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THERMAL NEUTRALISATION OF PHOSPHORUS CONTENT PESTICIDE CHEMICALS IN THE RECOVERING ENVIRONMENT

There had been presented the existing methods of neutralization of phosphorus content pesticide chemicals. There had been improved the methodic of their thermal neutralization in the natural gas environment which allows to obtain the commercial phosphor as secondary valuable product. There had been researched the influence of different factors on the processing process

Key words: *pesticides, pesticide chemicals, phosphorus content pesticide, phosphor organic compound, anthropological-ecological safety*

Urgency of the problem

On the territory of Ukraine there has been accumulated a significant amount of unusable and prohibited for usage pesticides, which makes the problem of environmental safety particular important. Among them are sulfur content, chlorine content, phosphorus content pesticide chemicals. The problem of their neutralization into the compounds which are safe for the environment and humans, and, if possible, practical use of the products of their processing, is extremely actual. Technology of neutralizing the sulfur content and chlorine content chamicals is more studied than that of phosphorus pesticide chemicals, which are in amount of over several dozen tons in Vinnytsia region. Technologies of their processing are known, but little used. Therefore the search for the environmentally and economically appropriate ways of their neutralizing is very important. The purpose of the work is the analysis of methods for neutralization of environmentally dangerous phosphorous content useless chemicals, and improvement of the methods of their thermal decontamination by natural gas, thus obtaining commercial phosphorus as a valuable secondary product; research of optimum parameters of this processing. Hence, the urgency of the problem of neutralization of phosphorus pesticide products is evident, as the solution of these issues will significantly increase the level of ecological safety of Ukraine and, in particular, Vinnytsia Region. Great variety of both, home and foreign researchers dedicated their works to the problem of neutralization of phosphorus content no organic substances, including phosphate fertilizer. However, there is not enough technologies of neutralization of phosphor organic compounds. Usually, these are high-temperature thermal methods, which do not take into account the environmental safety and formation of secondary products, which can be used in practice. However, there are some foreign publications dealing with specific local issues, but they do not solve the issue of neutralization of phosphorus pesticide products in general.

Key tasks:

1. Make a list of phosphorus content pesticide products (PPP), which are mostly used in Ukraine.
2. Analyze the most acceptable methods for the neutralization of PPP.
3. To improve the method of thermal neutralization of PPP in the presence of natural gas, which allows to receive commercial phosphorus as a valuable secondary product.
4. To explore the influence of all sorts of factors in the process of neutralization and to determine the optimal parameters of this processing.

Phosphorus organic compounds (POC) are rather intensively produced and used in agriculture. These include: aktelik, amidofos, amifos, antio, afos, afugan, bazudin, bayteks, volaton, gardona, gidrel, DDVF, difos, dibromo, demufos, dursban, ekamet, etafos, isdfenfos, karbofos, kaunter, kilval, kitatsin, coral, metaphos, metation, metilatsetofos, metilmerkaptofos, nekksion, ofunak, plondrel, primitsid, ritsid, sayfos, tokution, trihlormetafos-3, fenkopton, fozalon, phosphamid,

