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Desilication from illite by thermochemical activation①

JIANG Tao (姜 涛), CUI Zhi-xin(崔智鑫), LI Guang-hui(李光辉),
FAN Xiao-hui(范晓慧), HUANG Zhu-cheng(黄柱成), QUI Guan-zhou(邱冠周)
(School of Resources Processing and Bioengineering, Central South University, Changsha 410083, China)

Abstract: Illite occurs widely in bauxite ores and results in low alumina grade of the ores. Differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and X-ray diffraction analysis (XRD) show the OH groups split off from the structural framework of illite between 500 ℃ and 700 ℃. With the increase in temperature up to about 1 100 ℃, the layer structure of illite breaks up and Si in the layers is transformed into the amorphous state. Meanwhile, mullite comes out at 1 100 ℃. Quartz occurring in illite keeps unchanged in structure in the range of 500－1 200 ℃. A desilication process from illite by thermochemical activation followed by alkali leaching is therefore developed on the basis of the behavior that amorphous silica is alkali soluble. The investigation finds that the optimum parameters for desilication are activation temperature of 1 100－1 150 ℃, activation time of 90－120 min, leaching temperature of 95－110 ℃, leaching time of 90－120 min and concentration of caustic soda (Na_2O_k) 120－150 g/L. An overall desilication about 45% is attained under these conditions. XRD analysis confirms that the active amorphous SiO_2 has been dissolved in the alkali solution and removed from the samples, while quartz and mullite have not. The investigation also shows that the formation of mullite during activation and formation of sodium hydroaluminosilicates ($Na_{96}Al_{96}Si_{96}O_{384}$ and $0.95Na_2O \cdot Al_2O_3 \cdot 3.25SiO_2 \cdot 4.79H_2O$) during leaching lead to the relatively low desilication of illite.

Key words: illite; thermochemical activation; desilication
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1 INTRODUCTION

Bayer process is widely considered an efficient and economical technology to produce alumina from bauxite ores. But this process is economical only for the ores with A/S ratio (mass ratio of alumina to silica) larger than 8－10[1]. Although there are abundant bauxite ores in China, most of them are low-grade diaspore ores with the average A/S ratio below 6[2]. Therefore, to increase A/S ratio by pre-desilication is greatly important to alumina production by Bayer process.

At present, there are three main pre-desilication methods reported—physical, biological and chemical[2-5]. There are often low separation efficiencies by physical methods because the diaspore generally occurs in fine particles and is closely beset with silicon-bearing minerals such as kaolinite and illite in Chinese bauxite ores. There are drawbacks of slow desilication with biological process. Chemical pre-desilication is an available alternative to the treatment of such bauxite ores. Thermochemical activation is one kind of chemical pre-desilication methods. This process is based on that the aluminum silicate minerals are decomposed and silica in the matrix is transformed into the amorphous phase on heating, and the amorphous silica is soluble in dilute alkali solution and can be removed by leaching.

Thermochemical activation desilication has been applied to kaolinite type bauxite ores and good desilication results have been obtained[6-12]. But such a research on illite type ores has not been reported. An attempt has been made to study desilication technology and mechanism of illite by thermochemical activation in this paper.

2 EXPERIMENTAL

2.1 Chemical compositions of illite sample

The illite sample was obtained from Zhejiang province, China. The chemical composition of the sample is listed in Table 1.

It can be seen from Table 1 that the illite sam-

Table 1 Chemical composition of illite sample (mass fraction, %)

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O
36.04	47.60	0.15	0.34	9.32
Na_2O	CaO	MgO	Ignition loss	
0.35	0.15	0.25	5.43	

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Correspondence: LI Guang-hui; E-mail: liguangh@mail.csu.edu.cn

ple has a high K_2O content of 9.32%, which may result from K^+ compensation of the lack of positive charges induced by Al^{3+} substituting for Si^{4+} in the layers of silicon-oxygen tetrahedron of illite.

X-ray diffraction analysis shows that there are three main minerals in the samples: illite, quartz and muscovite. Their contents are 82%–85%, 8%–9% and 3%–5%, respectively.

