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INVESTIGATION OF PHASE TRANSFORMATIONS IN THERMAL PROCESSING OF PHOSPHATE ROCK

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The reaction mechanism of the hydrothermal sintering processing of hydroxyfluorapatite (HFA) was studied. Samples from an industrial rotary kiln and laboratory-made samples were investigated by thermal, X-ray and chemical analysis. It was found that HFA decomposes by a solid-solid reaction with Ca-Mg-phosphates and by interaction with fused clinker. Apatite decomposition is not accompanied by fluorine evaporation; it merely creates the main precondition for fluorine evolution from clinker.

The present study is related to an investigation of the chemistry of the hydrothermal sintering processing of hydroxyfluorapatite (HFA) from the Kovdor deposit (USSR). In the manufacturing of feed supplement from this apatite concentrate in a rotary kiln by thermal processing with phosphoric acid, problems appeared: the amount of melt formed was often too high, or an undesired product from the point of view of its residual fluorine content ($> 0.18\ \%$) was formed. This method is used to produce a feed phosphate or fertilizer from natural phosphates containing fluorapatite (FA) or fluorcarbonate-apatite (FCA) [1-4]. In addition to the different types of apatite, the dolomite and forsterite contents in Kovdor phosphate rock concentrates are relatively high. The formation of magnesium phosphates ($Mg(H_2PO_4)_2$, $Mg(PO_3)_2$, $Mg_2P_2O_7$, etc.) therefore takes place in the intermediate stage of the process and the system HFA-CaO-MgO-P_2O_5 is formed. Partial fusion of Ca-Mg-phosphates at the temperatures of the calcination process (700-1550°) [5-7] can influence the physico-chemical changes occurring in clinker (CL) during heating. In this paper the main attention is concentrated on the transformation of apatite and the formation of calcium phosphate.

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Experimental

HFA (P_2O_5 - 40.3 %, F - 0.99 %) was obtained from Kovdor, FA (P_2O_5 - 39.4 %, F - 3.1 %) from Kola, and FCA (P_2O_5 - 35.0 %, F - 3.2 %, CO_2 - 2.9 %) from Estonian apatite concentrates. CL samples were taken from an industrial rotary kiln (length 10 m). $Ca_2P_2O_7$ was prepared from $CaHPO_4 \cdot 2H_2O$ by heating. β - $Ca_3(PO_4)_2$ with varying magnesium contents (1.0-8.0 % MgO) was synthesized from $Ca_2P_2O_7$, CaO and MgO by heating their mixtures up to 1600° at a rate of 3-1 $deg \cdot min^{-1}$ and cooling at 10-5 $deg \cdot min^{-1}$. HFA, CL and HFA-$Ca,Mg)_3(PO_4)_2$ mixtures with a mass ratio of 1:1 were studied by simultaneous TG, DTG and DTA [8, 9], using a Derivatograph C apparatus (MOM, Hungary). Pure HFA and mixtures of HFA and $Ca_2P_2O_7$ (in which the CaO:P_2O_5 molar ratio was 3.00) were heated up to a certain temperature at a rate of 10 $deg \cdot min^{-1}$ and cooled at 30-20 $deg \cdot min^{-1}$.

Heating experiments with HFA were also carried out in a laboratory tube furnace in various atmospheres. The starting materials and the cooled heating products were examined by X-ray diffraction and chemical methods. X-ray powder diffraction patterns were taken with a DRON-0.5 ("Burevestnik" USSR) unit using FEK radiation. For quantitative phase analysis, samples were blended with AlF_3 as an internal standard.

