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TECHNICAL LECTURE SERIES, LECTURE 2

ALUMINA PLANT SCALING - TYPES, REACTION MECHANISM AND COMPOSITION

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 - MSc. in Chemical Engineering, Veszprém University of Chemical Engineering, Veszprém, Hungary, 1972
 - Patent Attorney, Postgraduate Institute of Budapest University of Economics, 1992
- **Present position: Senior Process Consultant, Alumina**
- **Work experience:.** Processing of bauxites of different types and grades. Techno-economic evaluations leading to Process Concept and Feasibility Studies. Co-ordination of research and development projects. Environmental aspects, utilisation of bauxite residue, prevention and removal of scale. Published about 50 papers. He is the principal inventor and driver of the ILTD (Improved Low Temperature Digestion) Process.

- **Mechanism of scale formation, DSP scale is the model**
- **Types of scales**
- **Equilibrium solubilities, prediction of scale types**
- **Composition of different alumina refinery scales**
- **Reaction mechanism considerations**
- **Conclusions**

Introduction

As you know, liquids and slurries are processed in the alumina refineries. The liquid phases have complex compositions, so have most of the solid phases, such as bauxites and bauxite residues. The temperatures and solid contents are other characteristics that vary at different places of the Bayer process.

The abrasive effects and scalings cause most of the headaches for the operators.

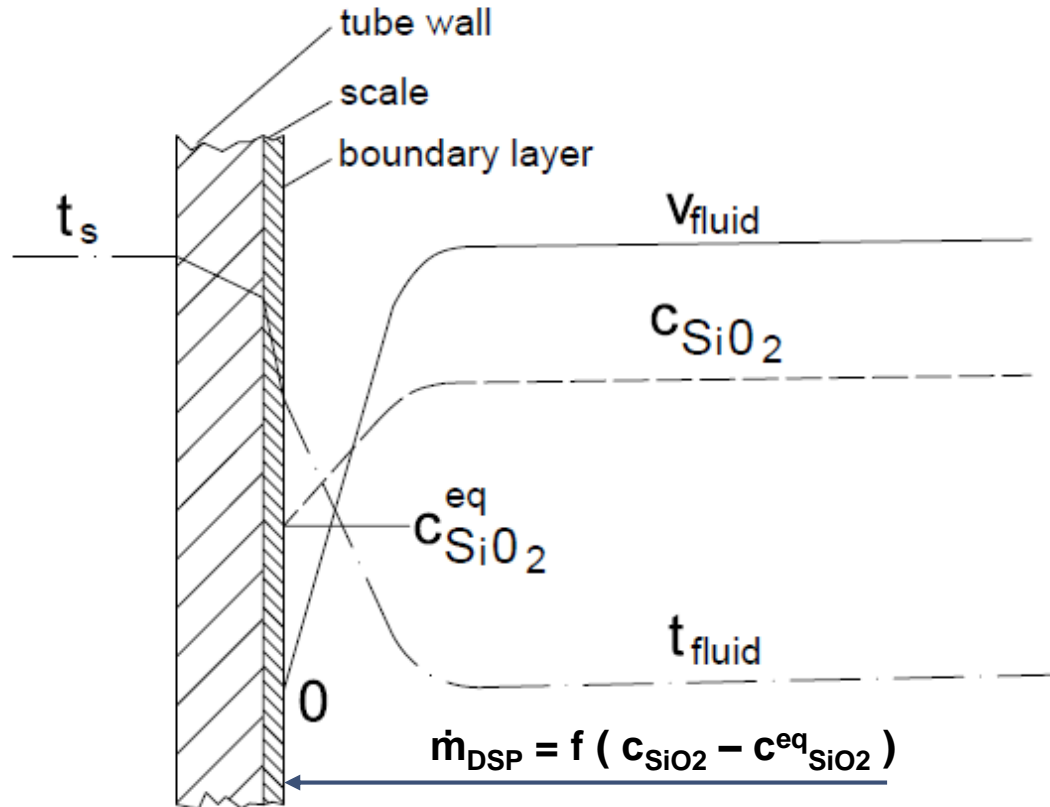
The objective of this presentation is to provide an insight to the formation mechanism of various scales of refineries.

Drawbacks of Scalings

- The scales reduce the inner diameters of tubes, may clog preheater tubes, reduce hydraulic and thermal performances. (The thermal conductivity of sodalite is 0.52 W/mK, while that of carbon steel is greater by almost two order of magnitudes, 43 W/mK)
- Need chemical and/or mechanical descaling, which is troublesome, sometimes incomplete.
- Spare equipment must be available, incur extra costs.
- Several types of scales exist.

