Powder Technology 333 (2018) 277–285

Contents lists available at ScienceDirect

Powder Technology

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

Calcification reaction of red mud slurry with lime

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ARTICLE INFO

Article history:
Received 2 September 2017
Received in revised form 21 December 2017
Accepted 14 April 2018
Available online 17 April 2018

Keywords:
Mechanism
Calcification
Calcification–carbonation process
Sodium aluminosilicate hydrate
Hydrogarnet

ABSTRACT

Calcification is a key step in the newly proposed calcification–carbonation process, which involves the recycling of alkali (Na_2O). In this study, the mechanism of calcification of red mud with lime (CaO) was elucidated thermodynamically, and the factors influencing the calcification were studied experimentally. The results showed that sodium aluminosilicate hydrate ($Na_2O\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O$) can be calcified with Ca^{2+} in red mud slurry, though not so with $Ca(OH)_2$ and CaO. Furthermore, calcification is mainly a solid–liquid reaction involving the transformation of sodium aluminosilicate hydrate to calcium hydrogarnet. Temperature increased the rate of CaO hydration and favored the calcification reaction. For reaction time equals 2 h, liquid–solid ratio equals 4, and the amount of lime added to dry red mud equals 30 wt%, at temperatures >160 °C, the content of Na_2O in the calcified slag reached <1%. When the reaction time reaches 90 mins, the content of Na_2O in calcified red mud slag became stable.

1. Introduction

In the Bayer process of alumina production, silica is found dissolved in sodium aluminate liquor, normally to the saturated state. The dissolved silica is separated from the liquor during the process of desilication, as a precipitate of sodium aluminosilicate hydrate (SAS), $Na_2O\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O$ [1,2]. The unsaturated coefficient x of SiO_2 (UCS) for the Bayer process normally lies in the range of 0–2 and varies according to the operating conditions, such as temperature and alkalinity. If SAS is precipitated as scales in pipe lines and heat exchangers, the alumina production operation can be affected significantly. However, SAS is mainly found as a precipitate in the residue (red mud) of this operation, and is the main component of red mud, which means that there are soda (Na_2O) and alumina (Al_2O_3) losses in the Al_2O_3 production process. SAS has three isomeric forms, namely the Linde type A zeolite, sodalite, and cancrinite. Of these three forms, Linde type A zeolite and sodalite forms are cubic with the space groups of $Fm\bar{3}c$ and $P\bar{4}3n$, respectively, whereas cancrinite is hexagonal with the space group of $P6_3$. Linde type A zeolite has a higher solubility than sodalite [3].

In the Bayer process, SAS is mainly in the form of sodalite and cancrinite. The amount of sodalite in SAS is higher at an elevated temperature (such as between 150 and 240 °C). In this process, the sodalite is formed first, which is then transformed slowly to cancrinite at a rate that increases with the increase in temperature. The activation energy for the formation of Linde type A zeolite from an amorphous phase lies in the range of 12–14 $kJ\cdot mol^{-1}$ [4], whereas for the crystal growth of pure sodalite and cancrinite, the values are 30 $kJ\cdot mol^{-1}$ and 52 $kJ\cdot mol^{-1}$, respectively [5,6].

When lime is added to a Bayer solution, SAS will react with lime in the solution to form a new precipitate, such as calcium hydrogarnet ($3CaO\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O$) [7,8]; note that hydrogarnet commonly exists in nature or can be synthesized from its constituents [9]. In this precipitation reaction, Na^+ in SAS is replaced by Ca^{2+}, and thus, soda is recovered and the loss of alkali is reduced. Hydrogaenet in the solution crystallizes in the space group Ia3d, and the crystals display a cubic unit cell structure. The structure of calcium hydrogarnet $3CaO\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O$ consists of a three-dimensional framework, which is made of octahedra $[Al(OH)_6]$, dodecahedra $[Ca(OH)_8]$ and tetrahedral $[(SiO_4)]$ [8,10]. The amount of hydrogaenet in the red mud residue depends on the quality of bauxite source and extraction conditions of alumina, such as temperature, amount of soda, and lime. As many studies have indicated, SAS in the residue is transformed to hydrogaenet [1,11,12], which thus, becomes the main constituent of red mud. The amount of lime added in the Bayer process is normally 3–7%, but exceeding this limit may result in the loss of Al_2O_3, although some loss of Al_2O_3 and alkali in red mud cannot be avoided.