ftalofos, hlorofos. Among the PPP there are poisonous substances (metaphos, merkaptofos) and highly toxic (fosfamid), the use of which has already been completely banned; there are compounds of medium toxicity (hlorofos, karbofos), which are used quite widely. Most of the POC, even of little toxicity, are characterized by accumulation effect and therefore may be of danger to human health [1]. The following insecticides and acaricide as amifos, antio, bazudin, bayteks, gardona, DDVF, karbofos, kilval, metaphos, metation, metilmerkaptofos, sayfos, trihlormetafos-3 , fenkopton, fozalon, fosfamid, ftalofos, hlorofos are the most used PPP in Ukraine, including in the Vinnytsia region. There are different ways of decontamination and disposal of hazardous wastes, which are characterized by not only the number of drawbacks, but also by the availability of products in the processing waste, which harmful to the environment as well as substances that are emitted in the biosphere. Therefore the traditional ways can not be obviously used for the decontamination of unsuitable pesticides, including phosphorus. Consequently, in connection with the above, there was a need to conduct an analysis of possible decontamination and recycling schemes to choose a possible way, equipment and technological modes of disposal and recycling of phosphorus pesticides. The main criterion for evaluating the efficiency of most schemes of decontamination and the elimination of pesticides is the content of toxic substances in products, which are emitted into biosphere after a process of decontamination. Final content of harmful impurities must not exceed their maximum allowed concentrations. The main methods for the neutralization of phosphorus products are thermal, biological (composting method), electric catalytic destruction, aerosol catalysis [2], etc. The essence of the methods of biological neutralization of useless pesticides lies in the microbiological composting or using algae or high water plants. This method provides for the neutralization of prohibited chemicals and unsuitable chemicals by the natural decomposition in organic-soil composts with further receiving of the organic mass [3]. Thermal method of neutralization is the most promising and cost effective. It is a traditional one which is widely used and is acceptable for the sanitary requirements, i.e, the final contents of harmful impurities after the thermal neutralization does not exceed the maximum allowable concentrations [4]. Phosphorus content pesticide chemicals can be neutralized by several of the existing thermal technologies, namely: neutralizing them in a chamber furnaces, revolving drum furnaces, plasma chemical method, thermal decomposition in the environment of glass formating furnace, etc. [5]. One of the perspective method of destruction is a plasma-chemical method, which has many advantages over the fire one. Plazmothermal converter - is a high temperature heat insulated reaction chamber, where the destruction of materials is carried out under the influence of plasma vortices, which are generated by the arc discharge [6]. It is possible to neutralize phosphorus content pesticides by thermal decomposition in their environment of glass formating furnace of such compounds: pesticide 5-25%, 40-60% silicon dioxide, carbonate or calcium oxide 5-10%, sodium carbonate or sodium hydroxide 15-25% [7]. Aerosol catalysis - the latest technology for the disposal of waste, including pesticides, the main provisions of which are: denial of Catalysis on the media, use of catalytically active particles in shallow dispersed condition; creation of aerosol moving particles in the zone of the reaction; recirculation of catalyst. The neutralisation of phosphorus content pesticide products takes place under the general scheme of the equation of reaction [8]:

$$RP+O_2+MeCO_3 \rightarrow CO_2+H_2O+Me_3(PO_4)_2$$

where R – the organic part of POC. Electrochemical oxidation of pesticides by electro catalytic destruction is realized in the electrolytes in the electrodes at low temperatures (20 ... 1000 ° C) and atmospheric pressure. The process of neutralization of phosphorus content pesticide products on the example of one of them by electro catalytic destruction takes place according to the equation of reaction [2]:

$$2(C_2H_5O)_2PO_2C_6H_4NO_2 + 23CaO + 26O_2 = 20CaCO_3 + 2CaHPO_4 + Ca(NO_3)_2 + 13H_2O.$$

The use of thermal method of PPP decontamination by natural gas is perspective. This method is known to be used for processing of phosphate fertilizers. It supports rather high temperatures, which guarantee the complete decomposition and combustion of organic components of pesticide chemicals and complete decontamination of inorganic components, controlled burning and pesticide resistance. The process is likely to generate the carbon dioxide, water, soot, and the presence of natural gas will contribute to the restoration of molecular phosphorus. If the PPP includes sulfur, then there will be observed the formation of sulfide phosphor R2S5 (R4S10). The overall scheme of process is represented by the following equations:

$$RP + CH_4 \xrightarrow{\sim 1000K} P_2 + CO_2 + H_2O;$$

$$RPS + CH_4 \xrightarrow{\sim 1000K} P_2S_5 + CO_2 + H_2O;$$

$$RP + C \xrightarrow{\sim 1000K} P_2 + CO_2 + H_2O;$$

$$RPS + C \xrightarrow{\sim 1000K} P_2S_5 + CO_2 + H_2O;$$

$$RPS + CH_4 \xrightarrow{\sim 1000K} P_2S_5 + CO + H_2;$$

$$RP + CH_4 + CaO \xrightarrow{\sim 1000K} Ca_3P_2 + CO_2 + H_2O;$$

$$RPS + CH_4 + CaO \xrightarrow{\sim 1000K} Ca_3P_2 + CaS + CO_2 + H_2O;$$

$$RP + CH_4 + CaCO_3 \xrightarrow{\sim 1000K} Ca_3(PO_4)_2 + CO_2 + H_2O.$$

If t> 1550 ° C, then the following processes are possible:

$$Ca_3P_2 + C \rightarrow CaC_2 + P_2 \ Etc.$$

If nitrogen is the part of pesticide, then the compounds of nitrogen will be formed (eg, oxides). Sulfide phosphorus and commercial phosphorus product have a wide range of use:

