ABSTRACT

of the dissertation on the topic:

"Complex processing of phosphorites with extraction of phosphorus and production of ferrosillicon and calcium carbide", submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D07160 – "Chemical technology of inorganic substances"

UTEYEVA RAISA AKYLBEKKYZY

The relevance of the problem. An analysis of the state of the problem shows that the total global reserves of phosphate raw materials amount to 84.5 billion tons, of which 82.7 billion tons are phosphorites. Kazakhstan ranks sixth in the world in terms of explored reserves of phosphorites. The total reserves of phosphorites in Kazakhstan, taking into account the forecast, amount to 8 billion tons, including 3 billion tons in the Karatau basin and 5 billion tons in the Aktobe basin. The content of P_2O_5 in phosphorus-containing ores of the Karatau basin is 15-30% (balanced phosphate ores) up to 0.5-1.0% phosphatized silicon. Moreover, balance ores account for only 60% of reserves. The phosphorites of the Aktobe deposit contain from 5.25 to 14% P_2O_5 and are characterized by a high content of SiO_2 - 52-55%, therefore they are not widely used for the production of phosphorus. They can become a resource for phosphorus electrothermy if a new technology is created for their processing with a high degree of integrated use of raw materials.

Kazphosphate LLP, based on Karatau phosphorites produces 60,000 to 80,000 tons of yellow phosphorus annually using the electrothermal method. Despite the high recovery rate of phosphorus into marketable products, which is approximately 90%, the electrothermal method of phosphorite processing generates waste in the form of slag. The amount of phosphorus slag produced during the processing of phosphorites is 9-10 tons per ton of phosphorus obtained. As a result, the degree of comprehensive use of raw materials does not exceed 50%, and phosphorus slag not only occupies significant land areas but also contributes to the deterioration of the environmental situation in the region. Its use in the construction industry is limited due to the presence of phosphorus and fluorine compounds.

In this regard, in order to increase the efficiency of phosphorite processing, it is relevant and timely to create new slag-free technologies that allow not only the extraction of phosphorus, but also the production of high-quality products from the non-metallic component during the electric smelting of phosphorites.

The purpose of the work.

The purpose of the dissertation work is to create a new slag-free technology for the complex electrothermal processing of phosphorites with an extremely high degree of complex use of raw materials, while simultaneously producing calcium carbide, silicon-containing ferroalloy, and extracting phosphorus into the gas phase in an electric furnace.

Research objectives:

- thermodynamic modeling of the interaction of tricalcium phosphate, Chulaktau and Chilisai phosphates with carbon and iron in the temperature range from 500 to

2100°C and pressure from 0.01 to 1 bar, with determination of the degree of distribution of elements in phosphorus, calcium carbide, silicons;

- establishing optimal conditions for producing calcium carbide, extracting phosphorus into the gas phase, and producing ferrosilicon;

- to establish optimal technological parameters (the ratio of coke and steel shavings) for the electric smelting of Chulaktau and Chilisai phosphorites, with simultaneous extraction of phosphorus into the gas phase to produce calcium carbide and ferrosilicon;

- Large-scale laboratory tests of electric smelting of Chulaktau and Chilisay phosphorites with phosphorus extraction, production of calcium carbide and silicon-containing ferroalloy, with an assessment of the technical and economic feasibility of the developed technology.

Research objects. Phosphorites from the Chulaktau and Chilisay deposits in the Karatau and Aktobe basins, calcium carbide, ferrosilicon

Research Methods

The following methods were used to accomplish the tasks set: computer thermodynamic modelling using the HSC-6.0 software package (Outokumpu, Finland), based on the principle of Gibbs energy minimisation; electric smelting in arc furnaces; experiment planning using a second-order rotatable plan (Box-Hunter plan); mathematical modelling of target product formation; construction of 3D and flat images, with optimisation based on them of the conditions for the simultaneous formation of calcium carbide, high-grade ferrosilicon and phosphorus extraction into the gas phase.

