

# Chemical resistance of the moulding of saponite/acriflavine complex after carbonization

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Powders of saponite/acriflavine complex (SAC) saponite/carbon black mixture (SKM) and saponite itself (Sap) were pressed into small discs (20 mm diameter  $\times$  3 mm), followed by heat treatment at 1073 to 1473 K under nitrogen or argon. Their chemical resistance to 10% NaOH, conc. HCl, conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub> solutions at room temperature was examined on the basis of weight loss. The resistance of the three samples to NaOH solution was found to increase with increasing heat-treatment temperature, and both SAC and Sap after heating to 1473 K exhibited only a slight weight loss even after soaking for 20 d. On the whole, SAC had the highest resistance among three. The three samples were more resistant to acid solutions than NaOH, the resistance of both SKM and Sap increasing with increasing heat-treatment temperature. The amorphous component and forsterite crystal in the samples after heating to high temperature were preferentially attacked by NaOH and acid solutions, respectively. These results are discussed on the basis of X-ray diffraction, SEM observation, carbon content, etc.

## 1. Introduction

Clay/organic complexes exhibit very different thermal degradation behaviour from the parent clays [1, 2]. For example, enstatite and forsterite crystals grow less favourably in saponite/organic complex on heating (carbonizing) than in saponite, resulting in a dense and homogeneous structure [3]. In addition, the electrical resistivity of moulding of the saponite/organic complex fell to 1  $\Omega$  cm or less, after carbonization at 1573 K [4], which is more effective in lowering the resistivity than the conventional method using carbon black or chopped carbon fibre [5, 6]. These phenomena suggest that a clay/organic complex might be an attractive raw material for a ceramic with unique properties. For practical use, of course, the moulding must be evaluated more comprehensively. From such a point of view, the chemical resistance of a moulding from saponite/organic complex was characterized by comparison with those from saponite/carbon black mixture and saponite itself.

## 2. Experimental procedure

### 2.1. Raw materials

Saponite  $[(\text{OH})_4(\text{Si}_{8-a}\text{Al}_a)(\text{Mg}_{8-b}\text{Al}_b)\text{O}_{20}]\text{Na}_{(a-b)}^+$  was synthesized by Kunimine Industries Co. Ltd and kindly supplied for this work. Its cation exchange capacity (CEC) is 71 meq/100 g and its chemical composition is shown in Table I [7]. The chemical formula of acriflavine hydrochloride (m.p. 533 K, dye content  $\sim$  90%) is C<sub>18</sub>NH<sub>7</sub>(NH<sub>2</sub>)<sub>2</sub> · 2HCl. An electrically conductive carbon black, Ketjenblack E.C. [8], was supplied by Lion Yushi Chemical Co. Ltd and some of its properties are shown in Table II.

### 2.2. Preparation of samples

Three aqueous sols were prepared: (i) a 2 to 3% aqueous sol (Sap); (ii) acriflavine hydrochloride was added to a 3 wt% saponite aqueous sol with an equivalent CEC value to Sap, followed by stirring at room temperature for 1 d to synthesize saponite/acriflavine complex (SAC); (iii) Ketjenblack was mixed with a saponite aqueous sol for 12 h at room temperature (SKM). The resulting three sols were spray-dried by Okawara Chemical Engineering Co. Ltd. The particles from SAC and Sap were about 10  $\mu$ m diameter.

Each powder sample was pressed into discs (20 mm diameter  $\times$  3 mm) at 600 kg cm<sup>-2</sup>. The water content of the powder was carefully controlled in order to produce a good mould. Heat-treatment (carbonization) was undertaken at 1073, 1273 K under nitrogen and 1473 K under argon. Heating rate and residence time at a prefixed temperature were 2 K min<sup>-1</sup> and 1 h, respectively. The discs were used in subsequent experiments after polishing with sandpaper (no. 400).

### 2.3. Measurements

#### 2.3.1. Chemical resistance

Solutions of 10 wt% NaOH, conc. HCl, conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub> were used. A disc was soaked in 70 ml solution and kept for a prefixed period at 298 K, followed by washing and drying to obtain weight loss. Weight loss is the average of data with almost no scatter.