2.2 Activation experiments

The thermal activation experiments were carried out in an electrically heated furnace. A Pt/Pt-Rh thermocouple was used to determine the temperature. Samples loosely packed in corundum crucibles were treated isothermally at a given temperature for a given period. The treated samples were cooled in air, and then ground to a fineness of 76 μm.

2.3 Alkali leaching experiments

The alkali leaching experiments of activated ores were conducted in a DY-8 autoclave. There are eight 150 mL stainless steel bombs that can rotate end to end (the rotating velocity varies from 20 r/min to 120 r/min) in a bath of glycerin as heating medium with the autoclave. Glycerin was electrically heated, and a thermostat was used to control the temperature of the bath.

At the beginning of each trail, caustic soda solution and activated ores were added to the steel bombs. The sealed bombs were soaked in the bath and agitated at 60 r/min. During leaching, the temperature of glycerin was maintained at a given temperature. Filtration was performed immediately and adequately after leaching. The concentration of SiO_2 and Al_2O_3 in the liquor and the solid residue was determined, respectively.

2.4 Instrumental techniques

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to observe the reactions taking place during the thermal treatment of illite. A TAS-100 thermal analyzer (made in Japan) was used. The pulverized sample was heated from ambient temperature to 1 300 ℃ at a rate of 10 ℃/min under static atmospheric conditions. Alumina calcined at 1 200 ℃ was used as reference.

Mineralogical analysis was carried out by X-ray diffraction (XRD) (made in Japan). Powder XRD patterns were recorded with CuK_α radiation at 50 kV and 100 mA, and a graphite monochromator was used. The goniometer was configured to scan over a diffraction angle range of 5 – 70° at a rate of 4°/min.

3 STRUCTURE AND PHASE TRANSFORMATION OF ILLITE ON HEATING

3.1 Thermal analysis(DTA and TGA)

DTA and TGA diagrams of the illite sample are shown in Fig. 1. There are a small endothermic vale and an obvious mass loss in the temperature range of 100–400 ℃. This is due to dehydration of free water (including absorbed water and layered water) in the sample. Another mass loss appears at 500–700 ℃ and the temperature of corresponding endothermic vale is 596 ℃ which is contributed to dehydroxylation of illite[13-15]. In the vicinity to 1 093 ℃, a special S-shaped ogee appears in the DTA curve. It is probably because the structure of illite is destroyed and turned into glass, which is an endothermic reaction; with the temperature up to 1 100 ℃ and higher, mullite comes out gradually, which is an exothermic reaction.

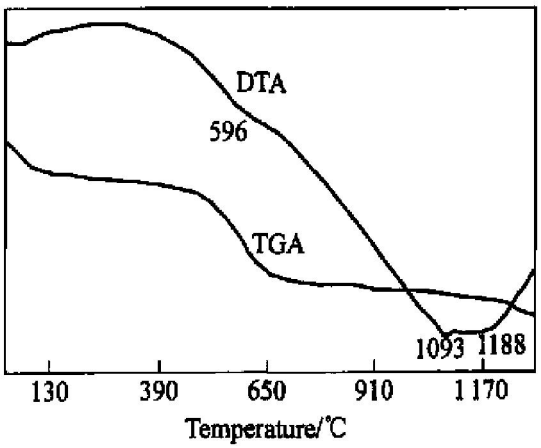

Fig. 1 Curves of DTA and TGA of illite sample

3.2 XRD analysis

XRD patterns of raw illite and illite treated at various temperatures (500–1 200 ℃) are shown in Fig. 2. The raw illite (Fig. 2(a)) presents a series of sharp and typical diffraction peaks, which indicates the illite crystallizes perfectly. Comparing Fig. 2(b) with Fig. 2(a), the intensity of diffraction peaks in Fig. 2(b) is improved. A probable reason is that the relative content of illite is increased after free water in the sample is removed. From Fig. 2(c) to Fig. 2(e), it can be observed that the elementary layer framework of illite remains unchanged. But Fig. 2(f) shows that illite treated at 1 100 ℃ has an obvious character of non-crystalline and the diffraction peaks of mullite starts to appear. In Fig. 2(g) and Fig. 2(h), the diffraction peaks of mullite get intenser and clearer and the non-crystalline phase still exists.

