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## Dissolution kinetics and removal mechanism of kaolinite in diasporic bauxite in alkali solution at atmospheric pressure

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**Abstract:** A new chemical pre-desilication process of kaolinite in diasporic bauxite in alkali solution at atmospheric pressure was proposed. The dissolution kinetics and mechanism were studied by chemical analysis, XRD and SEM. The kinetic results of dissolution process show that the kaolinite is symbiotic with diaspore but without cladding. The dissolution ratio of kaolinite is close to 100% at 100 °C for 90 min. The dissolution kinetic equation is  $1-(1-\alpha)^{1/3}=7.88\times10^{6}\exp[-64434/(RT)]t$ . With the low L/S (L/S= 10:1), the dissolution ratio of kaolinite decreases to 55%. This is due to the formation of lamellar hydroxyl—sodalite (OH—SOD) which is deposited on the surface of kaolinite and hinders the further dissolution of kaolinite. Under the optimum conditions, the A/S (mass ratio of Al<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub>) of dissolved residues is increased to 8.55, while the A/S of the bauxite is only 4.97. **Key words:** Bayer process; kaolinite; pre-desilication; dissolution kinetics; sodalite

### **1** Introduction

Bauxite is the main raw material of the alumina production industry, especially the main source of aluminum metal industry [1]. Depending on the difference of main alumina-bearing minerals, bauxites can be classified into three categories: gibbsitic bauxite (Al(OH)<sub>3</sub>), boehmitic bauxite ( $\gamma$ -AlO(OH)) and diasporic bauxite ( $\alpha$ -AlO(OH)). Other than that, there are other mineral components in bauxite such as kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), quartz (SiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), goethite (FeO(OH)), rutile/anatase (TiO<sub>2</sub>), calcite (CaCO<sub>3</sub>) and other impurities in minor or trace amounts [2,3].

Bayer process is the principal method to produce alumina from bauxite worldwide. In Bayer process, kaolinite is also dissolved with the digestion of the alumina hydrate-containing ores in caustic solution, resulting in a large amount of  $SiO_2$  entering the solution. The presence of  $SiO_2$  dissolved in Bayer liquors results in the formation of undesirable sodium aluminosilicate accumulated in the heat exchangers used in alumina refining plants, which is commonly known as desilication product (DSP) [4,5]. The formation of DSP not only causes the loss of aluminum and sodium in the solution, but also results in a pressure drop, flow restriction and energy consumption as well as serious fouling in the heat exchangers [5,6].

Several processes such as floating process [7,8], lime process [9-14], and roast-leach process have been developed and applied to producing alumina from lowgrade bauxite ore in the alumina refineries [14–16]. The flotation-Bayer process is the most widely used method for physical pre-desilication, but is generates more tailings simultaneously (25% of the initial bauxite ores in mass fraction) [17]. The lime Bayer process cannot effectively reduce the scale, and cannot treat low-grade bauxite with A/S<5 [18]. The roast-leach process has attracted more and more attention in recent years. This process can be described as the decomposition of kaolinite by roasting process, and formation of soluble silicon oxide and insoluble aluminum oxide. Then, the silicon oxide is dissolved in alkali solution to desilication. The desilicated bauxite is then used in the Bayer process with variation capable of digesting the alumina produced after being roasted [19-22]. During the roasting process, the stability of alumina in kaolinite, gibbsite and

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boehmite is increased. Therefore, it is more difficult for the roasted bauxite to be digested by the normal Bayer process. In order to solve this problem, the roasting process of bauxite has been studied in detail, and the digestion process of roasted products has also been discussed [23–27]. In addition, the effect of silica in roasted products on the digestion process was also discussed [22,28].

