PHYSICO-CHEMICAL TRANSFORMATIONS DURING THERMAL TREATMENT OF PHOSPHORITES AND SOLUBILITY OF THE PRODUCTS

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Abstract A comparative investigation of physico-chemical transformations taking place during heating up to 1300°C of calcareous and silico-calcareous phosphorites of different deposits (Kazakhstan, Russia, Uzbekistan, Israel, Estonia), and of the influence of thermal treatment on the solubility of products in processing by sulphuric and/or phosphoric acids was carried out by means of chemical, thermal, SEM, X-ray diffraction, IR spectroscopy and other methods of analysis.

INTRODUCTION

One of the possibilities of beneficiation of low quality phosphorites, particularly carbonaceous and silico-carbonaceous as well as high-level organic matter or pyrite containing phosphorites is their thermal treatment. For operating the thermal processing of phosphorites in optimum conditions, it is important to establish the transformations taking place during thermal treatment of phosphorites and their influence on the quality of the products.

The aim of our work was to establish optimum conditions for thermal treatment of the phosphorites studied, i. e. conditions which would guarantee the preservation of Ca and Mg oxides formed during decomposition of carbonates in the free form for the following removal of them¹, and to avoid the decrease in the solubility of apatite mineral and the increase in the solubility of accompanying minerals during acidic processing of the products. In this paper the results of studying the influence of thermal treatment on the solubility of phosphorites in the phosphoric acid are presented.

CHARACTERIZATION OF SAMPLES

Samples of phosphorites from different deposits were studied: Kokdzhon, Heres, Dzhanatas (Kazakhstan), Dzheroi-Sardara (Uzbekistan), Yegorjevsk, Kingisepp

(Russia), Nahal-Zin (Israel), Toolse, Kabala (Estonia). The solubility tests in phosphoric acid were carried out with the first six samples. The chemical composition of these samples is presented in the Table. The main constituent of the samples is fluorcarbonateapatite, the main accompanying minerals are dolomite, calcite, pyrite, quartz, organic matter, etc. The content of apatite as well as the impurities varied in a large range - the content of P_2O_5 from 16.9% (Heres) to 27.2% (Kingisepp), SiO_2 from 4.1% (Yegorjevsk) to 18.4% (Heres), etc. (Table).

In the solubility tests phosphoric acid of reactive grade quality, diluted to 20% of P_2O_5 was used.

TABLE.
CHEMICAL COMPOSITION OF THE SAMPLES

Content, % by mass	Kok- dzhon	Dzha- natas	Heres	Yegor- jevsk	Dzheroi- Sardara	Kingi- sepp
P_2O_5	22.7	25.2	16.9	29.2	22.2	27.2
CaO	40.0	42.1	38.0	47.2	45.5	43.5
MgO	4.1	4.0	8.2	1.5	0.7	3.1
Al_2O_3	1.2	0.7	0.7	1.0	2.5	0.2
Fe_2O_3	1.1	1.2	0.9	2.3	0.8	1.2
CO_2	9.7	7.9	18.4	6.1	9.2	8.3
C org.	0.15	-	0.18	0.87	0.98	0.30
SiO_2	12.8	11.7	10.7	4.1	7.5	17.4
SO_3	1.2	0.7	1.0	1.4	0.1	2.0
S^{2-}	0.18	0.18	0.16	0.57	0.05	0.53
F	2.7	2.4	1.2	4.2	2.9	3.2

METHODS AND EXPERIMENTAL

Thermal analysis with the simultaneous registration of TG, DTG, DTA and TGT curves was carried out in a Q-Derivatograph (MOM, Hungary) in the stream of oxygen or helium (10 dm^3 per hour) with absorption of evolved gases and titration of the solution at pH = 4.0 or 9.3 for determination of SO_2 or CO_2 in the evolved gases.^{2,3} The heating rate was 5 K per min and the mass of samples 300-350 mg.

Thermal treatment of the samples for determination of their solubility in the phosphoric acid was carried out in a laboratory tube furnace in a Pt-crucible at 900°, 1000°, 1100° during 15 minutes and at 1200°C during 2 hours in the stream of air. The

samples obtained as well as initial samples of phosphorites were treated with H_3PO_4 (mass ratio solid : liquid = 1:2.5) in a water basin at 75°C during one hour, filtered and washed. The insoluble in H_3PO_4 residue was treated with a 5%-solution of Na_2CO_3 for removal of silicon acid, filtered, the filtrates and washing waters were then connected and the content of P_2O_5 and SiO_2 (soluble in phosphoric acid SiO_2) in the obtained solution was determined. The solid residue after these procedures was heated to 1000°C (was fixed the content of quartz+insoluble silicates), and treated with HF-acid for determination of the total content of insoluble in phosphoric acid oxides: $\text{Me}_2\text{O}_3 + \text{MeO} + \text{Me}_2\text{O}$ (Me - cation).

RESULTS AND DISCUSSION

Based on the results of complex thermal analysis of the samples it was established that emission of CO_2 started at 200°C and continued up to $1250\text{--}1300^\circ\text{C}$, originating from the oxidation of organic carbon, decomposition of siderite, dolomite and calcite and rearrangements in the apatite structure. Emission of SO_2 which started at $400\text{--}450^\circ\text{C}$ and proceeded up to $1250\text{--}1300^\circ\text{C}$, originated from the oxidation of pyrite and organic sulphur and from the sulphates.

