JOURNAL OF MATERIALS SCIENCE 27 (1992) 2075–2082

Supplementary alkali extraction studies of 980 °C-heated kaolinite by X-ray diffraction analysis

A. K. CHAKRABORTY
Central Glass and Ceramic Research Institute, Calcutta 700 032, India

The alkali extraction process with the aim of leaching out free SiO_2 present in 980 °C-heated kaolinite has been re-examined by corroborating with X-ray diffraction analysis of the leached and heat-treated leached residues of Georgia kaolinite. The validity of the composition of the intermediate Si–Al spinel phase analogous to the composition of 3:2 mullite has been confirmed.

1. Introduction

The structural characterization of the most controversial spinel phase derived from the decomposition of kaolinite has been studied recently. The two groups of scientific researchers concerned had worked with different experimental tools (Table I) and they had been relying on their individual claims regarding the 980 °C spinel phase, i.e. either a simple γ-Al_2O_3 spinel or a Si-substituted spinel. This was discussed earlier [1, 2]. Most workers are nowadays inclined to believe in the formation of the latter type of spinel. In this context Chakraborty and Ghosh [1, 2] had shown the SiO_2 content of Si–Al spinel as 28%, whereas Okada *et al.* [3] and Sonuparlak *et al.* [4] microanalysed the alkali-leached residue by TEM and had shown that the spinel phase contained less than 10 wt % SiO_2. This challenges the validity of the mullite-like composition of Si–Al spinel as elucidated earlier by Chakraborty and Ghosh [1, 2]. It has now become necessary to discuss the reliability of their data [3, 4] theoretically.

TABLE I Different experimental tools used to characterize 980 °C-heated Si–Al spinel phase

Method	Objective
Physical changes: (i) density, (ii) dilatometry, (iii) DTA etc.	To ascertain the probable steps of thermal transformation of kaolinites
Solubility of SiO_2 and Al_2O_3 components	To reveal the nature and state of intermediate phases
Diffraction: powder X-ray, single-crystal X-ray and electron diffraction	To identify crystalline phases formed on heating, unit cell dimensions, and structure, and to ascertain the phase relationship
Microscopy: optical and electron microscopy	To exhibit the morphology of the phases
Thermodynamic approach	To calculate theoretically the changes in free energy, heat of reaction, lattice energy etc. of several possible reaction paths of kaolinite decomposition
Spectroscopy: IR, XRF, MASS-WMR etc.	To note the change of the co-ordination number of Al during the thermal process
RED measurement by X-rays	To correlate the RDF curves of various possible theoretical 980 °C reactions with the experimentally measured one
Alkali extraction	To estimate the amount of free SiO_2 liberated during heating of kaolinite

As a first step, the possibility of Si substitution in the γ-Al_2O_3 lattice from the crystallographic point of view is discussed. The structural formula of γ-Al_2O_3 can be written as

$$8Al[Al_{13\frac{1}{3}}\square_{2\frac{2}{3}}]O_{32}$$

When a certain portion of Si^{4+} is introduced in the γ-Al_2O_3 structure, the most probable sites the Si^{4+} will occupy in the γ-Al_2O_3 lattice are the tetrahedral interstices. In spinel there are eight such sites. Therefore the possible number of substitutions of Al^{3+} by Si^{4+} will be 8 at the maximum. One Si^{4+} will replace $1\frac{1}{3}$ Al^{3+} because of charge balancing, so there may be different compositions of spinel: either whole-number or different fractions of Si^{4+} and Al^{3+}, respectively, in the framework of oxygen taken as 32. For example

$$Al_{21\frac{1}{3}}O_{32}$$

$$SiAl_{20}O_{32}$$

$$Si_2Al_{18\frac{2}{3}}O_{32}$$

$$\cdot$$

$$\cdot$$

$$\cdot$$

$$\cdot$$

$$Si_8Al_{10\frac{2}{3}}O_{32}$$

The above conjecture leads one to believe that a continuous series of spinels is theoretically possible. The upper limit of the composition as shown above is γ-Al_2O_3 ($Al_{21\frac{1}{3}}O_{32}$) itself, and the lower limit is

0022-2461

$Si_8Al_{10\frac{2}{3}}O_{32}$. The composition of the last-named Si–Al spinel had been postulated earlier by Brindley and Nakahira [5]. The question now is why Okada *et al.* [3] and Sonuparlak *et al.* [4] suggested that only Si-substituted spinel of the composition $SiO_2 \cdot 6Al_2O_3$ can form on heating kaolinite, when there exist other possibilities. From the point of view of synthesis, Chakraborty [6] showed earlier that only Si–Al spinel of the composition of mullite had formed whatever the starting compositional ratio of Al_2O_3 and SiO_2 taken during gelation. This result disproves the validity of the Si–Al spinel composition put forward by Okada *et al.* [3] and Sonuparlak *et al.* [4] and further suggests a revision of their alkali leaching study. In the present leaching experiments more emphasis has been given to solubilizing the maximum amount of amorphous SiO_2 by NaOH solution present in the 980 °C-heated products of kaolinite, which is virtually a complex mass essentially containing both amorphous and crystalline silicates and aluminosilicates. Secondly, different methods for the detection of the end-point of alkali–amorphous SiO_2 interaction have been adopted in order to determine a semi-quantitative value for amorphous SiO_2 released from the decomposition of kaolinite at 980 °C *vis-à-vis* the composition of Si–Al spinel forming at the same temperature.

