

HIGH TITANIUM BAUXITES: SPECIFIC FEATURES OF MINERAL COMPOSITION AND BEHAVIOUR IN BAYER CYCLE (BY THE EXAMPLE OF INDIAN BAUXITES)

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Abstract

Currently alumina refineries of Ukraine, Russia, Azerbaijan and other CIS countries have started to process bauxites from Western coast of India (Gujarat and Maharashtra States). A specific feature of some of these bauxites is a high titanium oxide content in the form of anatase and rutile (3.5–6.5 mass %). Bauxites from Guinea, Australia, Brazil and other countries which are usually processed at CIS refineries have 2.0–2.7 mass % of TiO₂. Specific features of these bauxites required additional laboratory studies and industrial tests.

The studies have shown that the behaviour of anatase and rutile in Bayer cycle is different and depends on temperature and other conditions. Depending on lime addition etc, titanium minerals in the course of decomposition form different phases, such as hydrocassite, perovskite, titanium hydrogarnets, etc. In the absence of lime, gel-like sodium hydrotitanates are formed. This has a negative impact on kinetics and alumina recovery, specific alkali consumption, red mud sedimentation properties and alumina quality.

The behavior of titanium minerals and their impact on scaling of autoclave heating surfaces depending on temperature and bauxite type have been studied. It is demonstrated that scaling of heat-exchanging surfaces can be reduced by different methods.

The solubility of titanium of gibbsite-boehmitic bauxites from Shiloli deposit (Western Ghats, India), having TiO₂ content up to 6.5 mass %, was studied in a wide temperature and concentration range. It is demonstrated, that under proper processing conditions, titanium content in liquors will be at a normal level for gibbsitic bauxites processing and should not have negative impact on quality and technical properties of aluminium.

1. Introduction

Currently bauxites from Western coast of India (Gujarat and Maharashtra States) are starting to be used by alumina refineries of Ukraine, Russia, Azerbaijan and other CIS countries. A specific feature of some of these bauxites is a high titanium oxide content in the form of anatase and rutile (3.5–6.5 mass %). Bauxites from Guinea, Australia, Brazil and other countries that are usually processed at CIS refineries have 2.0–2.7 mass % of TiO₂. Specific features of these bauxites required special laboratory studies and industrial tests to study the influence of high-titanium bauxites on technical and economical indexes of the process.

Notation (Terminology)

α_C — a caustic ratio of solution (molecular)

$$\alpha_C = \frac{Na_2O * 1,645}{Al_2O_3} \quad (1)$$

μ_{Si} — a silica ratio of solution (mass)

$$\mu_{Si} = \frac{Al_2O_3}{SiO_2} \quad (2)$$

2. Minerals of Titanium in Bauxites and Titanium-containing Phases Formation in Bayer Process

Generally titanium in bauxites is represented by two minerals: *anatase* (TiO₂) and *rutile* (TiO₂). Both of them are polymorphous modifications of titanium oxide having a similar structure. The ratio of anatase and rutile content in bauxites from different deposits of the world varies from

10 : 1 to 1 : 2 (by mass). In some bauxites traces of *ilmenite* FeTiO₃, *brookite* TiO₂, *sphene* CaTiSiO₅ are available, however these minerals don't have much significance.

2.1 Reaction of Anatase and Rutile with Alkaline-Aluminate Liquor

In the Bayer process titanium minerals in bauxite react with alkaline-aluminate liquors with the following adverse effects:

- increase in TiO₂ concentration in liquor causing increased content of titanium in alumina and aluminium. This impurity impairs conductivity of aluminium, increases its brittleness which makes the metal unsuitable for wire, rods and foil production;
 - if lime addition is insufficient, *sodium hydrotitanates* of Na₂O·3TiO₂·2,5H₂O type or *sodium hydrometatitanates* of NaHTiO₃·H₂O type are formed. Both compounds have low solubility and settle with red mud. Under red mud thickening and washing conditions they hydrolyze causing the formation of titanium oxide gel TiO₂·H₂O, that often combines with sodium metatitanate and creates a gel-like complex TiO₂·nH₂O·NaHTiO₃. This has a negative impact on kinetics and depth of alumina recovery, specific alkali consumption, red mud sedimentation properties, quality of commercial alumina, etc.
- in the case of lime and other additions and depending on their dosage, type of bauxite, etc. the titanium minerals dissolve to form such phases as *hydrocassite* (Ca, Na, Mn)(Ti, Al, Mg, Fe)₂O₃(OH)₃ (3) *perovskite*