Kaolinite is 1:1 type phyllosilicate mineral, which is composed of tetrahedral SiO4 sheet and octahedral AlO<sub>2</sub>(OH)<sub>4</sub> sheet in each layer [29]. The hexagonal grid arrangement of tetrahedral SiO<sub>4</sub> in lattice of kaolinite makes a pseudo-hexagonal lamellar morphology appear in the microcrystalline of kaolinite. The dissolution mechanism of kaolinite is regarded as a three-stage process: kaolinite firstly is dissolved in alkali solution in the form of soluble silicate and aluminate, then the silicate in the alkaline solution reacts with the aluminate to form a metastable aluminosilicate. Finally, the aluminosilicate was precipitated when the concentration of silica exceeds its equilibrium concentration [30]. The reactive silica dissolution and stabilization of the active silica in concentrated NaOH-NaAl(OH)<sub>4</sub> solutions were investigated. Two distinct steps: active silica dissolution and DSP precipitation, control the whole leaching process of silica in NaOH-NaAl(OH)<sub>4</sub> media [31].

Based on the above analyses of kaolinite, transferring a large proportion of the kaolinite from bauxite directly into solution without roasting activation will be crucial for this process. In this work, a new chemical pre-desilication process for kaolinite-rich diasporic bauxite was proposed and investigated in detail. Under the atmospheric pressure, kaolinite can be dissolved by alkali solution, yet the diaspore cannot be dissolved so that the purpose of improving the A/S of concentrate can be achieved with very simple treatment steps: alkali dissolution and liquid-solid separation. The separated solution can be used to prepare zeolite products under certain conditions. Previous studies have shown that the solubility and dissolution ratio of kaolinite in alkali solution were strongly related to the dissolution conditions and the morphology of kaolinite. However, there is no detailed study on the dissolution process of kaolinite-rich diasporic bauxite in alkali solution at atmospheric pressure. This study aims to better understand the dissolution process of kaolinite at the atmosphere pressure in alkaline solution. This kind of kaolinite is associated with diaspore in bauxite. Characteristic of the dissolved residues was also studied to reveal reaction mechanisms. The final effect of the new chemical pre-desilication process would be determined through the A/S in the solid phase before and after dissolution.

#### **2** Experimental

Analytical-grade NaOH (Tianjin Kermel Chemical Reagent Co., Ltd.) was used for preparation of alkali solution with the purity of 98.0%. Unless otherwise stated, all chemicals used in this experiment were analytical reagent grade and all solutions in this experiment were prepared by deionized water.

In this experiment, kaolinite-rich diasporic bauxite from Shanxi province in China was studied after grounding to a particle size of less than 250 µm in diameter. All dissolution experiments were performed in a water bath heating device. Four-mouth flasks with a capacity of 500 mL were used and the condenser, agitation, thermocouple and feed switch were placed on four mouths, respectively. The whole dissolution process included dissolution, filtration separation, water washing of the dissolved residues and then drying at 90 °C. For each dissolution experiment, 300 mL of alkali solution with Na<sub>2</sub>O concentration of 230 g/L was heated to a certain temperature, and then a certain mass of kaolinite-rich diasporic bauxite was put into the alkali solution and dissolved for a certain time. After the dissolution reaction, the residue was filtrated and the filter cake was washed by hot deionized water to a pH value of 7. The concentrations of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in filter solution and the contents of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> of dissolved residues were analyzed.

The phase analysis was determined by X-ray powder diffraction (XRD, PANalytical PW3040/60) using Cu K<sub>a</sub> irradiation ( $\lambda$ =1.5406Å) at 40 kV with a scan speed of 0.05 (°)/s over 2 $\theta$  angle range of 5°–90°. The 2014 PDF database from BRUKER was used for reflection identification. The morphology analysis was observed by scanning electron microscopy (SEM, SHIMADZU SSX–550) and energy-dispersive X-ray spectroscopy (EDS, DX–4). The samples were gold-coated before SEM–EDS analysis. The X-ray fluorescence analysis (XRF) instrument was applied to determining the chemical composition of bauxite and dissolved residues.

The concentrations of  $Al_2O_3$  and  $Na_2O$  in solution were analyzed by the volumetric method, and the concentration of SiO<sub>2</sub> was analyzed on the basis of silicon-molybdenum blue spectrophotometry by a 722S spectrophotometer.

