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KINETIC REGULARITIES OF TRICALCIUM PHOSPHATE DECOMPOSITION BY CARBON TETRACHLORIDE

The paper investigates the impact of kinetic parameters of phosphorus oxychloride (V) distillation during $\text{Ca}_3(\text{PO}_4)_2$ interaction with CCl_4 . In the temperature mode of 350 – 550 °C a practically complete phosphorus oxychloride distillation has been achieved. It is shown that the phosphorus distillation process conversion into the mode of deoxidizing exchange with CCl_4 makes it possible to avoid application of energy-intensive phosphorus reduction process, to reduce the temperature and energy consumption of chemical transformations.

Keywords: phosphate raw materials, carbon tetrachloride, processing, chlorination, phosphorus distillation.

Introduction and problem statement

Absence of phosphorus production in Ukraine makes our country dependent on the import of insecticides, fungicides, sulfides, phosphorus chlorides and phosphorus derivatives. A potential source of providing Ukraine with phosphate raw materials are its own deposits of phosphorites and apatites, the explored reserves of which contain about 3.9 billion tons of P_2O_5 (reserves of phosphorite raw materials are discovered in the territory of 13 regions). Prognostic resources of phosphate deposits in Ukraine, expedient to be developed, are 516 million tons of P_2O_5 . Development of these deposits will make it possible to apply the required amount of phosphorus fertilizers for many decades – more than 2.4 million tons annually in terms of P_2O_5 [1 – 4]. However, domestic phosphate ores are characterized by a low content of P_2O_5 (4 – 10%) and the presence of significant amounts of carbonates, silicate, clay, and other impurities. Such ores are considered to be off-balance. The presence of rock-forming minerals in the domestic ores complicates the extraction and electrothermal processing of raw materials, worsens technical and economic indicators, leads to the formation of by-products and environmental pollution. At the same time, enrichment of phosphate raw materials can increase the content of P_2O_5 in apatite concentrates to 37 – 39.8% and in phosphorites – to 19.8 – 22.2%. Enrichment operations improve the quality of technological raw materials, but do not solve the problem of processing domestic phosphate ores, especially of carbonate-containing ores. The use of enriched phosphorites, e.g. of Nezviskoye and other deposits, in the technology of producing single or double superphosphate will increase sulfuric acid consumption 1.3 – 1.5 times due to the presence of significant amount of calcium carbonate. High content of calcium and magnesium carbonates, oxides of iron, silicon and aluminum predetermines increased expenses for scarce reagents and materials, leads to obtaining products with low content of P_2O_5 , their unsatisfactory properties and poor quality. Analysis of literature allows to come to a conclusion that the majority of open phosphate deposits in Ukraine are referred to off-balance ones and cannot be processed using electrothermal and, especially, acid methods. The above causes the necessity of finding a fundamentally new approach to processing phosphate ores in Ukraine. Therefore, new (non-acid) methods of thermal processing of phosphate raw materials are of considerable interest: they have a number of significant advantages, which make it possible to expand the raw material base of the phosphorous industry, to use phosphate raw materials with virtually any chemical-mineralogical composition (including carbonate-containing ores), to receive multicomponent mineral fertilizers [5, 6].

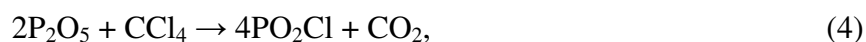
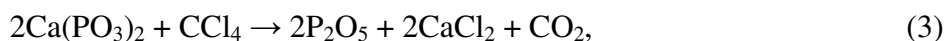
The research aim is to determine kinetic regularities of tricalcium phosphate decomposition with carbon tetrachloride.

Main material presentation

As the previous research has shown, phosphorus distillation from phosphate raw materials with carbon tetrachloride is possible in the temperature range of 300 – 700 ° C. At lower temperatures, this process is not expedient due to the possible condensation of the reagents and other substances, formed in the solid-phase products.

Carbon chlorides are stable up to the temperature of 600 ÷ 700 ° C. At higher temperatures, carbon chlorides decompose with liberation of chlorine and compounds with intermediate degrees of carbon oxidation. Such a process will be reduced from exchange to oxidation-reduction process. In the presence of carbon compounds of lower degrees, the latter must be oxidized by phosphate to the oxidation degrees of (+2) or (+4). This process will proceed hard enough, and a considerable amount of energy must be spent on such oxidation. The distillation of the reduced phosphorus through the layer of solid-phase products is complicated by the possible interaction of phosphorus with basic oxides. The flow of such a process is limited by internal diffusion processes. In the temperature range of 300 ÷ 700 ° C the carbonyl chlorides are in the gaseous state, which makes it possible to transform the process of phosphorus distillation from the phosphate raw material from the redox to exchange process and to obtain phosphorus compounds in the oxidation state (+5).

