BINDING OF SO_2 BY SYNTHETIC SUBSTITUTED APATITES

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Abstract

The reaction of SO_2 with synthetic apatites was studied by TG, XRD and IR analyses at 400–1000°C. Due to an interaction of apatite with SO_2, destruction of apatite and formation of $CaSO_4$ and diphosphate up to 750°C takes place. The further calcination leads to the formation of β-$Ca_3(PO_4)_2$ and a part of the SO_2 bound is lost again. The amount of SO_2 bound with apatite at calcination depends on the substitutions ($F^- \leftrightarrow OH^-$, $PO_4^{3-} \leftrightarrow CO_3^{2-}$, $Ca^{2+} \leftrightarrow Mg^{2+}$) in its structure.

Keywords: IR, sulphur oxide binding, synthetic substituted apatite, thermal analysis, XRD

Introduction

Calcination of phosphate rocks has been suggested for enrichment of the ore. During calcination of phosphate rocks sulphur containing admixtures (pyrite, organic matter etc.) decompose and gaseous sulphur and sulphur oxides evolve beside the decomposition of the accompanying carbonates (calcite, dolomite) [1, 2].

The main mineral of phosphate rocks – apatite (Ap) with a general formula $Ca_{10}(PO_4)_6F_2$ – may have several substitutions in the structure. The most common substitutions in the natural Aps are Mg^{2+} and Na^+ for Ca^{2+}, CO_3^{2-} for PO_4^{3-} and OH^- for F^- [3]. The reactivity of Ap depends on the substitutions in its structure. The main substituents that make the structure weaker are carbonate and magnesium. Fluorine, on the contrary, increases the stability of the structure and decreases the reactivity of Ap [3]. Formation of sulphate as well as sulphide-containing Aps was established by synthesis [3–6]. The sulphide in the Ap structure oxidises at 600–700°C and formation of $Ca_{10}(PO_4)_6SO_4$ takes place. The sulphate-substituted Ap is also very unstable and decomposes above 700°C [5]. Interactions of Estonian phosphorites with the products of thermal decomposition of pyrite have been studied and introduction of sulphur into the Ap structure was assumed [7].

The aim of our study was to examine the influence of Mg^{2+}, CO_3^{2-} and F^- substitutions in the apatite structure on the binding of sulphur dioxide with apatite on calcination.
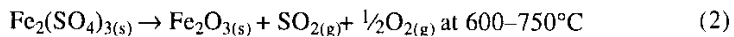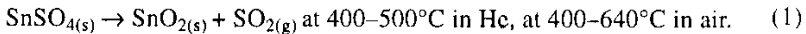
Materials

The Aps were synthesized by the wet method described in [8] and identified by IR and XRD analyses as B-type carbonateapatites (CO_3^{2-} substituted for PO_4^{3-}). The

chemical composition of the samples can be expressed with the formulas given in Table 1. The Aps differ in the substitution in the cation site as well as in CO_3/PO_4 and F/OH mole ratio.

Thermal transformations in the precipitated Aps were studied by FTIR-TG and thermogaschromatography analysis [8, 9]. H_2O is released stepwise below 550°C. The amount of CO_2 lost below 500°C is about 0.5% from the Ap mass. The tempera ture of CO_2 evolvement above 500°C depends strongly on the content of Mg^{2+} and CO_3^{2-} in the sample. The characteristic temperatures of the evolvement of H_2O and of the main amount of CO_2 are given in Table 1.

