Mechanism and kinetics of gibbsite-seeded sodium aluminosilicate crystallisation from synthetic spent Bayer liquor

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ABSTRACT

Despite a significant number of studies having been carried aimed at developing strategies for scale inhibition during the Bayer process, particularly in heat exchanger systems, there is still limited understanding of the underlying mechanisms and kinetics of scaling, in particular for single stream plants. The aim of this study was to further this understanding for sodium aluminosilicate crystallisation in spent Bayer liquor seeded with gibbsite. Gibbsite is present in pre-desilicated bauxite which is mixed with spent liquor and then passes through the heat exchanger system in single stream Bayer plant circuits.
The solution desilication rate, at 140 °C, was found to increase significantly with increasing seed loading (or surface area) from 45 g L^{-1} to 90 g L^{-1} even though partial, and in some cases complete, dissolution of the gibbsite seed resulted in increased liquor Si solubility. SEM, particle size distribution and X-ray diffraction analysis of the solid residues demonstrated that heterogeneous nucleation and growth of sodalite on the gibbsite seed results in reduced scaling on steel coupon surfaces as compared to without seeding. These findings suggest that the gibbsite, inherent in pre-desilicated bauxite, may be effective in reducing scale on heat exchanger surfaces in a single stream process environment.

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1. Introduction

The Bayer process is the predominant world-wide industrial process for the production of alumina (Al_2O_3) from bauxite ore (Webster et al., 2011). Aluminium-containing minerals in bauxite ore, such as gibbsite (γ-Al(OH)$_3$) and boehmite (γ-AlOOH), are extracted by digestion of the ore in concentrated sodium hydroxide solution at 140–250 °C to form 'pregnant' liquor. The pregnant liquor is then cooled to achieve supersaturation and seeded with gibbsite particles. Precipitation of gibbsite from the pregnant liquor takes place at 60–90 °C. The liquor is then concentrated through partial evaporation and the 'spent' liquor is re-heated as it passes through a series of heat exchangers (Addai-Mensah, 1997). In a double stream circuit the bauxite slurry is fed into a digester and mixed with the re-heated spent liquor. In contrast, in a single stream circuit, the slurry is combined with the concentrated spent liquor (or strong liquor) and is then reheated and digested as it passes through the heat exchangers (Sidrak, 2001).

A pre-desilication process prior to digestion is frequently employed to remove, via dissolution and reprecipitation, reactive silicate from the bauxite ore resulting in the production of desilication products (DSP). The DSP are eliminated from the circuit as part of the 'red mud'

during the clarification stage of the pregnant liquor subsequent to 'flashing' to atmospheric pressure (Addai-Mensah et al., 2004). Despite this aluminosilicate scaling remains a serious issue resulting in restrictions in liquor flow in vessels and pipes, decreases in heat exchanger efficiency and increases in energy consumption (Barnes et al., 1999c). However, it has been observed that seeding can markedly suppress scale formation (Barnes et al., 1999b).

The nature of the scale formed in double stream Bayer plants at 90–240 °C has been investigated, with sodalite and cancrinite being the main phases observed (Gerson and Zheng, 1997). These phases share a similar ring structure composed of a series of –Al–O–Si–O– making up interlocking cages in sodalite and cages and channels in cancrinite. Sodalite, which is the more soluble and less thermodynamically stable phase, undergoes a solution-mediated phase transformation to cancrinite over several hours at elevated temperature (>140 °C) (Addai-Mensah et al., 2004; Barnes et al., 1999c; Gerson and Zheng, 1997). Although sodalite and cancrinite have many diffraction peaks arising at similar d-spacings X-ray powder diffraction can be used to readily distinguish cancrinite from sodalite due to the presence of the 101 cancrinite diffraction peak, with no peak at similar d-spacing arising from sodalite (Barnes et al., 1999b).