The mechanism of chlorinating action of CCl₄ relative to tricalcium phosphate is complex. The investigated summary flow diagrams of the processes can not be used for final evaluation. During chlorination of salt systems with carbon chlorides, chlorides of alkali and alkaline-earth metals are primarily formed, which is confirmed by studies of successive phosphorus distillation from calcium orthophosphate. The mechanism of this transformation can be described by the following equations:



All the above overall reactions are possible and occur with high exoeffect. In addition to the presented schemes of reactions with possible tricalcium phosphate transformations, reactions with formation of various polyphosphates can also occur. This mechanism takes into account only transformations with the distillation of phosphorus from Ca₃(PO₄)₂. No less complicated transformations will occur during tricalcium phosphate chlorination with carbon tetrachloride. Not all possible transformations, associated with these schemes, were considered. Ca₃(PO₄)₂ chlorination with tetrachloromethane can occur with the formation of chlorine and carbon derivatives as well as of atomic chlorine and various types of radicals. The process can be reduced to that of a chain type.

During heat treatment of Nezvyskyi phosphorite, carbon (IV) oxide is liberated and the ratio between the oxides of the basic and acidic nature changes significantly (Table 1).

Table 1

Mole ratio of oxides of acidic and basic nature in Nezvyskyi phosphorite

Composition	Content of the components, %	Mole content in 100g of phosphorite	Molar proportion of oxides, %
P ₂ O ₅	24.5	0.1725	14,9
CaO	44.5	0.7946	68.6
SiO ₂	9.3	0.155	13.4
Al ₂ O ₃	0.89	0.0087	0.7
Fe ₂ O ₃	1.0	0.0063	0.5
Na ₂ O	1.36	0.0219	1.9
Bcero	81.55	1.1590	100

As can be seen from the calculation of mole ratio of acid and basic oxides, in the Nezvyskyi phosphorite the equivalent fractions of acid oxides constitute 0.316 equivalents and of the basic oxides – 0.684 equivalents, which is 0.368 g equivalents more than of the acid oxides. An increase in the content of basic oxides will also require an increase in the consumption of carbon tetrachloride during their decomposition. Therefore, to reduce the consumption of carbon tetrachloride, roasted Nezvyskyi phosphorite was pretreated with hydrochloric acid (in an appropriate ratio). During such treatment free basic oxides were bound to chloride salts. The phosphorite, treated with hydrochloric acid, was subjected to repeated roasting at 600 °C for 2 hours to eliminate moisture. The influence of the temperature and the process duration on the degree of phosphorus distillation from Nezvyskyi phosphorite, using carbon tetrachloride, has been investigated. The results of such experiments are presented below.

For the studies we used a sample of roasted phosphorite with a mass of 4 g. For complete distillation of phosphorus, 4.621 g of CCl₄ or $V_{\text{CCl}_4} = 2.912$ ml. must be passed through the reaction zone to such a sample (taking into account that the oxides of the basic and amphoteric character are already bound to chloride salts). This volume of CCl₄ is sufficient for complete decomposition of Ca₃(PO₄)₂ and of the available calcium silicate with obtaining calcium chloride and silicium (IV) oxide.

P₂O₅ content in the initial charge and reduced residues was determined by a titrimetric method [7] as well as by the colorimetric method according to standard procedures [8]. The chloride ion content in aliquot solutions was determined by an argentometric method using the standard procedure [9]. To find the content of chlorine in the solid residue, the sample of the product ~ 0.1 g was placed in a conical flask, dissolved with distilled water and then the operations were carried out in the same order as for chlorine determination.

Studies were conducted in the temperature range of 350 ÷ 550°C. At lower temperature increased condensation of the products was observed. The research results have shown (Fig. 1) that with temperature growth from 350 to 400°C a slight increase of phosphorus distillation degree is observed. Starting from 400°C, however, the phosphorus distillation degree remains practically constant as temperature increases. At the temperature of 450°C almost complete phosphorite conversion is achieved within 60 minutes.