2. Experimental procedure

Highly crystalline Georgia kaolinite was heat-treated to 1000 °C in an electric muffle furnace for 3 h, cooled, and ground to − 325 mesh powder in an agate mortar. Alkali leaching was carried out in the following two conditions:

(i) 3 gm of ground sample were placed in a round-bottomed flask containing 120 ml of 5% NaOH solution. The flask was placed in a boiling water bath and swirled occasionally for a few seconds.

(ii) The same conditions as in (i) except that instead of occasional swirling of the flask, the contents of flask were stirred continuously at about 1000 r.p.m. with an electric stirrer.

After leaching for a definite time, the flask containing the residue was cooled in running tap-water and centrifuged. The leachates were chemically analysed for SiO_2 and Al_2O_3. The residues were washed free of alkali and dried. In this way several leached residues of different leaching times were collected for both cases. These were first analysed by X-ray diffraction (XRD) to reveal the phases present and then successively heat-treated to 1200 and 1300 °C for 1 h and analysed by XRD to note the subsequent changes of phase development.

3. Results and discussion

3.1. Chemical analysis of the leachate

Extraction curves of both SiO_2 and Al_2O_3 of 1000 °C-heated *Bhandak* clay by 5% NaOH solution is shown in Fig. 1. It suggests that the alkali solution attacks SiO_2 as well as Al_2O_3. The rate of attack depends of course upon the nature and state of the two constituents present in 1000 °C-heated kaolinite. Generally, free SiO_2 and silica bonded to alumina will show reactivity towards alkali to a different degree, i.e. the rate of dissolution in alkali will vary. According to Fig. 1, the rate of dissolution of Al_2O_3 compared to SiO_2 is very slow at the beginning in the case of heated Bhandak kaolinite. After (say) 50 to 60 min of leaching, both SiO_2 and Al_2O_3 dissolve gradually with increase of leaching time. The slow rates of dissolutions of both SiO_2 and Al_2O_3 indicate that Al_2O_3 is going into alkali solution as sodium aluminate from aluminosilicate materials. The portion of SiO_2 leached out at the beginning of extraction is termed free SiO_2.

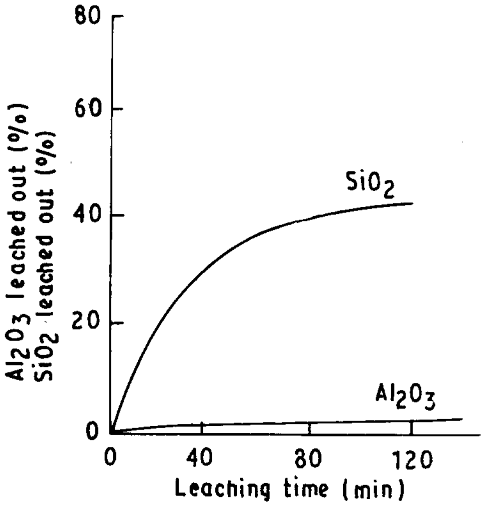

Figure 1 Alkali extraction of 980 °C heated Bhandak kaolinite at different durations of time.

The question now is how to ascertain the correct amount of free SiO_2 content by this leaching technique. During the extraction process it was observed that the two reactions, namely dissolution of SiO_2 by NaOH and interaction of NaOH with the aluminosilicate phase, proceed simultaneously from the commencement of the extraction. Thus the measured SiO_2 content at a given time in the extract consists mainly of free amorphous SiO_2 plus some amount of SiO_2 released by the attack of alkali on the aluminosilicate materials present in 980 °C-heated kaolinite. These two reactions are dependent upon the concentration of NaOH and the temperature of the extraction process for a particular heated clay.

It was observed that using 10 wt % NaOH solution and with an increase of temperature from boiling water bath to direct boiling, silica dissolution undoubtedly became more rapid but the reaction (i.e. attack on the aluminosilicate phase) became more marked as χ- and κ-type aluminas developed [7]. Formation of these phases is definitely unwanted. Selective leaching of amorphous SiO_2 *vis-à-vis* enrichment and less attack of spinel and other phases as far as practicable is our motto. To perform this, the temperature of extraction was first reduced from boiling conditions to water-bath conditions and secondly the concentration of NaOH was decreased from 10 wt % as used earlier [8] and by other researchers [3, 4] to 5 wt %. It was then observed that the time period to attain a steep rise of SiO_2 extraction in the leachate increased from 40–50 min to 60–70 min but the other reaction, i.e. dissolution of Al_2O_3 was considerably reduced, which is most desirable.

