

PROCESSING OF LOW-QUALITY BAUXITE FEEDSTOCK BY THERMOCHEMISTRY-BAYER METHOD

O.A. DUBOVIKOV¹, E.E. JASKELAINEN²

¹ Saint-Petersburg Mining University, Russia

² Norilsk Nickel Harjavalta Oy, Finland

The modern production of aluminum which by its global output ranks first among the non-ferrous metals includes three main stages: ore extraction, its processing into alumina and, finally, the production of primary aluminum. Alumina production from bauxites, being the primary raw material in the alumina industry, is based on two main methods: the Bayer method and the sintering method developed in Russia under the lead of an academician Nikolay Semenovich Kurnakov. Alumina production by the Bayer's method is more cost effective, but has higher requirements to the quality of the bauxite feedstock. A great deal of research has been carried out on low quality bauxites focusing firstly on finding ways to enrich the feedstock, secondly on improving the combined sequential Bayer-sintering method and thirdly on developing new hydrometallurgical ways for bauxites processing. Mechanical methods of bauxite enrichment have not yet brought any positive outcome, and a development of new hydrometallurgical high alkaline autoclave process faced significant hardware difficulties not addressed so far.

For efficient processing of such low quality bauxite feedstock it is suggested to use a universal thermochemistry-Bayer method, which was developed in St. Petersburg Mining University under the lead of Nikolay Ivanovich Eremin, allows to process different substandard bauxite feedstock and has a competitive costing as compared to the sintering method and combined methods. The main stages of thermochemistry-Bayer method are thermal activation of feedstock, its further desilicization with the alkaline solution and leaching of the resultant bauxite product under Bayer's method. Despite high energy consumption at the baking stage, it allows to condition the low quality bauxite feedstock by neutralizing a variety of technologically harmful impurities such as organic matter, sulfide sulfur, carbonates, and at the same time to remove crystalline hydrate and free water. Subsequent desilicization of thermally activated bauxite with an alkaline solution allows to regrade it from low quality bauxites to feedstock suitable for processing by the Bayer method.

Key words: N.S. Kurnakov, N.I. Eremin, kaolinite, chamosite, bauxite deposits, bauxite, silicon module, thermal activation, desilicization of baked bauxite, bauxite concentrate, the Bayer's method.

How to cite this article: Dubovikov O.A., Jaskelainen E.E. Processing of low-quality bauxite feedstock by thermochemistry-Bayer method. *Zapiski Gornogo instituta*. 2016. Vol.220, p.668-674. DOI 10.18454/PMI2016.5.668

Introduction. The quality of bauxites is determined by a number of factors affecting the alumina production costs. As specific consumption of bauxite and caustic alkali depends on the content of aluminum and silicon oxides, abroad the quality of bauxites is assessed by the base number $B = \{Al_2O_{3(act.)} - (SiO_{2(act.)} + CO_2)\}$, where: $Al_2O_{3(act.)}$ and $SiO_{2(act.)}$ – is the percentage of soluble aluminum oxide and silicon dioxide.

Since this formula does not reflect the loss of alkali with red mud, the Hungarian researchers have proposed to assess the quality of bauxite using the formula based on the ratio $\{(C - C^{Na_2O})/Q_b\}$, where C is a constant; C^{Na_2O} – is the cost of the alkali lost with the red mud and; Q_b – is an amount of dry bauxite consumed per a ton of alumina [15].

N.N. Tikhonov proposed a complex criterion to assess the quality of bauxites [4], according to which the bauxite equivalent is equal to $Q_b k Q_a$. The correction factor k accounts for a difference in the cost of alkali and bauxite, and specific consumption of bauxite Q_b and alkali Q_a per a ton of alumina is equal respectively to: $Q_b = 99/(A_b \eta_f)$ и $Q_a = 990(Si_b h + 1.45S_b \eta_s + 0.14C_b)/(A_b \eta_f)$, where percentage of aluminum oxide in bauxite is – A_b ; of sulfur – S_b ; of silicon dioxides – Si_b and carbon – C_b , actual extraction of alumina from bauxite is – η_f ; of silicon dioxide – h and of sulfur – η_s .

The main indicator of the bauxite quality is the silicon module or weight ratio of aluminum oxide to silicon dioxide in the bauxite feedstock, but the mineral resources base shows tendency not only towards deterioration in bauxite feedstock quality, but also towards increase in extraction costs.

Last century Russia-based studies aimed at development of technology for alumina extraction from low-grade bauxites were carried out in the Mining Institute and the Russian Institute of Applied Chemistry under the general lead of Nikolay Semenovich Kurnakov, an academician and a Professor of the Mining Institute. On September 14, 1929 the USSR Government for determining the final scope of aluminum production accepted recommendation given by N.S. Kurnakov to proc-

ess bauxites at Volkhov Aluminum Plant using Muller-Yakovkin-Lileev's sintering method and at Dnepr Aluminum Plant using Kuznetsov-Zhukovsky's method, proposed by A.N. Kuznetsov, Professor of the Mining Institute, and by his associate E.I. Zhukovsky.

