

MECHANISM OF REACTIONS IN MIXTURES OF CALCIUM POLYPHOSPHATE WITH APATITE AND ACCOMPANYING MINERALS DURING HEATING

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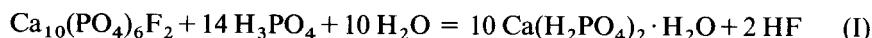
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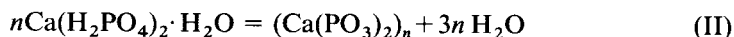
The thermal interaction of Kovdor apatite, calcite, dolomite and forsterite with calcium polyphosphate up to 1200 °C were studied by chemical, thermal (under dynamic and quasi-isothermal and isobaric conditions), X-ray, electronmicroscopic and chromatographic methods. It was found that the accompanying minerals of apatite react with calcium polyphosphate at lower temperature in comparison with apatite, complicating the process of thermal defluorination of apatite.

The thermal defluorination of phosphate rock after the preliminary addition of phosphoric acid is widely used in the U.S.S.R. for the production of feed phosphates. Until recently, the high-quality Kola apatite concentrate was used as raw material. The mechanism of the process in stages is described schematically by the following principal reactions (at a molar ratio $\text{CaO} : \text{P}_2\text{O}_5 = 3 : 1$ in the mixture equal) [1].

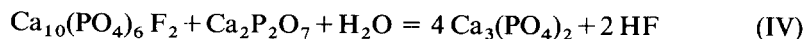
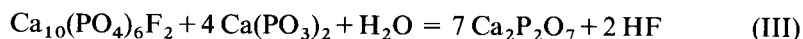
1. On the mixing of apatite with phosphoric acid:



2. On heating up to 600°:



3. On heating over 700°:



Overall reaction:



The product is mainly $\beta\text{-Ca}_3(\text{PO}_4)_2$ and does not contain more than 0.2% fluorine.

Due to the limited supplies of Kola apatite, the production of defluorinated feed phosphates is now involving the use of apatite from the Kovdor deposit, which contains considerable amounts of impurity minerals such as calcite, dolomite and forsterite in variable quantities. Further, the phosphatic mineral of this rock contains considerable amounts of impurity minerals such as calcite, dolomite and forsterite in variable quantities. Further, the phosphatic mineral of this rock contains less fluorine and is present as fluorhydroxyapatite. Defluorination of Kovdor apatite concentrate has turned out to be considerably more complicated, on account of agglomeration and accretion in the rotary kiln, and also incomplete defluorination of the product, particularly at high carbonate contents in the rock [2, 3].

The aim of our investigations was to establish the mechanism and conditions of the course of the reactions occurring when mixtures based on Kovdor apatite concentrates of different compositions and special mixtures are heated. It was established that in the first stage of the process carbonates and forsterite decompose to a greater extent than apatite, but far from completely. They partly pass over to the following stages of the process and influence the course of the reactions and phase transformations in these stages, particularly in the third stage. In the present paper the results of a comparative investigation of the thermal interaction of apatite, calcite, dolomite and forsterite with calcium polyphosphate under the conditions of the third stage of the process are given.

Chemical, thermal (MOM derivatograph, Hungary), X-ray (DRON-0.5, U.S.S.R.), electronmicroscopic (BS-300, Cz.S.S.R.) and chromatographic methods were used in the study.

For the dissolution and separation of polymeric phosphates, ion-exchange on Dowex 50W or a solution of EDTA at pH = 7 and chromatographic analysis were used [4]. The contents of free CaO and MgO were determined according to [5, 6], and the content of amorphous SiO_2 according to [7]. The contents of apatite and $\beta\text{-Ca}_3(\text{PO}_4)_2$ in the samples were determined on the basis of the intensities of the main reflexes in the diffractograms, at 2.80 and 2.86 Å, respectively.

In the experiments, high-molecular calcium polyphosphate $(\text{Ca}(\text{PO}_3)_2)_n$, and also $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, CaO and MgO, all of reagent grade, were used. The second components of the mixtures were samples of Kovdor apatite concentrate calcite, dolomite, magnesite and forsterite. Mixtures were heated in a laboratory electric furnace in a medium of air. The mixtures were made with a molar ratio $R = (\text{CaO} + \text{MgO}) : \text{P}_2\text{O}_5 = 3.0\text{--}3.1$.

