# SINTERING OF KAOLINITE WITH AMMONIUM FLUORIDE

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ABSTRACT

 The present work represents a study of the influence of ammonium fluoride on the thermal behaviour of kaolinite by using a derivatograph. The sintering of kaolinite with ammonium fluoride was found to be complicated. Different products of sintering are obtained, depending on the temperature and the amount of ammonium fluoride. They were identified microscopically and by using a Siemens Crystalloflex diffractometer. These include an ammonium aluminium fluoride complex, cryptohalite, aluminium fluoride, mullite, topaz and corundum. The DTA curves (using kaolinite and ammonium fluoride mixes of ratio 1 : 1) indicate the formation of the ammonium aluminium fluoride complex and cryptohalite at 120–280°C and the appearance of aluminium fluoride, topaz and mullite at 640°C. The intensive formation of topaz takes place at 750°C and its subsequent dissociation at 940°C with corundum formation. The very small endothermic peak at 1010°C represents the formation of mullite. In experiments using mixes of kaolinite–ammonium fluoride in the ratios 1 : 1 and 1 : 1.3 the end-product of sintering consists of corundum and mullite. When using mixes of the ratio 1 : 1.7, aluminium fluoride constitutes the main composition of the end-product.

INTRODUCTION

 The thermal behaviour of kaolinite is well known[1-5]. The DTA curve shows a sharp endothermic peak between 600 and 750°C, representing its dehydration and loss of constitutional OH radicals when its structure breaks down. When kaolinite is heated beyond 800°C, its layered structure is further disrupted and cannot be reconstructed by rehydration. The DTA curve shows also a sharp exothermic peak between 950 and 1000°C. The final products of decomposition are mullite and cristobalite.

 The fluorinating action of fluorine, fluorides and hydrogen fluoride are well known[6-12]. The solid fluorinating agents are very important, since they have many advantages. Ammonium fluoride and bifluoride have been paid much attention as important fluorinating agents. Their melting and evaporation temperatures are relatively low. The reactivity of ammonium bifluoride is close to that of anhydrous

hydrofluoric acid and it can be successfully applied as a fluorinating agent for many purposes[9, 10, 12].

The DTA curve of ammonium fluoride[8, 11] shows a small endothermic effect at 110 °C and two large and sharp endothermic peaks. The first at 158 °C corresponds to the liberation of ammonia and the formation of ammonium bifluoride. The second, at 225 °C, represents the dissociation of the resultant ammonium bifluoride into hydrogen fluoride and ammonia vapours. The thermal properties of ammonium bifluoride are well known[6-10, 12]. The DTA curve shows two large and sharp endothermic effects. The first effect at 126 °C represents its melting, the second, at 260 °C, indicates its decomposition.

The reaction of aluminium with ammonium bifluoride was reported to take place at 120 °C[12]. This temperature is practically identical with the melting point of ammonium bifluoride. The X-ray diffraction data for the reaction products indicate the presence of ammonium tetrafluoroaluminate and aluminium fluoride besides ammonium aluminium hexafluoride.

The reaction of silicon with ammonium bifluoride takes place at 80 °C[12]. The products of the reaction are ammonium silicon hexafluoride and a binary salt $(NH_4)_2$-$SiF_6 \cdot NH_4F$.

This work represents a derivatographic study of the influence of ammonium fluoride on the thermal behaviour of kaolinite. Also, the reaction of sintering and its mechanism were studied. Different products are obtained, depending on the temperature of sintering. They are identified microscopically and by X-ray diffraction analysis.

EXPERIMENTAL

This work was carried out with kaolinite collected from Kalabsha area, near Aswan, Egypt. Most mineral impurities such as quartz, rutile, and others were separated from it. Its chemical composition is given in Table 1. The kaolinite content was found to be 99.1 % in the purified product. Its X-ray diffraction pattern shows

TABLE 1

CHEMICAL COMPOSITION OF KAOLINITE

| Chemical component | Content (%) |
|---|---|
| $SiO_2$ | 46.34 |
| $Al_2O_3$ | 38.82 |
| $Fe_2O_3$ | 0.18 |
| $FeO$ | 0.10 |
| $MnO$ | 0.00 |
| $TiO_2$ | 0.21 |
| $CaO$ | 0.00 |
| $Na_2O$ | 0.04 |
| $H_2O$ | 14.26 |

only the kaolinite peaks, which are sharp and intense. No peaks of any mineral impurity have been detected. The X-ray powder diffraction data of the processed kaolinite agreed with those given in the ASTM index.

*Work techniques*

*Starting materials.* Starting materials usually consisted of kaolinite mixes. Kaolinite powder and ammonium fluoride were mixed together in particular amounts (corresponding to ratios of kaolinite: ammonium fluoride = 1:1, 1:1.3, and 1:1.7). Mixes were processed by repeated grinding in an automated agate mortar followed by sieving until all the powder passed through a 200-mesh sieve. The mixes were then ground with a pestle and mortar for 1 h to achieve homogeneity.

*Apparatus.* Experiments were carried out using platinum crucibles, heated in an electrical furnace with the removal of the evolved gases (namely, ammonia, silicon tetrafluoride, hydrogen fluoride), which resulted from the sintering reaction. The temperature was regulated automatically with an accuracy of $\pm 5\,°C$.