At present within the umbrella of one of the leading research schools of the Mining University the studies once held under the lead of Nikolay Ivanovich Eremin, the Head of the Light and Rare Metals Department in the Mining Institute, for enrichment of low quality bauxite feedstock, whose idea was to use the processes of thermal stimulation and subsequent selective leaching, allowing for targeted changes in chemical and mineralogical composition of bauxites and giving a possibility to process the resultant concentrates by conventional alkaline methods.

The quality of Bayer's bauxites in the first approximation is determined based on silicon module μ_{Si} , according to which theoretical alumina extraction by the Bayer's method is equal to $[(\mu_{Si} - 1) / \mu_{Si}] 100\%$ provided that total silicon dioxide present in the bauxite is fixed in the sodium hydroalumosilicate (SHAS) composed of $Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \cdot nH_2O$. In case of high concentrations of silicon dioxide in the bauxite it will be converted into the production wastes, i.e. the red mud in the form of SHAS, thus leading to high losses of alumina and alkali. After desilicization of the low-grade bauxites, the latter can be processed by the Bayer's method with recovery of not only alumina, but of a whole range of by-products based on silicon dioxide.

The use of mechanical beneficiation methods for increasing the silicon module depends on chemical and mineralogical properties of the processed feedstock. In some instances the Bayer's concentrate was received with Al_2O_3 recovery rate of 50÷70% and the concentrate yield of 60÷70%. Therewith inevitably the high-silicon product of low quality is produced with: $\mu_{Si} = 1.5 \div 2.5$, a while the amount of alumina entrained reaches 30÷50%.

Microbiological methods help to improve the quality of bauxites to some extent, but their industrial application due to the long process time at current stage is highly problematic [5].

Bauxite deposits. The main Russian fields with high concentration of the bauxites are: North Ural bauxite district, Timanskaya bauxite area Severoonezhsky bauxite district, Belgorod region, Krasnoyarsk region (see Figure 1) [3].

