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About development of a new method of processing of low-quality phosphate raw materials

Kazakhstan has huge reserves of phosphate raw materials. Nowadays high-grade phosphates are almost exhausted, and the ore is mainly represented by run-of-mine and low-grade phosphorites with small phosphorus content. Processing of low-grade phosphate raw materials by traditional methods is hindered. Formed large amounts of solid waste at phosphorus production require searching methods of their recycling or utilization. It also makes an urgent the search for new alternative ways of processing low-quality phosphate raw materials. Obtaining phosphorus oxyfluoride from low-grade phosphorites with its further processing into elemental phosphorus is one of ways of processing such phosphate raw materials, which allows to simplify the process and improve phosphates quality. According to the task, the process of calcium phosphates interaction with ammonium fluoride was investigated; thermodynamic analysis of possible reactions was carried out, which confirmed primary formation of monoammonium phosphate with the following its conversion into phosphorus oxyfluoride. The results of mass spectrometric analysis of samples of dicalcium phosphate and tricalcium phosphate in a mixture with ammonium fluoride confirmed the proposed mechanism of interaction. Based on the results obtained, possibility is shown and optimal parameters for processing low-grade phosphate raw materials into phosphorus were determined.

Keywords: low-grade phosphorites, phosphate raw material processing, phosphorus oxyfluoride, ammonium fluoride, thermodynamic analysis, isobar-isothermal potential.

Introduction

Phosphate raw material base of Kazakhstan is presented by a number of phosphorite deposits. It was primarily proposed to process large fractions of high-grade phosphate raw materials into yellow phosphorus and to direct small fractions for enrichment and further processing by acidic methods. Electrothermal (dry-process) method of phosphorite processing is characterized by physical-chemical process complexity due to phosphate raw material composition, i.e. its quality. High-grade phosphorites are mainly used for phosphorus production. The use of low-grade raw materials results in formation of a large amount of sludge, decrease of phosphorus quality and increasing energy expenses, what causes increasing the production cost. Presently there are large actual reserves of low-grade phosphate raw materials in Kazakhstan. This raw material processing by traditional technological methods is hindered. It is related to the complex mineralogical composition of these phosphorites, which requires the detailed study of initial ore chemical and mineralogical composition, deep investigations of raw material thermal preparation and its processing into a target product. That actualizes a search of new alternative methods of low-grade phosphate raw material processing [1]. Phosphorus oxyfluoride obtaining from low-grade phosphate raw materials with following processing into elemental phosphorus is one of ways of low-grade phosphate raw material processing, allowing to simplify a process and to improve phosphates quality compared to ones produced by dry- and wet-processes. Phosphorus oxyfluoride is colorless gaseous substance with condensation temperature 37 ºC, it is hydrolyzed in the moist air or in water [2]. The obtained gas can be processed into phosphates by hydrolysis, and hydrogen fluoride formed as a result of hydrolysis can be used for phosphorus oxyfluoride production. Results of research of phosphorus oxyfluoride production are presented in this work.

Materials and methods

Dicalcium phosphate, tricalcium phosphate and ammonium fluoride of «chemically pure» grade were used to carry out mass spectrometric analyses, and Karatau low-grade phosphorites for laboratory experiments. A basic procedure of suggested investigation is free associative instrumental method of an experiment which is one of most available and valid procedures. Based on theoretical and applied investigations certain scientifically grounded physical-chemical and technological bases of low-grade phosphate raw material processing can be developed.

An analysis of initial and additional raw materials, target products and materials was performed using up-to-datechemical and physical-chemical research methods. Gas-vapour phase composition when sample thermal processing was studied using mass-spectrometer MCX-3A adjusted to high-temperature investigation performance. The comparative analysis was carried out by means of mathematical treatment of experiment results.

Results and Discussion

In order to define perspectives of new technology development and determine the process thermodynamic probability, the thermodynamic analysis using Temkin-Shwartsman method has been performed for some possible reactions when phosphate raw materials processing by a fluoride treatment [3]. Changes of isobar-isothermal potential in the temperature interval 50–2000 K were calculated for reactions of fluor apatite interaction with ammonium, aluminum, iron, sodium, potassium and hydrogen fluorides forming phosphorus oxyfluoride:

$$Ca_{10}F_2(PO_4)_6 + 36NH_4F = 10CaF_2 + 6POF_3 + 36NH_3 + 18H_2O \quad (1)$$

$$Ca_{10}F_2(PO_4)_6 + 18NH_4HF_2 = 10CaF_2 + 6POF_3 + 18NH_3 + 18H_2O \quad (2)$$