The thermal investigation of the sintering of kaolinite with ammonium fluoride was studied by using the MOM derivatograph[13, 14]. This apparatus records simultaneously four curves; the change of temperature of the sample ($T$), differential thermal analysis (DTA), thermogravimetric analysis (TG) quantitatively in mg, and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

The parameters during the test were as follows: Platinum crucible, medium size; inert material, aluminium oxide. Weight of mix ranges from 0.5 to 1 g; temperature range, ambient up to 1200 °C, sensitivity of DTA circuit, 1/5, 1/10; sensitivity of DTG circuit, 1/10; weight used in TG curve, 1000 mg; heating rate, $10\,°C\ min^{-1}$. The DTA and temperature measuring thermocouples were Pt–Pt/Rh wire. The atmosphere was air and the volatile silicon tetrafluoride and other gases were removed as formed.

*Phase identification*

*X-ray procedure.* The phases of the products of kaolinite sintering with ammonium fluoride were identified both microscopically and by X-ray analysis using a Siemens Crystalloflex diffractometer. The finely ground sintered material was mixed with sodium chloride as a standard. Its peaks occurring at $2\theta = 31.38°$ and $45.44°$ were used for corrections. Nickel-filtered copper radiation was used. Exposure time was 1 h. Intensities were collected to maximum $2\theta = 85°$. The sensitivity of the experiment was $4 \times 10^4$ impl/min and the statistical error was 1.5%.

RESULTS AND DISCUSSION

For studying the influence of ammonium fluoride on the thermal behaviour of kaolinite, DTA experiments were carried out using different amounts of ammonium fluoride. Mixes of ratios kaolinite: ammonium fluoride = 1:1, 1:1.3 and 1:1.7 were used. The obtained thermal analysis records were evaluated on the basis of the
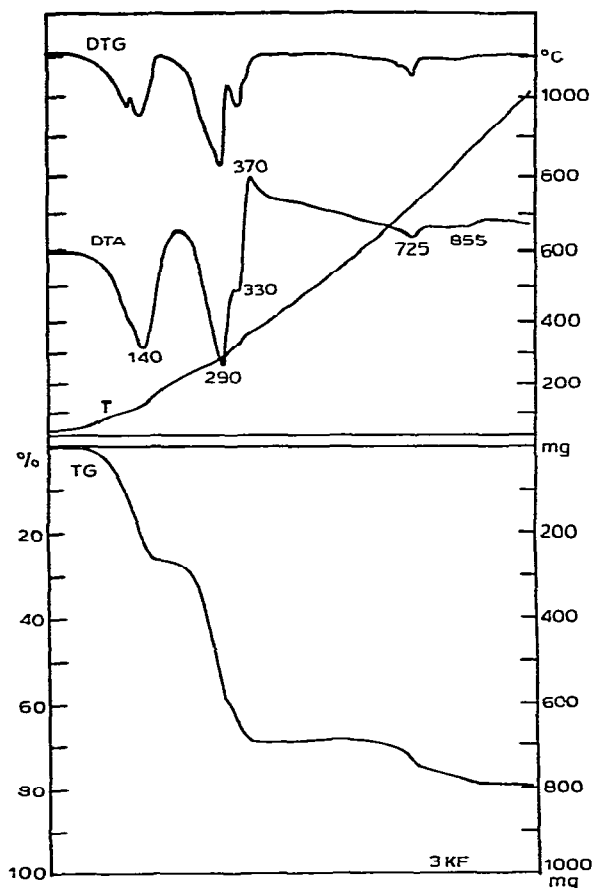
Fig. 1. Derivatogram of kaolinite sintering with ammonium fluoride of ratio 1 : 1.7. Weight of sample, 1000 mg; heating rate, 10°C min⁻¹; DTA, 1/10.

literature data[7-12, 15-20, 22], to explain the reactions which may be connected to certain peaks of the DTA curve.