– In the manufacturing of explosives;

– In the manufacturing of matches and flammable mixtures;

– As additives to oils;

– In pyrotechnics. phosphorus is also used in the production of the dial plates, medicine (for diagnosis), in agriculture for production of fertilizers to increase yields of plants, in the manufacturing of semiconductors, etc. Therefore, this technology allows not only to neutralize the useless phosphorus content pesticides, but also to get valuable secondary products. The scheme of laboratory-scale plant for the study of the neutralization of the PPP by the natural gas, developed in accordance with the research conditions, presented in Fig. 1. Sample pesticide id loaded in the ceramic shuttle – 1, which is located in the center of the reactor – 2. The reactor is a quartz tube with a working length of 0.8 meters and inner diameter of 0.02 m. Heating of the reactor takes place in the tubular electric furnace – 3, where the temperature in which was measured using the thermocouples platinum – platinum radium based – 4. The thermocouple is installed in the porcelain cover in the center of the reactor on the level of the sample under research. Temperature regulation in the electric furnace is made by potentiometer – 5. During the preparation of the plant to the experiments it is necessary to follow the following sequence of operations. First, it is necessary to switch furnace heating. After achieving the set temperature, the pesticide samples placed in the reactor. Then it is necessary to check the plant as for the air-tightness. Then, in order to prevent the formation of the explosive mixtures, the system shall be thoroughly washed by oxygen which is purified from nitrogen, after which the natural gas has to be supplied. Methane is passed through flushing devices – 7, 8 with potassium hydroxide to absorb the acid gases and concentrated sulfate acid to absorb moisture. Then, in calcium chloride tube – 9, it finally dries out,

and enters the reaction zone. Bulk loss of gas is regulated by reometrom – 6. Upon the completion of the experiment, the electric furnace is switched off, the supply of methane discontinues and the system is once again washed with the purified nitrogen for the rapid braking of the reaction. The shuttle with the neutralized pesticide moves into the cold part of the reactor and is transfered to the desiccators for final cooling. The gaseous reaction products are supplied through the ball sinks – 11, preceded by a filter of glass wool – 10.

