Scale Formation in Alumina Refineries

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Abstract

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 diaspore 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**:

$$\text{[Na-aluminosilicate ions]} \rightarrow \text{amorphous} \rightarrow \text{zeolite A} \rightarrow \text{sodalite} \rightarrow \text{cancrinite} \quad (1)$$

Sodalite and cancrinite is usually described with the same stoichiometry [9], $Na_6[AlSiO_4]_6 2NaX.nH_2O$, where X is ½ CO_3^{2-}, ½ 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 ß hydroxi-sodalite at temperatures of 50-90°C, and at higher temperatures, conversion of sodalite to cancrinite was revealed by Nemecz 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]:

$$\text{sodalite}_1 \quad \rightarrow \quad \text{sodalite}_2 \quad \rightarrow \quad \text{cancrinite} \qquad (2)$$

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-Rhonhof 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 ($Ca(OH)_2$) for various purposes. Karst bauxites contain some calcite and/or dolomite. Therefore, the behaviour of CaO, $Ca(OH)_2$ 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 $(Ca,Mg)(Ti,Fe,Al)_2O_4(OH)_2$. 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 $CaO.0.4MgO.0.3Al_2O_3.Ti_2O_4$.

Digester scale formed at 255°C in QAL was identified [26] mainly as cafetite, and its stoichiometry $(Na,Ca,Mg)_{2.2}(FeAl)_{2.5}(Ti,Si)_{3.1}O_{12.}3.7H_2O$. Cafetite stoichiometry was reported by Evans et al. [27] as $(Ca,Mg)(Fe,Al)_2Ti_4O_{12}.4H_2O$. Suss et al. claim [28] that where lime and other additives are added to the bauxite, the scales of preheated autoclaves comprise hydrocassite $(Ca,Mg,Mn)(Ti,Al,Mg,Fe)_2O_3(OH)_3$, perovskite $CaTiO_3$, alumino-calcium titanium hydrogarnets $Ca_3(Al,Fe)_2[(Si,Ti)O_4]_n(H_2O)_{(6-2n)}$, hydroxyapatite and apatite, $Ca_5[PO_4]_3(OH,Cl,F)$. 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 phase are summarized by Duncan et al. [32] and test results exhibited. A paper by the author [33] on the mechanism of the dissolution of gibbsite and the transformation of kaolinite to sodalite DSP could be also referenced. The parallel reactions of the dissolution of gibbsite and of kaolinite were described as a competition for the available reactive OH^- ions, which comprise the common driving force. The reactive OH^- concentration is defined by the following equation:

$$\text{Reactive } OH^- \text{ (g/l)} = 2 * 17\ ((c^{eq}_{Al2O3} - c_{Al2O3})/102 - c_{SiO2}/60) \qquad (3)$$

Where: c^{eq}_{Al2O3} equilibrium alumina concentration for gibbsite, g/L
c_{Al2O3} alumina concentration, g/L
c_{SiO2} silica concentration, g/L.

2. Mechanism of Scale Formation

The most important aspects of the formation of scales are shown schematically on Figure 1 taken from a previous study of the author [34].

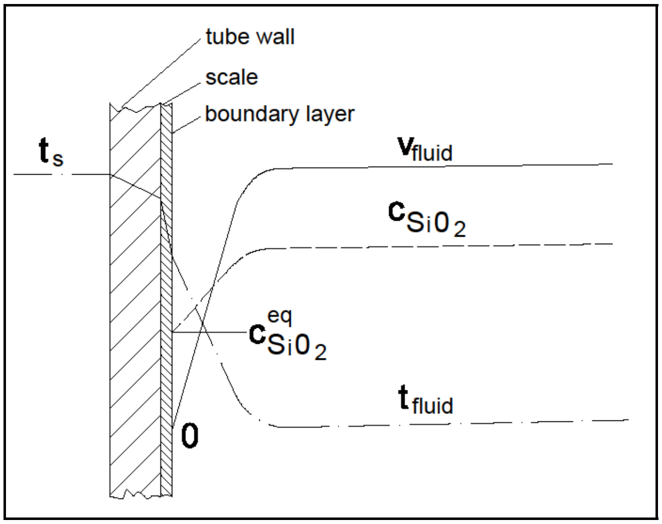

Figure 1. Fluid velocity, temperature profile and dissolved component concentration profile along a heated tube wall.

