Desilication of low alumina to caustic liquor seeded with sodalite or cancrinite

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ABSTRACT

The aim of this study was to improve understanding of scale formation mechanisms and to provide theoretical support for development of scale inhibition strategies. Sodium aluminosilicate scaling on plant surfaces is a critical problem in Bayer refineries, particularly within digesters and heat exchangers. Although numerous studies have been carried out to understand the mechanisms of scale formation and to develop scale inhibition strategies in double-stream circuit Bayer plants, there is still insufficient relevant research on single-stream Bayer plants. We have studied the desilication behavior of a liquor of similar composition to spent cleaning caustic liquor, for which the aluminate concentration and A/C are both less than heat exchanger liquor. These concentration conditions were chosen in order to investigate the early stage of scale formation in single-stream Bayer plants by increasing the component of aluminosilicate bulk precipitate upon seeding and decreasing the relative degree of scaling.

Solution desilication experiments were performed using spent cleaning caustic liquor at 140 °C either without seeding or with sodalite (seed loading 1.125 g L^{-1}) or cancrinite seeding (seed loadings 1.125 g L^{-1} and 2.850 g L^{-1}) in the presence of steel substrates. The solution desilication rate showed significant increase in the presence of seeds and was found to be greater in the presence of cancrinite seeds than sodalite of the same surface area. The desilication kinetics of the synthetic spent cleaning caustic liquor suggests predominant heterogeneous nucleation for unseeded desilication, a mixed secondary-nucleation and growth process for desilication on addition of sodalite seeding, and cancrinite seeding with both smaller and greater loading.

A first layer, possibly amorphous, with high Al and low Si concentrations was observed by SEM and FIB/SEM on the coupon surface after desilication with or without seeds. We note that this layers forms despite the low A/C and high Si supersaturation suggesting that under single-stream heat exchanger conditions this may also be the first layer to form. XRD confirmed that sodalite formed on the coupons in unseeded and sodalite seeded desilication systems while cancrinite formed on the coupons upon cancrinite seeded desilication with both smaller and greater seed loading. The coupon from the cancrinite seeded liquor with high seed loading is least covered by scale amongst the coupons, suggesting that cancrinite seeding may be a potential strategy for reducing scale formation in single-stream Bayer circuits.
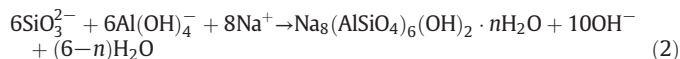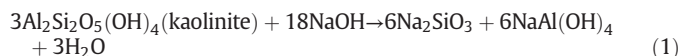
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1. Introduction

Refining of alumina (Al_2O_3) from bauxite ore via the Bayer process, invented and patented by Karl Josef Bayer in 1888 (Bayer, 1888), is the principal method for this purpose worldwide. The modern version of the Bayer process can be summarised as the digestion of Al-rich bauxite ore in hot caustic liquor after milling, separation of the insoluble components (red mud), followed by gibbsite precipitation and calcination of the gibbsite to alumina (Al_2O_3). The temperature required for digestion is relatively low (≈ 150 °C) when gibbsite ($Al(OH)_3$) is the main component of value or greater (≈ 220 °C) when boehmite (γ-AlO(OH)) is present in commercial quantities (Smith, 2009).

A pre-desilication stage (typically NaOH ≈ 5 M, 80–95 °C, ≈ 8 h) is often introduced prior to bauxite digestion to remove reactive silicates,

as insoluble desilication product (DSP), from the bauxite ore which are then expelled with the red mud (Hind et al., 1999; Smith, 2009). The reactive silicate is predominantly in the form of kaolinite, which during pre-desilication undergoes dissolution (Eq. (1)) and subsequent reprecipitation as less soluble silicate containing phases, for instance sodalite (Eq. (2)) (Cousineau and Fulford, 1987; Roach and White, 1988).

$$3Al_2Si_2O_5(OH)_4(kaolinite) + 18NaOH \rightarrow 6Na_2SiO_3 + 6NaAl(OH)_4 + 3H_2O \quad (1)$$

$$6SiO_3^{2-} + 6Al(OH)_4^- + 8Na^+ \rightarrow Na_8(AlSiO_4)_6(OH)_2 \cdot nH_2O + 10OH^- + (6-n)H_2O \quad (2)$$

X_2, given as $(OH)_2$ in the sodalite stoichiometry in Eq. (2), may be $\frac{1}{2}CO_3^{2-}$, $\frac{1}{2}SO_4^{2-}$, Cl^-, OH^- or other impurities. Pre-desilication usually results in removal of 80–90% of the reactive silicate (Smith, 2009)

but also results in the unwanted loss of both sodium hydroxide and aluminum from the process stream.

