



Characterisation of single-stream Bayer plant heat exchanger scale



Nobuyuki Kawashima^a, Lina Shi^a, Ning Xu^a, Jun Li^a, Andrea R. Gerson^{a,b,*}

^a Minerals and Materials Science & Technology, Mawson Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia

^b Blue Minerals Consultancy, Middleton, SA 5095, Australia

ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form 24 October 2015

Accepted 26 October 2015

Available online 30 October 2015

Keywords:

Bayer refinery
Single stream
Scale
Aluminosilicate
Titanate
Amorphous

ABSTRACT

During the Bayer process, deleterious scale formation, consisting largely of aluminosilicate and titanate phases, results in additional consumption of caustic soda and decreased heat transfer efficiency thereby increasing energy costs. However, little characterisation has been undertaken as to the nature of these scales, particularly from within single stream Bayer refineries. Five contrasting scale samples have been studied using SEM, EDS, XRD Rietveld analysis, and for three samples synchrotron XANES analysis. Cancrinite, perovskite or katoite were found as major crystalline phases in these scales; however, a significant amorphous content was also found to be present. In conjunction with XRD and EDS analyses, Al K-edges XANES linear combination analysis indicates that the amorphous component in the scale samples consists predominantly of poorly crystallised sodalite. Relatively minor components of hematite, found in all scales samples, and boehmite, found in some scales were distributed homogeneously. It appears that scale formation in single stream heat exchangers occurs via a mixed mechanism: precipitation of aluminosilicate phases, including amorphous components, and also on occasion katoite ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$) and perovskite (CaTiO_3) from the Bayer liquor plus cementation of pre-desilicated bauxite phases, e.g. DSP, hematite and boehmite from the slurry onto heat exchanger steel surfaces.

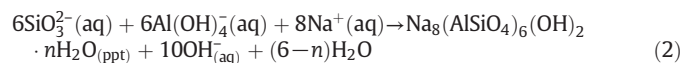
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Aluminium is one of the most widely used non-ferrous metals with 45.9 Mt produced globally in 2012 (Bray, 2012). In order to obtain aluminium, bauxite, the most common aluminium-containing ore, is refined to alumina (Al_2O_3) via the Bayer process, invented by Carl Josef Bayer in 1887 (Bayer, 1888; Hind et al., 1999). Bauxite ores consist of varying combinations of aluminium oxide/hydroxide, silica, iron oxide, titanium dioxide and clay minerals. Alumina is smelted by the Hall–Héroult process to produce aluminium metal (Hall, 1889).

The Bayer process (Fig. 1) is a closely integrated production circuit. Bauxite ore is mixed with post-evaporator spent caustic liquor (≈ 5 M NaOH) and is finely ground. The high solids content bauxite slurry is maintained at 80 to 95 °C for eight or more hours to enable dissolution of the reactive silica components, particularly kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Eq. (1)), and subsequent reprecipitation of sodium aluminosilicate phases (Eq. (2)) (Faneitte et al., 1990; Roach and Cornell, 1985; Roach and White, 1988). This process is termed the pre-desilication stage during which 80–90 % of the reactive silica components are usually transformed into desilication products (DSP). This process is used to

control silica in the Bayer liquor for protection of downstream heat exchangers, pipelines and reactors from scaling.



The slurry is then digested in hot caustic solution under pressure in order to dissolve the aluminium oxide/hydroxide components and convert the remaining reactive silica to DSP (Smith, 2009). The temperature required is relatively low (≈ 150 °C) when gibbsite ($\text{Al}(\text{OH})_3$) is the main component of value or greater (≈ 220 °C) when boehmite ($\gamma\text{-AlO}(\text{OH})$) is present, in commercial quantities (Paspaliaris et al., 1999).

The insoluble materials, including DSP and iron oxides, are filtered out as red mud and the gibbsite is then precipitated from the cooled and seeded supersaturated liquor. The gibbsite is then calcined to form alumina. For double-stream plants the spent liquor is heated to concentrate the soda by evaporation and recycled to the digester. For single stream Bayer plants the slurry resulting from pre-desilication is

* Corresponding author at: Blue Minerals Consultancy, Middleton, SA 5095, Australia.
E-mail address: Andrea.Gerson@bigpond.com (A.R. Gerson).

