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Control And Recovery of Phosphorous Pentoxide Emission in Zinc Phosphide Production Plant

التحكم والاستخلاص لأنبعاثات خامس أكسيد الفوسفور الناتج عن صناعة فوسفيد الزنك

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الملخص

يهدف هذا البحث إلى معالجة واستخلاص خامس أكسيد الفوسفور الناتج عن صناعة فوسفيد الزنك الذى يستخدم كمبيد للقوارض ، وقد صممت ونفذت وحدة تجارب نصف صناعية وتم إجراء التجارب عليها والتى تهدف إلى تحديد العوامل التى تؤدى لأقصى درجات التحكم والاستخلاص ، وقد تم تحديد هذه العوامل ، وهى معدل دخول الهواء المستخدم فى الاحتراق وكذلك معدل دخول المذيب فى برج الامتصاص وقد استنتج من التجارب أنه لابد من استخدام مادة لاستخلاص رذاذ حامض الفوسفوريك حتى نتمكن من الوصول إلى كفاءة الاستخلاص المطلوبة ، وقد استنتج من التجارب أن استخدام الدائرة المغلقة فى برج الامتصاص يؤثر بدرجة كبيرة على كفاءة الاستخلاص لغاز خامس أكسيد الفوسفور وتحويله إلى حامض الفوسفوريك بتركيزات عالية وقد تم أيضا عمل التصميمات المبدئية للمصنع ومؤشرات الربحية للمشروع .تم تنفيذ هذا المشروع بنجاح بشركة النصر للكيماويات الوسيطة بمنطقة أبو رواش بالجيزة.

Abstract

Control and recovery of phosphorous pentoxide emission as phosphoric acid in a zinc phosphide production plant was carried out. The control unit has been designed and fabricated on a semi-pilot scale .The results obtained showed that the water and air flow rates are important factors which affect the percentage recovery of P_2O_5 from the flue gases. Also, mist elimination is an important step in the pollution control efficiency. The obtained results revealed that recirculation of phosphoric acid are very efficient in the absorption of P_2O_5. Detailed engineering design and cost estimation for a full-scale system were carried out. The project was successfully implemented in Nasr Company for Intermediate Chemicals at Giza Governorate, Egypt.

Key words:

Zinc phosphide, rodenticide, P_2O_5 recovery.

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Introduction:

During the manufacture of zinc phosphide, in a chemical industrial plant in Egypt, batches of phosphorous / zinc mixtures are burned out-door and excess phosphorous is used to supply heat to start the reaction. Phosphorous pentoxide is emitted as a waste material at a rate of 10-15 tons/year.

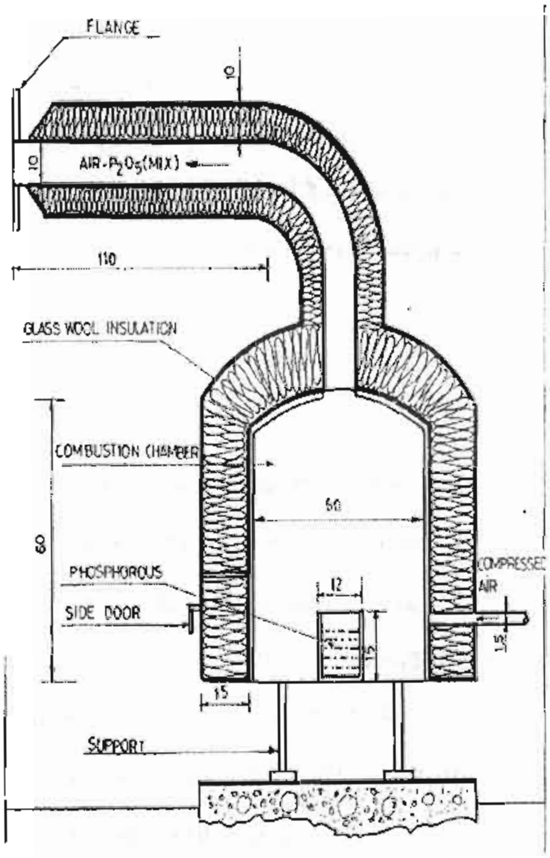
This emission is a source of air pollution in the area and represents a loss of red phosphorous, which is used in the production process. Control and recovery of wasted materials is the first logical step in tackling such a problem. Phosphoric acid is an important chemical, which is used by many industries and can be obtained by the reaction of phosphorous pentoxide with water. Therefore, the aim of this study is the control and recovery of phosphorous pentoxide in order to protect the environment and to gain benefit as much as possible from wasted materials.