Figure 1 gives the results of chromatographic and X-ray analysis of different phosphates in heated mixtures based on two samples of Kovdor apatite concentrate

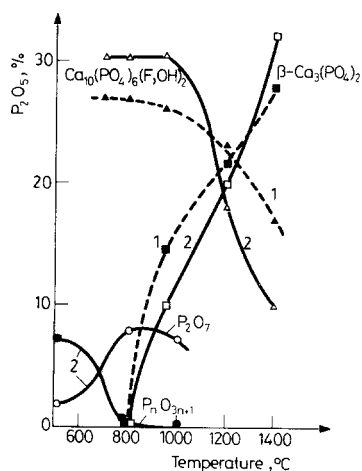


Fig. 1 Changing the content of different forms of phosphates at heating mixtures on the basis of carbonate-type (mixture 1) and forsterite-type (mixture 2) Kovdor apatite concentrate

(the carbonate type, containing 7.5% calcite, 7.6% dolomite and 1.6% forsterite, and the forsterite type, containing 2.9% calcite, 2.2% dolomite and 7.2% forsterite). It is obvious that the formation of $\beta\text{-Ca}_3(\text{PO}_4)_2$ proceeds strongly 800°, i.e. up to the beginning of decomposition of apatite. In the first mixture, based on the carbonate-type concentrate, the content of $\beta\text{-Ca}_3(\text{PO}_4)_2$ after heating up to 1200° is considerably higher than in the second mixture, based on the forsterite-type sample, but the residual content of apatite in the first mixture is also higher. Consequently, poly- and diphosphates of calcium react with impurity minerals, and particularly with carbonates, at a lower temperature and at a higher rate than with apatite. Additionally, the content of $(\text{Ca}(\text{PO}_3)_2)_n$ and $\text{Ca}_2\text{P}_2\text{O}_7$ in the mixture decreases and they are insufficient for complete reaction with apatite by reactions (III) and (IV).

On the other hand, it has been established that the decomposition of apatite and evolution of fluorine do not proceed in parallel: the degree of evolution of fluorine when the mixtures are heated is less than the degree of decomposition of apatite. Proceeding from the hypothesis of substitution of the OH group by fluorine in the crystal lattice of apatite, it is shown in Fig. 2 how the molar ratio of fluorine to decomposed apatite increases. This increase is again more considerable in the processing of the carbonate-type concentrate. The formation of new crystals of apatite in the end-products of heating has been established by electronmicroscopic study (Fig. 3). For removal of the residual fluorine, it is necessary to increase the heating temperature, but this may lead to the formation of liquid phase, the agglomeration of particles, and the increase of diffusion resistance. The indicator

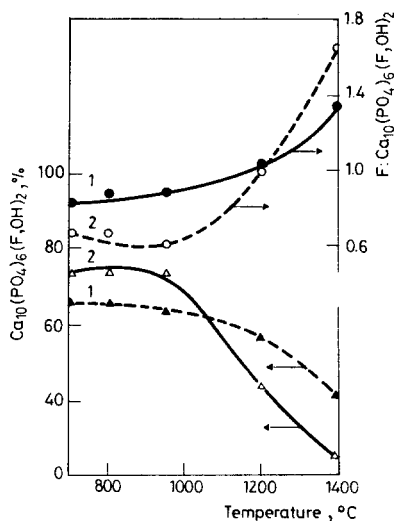


Fig. 2 Changing the content of apatite and molar ratio F: apatite at heating mixtures 1 and 2



Fig. 3 Electron-microscopic picture (enlargement 360 ×) heating end-product of the mixture 1

for liquid-phase formation was the increase of the electrical conductivity of compressed tablets of mixtures (Figs 6 and 9) and the decrease of the specific surface of the samples (by the BET method).

To specify the conditions of interaction of impurity minerals with calcium polyphosphate, thermal curves of their mixtures were taken under dynamic and quasi-isothermal-isobaric heating conditions. From the thermal curves of mixtures based on calcite (56.0% CaO, 44.0% CO₂), it follows (Fig. 4) that the decomposition of CaCO₃ in the mixture with calcium polyphosphate undergoing dynamic heating begins at a lower temperature than when calcite is heated alone.