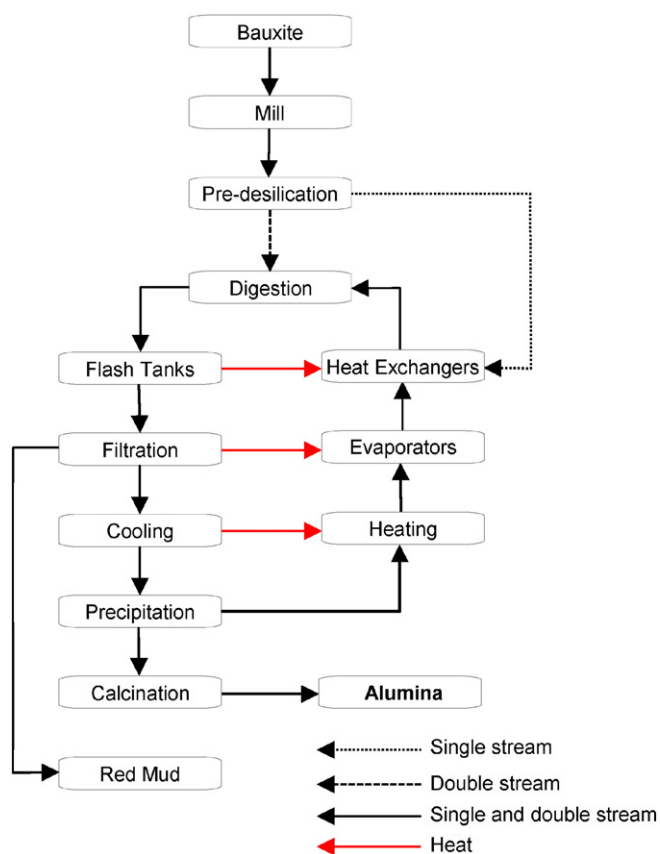


Fig. 1. Schematic of the Bayer process.

mixed with the heated and concentrated spent liquor which is the cycled through the heat exchangers prior to final digestion (Fig. 1).

Although the silica concentration in Bayer liquor is controlled at a relatively low concentration due to the pre-desilication and digestion DSP formation processes, as the silica solubility decreases as a result of the reduced aluminium concentration in the spent liquor (i.e. after gibbsite precipitation) the liquor can become supersaturated (Barnes et al., 1999a; Breuer et al., 1962; Pevzner et al., 1974; Zheng et al., 1998). This then results in scaling within downstream plant, particularly within evaporators and heat exchangers, due to faster kinetics of scaling at increased temperatures. Build-up of scale is a serious issue resulting in impeded slurry flow and reduced heat transfer to the process streams and results in the need for regular maintenance and equipment replacement (Roach and Cornell, 1985).

Since Bayer process conditions and concentrations of liquor impurities derived from different bauxite ores vary within plants over time and also between plants scaling issues and scale compositions can differ significantly. Scale management is therefore one of the highest priority issues for alumina refineries worldwide, as reported by the Alumina Technology Roadmap (Energetics Incorporated, 2001).

Breuer et al. (1962) examined Kaiser double stream scales and found sodalite (of generic formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 1/3(\text{Na}_2, \text{Ca})(\text{Cl}, \text{SO}_4, \text{CO}_3, \text{S}_x, \text{OH}, \text{etc.})$) to be present in a scale sample taken from a plant

evaporator ($>100^\circ\text{C}$) and three scale samples collected from 200°C digestion vessels. The basic-sodalite cubic unit cell parameter was determined to be 8.9 \AA , significantly different to noselite's (sulfate-sodalite) cubic unit cell parameter of 9.1 \AA or the hexagonal unit cell of cancrinite (Breuer et al., 1962). However, intermediate products of "basic noselite-cancrinite" were also identified in the three digester scale samples, indicating part conversion from noselite to cancrinite.

