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Desilication of hematite, goethite and iron powder seeded low alumina to caustic liquors

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ABSTRACT

Even though many studies have been carried out aimed at the development of methodologies for the inhibition of scale formation during the Bayer process there is still limited understanding of the underlying desilication processes and kinetics, in particular for the high solids density environment of single-stream heat exchangers. Our objective was to gain insight into the relative desilication due to nucleation and/or growth, and the kinetics of scale formation in the presence of typical solid phases. We have chosen a caustic aluminosilicate liquor composition in which both aluminate concentration and A/C are less than for heat exchanger feed liquor and hence aluminosilicate supersaturation is increased. These concentration conditions were chosen to investigate the early stage of scale formation in single-stream Bayer plant heat exchangers by increasing the component of aluminosilicate bulk precipitate upon seeding and decreasing the relative degree of scaling. The precipitation of aluminosilicate phases from this liquor at 140 and 180 °C seeded with hematite, goethite and iron powder crystals was investigated. Upon seeding rapid desilication took place with significant suppression of scale formation on steel coupon surfaces as compared to unseeded experiments. Seeding with hematite resulted in the most rapid reduction in aluminosilicate supersaturation. Additionally, the presence of hematite, in contrast to the other seed types, appears to promote the transformation of sodalite to cancrinite. Precipitation was found to occur predominantly via heterogeneous nucleation during the 240 min reaction time. The results of this study suggest that a seeding strategy, especially using hematite, may be effective in reducing scale formation on mild steel process equipment in a single-stream Bayer heat exchanger process environment.

1. Introduction

Sodium aluminosilicate scale caused by the processing of silicate-containing caustic aluminate liquor is a serious fouling problem for a wide range of Australian and international industries such as alumina refineries, pulp and paper industries and high level nuclear waste plants (Addai-Mensah et al., 2004). Scale growth leads to restrictions in liquor flow in process vessels and pipes, decreases in heat exchanger efficiency, increases in energy consumption and lost production capacity due to the necessity for downtime for scale removal (Barnes et al., 1999c).

The production of alumina (Al_2O_3) via the Bayer process requires the digestion of bauxite ores in hot concentrated NaOH solution for the extraction of aluminium hydrates (Webster et al., 2011). However, kaolin and other reactive silicates in the ore may also dissolve resulting in deleterious aqueous silicate within the caustic liquor (Gerson and Zheng, 1997). To mitigate this the majority of the reactive silicates are removed during a ‘pre-desilication’ stage. This is carried out prior to ore digestion and consists of the dissolution of the reactive silicates and their re-precipitation as desilication product (DSP). After digestion the liquor is cooled and the DSP is expelled from the circuit in the ‘red mud’ which also contains undissolved non-value components of the ore (Li et al., 2000). However, even with effective pre-desilication some silicate remains within the liquor. The liquor, at this stage, is supersaturated with respect to aluminium hydroxide (‘pregnant’ liquor) and upon seeding gibbsite ($Al(OH)_3$) is precipitated. The ‘spent’ caustic liquor is then concentrated by evaporation to increase the caustic concentration resulting in ‘strong liquor’ in industry terminology. This liquor is then reheated via a series of heat exchangers for further ore digestion. However, the dual effects of reduction in liquor aluminium concentration due to gibbsite precipitation and increased liquor silicate concentration results in increased aluminosilicate supersaturation (Armstrong and Dann, 2000). Upon reheating in the evaporators and heat exchangers scaling of silicate containing phases can be a serious issue.

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In a double-stream Bayer circuit, the slurry after pre-desilication is fed into a digester and is mixed with spent liquor that has passed through both the evaporators and the heat exchangers. In a single-stream circuit, the pre-desilicated slurry is combined with concentrated spent liquor from the evaporator and is then reheated and digested as it passes through the heat exchangers (Sidrak, 2001). Even though many studies have been carried out to develop methodologies for the inhibition of scale formation in the Bayer process, there is still limited understanding of the underlying desilication processes and kinetics, in particular for single-stream plants (Smith, 2009).

The sodium aluminosilicate phases that foul evaporators and heat exchangers are amorphous solid, zeolite A, sodalite and cancrinite (Addai-Mensah et al., 2004). Sodalite and cancrinite are the focus of this study as they are the main phases found in heat exchangers at high temperature (>140 °C). At elevated temperature (>180 °C) sodalite undergoes a dimorphic phase transformation to cancrinite over several hours (Addai-Mensah et al., 2004). This process is solution mediated, with the dissolution of the less stable phase, sodalite, and concomitant heterogeneous nucleation and growth of the more stable phase, cancrinite (Addai-Mensah, 1997). Both sodalite and cancrinite have the same framework stoichiometry composed of a series of ring structures made up by -Al-O-Si-O- units. The range of water molecules and anions and/or cations that can be located in the cages or channels forming the framework of these phase result in different chemical properties, diffraction peak intensities and variation in unit cell dimensions for each phase (Gerson and Zheng, 1997).

An oxide or oxyhydroxide layer is formed on the mild steel surfaces of heat exchangers due to their routine contact with caustic Bayer liquor. The major iron corrosion products constituting this oxidised layer are goethite (α-FeOOH) and hematite (α-Fe_2O_3), which may play an important role in the nucleation and growth mechanisms of scale (Hind et al., 1999). Goethite and hematite are also relatively abundant in bauxite and the structures of the two minerals are very similar: both have hexagonal close-packed O with octahedrally coordinated Fe (Goss, 1987). At relatively low temperatures (≈140 °C) these minerals are mostly inert and pass through the Bayer process undissolved and unreacted. However, the solubility of goethite increases significantly at greater temperatures (>180 °C), and goethite can transform into hematite, via dissolution and re-precipitation, given sufficient time and appropriate conditions (Murray et al., 2009).