The semi-quantitative value of amorphous SiO_2 was calculated in the following way. The total percentage of SiO_2 was first read from the graph in the steeply rising part of the extraction period up to 50 min. The amount of Al_2O_3 in the same leaching time was also found from the graph. Knowing this amount of Al_2O_3 the corresponding amount of SiO_2 was calculated, based on the mullite-like composition of the residue. Lastly this calculated amount of SiO_2 was subtracted from the total SiO_2. By this procedure the amount of amorphous SiO_2 liberated from Bhandak kaolinite at 980 °C exotherm was estimated to be 35 to 37%.

The earlier alkali extraction result [8] had been verified (i) by Moya *et al.* [9] in the thermal evaluation of halloysite rock and (ii) by Rincon *et al.* [10]. Brindley and Lemaitre [11] reviewed the earlier literature but wrongly quoted the present authors' [7] estimated free SiO_2 (~ 35–37%) as 42 wt %, and further very wrongly interpreted this 42 wt % value as closer to the amount expected if complete segregation of metakaolinite to Al_2O_3 and SiO_2 took place (see their Table 7.4). Actually our value of 35–37% is not at all close to the value of 54.5%, as expected from equation below:

$$Al_2O_3 \cdot 2SiO_2 \rightarrow Al_2O_3 + 2SiO_2 \qquad (1)$$

Okada *et al.* [3] used repeated alkali extraction on heated kaolinite. On leaching once with 7% NaOH solution for 40 min they showed that the amount of extractable SiO_2 was compatible with the data of the present author and the extracted residue was of the same composition as mullite. However, after twice leaching, the residue left was of a composition approaching 8 wt % SiO_2 which corresponds approximately to $SiO_2 \cdot 6Al_2O_3$ ($Si_{1.6}Al_{10.2}O_{32}$) as determined by analytical TEM. Similar data have also been put forward recently by Sonuparlak *et al.* [4]. In fact this confusion is due to performing the leaching technique in an exhaustive manner and not as per the schedule standardized earlier by Chakraborty and Ghosh [8]. As such, in their cases both amorphous binary aluminosilicate and Si–Al spinel present in 980 °C-heated kaolinite have been severely attacked.

3.2. XRD analysis of leached residues

Fig. 2 shows the XRD analysis of alkali-leached residues for different durations of leaching time. The following observations have been noted:

(i) The amorphous band in the region 22° 2θ CuK_α decreases with increase of leaching time. This suggests indirectly that the associated free amorphous SiO_2 is going into alkali solution. At about 50–60 min of leaching time, the amorphous band almost disappears. This time is taken to be a first indication of the end-point of the amorphous SiO_2–NaOH interaction.

(ii) Si–Al spinel gives two characteristic intense bands in XRD recordings, one at about 47° 2θ and the other at 67.2° 2θ with CuK_α radiation. Both these bands increase with increase of leaching time from 0–10–20–40–50 min and then attain more or less constant values. The leaching time of ~ 50 min may also be taken as a second indication of the end-point of amorphous SiO_2–NaOH reaction.

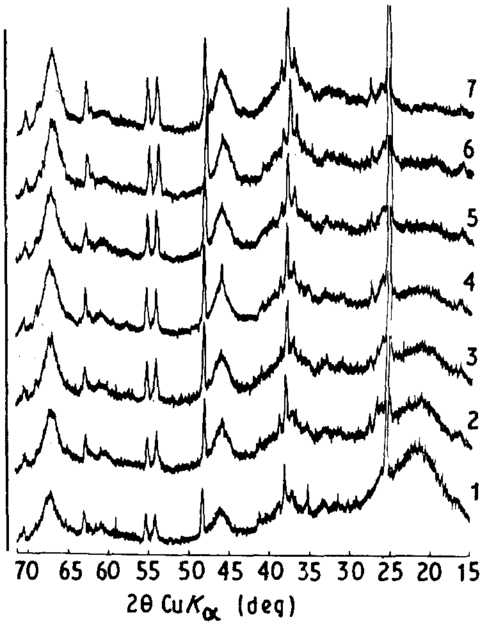

Figure 2 XRD recordings of Georgia kaolinite heated to 1000 °C for 3 h after alkali-leaching in 5% NaOH solution for different durations of time: (1) as heated, (2) Geo. 1 leached for 20 min, (3) Geo. 2 leached for 40 min, (4) Geo. 3 leached for 50 min, (5) Geo. 4 leached for 60 min, (6) Geo. 5 leached for 80 min, (7) Geo. 6 leached for 100 min.

