Journal of Thermal Analysis, Vol. 25 (1982) 117–125

A THERMAL STUDY OF THE PRECIPITATES FORMED IN AMMONIA NEUTRALIZATION OF ACIDIC SOLUTIONS OF DISSOLVED PHLOGOPITE

E. AITTA, L.H.J. LAJUNEN AND M. LESKELÄ*

Department of Chemistry, University of Oulu, SF-90570 Oulu 57, Finland

**Also at the Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland*

The precipitates containing mainly iron, aluminium and magnesium hydroxides, obtained from phlogopite dissolved in nitric acid by means of the neutralization procedure with ammonia, have been investigated by thermal analysis (TG, DTG and DTA). According to the present study, which is part of a larger investigation into the chemical utilization of Finnish mica minerals, the formation of solid solutions between iron and aluminium hydroxides in silt increases with an increasing neutralization temperature. Nitrogen exists mainly in the form of nitrate in silts, and magnesium forms mixed hydroxides with aluminium, which causes a separation between the iron hydroxide and magnesium aluminium hydroxide phases.

The present communication deals with the TG, DTG and DTA investigations of hydroxide precipitates containing mainly iron, aluminium and magnesium. The precipitate samples were obtained from phlogopite dissolved in nitric acid by means of the neutralization procedure with ammonia. The aim of the work was to study the effects of the precipitation temperature and the end pH of the neutralization especially on the composition of the coprecipitated nitrogen compounds and the formation of the different phases. The present paper continues our investigations into the factors affecting the chemical utilization of the Finnish mica minerals [1-3].

Different ways of utilizing mica minerals both mechanically and chemically have been investigated during the recent years.

Mica minerals belong to the net silicates, in which crystals are made up of parallel planes and exhibit strong two-dimensional and weak one-dimensional bonding. The net silicates split very easily into scales. One of the most common mica minerals is biotite, $K(Mg,Fe)_3Si_3(Al,Fe)O_{10}(OH,F)_2$. The mica in the biotite group is called phlogopite if the Mg/Fe ratio is greater than 2. Mineralogically, the mica studied here /mica of Siilinjärvi/ can be classified as phlogopite /the Mg/Fe ratio is 5.3/. It appears as mainly brown, shiny flakes less than 1 mm in cross section.

The goal of the chemical utilization of phlogopite is to separate MgO, K_2O, Al_2O_3 and Fe_2O_3 from the SiO_2 and each other, and further to convert the separated substances into marketable products. The potential products include magnesium oxide, aluminium oxide or hydroxide, potassium and magnesium salts /for fertilizers/, and different grades of silica.

The chemical utilization of phlogopite is made possible by the solubility of the cationic elements /Fe, Al, K, Mg/ in strong acids, e.g. nitric and sulfuric acids /only the pure SiO_2 skeleton is insoluble/.

According to our earlier investigations, the composition and filtration properties /e.g. the amounts of the coprecipitated magnesium and nitrogen/ vary significantly under different neutralization conditions. The use of X-ray methods for the investigations of iron and aluminium hydoxide precipitates is not possible, because these precipitates are usually highly amorphous. Hence, thermoanalytical methods were selected for the present work.

EXPERIMENTAL

Materials

The precipitate samples were obtained from earlier studies [1], and they were dried to the constant weight in a desiccator. The test solution was prepared by dissolving mica from Siilinjärvi in nitric acid. The concentrations of iron, aluminium, magnesium and potassium in this test solution were 15.0, 11.0, 30.0 and 19.3 g/dm^3, respectively. In addition, the solution contained fluoride ions 2.2 g/dm^3 and free acid /HNO_3/ 1.9 mol/dm^3.

Neutralization

In each neutralization experiment a 100 cm^3 sample of the stock solution was neutralized in a thermostated apparatus [1]. The desired amount of the neutralizing reagent, 25% aqueous ammonia solution, was added at a constant rate into the solution with a normal titration burette equipped with a peristaltic pump. The basic addition rate in the experiments was 0.5 cm^3/min. At this rate, the effect of the neutralization heat was negligible. At the same time, the slow addition rate improved the filtration rate of the precipitate. The solutions to be precipitated were mixed with a magnetic stirrer at a velocity of 300 rpm. Because the pH in concentrated solutions does not stabilize immediately, the end pH values were measured 10 min after the completion of the base addition. The precipitates were allowed to age for 15 min before filtration.

Methods

TG, DTG and DTA curves were recorded simultaneously in a dynamic air atmosphere (50 cm^3/min) with a Mettler TA-1 Thermoanalyzer. The heating rate was 10 deg/min, sample weight about 30 mg, DTA sensitivity 50 µV and DTG sensitivity 2 mg/min. For the DTA measurements, Al_2O_3 was used as a reference material.

Potassium and magnesium as well as iron and aluminium were determined in the precipitates by conventional atomic absorption spectrometry. In the filtrates, aluminium was analyzed by an indirect atomic absorption method based on iron absorption [4], and iron was analyzed spectrophotometrically by both the o-phenantroline method and the 1-hydroxy-4-sulfo-2-naphthoic acid method [5,6]. The fluoride ion concentrations were determined potentiometrically, using an ion selective fluoride electrode [7]. Total nitrogen was determined at Kemira Oy's Research Laboratory at Oulu, using a nitrogen analyzer. A Pye Unicam SP-900 atomic absorption spectrometer was used for the determinations.

