

THERMAL REACTIONS OF ALLOPHANE UNDER APPLIED ELECTRIC FIELDS

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ABSTRACT

DC electric fields applied to pellets of allophane from Derbyshire, U.K., during heating at 600–750°C were found to enhance their thermal reactions by assisting the removal of bound water and increasing the content of crystalline products, as measured by X-ray diffraction both in the pellet faces and in the bulk material. The degree of reaction at each end of the pellet is more strongly influenced by the direction of the inert gas stream used to purge the electrolysis cell than by the electrode polarity.

When initially formed, the mullite product phase is highly alumina-rich, but progressively approaches a $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition, with the separation of alumina. Other phases formed include kyanite (Al_2SiO_5), which further reacts with the impurity calcium present forming anorthite ($\text{CaAl}_2\text{SiO}_8$), and a transitory disordered mullite-like phase which appears at the positive electrode only. The reaction sequence, and crystallinity and microstructures of the products are not influenced by the electric field at the comparatively low temperatures used in this study.

INTRODUCTION

The thermal decomposition reactions of layer-lattice hydrous aluminosilicates such as kaolinite are known to be influenced by applying DC electric fields ($4\text{--}5 \times 10^4 \text{ V m}^{-1}$) to the sample during reaction. The dehydroxylation temperature of kaolinite and the apparent activation energy of dehydroxylation can thus be lowered by up to 60°C and 50 kJ mol⁻¹, respectively [1], probably by a mechanism involving the field-assisted migration of oxygenated proton-containing complexes [1]. The higher-temperature reactions of kaolinite are also influenced by applied electric fields; the temperature of an exothermic reaction at ~ 980°C is lowered by up to 15°C [2] and the physical properties of the high-temperature products are considerably improved, particularly at the negative electrode [3] due to the formation of a denser, interlocking microstructure in that region [4].

Although the effect of electric fields on the dehydroxylation of hydrous aluminosilicates with well-defined crystal structure has been documented, the influence of the crystal structure itself is unknown. For this reason, the

present study was undertaken of an X-ray amorphous hydrous aluminosilicate, allophane, using a well-characterized sample for which the thermal decomposition sequence has already been established [5]. The aim of the work was to discover the effect of electric fields both on the dehydration process and on the nature and crystallinity of the product phases, using X-ray diffraction, scanning electron microscopy (SEM) and IR spectroscopy as the principal analytical techniques.

EXPERIMENTAL

Material

The sample used in this study was an alumina-rich allophane formed by co-precipitation from solution on the walls and roof of the adit to the Odin Mine, Castleton, Derbyshire, U.K. A previous chemical analysis [5] takes no account of a substantial fluorine content, so a new analysis was made by atomic absorption spectroscopy and quantitative energy-dispersive X-ray analysis. A fluorine analysis was made by bombarding pellet samples with 2.5 MeV protons in an accelerator and detecting the γ -rays from the fluorine using a large NaI cryostat. The new chemical analyses are shown in Table 1. X-ray powder diffraction shows the material to be completely X-ray amorphous.

Electrolysis methods

Pellets of 10 mm diameter and 4.5 mm thickness were pressed at 500 bar, weighed, and heated in a silica electrolysis cell described elsewhere [3] at 600–750°C (chosen with reference to previous thermal analysis results [5]) for 1 h in a dynamic atmosphere of oxygen-free nitrogen (1 l min⁻¹). The removal of high concentrations of evolved water by the flowing gas atmosphere was an essential factor in preventing electrical flash-over between the

TABLE 1
Chemical analysis of Derbyshire allophane

Element	%	Element	%
Al ₂ O ₃	32.63	Fe ₂ O ₃	0.15
SiO ₂	17.75	MnO	0.10
CaO	2.73	PbO	2.53
MgO	0.17	ZnO	0.30
Na ₂ O	0.03	F	5.90
K ₂ O	0.04	H ₂ O	37.7
		Total	100.03