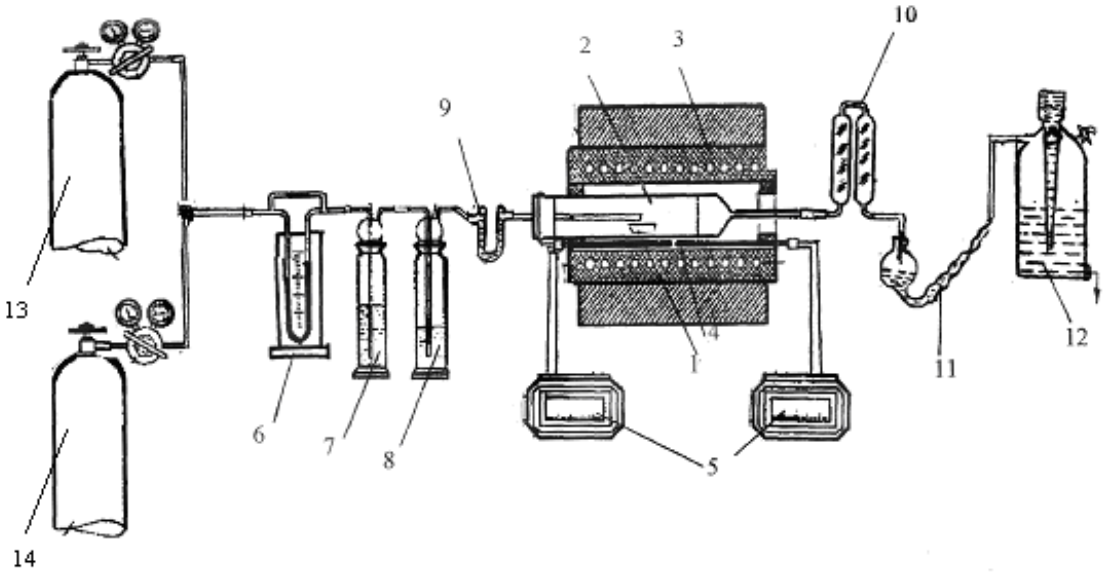

Fig. 1. A pilot plant for the removal of phosphorus pesticide products with natural gas: 1 –- shuttle, 2 – reactor, 3 – electric furnace, 4 – thermocouple, 5 – Potentiometers, 6 – rheometer; 7 – flushing devices with CON solution; 8 – flushing devices with solution N_2SO_4; 9 – calcium chloride tube, 10 – a filter of glass wool, 11 – absorber ball; 12 – gas meter; 13 – methane (CH_4), 14 – an inert gas (eg, N_2 or Ar).

The influence of factors on the kinetics of decomposition of phosphorus content pesticides chamicals

The neutralization of phosphorus content pesticide chemicals by natural gas is a heterogeneous process. The speed of the process depends on many factors. these are the temperature, the duration of the process, the losses of methane, granulometric content of PPP etc. To study the effects of temperature on the neutralization of phosphorus-PP by the natural gas, there was selected the temperature range 800–1100 ° C. In this interval the recovery takes place in a solid phase. The duration of the experiments was 60 minutes. Pilot studies were conducted in 50% of methane consumption and pesticide sample of 1g. The results of the researches are presented in Table 1 and graphically – in Fig. 2. The obtained data show that the neutralization of PPP at the temperature of 800 ° C takes place at high speed. With the temperature rising the process gets extremely intense, and at a temperature of 1000 ° C the degree of neutralization makes up 97,7%.

Table 1

Effect of temperature on the degree of neutralization of the PPP

Temperature, °C		800	850	900	950	1000	1050	1100
g, %	τ=30 min	94,12	95,09	95,47	95,82	96,13	94,96 meltback	94,10 meltback
	τ=60 min	95,24	96,07	96,80	97,39	97,70	94,96 meltback	94,10 meltback
	τ=90 min	95,59	96,60	97,02	97,41	97,75	94,96 meltback	94,96 meltback

In the temperature range 800-850 ° C the increase in the degree of neutralization makes up 0,83%, while in the temperature range 950-1000 ° C the increase - just 0.31%. Reducing the extent

of recovery with increasing temperature is related, probably, with the approach of the state of equilibrium, and so a slight increase in neutralization with increasing temperature at 50 ° C indicates the diffusion region of the process the neutralization of the PPP by natural gas. Rising temperatures above 1050 ° C does not lead to an increase in the degree of neutralization in connection with meltback and sintering of PPP. Meltback of PPP is stipulated by not only a relatively low temperature of melting, but, obviously, by the formation of eutectic mixtures. Consequently, the highest degree of neutralisation of PPP is achieved when T = 1000 ° C.

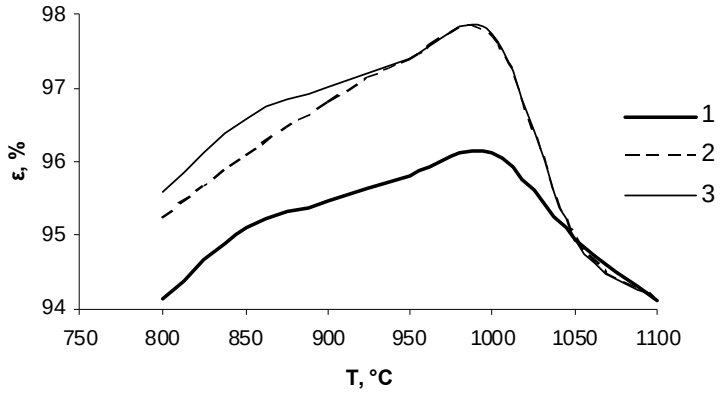

Fig. 2. The schedule of dependence of the degree of PPP neutralization on the temperature (1 - τ = 30 min, 2 - τ = 60 min, 3 - τ = 90 min)

One of the main factors determining the intensity of the neutralization process, is the duration for which the maximum output the final product is achieved. In order to study the influence of the duration of the process on the degree of neutralization of PPP by methane, there had been conducted a series of experiments. Change of the speed of the neutralization of PPP as for the duration of the process is presented in Table 2 and Fig. 3.