### **3** Results and discussion

### 3.1 Mineral analysis of kaolinite-rich diasporic bauxite

The chemical composition of kaolinite-rich diasporic bauxite is shown in Table 1, and the mineral

composition is shown in Fig. 1. Diaspore and kaolinite are the main mineral forms of alumina. In addition, anatase is the mineral form of titanium dioxide and calcite is the mineral form of calcium oxide. There is no quartz detected by XRD in kaolinite-rich diasporic bauxite, so all of the  $SiO_2$  are in the form of kaolinite in this bauxite. The calculated mineral composition is shown in Table 2. The A/S of the bauxite is 4.97, which is not suitable for digestion with the Bayer process.

Figure 2(a) shows the microstructure of the kaolinite-rich diasporic bauxite. The map scanning results of Al, Si, Ca, Ti and Fe elements are shown in Figs. 2(b-f), respectively, and then several typical phases in Fig. 2(a) are determined. The point of A in Fig. 2(a)

 Table 1 Chemical composition of kaolinite-rich diasporic

 bauxite (wt.%)

$Al_2O_3$	$SiO_2$	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	LOI	Others
63.85	12.84	2.93	3.64	0.60	14.14	2.00



Fig. 1 XRD pattern of kaolinite-rich diasporic bauxite

 Table 2 Mineralogical composition of kaolinite-rich diasporic

 bauxite (wt.%)

Diaspore	Kaolinite	Anatase	Calcite	Others
62.28	27.61	2.93	1.00	6.18



Fig. 2 SEM image of kaolinite-rich diasporic bauxite (a) and scanning maps (b)-(f)

indicates that the particle is anatase with massive structure and smooth surface. The crystallization is more complete and the size is more uniform. Iron is scattered in bauxite by permeating in kaolinite and diaspore, and the dense iron phases are symbiotic with anatase, as shown in Fig. 2(e). The point of *C* in Fig. 2(a) indicates that the particle is calcite. The kaolinite (short for K) is symbiotic with diaspore (short for D), as shown in area point by K+D. Figure 3(a) shows the magnified micromorphology of the square area in Fig. 2(a). A mixture phase of kaolinite and diaspore was formed because some of flake crystals covered on the surface of diaspore, as shown in Fig. 3(a). Kaolinite is a plate structure and it is stacked by layered crystals. The regional EDS analysis is shown in Fig. 3(b).



**Fig. 3** Magnified micromorphology of particles K+D (a) and EDS analysis (b)

### 3.2 Dissolution kinetics of kaolinite in diasporic bauxite

The dissolution process of kaolinite in alkali solution is a liquid–solid reaction. A solution containing 2 g/L of SiO<sub>2</sub> and 2 g/L of Al<sub>2</sub>O<sub>3</sub> was stirred for 5 h under the condition of 10 g/L seed at 90 °C, and the composition of the solution remained unchanged. Therefore, to avoid the formation of DSP, the concentration of 2 g/L SiO<sub>2</sub> was determined as the maximum value, so the liquid-to-solid ratio (short for L/S) of 70:1 was adopted. The dissolution kinetics of kaolinite was calculated according to the concentration of SiO<sub>2</sub> in solution, which was shown in Fig. 4(a). Three residues dissolved at 90, 95 and 100 °C for 120 min were analyzed by XRD and shown in Fig. 4(b). No DSP peak was found in the three residues. This indicated that no secondary reaction occurred under the L/S of 70:1.



**Fig. 4** Concentration of SiO<sub>2</sub> in solution (a) and XRD patterns of three dissolved residues (b)

When kaolinite entered the solution, it reacted with the alkali in the solution to form aqueous silicate and aluminate species, as shown in formula (1). Chemical thermodynamic calculations indicated that Na<sub>2</sub>SiO<sub>3</sub> was the main solution silicate specie and NaAlO<sub>2</sub> was the main aluminate specie [28].

$$Al_{2}O_{3} \cdot 2SiO_{2} \cdot 2H_{2}O + 6NaOH \rightarrow$$

$$2NaAIO_{2} + 2Na_{2}SiO_{3} + 5H_{2}O$$
(1)

The dissolution ratio of SiO<sub>2</sub> is expressed by  $\alpha$  and calculated by Eq. (2), as follows:

$$\alpha = \frac{x_{\rm S}V}{0.1284m} \times 100\% \tag{2}$$

where  $x_S$  is the mass concentration of SiO<sub>2</sub> in dissolution solution (g/L); *V* is the volume of dissolution solution (L); *m* is the total mass of kaolinite-rich diasport bauxite of input (g).