$$Ca_{10}F_2(PO_4)_6 + 12AlF_3 = 10CaF_2 + 6POF_3 + 6Al_2O_3 \quad (3)$$

$$Ca_{10}F_2(PO_4)_6 + 12FeF_3 = 10CaF_2 + 6POF_3 + 6Fe_2O_3 \quad (4)$$

$$Ca_{10}F_2(PO_4)_6 + 36NaF = 10CaF_2 + 6POF_3 + 18Na_2O \quad (5)$$

$$Ca_{10}F_2(PO_4)_6 + 36KF = 10CaF_2 + 6POF_3 + 18K_2O \quad (6)$$

$$Ca_{10}F_2(PO_4)_6 + 36HF = 10CaF_2 + 6POF_3 + 18H_2O \quad (7)$$

An analysis of performed calculations has shown that (1) and (2) reactions are more probable ones. ΔG_T^0 has positive value for these reactions at temperature 273 K. When temperature increases, ΔG_T^0 decreases and becomes equal to zero at temperatures 532 and 647 K correspondingly, i.e. these reactions become thermodynamically probable at temperatures 532 K and 647 K correspondingly. Reactions of fluor apatite interaction with aluminum, iron, sodium and potassium fluorides become thermodynamically probable at temperatures higher than 2000 K. Therefore these reactions are practically impossible. For reactions of flour apatite interaction with hydrogen fluoride ΔG_T^0 has negative value at temperatures lower than 257 K. Therefore the chemical reaction at temperatures above 257 K is thermodynamically impossible. From calculation data it is concluded that ammonium fluorides are most effective reagents for fluoride treatment of phosphate raw materials.

Then the possibility of calcium phosphate interaction with ammonium fluoride was investigated according to reactions:

$$Ca_3(PO_4)_2 + 6NH_4F = 3CaF_2 + 2NH_4H_2PO_4 + 4NH_3 \quad (8)$$

$$CaHPO_4 + 2NH_4F = CaF_2 + NH_4H_2PO_4 + NH_3 \quad (9)$$

$$Ca_3(PO_4)_2 + 12NH_4F = 3CaF_2 + 2POF_3 + NH_3 + H_2O \quad (10)$$

$$CaHPO_4 + 5NH_4F = CaF_2 + POF_3 + 5NH_3 + 3H_2O \quad (11)$$

Thermodynamic analysis of these reactions were also conducted by Temkin-Shwartsman method. Results of thermodynamic calculations have shown that reactions (8) and (9) are more thermodynamically probable ones. For these reactions ΔG_T^0 values become negative at temperatures 246 K and 155 K correspondingly whereas reactions (10) and (11) become thermodynamically probable at temperatures 515 K and 533 K correspondingly. Monoammonium phosphate formed in the course of (8) and (9) reactions can also interact with ammonium fluoride according to the reaction (12):

$$2NH_4H_2PO_4 + 6NH_4F = 2POF_3 + 8NH_3 + 6H_2O \quad (12)$$

Thermodynamic calculations have shown that reaction (12) becomes thermodynamically probable one at the temperature above 581 K (see Fig.).

Based on performed thermodynamic analysis of possible reactions of calcium phosphates interaction with ammonium fluoride, one can suppose that most probable interaction mechanism is primary monoammonium phosphate formation according to reaction equations (8) and (9) with subsequent phosphorus oxyfluoride formation according to the reaction equation (12).

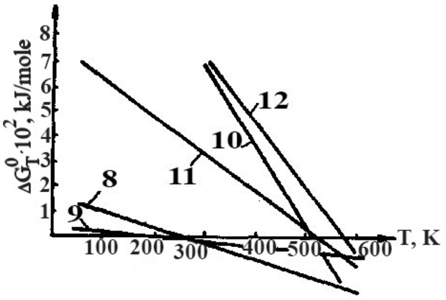

Figure. Dependence of isobar-isothermal potential on the process temperaturefor reactions 8–12

In order to confirm a conception about mechanism of calcium phosphates interaction with ammonium fluoride, the mass spectrometric analysis was performed for samples #1 (dicalcium phosphate mixed with excess of ammonium fluoride) and #2 (tricalcium phosphate mixed with excess of ammonium fluoride). The temperature interval of investigations is 0÷1350 ºC. Mass spectra registration in experimental conditions was carried out at step temperature rise with several soakings. A temperature mode was maintained with a block BPT-2.

Sample #1 studying has shown that ion currents with m/e = 16, 17, 19 and 20 match to NH_2^+, NH_3^+, F^+ and HF^+ ions are registered without furnace block heating up. In experimental conditions appearingly there was sufficient heat radiation of ion source cathode of the mass-spectrometer for ammonium fluoride sublimation. The reactor heating up at electric resistance furnace turn-on results in increasing ion current intensity. Therefore ion currents with m/e = 104, 85 and 69 interpreted as POF_3^+, POF_2^+ and PF_2^+ appear in the mass-spectra at temperature above 360 ºC. When temperature increasing up to 550 ºC ion currents with m/e= 66, 50 and 47 are registered in the mass-spectra. The noted ions are identified as POF^+, PF^+ и PO^+.