As a source of sulphur oxide, $SnSO_4$ and $Fe_2(SO_4)_3$ of analytical grade were used. Decomposition of the sulphates occurs by the following reactions:

$$SnSO_{4(s)} \rightarrow SnO_{2(s)} + SO_{2(g)} \text{ at } 400\text{--}500°C \text{ in He, at } 400\text{--}640°C \text{ in air.} \quad (1)$$

$$Fe_2(SO_4)_{3(s)} \rightarrow Fe_2O_{3(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \text{ at } 600\text{--}750°C \quad (2)$$

Experiment

The TG method used in the study of sulphur dioxide binding with an internal source of SO_2 was described in [10]. Three runs under the same conditions were performed: 1. apatite alone; 2. sulphate alone and 3. the two together. The amount of SO_2 bound is described approximately by curve 4 (Δm) that exhibits the difference between the summarised mass loss of Ap and sulphate (1+2, respectively, to their mass ratios in the mixture) and the real mass loss from the third run (Fig. 1).

As at temperatures above 650°C SO_3^{2-} is completely oxidized to SO_4^{2-} in air by the reaction (3), the calculations are performed with a presumption that SO_3 was bound.
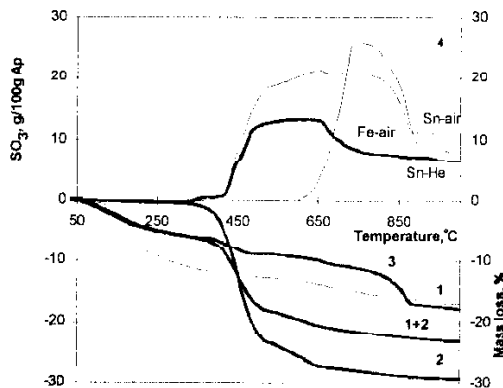
**Fig. 1** Thermogravimetric curves: 1 – apatite EM1; 2 – $SnSO_4$ in air; 3 – $SnSO_4$ + (Al_2O_3) + EM1 in layers in air; 1+2 – calculated curve (decomposition without interaction); 4 – Δm – calculated difference in masses of curves 3 and 1+2

Table 1 Chemical composition and thermal characteristics of the apatites

Sample	Formula	H$_2$O evolvement T_{end}/°C	CO$_2$ evolvement T_{start}/°C	character
AO	$Ca_{9.81}\square_{1.19}(PO_4)_{5.98}(CO_3)_{0.02}(OH)_{1.640}\square_{0.36}$			
C1	$Ca_{9.65}\square_{0.35}(PO_4)_{5.29}(CO_3)_{0.71}(OH)_2 \cdot 2.2H_2O$	450	570	continuous
C2	$Ca_{9.86}\square_{0.14}(PO_4)_{5.72}(CO_3)_{0.28}F_{0.50}(OH)_{1.50} \cdot 1.71H_2O$	550	570	continuous
C3	$Ca_{9.86}\square_{0.14}(PO_4)_{5.72}(CO_3)_{0.28}F_{0.89}(OH)_{1.11} \cdot 1.53H_2O$	550	700	continuous
C4	$Ca_{9.46}\square_{1.54}(PO_4)_{5.37}(CO_3)_{0.63}F_{1.56}\square_{1.44} \cdot 1.70H_2O$	520	520	max at 820
E4	$Ca_{9.33}\square_{0.67}(PO_4)_{4.85}(CO_3)_{1.05}F_{1.69}(OH)_{0.31} \cdot 1.44H_2O + 0.34\,CaCO_3$	440	580	max at 757, 885
EM1	$Ca_{7.13}Mg_{1.33}\square_{1.54}(PO_4)_{2.91}(HPO_4)_{1.98}(CO_3)_{1.11}(OH)_2 \cdot 6.67H_2O$	550	450	max at 690
EM4	$Ca_{7.82}Mg_{1.62}\square_{1.56}(PO_4)_{4.81}(CO_3)_{1.12}F_{1.59}(OH)_{0.4} \cdot 6.84H_2O$	450	450	max at 660

$\square$ vacancies in the formula

$$CaSO_{3(s)} + \frac{1}{2}O_{2(g)} \rightarrow CaSO_{4(s)} \tag{3}$$
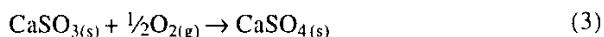
The experiments were carried out with MOM (Hungary) and SETARAM (France) equipment at a heating rate of 5 deg min^{-1} in an air and He atmosphere. The mass ratio of the materials was ~56 mg of SO_2 evolved from sulphate per 100 mg of Ap (100 or 15 mg of Ap. respectively. on equipment).