Results and discussion

Table 1 β -$Ca_3(PO_4)_2$ lattice parameters in synthezised samples in dependence of magnesium content

Content of MgO, %	$a_o \pm 0.001$ Å	C_o, Å
1.0	10.411	37.337 ± 0.010
2.0	10.392	37.252 ± 0.006
4.0	10.357	37.137 ± 0.012
6.0	10.333	37.198 ± 0.006
8.0	10.318	37.271 ± 0.005

The decrease in the synthesized $Ca_3(PO_4)_2$ unit cell Q_o value (Table 1) shows that substitution of calcium by magnesium has taken place [10]. It was found that, as a result of heating, the unit cell dimensions of HFA decrease in air and in a HF-containing atmosphere and increase in H_2O vapour. In the latter case replacement of F^- by OH^-, and in the H_2O-HF atmosphere replacement of OH^- by F^- in the HFA structure takes place (Table 2). In the case of pure HFA, differently from FA and FCA, the crystal perfection decreases (Fig. 1).

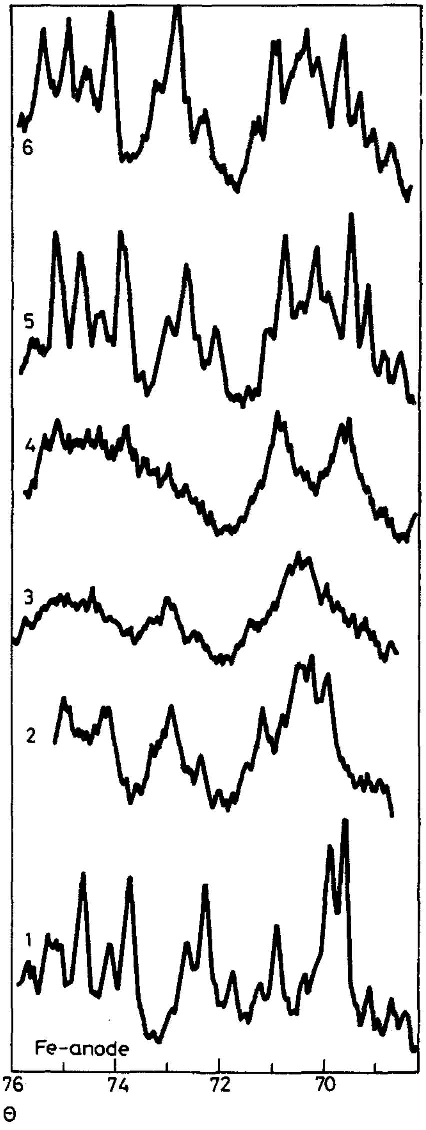

Fig. 1 X-ray diffraction patterns in the range of angles 68-76°. 1 - starting sample of HFA; 2 - HFA, heated up to 1300°C; 3 - HFA, heated up to 1500°; 4 - FA starting sample; 5 - FA heated up to 1500°; 6 - FCA starting sample; 7 - FCA heated up to 1500°

Table 2 Apatite lattice parameters in hydroxyfluorapatite starting and various heated samples

Heating		Content of F,	*F/AP molar ratio*	a_o ± 0.001	C_o ± 0.002
Temperature °C	Atmosphere and conditions	%	(RF)	Å	Å
		0.98	0.52	9.407	6.888
1000	air; 10°min	0.98	0.52	9.405	6.887
1300	air; 10°min	0.98	0.52	9.404	6.890
1500	air; 10°min	0.98	0.52	9.395	6.895
1300	air, 4 hours	0.98	0.52	9.400	6.882
1300	H_2O vapour; 4 hours	0.88	0.47	9.410	6.888
1200	$H_2O+HF=80:1$; 3 h.	3.55	1.9	9.372	6.884
1300	$H_2O+HF=25:1$; 4 h.	3.75	2.0	9.369	6.882

From the fluorine content and the RF and apatite values in all studied CL samples (Table 3), it was concluded that in the course of the process HFA transformation into FA takes place to various extents.