To understand the mechanism, the formation of DSP scale on a tube wall being heated with live steam or flash vapour is described. The schematics in Figure 1 shows the profile of the fluid velocity and the silica concentration at the wall. The fluid flowing inside the heated tube can be a slurry or a liquid. At a certain distance from the wall, the fluid has its bulk velocity, $\mathbf{v_{fluid}}$. Just at the wall, a so-called boundary layer exists. The velocity of the fluid within the boundary layer by definition is zero. Here there is theoretically infinite time, so the silica concentration reaches its equilibrium solubility, $\mathbf{c^{eq}_{SiO2}}$. In the bulk fluid the dissolved silica concentration, $\mathbf{c_{SiO2}}$ is higher. The difference between the two concentrations ($\mathbf{c_{SiO2}-c^{eq}_{SiO2}}$) constitutes the driving force for the formation of DSP scale. The temperature profile when the fluid is heated by steam/vapour through the outer wall is also shown. The saturation temperature of the steam/vapour is $\mathbf{t_s}$, the bulk temperature of the fluid is $\mathbf{t_{fluid}}$.

In an alumina refinery other scale compounds form, such as gibbsite, boehmite, hematite, various (CaMg)AlFeSi-titanates, etc. The scale formation, in general, is deemed to be driven by the supersaturation of the relevant component. The compounds which are prone to form scale are believed to be the intermediates of consecutive reactions. Some examples are shown here; the intermediate anions are in bold:

gibbsite, boehmite, diaspore → **aluminate anion** → gibbsite, boehmite (4)

kaolinite, quartz → **silicate anion** → DSP (sodalite, canrinite) (5)

goethite → **ferrite anion** → hematite (6)

anatase, rutile → **titanate anion** → perovskite, cafetite, kassite(?), hydrogarnet, apatite, etc. (7)

The Bayer process cycle for a typical low temperature digestion of gibbsitic bauxites is shown in Figure 2. Digestion is carried out at about 143°C with TTL of 250 g/L C (caustic expressed as Na_2CO_3) at an A/C ratio of 0.7. At this point the liquid phase is below the equilibrium solubility of gibbsite, though supersaturated for boehmite. Consequently, boehmite scale is expected in the digester autoclaves.

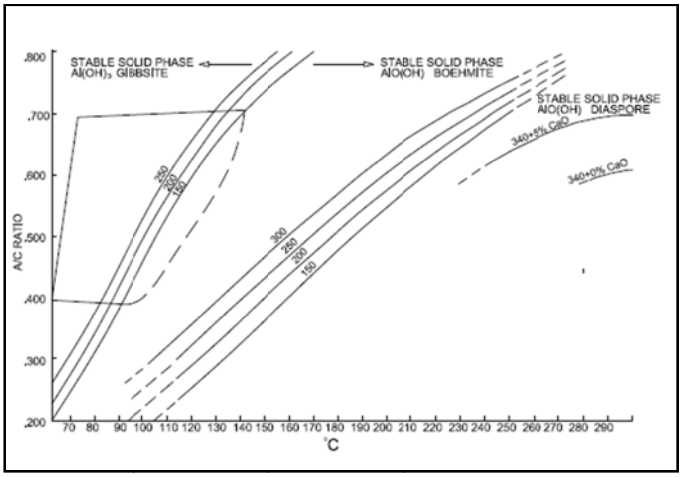

Figure 2. Typical low temperature Bayer cycle and equilibrium solubilites of dissolved alumina for gibbsite, boehmite and diaspore, from Kotte [4]

The formation of DSP scales have been studied by a number of researchers. There is a general consensus in the literature that DSP is formed following the dissolution of kaolinite (and of quartz at higher temperatures) after silicate anions have first formed.

When a pipe or some equipment is not heated, but cooled by the ambient temperature, the bulk temperature of the fluid is higher than the ambient temperature and the direction of the heat transfer is through the wall away from the bulk fluid.

In general, in tubular, or shell and tube type preheaters, the flow is usually turbulent. In the tanks/autoclaves, unless vigorously agitated, the flow is mainly laminar. It should be checked on a case by case basis whether the flow is laminar or turbulent since different equations may apply to describe the boundary layers. (The width of the boundary layer is not indicated in Figure 1.)

3. Experimental Results

3.1. High temperature (HT) digestion of boehmitic bauxites, single stream flowsheet

In the Hungarian aluminium industry the chemical and mineralogical analyses of scale samples started in the early 1970’s.

