Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 655–658

MONITORING OF THE EVOLVED GASES IN APATITE–AMMONIUM SULFATE THERMAL REACTIONS

Kaia Tõnsuaadu[1*], *J. Pelt*[2] *and Maria Borissova*[1]

[1]Tallinn University of Technology, 19086 Tallinn
[2]Tartu Observatory 61602 Tõravere, Estonia

Thermal reactions in natural fluorapatite or fluorcarbonate apatite and ammonium sulfate mixtures with mole ratio 1:4 at calcination up to 500°C were studied by simultaneous thermogravimetry and FTIR analysis of the evolved gases. The composition of natural apatite has little impact on the release of NH_3. Upon the evolution of NH_3 nitrous oxides were found in minor amounts. The release of SO_2 at temperatures above 400°C is more intensive and occurs at lower temperatures in the case of fluorapatite than of carbonate containing apatites. Evolution of CO_2 starts at 250°C with maximum at 350–360ºC.

Keywords: *apatite, CO_2, evolved gas analysis, FTIR, NH_3, $(NH_4)_2SO_4$, N_2O, SO_2*

Introduction

Thermal reactions in the mixture of apatite and ammonium sulfate (AS) have been studied since the early 1960s, with the main focus on the composition of solid product. It has been established that at calcination of apatite – AS mixture several simultaneous reactions take place that lead to the evolvement of NH_3, H_2O, SO_2, HF, and nitrous oxides [1–5].

Starting at 220°C, decomposition of $(NH_4)_2SO_4$ and a reaction between apatite and the products of $(NH_4)_2SO_4$ decomposition takes place resulting in NH_3, HF and H_2O release and the formation of calcium polyphosphate, $Ca_2(NH_4)_2(SO_4)_3$ and $CaSO_4$. In the temperature interval 290–450°C $Ca_2(NH_4)_2(SO_4)_3$ could react with calcium polyphosphate forming $CaNH_4P_3O_9$, or decomposition could take place (1)

$$Ca_2(NH_4)_2(SO_4)_3 \rightarrow 2CaSO_4 + 2NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \tag{1}$$

Also the simultaneous reaction of SO_3 decomposition (2) [6] takes place

$$SO_3 \rightarrow SO_2 + 1/2O_2 \tag{2}$$

Calcination of the mixture above 350°C causes decomposition of $CaNH_4P_3O_9$ resulting in a decrease in the content of water-soluble phosphorus and a release of NH_3 and SO_2 by the reactions (3) and (2):

$$2CaNH_4P_3O_9 + CaSO_4 \rightarrow 3Ca(PO_3)_2 + SO_3\uparrow + 2NH_3\uparrow + H_2O\uparrow \tag{3}$$

The reactivity of apatite is strongly influenced by its structural properties and the composition of the impurity minerals in natural apatite [7, 8]. Carbonate apatites decompose more readily at thermal treatment and then CO_2 is added to the evolved gases.

In our study the evolvement of gases during apatite – AS thermal interaction at temperatures up to 500ºC was investigated by means of coupled TG/DTA-FTIR analysis. AS reaction with natural Kola (Russia) and Sokli (Finland) fluorapatites, Kabala (Estonia) phosphorite (fluorcarbonate-apatite) and synthetic fluorapatite was studied.

Experimental

The composition of the natural apatite concentrates and the synthetic fluorapatite (FAp) used in the experiments is given in Table 1. In Kola apatite the main impurity is nepheline, while in Sokli apatite it is iron silicates and carbonates, and in Kabala apatite calcite and quartz. The chemical composition of apatites was determined by the standard methods of chemical analyses and the specific surface area (SSA) by BET method.

The $(NH_4)_2SO_4$ used was a chemical pure grade (NH_3 – 25.76; SO_3 – 60.61%). The mole ratio in the apatite – $(NH_4)_2SO_4$ mixtures was 1:4. The mixtures of apatite and $(NH_4)_2SO_4$ were mixed in an agate ball mill for 30 min.

The thermal analysis experiments were performed in the airflow 50 mL min^{-1} at the heating rate 10 K min^{-1} in a corundum crucible with Setaram LabSys 2000 equipment. The on-line gas composition was monitored using FTIR gas analyser (Interspectrum). The Ranger-AlP Gas cell S/N 23790 (Re-

---

[*] Author for correspondence: kaiat@staff.ttu.ee

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Chemical composition and specific surface area of apatites

Apatite	P_2O_5/%	CaO/%	MgO/%	CO_2/%	F/%	Fe_2O_3/%	SiO_2/%	SSA/m g^{-1}
Fluorapatite	56.03	46.40	0	0	3.00	0	0	1.00
Kola	39.27	52.32	0.12	0.06	2.96	0.60	1.53	0.57
Sokli	38.00	53.45	0.31	1.80	2.70	2.21	0.14	1.49
Kabala	30.57	45.27	1.56	5.54	2.27	1.58	11.35	4.94

flex Analytical Co.) with 8.8 m path length was maintained at temperature 150ºC. Spectra were recorded in the 600–4000 cm^{-1} region with a resolution of 4 cm^{-1} as 4 scan averages. The sample mass was about 20 mg.