Tube Wall, Scale, Fluid Velocity, Temperature and Concentration Profiles

Schematics of formation of DSP scales on tube walls

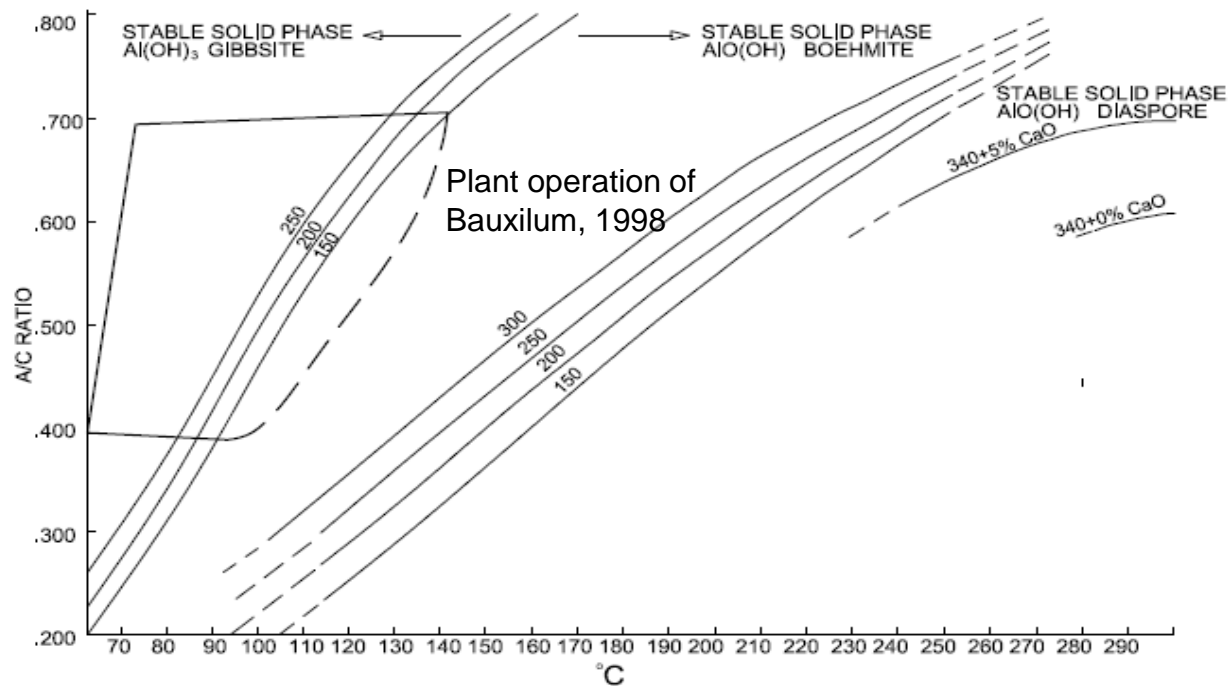


The chemical reactions in general can be described if the

- Equilibrium concentrations of the reagents and products
- Reaction equations (stoichiometry)
- Reaction kinetics
- Reaction mechanism
- Possible transformation of one modification to another one are known.

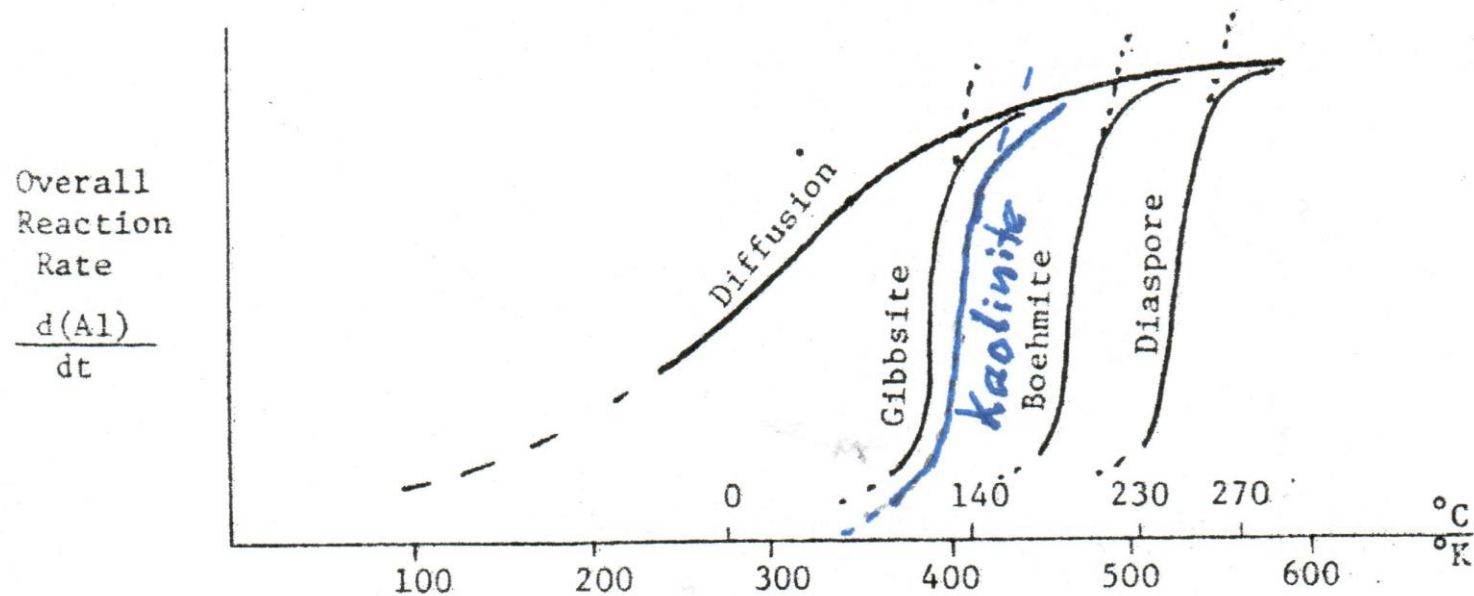
Let us start with reactions of the soluble alumina and reactive silica minerals.

Equilibrium Solubilities for Gibbsite, Boehmite and Diaspore. A/C Profile for a LT Bayer Process



J. Kotte, Light Metals 1981

Dissolution Reaction Rates of Soluble Alumina Minerals and Kaolinite



Principal Reaction Equations that may eventually Form Scales (1of2)

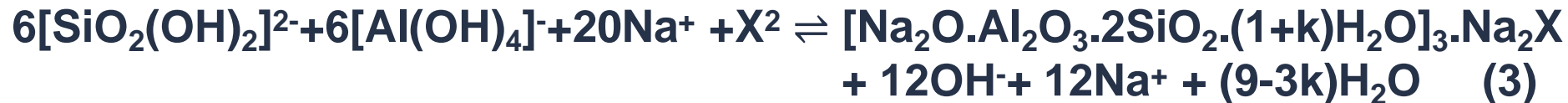
- Dissolution reaction of gibbsite



- Dissolution reaction of kaolinite

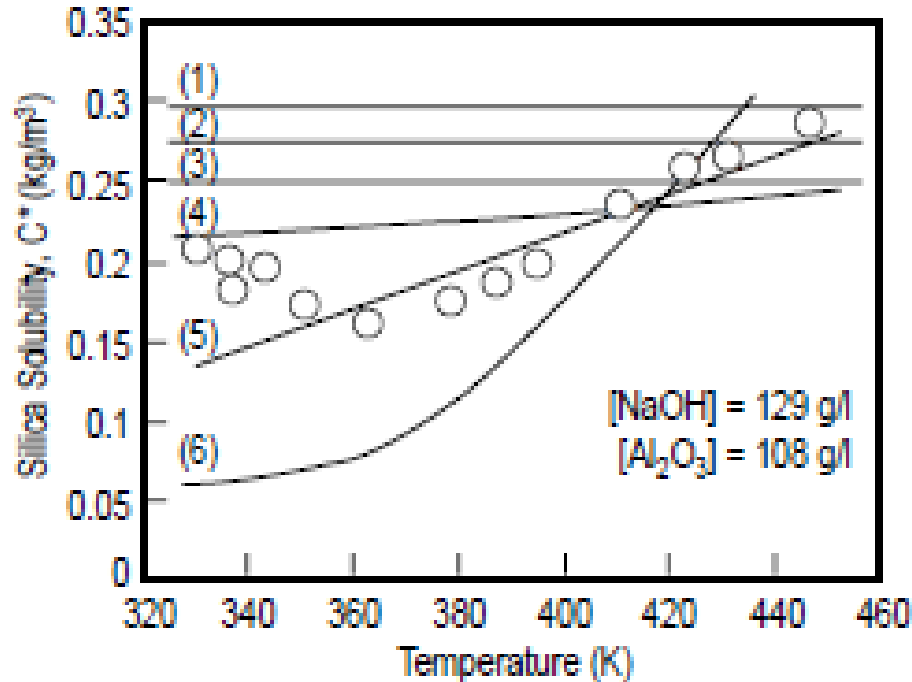


- DSP (sodalite) formation:



where X: 2OH^- , CO_3^{2-} , SO_4^{2-} , 2Cl^- , 2AlO_2^- , $k = 0 - 1$, $\sim 140\text{-}150^\circ\text{C}$ temp.

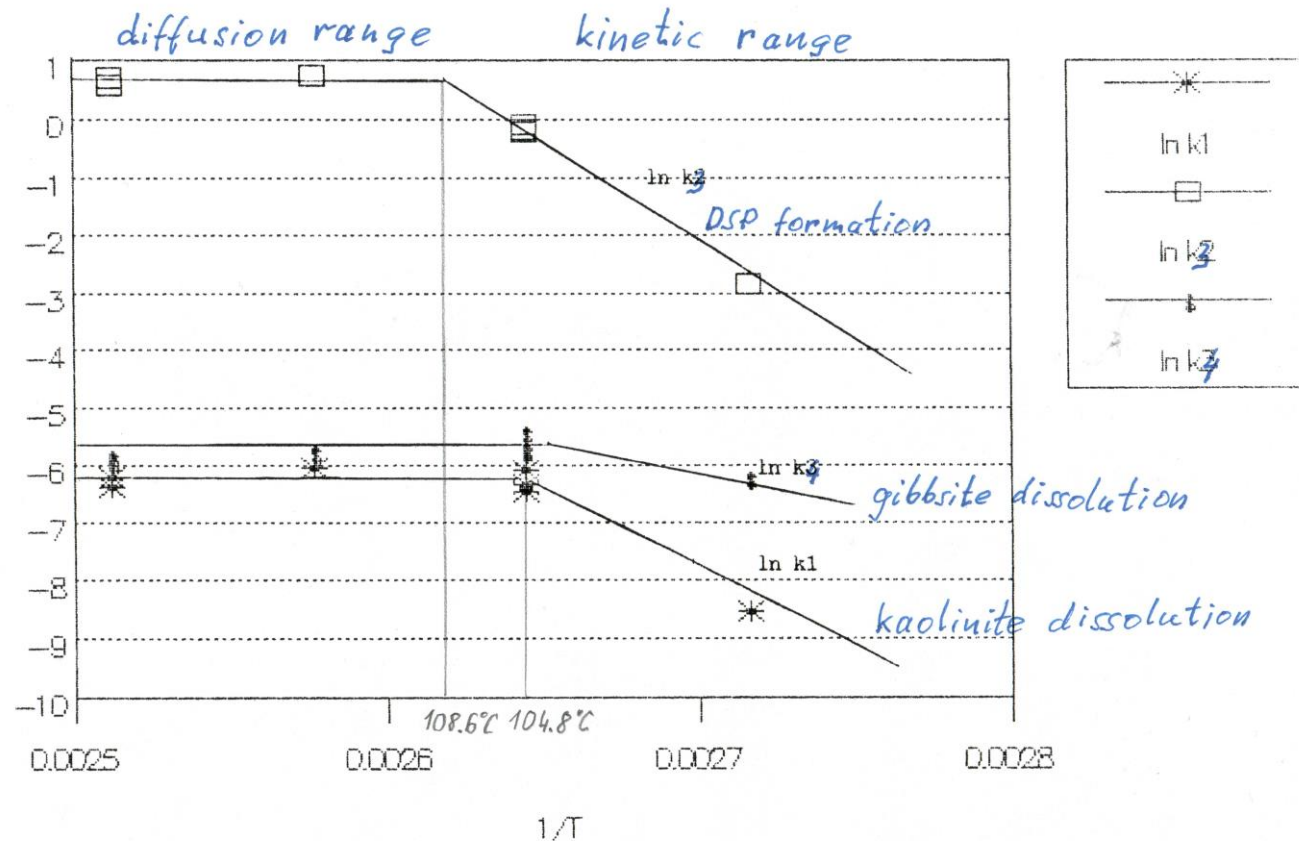
Silica Solubilities in the Function of Temperature by Various Authors



(1) Oku and Yamada (1971), (2) Adamson et al. (1964), (3) Leiteizen (1972), (4) Cresswell (1984), (5) Hewett et al. (1987), (6) Jamialahmadi and Müller-Steinhagen (1998). **The test results of Jamialahmadi and Müller-Steinhagen are shown with small circles.**

Source: Jamialahmadi M. and Müller-Steinhagen H. Determining Silica Solubility in Bayer Process Liquor. *JOM* November 1998, Volume 50, [Issue 11](#), pp 44–49.

Reaction rate constants in the function of predesilication temperature



Subsequent to dissolution of gibbsite and reactive silica, DSP (sodalite/cancrinite) forms as follows:

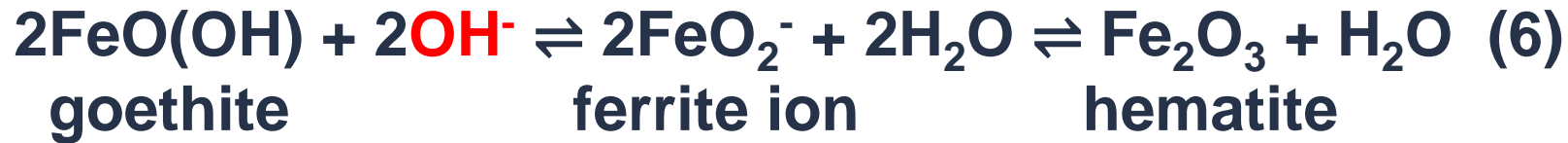
**[Sodium aluminate] + [Sodium silicate] →
[Na-aluminosilicate ions] → amorphous → zeolite A →
sodalite → cancrinite**