*Using mixes of kaolinite and ammonium fluoride of ratio 1 : 1.7*

The thermal analysis data for kaolinite mixes of ratio 1:1.7 are shown in Fig. 1. The first small endothermic peak at 120°C represents its reaction with kaolinite with the formation of ammonium aluminium hexafluoride and ammonium silicon hexafluoride (cryptohalite). This temperature is practically similar to the melting point of ammonium bifluoride. The endothermic peak at 140°C may represent the decomposition of ammonium aluminium hexafluoride with the formation of ammonium tetrafluoride. These processes are connected with a remarkable decrease in weight (TG curve) due to the volatilization of ammonia and other gases. The large and sharp endothermic peak at 290°C represents the intensive dissociation of cryptohalite and unreacted ammonium bifluoride. The weight of the sample sharply decreases due to the volatilization of silicon in the form of silicon tetrafluoride and the removal of ammonia and water vapours. The endothermic peak at 330°C may represent the dissociation of ammonium aluminium tetrafluoride with the formation of aluminium
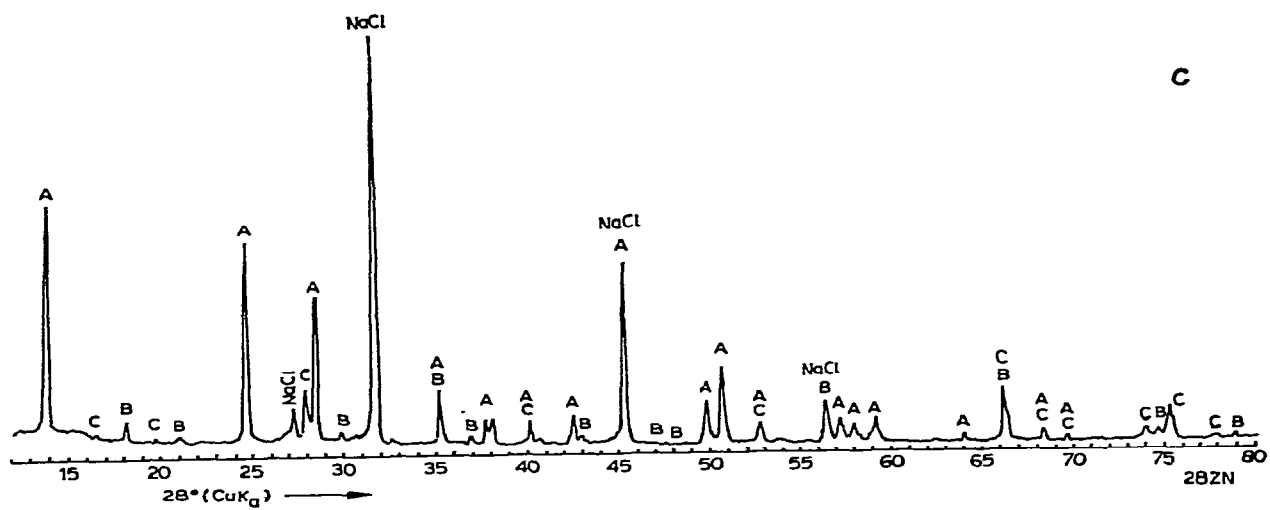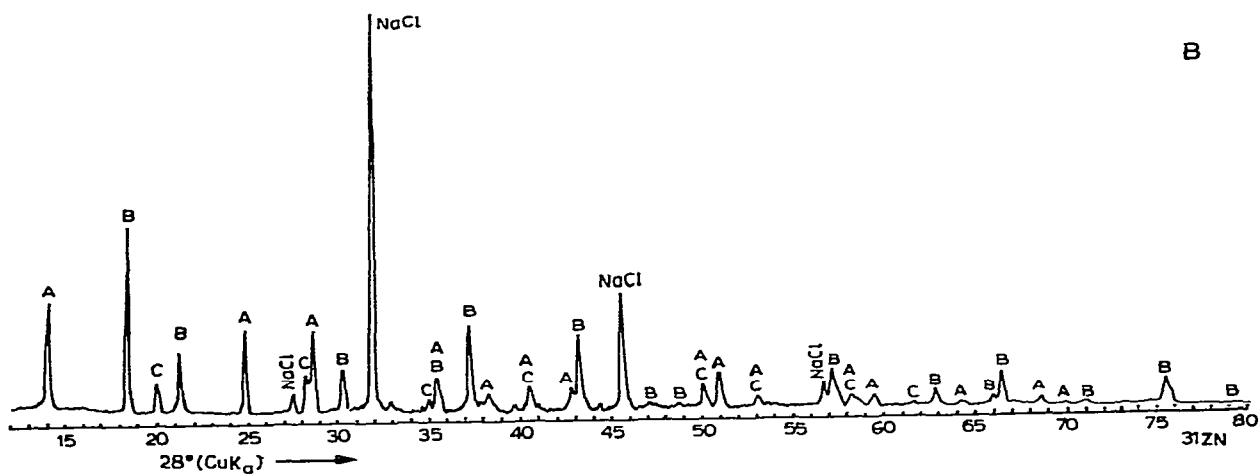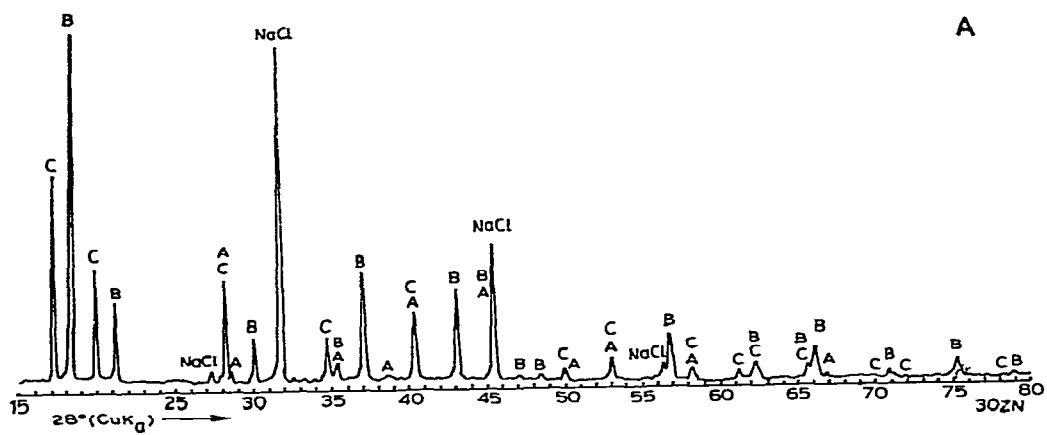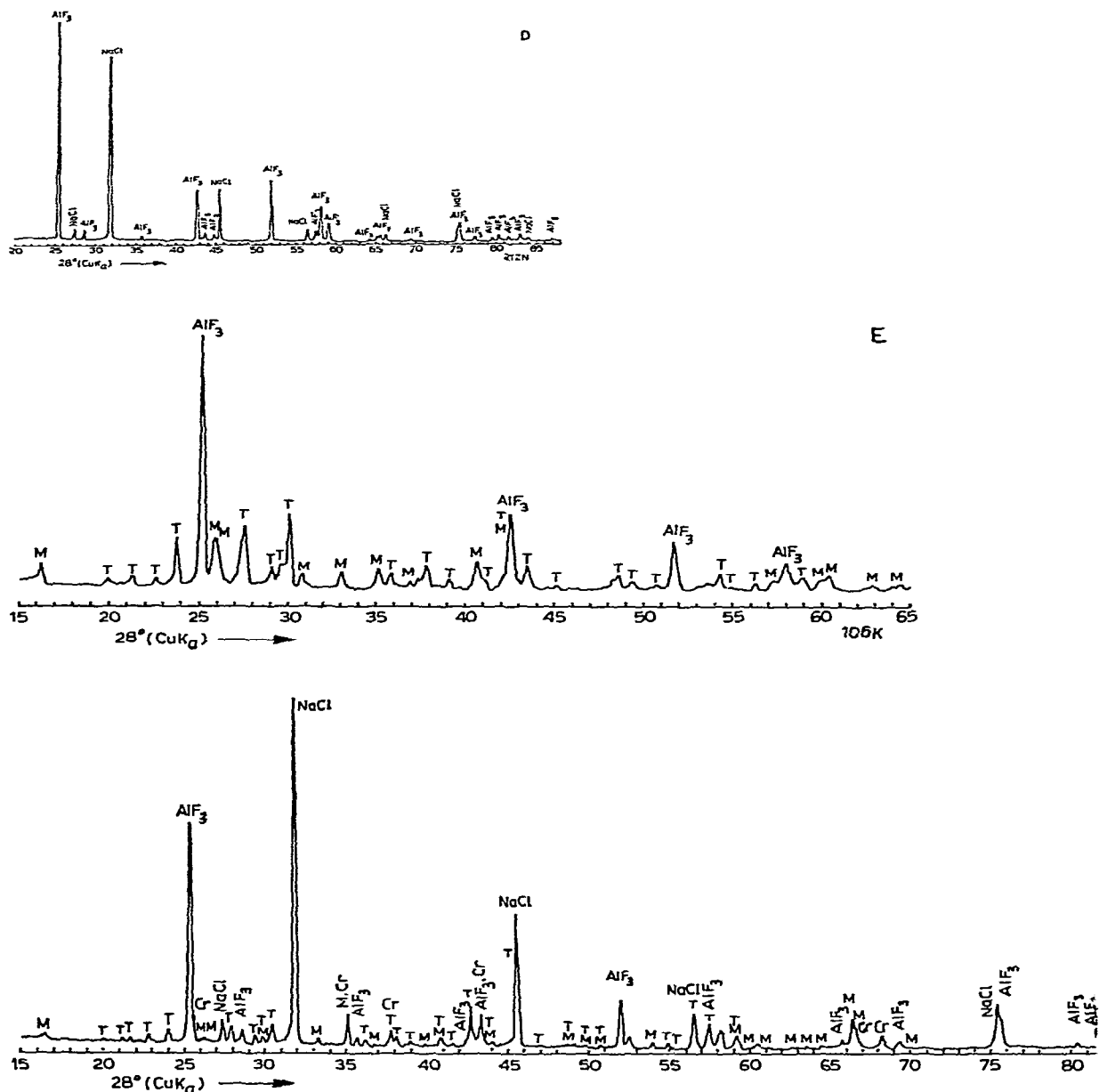
Fig. 2. X-ray powder diffraction patterns of the products of kaolinite sintering with ammonium fluoride of ratio 1:1.7. A, B, C, D, E and F at temperatures 120, 140, 290, 330, 725 and 855°C, respectively. A = NH₄AlF₄; B = (NH₄)₂SiF₆ (cryptohalite); C = (NH₄)₃AlF₆; T = topaz; M = mullite; and Cr = corundum.