4 TECHNOLOGY OF THERMOCHEMICAL ACTIVATION AND ALKALI LEACHING

4.1 Thermochemical activation conditions

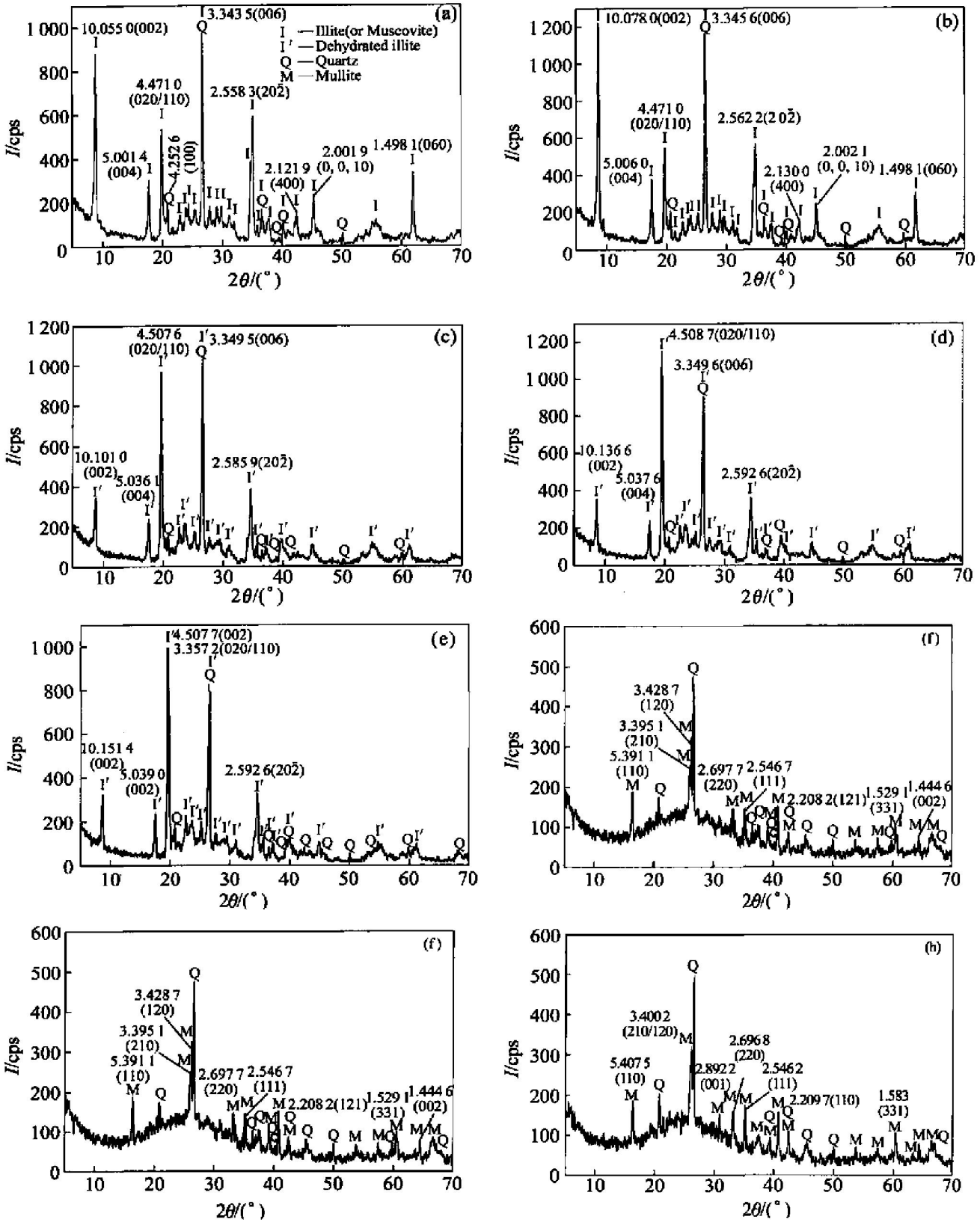

Fig. 2 XRD patterns of illite samples activated at different temperatures
(a) —Raw illite; (b) —500 ℃; (c) —800 ℃; (d) —1 000 ℃; (e) —1 050 ℃; (f) —1 100 ℃; (g) —1 150 ℃; (h) —1 200 ℃

The effects of activation temperature and time on desilication of activated illite are shown in Fig. **3** and Fig. **4**, respectively. The leaching conditions are the same in both figures. They are temperature of **95** ℃, time of **2** h, Na_2O_k concentration of **150** g/L and L/S (mass ratio of liquid to solid) of **5**.