The main experimental data were obtained using modern methods of physicochemical analysis: a JSM-6490LV series multi-purpose scanning microscope with an INSA Energy (Japan) energy-dispersive microanalysis system, inductively coupled plasma spectrometry IPS-MS Varian-820MS, differential thermal and thermogravimetric analyses (derivatograph Q-1500D) with computer control, and the mineralogical composition and microstructure of phosphorites and smelting products.

The main provisions submitted for defense

- The results of thermodynamic modeling of the effect of pressure on the equilibrium distribution of phosphorus, calcium, and silicon during the interaction of tricalcium phosphate, phosphates from the Chulaktau and Chilisai deposits, and their mixtures with carbon and iron, on the basis of which the optimal conditions for obtaining high-quality calcium carbide, ferrosilicon, and phosphorus distillation were determined.

- optimal technological conditions for the joint production of calcium carbide and ferrosilicon from phosphates of the Chulaktau and Chilisai deposits and their mixtures by electric smelting, with the extraction of phosphorus into the gas phase.

- The results of large-scale laboratory tests of the electric smelting of Chulaktau and Chilisai phosphates in the presence of various amounts of coke and steel shavings have established the optimal parameters for obtaining calcium carbide with a volume of up to 230 dm^3/kg and a calcium yield of more than 60-70%, as well as ferro-silicon grades FeSi50, FeSi45, and FeSi25 with a silicon yield of more than 70-80%;

- calculations of the technical and economic indicators of the developed technology.

The main results of the study.

Theoretical and applied studies on the processing of ordinary Chulaktau phosphorites and substandard Chilisai phosphorites have shown that the composition of the phosphorites and charge, the amount of iron-containing steel shavings, coke, and pressure have a significant impact on the technological parameters:

- A full thermodynamic analysis performed by computer modeling showed that when processing ordinary Chulaktau and Chilisai phosphorites, increasing the amount of iron increases the degree of silicon extraction into the alloy, increases the degree of calcium extraction into the carbide and its volume. Increased carbon content in the charge during processing of Chulaktau phosphorite has a positive effect on phosphorus, calcium extraction into calcium carbide and its volume. However, this reduces the extraction of silicon into the alloy and the concentration of this element in it. When processing Chilisai phosphorites, an increase in the carbon content of the charge increases the degree of formation of CaC_2 and its volume, as is the case with processing Chulaktau phosphorites;

- Reducing the pressure has a significant effect on the technological performance of processing Chulaktau phosphorites. Reducing the pressure from 1 to 0.01 bar reduces the temperature of complete phosphorus sublimation by 300°C (from 1500 to 1200°C), increases the degree of extraction of silicon into the alloy from 80 to 98%, with a decrease in the process temperature from 2200 to 1600-1800°C, and also increases the concentration of silicon in the alloy by almost 10%.

- By optimizing the technological parameters during the electric smelting of Chulaktau phosphorite, it was found that the formation of calcium carbide of the second and third grades, with a volume of 250 dm^3/kg, and FeSi25 ferro-silicon occurs in the presence of 24-38% steel shavings and 52-58% coke;

- When processing Chilisai phosphorite, depending on the amount of coke (50-58%) and steel chips (11-40%), calcium carbide with a degree of recovery of Ca 60% with a volume of 152-167 dm^3/kg and ferrosilicon of three grades FeSi50, FeSi45, and FeSi25 with a degree of recovery of Si 65% are formed during melting;

- Large-scale laboratory tests of the electro-smelting of Chulaktau phosphorites have demonstrated the possibility of obtaining calcium carbide with a volume of 190 dm3/kg, with a calcium extraction rate of up to 65% and phosphorus extraction rate of 94-97%, as well as FeSi25 ferrosilicon with a silicon extraction rate of 80%. When melting Chilisay phosphorite, two grades of ferrosilicon are produced: FeSi25 and FeSi45 with a silicon extraction rate of 82-85% and calcium carbide with a volume of >160% dm^3/kg with a calcium extraction rate in carbide of up to 60-65% and phosphorus in the gas phase of 94-98%.