Addai-Mensah, J., Li, J., Zbik, M. and Rosencrance, S.: Sodium Aluminosilicate Solid Phase Specific Fouling Behaviour. *2003 ECI Conference of Heat Exchanger Fouling and Cleaning. Fundamentals and Applications*. Santa Fe, New Mexico, USA. Year 2004, Paper 11

Formation of pseudo-boehmite (s_1) and boehmite (s_2)



Transformation of goethite into hematite



Reaction of anatase



The Key is the Supersaturation of Intermediate Anions of Consecutive Reactions

- gibbsite, boehmite, diaspore → **aluminate anion** → gibbsite, boehmite
- kaolinite, quartz → **silicate anion** → DSP (sodalite, canrinite)
- goethite → **ferrite anion** → hematite
- anatase, rutile → **titanate anion** → perovskite, cafetite, hydrokassite, hydrogarnet, etc.
- apatite, crandallite → **phosphate anion** → carbonate apatite, etc.

„Red side”

- Desilication products (sodalite, cancrinite)



- Boehmite, $\text{AlO}(\text{OH})$
- Hematite, Fe_2O_3
- Titanates, presented on the next slide
- Apatites $\text{Ca}_5[\text{PO}_4]_3(\text{OH}, \text{Cl}, \text{F})$
- etc.

„White side”

- gibbsite, $\text{Al}(\text{OH})_3$
- sodium fluoro-arseno-phosphato-vanadate

Titania Containing Scales of High Temperature Digesters

- Perovskite (CaTiO_3)
- $(\text{Ca,Mg})(\text{Ti,Fe,Al})_2\text{O}_4(\text{OH})_2$
- $\text{CaO} \cdot 0.4\text{MgO} \cdot 0.3\text{Al}_2\text{O}_3 \cdot \text{Ti}_2\text{O}_4$
- Cafetite $(\text{Na,Ca,Mg})_{2.2}(\text{Fe,Al})_{2.5}(\text{Ti,Si})_{3.1}\text{O}_{12} \cdot 3.7\text{H}_2\text{O}$
- Hydrokassite $(\text{Ca,Mg,Mn})(\text{Ti,Al,Mg,Fe})_2\text{O}_3(\text{OH})_3$
- Calcium alumino hydrogarnet
 $\text{Ca}_3(\text{Al,Fe})_2[(\text{Si,Ti})\text{O}_4]_n(\text{H}_2\text{O})_{(6-2n)}$

The composition of titania containing scales is sometimes extremely complex, depend on the composition of bauxite and liquor, temperature and addition of Ca.

The process technology, feedstocks and scales of some alumina refineries

High Temperature Digestion at Almásfüzitő Alumina Plant, Hungary (1971)

- Bauxite: 51% Al_2O_3 , 6.6% SiO_2 , 20.7% Fe_2O_3 .
- < 50% of av. Al_2O_3 in gibbsite, rest in boehmite and goethite
- ~40% of Fe_2O_3 in goethite, the rest in hematite
- Predesilication at 90°C for 6 hours
- Digestion trains (single stream digestion)
 - 5 vertical shell and tube heat exchangers (flash vapour)
 - 2 autoclaves (flash vapour)
 - 5 autoclaves (live steam), digestion at 225°C.

Chemical Composition of Digester Scales of Almásfüzitő Plant

Samples	Bauxite characteris	Shell and tube HXs, No.			Autoclaves, No.			
		1	3	5	1	3	5	7
Chemical compositions	Fejér county	Operating temperatures, °C			Operating temperatures, °C, typical			
	Hungary	88-98	108-118	128-138	145-155	170-186	200-214	224-226
Al ₂ O ₃ , %	51	31.2	29.1	26.5	32.4	15.9	15.1	16.1
SiO ₂ , %	6.6	22.3	26.1	24.2	5.1	3.9	3.8	4
Fe ₂ O ₃ , %	20.7	12.3	9.6	13	32.4	46.5	48.5	44.6
TiO ₂ , %	2.5	1.4	1.4	1.4	2.7	8.4	5.1	4.4
CaO, %	0.6	0.6	0.6	2.4	2.7	3.4	3.4	1.9
MgO, %	0.3	0.4	0.4	1.1	0.7	1.8	2	1.4
Na ₂ O, %	-	19.5	22.8	21.5	10	3	10.8	13.5
L.O.I., %	n.d.	12.3	10.1	9.8	13.7	12.1	10	12.8

Mineralogical Composition of Digester Scales of Almásfüzitő Plant

Samples	Shell and tube HXs, No.			Autoclaves, No.			
	1	3	5	1	3	5	7
Mineralogical compositions,	Operating temperatures, °C			Operating temperatures, °C, typical			
%	88-98	108-118	128-138	145-155	170-186	200-214	224-226
Al ₂ O ₃ , in sodalite	15.9	18.1	14.3	1.8	0.9	0.9	1.3
cancrinite	2.1	2.9	5.2	1.7	1.8	1.7	1.2
NaAlO ₂	0.2	1	0.9	1	tr.	4	5
Ca(Mg,Al)-titanate	-	-	-	tr.	1.2	0.6	0.7
boehmite	10	3.5	2.7	22	7.7	2.5	3.5
hematite	0.2	0.2	0.3	0.8	2	2.4	1
goethite	0.8	0.7	0.9	2	0.9	tr.	tr.
diaspore	2	2.3	2	2	1	0.5	2
illite	tr.	0.5	0.5	0.3	0.4	0.3	0.4
SiO ₂ , in quartz	2.3	2.3	2	0.5	tr.	tr.	-
sodalite	17.5	20	15.7	2	1	1	1.4
cancrinite	2.5	3.4	6.1	2	2.1	2	1.4
illite	tr.	0.4	0.4	0.2	0.3	0.2	0.3
Fe ₂ O ₃ , in hematite	6.2	5.6	7.9	17.5	39.1	47	43.3
goethite	4.6	4	5.1	10.9	5.4	1.5	1.4
maghemite	1.5	-	-	4	2	-	-
TiO ₂ , in anatase	1	0.8	0.8	-	-	-	-
rutile	0.4	0.4	0.2	-	-	-	-
Ca(Mg,Al)-titanate				1.3	6.4	3.5	3.7
perovskite				1.4	2.0	1.6	0.7
CaO, in Ca(Mg,Al)-titanate	-	-	-	1.7	7	4	3.9
perovskite	-	-	-	1	1.4	1.1	0.5
dolomite	0.4	0.4	1.3	-	-	-	-
calcite	tr.	tr.	1	-	-	-	-
Na ₂ O, in Na ₂ CO ₃ ·1-1/2H ₂ O	7.4	5	5.5	6	1.5	6.5	9
sodalite/cancrinite	12.1	13.8	10.8	1.4	0.7	0.7	1.0
Hematite/goethite ratio	1.3	1.4	1.5	1.6	7.2	31.3	30.9