It can be seen from Fig. **3** that desilication increases continuously with the increase of activation temperature in the range of **1 000** ~ **1 200** ℃ when activation time is less than **60** min. However, desilication increases quickly below **1 150** ℃ then decreases over **1 150** ℃ with temperature when activation time is over **90** min,

From Fig. **4**, it can be seen that desilication

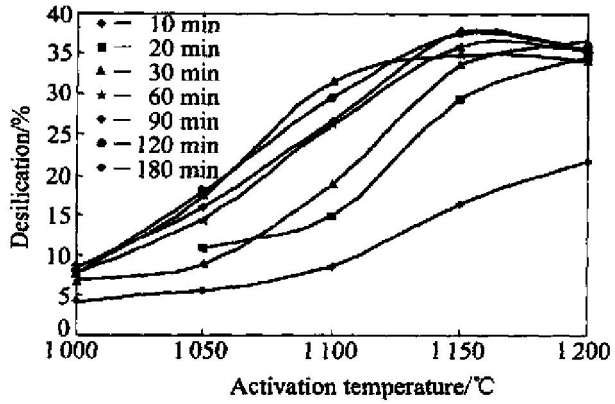

Fig. 3 Effect of activation temperature on desilication of illite
(Leaching conditions: 95 ℃, 2 h, 150 g/L Na_2O_k, L/S= 5)

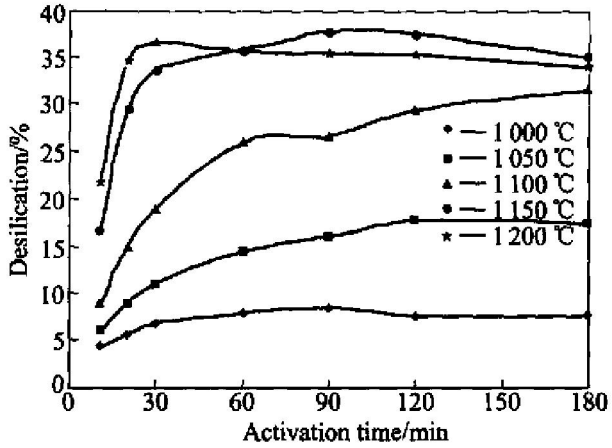

Fig. 4 Effect of activation time on desilication of illite
(Leaching conditions: 95 ℃, 2 h, 150 g/L Na_2O_k, L/S= 5)

increases slowly with activation time when the temperature is below **1 100** ℃. When the temperature is over **1 100** ℃, desilication increases sharply in the first **30** min, then maintains almost unchanged during the following period.

As a result, the suitable activation conditions should be **1 100 - 1 150** ℃ and **90 - 120** min.

4.2 Alkali leaching desilication conditions

The material used in the following alkali leaching experiments is the illite activated at 1 150 ℃ for 90 min.

4.2.1 Effect of leaching temperature

The effect of leaching temperature and time on desilication of illite is shown in Fig. 5.

It can be found that desilication rises clearly with leaching temperature. With provision for energy consumption and the material of leaching container, 95 - 110 ℃ and 90 - 120 min are suitable for the leaching of the activated illite.

4.2.2 Effect of Na_2O_k concentration

The effect of Na_2O_k concentration on desilication is shown in Fig. 6.