This suggests that there is no necessity for continued leaching beyond this specific leaching time of (say) 50 min. In addition, another question arises regarding the solubilization of SiO_2 in the alkali followed by the enrichment of Si–Al spinel concentration: whether the hot alkali solution has reacted with Si–Al spinel and aluminosilicate binary phase present in 980 °C-heated kaolinite? To reveal this, the 60 min alkali-leached mass was further alkali-treated with 10 wt % NaOH solution in a hot water bath for an additional duration of time. XRD analyses of these alkali-leached residues are given in Fig. 3. The following observations were noted:

(i) The areas of the peaks corresponding to Si–Al spinel phase at 67.2° and 47° 2θ CuK_α now decreased with increase of leaching time. This indicated that the spinel phase was attacked by NaOH and further indicated the futility of the leaching procedure.

(ii) Peaks corresponding to a zeolitic phase gradually developed, as noted by a gradual increase of its intensities from 20 min to 40 min. At 60 min leaching time the zeolite phase had fully developed.

Chemical analysis of the leached residues showed an increase in the concentration of Na_2O (SiO_2 = 14.59%, Al_2O_3 = 62.95%, TiO_2 = 6.37%, Fe_2O_3 = 0.54%, MgO = 1.53%, CaO = 2.88%, K_2O = 0.08%, Na_2O = 4.37% and loss on ignition = 6.37%) in contrast to very little concentration of Na_2O present originally in heated Georgia kaolinite itself (SiO_2 = 50.75%, Al_2O_3 = 42.93%, TiO_2 = 4.02%, Fe_2O_3 = 0.46%, MgO = trace, CaO = 0.51%, K_2O

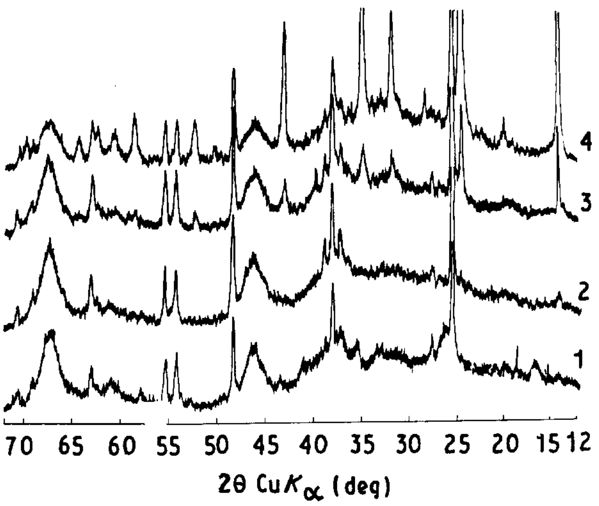

Figure 3 XRD recordings of 60 min alkali-leached 1000 °C-heated Georgia kaolinite with extended leaching time in 10% NaOH solution: (1) Geo. 8 leached for 10 min, (2) Geo. 9 leached for 20 min, (3) Geo. 10 leached for 40 min, (4) Geo. 11 leached for 60 min.

TABLE II *d* values of zeolitic phase formed during NaOH leaching of 1000 °C-heated Georgia kaolinite

d (nm)	I/I_0
0.622	80
0.444	30
0.363	100
0.313	5
0.281	60
0.256	80
0.237	30
0.209	80
0.1989	5
0.1888	5
0.1814	30
0.1737	40
0.1628	5
0.1573	30
0.1480	30
0.1439	30
0.1402	5
0.137	30
0.1317	30

= 0.04%, Na_2O = 0.08% and loss on ignition = 0.85%). Table II gives the XRD values of the zeolite phase.

The gradual diminution of the amorphous band due to solubilization of amorphous SiO_2 in NaOH thus observed in the XRD analysis of residues tallies well with that of Okada *et al.* [3]. The remaining amorphous band accounts for the presence of an amorphous aluminosilicate phase. However, Percival *et al.* [12] and Okada *et al.* [3] did not show enhancement of the XRD peak of Si–Al spinel in the case of the residue left after leaching, nor did they analyse by XRD the twice-leached residue or the residue leached after an extended period. On extended leaching (e.g. for more than 40 min leaching and with 10% NaOH in direct boiling conditions) a higher amount of SiO_2 (greater than 35–37%) goes into alkali solution and the residue is a mixture of newly-formed alumina and zeolite-type phase [7].

This result indicates that a portion of SiO_2 is definitely bonded to Al_2O_3 and it contradicts the contentions of Sonuparlak *et al.* [4] that (i) on extended leaching nearly all SiO_2 would go into alkali solution and (ii) that metakaolinite would transform at 980 °C to pure γ-Al_2O_3 spinel and amorphous SiO_2, although they showed only an Al peak in the energy-dispersive spectroscopy (EDS) (Fig. 7 of [4]) of leached samples after prolonged leaching time. They took XRD patterns of the alkali-leached residue in order to resolve the confusion, but they neither reproduced the X-ray data in their original paper [4] nor in their reply [13] to the present author's comment [14]. On the other hand they simply reproduced a microdiffraction pattern of 40 min leached residue which contained spinel, thereby claiming the persistence of γ-Al_2O_3.