- The estimated profit from processing Chulaktau and Chilisai phosphorites using the proposed technology ranges from 103,715 to 219,536 tenge per 1 ton of phosphorite, with an investment payback period of 2 to 4.5 years and a profitability rate of -24.98-42.26%.

Justification of the novelty and importance of the results obtained. The novelty of the dissertation work is the creation of a slag-free technology of complex electrothermal processing of phosphorites of the Chulaktau, Chilisai deposits and

their mixtures with simultaneous production of calcium carbide, ferrosilicon and extraction of phosphorus into the gas phase.

New scientific results are as follows:

- for the first time, it was found that the temperature of the beginning of the joint extraction of phosphorus and the formation of calcium carbide, iron silicides in the system $Ca_3(PO4)_2$-C-Fe-SiO_2 depends on the mole fraction of silicon in the forming iron silicide. When the mole fraction of silicon in the iron silicide increases from 0.375 to 0.66, the temperature of the beginning of the reaction increases from 1557 to 1631°C;

- the effect of temperature on the equilibrium degree of distribution of calcium, silicon, phosphorus and iron, as well as on the conditions of existence and quantitative ratios of the substances formed ($CaSiO_3$, $MgSiO_3$, Na_2SiO_3, K_2O*SiO_2, FeP_2, FeP, Fe_2P, Fe_3P, FeSi, Fe_5Si_3, $FeSi_2$, Fe_3Si, Si, Si(g), SiC, SiO(g), CaC_2, Ca(g), CaF_2, CaF, CaF_2(g), CaF(g), P_2(g), P_4(g), CO) in the production of calcium carbide, phosphorus and ferrosilicon from phosphorites of the Chulaktau and Chilisai deposits;

- It has been shown that the products of carbon-thermal reduction of SiO_2 in the presence of iron are not inert to tricalcium phosphate. The reactivity of SiO_2 reduction products decreases in the following order when they react with tricalcium phosphate to form phosphorus gas at 1600°C: (SiOg, Si)>SiC>$FeSi_2$>FeSi>Fe_3Si;

- The temperature sequence of the formation of products of the interaction of phosphates with carbon and iron has been found: initially, iron phosphides are formed at 900°C, then gaseous phosphorus is formed at 1100°C, iron silicides are formed at 1500°C, and calcium carbide is formed at 1800°C. Phosphorus completely turns into gas at a temperature of 1300-1500°C; ferrosilicon is formed at 1500-1800°C; calcium carbide is formed at 1800-2000°C;

- It has been found that when Chulaktau phosphates are electro-smelted in the presence of 52-58% coke and 24.4-38% steel shavings, calcium carbide with a volume of 245 to 248 dm^3/kg (second grade) and FeSi25 ferro-silicon with a silicon content of 20-30% are produced. At the same time, the degree of phosphorus extraction into gas ranges from 94 to 97%, calcium into calcium carbide from 60 to 70%, and silicon into ferroalloy from 70 to 80%;

- It was revealed that during electric melting of Chilisai CaC_2 phosphorites with a volume of 148-152 dm^3/kg and FeSi50 ferrosilicon are formed in the presence of 50.8-56.5% coke and 11.8-12.8% steel shavings; and calcium carbide with a liter from 149 to 165 dm^3/kg and FeSi45 grade is smelted at 51.2-54.2% coke and 12.5-18.4% of steel shavings; calcium carbide with a litre from 128 to 167 dm^3/kg and low-silicon ferrosilicon grade FeSi25 is formed at 53.4-58% coke and 38.7-40% steel shavings;

- When Chulaktau and Chilisai phosphates are electro-smelted, partial replacement of Chulaktau phosphate with Chilisai phosphate increases the silicon content in the ferroalloy to 41.4-42.6%, resulting in the production of FeSi45 ferro-silicon. This replacement allows the use of Chilisai phosphates, which are difficult to process using traditional electro-smelting methods due to their low P_2O_5 content.

The importance of the results obtained. The results obtained on the slag-free processing of phosphorites are important for the rational use of phosphate raw

materials (natural and technogenic). The developed technology allows for an increase in the complexity of raw materials from 43.9% to 84.3% and can be used not only for the processing of ordinary phosphorites, but also for the processing of phosphatized silicon, phosphate-silica rocks, and phosphorus slag.