fluoride. This is accompanied by weight loss (TG) corresponding to the evolution of ammonia and hydrogen fluoride. This reaction is accompanied by a substantial temperature increase as indicated by the exothermic effect at 370°C.

The results obtained are consistent with literature data[12], as the ammonium aluminium hexafluoride is stable only up to 100°C and begins to dissociate at higher

temperature, yielding first ammonium aluminium tetrafluoride and subsequently aluminium fluoride.

The small endothermic peak at 725 °C indicates the reaction between aluminium fluoride and relict grains of unreacted kaolinite with the formation of topaz. It was reported previously that the formation of topaz from the reaction between kaolinite and aluminium fluoride takes place at 750 °C[16-18, 21, 22]. Topaz loses silicon tetrafluoride at 855 °C, as indicated by some decrease of the sample weight at this temperature. In the presence of excess aluminium fluoride, the dissociation of topaz takes place simultaneously with its desilication with the formation of corundum or α-aluminium oxide. The results are in good agreement with literature data, as topaz loses silicon tetrafluoride on heating above 827 °C and its decomposition to corundum takes place at 950 °C[15-17, 22].

The products of the runs at 120, 140, 290, 330, 725, 855 and 1000 °C were identified both microscopically and by X-ray diffraction. By microscopic examination of thin sections of these products, it is observed that few kaolinite grains appear in the runs at 120, 140 and 290 °C, indicating fluorination of kaolinite with ammonium fluoride with the formation of silicon and aluminium complexes. At 725 °C, the product consists mainly of aluminium fluoride with topaz and few grains of mullite. At 1000 °C, aluminium fluoride constitutes the main composition of the end-product with a considerable number of corundum and mullite grains and few topaz grains.