However, this result does not mean that the binary aluminosilicate phase and Si–Al spinel phase are not attacked. The present author [7] had shown that an increase of time and temperature during leaching (direct boiling was used by Sonuparlak *et al.* [4]) attacked the binary aluminosilicate phase, Si–Al spinel along with the weakly crystalline mullite and new phase or phases developed. The amounts of the new phases increased with time and temperature. By XRD studies Chakraborty and Ghosh [8] have shown the transformations of the newly formed phases with rise of temperature. Furthermore, the cause of the persistence of 4 0 0 and 4 4 0 reflections of γ-Al_2O_3 had already been reported [14]. They overlooked this and suggested the γ-Al_2O_3 hypothesis to be true.

3.3. XRD analysis of heat-treated alkali-leached residues

Alkali-leached residues on further heating developed mullite, corundum and cristobalite depending upon their previous leaching conditions and are shown in Fig. 4. The relative development of phases on heat treatment at 1200 °C (Fig. 4a) and 1300 °C (Fig. 4b) of different leached residues as identified from the above XRD charts are shown in Table III. The following observations were noted.

(i) *Formation of corundum.* Traces of α-Al_2O_3 appeared on heating Geo. 4 at both 1200 and 1300 °C by the detection of a 0.208 nm peak in XRD recording. More and more development of corundum was observed on heating the alkali-leached residues collected with increase of leaching time (e.g. Geo. 5, Geo. 6 etc.). From these observations the end-point of alkali–SiO_2 reaction can be predicted to be less than 60 min. Beyond this time alkali leaching leads to the attack of both Si–Al spinel and binary aluminosilicate phase with liberation of an aluminous phase from which corundum develops on further heating.

(ii) *Cristobalite formation.* The amount of cristobalite formation decreases with increase of leaching time. This shows that free amorphous SiO_2 is going into alkali solution during the leaching process. At about 40 min time (Geo. 2), on further heating the 0.404 nm

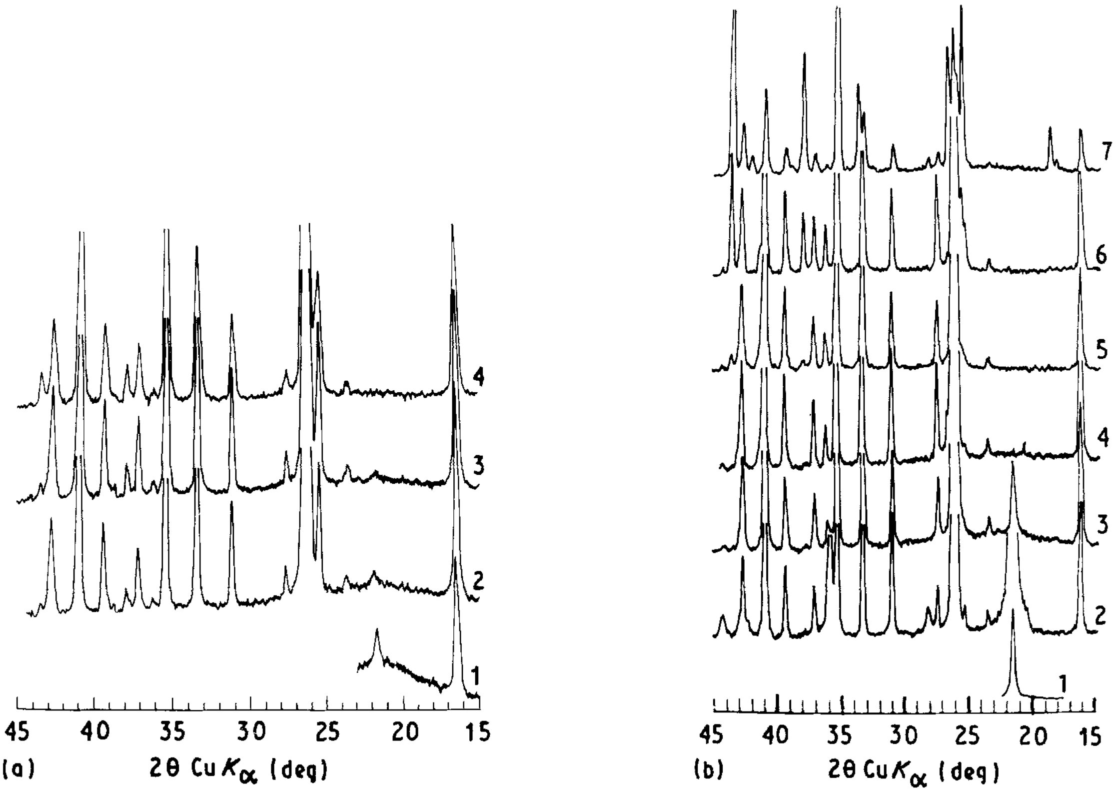

Figure 4 (a) XRD recordings of different alkali-leached residues heated to 1200 °C for 1 h: (1) as heated, (2) Geo. 1, (3) Geo. 2, (4) Geo. 4. (b) XRD recordings of different alkali-leached residues heated to 1300 °C for 1 h: (1) as-heated at 1×10^3 setting in XRD recording, (2) as-heated at 1×10^4 setting, (3) Geo. 1 as (2), (4) Geo. 2 as (2), (5) Geo. 4 as (2), (6) Geo. 5 as (2), (7) Geo. 6 as (2).