It is also worthwhile to note that an attempt has been made to transform SAS to hydrogarnet in the calcification–carbonation process for Al_2O_3 production from bauxite or red mud processing [2,12,13]. A large amount of lime was added to the digestion solution during the calcification step so that Na_2O could be recovered. Thereafter, the hydrogarnet was first decomposed by the carbonation by CO_2, due to

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https://doi.org/10.1016/j.powtec.2018.04.031
0032-5910/

which, Al_2O_3 could be recovered. A new phase of red mud mainly composed of calcium silicate, and calcium carbonate was obtained; note that small amounts of Al_2O_3 and Na_2O were also observed in the phase [12]. In the calcification process, further addition of lime led to the transformation of most of the silicon phase to hydrogarnet, thus avoiding the precipitation of scales in pipe lines and equipment. Although some Al_2O_3 in the red mud was transformed to hydrogarnet, the formation of hydrogarnet is only an intermediate step. The calcification–carbonation process was aimed at completely transforming SAS to hydrogarnet in order to prevent the loss of alkali in red mud. In the carbonation process to follow, the hydrogarnet was decomposed by CO_2 to recover Al_2O_3 in the same step. In this process, the amount of lime used was a significantly higher than in the Bayer process for the prevention of the loss of alkali in red mud.

In calcification–carbonation process, lime can be present in the form of Ca^{2+}, $Ca(OH)$, or CaO in red mud slurry. The calcification reactions are represented below by the following reaction Eqs. (R1)–(R3).

$$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 3Ca^{2+} + 4OH^- \rightarrow 3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 2Na^+ + 2H_2O \quad (R1)$$

$$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 3CaO + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 2NaOH \quad (R2)$$

$$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 3Ca(OH)_2 \rightarrow 3CaO \cdot Al_2O_3 \cdot xSiO_2 \cdot (6-2x)H_2O + 2NaOH + 2H_2O \quad (R3)$$

Many studies have been conducted to investigate the formation of SAS in the desilication process of Bayer liquor. Most of these studies [7,14,15] investigated the kinetics of SAS formation in desilication process. Further, some studies [16,17] investigated the mechanism of SAS scale formation in pipe lines and heat exchange equipment. But, only a few studies have reported the mechanism of the transformation of SAS into hydrogaenet which involves several end-results: the losses in Al_2O_3 and Na_2O, phase change of red mud, and recycling of red mud [18,19]. In this work, focusing on the calcification–carbonation processes, thermodynamic analysis and experimental studies are carried out to investigate the mechanism of the calcification reaction in red mud slurry. Finally, based on these results, the mechanism of calcification of SAS is discussed.

2. Thermodynamic analysis

2.1. Method for thermodynamic analysis

Gibbs free energy of formation is a property used to describe the thermodynamic behavior of chemical reactions in metallurgical engineering. One important application of Gibbs free energy is its use in the prediction of the direction of chemical reactions of minerals. For most simple minerals, the experimental data on Gibbs free energy are generally available. However, such data are not available for SAS and hydrogaenet, which are usually found in the constituents of red mud or scales in pipe lines/heat exchangers, due to their complex compositions. In this study, a method which was proposed previously by the present authors, is used for the analysis of the calcification reaction [20]. The equations for analyzing the reaction are summarized below.