KEY WORDS: bauxite, titanium oxide, digestion, scaling, alumina recovery

CaTiO_3 , aluminocalcium *titanium hydrogarnets* $\text{Ca}_3(\text{Al,Fe})_2[(\text{Si,Ti})\text{O}_4]_n(\text{H}_2\text{O})_{(6-2n)}$, *hydroapatite and apatite* $\text{Ca}_5[\text{PO}_4]_3(\text{OH, Cl, F})$, etc. These phases create scales at the heating surface of autoclaves that considerably impair heat transfer of surfaces, and thus cause an increase in specific heat consumption.

Despite their identical chemical composition and similar structural characteristics, anatase and rutile have quite different behaviour and scaling properties in Bayer cycle depending on temperature and other factors.

Below 100°C both minerals are inactive to alkali in liquors having concentration close to industrial.

In the course of reaction of anatase with alkaline liquor irrespective of its caustic ratio, sodium hydrotitanate starts to form at temperatures as low as 130°C, the curves being practically the same for liquors with very high and very low caustic ratios.

Rutile is less reactive with alkali. Scale formation starts at 150°C and continues up to 235°C. Decreasing liquor caustic ratio (α_C) significantly reduces its reactivity.

2.2 Scaling of Heating Surfaces

The presence of liquor silica derived from kaolin dissolution significantly passivates rutile and anatase by shifting the titanium scale formation zone to higher temperatures. In this case scales on heating surfaces at 130–160°C are represented by sodium hydroalumosilicates (desilication product or DSP) and recrystallized boehmite.

Under conditions of adequate desilication, decreased formation of DSP is observed however two other forms of scaling are observed:

- 1st — in the temperature range of 160–210°C, connected with formation of scales consisting of titanium-calcium compounds;
- 2nd — in the temperature range of 250–280°C, characterized by formation of scales with high concentrations of P_2O_5 and CaO .

Scaling rate depends on a number of factors, including:

- concentration of alumina in liquor: as its concentration increases (or caustic ratio decreases), average intensity of incrustation grows from 1–2 $\mu\text{m}/\text{day}$ to 3–3.5 $\mu\text{m}/\text{day}$;
- dosage of lime into raw bauxite slurry. The relationship here has a variable character. In the temperature interval of slurry heating from 165 to 210°C it is the following:

$$C_{\text{CaO}} \sim 1/V_{\text{SC}}, \quad (4)$$

where C_{CaO} — dosage of lime to digestion, kg/t;
 V_{SC} — scaling rate, $\mu\text{m}/\text{day}$.

In the temperature interval of 245–280°C:

$$C_{\text{CaO}} \sim V_{\text{SC}} \quad (5)$$

Addition of lime at digestion allows a reduction in the incrustation of heating surfaces by titanium scales at a temperature below ~240°C, however in this case, scaling of heating surfaces of first autoclaves by hydrogarnets is possible. This occurred at the Nikolaev Alumina Refinery (Ukraine) at a lime dosage of 4–5 mass % by weight of Jamaican bauxite, which was about 2 moles of lime per mole of titanium oxide present in the bauxite.

The behavior of rutile in the presence of calcium oxide is somehow different from behavior of anatase. Addition of calcium oxide intensifies the process of rutile decomposition and essentially changes the character of scaling by shifting its maximum into an area of lower temperature (from 255 to 210°C). Variation of CaO dosage over a wide range does not have a significant effect on the character of incrustation.

The value of temperature difference between slurry and steam (Δt) also has an effect. Scaling rate increases with increasing Δt in the area of higher temperatures.

Scale composition influences heat transfer coefficient of heating surfaces (k). Being extremely dense by their structure, titanium — calcium compounds essentially reduce the “ k ” value.

Composition of the incrustation on heating surfaces also depends on the type of bauxite. For example, processing of Guinean bauxite produces scales composed mainly of perovskite CaTiO_3 . Digestion of other bauxites, such as Jamaican, results in alkaline calcium hydroxotitanate scales of a hydrocassite type (3).