The gases evolved were identified by using characteristic infrared absorption wavelengths: for NH_3 at 930 and 963 cm^{-1}, SO_2 at 1345 and 1378 cm^{-1}, H_2O 1520, 1700 and 3855 cm^{-1}, CO_2 at 2359 and 669 cm^{-1} and N_2O at 2358 and 2242 cm^{-1} [9, 10]. As the spectra of the components of the gas mixture partially overlap, the less overlapped regions were chosen for the analysis of the evolvement of the components (Fig. 1). The profiles of evolvement of gases were obtained as temperature derivatives of the peak area integrated above the baseline from 900 to 984 cm^{-1} for NH_3, from 1309 to 1400 cm^{-1} for SO_2, from 2260 to 2406 cm^{-1} for CO_2 and from 2141 to 2286 cm^{-1} for N_2O. The shape of the SO_2 evolvement profile is slightly affected by releasing water. The high noise level in the water vapor spectrum and its overlapping with the NH_3 and SO_2 spectra makes the monitoring of the release of water useless. HF was not identified. Condensation of NH_4F in a cooler part of the furnace (<150°C) of the thermal analyzer could also take place.

Results and discussion

$(NH_4)_2SO_4$ thermal decomposition occurs mainly in two steps. The first step with maximum at 330°C was assigned to the loss of NH_3 and the second one at 420°C to the decomposition of the $(NH_4)HSO_4$ or H_2SO_4 formed, with release of NH_3, SO_2 and H_2O [4, 5, 11]. Remarkable thermal changes do not take place in studied apatites at temperatures up to 500°C.

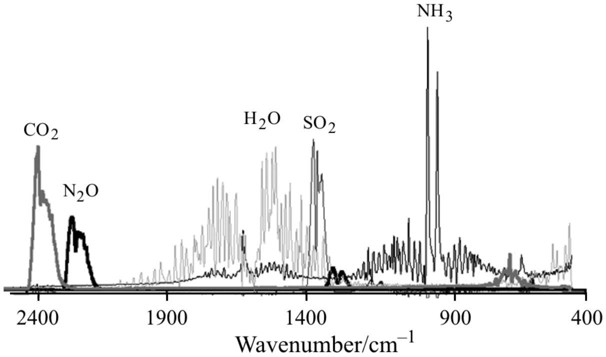

Fig. 1 Standard FTIR spectra of NH_3, H_2O, SO_2, N_2O and CO_2 [8]

TG-DTG and DTA curves (Fig. 2) of the apatite-AS mixtures as well as the curves of gas evolution reveal the differences of the apatites nature. The mass loss starts at calcination at 220–240°C and occurs at the highest speed mainly at 310–320 and 415–440°C in the mixtures studied. In the mixtures with apatites with a higher content of impurities, particularly carbonates (Kabala and Sokli) (Table 1) an additional relatively intensive mass loss area is observed at 350–400°C. Therefore, the total mass loss of these mixtures is up to 5–10% higher.

The evolved NH_3 profile shows the release of NH_3 in two steps (Fig. 3). The largest part of NH_3 evolves in the temperature interval of 230–320°C that corresponds to the first mass loss step – to AS decomposition [4]. The second maximum occurs in the interval of 320–400°C for natural apatites and at about 40°C higher temperature for synthetic FAp. Therefore, the impurities lower the temperature of NH_3 re-