The typical composition of bauxite processed in the Almásfüzitő Alumina Plant in 1971 is listed in Table 1. Almost 50% of the available alumina was gibbsitic, the rest boehmitic, along with some goethite. About 40 % of the iron oxide was goethite, the rest hematite. The Test Tank Liquor (TTL) contained 194 g/L $Na_2O_{caustic}$ (332 g/L C), its caustic molar ratio was 3.79 (A/C ratio 0.254). Pre-desilication operated at about 90°C with 6 hours retention time. The pre-desilication efficiency (conversion of kaolinite to DSP) was 44%. The digestion trains consisted of 5 stages of vertical shell and tube heaters, all heated with flash vapour. The slurry was then preheated in 7 autoclaves to 225°C. The first and second autoclaves were heated with flash vapour, the rest with live steam. Only indirect heating was used. The chemical and mineralogical analyses of the scale from each preheater and autoclave are shown in Table 1 and 2 [35].

The tube digester in the MOTIM Alumina Plant, Mosonmagyaróvár, consisted of 19 preheater units. A more detailed description of the tube digester of MOTIM can be found in the literature [36]. The first 15 units were heated with flash vapour and with condensate from the live steam heaters. Preheater units No. 16-19 used live steam. Between the preheater units No. 6 and 7 two vertical vessels without agitators were installed providing 12-13 minutes' retention time at 145-150°C to facilitate DSP formation. Between the preheaters No. 9 and 10, one more vertical retention vessel was installed to provide 6 minutes' additional retention time at about 180°C, to complete DSP formation before the further tubular preheaters. The use of intermediate retention time was patented by Suri et al. [37], and implemented in 1993. The objective of the scale study was to examine how successfully retention vessels minimized DSP scale [38]. The chemical and mineralogical analyses of the bauxite, the most important preheater unit scales, and the bauxite residue are shown in Tables 3 and 4.

3.2. Low temperature (LT) digestion of gibbsitic bauxites, double stream flowsheet

The "double stream" flowsheet is widely used for low temperature digestion of gibbsitic bauxites. Bauxite is slurried, and in most cases, ground in 10-15 % of the TTL. The thick slurry is then usually submitted to a pre-desilication stage. The rest of the TTL is preheated as a separate stream with flash and live steam, mostly in a series of large horizontal shell and tube preheaters to 160-170°C. The preheated TTL meets the thick bauxite slurry at the first digester autoclave. Some live steam is sometimes applied to attain the digestion temperature of about 143-145°C. The digesters' retention time is 30-60 minutes, depending on the reactive silica of the bauxite and whether pre-desilication is applied or not.

Scale from a live steam preheater, from a digester autoclave, and from other points in the Bauxilum alumina refinery, Venezuela were studied [39]. The bauxite processed in the refinery originated from the Los Pijiguaos mine and contained some 49 % Al_2O_3 (46 % Al_2O_3 as gibbsite). The total SiO_2 varied between 6 % and 10 %, out of which, only 1.2 % to 1.8 % SiO_2 was kaolinite. The caustic concentration of the TTL was 165 g/L Na_2O_{caust} (282 g/L C), the caustic molar ratio was 2.5 (A/C ratio 0.385). The dissolved silica concentration in the TTL was 0.84-0.9 g/L SiO_2. The pre-desilication temperature was about 98°C, the retention time 10-11 hours. The pre-desilication efficiency was 90 %. The digestion temperature was about 145°C, and retention time some 45 min. The caustic molar ratio in the digestion effluent was 1.29, (A/C ratio 0.75). The unreacted silica from pre-desilication dissolved and possibly 30 % of DSP that had formed during pre-desilication re-dissolved during digestion.

Table 1. Chemical composition of scale from a digester train of the Almásfüzitő Alumina Plant (1971)

Samples	Bauxite characteristic	Shell and tube type heat exchangers, No.					Autoclaves, No.						
		1	2	2	4	5	1	2	3	4	5	6	7
Chemical	Fejér county	Operating temperatures, °C, typical					Operating temperatures, °C, typical						
compositions	Hungary	88-98	98-108	108-118	118-128	128-138	145-155	155-166	170-186	185-198	200-214	210-225	224-226
Al_2O_3, %	51	31.2	30.7	29.1	29.3	26.5	32.4	31.6	15.9	17.4	15.1	14.9	16.1
SiO_2, %	6.6	22.3	21.3	26.1	27.4	24.2	5.1	3.8	3.9	3.9	3.8	4.6	4
Fe_2O_3, %	20.7	12.3	15.2	9.6	9	13	32.4	31.7	46.5	41.9	48.5	48.2	44.6
TiO_2, %	2.5	1.4	1.4	1.4	1.4	1.4	2.7	3.2	8.4	5.6	5.1	5.3	4.4
CaO, %	0.6	0.6	0.6	0.6	0.6	2.4	2.7	2.4	3.4	3.4	3.4	3.1	1.9
MgO, %	0.3	0.4	0.5	0.4	0.4	1.1	0.7	0.7	1.8	1.5	2	2	1.4
Na_2O, %	-	19.5	19.2	22.8	22.8	21.5	10	12.1	3	12.4	10.8	10.9	13.5
L.O.I., %	n.d.	12.3	11.4	10.1	9.4	9.8	13.7	14.5	12.1	12.1	10	10.2	12.8