IR spectra were obtained on a Carl Zeiss Jena IR 75 Spectrometer using the KBr pellets.

X-ray diffraction analysis was carried out with a DRON-4 Diffractometer using CuK$_\alpha$ radiation at 40 kV, 20 mA. The samples were scanned in the range of 8–60° with a step size 0.04°.

Results and discussion

Thermal analysis

The curves of the mass change (Δm) show that an increase in Δm begins with the beginning of decomposition of sulphate (Figs 1 and 2). In the experiments with $SnSO_4$ the mass loss of CaAps (C1, C4) is higher than of Ap alone in the temperature range 380–450°C. From the precipitated apatites water evolves at temperatures up to 450–550°C (Table 1). Therefore, an assumption could be made that volatilization of water is accelerated as a result of interaction of Ap with SO_2. From 450°C up to the end of decomposition of $SnSO_4$ (~650°C) Δm increases. The increase in the mass is higher in the air than in the He atmosphere as a result of oxidation of sulphites (Fig. 1). After 650°C slow mass loss begins, the course of which depends on the composition of the apatite.

In the experiments with $Fe_2(SO_4)_3$ (Fig. 1) Δm has the maximum value at 720–730°C. By the data of IR analysis evolvement of CO_2 under the effect of SO_2 was accelerated and occurs at lower temperatures. Therefore, the calculated amounts of the SO_3 bound are not exact. However, since the amount of CO_2 constitutes about 10% from the mass increase in the experiments with CaAps, and 20% on an average with Mg substituted Aps, the calculated amounts of the SO_3 bound could be used for caracterization of apatites.

The amount of SO_3 bound by an Ap at 400–600°C is smaller than the amount bound at 600–700°C, and reaching from 15.8 to 27.7 g per 100 g Ap at 750° and from 4.0 to 12.7 g at 1000°C (Table 2), depending on the sample. The degree of the SO_3 bound decreases with an increase in the fluorine content and increases with an increase in the carbonate content in the Ap structure at 750°C. At 1000°C fluorine has no remarkable effect on the amount of the SO_2 bound but the latter increases with an increase in the CO_3/PO_4 mole ratio in CaAp.

Mg substitution in the structure of Ap accelerates the sorption of SO_2 up to 750°C and its evolvement at higher temperatures similarly to the results obtained in the experiments with dolomite [11]. Promotion of the evolvement of SO_2 at lower temperatures could be a result of decomposition of $MgSO_4$ above 800–850°C, as the decomposition of $CaSO_4$ begins above 1200°C.

Table 2 The amount of SO_3 bound by apatite (g/100 g Ap) in air

Sample		A0	C1	C2	C3	C4	E4	EM1	EM4
Mole ratio	$(Ca+Mg)/P$	1.64	1.82	1.72	1.72	1.76	1.99	1.73	1.94
	CO_3/PO_4	0.004	0.135	0.049	0.049	0.117	0.285	0.227	0.230
	$(Ca+Mg):(P+C)$	1.63	1.61	1.64	1.64	1.58	1.69	1.41	1.58
Experiment									
With SnSO₄	at 750°C								
	SO_3		11.2			7.1		14.8	
Mole ratio	SO_3/CO_2		2.00			1.40		1.55	
	$(Ca+Mg)/P$		1.68			1.67		1.55	
	at 1000°C								
	SO_3		8.4			5.7		67	
Mole ratio	SO_3/CO_2		1.5			1.1		07	
	$(Ca+Mg)/P$		1.72			1.69		1.65	
With Fe₂(SO₄)₃	at 750°C								
	SO_3	26.7	27.7	22.0	20.5	15.8	19.0	26.0	25.3
Mole ratio	SO_3/CO_2	146.9	4.9	10.1	9.4	3.1	1.7	2.7	2.8
	$(Ca+Mg)/P$	1.31	1.48	1.45	1.47	1.56	1.75	1.41	1.62
	at 1000°C								
	SO_3	4.0	10.7	5.7	5.5	5.2	12.7	8.2	12.7
Mole ratio	SO_3/CO_2	22.0	1.9	2.6	2.5	1.0	1.1	0.9	1.4
	$(Ca+Mg)/P$	1.59	1.69	1.65	1.65	1.70	1.83	1.63	1.78

