Hydrometallurgy 108 (2011) 205–213

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

# Research on $NaCaHSiO_4$ decomposition in sodium hydroxide solution

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ARTICLE INFO

*Article history:*
Received 24 January 2011
Received in revised form 19 April 2011
Accepted 19 April 2011
Available online 28 April 2011

*Keywords:*
$NaCaHSiO_4$
CSH
Avrami
Tobermorite
Sodium
Red mud

ABSTRACT

The decomposition of $NaCaHSiO_4$ is an important step in the hydro-chemical process to recover sodium when treating red mud. In this study, the phase transformation during the $NaCaHSiO_4$ decomposition and the key influential factors, including sodium concentration, reaction temperature, CaO addition and particle size were investigated. In addition, the sodium content in the residue, where $NaCaHSiO_4$ had completely exhausted, was also studied. Finally, the kinetic data were fitted by the Avrami–Erofeev equation and the activation energy of the reaction was calculated.

## 1. Introduction

It is widely known that red mud, the residue of bauxite after leaching, rich in alkali and alumina, severely threatens the environment nearby, primarily because of the alkali it contains which results from DSP (desilication product), the main phase in red mud. It is also the main reason constraining the large-scale reutilization of red mud. Great efforts have been made to convert DSP into an alkali- and alumina-lean phase by some researchers (Whittington, 1996; Zhong et al., 2009; Zoldi et al., 1987) in order to recycle the valuable metals and reuse the disposed residue. Among these efforts, a hydro-chemical process, which was first proposed by researchers in the former USSR, is believed to be an effective method dealing with red mud. This process has recently been improved by Zhong et al. (2009). The phase transformation in the hydro-chemical process involves two steps, the first is to convert DSP to $NaCaHSiO_4$ to recover alumina. The second step is to decompose $NaCaHSiO_4$ to recover alkali. Based to this process, a facility capable of treating 10,000 tons of red mud per year has been built in Henan, China. The process of changing DSP into $NaCaHSiO_4$ has been studied in detail by Sun et al. (2008) and Zhong et al. (2009). However, the kinetics and mechanism of $NaCaHSiO_4$ decomposition have yet to be reported.

$NaCaHSiO_4$ is a stable phase when solution concentration is above 300 g/L $Na_2O$ and temperature around 200 °C in $Na_2O$-$SiO_2$-CaO-$H_2O$ system. Because solutions of such high alkali concentration have little industrial relevance in the traditional Bayer process in the past, the physiochemical behavior of $NaCaHSiO_4$ has attracted little attention except some reports from Soviet researchers (Ablamoff, 1988) in the 1960s. Their study has proposed that the $NaCaHSiO_4$ is the final phase after the extraction of aluminum from nepheline, generally described as $Na_2O\cdot 2CaO\cdot 2SiO_2\cdot H_2O$. Thereafter, in the 1970s, Gard et al. (1973) synthesized pure $NaCaHSiO_4$ by heating NaOH, $Ca(OH)_2$, finely ground quartz, and a very small proportion of water together at 180 °C, and determined its crystallographic structure by electron-microscope and X-ray diffraction. Their results showed that the crystal obtained was monoclinic and belongs to $P2_1$ or $P2_1/m$ space group with $a = 5.72$, $b = 7.06$, $c = 5.48$, $\beta = 122.5°$, $Z = 2$. Subsequently, Blakeman et al. (1974) investigated $Na_2O$-$SiO_2$-CaO-$H_2O$ system at 180 °C with a Ca/Si molar ratio of 0.83, and found that with the increase of NaOH concentrations and extension of curing time, the equilibrium phase was xonotlite (NaOH concentration 0–1.6 *M*, approximately), pectolite (NaOH concentration 1.5–5 M, approximately) and $NaCaHSiO_4$ (with little water), respectively. Recent research on $NaCaHSiO_4$ was carried out by Kenyon and Weller (2003), who refined the $NaCaHSiO_4$ XRD pattern and its structure. Their results revealed that the $NaCaHSiO_4$ consisted of $Si(O_3OH)$ tetrahedra which were hydrogen-bonded between neighboring groups to form a zigzag layer of chains. Further, the calcium coordination was octahedra and the sodium coordination was a distorted trigonal bipyramid.