#### 2.3.2. X-ray diffraction

X-ray diffraction was carried out using nickel-filtered

TABLE I Chemical composition (wt%) of saponite

SiO <sub>2</sub>	54.71
Al <sub>2</sub> O <sub>3</sub>	5.02
Fe <sub>2</sub> O <sub>3</sub>	0.03
MgO	30.74
Na <sub>2</sub> O	2.15
SO <sub>3</sub>	0.67
H <sub>2</sub> O	6.67
Total	99.99

CuK $\alpha$  radiation. The uncrushed disc was mounted on a sample holder.

### 2.3.3. SEM observation

Surfaces of the discs before and after soaking were observed by scanning electron microscopy (SEM).

### 2.3.4. Carbon content

The carbon content of the disc was measured by the combustion method using tin metal particles as a combustion accelerator.

## 3. Results

### 3.1. Discs before soaking

X-ray diffraction profiles of SAC and SKM before soaking are shown in Figs 1a and b (labelled "original" in the figures). The profiles of Sap are not shown, because they were analogous to those of SKM. Enstatite, with and without a small amount of forsterite, appeared in SKM after heating to 1083 K and 1273 K (Fig. 1a). After heating to 1473 K, a major crystal changed into forsterite. In SAC, on the other hand, only enstatite was observed even after heating to 1473 K (Fig. 1b).

Figs 2a to c show scanning electron micrographs of the 1473 K discs before soaking ("original" in the photographs). Rounded pores are observed in Sap discs (Fig. 2a), suggesting softening or semi-fusing during the heating process. A crystal can be seen in the pore as arrowed. A similar structure is also seen in SAC (Fig. 2c), but SKM seems to have a less sintered structure (Fig. 2b).

Table III shows the carbon content of the discs. SKM before soaking ("original") contained a somewhat larger amount of carbon than SAC. In both SAC and SKM, the discs before and after heating to 1073 K contained equal amounts of carbon, but this decreased on heating to higher temperatures.

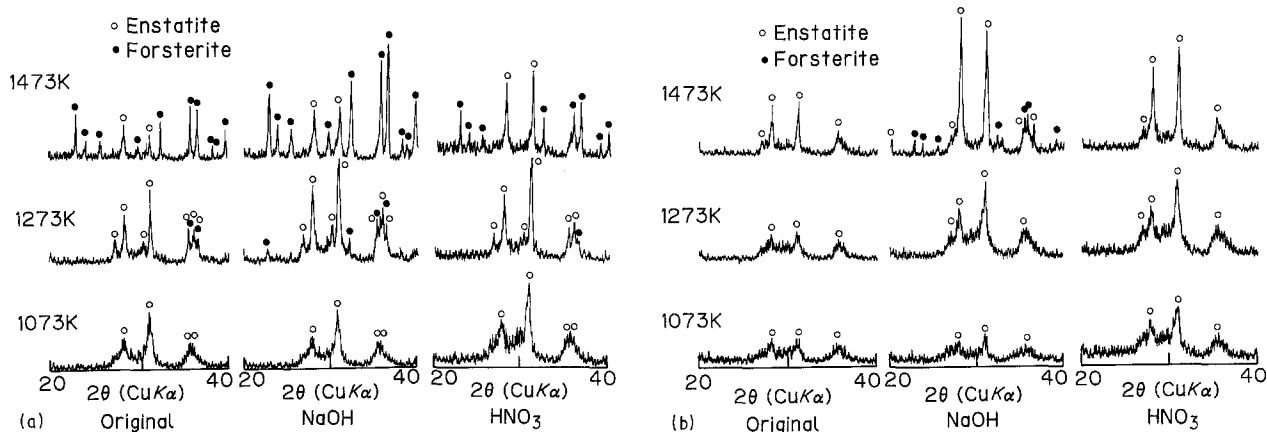


Figure 1 X-ray diffraction profiles (a) 1473 K SKM, and (b) 1473 K SAC, before and after soaking in NaOH and HNO<sub>3</sub> solutions for 20 d.

