

Scale Formation in Alumina Refineries

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Abstract

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Scales, in general, form due to the transport of the components from the bulk of the liquid phase to the walls of pipes and/or equipment. The liquid phase velocity at the walls, in the boundary layer, is practically zero, allowing the constituents to reach their equilibrium solubility. The species which are most important to scale formation are the intermediate compounds of consecutive reactions. This theoretical scheme describes the formation of desilication product (DSP), titania compounds and boehmite scales in the digester systems, gibbsite scale in clarification and bauxite residue washing, and in the “white side” of alumina refineries. Bauxite and/or bauxite residue particles can be trapped in scale. The study of the elements of scales has proven a useful tool in the understanding of titanium and iron mineral reactions. Chemical and mineralogical analyses of digestion scales from various alumina refineries are presented to support the theoretical considerations.

Keywords: alumina refinery scales; pipe incrustations; DSP, boehmite and gibbsite scale; titanium compounds.

1. Introduction

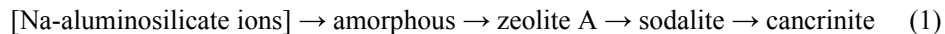
Scale formation, especially in the red side of alumina refineries, is a complex process. Desilication product (DSP) scale has dramatically lower thermal conductivity than steel, consequently its formation greatly hinders heat transfer when bauxite slurry or Test Tank Liquor (TTL) is preheated. Scales reduce the tube diameters and may clog preheater tubes, reducing their hydraulic and thermal performance. Scaling demands that spare equipment must be available. Removal of scales either by chemical and/or mechanical means is troublesome, sometimes incomplete, and incurs extra cost. The difficulties associated with scale are discussed by Fortin and Breault [1].

Roach and Cornell [2,3] point out the importance of liquor supersaturations, not only of alumina but also of silica and calcia at various stages of the process. Scales can be differentiated between the growth and settled scales, although this paper focuses on growth scales.

The equilibrium **alumina solubilities** for gibbsite, boehmite and diasporite have been summarized in a comprehensive diagram by Kotte [4].

Concerning the reactions of **kaolinite and quartz** in Bayer liquor, the classic papers of Adamson et al. [5], Breuer et al. [6], Oku and Yamada [7] should be mentioned. A large number of papers deal with various aspects of the formation and further reactions of **desilication product** (DSP), and there is insufficient space in this paper to present a comprehensive list of relevant publications.

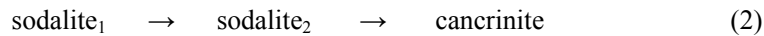
Addai-Mensah et al. [8] summarized the formation mechanism of **sodalite** and **cancrinite**:



Sodalite and cancrinite is usually described with the same stoichiometry [9], $\text{Na}_6[\text{AlSiO}_4]_6\text{NaX}\cdot n\text{H}_2\text{O}$, where X is $\frac{1}{2} \text{CO}_3^{2-}$, $\frac{1}{2} \text{SO}_4^{2-}$, Cl^- , OH^- and NO_3^- . Sodalite has a cubic space group crystal structure, while cancrinite's is hexagonal. The chemically combined water content of DSP described by Whittington is $n = 0-2$ [10].

The formation of an amorphous phase and transformation to zeolite A were shown to occur at temperatures lower than 85°C by Barnes et al. [11,12]. Previously, formation of zeolite A as an intermediate in the course of formation β hydroxi-sodalite at temperatures of $50-90^\circ\text{C}$, and at higher temperatures, conversion of sodalite to cancrinite was revealed by Nemezc et al. [13] in 1968. A thin amorphous layer and zeolite were detected during formation of sodalite and cancrinite at 140°C by Shi et al. [14].

Following the study of liquor preheater and digester scales, the latter at 255°C in Queensland Alumina Limited (QAL), the following mechanism was proposed for the transformation of sodalite to cancrinite by Gerson et al. [9]:



With respect to **iron minerals**, King [15] and later Basu [16] proposed that when goethite transforms to hematite, it is via sodium ferrite, NaFeO_2 .