The free energies and enthalpies of formation of complex minerals are represented by Eqs. (1) and (2), respectively.

$$\Delta G^0_{f\ (\text{complex minerals})} = \sum \Delta G^0_f\ (\text{binary composite oxide}) + \Delta G^0_r \quad (1)$$

$$\Delta H^0_{f(\text{complex minerals})} = \sum \Delta H^0_f\ (\text{binary composite oxide}) + \Delta H^0_r \quad (2)$$

The standard Gibbs free energy and enthalpy of calcification reactions are given by Eqs. (3) and (4), respectively.

$$\Delta G^0_{298} = \sum \left(ni\Delta G^0_{i,f,298}\right)(\text{produc}) - \sum \left(ni\Delta G^0_{i,f,298}\right)(\text{Reactant}) \quad (3)$$

$$\Delta H^0_{298} = \sum \left(ni\Delta H^0_{i,f,298}\right)(\text{product}) - \sum \left(ni\Delta H^0_{i,f,298}\right)(\text{Reactant}) \quad (4)$$

The Gibbs–Helmholtz equation is given by Eq. (5).

$$\Delta G^0_T = \Delta H^0_T - T\Delta S^0_T \quad (5)$$

The dependence of the isobaric molar heat capacity (C_p) of a material on temperature can be represented by Eq. (6).

$$C_P = a + b \cdot 10^{-3}T + c \cdot 10^5 T^{-2} + d \cdot 10^{-6}T^2 \quad (6)$$

The difference between the isobaric molar heat capacities of the products and reactants is given by Eq. (7).

$$\Delta C_P = \sum (niC_{P,i})(\text{product}) - \sum (niC_{P,i})(\text{Reactant}) \quad (7)$$

The temperature dependence of each of the variables, standard enthalpy, entropy and Gibbs free energy is represented by Eqs. (8)–(10), respectively.

$$\Delta H^0_T = \Delta H^0_{298} + \int_{298}^{T} \Delta C_p dT \quad (8)$$

$$\Delta S^0_T = \Delta S^0_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} dT \quad (9)$$

$$\Delta G^0_T = \Delta H^0_{298} - T\Delta S^0_{298} + \int_{298}^{T} \Delta C_p dT - T\int_{298}^{T} \frac{\Delta C_p}{T} dT \quad (10)$$

The Van't Hoff equation is given by Eq. (11).

$$\Delta G_T = \Delta G^0_T + RT\ \ln(a_{NaOH})^2 \quad (11)$$

In the above equations, ΔG^0_r and ΔH^0_r are the free energy and enthalpy changes of the reaction (kJ/mol), respectively; n_i is the number of moles of reactant or product i; a, b, c, and d are the temperature dependent coefficients of the heat capacities of materials; and a_{NaOH} is the activity of NaOH.

The standard Gibbs free energy of calcification reaction is a function of temperature and heat capacity as shown by Eq. (10). The heat capacity is also a function of temperature as shown by Eq. (6). Substituting Eq. (6) into Eq. (7) leads to the following equation.

$$\Delta C_P = \Delta a + \Delta b \cdot 10^{-3}T + \Delta c \cdot 10^5 T^{-2} + \Delta d \cdot 10^{-6}T^2 \quad (12)$$

Substituting Eq. (12) to Eq. (10) and computing the integrals, the relationship between the standard Gibbs free energy of calcification reaction and temperature can be represented by Eqs. (13)–(15).

$$\Delta G^0_T = -a \cdot T\ \ln T - \frac{1}{2}b \cdot 10^{-3}T^2 - \frac{1}{2}c \cdot 10^5 T^{-1} - \frac{1}{6}d \cdot 10^{-6}T^3 + \beta \cdot T + \alpha \quad (13)$$

where the integration constants α and β are defined as follows.

$$\alpha = \Delta H^0_{298} - a \cdot 298 - \frac{1}{2}b \cdot 10^{-3} \cdot 298^2 + c \cdot 10^5 \cdot 298^{-1} - \frac{1}{3}d \cdot 10^{-6} \cdot 298^3 \quad (14)$$