Table 3 Apatite and β-$Ca_3(PO_4)_2$ crystal characteristics in samples of * clinker

Clincer	Content, %		F/AP	Apatite		β-$Ca_3(PO_4)_2$	
nom.	AP	F		a_o ± 0.02 Å	C_o ± 0.003 Å	a_o ± 0.002 Å	C_o ± 0.007 Å
1	20.6	0.75	1.93	9.381	6.892	10.367	37.159
2	17.5	0.56	1.70	9.375	6.894	10.373	37.165
3	13.7	0.39	1.51	9.369	6.894	10.367	37.144
4	17.3	0.50	1.53	9.380	6.897	10.355	37.101

* the maximum temperature in rotary kiln was 1500-1600°C, H_2O and HF molar ratio in fuel gas was 67:1

The first liquid phase forms in CL-s at 1200-1250°, and the second at 1400-1470° (Fig. 2). For the determination of the effect of the melt of fluorine migration between phases, mixtures of HFA with Mg-containing β-$Ca_3(PO_4)_2$ were heated in the standard crucible. The thermograms of the studied mixtures (Fig. 3) show that $(Ca, Mg)_3(PO_4)_2$ presents a solid solution of three or more phosphates, one of which melts at 1390° and another at 1485°. Decomposition of HFA was found to take place (Table 4) at all temperatures. The main fluorine content remains in the CL and passes over into the HFA structure (RF changes from 0.52 to 1.82 and Q_o from 9.404 to 9.380-9.391 Å). At the same time, with the elevation of the temperature and the decomposition of the apatite, the magnesium content decreases in the $(Ca,Mg)_3(PO_4)_2$ formed.

The solid-state HFA decomposition was studied by heating HFA-$Ca_2P_2O_7$ mixtures at 1150° (the $Ca_2P_2O_7$ melting temperature is 1350°). The

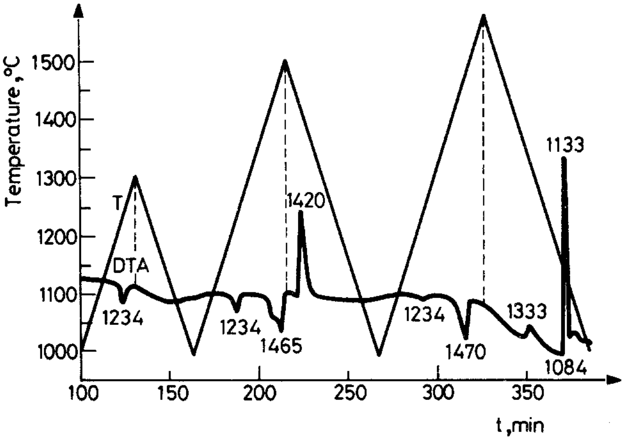

Fig. 2 Thermal curves of clinker, which contains P_2O_5–40.2, CaO–45.2 and MgO–4.6 %

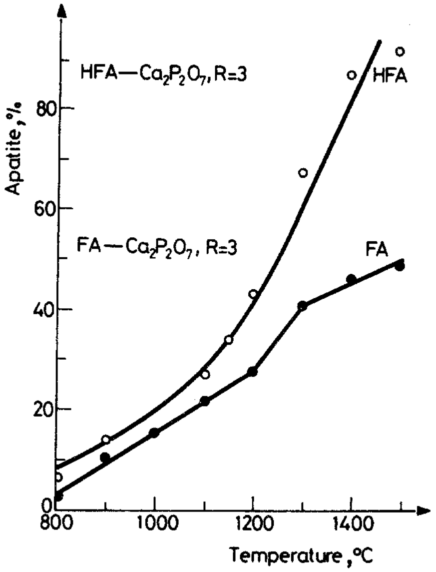

Fig. 3 DTA curve of mixture HFA with (Ca, Mg)$_3$(PO$_4$)$_2$, MgO content is 8 %, in mass ratio 1:1

results in Table 5 reveal that the reaction proceeds in an analogous way as in the liquid phase. The HFA reaction speeds up over 1200°. This phenomenon can be explained by the appearance of structural differences between HFA and FA at high temperatures (Fig. 1).