Under a certain L/S, the relationship between  $\alpha$  and time was consistent with the relationship between  $x_S$  and time in Fig. 4(a). With the increase of dissolution

temperature, the initial dissolution ratio of  $SiO_2$  increased and the time to reach equilibrium shortened. This indicated that the higher dissolution temperature promoted the dissolution of  $SiO_2$ .

The dissolution reaction was carried out in three steps. First, the liquid reactant diffused to the solid surface due to the concentration gradient in solution. It is usually called an external diffusion process. The second step was the reaction at the solid–liquid interface. The final step was to diffuse the product from the interface to the liquid through external diffusion [32].

When the dissolution process was controlled by chemical reaction or external diffusion, the dissolution kinetics equation was as follows:

$$1 - (1 - \alpha)^{1/3} = kt$$
 (3)

where  $\alpha$  (%) is the dissolution ratio of SiO<sub>2</sub> at the dissolution time of *t* and *k* is the apparent rate constant.

However, the raw material in this experiment was kaolinite-rich diasporic bauxite, and kaolinite was associated with diaspore. The dissolution process of kaolinite in diasporic bauxite was different from the pure kaolinite and it was affected by other minerals in bauxite. The presence of other components could affect the dissolution process of kaolinite, so the diffusion process becomes the restrictive step of the whole reaction. If there is no new phase generated, the dissolution kinetics equation can be described by the shrinking unreacted core model as follows:

$$1-2/3\alpha - (1-\alpha)^{2/3} = kt$$
 (4)

The calculated dissolution ratios of SiO<sub>2</sub> were substituted into Eqs. (3) and (4), the linear relationships obtained by fitting Eqs. (3) and (4) were shown in Fig. 5. The bigger the  $R^2$  is, the better the model fits the data. The results showed that the linear relationships between  $1-(1-\alpha)^{1/3}$  and t were better than those between  $1-2/3\alpha-(1-\alpha)^{2/3}$  and t. In this experiment, stirring method was used to reduce the influence of external diffusion. This indicated that the dissolution ratio was mainly affected by reaction at the solid–liquid interface.

The apparent activity energy was calculated by apparent rate constants at different temperatures. The dissolution kinetics equation of kaolinite in diasporic bauxite was obtained from the Arrhenius equation as follows:

$$\ln k = -E/(RT) + \ln A \tag{5}$$

where *E* is the activity energy (kJ/mol), *R* is the mole gas constant (8.314 J/(mol·K)), *T* is the dissolution temperature (K) and *A* is the pre-exponential factor.

According to k values at different temperatures, the Arrhenius curve of the dissolution process was obtained and shown in Fig. 6.



**Fig. 5** Linear relationships of  $1-(1-\alpha)^{1/3}$  vs t (a) and  $1-2/3\alpha-(1-\alpha)^{2/3}$  vs t (b) of kaolinite in bauxite at different temperatures



Fig. 6 Arrhenius curve of dissolution of kaolinite

As shown in Fig. 6, the line slope was -7.75 and intercept was 15.88. The activity energy of the reaction calculated by the Arrhenius equation (Eq. (5)) was 64.434 kJ/mol. According to the above discussion, for kaolinite in diasporic bauxite, the dissolution kinetic equation in alkali solution is expressed as

$$1 - (1 - \alpha)^{1/3} = 7.88 \times 10^6 \exp[-64434/(RT)]t$$
(6)

The result showed that the dissolution activity energy of the kaolinite-rich diasporic bauxite in alkali solution was 42–800 kJ/mol, which belonged to chemical reaction control. ROACH and WHITE [33] studied the dissolution kinetics of kaolinite in sodium aluminate solution, suggesting that the reaction rate of kaolinite dissolution was influenced by crystalline form and surface area. The activity energy of compact kaolinite dissolution in sodium aluminate solution was 99 kJ/mol, and the interfacial chemical reaction was a restrictive step.