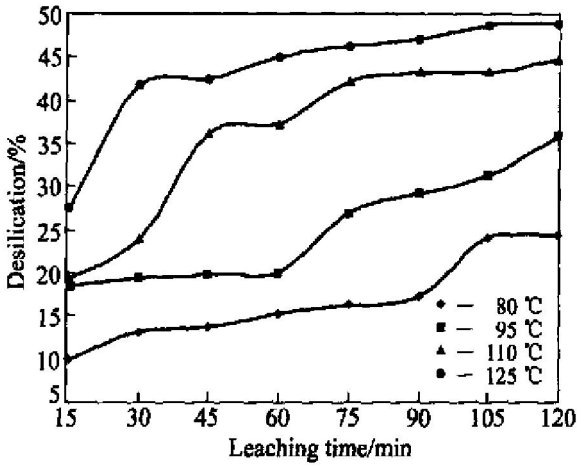

Fig. 5 Effect of leaching temperature on desilication of illite
(Leaching conditions: 2 h, Na_2O_k 150 g/L, L/S= 5)

Fig. 6 shows that desilication increases quickly when Na_2O_k concentration rises from 50 g/L to 200 g/L. The suitable Na_2O_k concentration should be 150 g/L. Moreover, desilication increases most quickly in the period of 60 - 90 min in each curve and the growth of desilication is almost held on after 90 min.

4.3 Effect of thermal activation on Al_2O_3 loss

Table 2 shows the effect of activation condi-

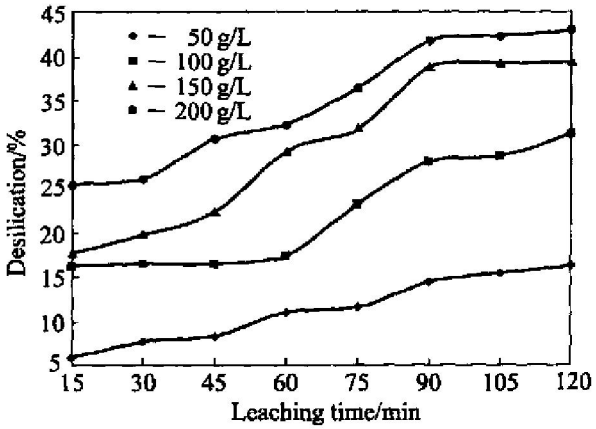

Fig. 6 Effect of Na_2O_k concentration on desilication of illite
(Leaching conditions: 95 ℃, 2 h, L/S= 5)

Table 2 Effect of activation conditions on alumina loss ratio(%)

Temperature/℃	Alumina loss ratio/%						
	10 min	20 min	30 min	60 min	90 min	120 min	180 min
1 000	1.17	0.74	0.85	0.67	0.61	0.69	0.65
1 050	1.07	0.52	0.61	0.50	0.52	0.52	0.62
1 100	0.57	0.49	0.68	1.54	1.52	2.52	2.65
1 150	0.55	0.62	0.60	0.53	0.70	0.68	1.41
1 200	0.78	0.68	0.65	0.65	0.69	0.69	1.93

tions on Al_2O_3 loss ratio. The same leaching conditions are temperature 95 ℃, time 2 h, Na_2O_k 150 g/L and L/S= 5. It can be found from Table 2 that Al_2O_3 loss of activated ores is very tiny, which is similar to that of unheated ores.

4.4 XRD research on leached illite

Compared to kaolinite, desilication of thermal activated illite is low. In order to find out the reason, XRD analysis has been made to the leached and the activated illite. The results are shown in Fig. 7.