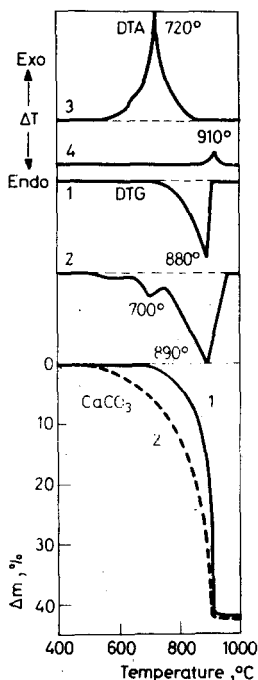


Fig. 4 Thermal curves of calcite (1), mixtures $(\text{Ca}(\text{PO}_3)_2)_n$ with CaCO_3 (2) and CaO (3), mixture $\text{Ca}_2\text{P}_2\text{O}_7$ with CaO (4)

The CaO formed reacts quickly with the phosphate component of the mixture, and its content in the mixture does not exceed 8.7% at the maximum possible content of 36.4%, calculated from the quantity of CO_2 evolved (Fig. 5). The reaction of CaO with calcium polyphosphate proceeds with maximum rate at 720° , but with $\text{Ca}_2\text{P}_2\text{O}_7$ at 910° .

The thermal curves for mixtures of calcium polyphosphate with dolomite (31.3% CaO , 20.3% MgO and 45.9% CO_2) and magnesite (44.3% MgO , 52.9% CO_2), recorded during dynamic heating (Figs 6 and 7), did not reveal that they decompose at lower temperatures in the mixtures than when the carbonates are heated alone (as in the mixture with CaCO_3). However, in the quasi-isothermal-isobaric heating of the mixtures (Fig. 8), calcium polyphosphate lowers the temperature of decomposition both of calcite and of dolomite. In the mixture with dolomite, and particularly with magnesite, the MgO formed during heating interacts with the phosphate component to a lesser extent in comparison with the reaction of CaO in the mixture with calcite (Fig. 5). In the mixture with magnesite, the content of MgO reaches its maximum at 700° (27.3%); on increase of the temperature up to 950° , the

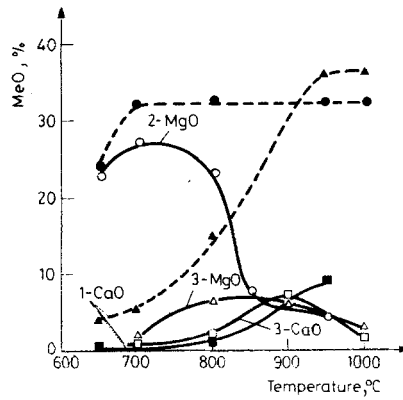


Fig. 5 Changing the calculated (-----) and actual (————) content of CaO and MgO in heated mixtures $(\text{Ca}(\text{PO}_3)_2)_n$ with calcite (1), magnesite (2) and dolomite (3)

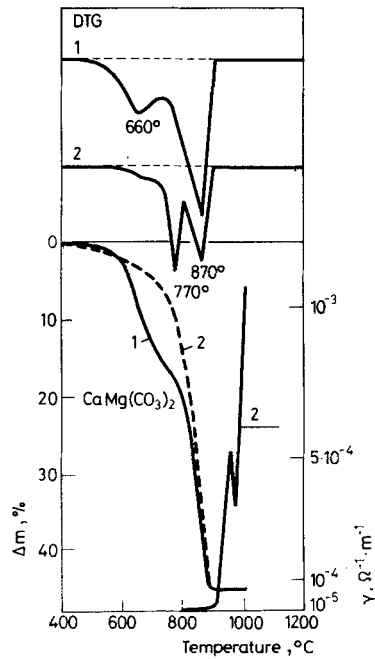


Fig. 6 Thermal curves of dolomite (1) and its mixture with $(\text{Ca}(\text{PO}_3)_2)_n$ (2) and the change of electrical conductivity of the mixture

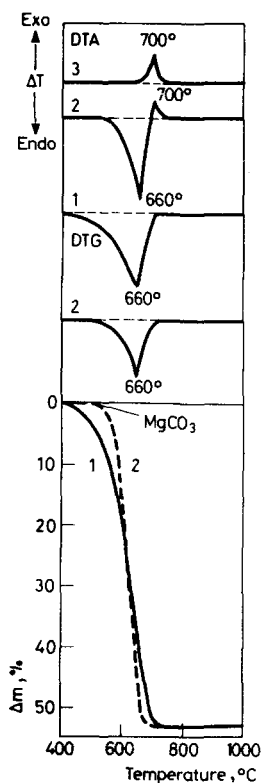


Fig. 7 Thermal curves of magnesite (1) and the mixtures $(\text{Ca}(\text{PO}_3)_2)_n$ with magnesite (2) and MgO (3)

content decreases to 4.4% which is equal to the content of CaO in the mixture with calcite heated up to the same temperature.