### 3.3 Reaction mechanism of kaolinite-rich diasporic bauxite in alkali solution

The above kinetic results were concerned with the dissolution reaction of kaolinite, so the L/S of the dissolution process was high enough without causing any secondary reaction. Bauxite refinery usually adopts lower L/S to reduce operating costs. However, in this experiment, a low L/S will lead to the formation of a large amount of DSP, which will reduce the pre-desilication effect and the A/S ratio of dissolved residues. Therefore, the L/S of 10:1 (100 g/L) was adopted and studied in detail, which could not cause the formation of a large amount of DSP, but also could be accepted by industrial production. In the dissolution process of kaolinite, the formation reaction (7) [4].

The formation of DSP in alkali solution:

xNa<sub>2</sub>SiO<sub>3</sub>(aq)+2NaAlO<sub>2</sub>(aq)+4H<sub>2</sub>O $\rightarrow$ 

$$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot (4-x)H_2O(s) + 2xNaOH(aq)$$
 (7)

With the dissolution of kaolinite, the formation of DSP was carried out simultaneously. The two chemical reactions were coinstantaneous in alkali solution. In fact, the DSP formed under different conditions varied greatly in compositions and structures. These DSPs were mainly in the forms of sodalite (SOD), zeolite (ZEO) and cancrinite (CAN) [26]. The zeolite (ZEO) and sodalite have the same cubic sodalite-structure, while cancrinite has a hexagonal structure [34].

Figure 7 shows the equilibrium phase diagram of Na<sub>2</sub>O-A1<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at 80 °C (where the solubility of SiO<sub>2</sub> is ignored). It shows the equilibrium solids of formation in the solution with different concentrations of A12O3 and Na2O. The equilibrium solid phase formation in solution with higher alkali concentration and higher molar concentration ratio of Na<sub>2</sub>O to A1<sub>2</sub>O<sub>3</sub> in solution (MR) is alkaline sodalite or hydroxyl-sodalite (OH-SOD) [2]. According to the above analyses, the DSP formed in alkali solution with the Na<sub>2</sub>O concentration of 230g/L was hydroxylsodalite, with molecular formula the of  $3(Na_2O \cdot A1_2O_3 \cdot 2SiO_2) \cdot 2NaOH \cdot 2H_2O.$ 



Fig. 7 Equilibrium phase diagram of Na<sub>2</sub>O–A1<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O system at 80 °C [2]

With L/S of 10:1, the single factor experiments of temperature and time were carried out. Chemical compositions of dissolved residues at different reaction temperatures and reaction time were shown in Table 3. Al<sub>2</sub>O<sub>3</sub> in residues mainly existed in three phases: OH—SOD, remnant kaolinite and non-reactive diaspore, and the contents were expressed by  $w_{A_S}^l$ ,  $w_{A_K}^l$  and  $w_{A_D}^l$  respectively. According to the chemical composition of the dissolved residues, the contents of Al<sub>2</sub>O<sub>3</sub> in each phase of residues were calculated by Eqs. (8)–(10), the contents of DSP in residues were calculated from the chemical formula of OH—SOD, and all results were listed in Table 3.

$$w_{A_{s}}^{1} = w_{N}^{1} / 62 / 4 \times 3 \times 102$$
(8)

$$w_{A_{K}}^{l} = (w_{S}^{l} - w_{N}^{l} / 62 / 4 \times 6 \times 60) / 60 / 2 \times 102$$
(9)

$$w_{A_{D}}^{1} = w_{A}^{1} - \left( \left( w_{S}^{1} - w_{N}^{1} / 62 / 4 \times 6 \times 60 \right) / 60 / 2 \times 102 \right) - \left( w_{N}^{1} / 62 / 4 \times 3 \times 102 \right)$$
(10)

where 102, 60 and 62 are relative molecular mass of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Na<sub>2</sub>O respectively;  $w_A^l$ ,  $w_S^l$  and  $w_N^l$  are the contents of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Na<sub>2</sub>O in residues, respectively. The DSP chemical formula was determined from OH—SOD as  $3Na_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot$  $2NaOH\cdot 2H_2O$ .