Table 2. Mineralogical composition of scale from a digester train of the Almásfüzitő Alumina Plant (1971)

Samples	Shell and tube type heat exchangers, No.					Autoclaves, No.						
	1	2	2	4	5	1	2	3	4	5	6	7
Mineralogical compositions,	Operating temperatures, °C, typical					Operating temperatures, °C, typical						
%	88-98	98-108	108-118	118-128	128-138	145-155	155-166	170-186	185-198	200-214	210-225	224-226
Al_2O_3, in sodalite	15.9	14.8	18.1	17.5	14.3	1.8	1	0.9	0.9	0.9	0.8	1.3
cancrinite	2.1	2.1	2.9	4.5	5.2	1.7	1.1	1.8	1.8	1.7	1.9	1.2
$NaAlO_2$	0.2	2	1	2	0.9	1	1.3	tr.	5	4	5.1	5
Ca(Mg,Al)-titanate	-	-	-	-	-	tr.	tr.	1.2	0.7	0.6	0.7	0.7
boehmite	10	9.1	3.5	3.2	2.7	22	23	7.7	5	2.5	3	3.5
hematite	0.2	0.2	0.2	0.2	0.3	0.8	1	2	2	2.4	2.4	1
goethite	0.8	1	0.7	0.6	0.9	2	1.5	0.9	0.5	tr.	0.5	tr.
diaspore	2	1.5	2.3	2	2	2	tr.	1	1	0.5	tr.	2
illite	tr.	1	0.5	0.7	0.5	0.3	0.5	0.4	0.5	0.3	0.5	0.4
SiO_2, in quartz	2.3	1.5	2.3	2.3	2	0.5	0.5	tr.	tr.	tr.	-	-
sodalite	17.5	16.3	20	19.2	15.7	2	1.1	1	1	1	0.9	1.4
cancrinite	2.5	2.5	3.4	5.3	6.1	2	1.3	2.1	2.1	2	2.2	1.4
illite	tr.	0.8	0.4	0.6	0.4	0.2	0.4	0.3	0.4	0.2	0.4	0.3
Fe_2O_3, in hematite	6.2	7.7	5.6	5.5	7.9	17.5	21.1	39.1	39.6	47	45.6	43.3
goethite	4.6	5.5	4	3.5	5.1	10.9	7.6	5.4	2.3	1.5	2.7	1.4
maghemite	1.5	2	-	-	-	4	3	2	-	-	-	-
TiO_2, in anatase	1	1	0.8	1	0.8	-	-	-	-	-	-	-
rutile	0.4	0.4	0.4	0.4	0.2	-	-	-	-	-	-	-
Ca(Mg,Al)-titanate						1.3	0.6	6.4	4.0	3.5	3.7	3.7
perovskite						1.4	2.6	2.0	1.6	1.6	1.6	0.7
CaO, in Ca(Mg,Al)-titanate	-	-	-	-	-	1.7	1.4	7	4.5	4	4	3.9
perovskite	-	-	-	-	-	1	1.8	1.4	1.1	1.1	1.1	0.5
dolomite	0.4	0.3	0.4	0.4	1.3	-	-	-	-	-	-	-
calcite	tr.	tr.	tr.	tr.	1	-	-	-	-	-	-	-
Na_2O, in $Na_2CO_3.1\text{-}1/2H_2O$	7.4	8	5	4.6	5.5	6	8	1.5	7.5	6.5	6.5	9
sodalite/cancrinite	12.1	11.2	13.8	13.2	10.8	1.4	0.8	0.7	0.7	0.7	0.6	1.0
Hematite/goethite ratio	1.3	1.4	1.4	1.6	1.5	1.6	2.8	7.2	17.2	31.3	16.9	30.9

Table 3. Chemical composition of tube digester scale from MOTIM Alumina Plant (1993)