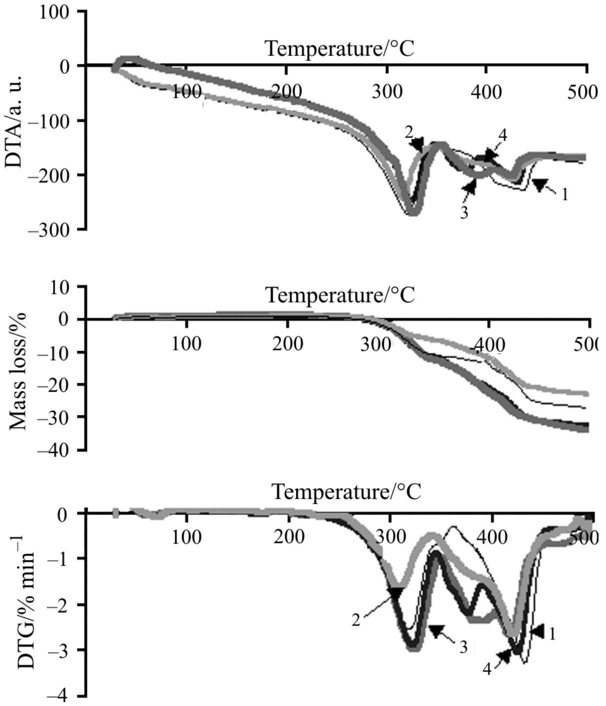

Fig. 2 Thermoanalytical curves of apatite – AS (mole ratio 1:4) mixtures. Heating rate 10 K min^{-1}, air flow 50 mL min^{-1}; 1 – FAp+AS; 2 – Kola+AS; 3 – Sokli+AS; 4 – Kabala+AS

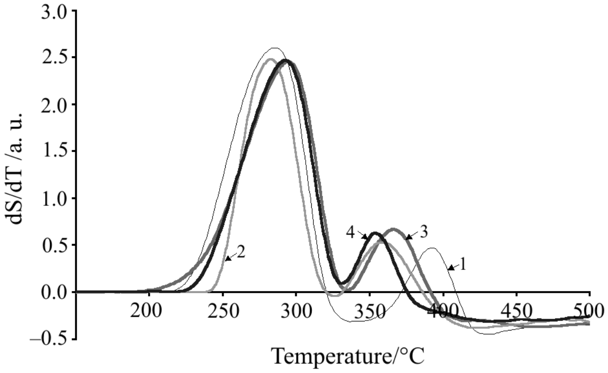

Fig. 3 Profile of evolved NH_3 from apatite+AS mixtures (mole ratio 1:4). Heating rate 10 K min^{-1}, air flow 50 mL min^{-1}; 1 – FAp+AS; 2 – Kola+AS; 3 – Sokli+AS; 4 – Kabala+AS

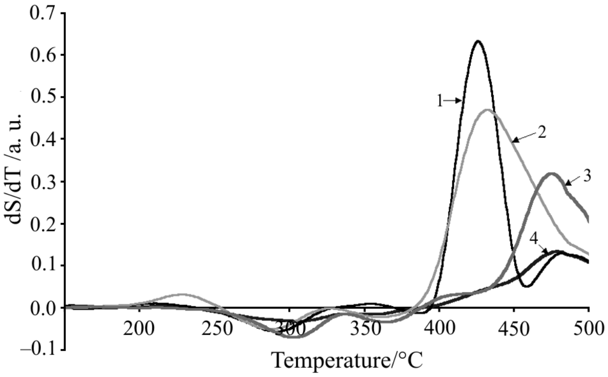

Fig. 4 Profile of evolved SO_2 from apatite+AS mixtures (mole ratio 1:4). Heating rate 10 K min^{-1}, air flow 50 mL min^{-1}; 1 – FAp+AS; 2 – Kola+AS; 3 – Sokli+AS; 4 – Kabala+AS

lease from the products of the reaction between apatite and AS.

More remarkable differences were found in SO_2 profiles for different apatites (Fig. 4). The release of SO_2 takes place with maxima at 430–435 and 480°C in the mixture with pure fluorapatites. For carbonate containing samples (with Sokli and Kabala apatites) the temperature of SO_2 release is at about 40°C higher. The shift of the temperature of SO_2 evolution in the mixtures of natural apatites is also attributed to the influence of the impurities in natural apatite concentrates. Due to the reactions with impurities the other phosphates could form [1, 12]. In the mixture with Kabala calcined up to 330°C, in addition to $CaNH_4P_3O_9$, the presence of $MgNH_4P_3O_9$ and $FeNH_4P_2O_7$ were established by XRD analysis.

The temperature of SO_2 release coincides with the third mass loss step that should correspond to the reaction (3) but no release of NH_3 was detected. On the contrary, the content of NH_3 decreases in the gas phase, beginning at 400°C when the content of SO_2 increases. This could be explained with the condensation, in a cooler part of furnace before IR analyzer, of AS formed as a result of the secondary reaction in the gas phase. For the same reason, no evolution of SO_2 was observed at temperatures below 400°C when the amount of NH_3 released exceeded the amount of SO_2 needed for the formation of AS in the gas phase.

Another explanation for an intensive release of SO_2 above 400°C is that a reaction between calcium polyphosphate and calcium sulfate could also occur.

The detection limit of the gas cell allowed monitor the release of CO_2 only in case of Kabala apatite where the content of CO_2 was 5.54%. In case of Sokli apatite the noise level was identical to the signal magnitude. The release of CO_2 was established in the temperature interval of 250–380°C, with two maximums (Fig. 5). The first maximum at 300°C corresponds to the first mass loss step and could be the result of calcite decomposition. The second maximum at 340°C could be related to carbonate-apatite decomposition.