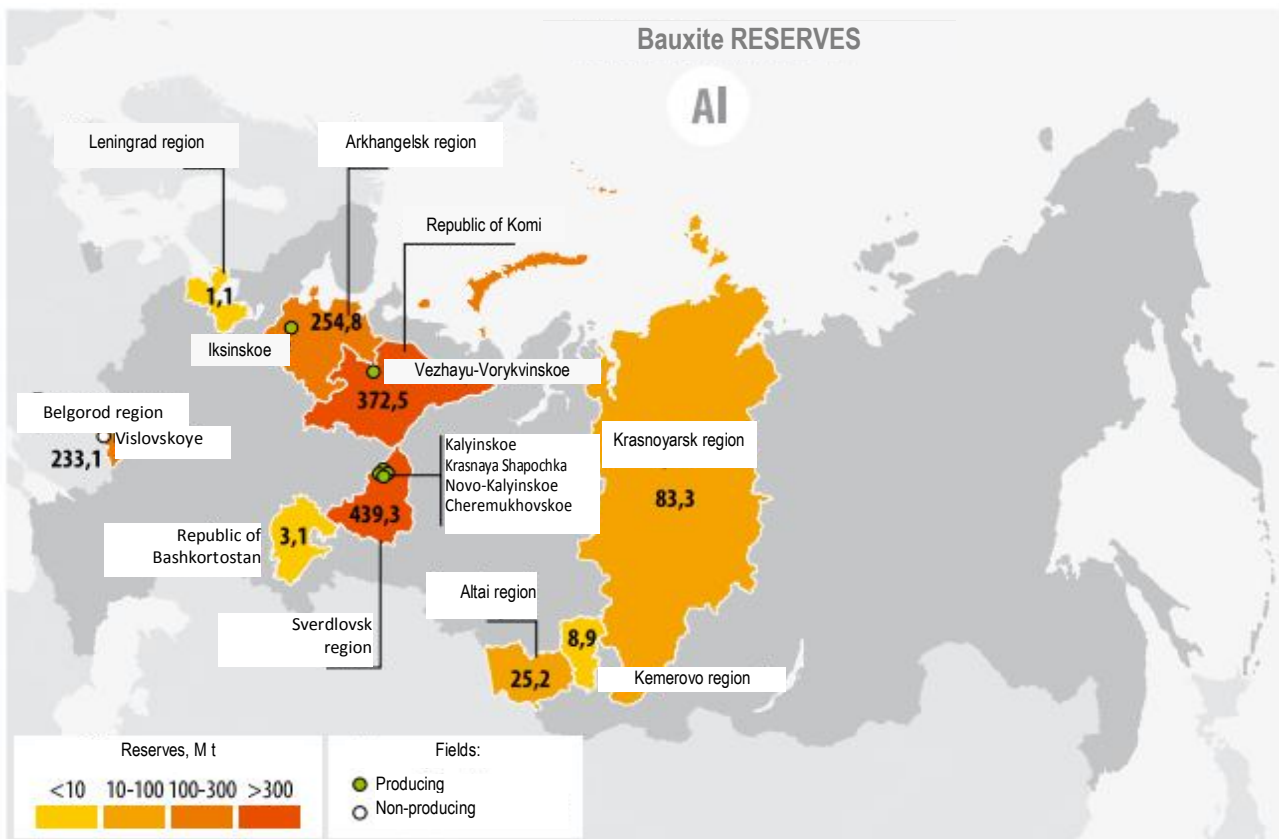


Fig. 1. Main bauxite fields, distribution of bauxite reserves and inferred resources (mln t) across constituent territories of the Russian Federation

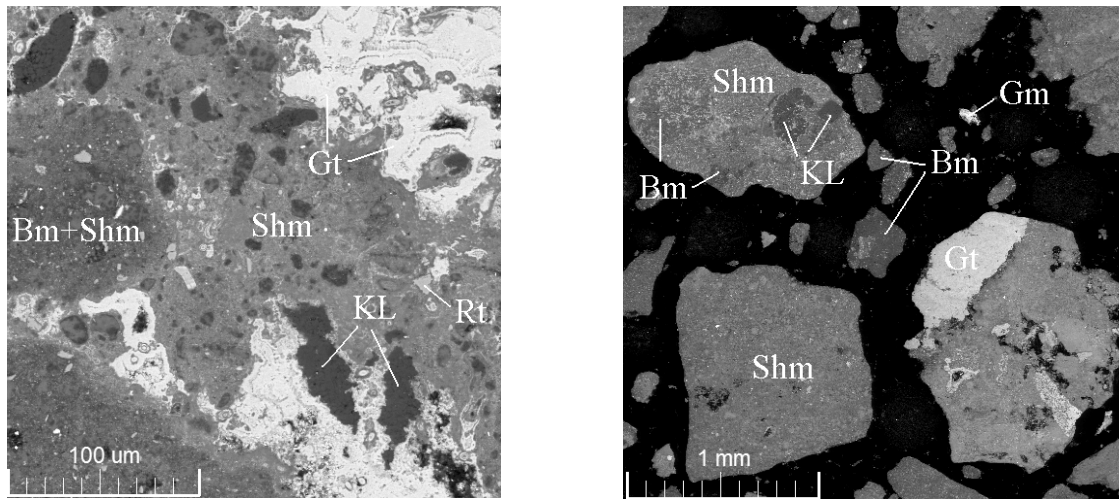


Fig.2. Bauxite of Vezhayu-Vorykviskoye field at different scale

Bm – boehmite / diaspore, Shm – chamosite, KL – kaolinite, Rt – rutile, Gt – goethite, Gb – gibbsite, Gm – hematite

About 26 % of the Russian bauxite reserves are concentrated in Timanskaya Bauxite Area (Republic of Komi). These are Vezhayu-Vorykviskoye field and fields Verkhne-Schugorskoye and Vostochnoye [12]. The bauxites in this area are highly ferrous and have silicon module from 3 to 6. Certain processing challenges are faced due to presence of sulfur in the form of pyrite. The bauxites are located close to the surface and can be extracted by open cast mining. The inferred resources of Timansk bauxite area comprise around 40 mln t.

Vezhayu-Vorykviskoye field is located in the area of Vorykva and Vezhayu rivers. Thickness of ore layers within the field varies from 1.0÷1.5 to 30÷32 m. The depth of ore deposits varies in range from 0.2÷0.5 to 132 m. The material composition of bauxites is as follows (% wt): SiO₂ 8.8-19; Al₂O₃ 41-48; Fe₂O₃ 21.9-29.8; FeO 3.5-7.4; TiO₂ 2.4-3.2; CaO 0.07-0.9; other impurities 11,6÷12,5. High content of rare metals Nb₂O₅ (0.005-0.009 %) and Ta₂O₅ (0.0003 %) has also been recorded. The main minerals are boehmite, kaolinite, chamosite and hematite (Figure 2). The field's bauxites belong to the industrial boehmite type.