It is established that in experimental conditions the peak intensities and ratios between noted ions are changed depending on temperature and time and attain maximal intensity in temperature interval 650–750 ºC. It has been discovered that, when ion currents POF_3^+, POF_2^+, POF^+, PF_2^+, PF^+ and PO^+ registering in the mass spectra, on one side, the intensity of ion currents HF^+ and F^+ essentially falls, but on the other side, the intensity of background ions with m/e = 17 and 18 (ions OH^- and H_2O^+) insignificantly increases. Thais confirms reactions (10) or (11) proceeding.

Mass-spectrometer investigation of #2 sample has shown that the qualitative composition of vapour-gas phase corresponds generally to #1 sample. Significant difference is observed in intensity and temperature intervals of registration of ion currents related to phosphorus oxyfluoride formation in vapour-gas phase. So, for #2 sample ions fixation in the mass spectra starts at temperature for 200 ºC above and these peaks intensities are of lower order compared to #1 sample. Maximal intensity of ion currents POF_3^+, POF_2^+ and PF_2^+ in #2 sample mass spectra is registered in the temperature interval 1000÷1150 ºC. However, it is evident that the fall of intensity of ion currents with m/e = 19 and 20 (F^+ and HF^+) for #2 sample is insignificant.

The mechanism of calcium phosphates interaction with ammonium fluoride stated on a basis of thermodynamic analysis of reactions (8)–(12) is confirmed by primary increasing the intensity of ion currents matched to NH_3^+ and NH_2^+ ions at constant background currents OH^- and H_2O^+ and at comparatively low temperatures, which proves the predominant course of the reaction (8) and (9). Increasing the intensity of ion currents matched to phosphorus oxyfluoride and it's fractions at temperature higher the 650 ºC speaks for primary proceeding the reaction (12).

Performed investigations allow to make a conclusion that calcium phosphates interaction with ammonium fluoride proceeds according to total reactions (10) and (11) through two stages forming ammonium phosphate according to reactions (8) and (9) at the first stage. At the second stage at higher temperatures further formed phosphate interaction with ammonium fluoride takes place forming phosphorus oxyfluoride according to the reaction (12).

We studied kinetics and the mechanism of calcium phosphates interaction with ammonium fluoride. Conducted experimental research has shown that phosphorus sublimation degree in the form of phosphorus oxyfluoride can attain 98 %.

To determine the probability of phosphorus oxyfluoride processing into phosphorus we performed the thermodynamic analysis of following reactions of elementary phosphorus formation from phosphorus oxyfluoride:

$$4POF_3 + 5C + 6H_2O = P_4 + 5CO_2 + 12HF \quad (13)$$

$$4POF_3 + 10C + 6H_2O = P_4 + 10CO + 12HF \quad (14)$$

$$4POF_3 + 10CO + 6H_2O = P_4 + 10CO_2 + 12HF \quad (15)$$

$$4POF_3 + 4NH_3 = P_4 + 4NO + 12HF \quad (16)$$

$$28POF_3 + 20NH_3 + 12H_2O = 7P_4 + 20NO_2 + 84HF \quad (17)$$

$$12POF_3 + 20NH_3 = 3P_4 + 10N_2 + 36HF + 12H_2O \quad (18)$$

Results of thermodynamic calculations have shown that reactions (14) and (18) are more thermodynamically probable ones. These reactions can take place at temperatures 817 ºC and 637 ºC correspondingly.

Thus the offered method of low-grade phosphate raw materials processing consists of thermal treatment of phosphate raw materials mixed with inorganic reagents with following processing the sublimate into elemental phosphorus. To decrease thermal treatment temperature and to improveproduct quality the phosphate raw materials is treated with ammonium fluoride excess amount, namely 110–200 % of stoichiometric norm for reactions (1) and (2). At more than 200 % excess of ammonium fluoride the sublimate amount rises sharply. In turn it hinds gases transporting and purification. At less than 110 % norm of ammonium fluoride the sublimation rate of ammonium fluoride is higher than the rate of phosphorus oxyfluoride formation. In addition to that at this norm the phosphorus oxyfluoride output falls sharply.

Thermal treatment is proposed to carry out at the temperature 300–600 ºC because temperature increasing above 600 ºC insignificantly effects on phosphorus oxyfluoride output. Obtained sublimates are purified from solid impurities and then they are cooled to 100–200 ºC and. Thereat phosphorus vapours are condensed, and liquefied phosphorus is formed. At the temperature above 200 ºC ammonium fluoride is sublimated.