Table 2

Influence of the duration on the degree of PPP neutralization

Time, min		15	30	60	90	120
g, %	T=800°C	46,72	94,12	95,24	95,59	96,03
	T=850°C	53,10	95,09	96,07	96,60	96,63
	T=900°C	55,21	95,47	96,80	97,02	97,05
	T=950°C	56,38	95,82	97,39	97,41	97,45
	T=1000°C	57,08	96,13	97,71	97,75	97,78

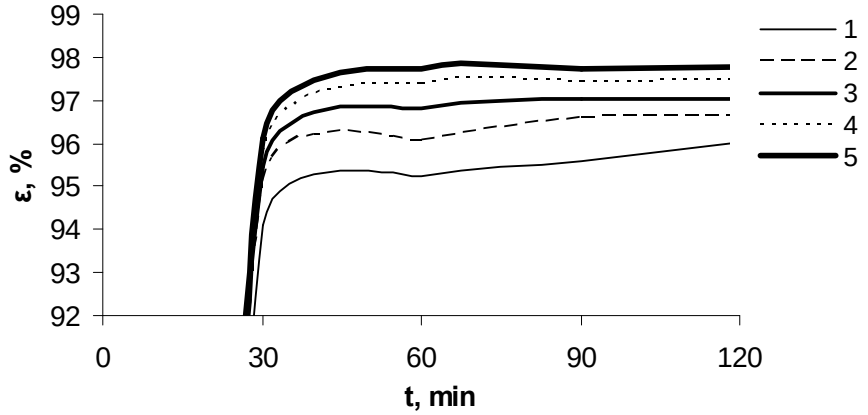

Fig. 3. The schedule of dependence of the degree of PPP neutralization on the duration of the process (1 – T = 800 ° C, 2 – T = 850 ° C, 3 – T = 900 ° C, 4 – T = 950 ° C, 5 – T = 1000 ° C)

The results of the experiments, given in Figure 5.2, show that the increase in the duration of the degree of PPP neutralization is increasing. When the temperature is 950 ° C and the duration of the process is 30, 60, 90 min., the degree of PPP neutralization is 95.82%, 97.39%, 97.41%. If we compare the degree of neutralization of PPP during 60 and 90 min., it is seen that it is growing by quite a small value of 0.02%. Therefore, it makes no sense to hold the neutralization of PPP in the furnace longer than 60 minutes. Because the increase in the degree of neutralization is small.

When studying the influence of temperature and duration of the process on the neutralization of PPP, it turned out that these factors are of great influence. The consumption of methane has also an influence on this process. The research was carried out with pesticide sample of 1 g. at a temperature of 950 ° C and the duration of 60 minutes. The results of the experimental data shown in Table 3 and graphically presented in Fig. 4.

Table 3

The dependence of the degree of PPP recovery on the methane consumption (T = 950 ° C, τ = 60 min, m = 1 g)

Consumption of methane sm3/min	1	2	3	4	5	6	7	8
ε, %	53,2	92,5	96,3	97,7	97,7	97,0	96,0	94,0

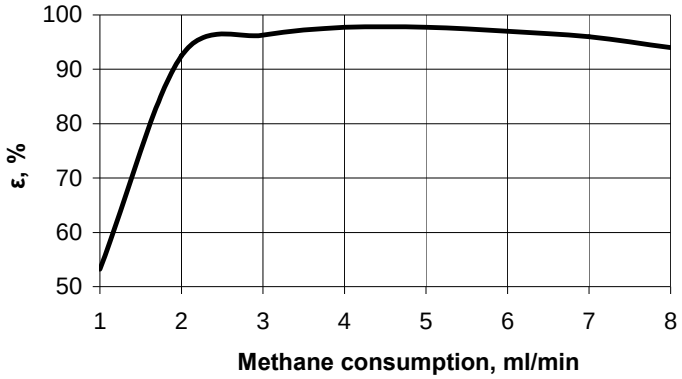

Fig. 4. The schedule of dependence of the degree of neutralization of the PPP on the methane consumption (T = 950 ° C, τ = 60 min, m = 1 g)