TABLE II Properties of Ketjenblack EC

I <sub>2</sub> -absorption	950 mg g <sup>-1</sup>
N <sub>2</sub> -BET surface area	1000 m <sup>2</sup> g <sup>-1</sup>
Volatile matter	1%
Ash content	0.5%
Particle size	30 $\mu$ m
Apparent density	150 g l <sup>-1</sup>

### 3.2. Discs after soaking

#### 3.2.1. NaOH

Fig. 3 shows the relationship between the weight loss and soaking period in 10% NaOH solution. On the basis of weight loss after 5 and 10 d soaking, the resistance of the three samples was clearly enhanced with increasing heat-treatment temperature. Each sample heated to 1073 and 1273 K showed analogous weight loss after 20 d soaking. Heating to 1473 K, however, resulted in a remarkable improvement of resistance, especially in Sap. On the whole, SAC has the highest resistance to NaOH solution.

As shown in Fig. 1, the diffraction intensities of enstatite and forsterite in both SKM and SAC increased after soaking for 20 d in NaOH solution. The relative intensity between both crystals in SKM was almost maintained throughout soaking, but forsterite appeared in the 1473 K SAC after soaking in NaOH. Such behaviour relates intimately to the results of SEM observation described below.

Structural change in the scanning electron micrographs through soaking was observed to be so remarkable in the 1473 K discs that it is shown in Figs 2a to c. No change was observed in SAC in contrast to the appearance of large crystals ( $\sim 10 \mu$ m) surrounded with fine crystals in Sap and SKM. The large and fine crystals are forsterite and enstatite, respectively, as reported previously [3]. 1473 K treated SKM showed similar behaviour, although the forsterite crystal is not as large as in the Sap disc. These results suggest that the amorphous component was attacked preferentially by NaOH solution. Such a preferential attack is not clear on the scanning electron micrograph of the SAC disc but possibly occurred in view of its X-ray diffraction profiles. As shown in Fig. 3, the rate of weight loss becomes gradually slower with soaking time, which is reasonably explained by more resistive crystals remaining after preferential removal of the amorphous component. The carbon contents of both SAC and