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doi:10.1016/j.hydromet.2011.04.010

Although $NaCaHSiO_4$ is stable in high alkali solution, it can be decomposed easily in low alkali solution when the $Na_2O$ concentration is below 100 g/L. This characteristic of $NaCaHSiO_4$ has been used to remove sodium in a hydro-chemical process. The decomposition product of $NaCaHSiO_4$ is amorphous calcium silicate hydrates, usually denoted as CSH, a precursor of many more ordered, well-defined phases when treated at a certain temperature and with long time curing. The CSH and related phases are the principal phases in concrete. There are about 30 stable crystalline phases, besides ill-crystallized materials in $CaO$-$SiO_2$-$H_2O$ system (Bonaccorsi and Merlino, 2005; Shaw et al., 2000). Many studies (Black et al., 2003; Hong and Glasser, 2004; Meller et al., 2007; Rios et al., 2009; Shaw et al., 2000) have been conducted to understand the relationship between CSH and related phases due to their importance in the cement industry. It shows that the Ca/Si molar ratio and temperature are the main parameters determining the formation of different phases. Fig. 1 presents a schematic stability diagram, showing the relative stabilities of some of these phases.

In this diagram, the CSH shows poorly ordered structure and variable chemical composition (Ca/Si molar ratio 0.8–2). However, if the molar ratio of Ca/Si is fixed to be 1, as the Ca/Si molar ratio in $NaCaHSiO_4$, the phase changes of CSH should gradually occur as follows at a certain temperature (El-Hemaly et al., 1977; Hong and Glasser, 2004; Shaw et al., 2000):

$$\begin{aligned}&\mathrm{CSH}\text{—tobermorite}\ (\mathrm{Ca_5Si_6O_{16}(OH)_2nH_2O})\\ &\quad\div\ \text{or Jennite}\ (\mathrm{Ca_9Si_6O_{18}(OH)_6 8H_2O})\text{—xonotlite}\\ &\qquad(\mathrm{Ca_6Si_6O_{17}(OH)_2})\ \text{or foshagite}\ (\mathrm{Ca_4(Si_3O_9)(OH)_2})\end{aligned}$$

Regarding the amorphous or semicrystalline state of CSH, there has been a lot of work reported (Bonaccorsi and Merlino, 2005; Chen et al., 2004; Gard and Taylor, 1976; Pellenq et al., 2008; Richardson, 2004, 2008; Smith et al., 1972) aiming at understanding the structural relations and formation mechanisms of CSH. Most of the present knowledge about CSH structure has been obtained from the study of the structure of tobermorite or jennite, which had been reviewed by Richardson(2004, 2008). Tobermorite has a dreierkette-like structure (Bonaccorsi and Merlino, 2005; Chen et al., 2004; Richardson, 2004) in which the same pattern of silica tetrahedra is repeated every three units on both sides of a central sheet of Ca octahedra which share oxygens with silicate tetrahedra. Water molecules and additional calcium cations occupy the interlayer. The variation in the length of the interlayer depends on the amount of water in the tobermorite structure, and structures with 1, 4 or 8 water molecules per unit cell have been reported. In addition, the structure of Jennite is almost the same as that of tobermorite, except that some silica tetrahedra of Jennite in the dreierkette chain is replaced by OH groups, causing substantial undulation in the Ca octahedra layer (Chen et al., 2004; Richardson, 2004). Consequently, CSH can be considered as a kind of tobermorite with a number of different types of defects, among which the missing tetrahedra and chain segments from the silicate chain are the most substantial.

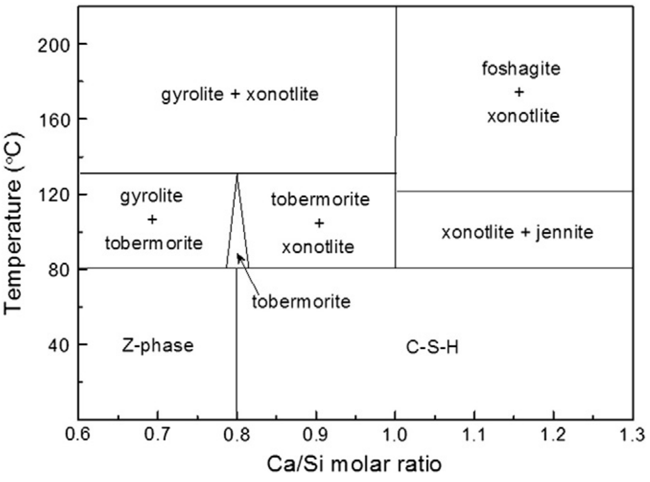

**Fig. 1.** Schematic stability diagram showing the relative stability of part of the hydrated calcium silicates (data are collected from Shaw et al., 2000, and Hong et al., 2004).