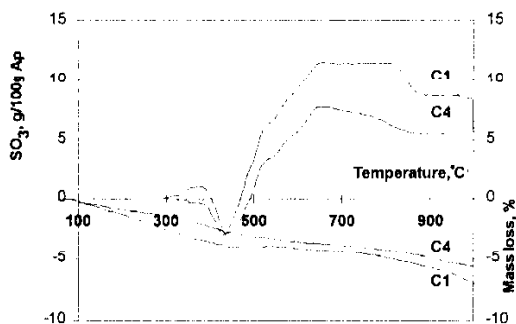**Fig. 2** TG and Δm curves for the samples C1 and C4 from the experiments with $SnSO_4$

The number of SO_3 moles bound exceeds the number of CO_2 moles in the Ap structure (Table 2). As a result of SO_2 binding and sulphate formation in the system, a part of the Ca^{2+} ions are lost from the phosphate. Therefore, in the samples with a low fluorine content (F/OH<0.8) the calculated mole ratio Cat/P decreases to less than 1.5 at temperatures up to 750°C. In $Ca_3(PO_4)_2$ the mole ratio of Ca/P=1.5, therefore formation of condensed phosphates is possible. Due to the partial loss of the bound SO_2 on calcination up to 1000°C, the value of the Cat/P ratio is restored up to 1.59–1.69, but it remains lower than the value in stoichiometric Ap - 1.67. The latter indicates the possibility of formation of $Ca_3(PO_4)_2$.

IR spectroscopy

In the spectra of HCAp after sorption of SO_2 at 400–600°C in air and calcination up to 650 and 750°C all the bands characteristic of carbonate Ap are retained [3]. Besides, weak bands at 635 and 670 cm^{-1} are observed, and the strong peak at 1000–1100 cm^{-1} is wider than the Ap peak is (Fig. 3a). The v_2 mode bands in the interval 500–400 cm^{-1} are shifted and stronger. These changes in the spectra could be caused by the v_3 and v_4 vibrations of SO_4^{2-} group bound to Ca [12] and the disordering of the Ap structure. The spectra of the samples used for sorption of SO_2 at 600–700°C and calcined up to 750°C differ in that the CO_3^{2-} bands at 1400–1500 cm^{-1} are absent and the bands characteristic for β-$Ca_2P_2O_7$ at 930–1010, 720 and 530 cm^{-1} appear. At the same time the SO_4^{2-} bands are also more intensive (Fig. 3a).

In the spectra of the samples calcined up to 1000°C the bands of HCAp disappeared (Fig. 3b). The peaks of SO_4^{2-} and β-$Ca_3(PO_4)_2$ (at 980–1100 and 545–605 cm^{-1}) are observed, though the relative intensities of SO_4^{2-} bands are decreased.

The changes in the spectra of HFCAp at sorption of SO_2 and calcination are analogous to the changes described above. Whereas fluorine makes apatite structure more resistant, the quantity of SO_3 bound is lower (Table 2) and, accordingly, the bands of SO_4^{2-} and $P_2O_7^{2-}$ are weaker. Existence of FAp at 1000°C is also observed.