The X-ray diffraction patterns of such products are shown in Fig. 2. The product of the run at 120 °C (Fig. 2A) consists of ammonium aluminium hexafluoride $(NH_4)_3AlF_6$ and cryptohalite $(NH_4)_2SiF_6$. The product of the run at 140 °C (Fig. 2B) consists mainly of ammonium aluminium tetrafluoride, $NH_4AlF_4$, and cryptohalite. At 290 °C (Fig. 2C), ammonium aluminium tetrafluoride constitutes the main composition of the product with little cryptohalite. At 330 °C (Fig. 2D), aluminium fluoride constitutes the total composition of the product with an unidentified phase. Topaz is present in a considerable amount with aluminium fluoride and little mullite, in the product of the run at 725 °C (Fig. 2E). Topaz peaks are less intense in the product of the run at 855 °C (Fig. 2F). Aluminium fluoride constitutes the total composition of such product with some corundum and few topaz and mullite grains. The aluminium fluoride peaks are narrow, sharp and intense, suggesting good crystallinity. The end-product of sintering at 1000 °C shows the intense peaks of aluminium fluoride and the very small peaks of corundum and mullite, as in the X-ray data at 855 °C, but here the topaz peaks have completely disappeared.

The microscopic study of the products of kaolinite sintering with ammonium fluoride is consistent with their X-ray diffraction patterns.

*Using mixes of kaolinite and ammonium fluoride of ratio 1 : 1.3*

The thermal analysis data for kaolinite mixed with ammonium fluoride of ratio 1 : 1.3 (Fig. 3) show similar peaks at similar temperatures to that obtained by using mixes of ratio 1 : 1.7, but here the end-product of sintering consists mainly of mullite and topaz with little amount of aluminium fluoride. This is due to the small amount
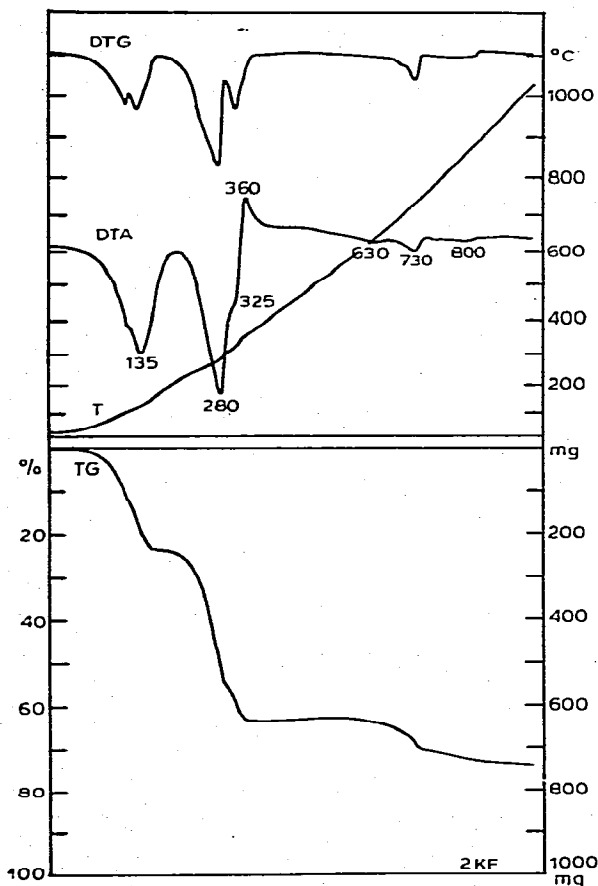
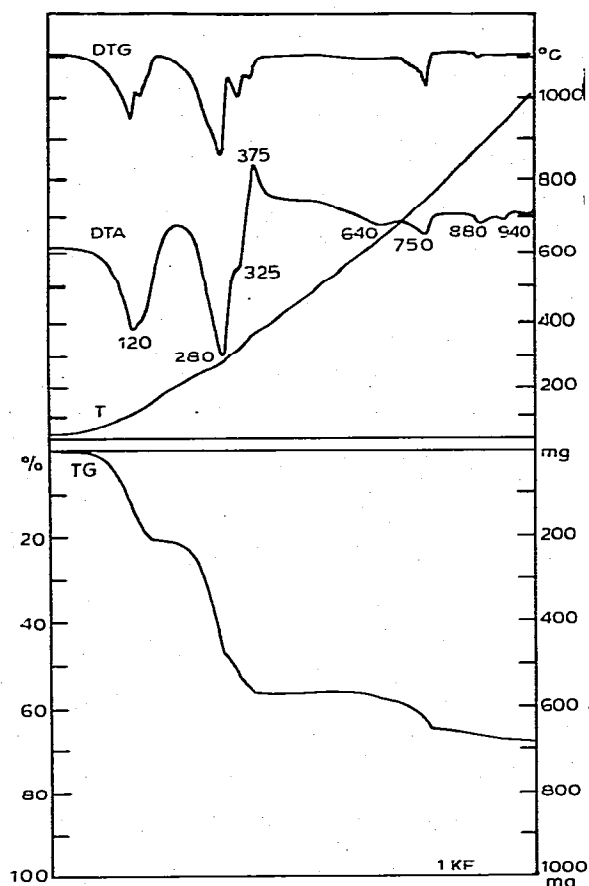Fig. 3. Derivatogram of kaolinite sintering with ammonium fluoride of ratio 1 : 1.3. Weight of sample, 1000 mg; heating rate, 10°C min⁻¹; DTA-1/10.