Material and Methods:

A control unit of P_2O_5 , based on a semi-pilot scale, has been designed and fabricated. The system consists of two parts:

* An efficient combustion system to facilitate the burning process and confinement into one single stream, which can be later, treated in a subsequent step as shown in Fig. (1). {1,2&3}

* Water scrubbers for the removal and possible recovery of P2O5 as phosphoric acid for further utilization (Figure 2). {1,3&4}



Dimensions in cm

Figure (1) Semi pilot plant for combustion chamber

Results and Discussion:

1-Effect of Water Flow Rate

Red phosphorous is putt in a special pot, which is placed in a combustion chamber. P_2O_5 resulting from the combustion chamber is fed to a scrubber of dimensions shown in (Figure 2) where the water is used as an absorbent fluid.

The recovery efficiency of P_2O_5 increases with increasing the liquid flow rate up to the value of 0.019-m^3/min.. If the liquid rate is greater than that value the removal efficiency of P_2O_5 decreases steadily as water flow rate increases as shows in table (1).

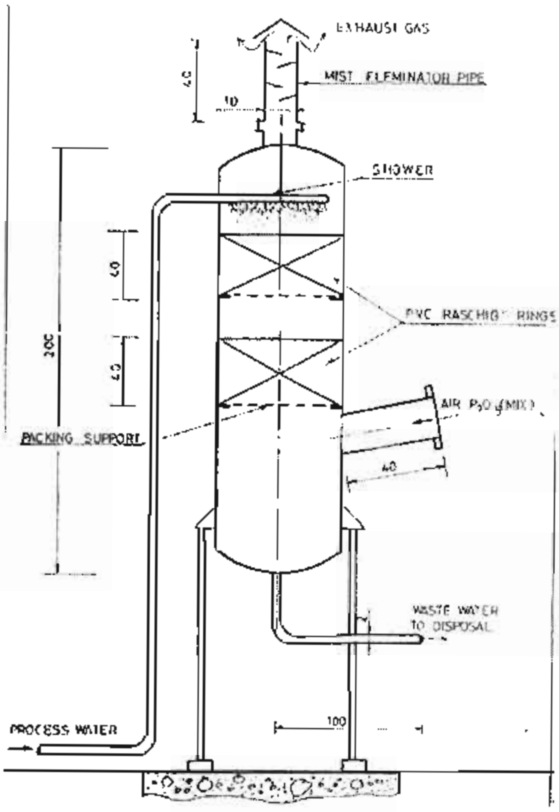


Figure (2) Semi Pilot Plant For Packed Absorption Tower

Apparently, water flow rate of 0.019 m3/min. results in the highest recovery efficiency of 16% when the weight of phosphorous in the sample is 0.5 kg as shown in fig. (3).

When the weight of phosphorous in the sample increased to 0.8 kg, the maximum recovery efficiency increased to 57.5% at a flow rate of 0.028 m3/min.

In both runs, the recovery efficiency was between 26-57% compared to a value of 12-16% for other runs as shown in table (2) and figure (3).

Table (1) Relation between water flow rate and removal efficiency of P_2O_5 for 0.5 kg phosphorus

Water flow rate, m^3/min.	Removal efficiency of P_2O_5
0.01	12%
0.019	16%
0.02823	15%
0.07	14%

This can be explained by the higher partial pressures of P_2O_5 in the water scrubber since the amount of phosphorous burned was higher.

Table (2) Relation between water flow rate and removal efficiency for 0.8 kg phosphorus

Water flow rate, m^3/min.	Removal efficiency of P_2O_5
0.01	26%
0.019	30%
0.02823	57%
0.07	45%
0.09	44%

This is accompanied by higher mass transfer coefficient and hence mass transfer rates (Gas phase controlling) in the scrubber. {4}

The decrease in the removal efficiency with increasing liquid flow rate maybe due to that the gas phase is controlling in this process.

The pressure drop across packing is increased and liquid is holding up which leads to process away from loading region. This phenomenon can decrease the mass transfer coefficients and hence mass transfer rate in the scrubber. {4}

2- Effect of Air Flow Rate

The air flow rate fed to the combustion chamber could not be measured directly. However, comparison between a run in which air is introduced by forced draft and another run in which air is introduced by natural draft shows that decreasing the air flow rate resulted in higher recovery efficiency due to the increase in P_2O_5 partial pressure inside the scrubber.