The content of  $Al_2O_3$  in diaspore was considered as an internal standard because of its insolubility in alkali solution at atmospheric pressure. The dissolution ratio of kaolinite ( $\delta_K$ ) and the formation ratio of DSP ( $\delta_S$ ) were calculated by Eqs. (11) and (12), and the results are shown in Fig. 8.

$$\delta_{\rm K} = \frac{(w_{\rm A_{\rm K}}^0 / w_{\rm A_{\rm D}}^0) - (w_{\rm A_{\rm K}}^1 / w_{\rm A_{\rm D}}^1)}{(w_{\rm A_{\rm K}}^0 / w_{\rm A_{\rm D}}^0)} \times 100\%$$
(11)

$$\delta_{\rm S} = \frac{(w_{\rm A_{\rm S}}^{\rm I} / w_{\rm A_{\rm D}}^{\rm I})}{(w_{\rm A_{\rm K}}^{\rm 0} / w_{\rm A_{\rm D}}^{\rm 0})} \times 100\%$$
(12)

The Al<sub>2</sub>O<sub>3</sub> in bauxite mainly existed in diaspore and kaolinite, and the contents were expressed by  $w_{A_D}^0$  and  $w_{A_V}^0$ , and the values were calculated from Table 2.

 Table 3 Chemical compositions of dissolved residues at different temperatures for different time (wt.%)

<i>T</i> / °C	t/ min	$w_{\rm A}^{\rm l}$	$w_{\rm S}^{\rm l}$	$w_{\rm N}^{\rm l}$	$w^{l}_{A_{s}}$	w <sup>1</sup> <sub>A<sub>K</sub></sub>	$w^1_{A_D}$	Content of DSP
80	60	60.30	9.36	0.38	0.47	7.49	52.34	1.48
85	60	66.08	9.40	0.39	0.48	7.51	58.09	1.52
90	60	64.46	8.60	0.43	0.53	6.78	57.15	1.68
95	60	64.19	8.09	0.74	0.91	5.96	57.31	2.89
100	60	63.00	8.08	1.46	1.80	5.07	56.13	5.70
90	75	66.55	8.06	0.44	0.54	6.31	59.70	1.72
90	90	62.58	7.35	0.48	0.72	5.53	56.33	1.87
90	120	65.39	7.65	0.81	1.00	5.5	58.89	3.16
90	150	67.99	8.68	1.42	1.75	5.63	60.61	5.54



**Fig. 8** Dissolution results at different temperatures for 60 min (a) and at 90 °C for different time (b)

As shown in Fig. 8(a), the dissolution ratio of kaolinite continuously increased with the increasing of dissolution temperature from 80 to 100 °C, which was consistent with the kinetic analysis. However, with the increasing of temperature, the formation ratio of DSP

also increased, especially when the temperature exceeded 90 °C. Although the increasing of temperature was beneficial to the dissolution of kaolinite, it also increased the formation of DSP. In order to improve the A/S of dissolved residues, suitable temperature of dissolution should be selected.

To determine the influence of dissolution time on dissolution result, single factor experiments of dissolution were carried out at 90 °C, as shown in Fig. 8(b). It showed that the dissolution ratio of kaolinite increased with the prolongation of dissolution time, and then tended to be stable. When the dissolution time exceeded 120 min the dissolution ratio of kaolinite remained stable. The precipitation ratio of DSP slowly increased with the increasing of dissolution time. When the dissolution time exceeded 120 min, the formation ratio of DSP increased rapidly.

The XRD patterns of dissolved residues at different temperatures are shown in Fig. 9(a). With the increase of reaction temperature, the characteristic peak intensity of kaolinite decreased. This indicated that the contents of kaolinite in the dissolved residues decreased.