However, the remaining reactive silicate can still result in severe down-stream scaling issues particularly within heat exchangers and digesters resulting in equipment downtime, reduced volume capacity and heat-transfer efficiency, lost production and de-scaling operations. The associated lost revenue has been estimated to be at least a quarter of the operational costs of an alumina refinery (Khan et al., 2010; Roach and Cornell, 1985; Sidrak, 2001).

The large decrease in Al concentration upon gibbsite precipitation results in a decrease in Si solubility and therefore greater relative Si supersaturation in the spent liquor and increased potential for desilication (Barnes et al., 1999b; Breuer et al., 1963). After gibbsite precipitation the spent liquor is concentrated in an evaporator to increase the caustic concentration, i.e. strong liquor in industry terminology. In a double-stream circuit the concentrated liquor, after being re-heated through a series of heat exchangers, is mixed with the bauxite slurry in a digester.

In a single-stream circuit the concentrated spent liquor is mixed directly with the bauxite slurry in the heat exchangers where the temperature in a train of heat exchangers typically varies from 90 °C to 220 °C prior to final digestion. This results in a number of benefits. The A/C ratio of the liquor stream rises step-wise throughout the entire heater train as the gibbsitic bauxite component dissolves. As a consequent very little gibbsite scaling results as alumina is either slightly under-saturated or saturated at each stage. The increasing A/C in the heat exchangers increases the silica solubility making the management of silicate-containing scale easier than in double-stream plants. In addition, the rising aluminate concentration reduces the free caustic concentration, reducing the demand on the construction of the heaters or digestion vessel and making the use of exotic metals unnecessary; the most significant advantage of single streaming. Furthermore, the scouring caused by the motion of the bauxite particles helps keep the pipes and vessels clean due to the reasonable amount of sandy material in bauxite. Single stream plants therefore are simpler and require less energy input than double stream plants (Hind et al., 1999; Smith, 2009). At present, approximately 40–45% of all alumina refineries are of the single stream design. However, despite these advantages scaling does remain a critical issue.

Currently there exist anti-scaling reagents that are highly effective for the low solids environment of double-stream Bayer process heat exchangers but are not as effective for the high solids environment of single-stream process heat exchangers (Heitner and Spitzer, 2011; Spitzer et al., 2010; Spitzer et al., 2004; Spitzer et al., 2008b). Moreover, 55–66% of bauxite reserves are sub-economic due to high levels of reactive silica (Sidrak, 2001; Smith, 2009), which improved silicate management strategies may make economically accessible.

The major forms of sodium aluminosilicate scale observed in Bayer plants are sodalite and cancrinite. The solubilities of both sodalite and cancrinite increase linearly with temperature with the solubility of sodalite always being greater than that of cancrinite (Zheng et al., 1998). Amorphous aluminosilicate and zeolite are relatively unstable and tend to transform into sodalite and subsequently cancrinite (Barnes et al., 1999b; Breuer et al., 1963; Yuhás et al., 1964). The conversion from sodalite to cancrinite was found to be more rapid at greater temperature, and was less complete at 90 °C than at 160 °C after 13 days (Barnes et al., 1999d; Zheng et al., 1998).