Then purified gases is suggested to be heated up to 640–1000 ºC and then to cool them to 300–250 ºC for production phosphorus condensation. When heating lower 640 ºC phosphorus reduction rate decreases acutely, and at the temperature above 1000 ºC energy expenses increase. Concerning cooling mode at the temperature above 400 ºC gaseous phosphorus condensation doesn't practically take place. Ammonium fluoride is precipitated at the temperature lower 250 ºC, what can result in production phosphorus pollution.

After phosphorus separation the ammonia is added to the rest gas in the stoichiometric amount for the reaction of ammonium fluoride formation. Gases are cooled to 100–180 ºC and ammonium fluoride is separated. It is recycled to the process top. The rest gases are discharged into the atmosphere after sanitary purification.

Conclusion

The possibility of low-grade phosphate raw materials processing into elemental phosphorus is proved on the basis of results of thermodynamic calculations, mass-spectrometer and laboratory investigations. Optimal parameters of the process were determined and the technological scheme of offered technology was developed.

The offered technology of low-grade phosphate raw materials processing gives an opportunity to solve both ecological and economical problems. On one side, the developed technology allows to process low-grade raw materials and to eliminate sludge formation, and from the other side, it results in essential energy consumption decreasing.

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Төмен сапалы фосфат шикізатын өңдеудің жаңа әдісін әзірлеу туралы

Қазақстан фосфат шикізатының үлкен қорына ие. Қазіргі уақытта бай фосфориттер іс жүзінде таусылған және кен негізінен құрамында фосфор аз қатардағы және төмен сортты фосфориттермен ұсынылған. Төмен сапалы фосфат шикізатын дәстүрлі әдістермен өңдеу қиын. Фосфор өндірісі нәтижесінде пайда болатын қатты қалдықтардың мөлшері оларды өңдеу, пайдаға жарату туралы зерттеуді қажет етеді. Бұл сондай-ақ төмен сапалы фосфат шикізатын қайта өңдеудің жаңа дәстүрлі емес әдістерін іздестіруді өзекті етеді. Процесті жеңілдетуге және фосфаттардың сапасын жақсартуға мүмкіндік беретін төмен сапалы фосфат шикізатын өңдеу жолдарының бірі одан фосфордың оксифторидін алу болып табылады, одан әрі оны қарапайым фосфорға қайта өңдеу болып табылады. Қойылған міндетке сәйкес кальций фосфатының аммоний фторидімен өзара әрекеттесу процесі зерттелді; моноаммонийфосфаттың түзілуінің басымдығын растап, оны кейіннен фосфордың оксифторидіне айналдыра отырып, ықтимал реакцияларға термодинамикалық талдау жүргізілді. Аммоний фторидімен қоспадағы дикальцийфосфат және трикальцийфосфат үлгілерінің масс-спектрометриялық талдауының нәтижелері өзара әрекеттесудің болжамды механизмін растады. Алынған нәтижелердің негізінде төмен сапалы фосфатты шикізатты фосфорға өңдеудің мүмкіндігі және оңтайлы параметрлері анықталды.

Кілт сөздер: төменсұрыпты фосфориттер, фосфатты шикізаттарды өңдеу, фосфор оксифториді, аммоний фториді, термодинамикалық талдау, изобара-изотермиялық потенциал.

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О разработке нового метода переработки низкокачественного фосфатного сырья

Казахстан обладает огромными запасами фосфатного сырья. В настоящее время богатые фосфориты практически исчерпаны, и руда представлена главным образом рядовыми и низкосортными фосфоритами с низким содержанием фосфора. Переработка низкокачественного фосфатного сырья традиционными методами затруднена. Образующиеся объемы твердых отходов производства фосфора требуют проведения исследований по их переработке или утилизации. Это делает также актуальным поиск новых нетрадиционных способов переработки низкокачественного фосфатного сырья. Одним из путей переработки низкокачественного фосфатного сырья, позволяющим упростить процесс и улучшить качество фосфатов, является получение из него оксифторида фосфора с дальнейшей переработкой его на элементарный фосфор. В соответствии с поставленной задачей исследован процесс взаимодействия фосфатов кальция с фторидом аммония; проведен термодинамический анализ возможных реакций, который подтвердил преимущественное образование моноаммонийфосфата с последующим превращением его в оксифторид фосфора. Результаты масс-спектрометрического анализа образцов дикальцийфосфата и трикальцийфосфата в смеси с фторидом аммония подтвердили предполагаемый механизм взаимодействия. На основании полученных результатов показана возможность и определены оптимальные параметры переработки низкокачественного фосфатного сырья в фосфор.

Ключевые слова: низкосортные фосфориты, переработка фосфатного сырья, оксифторид фосфора, фторид аммония, термодинамический анализ, изобарно-изотермический потенциал.

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