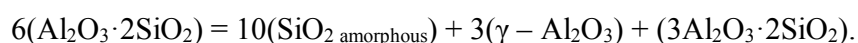
Vostochnoye field is located to the east of Vezhayu-Vorykviskoye field and is virtually its continuation. The bauxite deposits of Vostochnoye field are at the depth from 78 to 400 m, layer thickness varies from 1.5 to 46 m. The average composition of bauxites is as follows (% wt): Al₂O₃ – 50.26; SiO₂ – 7.39; Fe₂O₃ – 27.8; TiO₂ – 2.6. Also high content of rare metal and rare earth elements is recorded: Nb₂O₅ (up to 0.0093 %), Ta₂O₅ (0.0002 %); Ga (up to 100 g/t); Sc (up to 120 g/t); V (up to 630 g/t). The minerals present include boehmite, diaspore, kaolinite, chamosite and hematite. Bauxites are of boehmite and diaspore-boehmite type.

The Verkhne-Schugorskoye field is located to the north-west from the Vezhayu-Vorykviskoye field, upstream the Schugor river. Deposit thickness varies from 0.4 to 50 m. Concentration of Al₂O₃ is 49.76 %, of SiO₂ is 6.61 % and of Fe₂O₃ is 28.03 %. The main minerals are boehmite, diaspore, kaolinite and hematite. The industrial type – monohydrate boehmite bauxites.

The main silicious minerals of Timanskaya bauxite area are kaolinite and chamosite.

Kaolinite behavior during bauxite processing by thermochemistry-Bayer method. The process of thermochemical desiliconization of kaolinite feedstock relies on the kaolinite ability to disintegrate at temperatures higher than 900 °C into aluminosilicate with silicon dioxide content lower than in kaolinite and amorphous free silicon dioxide, well soluble in alkaline solutions [1, 2, 6, 8-10].

Along with the X-ray diffraction and crystal optical analysis techniques N.I. Eremin in order to examine the mechanism of kaolinite thermal activation used a simple and reliable chemical method. It was demonstrated that the products of kaolinite baking at 925÷1000 °C are amorphous SiO₂, γ-Al₂O₃ and mullite with almost even quantitative distribution of the aluminum oxide between them according to the reaction and the graphic interpretation (Figure 3):



Thus in theory it is possible that silicon dioxide extraction through the process of baked kaolinite desiliconization may be beyond 80 %.

Chamosite behavior during bauxite processing by thermochemistry-Bayer method. While kaolinite behavior during thermal treatment was crystal clear, a question of chamosite thermal transformations remained understudied. Chamosite behavior ($\text{Fe}^{2+}, \text{Fe}^{3+}$) $_3 \cdot [\text{AlSi}_3\text{O}_{10}] \cdot (\text{OH})_2 \times \{(\text{Fe}, \text{Mg})_3(\text{O}, \text{OH})_b\}$ within the scope of thermochemistry-Bayer method to a large extent depends on process parameters [7, 11, 13, 14]. Research samples with different level of oxidation and different orthogonal to monoclinic modifications ratio were taken from the Belgorod territory of the Kursk Magnetic Anomaly (Table 1).

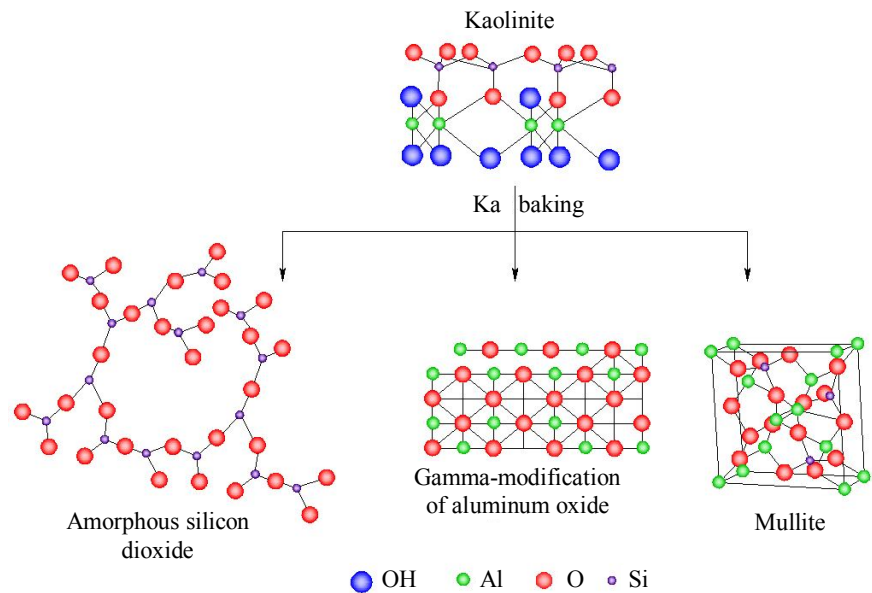


Fig.3. Graphic interpretation of kaolinite thermal decomposition

Table 1

Material composition of chamosite

Sample N	Concentration, %							Oxidation*	Modifications ratio (O/M)**
	Other impurities	A ₂ O ₃	SiO ₂	Fe ₂ O ₃	FeO	R ₂ O	TiO ₂		
1	8.08	18.26	15.30	54.56	29.61	0.16	1.19	0.46	2.1
2	15.58	31.75	26.00	21.40	8.43	0.25	1.96	0.61	2.0
3	10.52	23.72	22.40	39.10	23.30	0.20	0.61	0.40	9.0

* Level of oxidation $(\text{Fe}_2\text{O}_3 - \text{FeO}) / \text{Fe}_2\text{O}_3$; ** (O/M) – orthogonal / monoclinic.