In addition to the expected components of the gas phase, nitrogen oxides were also detected in the case of mixtures with FAp and Kola apatite (Fig. 6). The highest content of N_2O was observed above 390°C when the emission of SO_2 was the highest. The emergence of nitrous oxides could be a result of the secondary reaction in the gas phase. The oxidation of NH_3 could occur when the SO_3 released decomposes into SO_2 and O.

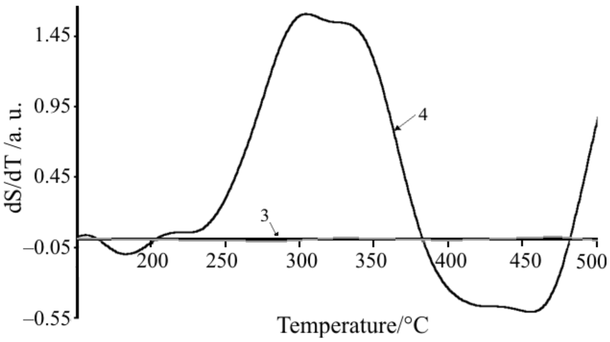

Fig. 5 Profile of CO_2 evolvement from apatite+AS mixtures (mole ratio 1:4). Heating rate 10 K min^{-1}, air flow 50 mL min^{-1}; 3 – Sokli+AS; 4 – Kabala+AS

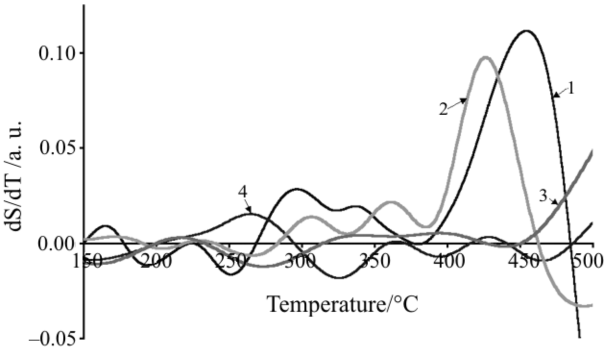

Fig. 6 Profile of N_2O evolvement from apatite+AS mixtures (mole ratio 1:4). Heating rate 10 K min^{-1}, air flow 50 mL min^{-1}; 1 – FAp+AS; 2 – Kola+AS; 3 – Sokli+AS; 4 – Kabala+AS

Conclusions

The composition of natural apatite has little impact on the release of NH_3. Minor amounts of nitrous oxides were detected simultaneously with the evolvement of NH_3 due to the oxidation reaction of NH_3. The release of SO_2 at temperatures above 400°C is more intensive and occurs at lower temperatures in the case of fluorapatite than that of carbonate containing apatites. The evolvement of CO_2 starts at 250°C and the maximum occurs at 350–360ºC.

Despite the imperfection of the analytical system, where partial condensation of the products of the reactions, like ammonium sulfate, occurs, monitoring of the evolved gases by FTIR makes it possible to define the thermal reactions in natural apatite – ammonium sulfate mixture more precisely than it is possible in the case of thermal analysis alone.

Acknowledgements

The help provided by M. Einard in carrying out chemical analyses and the support of the Estonian Science Foundation (Grants No. 5648 and 4697) are gratefully acknowledged.

References

1 A. V. Ekshtelis and A. K. Il'yasova, Izvestiya Akademii Nauk Kazakhskoi SSR, Seriya Khimicheskaya, 24 (1974) 5 (in Russian).
2 M. Marraha, M. Heughebaert, J.-C. Heughebaert and G. Bonel, Biomat. Biomechanics, 5 (1983) 445.
3 A. J. E. Welch, Proceedings - International Congress on Phosphorus Compounds, 2nd (Boston, USA, 1980), pp. 363–369.
4 K. Tõnsuaadu, M. Borissova, V. Bender and J. Pelt, Phosphorus, Sufur, Silicon Relat. Elem., 179 (2004) 2395.
5 Y. Pelovski, V. Petkova and I. Dombalov, J. Therm. Anal. Cal., 72 (2003) 967.
6 K. H. Stern and E. L. Weise, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) NSRDS-NBS 7 (1966).
7 J. C. Elliot, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Elsevier, Amsterdam 1994, p. 389.
8 M. Veiderma, Proc. Estonian Acad. Sci. Chem., 49 (2000) 5.
9 NIST/EPA Gas-Phase Infrared Database. www.http://www.nist.gov/srd/nist35.htm.
10 Gases and Vapours Database (code GS), BioRad (Sadtler).
11 M. Statheropoulos and S. A. Kyriakou, Anal. Chim. Acta, 409 (2000) 206.
12 M. Arasheva and I. Dombalov, J. Thermal Anal., 43 (1995) 359.