Samples	Bauxite, characteristic	Scales of the Tube digester, preheater, No of unit								Bauxite
		7	8	10	16	17	18	19	at CaO dosage	residue
	Fenyőfő	**Operating temperatures, °C, typical**								
Chemical compositions		**140-150**	**164**	**182**	**202**	**210**	**220**	**240**	**240**	**240**
Al_2O_3, %	**51**	31.1	9.2	10.3	8.9	8.2	7.7	6.4	6.8	15.5
SiO_2, %	**7.2**	1.6	1.5	3	0.3	0.8	0.5	1.7	2.8	13.5
Fe_2O_3, %	**17.2**	21	17	15.2	19.8	22.5	24.3	24.3	22.5	39.4
TiO_2, %	**2.6**	15.8	33.5	32.9	34.5	33.8	33.8	33.2	10.8	5.1
CaO, %	**0.8**	9.2	16	16.3	14.5	14.2	14.4	13.1	30	5
MgO, %	**0.4**	2.9	3.9	5	4.9	4	3.9	3.7	0.7	n.d.
Na_2O, %	**-**	1.1	0.7	1	0.2	0.6	0.5	1	3	8.8
P_2O_5, %	**n.d.**	0.72	0.5	1	0.19	0.17	0.34	0.39	10.3	n.d.
L.O.I., %	**n.d.**	12.1	10.2	12.5	11.6	10.7	10.4	9	8.2	8.3

Table 4. Mineralogical composition of tube digester scale from MOTIM Alumina Plant (1993)

Samples	Bauxite,	Scales of the tube digester preheaters, No. of unit								Bauxite
	characteristic	7	8	10	16	17	18	19	at CaO dosage	residue
	Fenyőfő	**Operating temperatures, °C, typical**								
Mineralogical compositions, %		**140-150**	**164**	**182**	**202**	**210**	**220**	**240**	**240**	**240**
Al_2O_3, in gibbsite	**20.9**	-	-	-	-	-	-	-	-	-
boehmite	**22.8**	27.7	-	-	-	-	-	-	-	0.5
diaspor	**0.4**	-	-	-	-	-	-	-	-	0.5
kaolinite	**5.8**	-	-	-	-	-	-	-	-	-
goethite	**0.9**	-	-	-	-	-	-	-	-	1.5
crandallite	**0.4**	-	-	-	-	-	-	-	-	-
sodalite/cancrinite	-	1.4	0.8	2.3	0.2	1.5	0.8	1.2	0.7	10.8
Ca-aluminosilicate	-	-	2.4	1.6	3	1	1.3	0.7	5.6	2.2
(CaMg)Al-titanate	-	2	6	5.1	5.7	5.7	5.6	5.7	0.5	-
SiO_2, in kaolinite	**6.7**	-	-	-	-	-	-	-	-	-
quartz	**0.5**	-	-	-	-	-	-	-	-	-
sodalite/cancrinite	-	1.6	1	2.4	0.2	0.8	0.5	1.4	0.8	12.8
Ca-aluminosilicate	-	-	0.5	0.6	0.1	-	-	0.3	2	0.7
Fe_2O_3, in hematite	**9.5**	19.5	15.5	14	19.8	21	23.3	23.5	20.3	26.9
goethite	**7.7**	1.5	1.5	1.2	-	1.5	1	0.8	2.2	12.5
TiO_2, in anatase	**1.8**	-	-	-	-	-	-	-	-	-
rutile	**0.8**	-	-	-	-	-	-	-	-	3.1
(CaMg)Al-titanate	-	12.3	33.5	32.8	34.5	33.8	33.8	33.2	4.4	-
perovskite	-	3.5	-	-	-	-	-	-	6.4	2
CaO, in dolomite	**0.6**	2.3	-	2	-	0.3	0.3	-	-	-
crandallite	**0.2**	-	-	-	-	-	-	-	-	-
Ca-aluminosilicate	-	-	4	2.6	4.9	1.6	2.1	1.2	9.2	3.6
(CaMg)Al-titanate	-	4.4	12	11.7	9.6	12.3	12	11.9	4.2	-
perovskite	-	2.5	-	-	-	-	-	-	3.1	1.4
apatite	-	-	-	-	-	-	-	-	13.5	-
MgO, in dolomite	**0.4**	1.6	-	1.4	-	0.2	0.2	-	-	-
(CaMg)Al-titanate	-	1.3	3.9	3.5	4.9	3.8	3.7	3.7	0.7	-
Na_2O, in sodalite/cancrinite	-	1.1	0.7	1.6	0.2	0.6	0.4	1	0.6	8.8
P_2O_5, in crandallite	**0.3**	-	-	-	-	-	-	-	-	-
OH-apatite	-	-	-	-	-	-	-	-	10.3	-
Hematite/goethite ratio	1.2	13.0	10.3	11.7	n.a.	14.0	23.3	29.4	9.2	2.2

The front and rear view of the same scale sample taken from a live steam preheater after 3 days of operation are shown in Figure 3 and 4. The mineralogical compositions of the newly formed bright surface, i.e. the liquor side of the scale, the middle part and also the dark surface (the rear of the scale) were investigated. The latter was the "oldest" and had been closely attached to the inner wall of the heated tube.