The kinetics of desilication of self-nucleating and seeded spent Bayer liquors has been the subject of several investigations (Addai-Mensah et al., 2003; Addai-Mensah et al., 2004; Armstrong and Dann, 2000; Barnes, 1999; Barnes et al., 1999a; Barnes et al., 1999b; Duncan et al., 1995; Gerson et al., 1996; Gerson and Zheng, 1997; Grujić et al., 1989; Hermeler et al., 1991; Kraus et al., 1968). In unseeded reactions, the rate of desilication with low initial silicate concentration (<10 mM) is extremely slow at temperatures below 180 °C. As a result, accurate determination of the relative occurrence of nucleation and/or growth, and kinetics of desilication is difficult. Upon seeding, the rate of desilication is sufficiently rapid to enable the measurement of more reliable kinetic data (Barnes, 1999). Previous studies have examined the effect of seeding with pre-desilicated bauxite, zeolite, sodalite, cancrinite or their mixtures, with observation of different and/or conflicting desilication kinetic behaviours (precipitation reaction orders from 1 to 5 and activation energies ranging from 17 to 142 kJ mol^{-1}). Much of the variation may be attributed to the differences in crystallographic characteristics of the seed phase types (Barnes, 1999). However, all the studies suggest that the addition of seed greatly accelerates desilication and markedly suppresses scale formation (Barnes et al., 1999d).

In this study, in accordance with the rational provided in Ruan et al. (2016) based on the published studies by Barnes et al. (1999a) and others, desilication with third-order or greater dependence on aluminosilicate supersaturation (defined as a function of solution silicate concentration) is interpreted to be predominantly due to nucleation. This may be either heterogeneous (i.e. where crystallisation is induced by foreign bodies of phase different to the solute crystals) or secondary (i.e. nucleation promoted by the presence of seed crystals of the same phase as the solute crystals) depending on seed type. Desilication with aluminosilicate 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 hematite, goethite or iron powder seeded caustic aluminosilicate liquor have been reported. Both goethite and hematite are present in pre-desilicated bauxite and will pass through the heat exchanger with the concentrated spent liquor in a single-stream circuit. Iron powder seeding has also been examined to investigate whether provision of a large surface area of iron, which has similar surface properties to the steel surface of heat exchangers, can lead to reduced scale formation.

2. Experimental

2.1. Liquor preparation

Silicate-free synthetic caustic aluminate liquor was prepared from aluminium hydroxide (Cytec, purity 99 wt.%); sodium hydroxide pellets (Chem-supply, Analytical Reagent, minimum assay 97 wt.%, maximum limit of Na_2CO_3 1 wt.%); sodium sulfate anhydrous powder (Sigma-Aldrich, AR grade); anhydrous sodium carbonate (Yixin chemical company, China, 97 wt.%) and Milli-Q water (surface tension of 72.8 mN m^{-1} at 20 °C and specific conductivity <0.5 μS cm^{-1}). To prepare this liquor the required amount of sodium hydroxide pellets was dissolved in Milli-Q water in a stainless steel vessel. The aluminium hydroxide powder was then added to the hot sodium hydroxide solution. The vessel containing this solution was wrapped with aluminium foil and maintained at 105 °C. The desired masses of sodium carbonate and sodium sulfate were then dissolved separately in hot water and added to the clear sodium aluminate solution on complete dissolution of the aluminium hydroxide. The solution was stirred at 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.

Liquid sodium silicate (D grade, 14.7 wt.% Na_2O + 29.4 wt.% SiO_2; PQ Australia Pty Ltd.) was added to the diluted solution immediately prior to experiment commencement. Addition of silicate earlier in the solution preparation process gives rise to aluminosilicate precipitation. The final caustic aluminosilicate liquor was of the composition 1.80 M $Al(OH)_3$, 6.23 M total NaOH (1.80 M $NaAl(OH)_4$, 4.41 M free NaOH), 0.44 M Na_2CO_3, 0.07 M Na_2SO_4, and 17.7 mM Na_2SiO_3. This liquor has similar composition to a spent cleaning caustic liquor with lower aluminate concentration and A/C ratio of 0.28 (aluminium is expressed as Al_2O_3 g L^{-1} divided by sodium expressed as g L^{-1} Na_2CO_3) than typical of the slurry passing through single-stream Bayer heat exchangers (A/C of ≈0.5), resulting in increased aluminosilicate supersaturation. This liquor was chosen so that the degree of bulk precipitation would be increased relative to scaling enabling the first stages of scaling to be more specifically examined.

2.2. Batch desilication experiments

The unseeded and seeded desilication experiments were carried out using a set of high pressure Parr bombs (Parr Instrument Company, U.S.A.) into which Teflon liners, volume 27 mL, were placed. The Parr bombs were inserted into the specifically designed apertures of a thermostatically controlled heater. The heater, with Parr bombs inserted, was fixed onto a shaker table, which provided constant shaking (1800 rph) for the duration of the experiment. The experiments were run for 4 h at 140 or 180 °C (±0.3 °C) with periodic removal of a Parr bomb to monitor the silicate concentration of the liquor. Solution silicate concentration analysis was carried out using the molybdate blue method and UV–vis spectroscopy. Each experiment was carried out twice. Coupons of 1020 mild carbon steel (Metal Samples Company)