electrodes. On reaching the soaking temperature, monitored by an independent thermocouple located within the cell, a potential difference of 2.1 kV was applied to the platinum electrodes from a Philips PW4022 EHT power supply. Since the applied voltage tended to decrease with time, particularly at the higher temperatures, the voltage/time relationship was continuously recorded. Three experiments were carried out at each temperature: one in which the positive electrode face was toward the gas outlet (called +ve outlet); one at reversed polarity (+ve inlet); and an unelectrolysed control experiment. At the end of an electrolysis experiment, the applied voltage was maintained until the sample had cooled to $< 150^{\circ}\text{C}$. The pellets were then re-weighed and each electrode face was examined by X-ray diffraction, SEM and IR spectroscopy (of small scrapings from the face). The pellets were then ground and quantitative X-ray analyses made of the bulk composition using 5% ZnO as the internal standard. The cell dimensions of the mullite products were also measured from slow X-ray scans by processing the indexed mullite peak positions (corrected with reference to the ZnO standard) in a computer program of Appleman and co-workers [6]. The cell dimensions thus derived were used to deduce the composition of the mullite product, using the relationship determined by Cameron [7].

RESULTS AND DISCUSSION

X-ray examination of the reacted pellet faces

The crystalline phases formed in both electrolysed and non-electrolysed samples were predominantly mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), with smaller amounts of fluorite (CaF_2) and kyanite (Al_2SiO_5) appearing at higher temperatures. Two other phases were observed only at the positive faces of the electrolysed samples; one of these was characterized by an X-ray reflection at 3.50 \AA and will be discussed below. The other phase was corundum ($\alpha\text{-Al}_2\text{O}_3$).

Semiquantitative peak-height estimates of the relative amounts of mullite formed at each face of the reacted pellets are shown in Fig. 1, from which the following points emerge:

- (i) At all temperatures, the degree of mullite formation is greater in the electrolysed pellets than in those unelectrolysed;
- (ii) The gas flow direction strongly influences the degree of mullite formation, the greatest amount of mullite always occurring at the gas outlet face, irrespective of the polarity of the electrolysing field.

By analogy with previous results for kaolinite dehydroxylation [1], the major effect of the field should be to assist the transfer of protons through the pellet. The highest proton concentrations would be expected at the negative face, where recombination to form water should lead to enhanced nucleation of crystalline phases in that region. The role of the field in

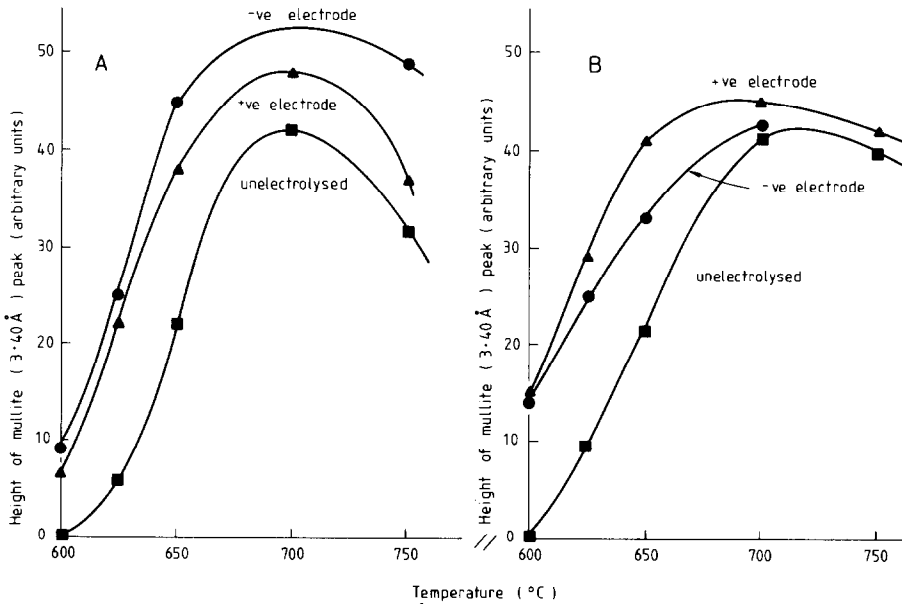


Fig. 1. Relative peak heights of the 3.40 Å mullite X-ray peak in the faces of electrolysed and unelectrolysed allophane pellets as a function of temperature. Electrolysis time, 1 h; mean field strength; $3.2 \times 10^5 \text{ V m}^{-1}$; atmosphere; dynamic oxygen-free nitrogen, 1 l min^{-1} . (A) Gas flow from positive to negative electrode; (B) gas flow from negative to positive electrode.