The practical significance and technological novelty of the developed method for processing Chulaktau and Chilisai phosphorites are confirmed by the RK patent for inventions No. 35033, "Method for Processing Phosphorite," and the utility model patent No. 8853 KZ, "Method for Processing Ordinary Phosphorite by Electric Melting."

When implementing the developed technology at the existing Kazphosphate LLP (NDFZ) enterprise, at current emission rates, it is possible to reduce annual payments by approximately 4.2 million tenge by reducing the fee for storage in electrothermal phosphorus slag dumps. In addition, reducing the number of slag dumps will improve the environmental situation in the region.

Compliance with scientific development trends or government programs.

The dissertation is an integral part of the research and development plan under grant AR14869066 "Development of a resource-saving slag-free technology for electrothermal processing of phosphorites" under the program of applied research of the Ministry of Education and Science of the Republic of Kazakhstan "Scientific and (or) scientific and technical activities for 2022-2025", priority "Deep processing of raw materials and products" (state registration no. 0122RK00424) and plans for state-funded research and development at the M.Auezov Moscow State University, in which the applicant was a performer.

The doctoral student's personal contribution to each publication.

Based on the results of research conducted as part of the dissertation, 20 scientific papers have been published, including 2 patents of the Republic of Kazakhstan (1 patent for an invention and 1 patent for a utility model), 1 monograph, 1 article in scientific journals recommended by the authorized body (CQASHE MSHE RK), 5 articles in international peer-reviewed scientific journals indexed in Scopus, 2 articles in international journals, and 9 publications in collections of international scientific conferences, including 2 articles published abroad. As a result of the research, two acts were issued (No. 2 and No. 3 dated June 24, 2024) on the conduct of large-scale laboratory tests of the electric smelting of Chulaktau and Chilisai phosphates. The results of the work have been implemented in the educational process: acts No. 343, No. 346, and No. 347 dated June 2, 2023; act No. 56 dated April 10, 2024; and act No. 205 dated July 16, 2025.

1. In the article "Electrothermal co-Production of Ferrosilicon, Calcium Carbide and Qaseous Phosphorus from the Chilisay Phosphorite" in the journal Metalurgija, the calculation and analysis of data, obtaining and processing of results, as well as the preparation of the blend for electric smelting were carried out.

2. In the article "Interaction of Tricalcium Phosphate with Products of Carbothermic Reduction of Silicon Oxide" published in the journal "Metalurgija", a review and analysis of literature data, calculations on $\Delta G0$, $\Delta H0$, and processing of results were carried out.

3. In the article "Production of Ferroalloys, Calcium Carbide, and Phosphorus from High-Silicon Phosphorite" in the journal "Rasayan J. Chemistry", she prepared a literature review, summary, calculations, and data processing.

4. In the article "Thermodynamic Picture of Interaction of a Mixture of Phosphorites of Karatau and Aktobe with Obtaining Phosphorus, Calcium Carbide and Ferrosilicon" in the journal "Izvestiya of Tomsk Polytechnic University" carried out the preparation and analysis of a literature review, calculations and processing of the results.

5. In the article "Processing of Phosphorites with Extraction of Phosphorus, Obtaining Calcium Carbide and Ferroalloy" in the journal "Physicochemical Problems of Mineral Processing" carried out thermodynamic calculations, discussion and experiments in a single-electrode arc electric furnace.

6. The article "Electric Smelting of Phosphorites with Production of a Ferroalloy, Calcium Carbide and Sublimation of Phosphorus" in the Engineering Journal of Satbayev University conducted thermodynamic calculations, discussions, and experiments in a single-electrode arc electric furnace using Chulaktau phosphorites.

Structure and volume of the dissertation. The dissertation work of 167 pages includes 35 tables and 88 figures. Structurally, the work consists of an introduction, five chapters, a conclusion, a list of used sources, including 93 titles, and 10 applications.