Formation of this phase results in secondary losses of caustic soda and alumina.

The X-ray characteristics of this compound are close to natural mineral cassite $\text{CaTi}_2\text{O}_4(\text{OH})_2$ (ASTM 20-243), but are slightly different. The main characteristic peaks in nm (in brackets, intensity in %) are the following: 0,331 (100); 0,176 (100); 0,478 (50).

Replacement of perovskite scales by mostly hydrocassite ones results in increased rate of incrustation. For example, the scaling rate from processing Brazilian bauxite from Trombetas mine is up to 3 times higher as compared with Guinean bauxite (mostly perovskite scales).

The abovementioned shows, that in the course of processing gibbsitic bauxites at the temperature of ~150°C, there are no specific problems with titanium. In the processing of boehmitic bauxite (temperature of digestion ~210°C), high titanium content can create a number of process difficulties. In this context, investigation of Indian bauxites such as bauxite of Shiloli deposit can be of interest.

3. Shiloli Bauxite Deposit — Brief Information

In the years of 2000–2001 VAMI and Zaporozhye aluminium smelter (Ukraine) have carried out laboratory investigations of Indian bauxite from Shiloli deposit in order to determine amenability of this gibbsite-boehmitic high-titanium bauxite for processing at ZAIK.

The Shiloli bauxite deposit is located in Kolhapur administrative district of Maharashtra State at a distance of ~450 kilometers from the State capital — city of Bombay (Fig. 1) at an altitude between 300 and 350 meters above sea level.

The ore body is located on the top of a flat mountain. The deposit extends from the North to the South for ~2.5 kilometers. Its width is variable, averaging about 300 meters. The orebody is practically free from overburden (Fig. 2).

Thickness of bauxite orebody is about 8 meters. Bauxite occurs directly on basalt parent rocks.

The exploration of Shiloli bauxites and calculation of reserves have been carried out by a government organization — Geological Survey of India (GSI) in 1983–85. The estimated bauxite reserves of this deposit are about 12–14 million tonnes.

Results of investigation of chemical and mineral composition of composite bauxites samples taken by belt method at two different levels are shown in Table 1.

The above results show these bauxites to be of high quality (Silica Ratio $\mu_{\text{Si}} = 46\text{--}78$). But on the other hand, there are a few specific features to be noted:

- high content of titanium dioxide (TiO_2) up to 6,5 mass %, mainly in the form of anatase;
- comparatively high content of monohydrate minerals of alumina — mainly boehmite $\gamma\text{-AlO}(\text{OH})$ — up to 8.0 mass % and impurity of diasporite $\alpha\text{-AlO}(\text{OH})$ — up to 1 mass %;
- upper horizon bauxites have increased content of P_2O_5 — up to 0.42 mass %.



Figure 1 — Location of Shiloli bauxite deposit



Figure 2 — Typical view of Shiloli bauxite deposit in a dry season — bauxite and laterite come to the surface

Table 1 — Chemical composition of representative bauxite samples from Shiloli deposit

Sample	Content of main oxides, mass. %								
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	V ₂ O ₅	Cr ₂ O ₃	MnO	μSi
Depth 0–2 m	50,2	1,1	17,5	5,0	0,21	0,16	0,05	0,05	46
Depth 2–4 m	54,7	0,70	8,4	6,0	0,11	0,11	0,04	0,02	78
Composite, 0–4 m	52,7	0,93	13,0	5,6	0,16	0,14	0,05	0,04	57

Note: in all samples CaO <0,05 mass %; MgO <0,02 mass %; Na₂O <0,15 mass %; K₂O <0,15 mass %.

As the depth increases, the content of gangue and harmful impurities (SiO_2 , Fe_2O_3 , P_2O_5 , V_2O_5 , Cr_2O_3 and MnO) decreases, and Al_2O_3 content increases.

The only undesirable chemical element is TiO_2 , the content of which increases from 5 to 6 mass % as the depth increases.

Average boehmite content in Shiloli bauxite equals 6.3 mass % which shows that for complete extraction of alumina from this bauxite special process conditions are required (digestion temperature not less than 210°C , addition of lime, higher retention time at reaction temperature, higher rated caustic ratio of liquor after digestion, etc.).

In order to investigate special features of boehmite and TiO_2 behavior of these bauxites in the Bayer cycle and influence of the process parameters on them, laboratory tests have been carried out.