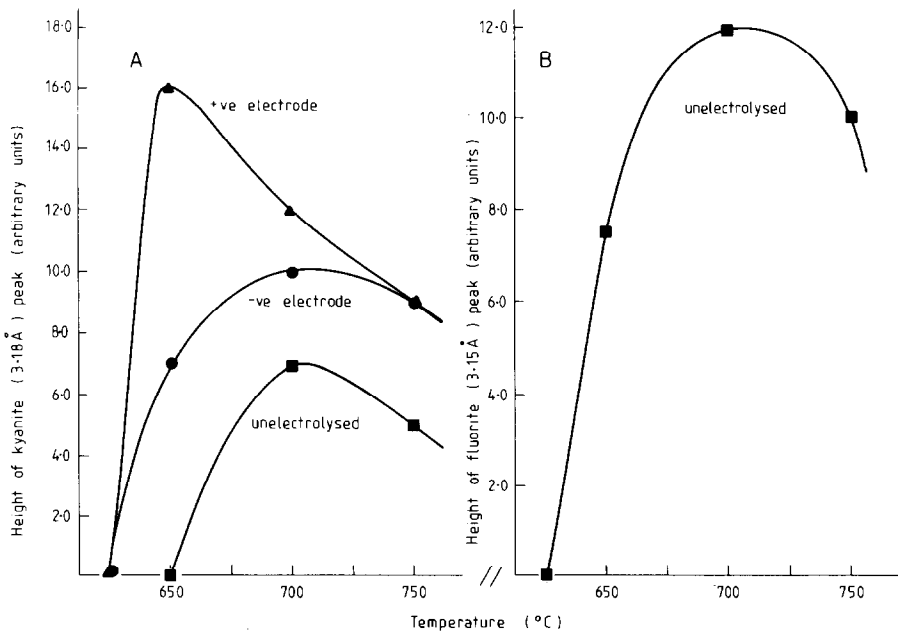


Fig. 2. (A) Relative peak height of the 3.18 Å kyanite X-ray peak in the faces of electrolysed and unelectrolysed allophane pellets as a function of temperature. Reaction conditions as for Fig. 1. Gas flow from positive to negative electrode. (B) Relative peak height of the 3.15 Å fluorite X-ray peak in the faces of unelectrolysed allophane pellets as a function of temperature. Similar results are found in electrolysed pellets.

assisting the elimination of water is also reflected in the weight losses of the electrolysed pellets, which over the whole temperature range lose $\sim 1.5\%$ more weight than the corresponding unelectrolysed pellets. Under dynamic gas flow conditions, a vapour gradient would be expected to exist across the pellet, with the highest concentrations of volatile products occurring at the outlet face, where enhanced nucleation should also occur. Figure 1 shows the gas flow effect to be dominant; the highest mullite concentrations occur where the effects of electrolysis and gas flow reinforce each other (in the samples where the outlet face is negatively charged).

Figure 2A shows the development of kyanite in the faces of unelectrolysed and electrolysed pellets, for the case where the gas flow is from the positive to the negative faces. A similar result is found when the gas flow is reversed with respect to the electrolysing polarity. The appearance of kyanite is transitory, reaching a maximum at $\sim 700^\circ\text{C}$ then decaying away to zero by 850°C . Similarly, the appearance in the pellet faces of fluorite (Fig. 2B) is also transitory, but unlike kyanite, fluorite occurs in similar amounts in both electrolysed and unelectrolysed samples, and is independent of gas flow direction. Like kyanite, fluorite is not found in samples fired above 750°C .

Figure 3 shows the behaviour of the two phases which were found only at the positive faces of the electrolysed pellets, irrespective of the gas flow direction.

The concentration of corundum increases with increasing temperature; although this phase does not appear in unelectrolysed samples even at 850°C , it is formed in unelectrolysed samples heated at higher temperatures (1150°C), confirming an earlier observation [5].