Barnes et al. (1999d) found that the solubilities of sodalite and cancrinite increased linearly with increasing temperature, with the equilibrium Si solubility of sodalite being greater than that of cancrinite at all temperatures. The solubilities of both cancrinite and sodalite in

synthetic spent Bayer liquor have also been found to increase with increasing Al concentration in the Al/NaOH molar ratio range 0.2–0.7 (Addai-Mensah et al., 2004; Barnes et al., 1999d). In Bayer alumina refineries, the dissolved Al concentration is prone to variation, in spent liquors typically from 1.35 to 2.20 M (Barnes, 1999).

The kinetics of nucleation and growth of aluminosilicate for both unseeded and seeded spent Bayer liquors has been the subject of a significant number of investigations (summarised in Tables 1 and 2, respectively). Secondary nucleation (i.e. nucleation promoted by the presence of seed crystals of the same phase as the solute crystals) and growth of sodium aluminosilicate from synthetic spent Bayer liquor have been studied using different seed types such as pre-desilicated bauxite (Cresswell, 1984; Oku and Yamada, 1971), aluminosilicate phases (Addai-Mensah et al., 2002; Barnes et al., 1999a,b; Grujić et al., 1989) and mixtures of aluminosilicate phases (Barnes et al., 1999b; Duncan et al., 1995; Murakami et al., 1992). The significant variation in the orders of reaction of desilication with respect to Si supersaturation, most probably for the same or similar reaction mechanisms, may be due to differences in the phases and characteristics of the seed used, and variation in the Si supersaturations at which the experiments were undertaken (Barnes, 1999).

A second order dependence of desilication on Si supersaturation has been derived mathematically for aluminosilicate scale fouling on heat exchanger surfaces in double stream Bayer circuits (Duncan et al., 1995; O'Neill, 1986). Upon zeolite, sodalite and cancrinite seeding, desilication reaction orders of four or greater have been reported for secondary nucleation of these phases (Addai-Mensah et al., 2002; Gualtieri and Venturelli, 1999). Orders of desilication with respect to Si supersaturation between one and three have been reported for aluminosilicate crystal growth upon seeding with bauxite, red mud, DSP, sodalite and cancrinite (Adamson et al., 1963; Barnes et al., 1999a,b; Cresswell, 1984; Duncan et al., 1995; Murakami et al., 1992; Oku and Yamada, 1971).

In this study, in accordance with the published studies by Barnes (1999) and others (Tables 1 and 2), desilication with third-order or greater dependence on Si supersaturation is interpreted to be predominantly due to nucleation, either primary heterogeneous (where crystallisation is induced by foreign bodies of phase different to the solute crystals) or secondary, depending on seed type. Desilication with Si supersaturation dependence less than third-order is interpreted to be predominantly due to aluminosilicate crystal growth.

As far as the authors are aware no desilication studies involving gibbsite seeded spent Bayer liquor have been reported even through gibbsite is always present in single steam heat exchanger slurries. Hence the aim of this study was to examine the kinetics and mechanism of gibbsite-seeded aluminosilicate precipitation from synthetic Bayer spent liquor with the longer-term objective of scaling remediation.

2. Experimental methodology

2.1. Liquor preparation

The synthetic spent liquor used for the desilication experiments was of composition: 1.8 M NaAl(OH)$_4$, 4.41 M free NaOH, 0.44 M Na$_2$CO$_3$, 0.065 M Na$_2$SO$_4$, and 17.7 mM Si (added as liquid sodium silicate, D grade, 14.7 wt.% Na$_2$O + 29.4 wt.% SiO$_2$; PQ Australia Pty Ltd.). This liquor composition was derived using the ratio of concentrations of an industrial pre-desilicated slurry solution (primer slurry) to concentrated spent liquor of 0.35:1 (wt.%/wt.%) to simulate the liquor concentration within single stream Bayer process heat exchangers.