Table 4 Apatite and β-$Ca_3(PO_4)_2$ crystal characteristics in various heated hydroxyfluorapatite and calcium-magnesium phosphate (8 % MgO) mixtures (1:1 by mass)

Heating temp. °C	Content, % AP	F	FA/P	Apatite a_o ± 0.03 Å	C_o ± 0.003 Å	β-$Ca_3(PO_4)_2$ a_o ± 0.002 Å	C_o ± 0.009 Å
1100	26.2	0.41	0.83	9.387	6.883	10.322	37.250
1200	19.8	0.45	1.21	9.390	6.880	10.332	37.094
1300	15.1	0.45	1.58	9.380	6.887	10.344	37.093
1400	13.1	0.45	1.82	9.391	6.882	10.354	37.102

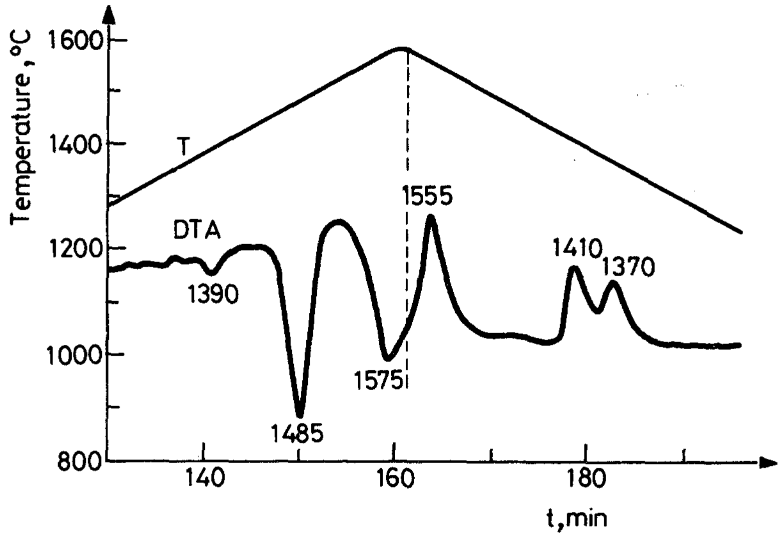

Fig. 4 Decomposition dependence of HFA and FA by $Ca_2P_2O_7$ from temperature

Thus, it was found that the reason for getting a nondefluorinated product is the formation of too large an amount of FA, which reacts at a much lower rate than HFA. The chemistry of the thermal process described [1, 2, 3, 5] did not give any conclusive evidence. HFA decomposes by a reaction with Ca-Mg-phosphates in the solid state and by interaction with liquid CL.

Apatite decomposition is not accompained by fluorine evaporation; it merely creates the main precondition for fluorine evolution from CL.

Table 5 Apatite and β-$Ca_3(PO_4)_2$ crystal characteristics in heated hydroxyfluorapatite and $Ca_2P_2O_7$ mixtures at temperature 1150°C

Heating temp.	Content, %		FP/A	Apatite		β-$Ca_3(PO_4)_2$	
°C	AP	F		$a_o \pm 0.002$ Å	$C_o \pm 0.003$ Å	$a_o \pm 0.002$ Å	$C_o \pm 0.015$ Å
30	38.2	0.64 0.64	0.89	9.397	6.888	10.403	37.360
60	28.0	1.21	1.21	9.386	6.886	10.424	37.374
120	24.7	0.53	1.14	9.380	6.885	10.418	37.383

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Zusammenfassung — Es wurde der Reaktionsmechanismus des hydrothermischen Sinterverfahrens von Hydroxyfluorapatit (HFA) untersucht. Proben aus einem Industriedrehofen und aus dem Labor wurden mittels Thermo-, röntgenographischer und chemischer Analyse untersucht. Es wurde gefunden, daß HFA durch eine Feststoffreaktion mit Ca-Mg-Phosphaten und mittels einer Wechselwirkung mit geschmolzener Schlacke zerfällt. Die Zersetzung von Apatit wird von keiner Abdampfung von Fluor begleitet; es schafft lediglich die Hauptvoraussetzung für die Freisetzung von Fluor aus Schlacke.