Fig. 4. Derivatogram of kaolinite sintering with ammonium fluoride of ratio 1 : 1. Weight of sample, 1000 mg; heating rate, 10°C min⁻¹; DTA-1/10.

of ammonium fluoride in the initial mixture and consequently the deficiency of fluorine.

## Using mixes of kaolinite and ammonium fluoride of ratio 1 : 1

The thermal analysis data for kaolinite mixed with ammonium fluoride of ratio 1 : 1 are shown in Fig. 4. The first two large and sharp endothermic peaks at 120 and 280°C represent the formation of ammonium aluminium hexafluoride and crypto-halite and their subsequent dissociation into ammonium aluminium tetrafluoride and silicon tetrafluoride and ammonia, respectively. This is accompanied by a considerable decrease in weight due to the liberation of ammonia, silicon tetrafluoride, hydrogen fluoride and water vapours. The small and wide endothermic peak at 640°C represents the reaction between kaolinite and the resulted aluminium fluoride or due to the dehydroxylation of kaolinite. The latter process is greatly delayed in the presence of aluminium fluoride. Earlier studies[9] refer to a possible explanation of this phenomenon by a bond formation between kaolinite and aluminium fluoride and the
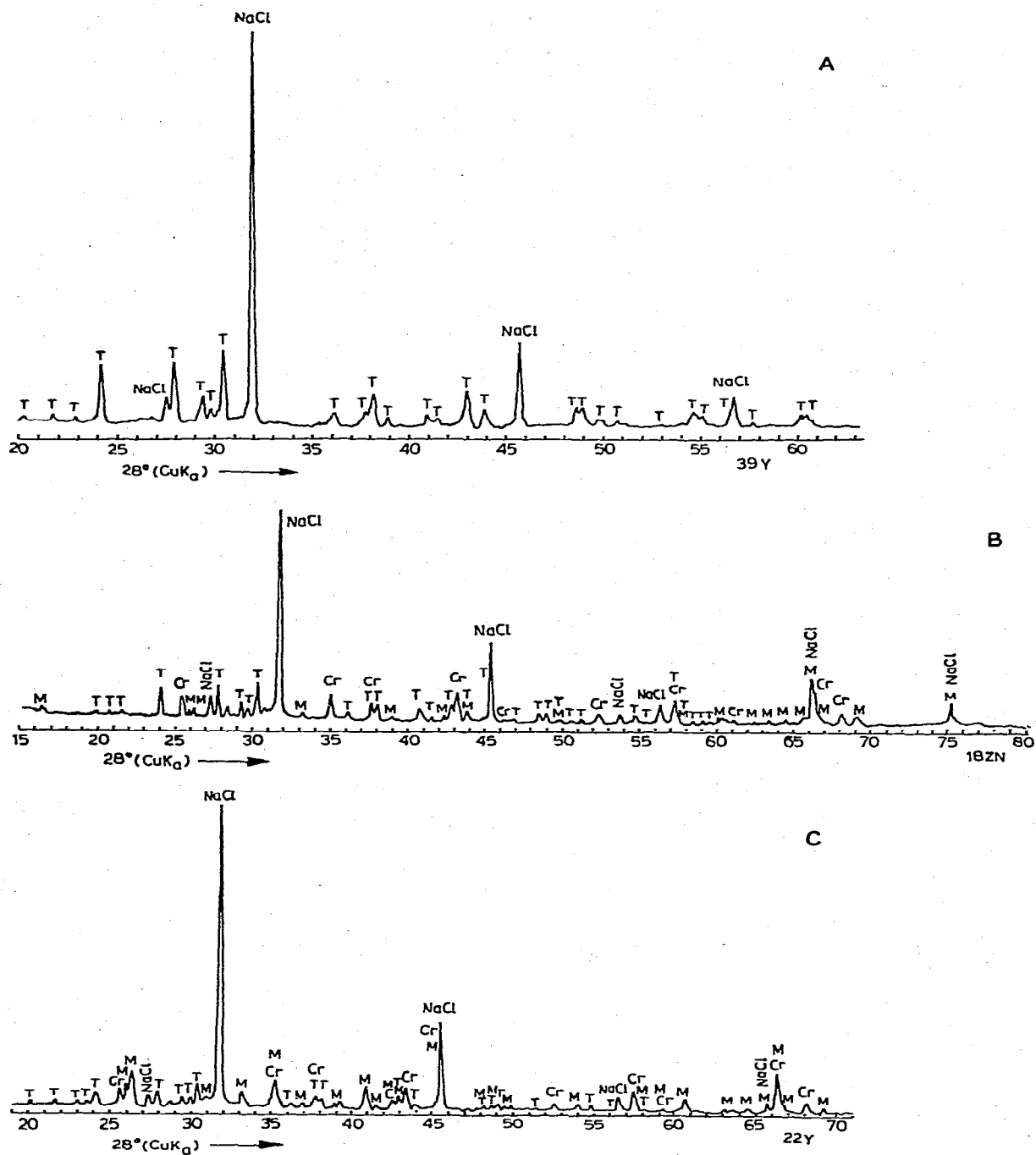
Fig. 5. X-ray diffraction patterns of the products of kaolinite sintering with ammonium fluoride of ratio 1:1. A, B and C at temperatures 750, 940 and 1010°C, respectively. T = topaz, M = mullite and Cr = corundum.

eventual development of a fluoride containing the aluminium fluorosilicate phase during the reaction. Under dynamic conditions, this amorphous phase may develop only in a much lower quantity, as in the range concerned, the period of heat treatment is short.

