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Technical note

Transformation of $NaCaHSiO_4$ to sodalite and katoite in sodium aluminate solution

Shaowei You [a,b,c], Yifei Zhang [a,b,*], Fangfang Chen [a,b], Shaotao Cao [a,b], Yi Zhang [a,b]

[a] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

The decomposition of $NaCaHSiO_4$ in sodium aluminate solution was investigated. $NaCaHSiO_4$ transformed to sodalite and katoite during decomposition. Parameters, such as Na_2O concentration, reaction time, temperature and Al_2O_3 concentration, had a significant influence on the $NaCaHSiO_4$ decomposition. The optimal Na_2O concentration and reaction time for the $NaCaHSiO_4$ decomposition were 150 g/L and 105 min, respectively. The extent of $NaCaHSiO_4$ decomposition largely depended on Al_2O_3 concentration in sodium aluminate solution. Reaction products were composed of thin flakes with a loose structure at 50 g/L of Na_2O concentration, and were agglomerates with a compact surface composed of tabular and rod crystals at 150 g/L of Na_2O concentration.

1. Introduction

Red mud is the insoluble solid residue left after the digestion of bauxite ores with caustic soda during alumina production, like the Bayer process. Producing 1 t of alumina will generate 1–1.5 t red mud, even 2.5 t for treating low-grade bauxite ores (Borges et al., 2011; Brunori et al., 2005; Ghosh et al., 2011; Liu et al., 2009; Poulin et al., 2008). It is estimated that the global inventory of red mud has been over 2.7 billion tons (Power et al., 2011), and is continuously growing. Red mud is characterized by very high alkalinity and aluminum content, and, if not properly treated, it is a serious environmental hazard. The appropriate management of red mud seems to be particularly important. The current disposal method for red mud is stacking (Power et al., 2011). This improper disposal has serious environmental risk due to the characteristic of high alkalinity, such as the widespread contamination to the surrounding environment. In addition, this approach also causes a waste of red mud as a secondary aluminum resource. The reuse of red mud is an urgent problem to be solved. To minimize the damage to the environment and the waste of the secondary aluminum resource, great efforts have been made to recover alkali and alumina from red mud (Cresswell and Milne, 1982; Cresswell et al., 1987; Hrishikesan, 1977; Meher et al., 2011; Xu and Smith, 2012; Zhang et al., 2011a).

A mild hydro-chemical process to recover alumina and sodium oxide from red mud, which has been applied in a demonstration project in China's Henan Province, was proposed (Zhong et al., 2009). The hydro-chemical process includes two steps: alumina extraction from raw red mud followed by sodium oxide extraction from the secondary residue obtained after alumina extraction. During the first step for alumina extraction, aluminiferous desilication product (DSP) is converted to $NaCaHSiO_4$ that is the principal ingredient of the secondary residue and is generally described as $Na_2O\cdot 2CaO\cdot 2SiO_2\cdot H_2O$ (Gard et al., 1973; Zhang et al., 2011b; Zhong et al., 2009). In actual production, scale layer formed inside the heating pipelines during the first step consists mainly of $NaCaHSiO_4$ that is hard and difficult but needs to be removed periodically. However, $NaCaHSiO_4$ is unstable in low alkali solution (Zhang et al., 2011b), and that characteristic of $NaCaHSiO_4$ can be used in scale removal. In addition, due to the characteristic, $NaCaHSiO_4$ formed during the first step reacts easily with sodium aluminate solution carried by the secondary residue during residue washing. The secondary reaction of $NaCaHSiO_4$ and sodium aluminate solution reduces the percent conversion of DSP to $NaCaHSiO_4$, thus decreasing the efficiency of the first step for alumina extraction. Furthermore, there is little study on the decomposition of $NaCaHSiO_4$ in sodium aluminate solution although the process of $NaCaHSiO_4$ decomposed in sodium hydroxide solution has been recently researched by Zhang et al. (2011b).

The aim of this work was to investigate the decomposition process of $NaCaHSiO_4$ in sodium aluminate solution. The influence of parameters such as alkali concentration, temperature, and reaction time as well as Al_2O_3 concentration on the decomposition process was investigated.

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* Corresponding author at: National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. Tel./fax: +86 10 82544826.
E-mail address: yfzhang@home.ipe.ac.cn (Y. Zhang).

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2. Experiment

2.1. Materials

$NaCaHSiO_4$ raw material used in the experiments was from the pilot plant in China's Henan Province. Its chemical composition is shown in Table 1. XRD analysis (Fig. 1) indicates that a small amount of Al_2O_3 is in the form of sodalite $Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$ that accounts for approximately 9.44% of the raw material. Sodium hydroxide, aluminum hydroxide, anhydrous sodium carbonate, sodium borate and hydrochloric acid were all of analytical grade, and produced by Shantou Xilong Chemical Industry Co Ltd.

2.2. Experimental methods

Sodium aluminate solution was prepared in a nickel vessel by dissolving sodium hydroxide and aluminum hydroxide in pure water in different proportions according to experimental conditions. Experiments of $NaCaHSiO_4$ decomposed in sodium aluminate solution were carried out in a 500 mL cylindrical reactor made of Teflon with a Teflon propeller driven by a dynamoelectric stirring apparatus. The stirring speed was set at 400 rpm to ensure full mixing of reactive system. Temperature was accurately controlled by an automatic constant temperature electric heater. Each experiment was performed with 10 g of $NaCaHSiO_4$ raw material in 200 mL of sodium aluminate solution or sodium hydroxide solution, and detailed conditions are listed in Table 2.