The reactions of **titania** minerals in caustic solutions were published by Wefers [17], Schultze-Rhnhof and Winkhaus [18,19], Hazainé Borsiczky and Solymár [20], Malts [21], Croker et al. [22] and others.

Lime is widely used in the Bayer process as quicklime (CaO), or in hydrated form ($\text{Ca}(\text{OH})_2$) for various purposes. Karst bauxites contain some calcite and/or dolomite. Therefore, the behaviour of CaO , $\text{Ca}(\text{OH})_2$ and other calcium and magnesium compounds is an important aspect of the Bayer process. P. Smith [23] recently published a comprehensive review of the equations and reaction paths of lime with alumina, silica, titania, iron and other species, with an emphasis on high temperature digestion.

Sajó et al. [24] described and determined the crystallographic features of the principal constituent of scale taken from the piping providing the residence time of the high temperature tube digester in Hungary. The approximate formula was $(\text{Ca},\text{Mg})(\text{Ti},\text{Fe},\text{Al})_2\text{O}_4(\text{OH})_2$. The tentative composition of the calcium-magnesium-alumino-titanate in preheater scales from the Hungarian tube digester was claimed by Ferenczi and Kálmán [25] to be $\text{CaO}\cdot 0.4\text{MgO}\cdot 0.3\text{Al}_2\text{O}_3\cdot \text{Ti}_2\text{O}_4$.

Digester scale formed at 255°C in QAL was identified [26] mainly as cafetite, and its stoichiometry $(\text{Na},\text{Ca},\text{Mg})_{2.2}(\text{FeAl})_{2.5}(\text{Ti},\text{Si})_{3.1}\text{O}_{12}\cdot 3.7\text{H}_2\text{O}$. Cafetite stoichiometry was reported by Evans et al. [27] as $(\text{Ca},\text{Mg})(\text{Fe},\text{Al})_2\text{Ti}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$. Suss et al. claim [28] that where lime and other additives are added to the bauxite, the scales of preheated autoclaves comprise hydrocassite $(\text{Ca},\text{Mg},\text{Mn})(\text{Ti},\text{Al},\text{Mg},\text{Fe})_2\text{O}_3(\text{OH})_3$, perovskite CaTiO_3 , alumino-calcium titanium hydrogarnets $\text{Ca}_3(\text{Al},\text{Fe})_2[(\text{Si},\text{Ti})\text{O}_4]_n(\text{H}_2\text{O})_{(6-2n)}$, hydroxyapatite and apatite, $\text{Ca}_5[\text{PO}_4]_3(\text{OH},\text{Cl},\text{F})$. The rationale for lime addition to digestion was probably to facilitate the goethite-hematite conversion of gibbsitic bauxites which have high goethite content (such as some from Guinea or Jamaica). Scale compounds/minerals, especially in high temperature digestion in the presence of lime, can be extremely complex.

For predicting the decay of heat transfer coefficients due to scale formation by mathematical modeling, the papers of O'Neill [29] [27], Müller-Steinhagen et al. [30] and Duncan et al. [31] should be mentioned. Several attempts on the kinetics of desilication in the digestion liquor

Equilibrium solubilities can be described just at the walls of the tubes/equipment, provided that they have been measured appropriately. The bulk concentrations are subject to the kinetics of the consecutive reactions of each species.

The driving force for the mass transfer that results in scale is the difference between the bulk and equilibrium concentrations of the relevant species.

The study of scales can be a useful tool in understanding the mechanism of various reactions. The large hematite content in scale (in cases extremely high hematite/goethite ratios compared with that of bauxite and bauxite residue) supports the hypothesis that conversion of goethite to hematite takes place via ferrite anion. Similar patterns apply to the formation of various titania containing scale formed from anatase and rutile.

Having formed the scale, which may remain in-situ for a long period, the long retention time (and possibly increasing wall temperature) are favourable for the transformation of one mineral to another one, e.g. sodalite to cancrinite.

Solid particles (in this case bauxite and/or bauxite residue) can be entrapped in the scale and their mineral constituents may react afterwards.

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