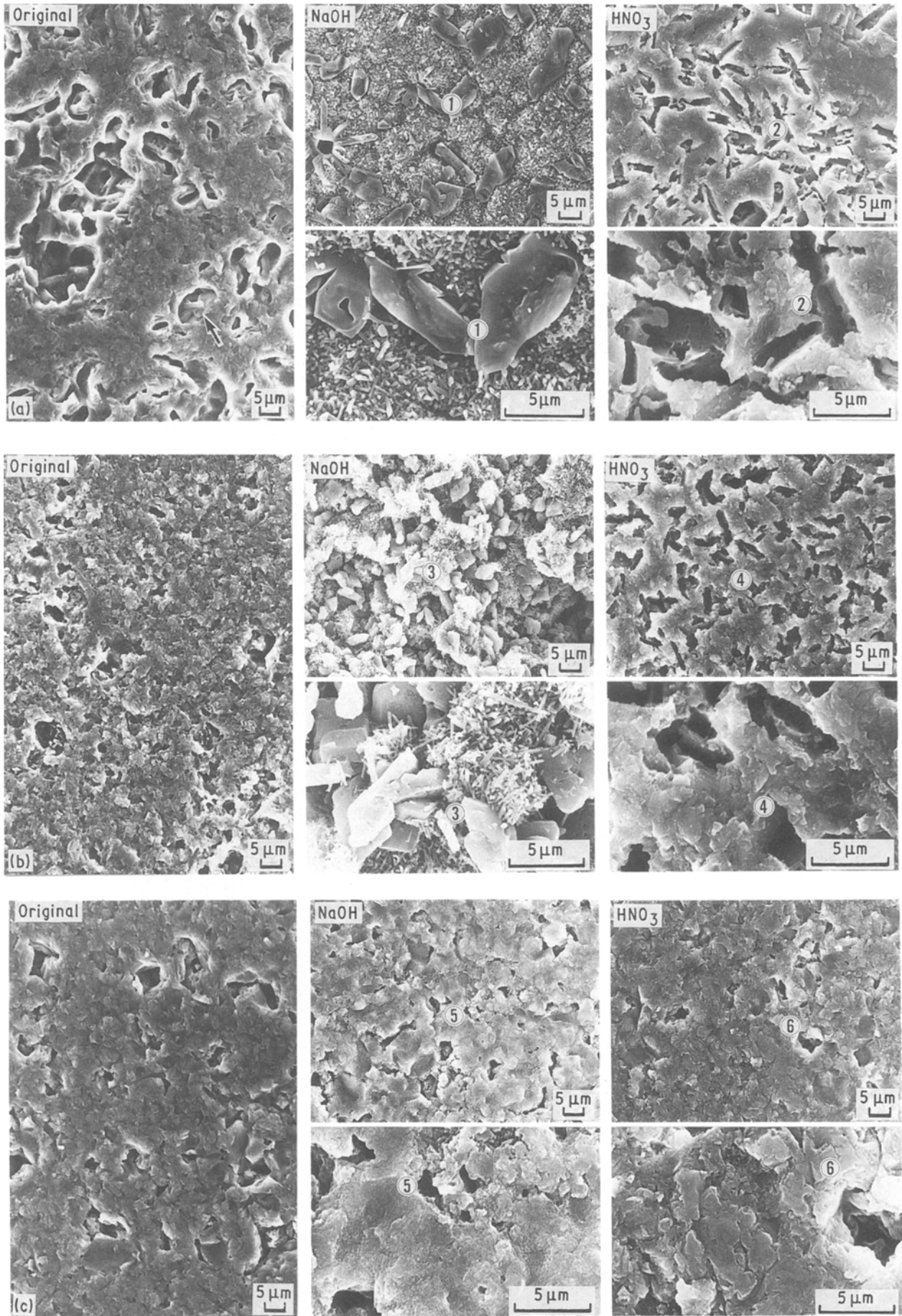


Figure 2 Scanning electron micrographs of (a) 1473 K Sap, (b) 1473 K SKM, and (c) 1473 K SAC, before and after soaking in NaOH and HNO<sub>3</sub> solutions for 20d.

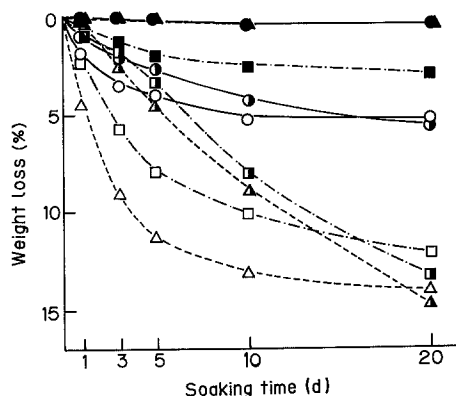


Figure 3 Relationship between weight loss and soaking time in NaOH solution. (○) 1073 K SAC, (●) 1273 K SAC, (●) 1473 K SAC, (□) 1073 K SKM, (■) 1273 K SKM, (■) 1473 K SKM, (△) 1073 K Sap, (▲) 1273 K Sap, (▲) 1473 K Sap.

SKM increased after soaking in NaOH solution, as shown in Table IV. It was difficult to identify the carbon on micrograph. It must exist at sites where carbon is not removed easily by preferential attack of the amorphous region by NaOH solution.

### 3.2.2. Acids

Table V shows weight loss of the discs after soaking in acid solutions for 20 d. On the whole, weight loss increased in the order  $HCl > HNO_3 > H_2SO_4$ , although the difference is small. When heat-treatment temperature is low, SAC exhibited higher resistance than the other two samples, but such a tendency was changed in the samples heated to high temperature.

As shown in Fig. 1a, the strength of the diffraction pattern of forsterite in SKM decreased after soaking, indicating preferential removal of forsterite by  $HNO_3$  solution. Such behaviour became clearer on comparing it with results of SEM observation shown in Fig. 2. In SAC shown in Fig. 2c, the irregular-shaped particles became slightly clearer after soaking in  $HNO_3$ . In the SKM and Sap discs, on the other hand, angular pores, corresponding to forsterite crystal, appeared after soaking (Figs 2a and b). By comparing this with X-ray diffraction results given above, it is concluded that forsterite crystal is preferentially removed. The resistance of the amorphous component to acid is not so clear. Table IV shows the carbon contents of the discs after soaking in acid solutions for 20 d. There is no marked change before and after soaking.

## 4. Discussion

The results may be summarized as follows.