The prepared solution of fixed volume was introduced into the Teflon reactor, and then the dynamoelectric stirring apparatus and the electric heater were started. After solution temperature reached set value and kept constant for 15 min, 10 g of raw material was added and reaction time was recorded. Thereafter suspension samples were withdrawn from the reactor at regular intervals, filtered immediately and washed with pure water. The obtained solid residue samples were dried in an oven for element composition and phase analysis.

The dried solid samples mixed uniformly with fluxing agent, a mixture of anhydrous sodium carbonate and sodium borate, were melted in platinum crucibles placed in a muffle furnace at 950 °C for 15 min, and then dissolved in hydrochloric acid solution to permit chemical analysis for Al_2O_3, SiO_2 and CaO. Additionally, dried solid samples were directly dissolved in hydrochloric acid solution and filtered to remove the insoluble parts. The obtained filtrate was analyzed to determine the Na_2O content. The contents of Na_2O, Al_2O_3, SiO_2 and CaO in solid samples were all determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 5300 DV, Perkin Elmer). Crystal phases of reaction products were identified by XRD using an X' Pert Pro MPD diffractometer with Cu Kα radiation, and morphology was examined using a field-emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan).

3. Results and discussion

3.1. Phase transformation

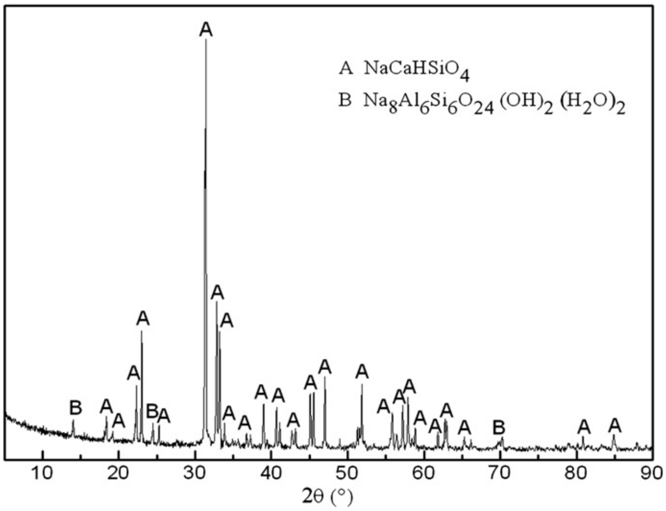

Fig. 1. XRD pattern of $NaCaHSiO_4$ raw material used in experiments.

XRD phase analysis of $NaCaHSiO_4$ raw material and reaction products before and after decomposition is shown in Fig. 2. Results show that the obtained reaction products are composed of sodalite $Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$ and katoite $Ca_{2.93}Al_{1.97}(Si_{0.64}O_{2.56})(OH)_{9.44}$ with incompletely reacted $NaCaHSiO_4$. Katoite is a member of the hydrogarnet family. Hydrogarnet has the general formula $Ca_3Al_2(SiO_4)_n(OH)_{12-4n}$ where n indicates the degree of silica substitution into the hydrogarnet structure (Whittington, 1996). This silica substitution ($n = 0.64$) is consistent with the literature (Whittington and Fallows, 1997).

Table 1
Chemical composition of $NaCaHSiO_4$ raw material used in experiments.

Composition	Na_2O	Al_2O_3	SiO_2	CaO	A/S[a]
Content (wt.%)	20.48	2.99	32.31	32.07	0.092

[a] A/S is the Al_2O_3-to-SiO_2 mass ratio.

After reaction, the characteristic peaks of $NaCaHSiO_4$ become weak, and instead the intensity of diffraction peaks of sodalite at 2-theta of 14.1° and 24.5° increases. Meanwhile, diffraction peaks representing katoite can be observed. As is shown in Fig. 2, these peaks are at 17.5°, 20.3°, 26.9°, 28.9°, 35.5°, 39.9°, 45.2°, 51.2°, 53.4°, 55.6°, 59.8° and 67.9°. During decomposition, $NaCaHSiO_4$ transforms to sodalite and katoite, which is the major cause of the increase of aluminum content in secondary residue in a hydro-chemical process. The reaction of $NaCaHSiO_4$ decomposed in sodium aluminate solution can be written as follows:

$$6NaCaHSiO_4(s) + 6Al(OH)_4^- \rightarrow Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O \text{ (sodalite)} + 6Ca^{2+} + 4Na^+ + 16OH^- + 4H_2O \quad (1)$$

$$3NaCaHSiO_4(s) + 2Al(OH)_4^- + (1-2n)OH^- \rightarrow Ca_3Al_2(SiO_4)_n(OH)_{12-4n} + (3-n)SiO_3^{2-} + 3Na^+ + nH_2O. \quad (2)$$

The product of $NaCaHSiO_4$ decomposition in sodium aluminate solution is completely different from that of $NaCaHSiO_4$ decomposition in sodium hydroxide solution where the product is amorphous calcium silicate hydrates (CSH), such as tobermorite and foshagite (Zhang et al., 2011b).

Table 2
Conditions of $NaCaHSiO_4$ decomposition in sodium aluminate solution.

Parameters	Value(s)
Na_2O concentration (g/L)[a]	50–350
Reaction time (min)	180
Temperature (°C)	50–110
Al_2O_3 concentration (g/L)[b]	0–43.86
Stirring speed (rpm)	400

[a] Na_2O concentration is the concentration of sodium hydroxide in sodium aluminate solution.

[b] Al_2O_3 concentration is the concentration of aluminum hydroxide in sodium aluminate solution.