Comments to the Scales from the Almásfüzitő Alumina Plant

- Sodalite and to a lesser extent, cancrinite comprise the main constituents of scales in the preheaters at temperatures up to 140°C. At temperatures higher than about 160°C, cancrinite becomes dominant over sodalite. The sum of sodalite and cancrinite significantly decreases in the autoclaves operating at 150°C and higher since transformation of reactive silica ended.
- In the autoclaves at temperatures of 145-166°C, boehmite deposits due to the local supersaturation of Na-aluminate for boehmite. At higher temperatures the liquor becomes unsaturated and dissolves boehmite.
- The goethite to hematite transformation starts at about 160°C; hematite becomes the principal iron constituent of the scale whilst goethite content gradually diminishes. The hematite/goethite ratios dramatically increase at temperatures higher than about 180-190°C. This supports that the conversion of goethite to hematite takes place via liquid phase.
- Calcite, and possibly dolomite and anatase, react 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 range of 90-140°C.

- **Bauxite composition presented on the following sheets**
- **Tube digester (single stream):**
 - **15 horizontal tubular preheater units (flash vapour and live steam condensate)**
 - **4 horizontal tubular preheater units (live steam)**
 - **after the 6th preheater unit, vessels were installed to provide 12 minutes retention time at 145-150°C, after 9th preheater units, a vessel for 6 minutes additional desilication at 180°C**
 - **digestion temperature 240-250°C.**

Chemical Composition of Tube Digester Scales from MOTIM Plant (1993)

Samples	Bauxite, characteristic	Scales of the Tube digester, preheater, No of unit					Bauxite residue
		7	10	17	19	at CaO dosage	
	Fenyőfő	Operating temperatures, °C, typical					
Chemical composition		140-150	182	210	240	240	240
Al ₂ O ₃ , %	51	31.1	10.3	8.2	6.4	6.8	15.5
SiO ₂ , %	7.2	1.6	3	0.8	1.7	2.8	13.5
Fe ₂ O ₃ , %	17.2	21	15.2	22.5	24.3	22.5	39.4
TiO ₂ , %	2.6	15.8	32.9	33.8	33.2	10.8	5.1
CaO, %	0.8	9.2	16.3	14.2	13.1	30	5
MgO, %	0.4	2.9	5	4	3.7	0.7	n.d.
Na ₂ O, %	-	1.1	1	0.6	1	3	8.8
P ₂ O ₅ , %	n.d.	0.72	1	0.17	0.39	10.3	n.d.
L.O.I., %	n.d.	12.1	12.5	10.7	9	8.2	8.3

Mineralogical Composition of Tube Digester Scales from MOTIM Plant

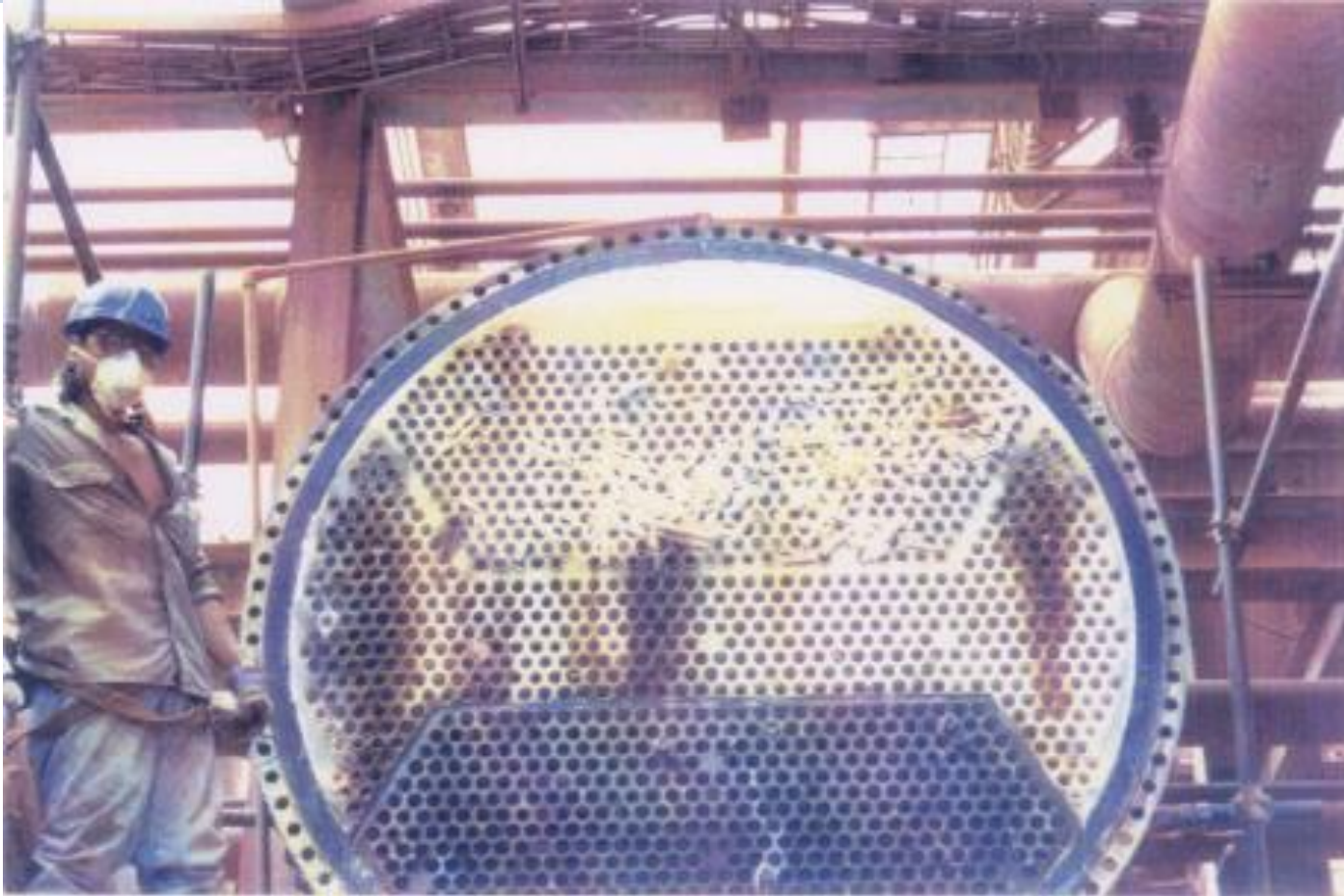
Samples	Bauxite, characteristic	Scales of the tube digester preheaters, No. of unit					Bauxite residue
		7	10	17	19	at CaO dosage	
	Fenyőfő	Operating temperatures, °C, typical					
Mineralogical compositions,		140-150	182	210	240	240	240
Al ₂ O ₃ , in gibbsite	20.9	-	-	-	-	-	-
boehmite	22.8	27.7	-	-	-	-	0.5
kaolinite	5.8	-	-	-	-	-	-
sodalite/cancrinite	-	1.4	2.3	1.5	1.2	0.7	10.8
Ca-aluminosilicate	-	-	1.6	1	0.7	5.6	2.2
(CaMg)Al-titanate	-	2	5.1	5.7	5.7	0.5	-
SiO ₂ , in kaolinite	6.7	-	-	-	-	-	-
sodalite/cancrinite	-	1.6	2.4	0.8	1.4	0.8	12.8
Ca-aluminosilicate	-	-	0.6	-	0.3	2	0.7
Fe ₂ O ₃ , in hematite	9.5	19.5	14	21	23.5	20.3	26.9
goethite	7.7	1.5	1.2	1.5	0.8	2.2	12.5
TiO ₂ , in anatase	1.8	-	-	-	-	-	-
rutile	0.8	-	-	-	-	-	3.1
(CaMg)Al-titanate	-	12.3	32.8	33.8	33.2	4.4	-
perovskite	-	3.5	-	-	-	6.4	2
CaO, in dolomite	0.6	2.3	2	0.3	-	-	-
Ca-aluminosilicate	-	-	2.6	1.6	1.2	9.2	3.6
(CaMg)Al-titanate	-	4.4	11.7	12.3	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	-	-	-
(CaMg)Al-titanate	-	1.3	3.5	3.8	3.7	0.7	-
Na ₂ O, in sodalite/cancrinite	-	1.1	1.6	0.6	1	0.6	8.8
P ₂ O ₅ , in OH-apatite	-	-	-	-	-	10.3	-
Hematite/goethite ratio	1.2	13.0	11.7	14.0	29.4	9.2	2.2