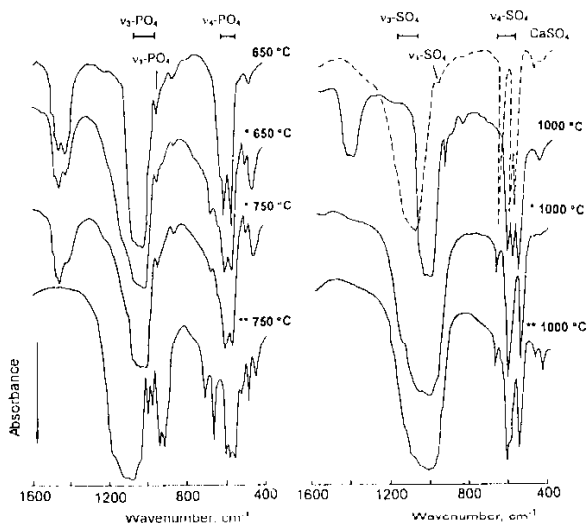**Fig. 3** IR spectra of sample C1 calcined up to given temperature: * – SO_2 bound at 400–600°C; ** – SO_2 bound at 600–700°C

XRD analysis

In the samples calcined up to 750°C, after SO_2 binding, inherence of $CaSO_4$, diphosphate ($Ca_2P_2O_7$ or $CaMgP_2O_7$) and HFAp or traces of HAp are identified. In the spectra of the samples calcined up to 1000°C the peaks of diphosphate and HAp disappear and the peaks of β $Ca_3(PO_4)_2$ [($Ca,Mg)_3(PO_4)_2$ with Mg substituted Aps] appear. Substitution of SO_4^{2-} ions into the Ap structure in the mixture of phases was not established.

Conclusions

Due to an interaction of apatite with SO_3, destruction of apatite, primarily of HCAps, and formation of $CaSO_4$ and diphosphate up to 750°C take place. The further calcination leads to reaction between diphosphate and $CaSO_4$ and to the formation of β-$Ca_3(PO_4)_2$ (of ($Ca,Mg)_3(PO_4)_2$ with Mg substituted Aps) and a part of the SO_2 bound is lost again.

The amount of SO_3 bound with apatite at calcination depends on the substitutions in its structure. The amount of SO_2 bound is bigger when the content of CO_3^{2-} is higher and the content of F^- ions in the apatite structure is lower. The content of SO_4^{2-} ions remaining at 1000°C does not depend on the fluorine content, although it is higher with a higher CO_3^{2-} content in the apatite. The evolvement of SO_2 from magnesium-substituted apatites proceeds more extensively.

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References

1 T. Kaljuvee, R. Kuusik and M. Veiderma, Int. J. Miner. Process, 43 (1995) 113.
2 R. Knubovets, Y. Nathan, S. Shoval and J. Rabinowitz, J. Thermal Anal., 50 (1997) 229.
3 J. C. Elliot, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates (1st Edn), Elsevier, Amsterdam 1994, p. 389.
4 J. C. Trombe and G. Montel, Ann. Chim. Fr., 5 (1980) 443.
5 J. C. Trombe, J. Szilagyi and G. Montel, C. R. Acad. Sci. Paris, 283 (1976) 199.
6 M. C. Apella and E. J. Baran, Z. Naturforsch., 34 b (1979) 1124.
7 M. E. Põldme, J. H. Põldme, K. R. Utsal and J. E. Kirs, Zh. Neorgan. Khim., 30 (1985) 877. (In Russian)
8 K. Tõnsuaadu, M. Peld, T. Leskelä, R. Mannonen, L. Niinistö and M. Veiderma, Thermochim. Acta, 256 (1995) 55.
9 M. Koel, M. Kudrjashova, K. Tõnsuaadu and M. Veiderma, J. Chromatography, 819 (1998) 75.
10 R. Kuusik and A. Trikkel, J. Thermal Anal., 44 (1995) 111.
11 T. Kaljuvee, A. Trikkel and R. Kuusik, Proc. Estonian Acad. Sci. Chem., 43 (1994) 146.
12 R. A. Nyquist, C. L. Putzig and M. A. Leugers, Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts, I. Academic Press, USA 1996, p. 107.