By contrast, the phase characterized by an X-ray reflection at 3.40 \AA decreases with increasing temperature, concomitant with an increase in mullite formation (Fig. 3). A similar peak at 3.50 \AA was reported in the cathode faces of electrolysed kaolinite pellets [3], in which it was tentatively

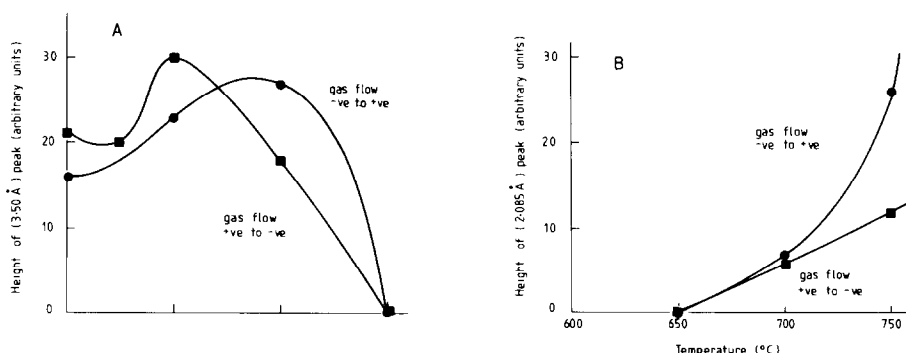


Fig. 3. Relative peak height of the 3.50 \AA X-ray peak of disordered mullite-like phase and the 2.085 \AA corundum X-ray peak in the faces of electrolysed allophane pellets as a function of temperature. Reaction conditions as for Fig. 1 (these phases are not found in unelectrolysed samples over this temperature range). (A) Disordered mullite-like phase; (B) corundum.

attributed to a distorted mullite-like phase containing additional cations in the (120) plane. Figure 3 shows that this distorted phase reaches a maximum intensity at 650–700°C, then disappearing at higher temperatures in a similar manner to kyanite (Fig. 2).

Quantitative X-ray diffraction of the bulk pellet material

Figure 4 shows the results of quantitative mullite analyses of the bulk pellet material, expressed as area ratios of the 3.40 Å mullite peak to the 2.816 Å ZnO internal standard peak. The differences in the bulk mullite contents of samples electrolysed under different polarities are much less marked than at the electrode faces (Fig. 1); nevertheless, all the electrolysed samples have greater bulk mullite contents than the corresponding unelectrolysed samples.

The bulk analyses also indicate the presence of kyanite and the disordered mullite phase in similar proportions to that observed in the electrode faces, but the calcium fluoride found in the electrode faces was not present in the bulk material in sufficient concentration to be detected by XRD. Fluorite formation thus appears to be a surface reaction, and its mineralizing effect may account for the enhanced formation of the other phases at the electrode surfaces.

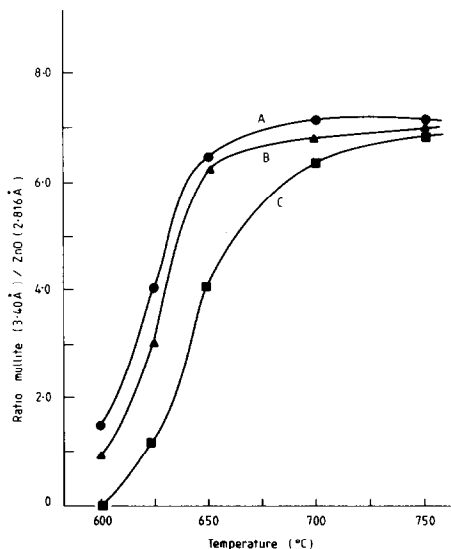


Fig. 4. Quantitative X-ray analysis for bulk mullite in electrolysed and unelectrolysed allophane pellets as a function of temperature. (A) Gas flow from negative to positive electrode; (B) gas flow from positive to negative electrode; (C) unelectrolysed.

The composition of the mullite product

On the assumption that the relationship deduced by Cameron [7] between the cell edge a or cell volume and the mullite composition can be extended to mullites derived from lower-temperature mineral decompositions, the a parameters measured for the present mullites were used to deduce their composition. The results are shown in Fig. 5, from which the following points emerge.

(i) The alumina content of the mullite product decreases with increasing reaction temperature, irrespective of the electric field and gas flow direction.

(ii) At 600°C the mullite, which is formed only in electrolysed samples at this temperature, is of much higher alumina/silica mole ratio ($\sim 5:2$) than is the allophane starting material ($\sim 3:2$). In this respect, the reaction is similar to that of kaolinite, in which the initially formed mullite is of high alumina content (unpublished results).

As the reaction temperature increases, the excess amorphous silica forms kyanite, and the composition of the co-existent mullite approaches 2:1 (Fig.