Comments to the Tube Digester Scales of MOTIM Alumina Plant

- Sodalite, and to a lesser extent cancrinite comprise the main constituents in the tubular slurry heat exchangers at operating temperatures up to 150°C, from previous experience. The vessels which provided retention time of 12-13 minutes at about 145°C reduced the sodalite/cancrinite scale in the preheaters operating at higher temperatures to a fraction.
- 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, goethite is negligible. The hamatite/goethite ratio is about 10 times greater than in bauxite. This supports that goethite-hematite conversion takes place via liquid phase, this is why hematite deposits.
- (Ca,Mg)Al-titanate, sometimes perovskite (CaTiO_3) appear in scales. Rutile can “survive” the digestion process, as found in the bauxite residue (BR).
- A significant amount of OH-apatite and hematite have been found in scale where the Ca(OH)_2 was added at 240°C.

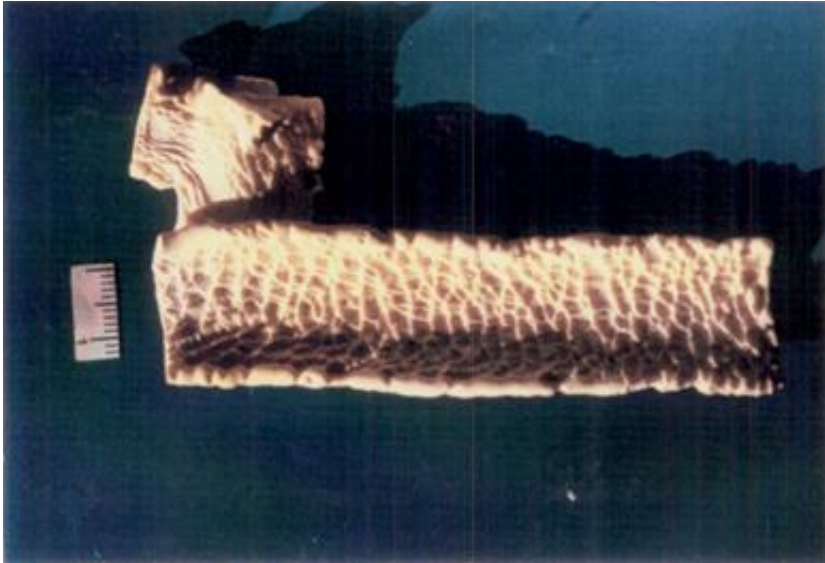
- Bauxite: T. Al_2O_3 49%, T. SiO_2 8-10%, R. SiO_2 1.2-1.8%
- Test Tank Liquor 282 g/L C, A/C 0.385
- Pre-desilication of dense slurry: 98°C, 10-11 hours
- Double stream digestion
- Preheating of some 90% of TTL up to 170°C with flash vapour then with live steam
- Three operating large autoclaves, digestion temperature 145°C, retention time 45 min.