3- Effect of Phosphoric Acid Circulation

It was reported in literature that the absorption of P_2O_5 in phosphoric acid is faster than the absorption in water and therefore recirculation of the solvent is usually employed in phosphoric acid plants to enhance the absorption process{5}.

To test the effect of recirculation on the removal rate, two tests were carried out using batches of 2 kg of the phosphorous/zinc mixtures (1:3 ratio) and using the same liquid flow rate of 0.019 m^3/min. In the first experiment tap water was used as the solvent but in the second case H_3PO_4 produced is recirculated.

The accumulating H_3PO_4 in the effluent stream of the second experiment was 350 mg/l indicating an increase of the absorption rate by 5 times upon recirculation.

4- The Need to Use a Mist Eliminator

Initial experiments showed that in the absence of a mist eliminator, a persistent white smoke is present in the stack in spite of the fact that P_2O_5 reacts vigorously with water. It has been stressed in literature that mist elimination of the fine H_3PO_4 droplets is necessary(1&6).

Incorporation of a 5 mm thick glass wool layer and a short stack with tapered plates at the top of the scrubber was effective. This was obvious from the absence of any visible smoke, which is a characteristic of the H_3PO_4 mist.

5-Presence of Zinc Phosphide in the Flue Gas:

Samples of the effluent gases were analyzed for the presence of zinc phosphide. Although the phosphide radical was detected in the samples, no evidence for the presence of zinc radical was detected. This can be explained by the fact that the boiling point of Zn_3P_2 is 1100 °C, which is higher than the actual flame temperature, (measured during the experiments using special thermocouple), by about 100 °C. Other metal phosphides e.g. iron phosphide, which might result from the slow attack on the pot walls, could be the source of the phosphide radical in the effluent gas.

Design of Full Scale Unit:

The outcome of our experimental study was encouraging and based on these results and other engineering considerations a full-scale unit was designed, fabricated and installed. Sizing was based on standard procedures {1,2,7&8}. The main components of that unit are: Furnace, scrubber, phosphoric acid, cooler, mist eliminator and chimney.

This unit has been installed in conjunction with the manufacturing process of zinc phosphide. The mixture of zinc powder and red phosphorous is prepared manually in special area at the ratio of 3: 1.

Pots of 80 kg capacity are used and 20 pots are used each time. Manual mixing and feeding are needed to avoid electric sparks which may cause explosions if moving parts are used since phosphorous catches fire easily at any slight friction.

The pots are arranged inside the furnace in pre-formed troughs which allow enough space for operators to enter and leave conveniently and in the same time to keep the pots as close as possible to guarantee that all pots reach a uniform temperature and combustion to proceed evenly.

Horizontal oil burners in the sides of the furnace are used to heat the pots to reach the spontaneous ignition temperature of phosphorous which produce enough heat for the zinc/ phosphorous reaction to proceed.

This reaction is exothermic and produces a considerable amount of heat in addition to the byproduct P_2O_5 .Air for combustion introduced from side holes and the reaction is proceeds at a faster rate than the previous practice (i.e. out-doors combustion).

The pots are observed from side-windows to insure that all pots catch fire and to observe the progress of combustion. Hot gases containing P_2O_5 rises and leave the furnace through a steel pipe to the adjacent scrubber. Normally, the reaction in the furnace takes about 30 minutes to complete. Introduction of combustion air by induced draft mechanism accelerates the reaction, allows shorter time for the conversion to zinc phosphide and avoids the leaving the exhaust gases from furnace door.

When the reaction is complete, cooling with air continues until the temperature in the furnace falls down to room temperature where doors are opened and pots are removed manually where they are emptied of their content and recharged for another batch. Zinc phosphide powder is then sent to grinding and packaging area.

Hot gases containing P_2O_5 passes to the scrubber where they meet phosphoric acid solution, which absorbs P_2O_5 vigorously, and heat of reaction evolves where it is reported that absorption in phosphoric acid is faster than in fresh water.

Phosphoric acid collects at the bottom of the tower and passes to an intermediate storage tank, which receives dilute phosphoric acid solution from the mist eliminator. Phosphoric acid from the intermediate tank is circulated to scrubber passing through a cooler using a centrifugal pump and make-up water is introduced into the tank.