The reaction about decomposition of $NaCaHSiO_4$ in alkali solution can be expressed as follows (Bi and Yu, 2006):

$$\mathrm{NaCaHSiO_4} + \mathrm{OH^-} = \mathrm{SiO_3^{2-}} + \mathrm{Na^+} + \mathrm{Ca(OH)_2} \tag{1}$$

$$\mathrm{SiO_3^{2-}} + \mathrm{Ca(OH)_2} + \mathrm{H_2O} = \mathrm{CSH} + \mathrm{OH^-} \tag{2}$$

When alkali is added into the $CaO$-$SiO_2$-$H_2O$ system, $Na^+$ would prevent the conversion of nearly amorphous CSH into well-developed final phases, which are expected to be formed at stoichiometric Ca/Si molar ratio (Lodeiro et al., 2009, 2010; Nelson and Kalousek, 1977; Nocun-Wczelik, 1999). Generally, the transition of CSH to other crystalline phases would occur in several hours (Nocun-Wczelik, 1999; Shaw et al., 2000). Owing to the presence of $Na^+$ in solution, the transformation of CSH into corresponding phase at a certain temperature evolves slowly and could last days without significant change.

In addition, from the reaction equations it could be concluded theoretically that the decomposition extent can be determined by the sodium content in the residue. However, in alkali solution, the $Na^+$ can be incorporated into the CSH and difficult to wash off (Nelson and Kalousek, 1977; Nocun-Wczelik, 1999), so it is hard to determine the decomposition extent by elemental analysis. Therefore, in this study, the matrix-flushing method (Chung, 1974) – quantitative analysis of XRD with corundum as internal standard – has been used to determine the decomposition extent. Moreover, the Avrami–Erofeev equation was used to fit the kinetic data of decomposition of $NaCaHSiO_4$.

In view of the significance of the decomposition of $NaCaHSiO_4$ in a hydro-chemical process and limited research on it, the main aim of this work is set to investigate the transformation of $NaCaHSiO_4$ to CSH as a function of the alkali concentration, temperature, $NaCaHSiO_4$ particle size and CaO addition. Furthermore, detailed reaction kinetics were analyzed.

## 2. Experiments and methods

The $NaCaHSiO_4$ used in the experiments was synthesized from chemical regents. The following substances of analytical purity were used: NaOH, CaO and $Na_2SiO_3 \cdot 9H_2O$. All the reactants were produced by Xilong Chemical Co. Ltd., Guangzhou, China. Deionized water was used throughout all experiments.

The operation conditions of $NaCaHSiO_4$ synthesis were reported in a previous publication (Zhong et al., 2009). The hydro-chemical reaction was conducted in 30% $Na_2O$ solution at 230 °C for 2 hours. The mass ratios of $Na_2O$ to $SiO_2$ and CaO to $SiO_2$ reached 8 and 1, respectively. After the reaction, the slurry was filtered and the wet filter cake was thoroughly dispersed in deionized water at 60 °C to wash off sodium ions attached to the sample, followed by further filtration. After repeating the rinsing 4 times, the sample was dried in an oven at 80 °C overnight. The dried sample was then crushed and ground to below 106 μm. The chemical composition (analyzed by ICP-OES, optimal 5300DV of PerkinElmer instruments), XRD pattern (examined by X' Pert Pro MPD of Panalytical Company, 40 kV, 30 mA, CuK$\alpha$ as X-ray source), SEM micrograph (determined by Sirion 200 of FEI) and particle size distribution (measured by Mastersizer 2000 of Malvern) of the synthetic sample are shown in Table 1 and Figs. 2–4, respectively.