TABLE III XRD intensities of mullite and cristobalite formed on heating alkali-leached residues obtained during leaching at 1000 °C for 3 h of heated Georgia kaolinite

Leaching time for heated Georgia kaolinite (min)	Mullite formed as a measure of 0.537 nm peak (scale divisions from XRD chart)		Peak height (0.537 nm) of standard mullite (Fig. 5)	Cristobalite formed as a measure of 0.404 nm peak (scale division from XRD chart)		Peak height (0.404 nm) of standard cristobalite (Fig. 5)
	1200 °C	1300 °C		1200 °C	1300 °C	
0	36[a]	60[a]	38[b] ($38 \times 4 = 152$)[a]	10[a]	28[c] ($28 \times 10 = 280$)[a]	88[c] ($88 \times 10 = 880$)[a]
20	55[a]	43[a]		5[a]	22[a]	
40	60[a]	57[a]		3[a]	3[a]	
60	45[a]	30[a]		Nil	Nil	
80	–	40[a]		–	–	
100	–	13[a]		–	–	

[a] At 1×10^3 setting in XRD recording.
[b] At 4×10^3 setting.
[c] At 1×10^4 setting.

peak of cristobalite vanishes. These results suggest that complete removal of amorphous SiO_2 takes place within 40 to 50 min of leaching time.

(iii) *Mullite formation.* It was observed that the amount of mullite developed on heating the leached residue increased with increase of leaching time upto 40 min duration, after which it decreased even on further leaching (Table III). Therefore, roughly 40–50 min time is enough to leach out the associated free amorphous SiO_2 present in 980 °C-heated Georgia kaolinite. Furthermore, on comparing the mullite formation of alkali-leached residues at two different temperatures, namely 1200 and 1300 °C, it was observed that the amount of mullite so developed on firing at 1200 °C decreased on further heating to 1300 °C. It has been noted previously that with an increase of leaching time, gradually more and more Na_2O is introduced into the residue. Probably this Na_2O fraction hinders mullite development or it facilitates conversion of mullite into glass. The decrease in the quantity of mullite was observed by comparing the mullite development of heated alkali-leached residues with that of a standard as shown in Fig. 5. From Table III, mullite formation from leached residues on heating to 1300 °C is not found to attain a constant level. It is therefore apparent that the end-point of alkali–SiO_2 interaction has not been properly detected by observing mullite formation occurring on heating the leached residue obtained in the first leaching operations.

3.4. XRD analysis of heat-treated alkali-leached residues obtained by continuous stirring

Following the above leaching treatment, the silica content of leached residues collected at different durations of leaching time were analysed gravimetrically and the results are shown in Fig. 6. The nature of the curve of wt % SiO_2 versus leaching time for different residues was found to be analogous to the direct compositional analysis by EDS in an analytical TEM used by Sonuparlak *et al.* [4]. The dissolution of amorphous SiO_2 under these continuous stirring conditions was found to be comparatively more rapid than in the leaching procedure followed previously. From their extraction curve (Fig. 6 of [4]) Sonuparlak *et al.* suggested that at extended leaching times (~ 25 min) the rate of leaching of SiO_2 approached zero, below 10 wt % SiO_2. Accordingly they concluded that the spinel contained not more than 10 wt % SiO_2. Here arises a question: what was the justification and/or reason behind the choice of 25 min leaching time as the end-point of amorphous SiO_2–5% NaOH solubilization reaction? To answer the above question, the crystallization behaviour of alkali-leached residues was been studied in the usual way. Fig. 7 and Table IV show the XRD analysis of heat-treated residues.

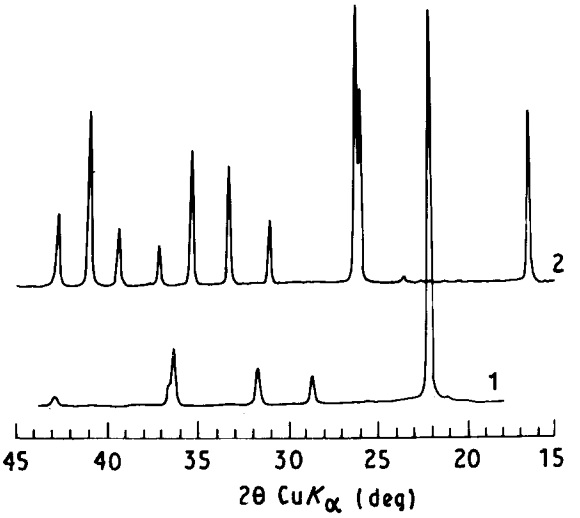

Figure 5 XRD recordings of (1) standard cristobalite, (2) mullite.