1. SAC exhibited higher resistance to NaOH solution than the other two samples. The resistance of all samples improved with increasing heat-treatment tem-

TABLE III Carbon content of samples before and after heating

Sample	Carbon content (wt %)			
	Before heating	1073 K	1273 K	1473 K
SAC	3.9	4.0	3.3	3.3
SKM	4.5	4.5	4.1	4.2
Sap	0.0	0.0	0.0	0.0

TABLE IV Carbon content of samples before and after soaking

Sample	Carbon content (wt %)				
	Before soaking	NaOH	HCl	$HNO_3$	$H_2SO_4$
1073 K SAC	4.0	5.2	4.3	4.4	4.3
1273 K SAC	3.3	4.1	3.6	3.4	3.4
1073 K SKM	4.5	5.4	4.7	4.7	4.5
1273 K SKM	4.1	5.2	4.3	4.4	4.3

perature, and the 1473 K SAC and 1473 Sap exhibited no weight losses even after soaking for 20 d.

2. The resistance of the three samples to acid solutions was very high. Both Sap and SKM had improved resistance with increased heat-treatment temperature.

3. NaOH and acid solutions preferentially attacked the amorphous component and forsterite, respectively.

The factors controlling reactivity of the disc are: (i) the reaction area, (ii) the kind of crystal, (iii) the chemical composition of the amorphous component, (iv) the content and physical state of carbon, etc.

Resistance to NaOH is first discussed on the basis of these factors. The resistance, on the whole, increased in the order of  $SAC > SKM = Sap$ . The reaction area of the disc is not clear, but the difference between the three samples seems to be not so large, from the scanning electron micrographs.

The crystals formed in the samples are forsterite and enstatite which are resistant to NaOH solution. As stated above, NaOH solution attacks the amorphous component preferentially. Raw saponite includes about 2%  $Na_2O$  which remains in both Sap and SKM samples, but not in the SAC sample, throughout the cation exchange reaction [8, 9]. It is well known that  $Na_2O$  is effective in melting the oxide at lower temperatures. After crystallization,  $Na_2O$  is concentrated in the amorphous component, leading to lowering of the resistance to NaOH solution [10, 11].

X-ray diffraction showed that SAC consists of a larger amount of the amorphous component than others. The amorphous component, without  $Na_2O$ , derived from SAC by thermal decomposition is more difficult to crystallize because of its lower fluidity. Such an amorphous component has a higher resistance to NaOH solution than the amorphous component including  $Na_2O$  [10, 11].

TABLE V Weight loss of samples after soaking in acids for 20 d

Sample	Weight loss (wt %)		
	HCl	$HNO_3$	$H_2SO_4$
1073 K SAC	2.2	1.1	0.0
1273 K SAC	3.0	1.5	0.4
1473 K SAC	3.5	1.0	0.2
1073 K SKM	5.0	2.9	1.1
1273 K SKM	3.0	3.2	0.3
1473 K SKM	0.6	0.7	+ 0.5
1073 K Sap	4.3	2.4	1.3
1273 K Sap	0.7	0.6	0.1
1473 K Sap	0.5	0.3	0.0

The carbon material is well known to be very resistant to chemicals. As shown in Table IV, the carbon content increased after soaking in NaOH solution. The disc covered with the carbon must be very resistant to NaOH solution. Table IV shows that SAC contains a smaller amount of carbon than SKM. However, the carbon particle in SAC derived from acriflavine is far finer than the Ketjenblack particle (30  $\mu\text{m}$ ), which will be reported later [12]. Fine carbon particles dispersed throughout the disc are more effective in preventing attack by NaOH solution.

Both Sap and SKM, especially the former, after heating to high temperature had an improved resistance up to nearly the same level as SAC. Both Sap and SKM were sintered to decrease the reaction area. However, Ketjenblack in SKM somewhat hinders the sintering, as shown in the scanning electron micrographs, possibly resulting in the structure with a somewhat larger reaction area.

On the other hand, SKM and Sap had lower resistance to acids with increasing heat-treatment temperature, which is the opposite trend to SAC. As noted in Fig. 2,  $\text{HNO}_3$  solution preferentially attacks forsterite crystal. Because the matrix consisting of the amorphous component and fine enstatite crystals has a higher resistance, a pore forms after preferential removal of forsterite crystal. The amount of forsterite in SAC is small and the crystal is so fine as to be never observed by SEM. Preferential removal of such fine forsterite crystals may result in the separation of the matrix from the disc, leading to larger weight loss. In contrast to Sap

and SKM, the resistance of SAC was not improved with increasing heat-treatment temperature. This is because  $\text{Na}_2\text{O}$  accelerates the sintering of the disk but does not lower the resistance to acid solutions.

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