Analyzing the experimental data, we see that with an increase in methane consumption up to 4 sm^3/min, the degree of PPP neutralization is growing, but when the methane consumption is 4 sm^3/min, it is 97,7%, that is the most effective. During the increase of the methane consumption level of PPP neutralization remains unchanged for some time and then gradually decreases and with the consumption of 8 sm^3/min ε is 94%. A significant influence on the efficiency of the process is exerted by the degree of grinding of all the components of pesticides. Thus, during the experimental studies it became clear that when the temperature is 950 °C, during 60 minutes the degree of neutralization for phosphorus content pesticide chemicals with an average particle size of 0,25 mm was 97,39%, and for PPP with the particle size of 0,5 mm –- only 31,84%. When the temperature is 1000 °C, during 60 minutes the degree of neutralization increases by a small amount. Table 4 shows the results of researches of influence of grain size on the effectiveness of the PPP neutralization. The dependence of the degree of PPP neutralization on grain size pesticide is shown in Fig. 5.

Table 4

The dependence of the degree of PPP neutralization on grain size (τ = 60 min.)

Particle size, mm	1,0, and more	0,5	0,4	0,3	0,25 and less
ε, % T=950°C	24,51	31,84	48,63	79,20	97,39
ε, % T=1000°C	27,1	36,01	52,30	80,11	97,70

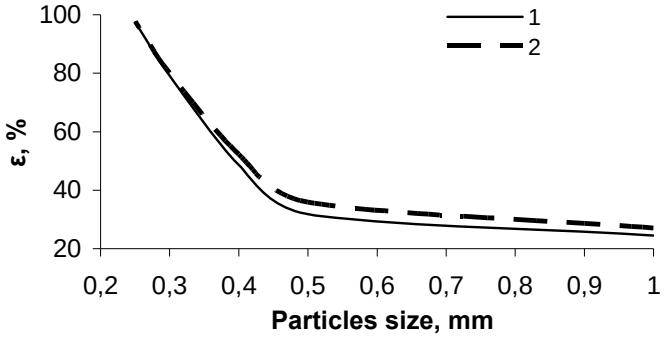

Fig. 5. Graph of dependable of degree of PPP neutralization on their grain size (T = 950 ° C, τ = 60 min, m = 1 g)

As it is seen from the results of the experimental researches, the increase in the size of grains results in the reduction of the reaction area of the contact components of pesticide products, and respectively, in the reduction of the intensity of massheatexchange, which in turn leads to the reduction of neutralization of PPP components as a whole.

Conclusions

1. There had been considered the main methods of phosphorus content pesticide chemicals, including thermal, biological methods, aerosol catalysis, electro catalytic destruction, thermal decomposition in the environment glass formation furnace. The most effective method for the neutralization of organ phosphorus compounds in terms of techno-economic factors is the method of thermal method of decomposition, in particular, restoration by natural gas.

2. In the results there had been improved the laboratory-scale plant for the thermal decomposition of phosphorus content pesticide chemicals in the conditions of natural gas (methane).

3. There had been researched the effect of temperature, the duration of the process, natural gas consumption and grain size of phosphorus content pesticide chemicals on the process of their neutralization.

4. Rising temperature increases the degree of PPP neutralization. The most optimal process temperature is 1000 °C. Exceeding this boundary, the degree of PPP neutralization and the output of recovery products (phosphorus sulfide or phosphorus) is slowing down.

5. During 30 minutes, there takes place more than 96% PPP neutralization, but with the further processing up to 60 minutes – no more than 97,7%, after further increasing the duration of the process becomes economically inefficient.

6. The best flow rate of methane consumption is 4 ml/min. In doing so, the extent of PPP neutralization goes up to 97,7%.

7. The more the PPP components are reduce to fragments, the more intense is the process of neutralization, that is, the degree of neutralization increases.

8. There had been substantiated that the use of thermal method of neutralization of phosphorus content pesticide chemicals by natural gas allowed to obtain valuable secondary products, for example, to restore phosphorus, which is widely used in various industries: agriculture, industry, military, medicine, etc.

9. The results of the conducted researches allow to recommended the developed and improved methodic for neutralization of phosphorus content pesticide chemicals, accumulated in the Vinnytsia region, which significantly reduces the technological and anthropological pressures on the environment and humans.

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