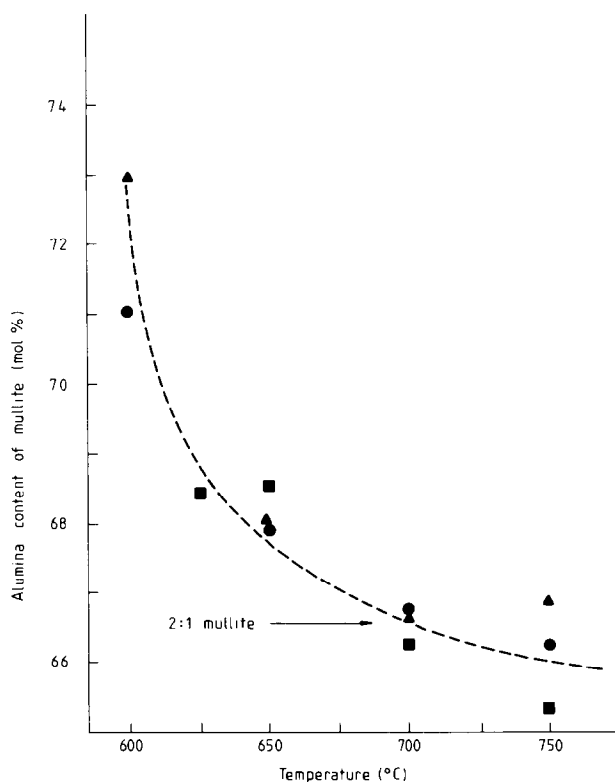


Fig. 5. Composition of mullites formed in electrolysed and unelectrolysed allophane as a function of temperature, deduced from Cameron's relationship [7]. (▲) Gas flow from positive to negative electrode; (●) gas flow from negative to positive electrode; (■) unelectrolysed.

5). By 850°C the kyanite is no longer present, the only crystalline phase detectable at this temperature being mullite. The disappearance of the kyanite could be due either to (a) its conversion to mullite (a reaction which normally occurs at considerably higher temperatures) or (b) its reaction with the calcium present to form an X-ray amorphous phase. Possibility (a) is ruled out by the measurements of the a parameter of this mullite, which indicates an alumina content of 66.1 mol%, i.e., a 2 : 1 mullite; if all the silica and alumina released by the decomposition of the kyanite combined with the mullite already present, the product would be even more silica-rich than 3 : 2. Possibility (b) is more likely, since if the 1.9% Ca originally present reacted to form a phase of anorthite of composition $(\text{CaAl}_2\text{Si}_2\text{O}_8)$, the remaining alumina/silica ratio would be 2 : 1, consistent with the mullite composition measured at 850°C. Further support for (b) is provided by samples heated to 950°C and 1150°C, in which crystalline anorthite is found. Isothermal studies [8] show that although crystallization of a phase of anorthite composition would not be expected at 850°C, crystallization will occur between 950 and 1150°C, and should be particularly efficient in systems containing mineralizing agents such as fluoride. Cell dimension measurements indicate that the mullite composition at 950°C is still 2 : 1, whereas at 1150°C it has moved nearer to 3 : 2 (62.5 mol% Al_2O_3). Thus, the 3 : 2 mullite composition preferred by this system at higher temperatures is progressively approached by the separation of alumina, which appears as corundum in the X-ray pattern of samples fired at 1150°C. These results are consistent with those reported previously [5].

Infrared spectroscopy

Typical IR spectra of face scrapings from electrolysed and unelectrolysed allophane pellets are shown in Fig. 6. The spectra of samples electrolysed at lower temperatures (Fig. 6B) are much sharper and well defined than the corresponding unelectrolysed samples (Fig. 6A), indicating improved crystallinity in the former. No differences attributable to electrolysis polarity or gas flow direction could be distinguished by IR spectroscopy in the two faces of any pellet. The spectra all show bands similar to those of other partly reacted, hydrous aluminosilicates [9], the appearance at 625–650°C of the diagnostic 880–90 cm^{-1} mullite band confirming the X-ray result that mullite is formed at these low temperatures. Although the intensities of the water bands at $\sim 3400 \text{ cm}^{-1}$ are not fully quantitative, they confirm that at all temperatures, a greater degree of water loss has occurred in the electrolysed samples.