The change in phosphate composition when mixtures of calcium polyphosphate with carbonates are heated is illustrated by the data in the Table. For a more complete dissolution of mono- and diphosphates (for subsequent chromatographic separation on paper), the method of ion-exchange with the application of cationite Dowex is used, but for the dissolution of polyphosphates ($n \geq 3$) the samples are processed with a solution of EDTA. It has been established that the polyphosphate content in the heated mixtures decreases as the temperature increases, and approaches zero at 920° . The diphosphate content in the mixtures reaches its maximum in the interval $850\text{--}950^\circ$, depending on the composition of the mixture, and then decreases. The monophosphate content increases with increase of temperature, to a greater extent in the mixtures with calcite than those with dolomite and magnetite. Variation of the phosphate composition of the samples

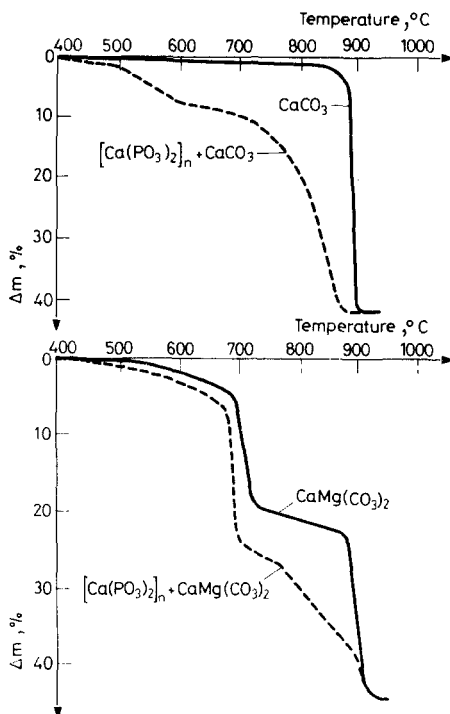
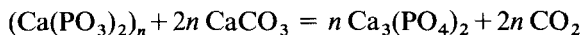


Fig. 8 Curves of losses of masses of calcite, dolomite and their mixtures with $(\text{Ca}(\text{PO}_3)_2)_n$ at quasi-isothermal-isobaric heating

also has an effect upon the solubility of the phosphates in the different methods of processing the samples (by means of cation-exchange or dissolution with EDTA).

The overall reaction in the mixture of calcium polyphosphate with calcite is represented by the equation:



The product of interaction of the components in the mixture with calcite in the intermediate stage is $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, and that in the final stage is $\beta\text{-Ca}_3(\text{PO}_4)_2$, while in the mixtures with dolomite and magnesite (in accordance with the shifts and changes in intensity of the reflexes in the diffractograms) the products are $(\text{Ca}, \text{Mg})_2\text{P}_2\text{O}_7$ and $(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$.

The differences between the thermal curves of the mixture of calcium polyphosphate with forsterite and those of forsterite alone (Fig. 9) indicate the interaction in this mixture too, but it is less intensive and more complicated than in the mixtures with carbonates. The lower rate of interaction is indicated by the increased content of polyphosphates in samples heated up to 750–920° (see the

Table 1 Solubility and phosphatic composition of products of heating mixtures $(\text{Ca}(\text{PO}_3)_2)_n$ with CaCO_3 , MgCO_3 , $\text{CaMg}(\text{CO}_3)_2$ and Mg_2SiO_4 at $R = 3$ (in relative percentage of the mass P_2O_5)

	$\text{CaCO}_3 + (\text{Ca}(\text{PO}_3)_2)_n$			$\text{MgCO}_3 + (\text{Ca}(\text{PO}_3)_2)_n$			$\text{CaMg}(\text{CO}_3)_2 + (\text{Ca}(\text{PO}_3)_2)_n$			$\text{Mg}_2\text{SiO}_4 + (\text{Ca}(\text{PO}_3)_2)_n$		
	750	850	920	850	950	1000	700	800	920	750	850	920
	°C			°C			°C			°C		
Solubility at cationic exchange, %	25.7	84.8	87.5	51.2	92.2	93.0	5.2	26.8	91.2	—	—	—
*Solubility at processing with EDTA, %	86.6	67.8	55.0	—	—	—	64.6	56.8	46.1	79.9	68.5	49.3
Content, %												
of monophosphate	2.9	32.8	45.5	6.4	18.7	42.1	5.2	10.4	31.7	$x_{2.4}$	$x_{2.4}$	$x_{10.8}$
of diphosphate	18.6	38.3	37.3	19.2	73.5	50.9	0	16.4	59.5	$x_{9.5}$	$x_{20.6}$	$x_{19.1}$
of polyphosphate ($n \geq 3$)	$x_{71.8}$	$x_{32.8}$	$x_{2.4}$	—	—	—	$x_{63.0}$	$x_{45.4}$	$x_{0.6}$	$x_{68.0}$	$x_{45.6}$	$x_{19.3}$