At the relatively low temperature of 120°C boehmite was found to be the predominate component in scale formed in a double stream Bayer plant (Gerson and Zheng, 1997). Three sodium aluminosilicate phases were found to form between 150 and 255°C , sodalite₁ (cubic, $a \approx 8.98 \text{ \AA}$, high CO_3^{2-} concentration), sodalite₂ (cubic, $a \approx 8.89 \text{ \AA}$, low CO_3^{2-} concentration) and cancrinite (hexagonal, $a \approx 12.70 \text{ \AA}$, $c \approx 5.18 \text{ \AA}$) although thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and calcite (CaCO_3) were also observed (Gerson and Zheng, 1997). The scale phases found in a cross section of plant scale formed at 150°C show an increase of sodalite₂ and cancrinite content with increasing in situ age of the scale, revealing that the transformation from sodalite₂ to cancrinite was the rate determining step in sodalite₁ \rightarrow sodalite₂ \rightarrow cancrinite transformation process.

Armstrong and Dann (2000) examined scale samples removed from various locations within a high temperature ($>200^\circ\text{C}$) and a low temperature ($100\text{--}140^\circ\text{C}$) Bayer process plant (it was not stated whether this was single or double-stream) and observed that the scales formed at $\geq 200^\circ\text{C}$ are primarily carbonate cancrinite with typical hexagonal rod morphology with very minor sulfate content. At the low temperature the scales crystallised predominantly as natrodavynite (intergrowths between sodalite and cancrinite) with plate-like morphology. Sodium was found to be the major cation present with minor K and Ca in both high and low temperature scales. Surprisingly, most organics, e.g. the large concentration of oxalate ions present in Bayer liquor, have relatively little effect on the nature of the scales formed and do not appear to promote scale formation (Armstrong and Dann, 2000).

Formation of very hard titanate scale, in addition to sodium aluminosilicate scale, particularly in high temperature heat exchangers and digesters, is an issue encountered when titania is present in the bauxite (Chester et al., 2009; Dudek et al., 2009). For example, the majority of a digester scale, formed at 255°C , was found to be cafetite ($(\text{Na,Ca,Mg})_{2.2}(\text{Fe,Al})_{2.5}(\text{Ti,Si})_{3.1}\text{O}_{12} \cdot 3.7\text{H}_2\text{O}$; unit cell $a = 9.098 \text{ \AA}$, $b = 9.428 \text{ \AA}$ and $c = 5.250 \text{ \AA}$) with a small component of haematite (Gerson and Zheng, 1997). Kshatriya et al. (2006) identified boehmite, gibbsite, goethite, sodalite and hematite in heat exchangers scales ($135\text{--}140^\circ\text{C}$); and cancrinite, sodalite and calcium titanate in a digester scale (240°C). Titanate scales have been reported as a significant issue at the Eti Aluminium Inc. Seydisehir plant (Konya, Turkey) where the bauxite ore contains significant components of boehmite, hematite, anatase and kaolinite (Akpınar et al., 2012). Cancrinite, calcium titanate, calcium magnesium and hematite were identified as major phases in preheater and digester scale with rutile also being identified in the digester scale (Akpınar et al., 2012).

Although scaling is a widespread issue within the Bayer industry little characterisation of real industrial plant scale has been reported for double stream plants (Fortin and Breault, 2003; Gerson and Zheng, 1997) and even less for single stream plants. Suss et al. (2004) identified four temperature zones that give rise to different phases of scaling in tube digesters, i.e. single stream Bayer plants: $<170^\circ\text{C}$ sodium

Table 1
Conditions of industry scale formation.

Scale sample	Refinery (#) – location in refinery	Temperature ($^\circ\text{C}$)	Other notes
A	#1 – inner wall of spent liquor heat exchanger tube	≈ 200	After installation of a new tube and two weeks of operation. Orientation identified.
B	#1 – spent liquor heat exchanger end cap	194	Orientation unknown.
C	#2 – spent liquor heat exchanger tube	180	Orientation unknown
D	#3 – spent liquor heat exchanger tube	88–93	Orientation identified
E	#4 – heat exchanger tube	148	Orientation unknown

Download English Version:

<https://daneshyari.com/en/article/211905>

Download Persian Version:

<https://daneshyari.com/article/211905>

[Daneshyari.com](https://daneshyari.com)