Fig. 9 XRD patterns of dissolved residue at different temperatures for 60 min (a) and at 90 °C for different time (b)

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When the reaction temperature reached 100 °C, the DSP was found in dissolved residues. This indicated that the increasing of temperature promoted the formation of DSP. Figure 9(b) shows the XRD patterns of dissolved residues for different time, and DSP was detected in the dissolved residue with the reaction time of 150 min. The chemical composition (see Table 3) of the dissolved residues showed that the DSP precipitated into the dissolved residues, but the content of DSP was not enough to be analyzed by XRD when the dissolution time was less than 120 min. The dissolution results at different temperatures and time showed that the dissolution of kaolinite and the formation of DSP were simultaneous. When the content of Na<sub>2</sub>O in the dissolved residues exceeded 5%, the characteristic peak of DSP in dissolved residues could be detected by XRD. So the DSP phase was found only in the residues dissolved at 100 °C for 60 min and at 95 °C for 150 min.

From the XRD patterns of the dissolved residues, the crystallinity of a crystal plane was obtained by Jade software. According to the crystallinity of main crystal plane of kaolinite in dissolved residues, the solubility of crystal plane was calculated by Eq. (13) as follows:

$$\gamma_{hkl} = \frac{(I_{\rm K}^0 / I_{\rm D}^0) - (I_{\rm K}^1 / I_{\rm D}^1)}{(I_{\rm K}^1 / I_{\rm D}^1)} \times 100\%$$
(13)

where  $\gamma_{hkl}$  is the solubility of crystal plane of kaolinite;  $(I_{\rm K}^0 / I_{\rm D}^0)$  and  $(I_{\rm K}^1 / I_{\rm D}^1)$  are the relative crystallinity of a crystal plane of kaolinite in raw materials  $(I_{\rm K}^0 / I_{\rm D}^0)$ and in dissolved residues  $(I_{\rm K}^1 / I_{\rm D}^1)$ , respectively.

Figures 10 (a) and (b) showed the effect of time and temperature on the solubility of (001) and (110) crystal planes of kaolinite, respectively. It showed that the solubility of the (001) crystal plane was much higher than that of the (110) crystal plane. This indicated that the (001) crystal plane was more likely to been destroyed than the (110) crystal plane by alkali. With the increase of reaction temperature, the solubility of the (001) crystal plane increased gradually. The results also indicated that the dissolution of kaolinite was promoted by increasing temperature.

The fundamental structure unit of kaolinite is composed of a plane of tetrahedral SiO<sub>4</sub> linked by oxygen atoms parallel to a plane of octahedral AlO<sub>2</sub>(OH)<sub>4</sub>. The hexagonal grid arrangement of tetrahedral SiO<sub>4</sub> in the lattice of kaolinite makes a pseudo-hexagonal lamellar morphology appearing in the microcrystalline of kaolinite (see Fig. 1). In general, for kaolinite, there are main basal planes at (001) with  $2\theta$ =12.5°, (002) with  $2\theta$ =24.8° and also the prism planes at (020) with  $2\theta$ =19.9°, (110) with  $2\theta$ =21.2° (Reference code 00-003-0052). For a hypothetical kaolinite crystal, if the (001) crystal plane is defined as a horizontal crystal surface, it can be seen as the horizontal



**Fig. 10** Solubility of crystal plane of kaolinite at 90 °C for different time (a) and at different temperatures for 60 min (b)

extension of a plane of tetrahedral SiO<sub>4</sub> or a plane of octahedral AlO<sub>2</sub>(OH)<sub>4</sub>. The (110) crystal plane can be seen as the connection plane of the tetrahedral SiO<sub>4</sub> and octahedral AlO<sub>2</sub>(OH)<sub>4</sub> with H-bond as a force. It should be noted that the calculating of solubility of (110) plane may be affected by (020) plane because they are close to each other. In this work, this effect was neglected, because they were prismatic planes, more deeply research is still under way. The solubility of the crystal planes in Fig. 10 showed that the dissolution process of kaolinite in alkali solution was carried out by the way of peeling damage on crystal planes and insertion damage in interlayer synchronously. In addition, the peeling damage on crystal planes exceeded insertion damage in interlayer.

The SEM image of the dissolved residue was shown in Fig. 11, and the particle size in dissolved residue was smaller than that of raw material (Fig. 2(a)).