At $> 700^\circ\text{C}$, splitting of the Si–O stretching band at 1140–60 cm^{-1} occurs; based on the IR observations of Cameron [7], the changes in the relative intensities of these two peaks indicate a progressive decrease in the alumina content of the mullite as the reaction progresses, consistent with the

X-ray results. At 700–750°C, differences appear in the electrode-face spectra of the electrolysed pellets, irrespective of gas flow direction (Fig. 6D and E). The additional peaks at 360, 460 and 640 cm^{-1} in the spectra of the positive faces (Fig. 6E) and the shifts of the peaks at $\sim 580 \text{ cm}^{-1}$ to higher wavenumbers are consistent with the development of a corundum spectrum [10].

In summary, the IR spectra confirm the X-ray findings that electrolysis assists the elimination of water and the formation of mullite, but does not produce significant polarization, except in the case of corundum formation, which appears predominantly at the positive electrode.

Scanning electron microscopy (SEM)

The foregoing conclusions were supported by an SEM investigation of the pellet faces, which showed that the crystallinity increased with increasing

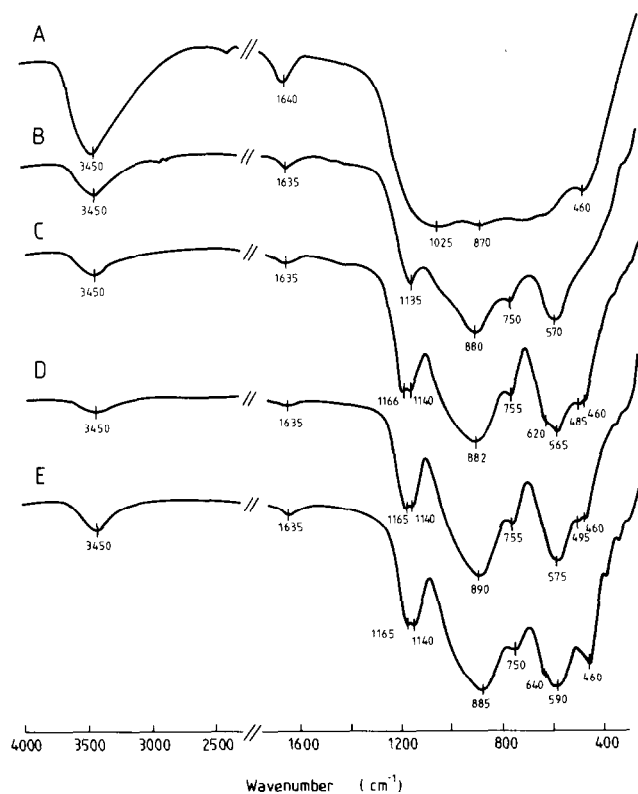


Fig. 6. Typical IR spectra of scrapings from faces of electrolysed and unelectrolysed allopahane pellets. (A) Unelectrolysed, 600°C; (B) electrolysed, negative face, 600°C; (C) unelectrolysed, 750°C; (D) electrolysed, negative face, 750°C; (E) electrolysed, positive face, 750°C.

temperature, the electrolysed samples being more crystalline than their unelectrolysed controls, especially at the lower temperatures. No crystallinity differences were detected between the positive and negative electrode faces, neither were any composition differences detected by EDAX in the electrode faces of any of the electrolysed pellets, ruling out any significant polarization phenomenon. However a narrow outer ring composed of much less crystalline material with significantly lower Al content was observed in all pellets, irrespective of electrolysis. This was more pronounced in the lower-temperature samples, and appears to be related to the annular loss of a volatile component. To further investigate this possibility, the outlet gas was bubbled through a water-filled trap and the solution analysed by ion chromatography at the conclusion of each run. Concentrations of F^- as high as 17.8 mg g^{-1} of allophane were detected, the concentrations generally increasing with increasing temperature, irrespective of electrolysis. These results suggest that the removal of an appreciable proportion of the fluorine originally present occurs via the vapour phase, conceivably as a volatile fluoride such as AlF_3 .

The effect of electrolysis on the reaction mechanism

When pellets of the present allophane are heated in the absence of an electric field, the following reactions occur.

(i) The bonds by which water is held in association with the aluminosilicate are broken, the water thus released diffusing to the pellet surfaces and dispersing into the reaction atmosphere. Because of the wide range of bond strengths involved, this reaction occurs over a wide temperature range.