A great influence of the temperature of thermal treatment of phosphorites on the composition and physico-chemical properties, especially on the solubility in H_3PO_4 of the silica-containing part of phosphorite was observed. The total content of soluble SiO_2 in Yegorjevsk phosphorite increased from 0.85% in initial sample to 3.95% in the sample thermally treated at 1200°C or from 20.7% to 96.3% of the total content of SiO_2 in the sample (FIGURE 1). The same values for Kokdzhon phosphorite increased from 4.2% to 12.3% or, relatively, from 32.5% to 96.0% of the total SiO_2 content. So, the relative content of soluble SiO_2 which varies in initial samples in the range of 15-16% (Dzhanatas, Heres) to 40% (Dzheroi-Sardara) increased during thermal treatment at 900°C up to 25-65% and at $1100\text{--}1200^\circ\text{C}$ up to 95-99% as calculated from the total content of SiO_2 in phosphorites. Exception to the phosphorites studied was Kingisepp, solubility of the silica part of which increased only from 6% in the initial sample to 35% of the total content of SiO_2 in the sample treated at 1200°C .

As a result, the insoluble part of silica in the phosphorite samples thermally treated decreased and in the samples heated at $1100\text{--}1200^\circ\text{C}$ it was only 0.2-0.5%, except for Kingisepp phosphorite in which it was 7.5% (FIGURE 2A). By X-ray data the SiO_2 in the initial sample of Kingisepp phosphorite is presented mainly as well-crystallized quartz, in the other phosphorites besides not well-crystallized quartz also as

wollastonite and, possibly, as albite or microcline.

FIGURE 1. Influence of temperature of thermal treatment of samples on the solubility of silica in the phosphoric acid: 1 - Kokdzhon, 2 - Dzhanatas, 3 - Heres, 4 - Dzheroi-Sardara, 5 - Kingisepp, 6 - Yegorjevsk.

During heating of phosphorites great changes took part in the composition of insoluble part of phosphorite as well, and they were different for different phosphorites. A poor increase in the content of insoluble oxides was observed in Kokdzhon and Heres phosphorites and about 1.5 times increase (from 1.8 to 2.7%) in Dzhanatas phosphorite heated at 900-1000°C and a poor decrease of it in Yegorjevsk and Dzheroi-Sardara phosphorites at these temperatures (FIGURE 2B). The following increase in the temperature resulted in rapid decrease in the content of insoluble oxides in Kokdzhon (from 4.1% to 0.38%), Dzhanatas (from 2.7% to 1.3%) and Dzheroi-Sardara phosphorites (from 2.5% to 0.61%). In Heres phosphorite the content of insoluble oxides also decreased, but it stopped and stayed nearly constant at 1100-1200°C on the level of 1.7%. Only in Kingisepp phosphorite the increase in temperature was followed by the increase in the content of insoluble oxides - from 1.5% in the initial sample to 4.8% in the sample heated at 1200°C.

So, the relative content of insoluble in H_3PO_4 oxides in insoluble part of phosphorites (quartz + insoluble silicates) increased from 13.5-35.0% in initial sample to

FIGURE 2. Influence of temperature of thermal treatment of samples on the content of insoluble in phosphoric acid oxides ($\text{Me}_2\text{O}_3 + \text{Me}_2\text{O}$) (A) and silica (B): 1 - Kingisepp, 2 - Heres, 3 - Dzhanatas, 4 - Kokdzhon, 5 - Dzheroi-Sardara, 6 - Yegorjevsk.

73.9-76.9% of Kokdzhon, Dzhanatas and Yegorjevsk phosphorites heated at 1200°C and from 16.3-31.5% to 96-97% in Heres and Dzheroi-Sardara phosphorites. In Kingisepp phosphorite the content of insoluble oxides increased from 8.4% in initial sample to 39.2% in thermally treated at 1200°C sample.

These changes in the solubility of SiO_2 and in the composition of insoluble part of phosphorites correlated well with the results of X-ray analysis of the samples. The X-ray data indicated that at higher temperatures (over 900°C) an interaction between silica part of phosphorites and Ca and Mg oxides formed during the decomposition of carbonates takes place. At 1100-1200° in the thermally treated samples, in addition to apatite mineral and to a little content of diopside the presence of akermanite, brownmillerite and merwinite which all are well-soluble in phosphoric acid was determined. The X-ray data confirmed that besides of apatite mineral the sample of Kingisepp phosphorite heated at 1200°C contained quartz and diopside which are both hardly-soluble in phosphoric acid.

CONCLUSIONS

An increase in the solubility of silica with increasing the temperature of thermal treatment of phosphorites was observed. Consequently, Ca and Mg oxides formed as well as other metal oxides contained in phosphorites react with the silica part of phosphorites. At that the formation of well-soluble in phosphoric acid compounds as akermanite, brownmillerite, merwinite takes place. Only the sample of thermally treated Kingisepp phosphorite contained a high amount of unreacted quartz and newly formed mineral - diopside, both hardly-soluble in phosphoric acid.

So, the optimum thermal treatment temperature of the studied phosphorites for the following extraction of phosphoric acid seems to be 850 - 900°C. Below 850° C decomposition of carbonates is not complete. The use of higher temperatures is accompanied by an increase in the solubility of silicates and the other secondary compounds which leads to technological complications in the manufacturing of phosphoric acid and to contamination of products based on the use of H_3PO_4 . The solubility of apatite mineral was in the range of 95-99% of the total content of P_2O_5 in the initial samples.

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