devices in the phosphine generator

The generator may only be operated by certified fumigators who have been specifically trained to use this equipment. If there is insufficient flow of carbon dioxide, or the pressure in the internal chamber is excessive, or the temperature in the reaction chamber becomes too high or too low, or there is power failure, the generator will automatically stop production of phosphine gas. Should any of these conditions develop, an audible alarm will sound.

12. Technical parameters of phosphine generator

Working sites: indoor or outdoor. Environment temperature: 0°C ~ 45°C. Environment relative humidity: 20 ~ 90% r.h. Environment height above sea level: ≤1000 meter. Category of pesticide: aluminum phosphide pesticide, tablets or pellets. Diameter of the tablets or pellets: less then 10 mm. Content of aluminum phosphide in pesticide tablets or pellets: 56%. Maximum weight of aluminum phosphide in once fumigation process: ≤8 kg. Speed of aluminum phosphide tablets immersed into the water of the

reaction container: 12~72 g/min. The detect range of CO_2 flow rate by CO_2 flow meter: 100~ 600 L/min (200 ~1200 g/min). Design pressure of container: 200 kPa. Working pressure of container: 2~5 kPa (Depending on the gas resistance from the outlet of phosphine generator to fumigation sites). Safety valve threshold pressure: 80~90 kPa. Working temperature: 35 ~ 60°C. Noise of equipment: <70dB. Electrical source (AC): 230 V±10% /50 Hz ±1 Total power: 3.7 kW. Power rate of the 5 units carbon dioxide supply valve are 1.5 kW. Power rate of the electricity heater for phosphine generator is 2.0 kW. Power rate of the controller of phosphine generator is 0.08 kW. Power rate of the timing motor 0.12 kW. Size of equipment: length 160 cm × width 70 cm × high 170 cm. Net weight t: 350 kg. Gross weight: 400 kg. Water volume: 180 kg (reaction container: 100 kg, filtration container: 80 kg). Carbon dioxide supply valves: 6 units. Percentage of gas mixture: phosphine 2%; carbon dioxide 98%

13. Technical parameter of carbon dioxide supply valve

Inlet pressure: 0~15,000 kPa. Outlet pressure: 0~500 kPa. Gas flow rate: 0~120 L/min or 0~240 g/min. Voltage of electric heater: 230 V±10% / %/50 Hz±1. Power of electric heater 1 unit: 0.30 kW; 5 unit total power: 1.5 kW. Safety valve threshold pressure: 800~1000 kPa. Cut-off temperature of heat electric relay: 50±5°C.

14. Recirculation Fan

The recirculation fan is used in recirculation fumigation system. When the recirculation fan is in operation, the mixture gas of phosphine and carbon dioxide supplied from the phosphine generator is directly added to the outlet of recirculation fan and the flowing air carries the mixture gas into the ventilation system on the bottom of grain storage. By using the recirculation fan the phosphine gas is introduced into the stored commodity. Through the ventilation system the phosphine gas can be made uniform distribution.

15. Phosphine concentration monitors

Phosphine concentration monitors are used to detect the phosphine concentration during the fumigation process. Its detection range is 0 ~1000 ppm. The electrochemical sensor has been used in the detector that measures the concentration of target gas continuously and sends sound-light alarms once the threshold was achieved (Fig. 4).

16. Phosphine alarm

Phosphine alarm is a specially designed pocket sized instrument to protect workers from the hazards of phosphine gas inhalation during the fumigation process. If the concentration of phosphine around the work site is over 0.3 ppm, it will sound and light the alarm (Fig. 5).

Figure 4 Gas distributor.

Figure 5 Recirculation fan.

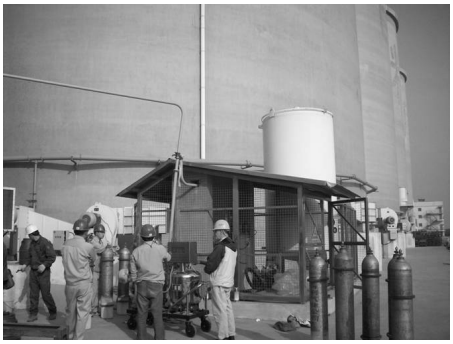

Figure 6 Phosphine recirculation fumigation system on big silo.

Figure 7 Phosphine recirculation fumigation system on big storehouse.

Figure 8 Phosphine recirculation fumigation system on big stack.