4. Digestion tests of Shiloli Bauxite

Process properties were investigated on a composite sample from the depth of 2-4 meters (obtained by blending of 4 individual samples), as it contained the maximum titanium oxide. The influence of the following factors on the parameters of Shiloli bauxites processing have been investigated:

- digestion temperature (varying from 150 to 230°C);
- dosage of lime (CaO act.) at the digestion stage — from 0 till 5 mass % (from the dry bauxite weight).

The digestion was carried out using industrial spent liquor from the Zaporozhye Aluminium Smelter (ZAIK, Ukraine) of the following composition (g/dm^3): Na_2O titr. — 259.0; Na_2O carb. — 21.1; Na_2O cst. — 237.9; Al_2O_3 — 120.1; SiO_2 — 0.98; TiO_2 — 0.0015; Caustic Ratio α_C — 3.26. The liquor was diluted keeping in mind the open steam heating of liquor at the Plant. Rated caustic ratio of liquid phase of digested bauxite slurry was 1.55.

Table 3 summarises results of Shiloli bauxite digestion at a retention time of 60 minutes.

The results of laboratory studies have shown the following.

- **Yield of Al_2O_3 .** At digestion temperature of 150°C alumina yield is low due to non extraction of boehmite. Extraction of alumina from boehmite starts at 210°C (Table 3). Further increase in the reaction temperature from 210 till 230°C is not effective.
- **Extraction of TiO_2 into liquor.** Digestion of Shiloli bauxite results in titanium oxide in the liquor increasing from 0.0015 till ~ 0.0035–0.0065 g/dm^3 (Fig. 3 and Table 3). If addition of lime is made at digestion, amount of TiO_2 in liquor decreases.
- **Specific Caustic Alkali Consumption.** Increase of digestion temperature results in increase of alkali consumption (100% NaOH) per 1 tonne of alumina (Fig. 4, Table 3). Increase of lime dosage for digestion leads to growth of specific alkali consumption

Table 2 — Mineral composition of representative bauxite samples from Shiloli deposit

Sample	Content of mineral, mass %									
	Gibbsite	Boehmite	Diaspore	Quartz	Kaolinite	Al-goethite		Hematite	Anatase	Rutile
						Content, mass. %	degree of isomorphous substitution, molar %			
Depth 0–2 m	base	7,3	0,7	0,2	1,9	19,1	15	3,2	4,1	0,9
Depth 2–4 m	base	3,8	1,0	traces	1,5	7,8	12	2,4	5,1	0,9
Composite, 0–4 m	base	6,3	0,9	0,2	1,5	13,4	15	3,0	4,6	1,0

Table 3 — Digestion of bauxite from Shiloli deposit

#	Conditions		Composition of liquors after digestion, g/dm^3							α_C	μ_{Si}	Na_2O	Yield of Al_2O_3		Red mud yield, t/t of Al_2O_3	Bauxite consumption, t/t of Al_2O_3	NaOH consumption, kg/t
	$^\circ\text{C}$	CaO , %	Na_2O titr.	Na_2O carb.	Na_2O cst	Al_2O_3	TiO_2	SiO_2	SiO_2				actual	after desilication			
1	150	0	249,5	21,9	227,6	229,5	0,0058	2,74	1,6	88	0,804	85,9	84,8	0,525	2,16	18,3	
2	150	1,5	251,1	21,9	229,2	234,1	0,0050	2,63	1,6	89	0,511	85,1	84,0	0,576	2,18	17,3	
3	150	3	250,5	21,7	228,8	229,5	0,0042	2,69	1,6	85	0,83	84,9	83,9	0,612	2,18	18,6	
4	150	5	250,5	21,4	229,1	233,6	0,0036	2,81	1,6	83	0,717	84,4	83,4	0,662	2,19	18,3	
5	210	0	245,9	22,5	223,4	236,2	0,0044	1,99	1,6	119	1,273	94,3	93,4	0,373	1,71	22,2	
6	210	1,5	247,4	22,5	224,9	240,7	0,0048	2,07	1,5	118	1,214	95,1	94,4	0,402	1,94	24,3	
7	210	3	245,9	21,4	224,5	238,3	0,0034	2,00	1,6	119	1,308	94,8	94,0	0,424	1,94	24,8	
8	210	5	241,7	21,3	220,4	236,0	0,0036	2,02	1,5	117	1,059	94,7	94,1	0,488	1,65	26,8	
9	230	0	245,9	22,5	223,4	238,9	0,0064	1,97	1,5	121	1,25	95,2	94,3	0,352	1,94	22,3	
10	230	1,5	247,4	22,5	224,9	238,3	0,0058	1,95	1,6	122	1,333	95,3	94,5	0,423	1,93	24,2	
11	230	3	248,0	23,5	224,4	236,2	0,0048	2,01	1,6	118	1,286	94,9	94,2	0,424	1,94	25,3	
12	230	5	243,2	19,6	223,6	238,3	0,0040	1,89	1,5	126	0,762	96,4	96,0	0,441	1,68	24,6	