RESULTS AND DISCUSSION

The thermal behaviour of the mixed hydroxide precipitates studied is shown in Fig. 1. The part *a* of the figure shows the DTA and TG curves of the dried mixed hydroxides, when the end pH of the neutralization is 5 and the temperature rises from 40 to 80°. The DTA curves show endoterms at 40-175° and 180-250°.

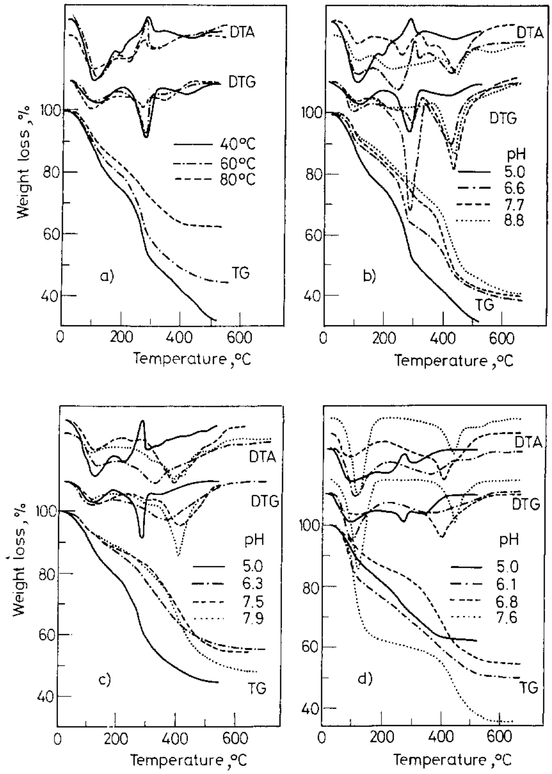

Fig. 1. TG, DTG and DTA curves of the hydroxide precipitates studied. *a* : the end pH of neutralization was 5 and the precipitation temperatures 40, 60 or 80°; *b*, *c* and *d*: the neutralization temperature was either 40 *(b)* 60 *(c)* or 80° *(d)* and the end pH of precipitation varied between 5 and 9.

The former is caused by the adsorbed water and the latter by the constitutional water [8]. The exoterm at 250-305° shows the decomposition of the loosely bound nitrate and perhaps the crystallization of microcrystallized oxides [9]. The maximum of the exoterm shifts towards higher temperature when the amount of magnesium increases in the silt /Table 1/. This indicates the beginning of the formation of magnesium/aluminium hydroxide $[Mg_4Al_2(OH)_{12}](NO_3)_2 \cdot \underline{n}H_2O$ in the silt. Both the pure aluminium hydroxide and the magnesium aluminium hydroxide bind nitrate, but the former binds it more loosely than the latter [10, 11].

Table 1

Composition of silt as a function neutralization temperature and end pH. Metal oxides have been analyzed from silts heated up to 500°. Nitrogen has been analyzed of vacuum dried silts

T, °C ($\pm$2°C)	pH ($\pm$0.05)	Fe_2O_3 %	Al_2O_3 %	MgO %	N %
40	5.0	33.1	33.0	13.5	10.6
"	6.6	26.8	27.8	24.6	10.4
"	7.7	22.0	22.2	38.7	9.9
"	8.8	19.6	20.7	47.3	9.9
60	4.9	42.7	40.1	6.3	6.7
"	6.2	28.7	29.3	30.0	4.6
"	7.5	23.0	23.4	39.3	4.8
"	7.9	21.0	21.0	43.1	6.4
80	4.9	49.0	40.3	1.3	2.45
"	6.1	32.8	31.6	25.5	2.37
"	6.8	24.4	24.1	41.3	2.86
"	7.5	20.0	20.3	50.6	2.47

The loosely bound nitrate in aluminium hydroxide decomposes more easily thermally than the ionically bound nitrate in magnesium aluminium hydroxide. In an earlier study, a microanalysis of the silt granules also showed two phases, of which one contained much more magnesium than the other [2].

There are three distinct regions in the TG curves: region I /40-250°/, region II /250-305°/ and region III /over 305°/. In region I the weight change /%/ diminishes when the neutralization temperature rises, which shows an increase of the solid solution in the silt. In region II the weight change is caused principally by the loosely bound nitrate /Table 2/. The weight changes calculated from the total nitrogen concentration in dried silts agree well with those measured from the TG curves. The development of brown nitrogen dioxide gas is a qualitative support for the result. The TG curves show a slight shift of the weight change towards higher temperatures when the amount of magnesium increases in the silt.