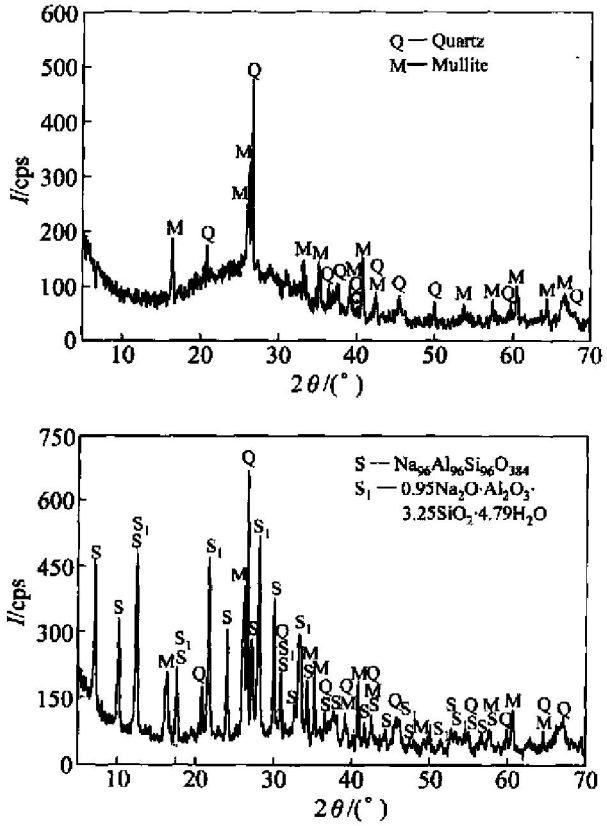

Fig. 7 XRD patterns of activated and leached illite
(a) —XRD pattern of activated illite (1 150 ℃, 90 min)
(b) —XRD pattern of illite leached after activation(1 150 ℃, 90 min)

Figs. 7(a) and (b) are the XRD patterns of illite activated at 1 150 ℃ for 90 min and illite leached after activation at the same conditions respectively. It can be seen from Fig. 7(a) that dehydrated illite has transformed into non-crystals, accompanied by the formation of mullite. Quartz keeps in still.

Fig. 7(b) shows that all diffraction peaks of the non-crystals in Fig. 7(a) disappear, whereas those of mullite still exist. This suggests that non-crystal SiO_2 formed during thermal activation has dissolved in alkali solution and been removed. But there appears two sodium hydroaluminosilicates in Fig. 7(b). XRD analysis finds that their formulas are $Na_{96}Al_{96}Si_{96}O_{384}$ (S) and $0.95Na_2O \cdot Al_2O_3 \cdot 3.25SiO_2 \cdot 4.79H_2O$ (S_1) respectively. The formation of sodium hydroaluminosilicates may be described by following reactions:

$$Na_2SiO_3 + NaAl(OH)_4 + aq \longrightarrow NaOH + Na_{96}Al_{96}Si_{96}O_{384}\downarrow + H_2O + aq$$

$$Na_2SiO_3 + NaAl(OH)_4 + aq \longrightarrow NaOH + 0.95Na_2O \cdot Al_2O_3 \cdot 3.25SiO_2 \cdot 4.79H_2O\downarrow + H_2O + aq$$

Therefore, the reasons for low desilication of activated illite includes the formation of sodium hydroaluminosilicates in leaching and the formation of mullite insoluble in alkali solution in activation when the temperature is above 1 100 ℃, as well as the presence of quartz.

4 CONCLUSIONS

1) Thermal analysis (DTA and TGA) and XRD analysis show that the OH groups split off from the structural framework of illite between 500 ℃ and 700 ℃. With the increase in temperature up to about 1 100 ℃, the layer structure of illite breaks up and Si in the layers is transformed into the amorphous state. Meanwhile, mullite comes out at 1 100 ℃. Quartz occurring in illite keeps unchanged in structure at 500 – 1 200 ℃.

2) A desilication process from illite by thermo-chemical activation followed by alkali leaching is developed on the basis that amorphous silica is alkali soluble. The optimum parameters are found to be activation temperature of 1 100 – 1 150 ℃, activation time of 90 – 120 min, leaching temperature of 95 – 110 ℃, leaching time of 90 – 120 min and Na_2O_k concentration of 120 – 150 g/L. An overall desilication about 45% is attained under these conditions.

3) XRD analysis shows that the amorphous SiO_2 dissolves in alkali solution and is removed from the activated illite, while quartz and mullite hardly dissolve in the solution. XRD analysis also finds that two sodium hydroaluminosilicates ($Na_{96}Al_{96}Si_{96}O_{384}$ and $0.95Na_2O \cdot Al_2O_3 \cdot 3.25SiO_2 \cdot 4.79H_2O$) are formed in leached illite. The formation of mullite during activation and formation of sodium hydroaluminosilicates during leaching as well as the presence of quartz lead to the relatively low desilication of illite.

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