(ii) The alumina and silica units freshly activated by dehydration combine, forming compounds with mullite-like structure (i.e., columns of AlO_6 octahedra cross-linked by SiO_4 and AlO_4 tetrahedra [11]). Initially, the alumina content of these mullite-like regions is high, suggesting that this reorganisation originates in the aluminous regions. At higher temperatures, the mullite composition approaches an alumina/silica ratio of 3 : 2, the excess alumina appearing as corundum at $\sim 1150^\circ\text{C}$.

(iii) At $> 625^\circ\text{C}$, reaction in the siliceous regions produces a comparatively silica-rich aluminosilicate (kyanite), which at higher temperatures progressively reacts with the calcium present to form an X-ray amorphous phase of anorthite of composition $(CaAl_2Si_2O_8)$. This phase becomes crystalline at $> 950^\circ\text{C}$.

(iv) The appreciable fluorine content of this allophane is reflected in the appearance at $\sim 650^\circ\text{C}$ of fluorite at the pellet surfaces. Above $\sim 750^\circ\text{C}$ this phase is progressively dissociated, the calcium reacting to form anorthite and the fluorine being removed as volatile fluorides.

The degree to which all these reactions are influenced by electrolysis depends on the temperature, as does the effect of dynamic gas atmospheres. The results reported here represent a complex balance between all these

factors. Reaction (i) above would be expected to be the one most influenced both by electrolysis and gas flow conditions, particularly at low temperatures. This is confirmed by the observation that at the lower temperatures the system appears to have an overall higher electrical conductance when the gas flow direction is from the negative to the positive electrode, but by 650°C this effect has been swamped by the effect of temperature, and the conductance becomes independent of gas flow direction. The charge-carrying mechanism is thus related to the removal of a volatile species (water), which, if the charge carriers are assumed to be protons, should be facilitated when the negative electrode is downstream of the gas flow; the resulting overall depletion of charge-carriers will result in a lower bulk conductivity, as is observed with this configuration of gas flow and electrode polarity.

The possibility of significant F^- electromigration is ruled out by the appearance of CaF_2 in both faces of electrolysed (and unelectrolysed) pellets, and the fact that the concentration of volatile fluorides in the reaction atmosphere is unaffected by electrolysis.

As was found for kaolinite [3], the enhanced removal of bound water by electrolysis also influences the formation of the crystalline phases, which are formed more readily in electrolysed samples because of the well-known nucleating effect of water vapour. However, by contrast with kaolinite, the only evidence of polarizing effects or enhanced phase formation attributable solely to the effect of electrolysis is the formation in the electrode region of a transitory disordered mullite-like phase and corundum. The lack of detectable differences in the microstructure or physical properties of electrolysed and unelectrolysed allophane pellets is probably due to the low temperature range of this study rather than to any fundamental difference in the electrolysis behaviour of this material and that of the crystalline hydrous aluminosilicates.

CONCLUSIONS

(1) The thermal reactions occurring in allophane pellets can be assisted by the application of DC electric fields, which enhance the removal of bound water by electrolysis of protons to the negative electrode where they are discharged. The formation of the principal crystalline product (mullite) throughout the pellet is enhanced by electrolysis, but the direction of the gas flow through the electrolysis cell exerts a greater influence on the differential formation of the crystalline phases at the two ends of the pellet than does the polarizing effect of the electric field.

(2) The mullite product initially contains a higher proportion of alumina than the allophane starting material, but progressively approaches the conventional 3 : 2 composition with the separation of the excess alumina, which eventually crystallizes as corundum. An aluminosilicate of much lower

alumina content (kyanite) is also formed, subsequently reacting with the calcium present to form anorthite. The fluorine present initially appears as fluorite at the pellet faces, but later decomposes to volatile fluorides which are removed by the flowing gas atmosphere. The sequence of these reactions and the nature of their products are not influenced by electric fields.

(3) Two crystalline phases which are only observed in the positive electrode region of electrolysed pellets are a transitory, disordered mullite-like phase and corundum. The former progressively disappears as the crystallinity of the mullite in the pellet bulk improves, but the concentration of corundum progressively increases. At much higher temperatures ($\sim 1150^{\circ}\text{C}$), crystalline corundum is observed in all samples.

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