Table 2

Weight change /%/ in the temperature range 250-310°
/calculated and measured/ in Fig. 1(a)

Characteristics of the precipitate			Weight change as loss of NO, %	
T, °C	end pH	N%	$NO_{calc.}$	$NO_{meas.}$
40	5.0	10.6	22.7	22.0
60	4.9	6.7	14.4	14.5
80	"	2.45	5.3	5.5

In region III the appearance of the TG curves changes from the $Al(OH)_3$-type to the FeOOH-type when the neutralization temperature rises, which partly supports the assumption of an increase of the solid solution in the silt [2]. To study the effect of the end pH of the neutralization, a thermal analysis was made on silts precipitated at three different temperatures /40, 60 and 80°/. In connection with it, particularly the exoterm caused by the loosely bound nitrate and the appearance of the TG curves were examined.

Fig. 1b shows the thermal analysis curves of the silts neutralized at 40° with varying end pH values of neutralization. From DTA it can be seen that the amount of bound water diminishes and that of constitutional water increases with increasing end pH. At the same time the exoterm caused by the loosely bound nitrate shifts towards higher temperatures and the highest pH it may even disappear. According to this, the amount of constitutional water increases and the decomposition of loosely bound nitrate is retarded as magnesium increases in the silt.

The TG curves show that the loosely bound nitrate diminishes and its decomposition temperature rises with the increasing magnesium content. At the same time, the appearance of the curves changes gradually from the FeOOH-type to $Al(OH)_3$-type. This indicates a separation between the iron and magnesium/aluminium hydroxide phases.

Fig. 1c shows the effect of the end pH at 60°. The curves behave in much the same way as at 40°. However, there are differences, particularly in the disappearance of loosely bound nitrate, which takes place then at 40°. The shape of the TG curves also changes more clearly with a rising end pH than at the lower temperatures.

Fig. 1d shows the effect of the end pH at 80°. It appears that loosely bound nitrate only exists at an end pH value of 5 /DTA/. However, the TG curves at end pH 6.8 are of the same type, representing the solid solution. The other two curves show the separation between the phases. It seems that the formation of the solid solution between iron and aluminium hydroxide and the decrease of total nitrate in the silt delays the separation between the iron and magnesium/aluminium phases.

CONCLUSION

The results show that the formation of solid solutions between iron and aluminium hydroxides in silt increases with a rising neutralization temperature. Nitrogen exists mainly as nitrate in the silts. Magnesium forms mixed hydroxides with aluminium, which causes a separation between the iron hydroxide and magnesium aluminium hydroxide phases. At the same time, nitrate is bound to the latter phase and its thermal decomposition is retarded.

REFERENCES

1. L.H.J. Lajunen and E. Aitta, Kem.-Kemi, 8/1981/5.
2. E. Aitta, M. Leskelä and L.H.J. Lajunen, Oulun Yliopiston Kem. Laitoksen Raporttisar., 3/1981/8.
3. E. Aitta, M. Leskelä and L.H.J. Lajunen, Kem.-Kemi, 8/1981/411.
4. O. Lindsjö and M. Riekkola, Atomiabsorptionspektrometria, Teknillisten Tieteiden Akatemia, Helsinki, 1976.
5. N.H. Furman /Ed./ Scott's Standard Methods of Chemical Analysis, 6.ed., D. van Nostrand Company, New York 1965.
6. L.H.J. Lajunen and E. Aitta, Talanta, 28/1981/603.
7. Finnish Standard SFS 3027 /1976-09-03/.
8. B. Mani and V. Sitakara, Thermochim. Acta, 53/1982/175.
9. A. Spinzi and I.V. Nicolescu, Rev. Roum. Chim., 20/1975/387.
10. G.W. Brindley and S. Kikkawa, Thermochim. Acta, 27/1978/385.

ZUSAMMENFASSUNG - Die von in Salpetersäure gelöstem Phlogopit durch Neutralisierung mit Ammoniak erhaltenen, hauptsächlich Eisen-, Aluminium- und Magnesiumhydroxid enthaltenden Niederschläge wurden thermoanalytisch (TG, DTG und DTA) untersucht. In der vorliegenden Arbeit, die Teil einer grossangelegten Untersuchung zur chemischen Nutzung finnischer Glimmermineralien ist, wird gezeigt, dass die Bildung fester Lösungen von Eisen- und Aluminiumhydroxiden in Schluff mit zunehmender Neutralisationstemperatur ansteigt. Stickstoff kommt in Schluff hauptsächlich in Form von Nitraten vor, und Magnesium bildet Mischhydroxide mit Aluminium, was eine Trennung der Eisenhydroxidphase von der Magnesium-Aluminium-Hydroxidphase bewirkt.

Резюме - Методами ТГ, ДТГ и ДТА исследованы осадки, содержащие главным образом гидроокиси железа, алюминия и магния. Осадки были получены растворением флогопита в азотной кислоте с последующей нейтрализацией аммиаком. Согласно проведенных исследований, являющихся частью комплексного исследования по химическому использованию финских минералов, образование твердых растворов между гидроокисями железа и алюминия в осадке увеличивается с увеличением температуры нейтрализации. Азот находится в осадке, главным образом, в форме нитрата, а магний образует смешанные гидроокиси с алюминием, что вызывает разделение между гидроокисью железа и смешанной гидроокисью магний алюминия.