Based on the results of the X-ray phase analysis the examined chamosite samples belong to kaolinite type, as there is no diffraction peak corresponding to the interplanar distance $d = 1.4$ nm, characteristic of chlorites. In radiographs of all initial samples the basic chamosite reflexes are seen: $d = 0.7$; 0.35 ; 0.25 ; 0.24 nm. It was also found that samples contain hematite ($d = 0.369$ nm), the samples 2 and 3 contain kaolinite ($d = 0.712$; 0.443 ; 0.356 nm), the samples 1 and 3 contain small amounts of siderite ($d = 0.279$ nm), the sample 2 contains gibbsite ($d = 0.483$ nm) and quartz ($d = 0.334$ nm).

Difference in correlation between reflection intensities, especially as concerns reflexes corresponding to interplanar distances $d = 0.251$ nm and $d = 0.240$ nm, is associated with different ratio of orthogonal to monoclinic forms of chamosite mineral across the samples. Reflection typical for the orthogonal form is $d = 0.251$ nm, while for the monoclinic one it is $d = 0.240$ nm. In order to compare intensities of reflections $d = 0.251$ nm and $d = 0.240$ nm the X-ray phase analysis results were presented in the form of line diagrams, where lines correspond to the height of peaks in the diffraction pattern as compared to the spectral background. Correlation between intensities of the said reflections is proportional to the ratio of forms in the sample. At $I_{d=0.240} > I_{d=0.251}$ the monoclinic form is predominant, while at $I_{d=0.240} < I_{d=0.251}$ the dominating form is orthogonal. Как правило, ортогональная форма преобладает в шамозите. Diffraction peaks 0.7 ; 0.35 nm are typical for both structural forms.

Thus by comparing correlation between reflection intensities $I_{d=0.251} / I_{d=0.240}$ for samples № 1; 2; 3 respectively we obtained the following reflection intensity ratios: 2.1; 2.0; 9.

Chamosite samples were crushed to a particle size of minus 0.147 mm. Then some of them were baked. Diffraction patterns of initial and baked chamosite are shown in Fig.4.

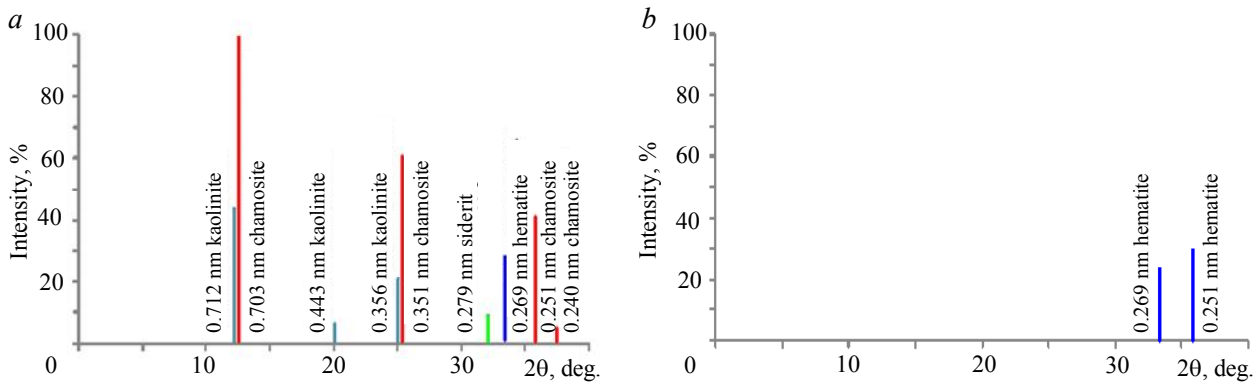


Fig.4. Typical line diagram of chamosite before (a) and after baking at temperature 600°C (b)
 $d = 0,251$ nm – orthogonal form, $d = 0,240$ nm – monoclinic form

Then initial and baked chamosite samples underwent leaching with different process parameters (Table 2).