There have been a number of publications concerning the mechanism and kinetics of aluminosilicate scale formation under industrially relevant double-stream conditions (Duncan et al., 1995a; Duncan et al., 1995b; Müller-Steinhagen et al., 1994; Müller-Steinhagen et al., 1993; Prakash and Horvath, 1979; Watanabe, 1981; Wefers, 1971). Kinetic analysis of the crystallisation of sodium aluminosilicate from both synthetic spent Bayer liquor and plant liquor has been investigated both without seeds and with a variety of seeds including DSP, pre-desilicated bauxite and red mud. The reaction order of desilication with respect to Si supersaturation in synthetic spent Bayer liquor seeded

with zeolite, sodalite or cancrinite has been reported to range from 1 to 4 (Addai-Mensah et al., 2002a; Barnes et al., 1999a; Cousineau and Fulford, 1987; Gualtieri et al., 1997). Based on these studies a first or second order dependency of desilication on Si supersaturation can be attributed to predominant crystal growth. A third-order or greater desilication dependency on Si supersaturation can be interpreted as resulting from a nucleation dominated process, either heterogeneous (i.e. nucleation in the presence of foreign substances) or secondary (also termed breeding of nuclei, i.e. nucleation in the presence of crystalline solute material) depending on seed type.

To date, there have been few studies of heat exchanger scaling within single-stream Bayer processes. The two that the authors are aware of concern high titanium bauxite (Suss et al., 2002) and scale removal/inhibition strategies (Suss et al., 2004). In the latter publication a variety of industrial scale phases are identified but the mechanism of scaling is not examined. We have studied five scale samples located at different areas of the heat exchanger train from a single-stream refinery using a variety of characterisation techniques. Cancrinite, perovskite or katoite were found as major crystalline phases in these scales; however a significant amorphous content was also found to be present proposed to be predominantly poorly crystallised sodalite. Elevated Al concentration (25 at.%) was observed in the tube side of the scale which significantly decreased over 50 μm toward the slurry side of the scale (Kawashima et al., 2016).

As the temperature increases from 90 °C to 220 °C and A/C increases through the heat exchanger train in order we intend to study the kinetics and characteristics of scale formation in Bayer liquors with differing concentrations of aluminate: 1) spent cleaning caustic liquor (50% NaOH w/w raw caustic diluted with plant liquor and used for dissolving scale from the pipes and tanks at temperatures lower than 100 °C before being mixed with spent liquor and recycled to digestion); 2) digester feed liquor of a single-stream refinery and 3) the later stages of single-stream heat exchanger liquor prior to the final digestion (Rothenberg and Cywar, 2016).

In single-stream plants the pre-desilicated bauxite passes through the heat exchangers with the concentrated spent liquor and therefore the DSP and phases formed due to subsequent transformations may act as seeds during subsequent desilication. Although there are a number of studies regarding the kinetics of scale formation in spent liquor (Barnes et al., 1999e; Zheng, 1997) the mechanism of the initial scaling-stage is still unclear. Decreasing aluminate concentration results in decreasing Si solubility and thus increasing initial supersaturation with respect to aluminosilicate. When the initial supersaturation is greater than that needed for only growth, rapid nucleation will also occur initially (Addai-Mensah et al., 2002b; Barnes et al., 1999a). The aims of this study, therefore, were to 1) examine the kinetics and mechanism of aluminosilicate precipitation from synthetic spent cleaning caustic liquor in the presence of sodalite or cancrinite, 2) explore the early stages of scaling by reducing the aluminate concentration (spent cleaning caustic liquor) to accelerate bulk nucleation with seeding and to slow down the scaling event on steel coupons which mimics the heat-exchanger wall in experiments.

2. Methodology

2.1. Materials and preparation of spent cleaning caustic liquor

The following chemicals were used in the preparation of caustic aluminosilicate liquors and seeds: sodium hydroxide (Ajax Chemicals, Australia, laboratory reagent, 97.5 wt.%, <2.5 wt.% Na_2CO_3); gibbsite (KB-30, Alcoa World Alumina- Australia, 99.5–99.7 wt.%); sodium carbonate (BDH Chemicals, Australia, analytical reagent, 99.9 wt.%); sodium sulfate (BDH Laboratory Chemicals Division Poole England, analytical reagent, 99.0 wt.%); liquid sodium silicate (D grade, 14.7 wt.% Na_2O + 29.4 wt.% SiO_2); nitric acid (RCI Labscan Ltd., 70 wt.%) and milli-Q water (specific conductivity <0.5 μS cm^{-1}).