The endothermic peak at 750°C represents the intensive formation of topaz, due to the reaction between the resultant aluminium fluoride and the unreacted kaolinite. The small endothermic peak at 880°C may correspond to the reaction between mullite and aluminium fluoride. The small endothermic peak at 940°C indicates the decomposition of topaz, accompanied by a little decrease in weight, due to the removal of volatilized silicon tetrafluoride. The very small endothermic peak at 1010°C represents the formation of mullite from the dissociation of topaz in the absence of aluminium fluoride.

The products of the runs at 120, 280, 325, 640, 750, 880, 940 and 1010°C were studied and identified microscopically and by X-ray diffraction. It is found that the products obtained at 120, 280 and 325°C are of the same composition as those obtained in sintering experiments using mixes of kaolinite and ammonium fluoride of ratio 1:1.7. The product of the run at 120°C consists of ammonium aluminium hexafluoride and cryptohalite. Ammonium aluminium tetrafluoride constitutes the main composition of the product at 280°C with few grains of cryptohalite. The product obtained at 325°C consists of unreacted kaolinite with aluminium fluoride.

By microscopic examination of thin sections of the sintering products at 640, 750, 940 and 1010°C, it is observed that aluminium fluoride is present in a considerable amount with topaz and some mullite in the product obtained at 640°C. At 750°C, the product consists mainly of topaz, with few grains of mullite. No aluminium fluoride grains were detected. The products of sintering at 940 and 1010°C consist mainly of mullite and corundum, with few topaz grains.

The X-ray diffraction patterns of the products of sintering at 750, 940 and 1010°C are shown in Fig. 5. Topaz constitutes the total composition of the product at 750°C (Fig. 5A). Faint peaks of mullite are observed and all aluminium fluoride peaks disappeared in this product, indicating its absence. This means that all the resultant aluminium fluoride is consumed in the formation of topaz. The product of the run at 940°C (Fig. 5B) consists mainly of corundum and topaz with some mullite. Mullite is the end-product of sintering at 1010°C (Fig. 5C) with some corundum and topaz. Mullite peaks are well defined and intense. This is in good agreement with the microscopic study of its thin section. No aluminium fluoride peaks have been detected.

Therefore, the main product of sintering of kaolinite with ammonium fluoride of ratio 1:1 at 1010°C is mullite due to the deficiency of fluorine. This means that the dissociation of topaz in the absence of aluminium fluoride takes place with the formation of mullite. This is in good agreement with literature data, as topaz liberates fluorine on heating to 900°C and mullite is produced[19].

In general, the X-ray peaks of the products of sintering of kaolinite with ammonium fluoride, (namely, ammonium aluminium fluoride complexes, crypto-halite, aluminium fluoride, topaz, mullite and corundum or α-aluminium oxide) are narrow and intense, suggesting good crystallinity. The X-ray data of these synthetic minerals are consistent with those of the corresponding ASTM values of the natural minerals.

The products of the reaction of kaolinite with ammonium fluoride are different, depending upon the temperature of sintering and the amount of ammonium fluoride. The mechanism of the reaction is complicated and can be considered as the following. *At 120°C:* The reaction of kaolinite with ammonium fluoride takes place with the formation of ammonium aluminium hexafluoride and cryptohalite.

$$Al_2Si_2O_5(OH)_4 + 24\,NH_4F \rightarrow 2\,(NH_4)_3AlF_6 + 2\,(NH_4)_2SiF_6 + 14\,NH_3 + 9\,H_2O$$

*At 140°C:* Ammonium aluminium hexafluoride is unstable and begins to decompose at a higher temperature, yielding the more stable ammonium aluminium tetrafluoride, according to

$$(NH_4)_3AlF_6 \rightarrow NH_4AlF_4 + 2\,NH_3 + 2\,HF$$

or *the reaction of kaolinite with ammonium fluoride takes place at 140°C, according to*

$$Al_2Si_2O_5(OH)_4 + 20\,NH_4F \rightarrow 2\,NH_4AlF_4 + 2\,(NH_4)_2SiF_6 + 14\,NH_3 + 9\,H_2O$$

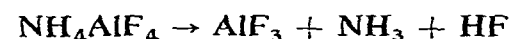*At 290°C:* Cryptohalite is unstable and dissociates with the liberation of ammonia, silicon tetrafluoride and hydrogen fluoride

$$(NH_4)_2SiF_6 \rightarrow 2\,SiF_4 + 2\,NH_3 + 2\,HF$$

or the reaction of kaolinite with ammonium fluoride takes place at 290°C, according to

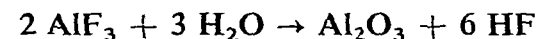$$Al_2Si_2O_5(OH)_4 + 16\,NH_4F \rightarrow 2\,NH_4AlF_4 + 2\,SiF_4 + 14\,NH_3 + 9\,H_2O$$
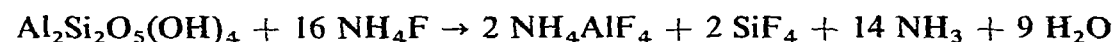
*At 330°C:* The dissociation of ammonium aluminium tetrafluoride takes place with the formation of aluminium fluoride

$$NH_4AlF_4 \rightarrow AlF_3 + NH_3 + HF$$

or

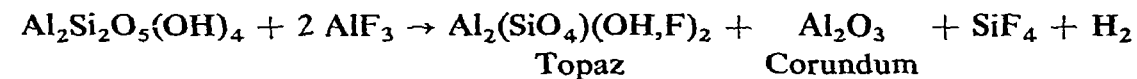$$Al_2Si_2O_5(OH)_4 + 14\,NH_4F \rightarrow 2\,AlF_3 + 2\,SiF_4 + 14\,NH_3 + 9\,H_2O$$