Si-free synthetic spent Bayer liquor (concentrations as given above) was prepared using gibbsite (Cytec Industries Ltd., purity 99 wt.%), sodium hydroxide pellets (Chem-supply, Analytical Reagent, minimum assay 97 wt.%, maximum limit of Na$_2$CO$_3$ 1 wt.%), sodium sulphate anhydrous powder (Sigma-Aldrich, AR grade), sodium carbonate anhydrous (Yixin chemical company, China, 97 wt.%) and Milli-Q water (surface tension of 72.8 mN m^{-1} at 20 °C and a specific conductivity less than 0.5 μS cm^{-1}). To prepare this liquor the required amount of NaOH pellets were dissolved in Milli-Q water in a stainless steel vessel. Gibbsite powder was then added to the hot sodium hydroxide solution. The vessel was wrapped with Al foil and the temperature was maintained at approximately 105 °C. The required masses of sodium carbonate and sodium sulphate were then dissolved separately in hot water and added to the clear sodium aluminate solution on complete dissolution of the gibbsite. The solution was stirred (400 rpm) at 90 °C for 3 h. The hot solution was then vacuum-filtered through a caustic resistant 0.2 μm membrane before being diluted to the required concentration.

2.2. Preparation and characterisation of sodalite and gibbsite

Sodalite was synthesised over 48 h at 90 °C from liquor with initial composition 0.2 M Si (added as liquid sodium silicate), 1.7 M Al, 4.0 M NaOH, and 0.38 M Na$_2$CO$_3$. Greater crystallisation times (>48 h) result in significant transformation of sodalite to cancrinite. The solution was agitated (≈400 rpm) in a stainless steel reactor vessel. The product slurry was filtered through a 0.2 μm membrane. The solid component was washed three times each with 10 wt.% aqueous ammonia solution (Sigma-Aldrich, ACS reagent, 28–30 wt.% NH$_3$) and ethanol (Sigma-Aldrich, ACS reagent, ≥99.5 wt.%), and dried in an oven overnight at 120 °C. Rietveld analysis of the powder X-ray diffraction (XRD, Section 2.5) data confirmed that the product was sodalite with cancrinite content less than 3 wt.% and amorphous content less than 5 wt.%.

The specific surface area of the gibbsite seed and sodalite were determined to be 0.12 ± 0.01 m^2 g^{-1} and 24.08 ± 0.06 m^2 g^{-1}

Table 1
Kinetic parameters reported in the literature for nucleation of sodium aluminosilicate.

Authors	Experimental conditions	Order (n)	E_a (kJ mol^{-1})
O'Neill (1986)	Plant liquor, neat exchanger scaling, Si 0.006–0.008 M	2	51
Duncan et al. (1995)	Synthetic liquor, heat exchanger scaling, Si 0.0315 M,	2	77
Antonić et al. (1994)	Zeolite A nucleation	–	12–44
Barnes (1999)	Sodalite nucleation from: 3.87 M NaOH, 0.38 M Na$_2$CO$_3$, 0.1 M Si, 1.67 M Al(OH)$_3$, 90–240 °C.	–	95
Gualtieri et al. (1997)	Sodalite nucleation from a clear solution: 1 M NaOH (dissolved kaolinites in 4 M NaOH, then diluted into 1 M NaOH concentration) at 100–130 °C.	5	71–142
Grujić et al. (1989)	Sodalite nucleation from a zeolite A seeded solution: 8 M NaOH at 70–85 °C.	–	104
Barnes (1999)	Cancrinite nucleation from a sodalite seeded solution: 3.87 M NaOH, 0.38 M Na$_2$CO$_3$, 0.05 M Si and 1.67 M Al(OH)$_3$ at 180–240 °C.	2	133
Addai-Mensah et al. (2002)	Zeolite nucleation from a zeolite seeded solution: 4 M NaOH, 1 M NaNO$_2$, 0.175 M Si and 0.188 M Al at 30 and 65 °C.	4	47
Addai-Mensah et al. (2002)	Sodalite nucleation from a sodalite seeded solution: 4 M NaOH, 1 M NaNO$_2$, 0.175 M Si and 0.188 M Al at 30–130 °C.	4	49
Addai-Mensah et al. (2002)	Cancrinite nucleation from a cancrinite seeded solution: 4 M NaOH, 1 M NaNO$_2$, 0.175 M Si and 0.188 M Al at 30–130 °C.	4	82