The chemical and mineralogical compositions of the bauxite and the bauxite residue, scale from the live steam preheater, digester autoclave, 1st and last flash vessel and the overflow pipe of the Washer No 1 are also shown in Table 5 and 6. The typical operating temperatures of the fluids are also indicated.

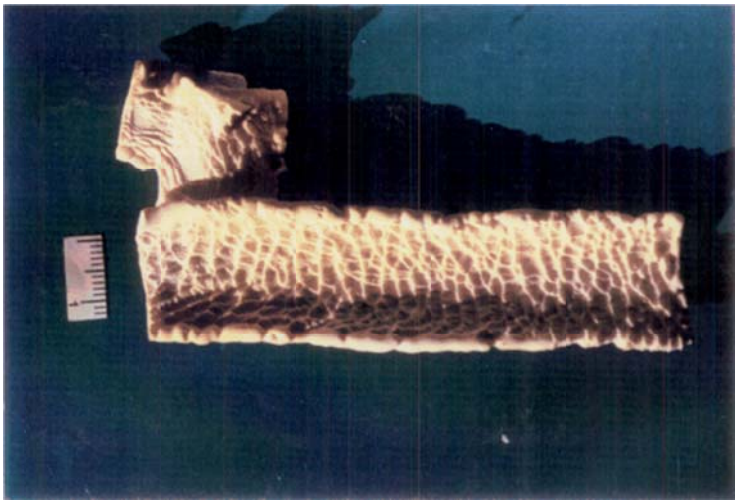

Figure 3. Front view of the scale taken from live steam heater tube band wall

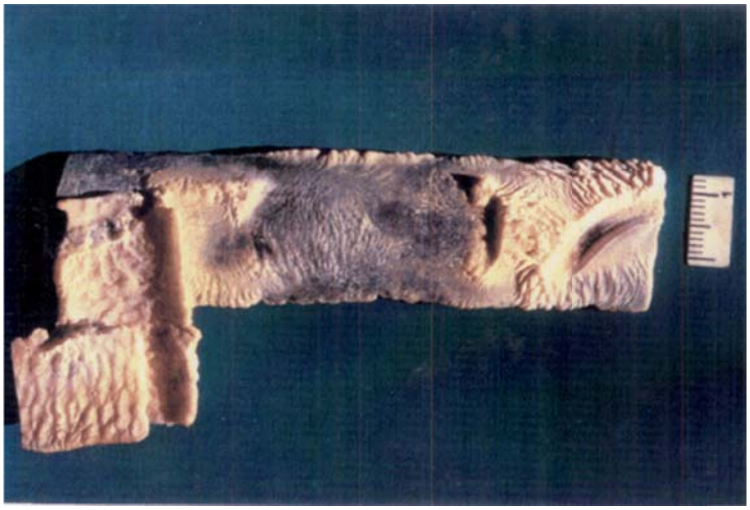

Figure 4. Rear view of the scale taken from live steam heater tube band wall

Table 5 Chemical composition of bauxite, scale and bauxite residue, Bauxilum (1997)

Samples	Bauxite, characteristic	Scale of the live steam heater			Digester scale	1st flash tank	Last flash tank	Washer No 1, O/F pipe	Bauxite residue
		Liquor side	Middle part	Tube side					
	Los Pijiguaos	Operating temperatures, fluids, ^{o}C							
Chemical compositions	08/97	170			145	~125	115	88	145
Al_2O_3, %	**52.1**	30.5			39.4	41.1	50.6	61.2	12.4
SiO_2, %	**5.9**	31.8			16.8	14.7	9.9	0.3	24.4
Fe_2O_3, %	**12.7**	-			20.8	14.9	14.9	2.2	48
TiO_2, %	**1.2**	-			n.d.	2.4	2	0.3	1.6
CaO, %	**n.d.**	0.35			n.d.	0.4	0.6	0.7	n.d.
Na_2O, %	-	23.5			11.6	12	4.4	1.8	3
L.O.I., %	**28.4**	7.5			9.5	12	15.8	33.4	6.8

Table 6. Mineralogical composition of bauxite, scale and bauxite residue, Bauxilum (1997)