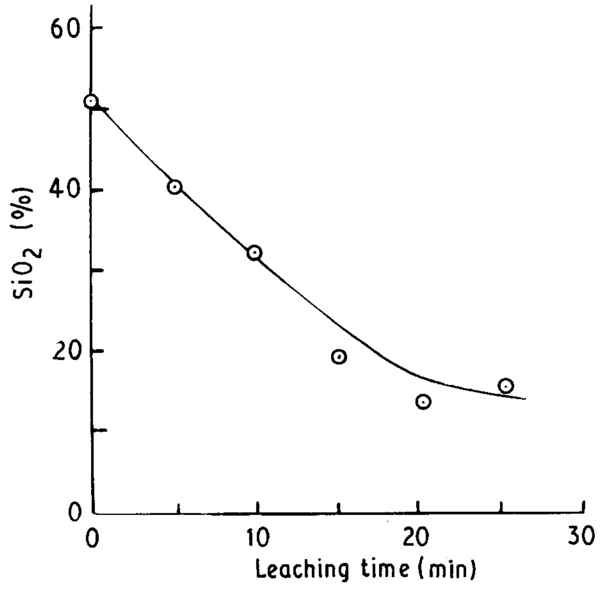

Figure 6 Percentage of SiO_2 in the leached residue versus time of leaching.

Figure 7 XRD recordings of different heat-treated residues obtained by alkali leaching of heated Georgia kaolinite with different durations of time for continuous stirring. (a) Heating to 1200 °C for 1 h: (1) Geo. 19 leached for 5 min, (2) Geo. 20 leached for 10 min, (3) Geo. 22 leached for 15 min, (4) Geo. 23 leached for 20 min, (5) Geo. 24 leached for 25 min. (b) Heating to 1300 °C for 1 h: (1) Geo. 19 at 1 $\times 10^3$ setting in XRD recording, (2) Geo. 20 as (1), (3) Geo. 22 as (1), (4) Geo. 23 as (1), (5) Geo. 24 as (1), (6) Geo. 19 at 1×10^4 setting.

3.4.1. Cristobalite formation

The development of cristobalite during heating of the leached residue is a direct index of the presence of free amorphous SiO_2. According to this, alkali-leached samples collected at different durations show a gradual diminution in their cristobalite content on heating (Table IV). On heating the residue to (say) 1200 °C for 1 h, the 0.404 nm peak height decreases from peak height 11 divisions (arbitrary diffractogram scale) in 5 min leaching time to 3 divisions in 10 min leaching time, and disappears completely at about 15 min time. Therefore, the amount of SiO_2 leached out in the time interval 10–15 min is to be considered as free SiO_2 present in 980 °C-heated Georgia kaolinite. In other words, the amount of SiO_2 present in the leached residue after the above time interval is to be regarded as chemically bonded SiO_2. The composition of the residues in between the leaching period encompasses the composition of mullite. In this way,

TABLE IV XRD intensities of mullite and cristobalite developed on heating alkali-leached residues collected during continuous stirring

Sample	Leaching time for Georgia kaolinite heated to 1000 °C for 3 h. (min)	Mullite formed as measured from 0.537 nm peak height (scale divisions from XRD chart)			Cristobalite developed as measured from 0.404 nm peak height (scale divisions from XRD chart	
		1100 °C	1200 °C	1300 °C	1200 °C	1300 °C
Geo. 19	5		45[b]	45[b]	11[b]	12[c] ($12 \times 10 = 120$)[b]
Geo. 20	10		63[b]	74[b]	3[b]	Nil
Geo. 22	15	20[a] (40)[b]	39[a] (78)[b]	43[a] (86)[b]	Nil	Nil
Geo. 23	20	25[a] (50)[b]	24[a] (48)[b]	35[a] (70)[b]		
Geo. 24	25	13[a] (26)[b]	20[a] (40)[b]	22[a] (44)[b]		

[a] At 2×10^3 setting in XRD recording.
[b] At 1×10^3 setting.
[c] At 1×10^4 setting.

the amount of free SiO_2 and bonded SiO_2 present in 980°-heated clay have been differentiated. The percentage of SiO_2 leached out beyond 15 min time (Fig. 6) could be accounted for by the breakdown of both Si–Al spinel and binary aluminosilicate phases. To corroborate the above findings the second procedure was followed.