Samples of the acid are withdrawn from the tank and analyzed and when the concentration reaches 85% product phosphoric acid is sent to main storage tank.

Gases leaving the scrubber are now free from most of the P_2O_5 but contain appreciable amount of phosphoric acid mist. This is removed in a mist eliminator, which is capable of condensing and trapping the phosphoric acid mist. It collects at the bottom of the mist eliminator and pass to the intermediate storage tank.

All parts in contact with phosphoric acid solution are made of 316 stainless steel to reduce the rate of corrosion. Packing material is made of ceramic material resistant to hot phosphoric acid solution (porcelain).

Gases leaving the mist eliminator leave to the chimney where they leave at a sufficient height that reduces the ambient concentration resulting from any P_2O_5 traces in the stack gases.

Cost Estimation and Payback Period Prediction:

Using a Lange Factor of 3.63, the estimated fixed capital investment is EGP 2,790,000 {1}. For a total production of 462 tons/year of zinc phosphide, the total production cost per kg of zinc phosphide is L.E 8.11. The selling price of zinc phosphide product is EGP 12/Kg and of phosphoric acid product is EGP 2.35/kg. Hence, the total annual profit after taxes is EGP 1,449,000.

The payback period therefore is 1.65 years if the service life of the plant is 20 years and the plant runs at full capacity. {9&10}

Conclusion and recommendations:

A semi-pilot unit has been tested for the removal of P_2O_5 from gaseous emissions from zinc phosphide manufacturing plant and its recovery as phosphoric acid. Experiments showed the effects of the important design parameters and indicated the need of recirculation and cooling of phosphoric acid product and the necessity to use a mist eliminator to capture phosphoric acid droplets.

The economical study showed that the estimated fixed capital investment is EGP 2,790,000 and a project payback period of 1.66 years. A full-scale unit was designed, fabricated, installed and operated efficiently.

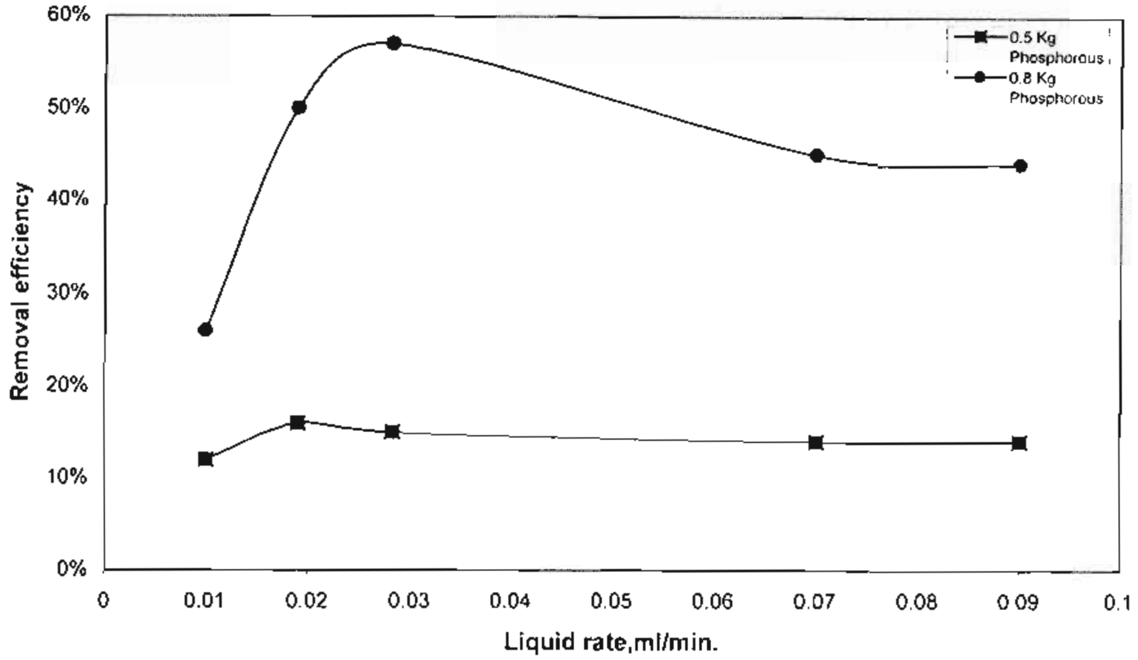


Figure (3) Effect of liquid rate on the removal efficiency of P2O5

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