In Fig. 11, four typical particles of A, C, D and S were selected for detailed observation and composition analysis. The results of micromorphology and EDS analysis of these particles were shown in Figs. 12(a)–(h) respectively. According to the results of EDS analysis, it was determined that the composition of point A was



Fig. 11 SEM image of dissolved residue at 90 °C for 120 min

anatase associated with kaolinite and diaspore. The composition of point C was calcite. The composition of point D was diaspore with a small amount of kaolinite. The composition of S was OH—SOD associated with kaolinite.

Figure 12(g) showed that the crystal particle of DSP was attached to kaolinite. It was observed that lamellar crystals interlaced each other and combined in the form of edge-face, and then grew on kaolinite body. In the dissolution process by alkali solution, kaolinite structure was broken and has a large number of defects with high surface energy. These fresh defects promoted the nucleation process of DSP and precipitation reaction.



**Fig. 12** Micromorphologies of dissolved residue (a, c, e, g) and corresponding EDS analyses (b, d, f, h) of point A (a, b), point C (b, d), point D (e, f) and point S (g, h) in Fig. 11

DSP precipitated on the surface of kaolinite, and resulted in wrapping and covering the kaolinite surface. The precipitation of DSP made the dissolution process of kaolinite more difficult. The kinetic studies showed that the increase of temperature promoted the dissolution of kaolinite, but also promoted the formation of DSP. So that SiO<sub>2</sub> was returned to the dissolved residues and the A/S of the residues was decreased. Above analysis was confirmed by the results of single factor experiments, as shown in Fig. 8. The morphology of precipitates was consistent with Ref. [28]. The lattice parameters of hydroxyl–sodalite precipitated in this experiment agreed with those in Ref. [35]. The *d*-spacings in lattice plane of (211) and (110) were 0.3634 and 0.6275 nm respectively, which were 0.3633 and 0.6275 nm.

#### 4 Conclusions

(1) The dissolution kinetics of kaolinite-rich diasporic bauxite in alkali solution at atmospheric pressure was studied. The results show that the dissolution process of kaolinite is mainly controlled by chemical reaction, and the effective way to improve the dissolution ratio is to increase the temperature. The dissolution kinetic equation is  $1-(1-\alpha)^{1/3}=7.88\times10^6\times$  exp[-64434/(*RT*)]*t*. The dissolution ratio of kaolinite is close to 100% at 100 °C for 90 min with the L/S of 70:1.

(2) Analysis of dissolved residues showed that the dissolution process of kaolinite in alkali solution was carried out by peeling damage on crystal plane and insertion damaged in interlayer synchronously. The DSP formed in this experiment was hydroxyl-sodalite with lamellar structure, which precipitated on kaolinite and hindered the dissolution of kaolinite.

(3) Because of the precipitation of DSP, the dissolution ratio of kaolinite was decreased. Under the optimum dissolution condition, the dissolution ratio of kaolinite reached 55%. The A/S of dissolved residues was increased to 8.55, while the A/S of the bauxite was only 4.97.

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# 一水硬铝石型铝土矿中高岭石的常压碱溶动力学与溶出脱除机理

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**摘 要:**提出一种一水硬铝石型铝土矿中高岭石的常压化学预脱硅新工艺。通过化学分析、XRD和 SEM 对溶出 过程动力学及溶出机理进行研究。溶出动力学结果表明,高岭石与一水硬铝石虽嵌布共生,但并无包覆现象。因 此,在100 ℃下,高岭石溶出 90 min 的溶出率可接近100%。溶出动力学方程为1-(1-a)<sup>1/3</sup>=7.88×10<sup>6</sup>exp[-64434/ (*RT*)]t。低液固比(L/S=10:1)条件下,高岭石的溶出率降低到55%。这是由于形成层状羟基方钠石(OH—SOD),并 沉淀在高岭石的表面,阻碍高岭石进一步被溶出。在最优条件下,可以将溶出渣的铝硅比提高到8.55,而原矿中 铝硅比仅为4.97。

关键词:拜耳法; 高岭石; 预脱硅; 溶出动力学; 方钠石

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