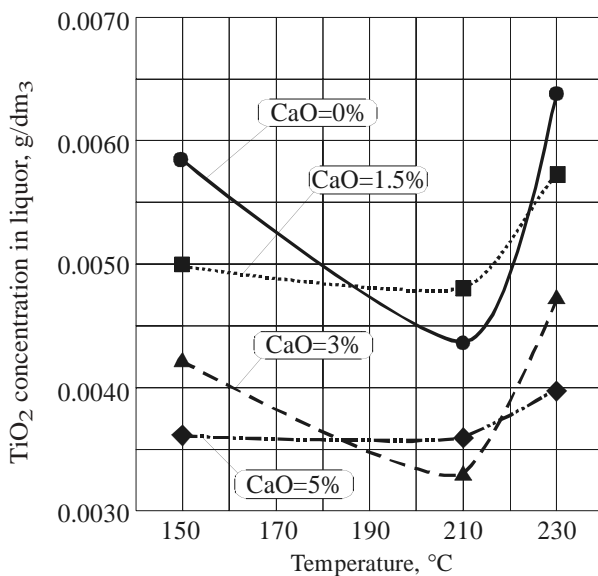


Figure 3 — Relation between TiO₂ content in the liquor (g/dm³) and temperature

due to formation of alkaline calcium hydroxo-titanates — hydrocassite, containing both Na₂O and Al₂O₃, as well as due to quartz decomposition with following DSP formation at 210–230°C. As temperature increases from 210°C to 230°C, no significant increase in alkali consumption is observed.

5. Conclusions

In connection with gibbsite-boehmitic bauxites from Shiloli deposit (Western Ghats, India), having TiO₂ content

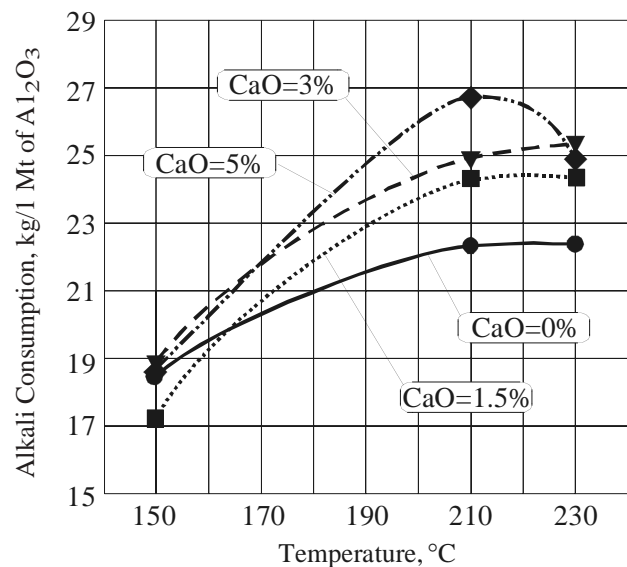


Figure 4 — Relation between specific alkali consumption (kgs per 1 Mt of Al₂O₃) and temperature

up to 6.5 mass %, solubility of titanium was studied in a wide temperature and concentration range. It is shown, that at proper processing conditions, content of titanium in liquors will be at expected levels for processing of gibbsitic bauxites and should not have any negative impact on quality and technical properties of aluminium.

Processing of such bauxites by indirect heat transfer in the autoclave is not recommended. Heating of bauxite slurry in the temperature range of 160–210°C should be performed by direct steam ejection into the bauxite slurry.