Table 2

Composition of leaching products

Baking, °C	Leaching conditions: Temperature °C, Na ₂ O _K г/л and α _K	Content in leaching residuals, %					Na ₂ O	Na ₂ O* SiO ₂ Moles
		Other impurities	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	FeO		
<i>Sample 1</i>								
Not baked	95 °C, 150 g/l	8.80	17.51	14.60	53.55	20.64	1.25	0.080
400	95 °C, 150 g/l	4.75	18.83	16.00	59.02	9.12	1.30	0.080
600	95 °C, 150 g/l	8.11	15.12	14.40	56.54	1.68	5.80	0.390
<i>Sample 2</i>								
Not baked	80 °C, 150 g/l	–	28.00	26.40	22.50	15.10	1.40	0.051
Not baked	80 °C, 150 g/l и 3,5	–	28.70	27.00	23.20	15.43	1.00	0.001
Not baked	95 °C, 150 g/l	11.96	27.56	26.20	21.58	14.36	6.30	0.230
400	95 °C, 150 g/l	12.20	27.75	26.00	21.70	7.90	6.30	0.230
600	95 °C, 150 g/l	13.06	21.93	24.40	20.58	2.88	12.00	0.480
<i>Sample 3</i>								
Not baked	95 °C, 150 g/l	6.56	22.14	22.40	40.55	25.75	0.65	0.030
400	95 °C, 150 g/l	8.22	23.12	23.40	41.30	11.52	2.56	0.100
600	95 °C, 150 g/l	11.10	21.65	20.00	36.08	3.84	8.00	0.390

* Upon chamosite decomposition and emergence of SHAS composed of Na₂O:Al₂O₃:SiO₂ = 1:1:(2÷2.4) Molar ratio Na₂O/SiO₂ is equal to (0.50÷0.42)

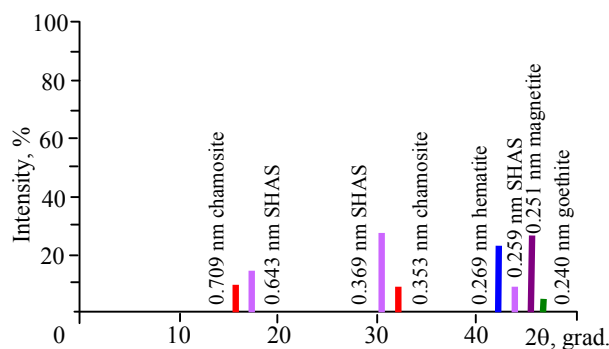


Fig.5. Line diagram for leaching products of sample 3 baked at 600°C

X-ray diffraction analysis of leaching products (Figure 5) has revealed that the main products are SHAS having the following molecular ratio Na₂O:Al₂O₃:SiO₂ = 1:1:(2÷2.4), and ferrous minerals.

Degree of decomposition, one of indicators of which is Na₂O to SiO₂ ratio in solid phase, for samples baked at 600 °C and leached at 95 °C is higher than even after the samples processing in autoclave conditions without prior baking, which made it possible to make the graphical interpretation of chamosite thermal decomposition (Figure 6).

Simultaneously with thermal transformations of aluminosilicates during bauxite baking, alumina-containing phases also undergo changes. According to literature sources, the phase transition temperatures either in the process of thermal decomposition of aluminosilicates or in the course of aluminum oxide transformations depend on several factors, including the heat treatment conditions, degree of material dispersion, presence of solid and gaseous mineralizers [11].

Thermochemical conditioning of bauxites from Vezhayu-Vorykvinskoye field. In-process monitoring of bauxite baking conditions was performed with the simplest and most informative chemical method.

With increase in the baking temperature for bauxite from Vezhayu-Vorykvinskoye field a more drastic desiliconization is observed. A short flat segment in the area of 500÷800 °C can be explained by the presence of chamosite in these bauxites and by its thermal decomposition, resulting in the emerged amorphous free oxides of aluminum and silicon freely passing into the alkali solution. This is also proven by the fact that the flat segment in the silicon dioxide extraction curve coincides with that of the aluminum dioxide.

Further increase in the degree of baked bauxite desiliconization is attributable to thermal decomposition of metakaolinite emerged from kaolinite, while decrease in aluminum oxide extraction rate is due to its polymorphic transformations, making it more inert to alkaline solutions.

The longer thermal exposure during baking after the set temperature is reached produces the same effect as when the temperature is increased (Figure 7). This is evidenced by the relative position of dots (unshaded and shaded dots stand respectively for no exposure and an hour-long exposure to the set temperature). But the effect is minor.