*Topaz formation:* The resulted aluminium fluoride may react with kaolinite in hydrolysis-like manner or with the water produced by dehydroxylation of kaolinite. Above 300°C, aluminium fluoride will hydrolyze even under the effect of atmospheric moisture[23].

$$2\,AlF_3 + 3\,H_2O \rightarrow Al_2O_3 + 6\,HF$$
$$Al_2Si_2O_5(OH)_4 + 6\,HF \rightarrow Al_2(SiO_4)(OH,F)_2 + 3\,H_2O + SiF_4 + H_2$$

or,

$$Al_2Si_2O_5(OH)_4 + 2\,AlF_3 \rightarrow \underset{\text{Topaz}}{Al_2(SiO_4)(OH,F)_2} + \underset{\text{Corundum}}{Al_2O_3} + SiF_4 + H_2$$
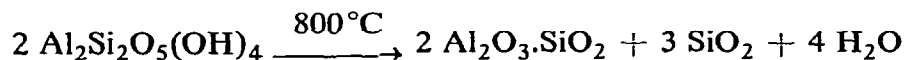
The reaction of kaolinite with aluminium fluoride with the formation of topaz takes place at 725–750°C.

*Mullite formation:* Under dynamical conditions, mullite formation proceeds in two ways. One starts from kaolinite, due to the deficiency of fluoride ion
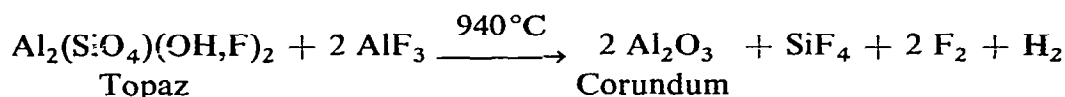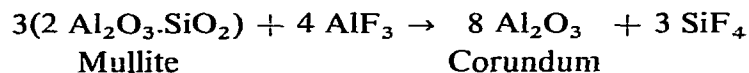
$$2 \; Al_2Si_2O_5(OH)_4 \xrightarrow{\;800\,°C\;} 2 \; Al_2O_3.SiO_2 + 3 \; SiO_2 + 4 \; H_2O$$

or,

$$Al_2Si_2O_5(OH)_4 + 2 \; AlF_3 \rightarrow 2 \; Al_2O_3.SiO_2 + SiF_4 + 2 \; HF + H_2O$$

The second, from the dissociation of topaz, as indicated by the very small endothermic peak at 1010°C

$$Al_2(SiO_4)(OH,F)_2 \rightarrow 2 \; Al_2O_3.SiO_2 + F_2 + 2 \; OH$$
$$\text{Topaz} \qquad\qquad \text{Mullite}$$
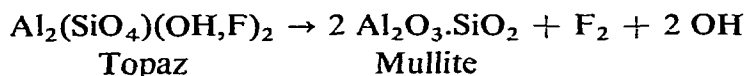
*Corundum formation:* Corundum or α-aluminium oxide may be formed in different ways, either by the hydrolysis of aluminium fluoride or the desilication of topaz or mullite with aluminium fluoride according to the following equations

$$Al_2(SiO_4)(OH,F)_2 + 2 \; AlF_3 \xrightarrow{\;940\,°C\;} 2 \; Al_2O_3 + SiF_4 + 2 \; F_2 + H_2$$
$$\text{Topaz} \qquad\qquad\qquad\qquad \text{Corundum}$$

Also,

$$3(2 \; Al_2O_3.SiO_2) + 4 \; AlF_3 \rightarrow 8 \; Al_2O_3 + 3 \; SiF_4$$
$$\text{Mullite} \qquad\qquad\qquad \text{Corundum}$$

From the results, it can be concluded that topaz dissociates at 1010°C with the liberation of fluorine and hydroxyl groups with the formation of mullite. In the presence of aluminium fluoride, desilication of topaz takes place at 940°C with the formation of corundum or α-aluminium oxide.

CONCLUSIONS

The thermal analysis study of sintering of kaolinite with ammonium fluoride has revealed that the reaction mechanism is a complicated one. Different products of sintering are obtained, depending on the temperature and amount of ammonium fluoride. Using mixes of kaolinite and ammonium fluoride of ratios 1:1, 1:1.3 and 1:1.7, the products are identical at low temperature. The DTA curves show an endothermic peak at 120°C, representing the formation of ammonium aluminium hexafluoride and cryptohalite. The endothermic peak at 280–290°C represents the dissociation of cryptohalite and the rest of the ammonium aluminium hexafluoride, with the formation of ammonium aluminium tetrafluoride. The last product decomposes at 330°C, with the formation of aluminium fluoride. The intensive formation of topaz takes place at 725–750°C, with its subsequent dissociation at 940°C. At temperatures, higher than 900°C, the end-products of sintering are different:

(1) Using mixes of ratio (1 : 1), mullite is the end-product of sintering at 1010°C with corundum and topaz impurities. This is due to the deficiency of fluorine.

(2) Using mixes of ratio (1 : 1.3), the end-product consists mainly of mullite, corundum and topaz with little aluminium fluoride.

(3) Using mixes of ratio (1 : 1.7), aluminium fluoride constitutes the total composition of the end product of sintering with mullite and corundum impurities.

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