3.4.2. Mullite formation

Mullite will form jointly from Si–Al spinel and binary aluminosilicate phase, respectively [2]. The accumulation of mullite during the heating of leached residue is an indirect index of the presence or absence of free SiO_2. For example, the concentration of mullite increases on heating the residues collected after 5 to 10 min and lastly up to 15 min leaching time; after that it decreases (Table IV). This result definitely indicates that with removal of SiO_2, the concentration of mullite has almost attained a maximum with 15 min leaching time. Afterwards, with increase of time, SiO_2 further exsolves out by break-up of both the aluminosilicates, and ultimately the formation of mullite decreases. Therefore, a leaching time not exceeding 15 min may be regarded as the end-point of alkali–amorphous SiO_2 reaction in this complex situation. The advantage of this leaching technique is that the formation of a zeolitic-type phase during the leaching process has been completely eliminated, since the chemical analyses of Na_2O in the leached residues (e.g. 0 min–0.08 wt %, 5 min–0.37 wt %, 10 min–0.57 wt %, 15 min–0.84 wt % etc.) do not show much increment of Na_2O in contrast to the previous leaching process. Secondly, as per expectation, the alkali–SiO_2 reaction is much more predominant but the possibility of decomposing the Si–Al spinel phase may still remain. Nevertheless, the percentage of SiO_2 in the Si–Al spinel phase has been confirmed to be about 28 wt % unlike the value of 10 wt % obtained by both Sonuparlak *et al.* [4] and Okada *et al.* [3].

4. Conclusion

The total amount of SiO_2 present in 980 °C-heated kaolinite remains partly in the Si–Al spinel phase and partly in an amorphous binary aluminosilicate phase. Both these transform to mullite on further heating, and the rest which is present as free SiO_2 ultimately converts to cristobalite and glass. With this in view, the alkali leaching process has been deployed to mostly remove the free siliceous portion out of the matrix of 980 °C-heated kaolinite. Several reactions proceed during the leaching process. The major problem arises in determining the end-point, particularly of NaOH solution–free amorphous SiO_2 reaction in the presence of other reactions.

During leaching it has been shown that the amorphous band which is characteristic of free SiO_2 in XRD recording decreases with increase of leaching time and then attains a constant value; conversely, the concentration of Si–Al spinel phase increases as noted by the increase in XRD intensity of the peaks of Si–Al spinel phase followed by the removal of SiO_2. On continued leaching, its intensity again decreases with subsequent development of an aluminous phase and a zeolitic-type phase. During heating of the leached residues, it has been observed that the amount of cristobalite development decreases with increase of leaching time (which is quite likely as free SiO_2 is being dissolved in hot alkali) and ultimately the cristobalite formation completely ceases. Side by side the concentration of mullite development during heating of residues increases with increase of leaching time, and reaches its highest level when complete removal of free SiO_2 has been attained. Its concentration decreases further due to the decomposition of Si–Al spinel and binary aluminosilicate by hot NaOH on continued leaching. During continuous stirring at about 15 min leaching time, the leached residue shows complete removal of the amorphous XRD band on one hand, and on the other hand complete elimination of cristobalite formation takes place on heating the residue. Thus 15 min time of leaching can be taken as the approximate end-point of the above reaction. Further, the residue obtained for this leaching period shows maximum mullite enrichment during onward heating. The amount of bonded SiO_2 which accounts for maximum mullite formation has been assessed from the leaching curve to be little less than 15 min duration, because of a correction factor taken into consideration for TiO_2

originally present in Georgia kaolinite which will ultimately be incorporated into mullite. On average, the end-point of the alkali–free SiO_2 reaction will be attained during 12 to 14 min, i.e. with a time of less than 15 min duration. Accordingly the composition of the residue left after 12–14 min leaching becomes nearly equal to the composition of 3:2 mullite.

References

1. A. K. CHAKRABORTY and D. K. GHOSH, *J. Amer. Ceram. Soc.* **62** (1979) 52.
2. *Idem, ibid.* **74** (1991) 1401.
3. K. OKADA, M. OTSUKA and J. OSSAKA, *ibid.* **69** (1986) C-251.
4. B. SONUPARLAK, M. SARIKAYA and I. A. AKSAY, *ibid.* **70** (1987) 837.
5. G. W. BRINDLEY and M. NAKAHIRA, *ibid.* **42** (1959) 319.
6. A. K. CHAKRABORTY, *ibid.* **62** (1979) 120.
7. A. K. CHAKRAVORTY and D. K. GHOSH, *ibid.* **61** (1978) 90.
8. *Idem, ibid.* **61** (1978) 170.
9. J. S. MOYA, C. J. SERNA and J. E. IGLESIAS, *J. Mater. Sci.* **20** (1985) 32.
10. J. Mq. RINCON, G. THOMAS and J. S. MOYA, *J. Amer. Ceram. Soc.* **69** (1986) C-29.
11. G. W. BRINDLEY and J. LEMAITRE, in "Chemistry of Clays and Clay Minerals", edited by A. C. D. Newman, Monograph No. 6, (Mineralogical Society, London, 1987), p. 319.
12. H. S. PERCIVAL, J. F. DUNCAN and P. K. FOSTER, *J. Amer. Ceram. Soc.* **52** (1974) 57.
13. I. A. AKSAY, M. SARIKAYA and B. SONUPARLAK, *ibid.* **72** (1989) 1572.
14. A. K. CHAKRABORTY and D. K. GHOSH, *ibid.* **72** (1989) 1569.

Received 6 December 1990
and accepted 26 July 1991