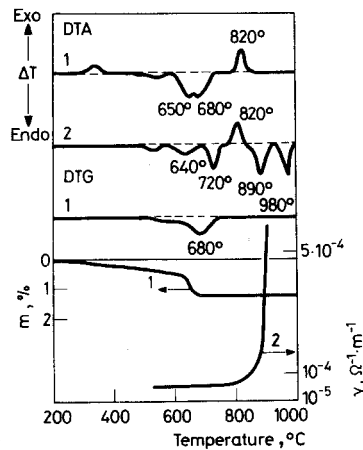


Fig. 9 Thermal curves of forsterite (1) and its mixtures with $(\text{Ca}(\text{PO}_3)_2)_n$ (2) and the change of electrical conductivity of the mixture

Table). In the mixture an amorphous SiO_2 is formed, comprising 9.3% of the total content of SiO_2 in the mixture at 850° . The diffractogram data show that $(\text{Ca}, \text{Mg})\text{P}_2\text{O}_7$ is formed in the intermediate stage of heating, while $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$ has been identified at temperatures above 1000° [8]. The formation of silicophosphates of calcium and magnesium is also possible. Because of the close conditions of the reactions of $(\text{Ca}(\text{PO}_3)_2)_n$ with forsterite and apatite, the influence of forsterite on the process studied is less considerable than those of carbonates. SiO_2 in the mixture promotes the decomposition and defluorination of apatite. However, the admixture of forsterite and of dolomite increases the fusibility of the mixture, but it also complicates the intensive process of defluorination of Kovdor apatite. The sudden increase in electrical conductivity of the mixture $(\text{Ca}(\text{PO}_3)_2)_n$ with forsterite takes place even at 900° , while that of the mixture with dolomite is at 950° (Figs 6 and 9).

Thus, the investigation has shown that the accompanying minerals in Kovdor apatite concentrate react with calcium polyphosphate at lower temperatures in comparison with apatite, complicating the process of thermal defluorination of this kind of phosphate rock. It is necessary to perfect the processes of concentrating Kovdor complex ores and to decrease the content of impurity minerals in the apatite concentrate.

References

- 1 M. A. Veiderma, Chem. Ind., (4) (in Russian), (1971) 279.
- 2 O. K. Tynsuaadu, M. E. Pyldme and M. A. Veiderma, Proc. Ac. Sc. U.S.S.R., Inorg. Mat., 19 (1983) 978.
- 3 O. K. Tynsuaadu, M. A. Veiderma and M. E. Pyldme, Proc. Ac. Sc. E.S.S.R., Chem., 32 (1983) 237.
- 4 M. A. Veiderma and J. H. Pyldme, J. Inorg. Chem., (in Russian), 21 (1976) 10.
- 5 J. H. Reispere, Transact. of Tallinn Polytechn. Inst., ser. A, 245 (1966) 73.
- 6 N. A. Toropov, Chemistry of Cements, Moscow 1956, p. 26.
- 7 N. T. Polejaev. In Coll.: Determination of Free Dioxide of Silicon in Rocks and Mine Dust. Moscow 1958, p. 23.
- 8 I. Jun, J. Res. Nat. Bur., 72 (1968) 355.

Zusammenfassung — Die thermische Wechselwirkung von Kovdor-Apatit, Calcit, Dolomit und Forsterit mit Calciumpolyphosphat bei Temperaturen bis 1200 °C wurde durch chemische, thermische (unter dynamischen, quasiisothermen und isobaren Bedingungen), röntgenographische, elektronenmikroskopische und chromatographische Methoden untersucht. Es wurde festgestellt, daß die Begleitminerale des Apatits im Vergleich zum Apatit selbst bei niedrigeren Temperaturen mit Calciumpolyphosphat reagieren und so den Prozeß der thermischen Entfluorierung von Apatit komplizieren.

Резюме — Изучено термическое взаимодействие ковдорского апатита, кальцита, доломита и форстерита с полифосфатом кальция при нагреве до 1200° с использованием химического, термического (в условиях динамического и квазиизотермического и квазиизобарного нагрева), рентгенофазового, электронно-микроскопического и хроматографического методов анализа. Установлено, что сопутствующие апатиту примесные минералы реагируют с полифосфатом кальция при более низких температурах по сравнению с апатитом, осложняя тем самым процесс термического обесфторивания апатита.