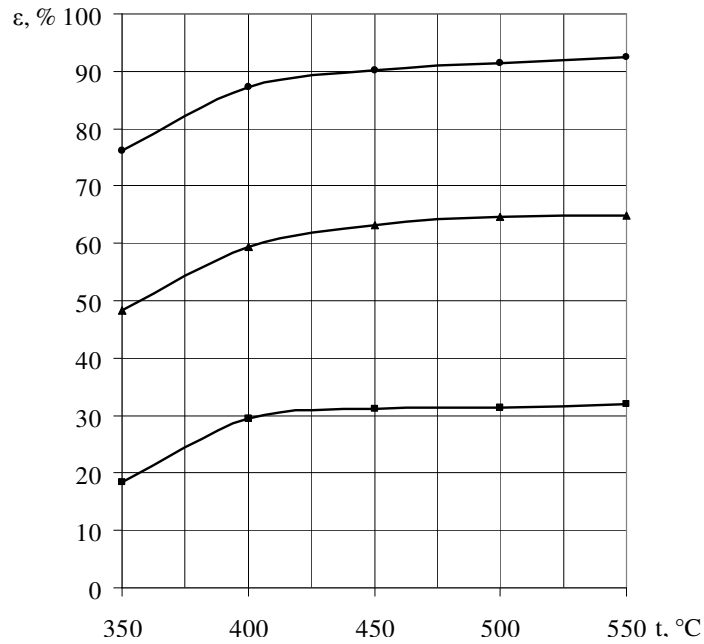


Fig. 1. Influence of the temperature on the degree of phosphorus distillation with tetrachloromethane from Nezvyskyi phosphorite ($\text{CCl}_{4,2}$ consumption – 9 ml, phosphorite sample – 4 g): ■ – 20 min., 40 min, ● - 60 min.

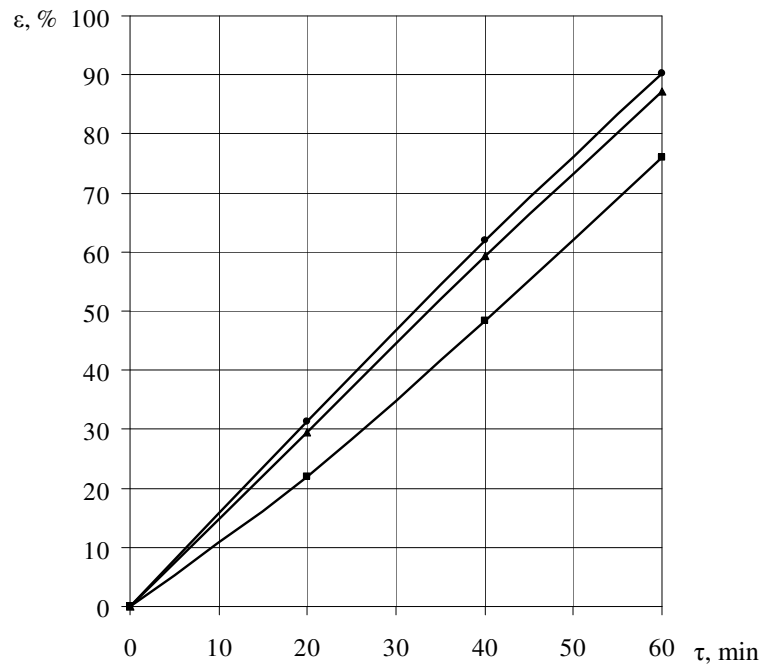


Fig. 2. The process duration influence on the degree of phosphorus distillation from Nezvi phosphorite with tetrachloromethane at different temperatures (°C): ■ – 350, – 400, ● - 450.

As it is evident from Fig. 2, the time dependencies of phosphorus distillation from $\text{Ca}_3(\text{PO}_4)_2$ at temperatures 350, 400 and 450°C are of identical character and the process rate is constant over time. At the temperatures of 350 and 450°C a practically complete conversion of Nezvyskyi phosphorite was achieved. Difference in the reduction degrees, achieved within 60 minutes, is determined by the difference in the condensation of products at the cold end of the reactor, which is the largest at 350° and is within $8 \div 9\%$ of that absorbed in the absorbers.

Conclusions

Based on the studies of phosphorus distillation from tricalcium phosphate with carbon tetrachloride, the following conclusions can be made:

1. The chlorinating ability of carbon tetrachloride is possible in the gas phase. Carbon tetrachloride is lyophobic with respect to a number of substances – polar substances (for example water) and substances with an ionic type of bond – up to the boiling point, which leads to reactive inertness of CCl_4 .
2. With the transfer of carbon tetrachloride to the gaseous state, its chlorinating ability increases with a high energy gain, i.e. with a significant exoeffect.
3. Interaction of CCl_4 with $\text{Ca}_3(\text{PO}_4)_2$ is extremely effective in the gaseous state to the temperatures of $350 \div 500$ °C. As the temperature rises, the chlorinating activity decreases as a result of dissipation of the molecules, and the exchange process passes into the oxidation-reduction mode.
4. The process of phosphorus distillation from tricalciumphosphate is described by a first-order equation. This is confirmed by a linear character of the phosphorus distillation degree dependence on the process duration. This linear dependence is observed in the temperature range of $350 \div 550$ °C under study. The process is limited by carbon tetrachloride delivery (diffusion) to $\text{Ca}_3(\text{PO}_4)_2$, i.e. the process proceeds in the diffusion region.
5. Chlorinating ability of carbon tetrachloride is also dependent on the nature of chlorinating reagents. Salts are chlorinized first and then oxides with amphoteric and acidic properties. This is confirmed by interaction of aluminosilicates with CCl_4 after $\text{Ca}_3(\text{PO}_4)_2$ chlorination.

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