Samples	Bauxite, characteristic	Scale of the live steam heater			Digester scale	1st flash tank	Last flash tank	Washer No 1, O/F pipe	Bauxite residue
		Liquor side	Middle part	Tube side					
	Los Pijiguaos	Operating temperatures, fluids, ^{o}C							
Mineralogical compositions, %	08/97	170			145	~125	115	88	145
Al_2O_3, in gibbsite	**51**	1.3	-	-	1.3	1	2	60.9	3.9
boehmite	**0.4**	-	-	-	21.3	26.5	43.9	-	-
kaolinite	**0.6**	-	-	-	-	-	-	-	-
goethite	**1.2**	-	-	-	2.6	0.5	0.5	-	4.7
sodalite	-	20.2	22.6	15.5	-	13.1	4.3	0.3	3.7
cancrinite	-	3.1	3.7	10.9	14.3				-
OH-grossular	-	2.5	2.5	2.5	-	-	-	-	-
sodium aluminate hydr.		3.7	-	-	-	-	-	-	-
SiO_2, in kaolinite	**0.7**	-	-	-	-	-	-	-	-
quartz	**3**	-	-	-	-	-	5.2	-	20
sodalite	-	23.8	26.7	18.3	-	14.7	4.7	0.3	4.4
cancrinite	-	3.7	4.4	12.8	16.8				-
OH-grossular	-	2.2	2.2	2.2	-	-	-	-	-
Fe_2O_3, in hematite	**4**	-	-	-	10	7.9	8.4	-	20
goethite	**7.7**	-	-	-	10.8	7	6.5	-	26.5
ilmenite		-	-	-	-	-	-	-	1.6
TiO_2, in anatase	**0.7**	-	-	-	-	2.4	2	-	-
rutile	**0.1**	-	-	-	-	-	-	-	-
ilmenite	-	-	-	-	-	-	-	-	1.6
CaO, in OH-grossular	-	4.1	4.1	4.1	-	-	-	-	-
Na_2O, in sodalite	-	16.3	18.4	12.6	-	10.6	3.4	0.5	3
cancrinite	-	2.5	3	8.8	11.6				-
sodium aluminate hydr.		2.3	-	-	-	-	-	-	-
H_2O, in gibbsite	**27**	0.7	-	-	0.7	0.5	1.1	32.3	2.1
boehmite	**0.1**	-	-	-	3.8	4.7	7.7	-	-
kaolinite	**0.2**	-	-	-	-	-	-	-	-
goethite	**1.1**	-	-	-	1.7	0.8	0.7	-	3.0
sodalite	-	4.8	5.3	3.7	-	3	0.9	0.1	0.9
cancrinite	-	0.7	0.9	2.6	3.4				-
OH-grossular	-	1.3	1.3	1.3	-	-	-	-	-
sodium aluminate hydr.	-	2	-	-	-	-	-	-	-
Hematite/goethite ratio	**0.5**	-	-	-	**0.9**	1.1	1.3	-	0.8

4. Discussion

4.1. Scale from HT temperature digestion of boehmitic bauxites, single stream flowsheet

4.1.1. Scale from the Almásfüzitő Alumina Plant as of 1971 (Tables 1 and 2)

- Sodalite and to a lesser extent, cancrinite comprise the main constituents in the shell and tube slurry preheaters at temperatures up to 140°C. At temperatures higher than about 160°C, canrinite becomes dominant over sodalite. The sum of sodalite and cancrinite significantly decreases in the autoclaves operating at 150°C and higher.
- In the first autoclaves at temperatures of 145-166°C, boehmite deposits due to the local supersaturation of aluminate for boehmite. At higher temperatures the liquor becomes unsaturated and is able to dissolve boehmite.
- The goethite to hematite transformation starts at about 160°C; hematite starts to be the principal iron constituent of the scale, goethite content gradually diminishes. The hematite/goethite ratios in Table 2 dramatically increase at temperatures higher than about 180-190°C. The significant and growing amount of hematite over goethite supports the mechanism that the conversion of goethite to hematite takes place via liquid phase, as proposed by King and Basu [15,16]; the hematite deposits from the liquid phase.
- Calcite, and possibly dolomite and anatase, react in the shell and tube heat exchangers at temperatures below 140°C, perovskite and (Ca,Mg)Al-titanate compounds appear in the scales formed at higher temperatures.
- Some bauxite particles were entrapped in the scale, especially in the range of 90-140°C.

4.1.2. Scale from the tube digester of MOTIM Alumina Plant as of 1993 (Tables 3 and 4)

- Sodalite, and to a lesser extent cancrinite comprise the main constituents in the tubular slurry heat exchangers at operating temperatures up to 140-150°C. This is from previous experience with tube digester, also supported by Table 1 and 2.