Front View of a 1200 m² Shell and Tube Live Steam Heater, Bauxilum



After 3 days
of operation

Front view



Rare view



Operating temperature: 170 °C

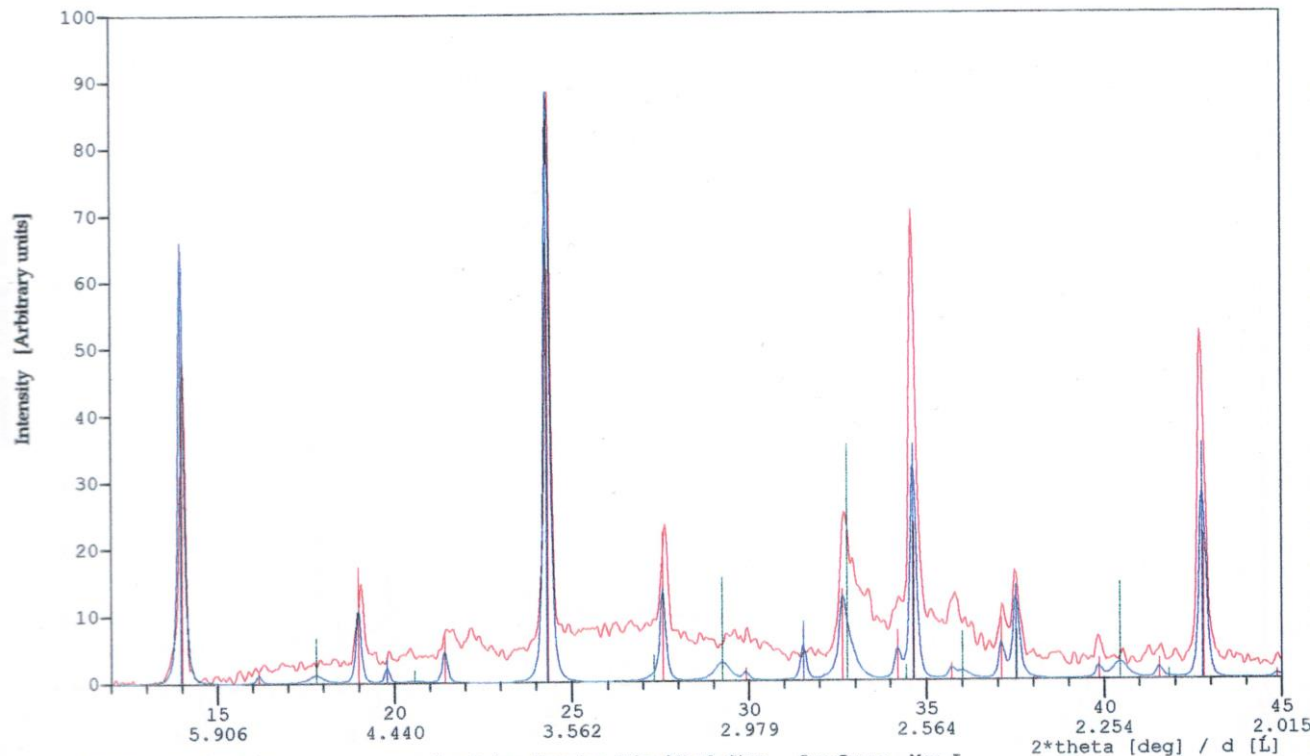
Chemical Composition of Bauxilum Scales

Samples	Bauxite, characteristic	Live steam heater scale		Digester scale	Last flash tank	Washer No 1, O/F pipe	Bauxite residue
		Liquor side	Tube side				
	Los Pijiguaos	Operating temperatures, fluids, °C					
Chemical compositions	08/97	170		145	115	88	145
Al ₂ O ₃ , %	52.1	30.5		39.4	50.6	61.2	12.4
SiO ₂ , %	5.9	31.8		16.8	9.9	0.3	24.4
Fe ₂ O ₃ , %	12.7	-		20.8	14.9	2.2	48
TiO ₂ , %	1.2	-		n.d.	2	0.3	1.6
CaO, %	n.d.	0.35		n.d.	0.6	0.7	n.d.
Na ₂ O, %	-	23.5		11.6	4.4	1.8	3
L.O.I., %	28.4	7.5		9.5	15.8	33.4	6.8

Mineralogical Composition of Bauxilum Bauxite, BR and Scales

Samples	Bauxite, characteristic	Live steam heater scale 3 days		Digester scale	Last flash tank	Washer No 1, O/F pipe	Bauxite residue
		Liquor side	Tube side				
	Los Pijiguaos	Operating temperatures, fluids, °C					
Mineralogical compositions, %	08/97	170		145	115	88	145
Al ₂ O ₃ , in gibbsite	51	1.3	-	1.3	2	60.9	3.9
boehmite	0.4	0	-	21.3	43.9	0	0
kaolinite	0.6	-	-	-	-	-	-
goethite	1.2	-	-	2.6	0.5	-	4.7
sodalite	-	20.2	15.5	-	4.3	0.3	3.7
cancrinite	-	3.1	10.9	14.3			0
SiO ₂ , in kaolinite	0.7	-	-	-	-	-	-
quartz	3	-	-	-	5.2	-	20
sodalite	-	23.8	18.3	-	4.7	0.3	4.4
cancrinite	-	3.7	12.8	16.8			0
Fe ₂ O ₃ , in hematite	4	-	-	10	8.4	-	20
goethite	7.7	-	-	10.8	6.5	-	26.5
TiO ₂ , in anatase	0.7	-	-	-	2	-	-
rutile	0.1	-	-	-	-	-	-
CaO, in OH-grossular	-	4.1	4.1	-	-	-	-
Na ₂ O, in sodalite	-	16.3	12.6	-	3.4	0.5	3
cancrinite	-	2.5	8.8	11.6			0
H ₂ O	28.4	7.5	7.5	9.5	15.8	33.4	6.8
Hematite/goethite ratio	0.5	-	-	0.9	1.3	-	0.8
Cancrinite/(sodalite+cancrinite), rel%		13.4	41.2	100.0			0.0
Gibbsite/(gibbsite+boehmite), rel%		99.2		7.4	4.4	100.0	100.0

XRD Pattern of the Rare Part of a Live Steam Preheater Scale from Bauxilum



[FileName]	Sample Id.:	MeasDate	Wavelen	Tube	kV	mA	Step	ScanRange	Max.I
[BXL-SC02]	Live steam heater scale,2	10-01-97	1.54186	Cu	40	30	0.04	4.9-69.9	839
[BXL-SC02]	Live steam heater scale,2	04-03-98	1.54186	(SIMUL)			0.04	4.9-69.9	839

Reference patterns:

Private BCan Cancrinite, Bayer process
 Private BSod Sodalite (Bayer process)
 Calcula GroH HydroGrossular,i; 1.5:1.5

[BXL-SC02] Live steam heater scale,2

Phase%	SUM	BCan	BSod	GrOH	Chem Anal	Diff
CaO%	95.00	35.00	50.00	10.00	4.06	0.35 -3.71
SiO ₂ %	4.06			4.06	31.80	-1.44
Al ₂ O ₃ %	33.24	12.79	18.27	2.18	30.50	1.68
Na ₂ O%	28.82	10.85	15.51	2.46	23.50	2.14
H ₂ O%	21.36	8.80	12.57			
LOI %	7.51	2.56	3.65	1.30	7.50	-0.01