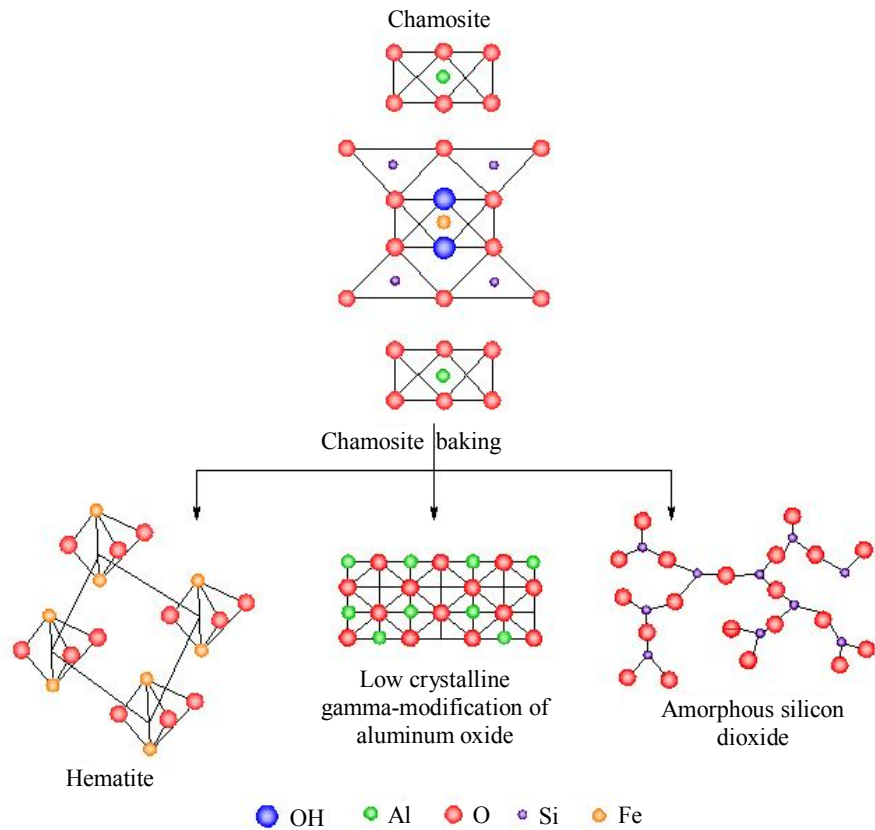


Fig.6. Graphic interpretation of chamosite thermal decomposition

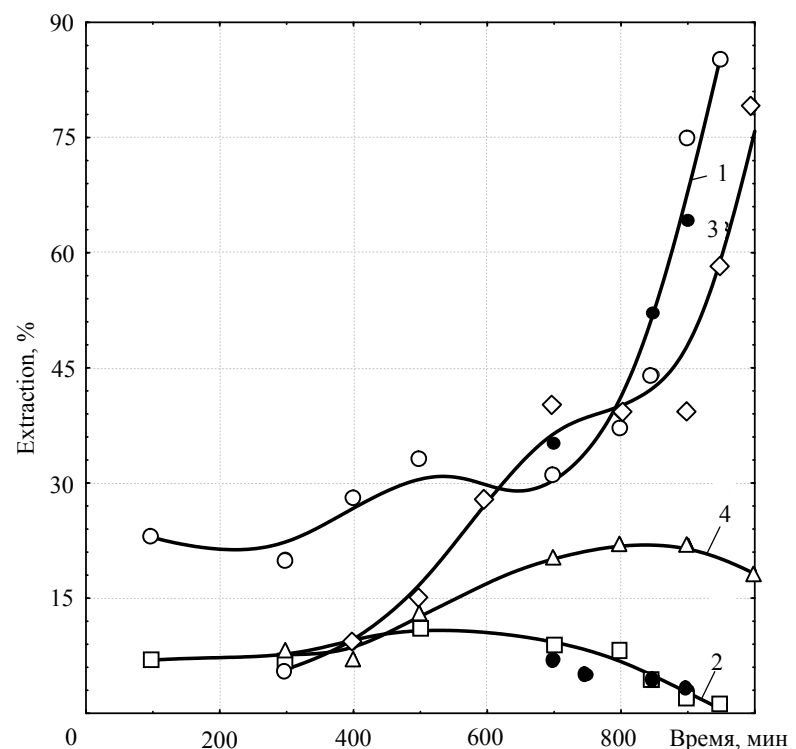


Fig.7. Extraction of SiO₂ (1, 3) and Al₂O₃ (2, 4) from bauxites with modules: $\mu_{Si} = 5.06$ (1, 2) and $\mu_{Si} = 2.27$ (3, 4) depending on the baking temperature



Conclusions. Examination of behavior of the main siliceous minerals during thermochemical conditioning of the low quality bauxites resulted in a number of valuable scientific findings:

- chemical conditioning of bauxite not exposed to baking, based on dissolution of hydrous silicates and aluminosilicates in alkali and aluminate solutions, is efficient, but only for the bauxites with a silicon module greater than 5 and containing a limited amount of impurities technologically detrimental to the Bayer's process, such as organic substances, carbonates and sulfides;
- the thermochemistry-Bayer's method shall be recognized as energy intensive, yet universal;
- the products of kaolinite baking at 925÷1000°C are amorphous SiO₂, γ-Al₂O₃ and the mullite, which make it possible to recover from the baked kaolinite to the alkali solution of more than 80 % SiO₂;
- degree of chamosite decomposition upon interaction with alkali and aluminate solutions depends on the ratio of its polymorphic modifications and level of its oxidation: 1) higher level of oxidation leads to higher structural disorder, while orthogonal modification manifests higher resistance in the alkali solutions; 2) chamosite baking at temperature above 600 °C levels down these differences due to chamosite decomposition and emergence of amorphous oxides of aluminum and silicon;
- a dependency has been revealed between the desiliconization intensity of thermally activated bauxites and the temperature of their baking.

More than a dozen of invention certificates and patents of the Russian Federation have been obtained for the technologies and technical solutions developed in the Mining University for the processing of low quality bauxite feedstock by thermochemistry-Bayer method.

REFERENCES

1. Brindli G.V., Nakakhira M. Reaction Series Kaolinite-Mullite. Issues of Clay Mineralogy. Moscow: Inostrannaya literatura, 1962, p.90-135 [in Russian].
2. Budnikov P.P., Keshimyan T.N., Volkova A.V. Studies of the Effect of Small Admixtures on the Kinetics of Mullite Formation Process at Low Temperatures. Zhurnal prikladnoi khimii. 1963. N 5, p.1064-1068 [in Russian].
3. State Report on Condition and Use of Mineral Resources in the Russian Federation in 2013. 2014. Available at: <http://www.mnr.gov.ru/upload/iblock/914/Report2014.pdf> [in Russian].
4. Dubovikov O.A., Sizyakov V.M. Efficient Processing Technologies for Low Quality Bauxites. Natsional'nyi mineral'no-syr'evoi universitet «Gornyi». St. Petersburg. 2012, p.195 [in Russian].
5. Dubovikov O.A., Andreev E.E., Nikolaeva N.V. Microbiological Conditioning of Bauxites. Obogashchenie rud. 2011. N 5, p.19-23 [in Russian].
6. Dubovikov O.A., Nikolaeva N.V. Mathematical Description of Kaolinite Decomposition with Alkali Solutions. Zapiski Gornogo instituta. 2011. Vol.192., p.73-76 [in Russian].
7. Dubovikov O.A., Nikolaeva N.V. Chamosite Behavior in the Process of Chemical and Thermochemical Conditioning. Zapiski Gornogo instituta. 2011. Vol.192, p.49-53[in Russian].
8. Eremin N.I., Erusalimskii M.I. Examination of Kaoline Thermal Transformations by Chemical Method. Zhurnal prikladnoi khimii. 1969. Iss.42. N 3, p.497-501[in Russian].
9. Kalinina A.M. High-Temperature Transformations of Synthetic Kaolinite. Zhurnal neorganicheskoi khimii. 1963. Iss.12. N 8, p.2675-2684 [in Russian].
10. Kalinina A.M. On Transformations of Synthetic Kaolinite upon Heating. Khimiya i tekhnologiya glinozema. NTI SNKh. Erevan, 1964, p.63-80 [in Russian].
11. Sizyakov V.M., Dubovikov O.A., Nikolaeva N.V. et al. On the Role of Mineralizing Additives in the Processes of Alumina Phase Transformations. Zapiski Gornogo instituta. 2013. Vol.202, p.48-56 [in Russian].
12. Plyakin A.M., Belyaev V.V. Solid Minerals in Timan: Handbook. UGTU. Ukhta, 2005, p.92 [in Russian].
13. Sizyakov V.M., Dubovikov O.A., Nikolaeva N.V. et al. Preparation of Bauxites for Exploring the Possibility of Red Mud Processing for Application in Iron and Steel Industry. Tsvetnye metally. 2013. N 2, p.57-62 [in Russian].
14. Sizyakov V.M., Dubovikov O.A., Loginov D.A. Theory and Practice of Thermochemical Beneficiation of Low Quality Bauxites. Obogashchenie rud. 2014. N 5, p.10-17[in Russian].
15. Zambo J. Bauxitoh kavasavtartalmanah esohhentese aluminatlugos heselfessel. Femipari kutato int koze. 1960. Vol.4, p.57-63.

Authors: O.A. Dubovikov, Dr. of Engineering Sciences, Senior Researcher, dubovikov_oa@mail.ru (Saint-Petersburg Mining University, Russia), E.E. Jaskelainen, Dr. of Engineering Sciences, Professor, eduard.jaskelainen@nornik.fi (Norilsk Nickel Harjavalta Oy, Finland).

The paper was accepted for publication on 13 September, 2016.