  The vessels which provided retention time of 12-13 minutes at about 145°C reduced the sodalite/cancrinite scale in the tubular preheaters operating at higher temperatures to a fraction. The second retention vessel at a temperature of 180°C was not of much use;
- A temporary boehmite supersaturation caused boehmite deposition in the range of 140-150°C;
- The (Ca,Mg)Al-titanate compound has been found in the largest amounts in scale formed at temperatures higher than 164°C;
- The amount of hematite is significant at 140-150°C and higher, and the goethite content in scale is negligible. This finding supports the argument that the goethite-hematite conversion takes place via liquid phase, this is why hematite deposits. Hematite/goethite ratios are shown in the Table 4. The goethite-hematite conversion starts at about 140-150°C.
- Anatase and rutile cannot be found in scales, (Ca,Mg)Al-titanate, sometimes perovskite ($CaTiO_3$) appear instead. Rutile can "survive" the digestion process, as it is found in the bauxite residue.
- A minor amount of calcium-alumino-silicate has been found at 164°C and higher. The calcium-alumino-silicate is referred to as Bayer-hydrogarnet by Smith [23].
- A significant amount of OH-apatite and hematite have been found in scale where the $Ca(OH)_2$ was added at the digestion temperature of 240°C.

4.2. Scale from a typical LT temperature digestion, double stream flowsheet

Scale from the Bauxilum alumina refinery as of 1997 (Tables 5 and 6)

- The surface of the scale which was contacted with the TTL consisted of primarily sodalite, though cancrinite and other minor compounds were also found. The composition of the middle part of the scale was very similar to the surface, the sodium aluminate hydrate was missing. The rear side of the scale (dark surface) was attached to the inner wall of the heated tube, and consequently the "oldest", showed a different composition. The quantity of sodalite and cancrinite combined was exactly the same as that in the middle part, however, cancrinite significantly increased at the expense of sodalite. The thermal conductivity of the carbon steel is around 43 W/Mk [40], while that for the DSP scale is only 0.52 W/mK [29]. Due to this much smaller thermal conductivity of DSP scale compared to carbon steel, it can be reasonably concluded that the temperature at the rear side of the scale was higher than that of the liquor i.e. 170^{o}C. This confirms the transformation of sodalite to canrinite over time and at higher temperatures as experienced by Gerson and Zheng [26] and others.
- The appearance of the scale surface which was in contact with the TTL is interesting. The highly uneven surface, like ocean waves, suggests turbulent flow.
- No cancrinite has been found in the bauxite residue, only sodalite. This observation confirms that sodalite forms first, at least at the conditions of low temperature digestion. More detailed analysis of the XRD could reveal whether the bauxite residue gibbsite content is due to incomplete digestion or precipitation during sampling or sample treatment, or both.
- The scale from the digester autoclave consists of cancrinite and boehmite. The fact that sodalite is missing confirms the theory of the transformation of sodalite to cancrinite over time, even at relatively low temperature, i.e. 145^{o}C. Boehmite is formed due to the supersaturation of the dissolved alumina for boehmite. It is hypothetised that while sodalite and boehmite were deposited, the scale trapped fine bauxite residue particles. The goethite of the fine residue particles only partly transformed to hematite due to the limiting reactive OH^- ion concentration. The fine bauxite residue particles either did not contain a noticeable amount of quartz, or the quartz gradually transformed to sodalite and then to cancrinite.
- The most characteristic constituent of the flash vessel scale is boehmite. The aluminate in the liquid phase is supersaturated for gibbsite and boehmite. It is not clear whether boehmite is precipitated directly from the liquid, or transformed from precipitated gibbsite. Another constituent is sodium alumino hydrosilicate (sodalite and/or cancrinite). The cooler the flash vessel, the more boehmite and the less sodium aluminium hydrosilicate are found. A few percent of bauxite residue may have been entrapped in this scale. The hematite to goethite ratio is somewhat higher than those in the bauxite and bauxite residue. This shows that minimal transformation of goethite to hematite takes place within the scale over time at the prevailing process conditions.
- Scale taken from the overflow pipe of the Washer No. 1 is gibbsite. The supersaturation for gibbsite is evident, and at this temperature formation of gibbsite seems to be favoured.

5. Conclusions

Many factors are important in influencing scale formation during various stages of the Bayer process including; the fluid velocity adjacent to the boundary layer of the wall; the direction and the intensity of heat transfer and the equilibrium and the bulk concentrations of solutes; these factors should be considered in a holistic way.

The species which play important roles in scale formation are deemed to be the intermediate compounds of various consecutive reactions, such as aluminate, silicate, ferrite and titanate anions.

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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