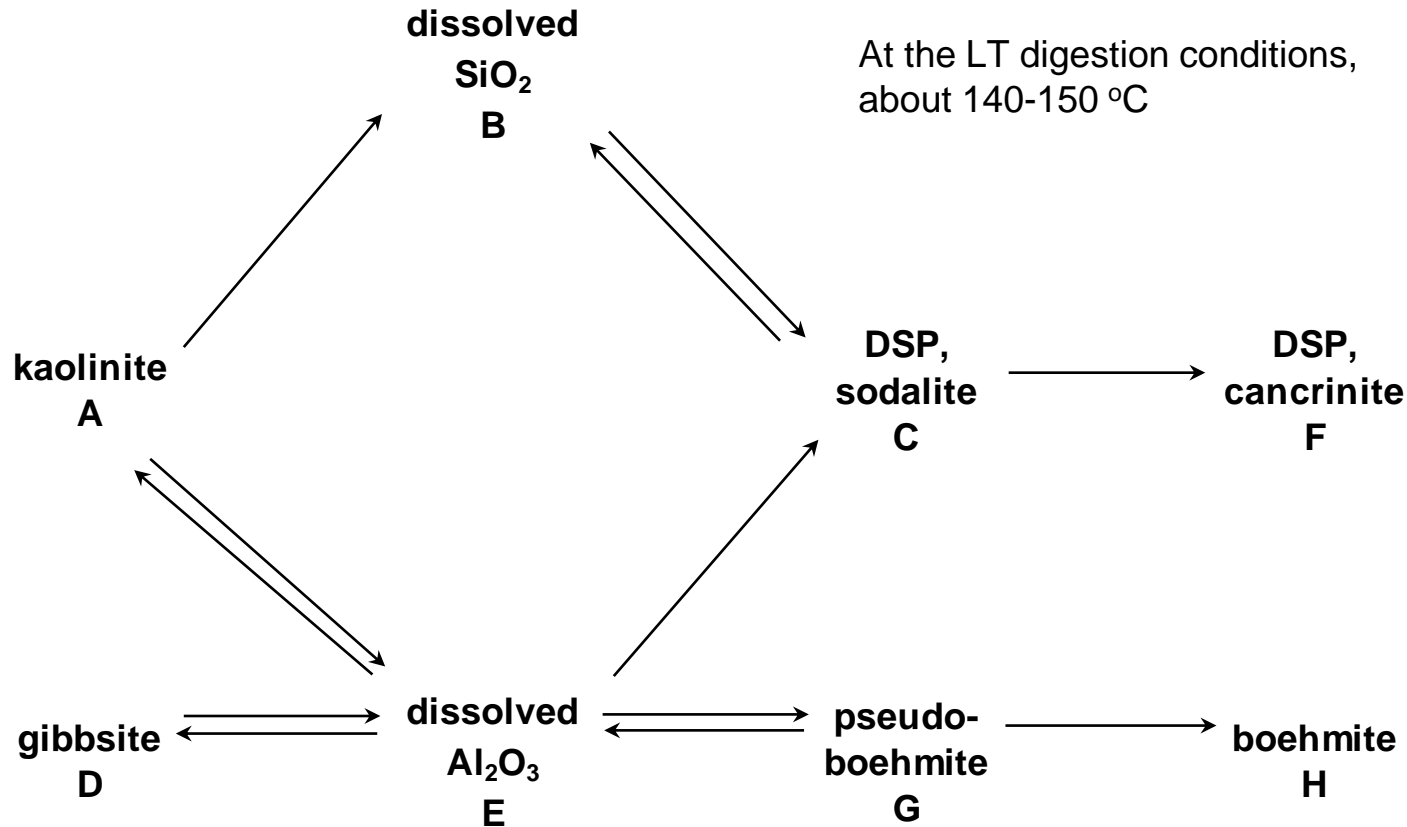
Comments to the Scales from the Bauxilum Alumina Refinery (1 of 2)

- The surface of scale which was in contact with the TTL consisted of primarily sodalite. The rear side of the scale attached to the inner wall of the heated tube was 3 days „old”. The amount of cancrinite increased at the expense of sodalite, it formed from sodalite.
- The uneven surface of scale in contact with the TTL, look like ocean waves, suggests turbulent flow.
- No cancrinite has been found in BR, only sodalite. This confirms that sodalite forms at the conditions of low temp. (LT) digestion.
- Scale from the digester autoclave consists of cancrinite and boehmite. Sodalite is missing, this confirms the transformation of sodalite to cancrinite over time, even at relatively low temperature, i.e. 145°C. Boehmite is formed due to the supersaturation of dissolved alumina for boehmite. Meanwhile sodalite and boehmite were deposited at first, fine bauxite residue particles may have been trapped in scale.

Comments to the Scales from the Bauxilum Alumina Refinery (2 of 2)

- The most characteristic constituent of the flash vessel scale is boehmite. The aluminate in the liquid phase is supersaturated for gibbsite and boehmite. Boehmite has probably been precipitated directly from the liquid. Another constituent is sodium aluminosilicate (sodalite and/or cancrinite). The cooler the flash vessel, the more boehmite and the less sodium aluminium silicate are found. A few percent of bauxite residue has probably been entrapped in this scale as well.
- Scale taken from the overflow pipe of the Washer No. 1 is gibbsite. The supersaturation for gibbsite is evident. At this temperature formation of gibbsite is favoured.

Reaction mechanism of dissolution of gibbsite, formation of (pseudo-) boehmite, transformation of kaolinite to DSP (sodalite/cancrinite)



Important factors of scale formation in the Bayer process:

- fluid velocity in the bulk of solute;
- direction and intensity of heat transfer; temperature profile
- equilibrium and bulk concentrations of solutes;

The factors should be considered in a holistic way.

- Species which play decisive roles in scale formation are intermediate compounds of consecutive reactions.
- The driving force for the mass transfer that result in scales is the difference between the bulk and equilibrium concentrations.
- After formation, scales may remain in-situ for long periods, or can transform from one mineral to another.
- Solid particles can be entrapped in scales.
- The study of scales along with reaction kinetics is a useful tool in understanding the mechanism of several reactions.

Bánvölgyi, Gy.: Scale Formation in Alumina Refineries. Proceedings of the 34th International Conference and Exhibition of ICSOBA, 3-6 October, 2016, Quebec City, Canada. No 45. pp. 101-114.



Thank you for your attention

Questions, Comments are Welcome

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