BR09 - Technology of Scandium Oxide Production from Bauxite Residue

Alexander Suss[1], Alexander Kozyrev[2], Natalia Kustensova[3], Alexander Damaskin[4], Sergey Pishchalnikov[5], Andrey Panov[6], Sergey Ordon[7] and Oleg Milshin[8]
1. Department Director
2. Chief Researcher
3. Senior Researcher
4. Chief Researcher
6. Director R&D Alumina
7. Deputy Director General (Alumina & Ecology)
RUSAL Engineering and Technology Center, Saint Petersburg, Russia
5. Project Manager
RUSAL Engineering and Technology Center, Krasnoturinsk, Russia
8. Project Group Manager
RUSAL Management, Moscow, Russia
Corresponding author: Aleksandr.Suss@rusal.com

Abstract

Bauxites in the North of European Russia (i.e. North Urals bauxites – SUBR, Middle Timan bauxites – STBR, North Onega bauxites – SOBR) are characterized by a high scandium content (up to 350 ppm calculated as Sc_2O_3). Most of scandium is isomorphically embedded into the structure of aluminum-containing minerals (boehmite and diaspore), as well as into zircon $ZrSiO_4$ and apatite. These minerals break down during the pressure digestion of the bauxites, so scandium is re-precipitated in form of oxyhydroxide ScO(OH) and sorbed on the surface of bauxite residue particles. UC RUSAL has develop and pilot tested the extraction of scandium oxide from bauxite residue using a sodium bicarbonate solution that enables to dissolve up to 50 % of scandium into the solution followed by precipitation of the concentrate and purification to obtain 99.0 % Sc_2O_3. The extraction uses actual liquors from alumina production and flue gases. SUBR and STBR bauxites contain a number of REM elements (e.g. zircon, titanium, hafnium, copper, yttrium, thorium, etc.). Chemical behaviour of said REMs during the sodium bicarbonate digestion is similar to the behaviour of scandium. To obtain pure scandium oxide (2N) ($Sc_2O_3 \geq 99.0$ wt.%) without radioactive impurities effective purification of Sc-containing concentrate was developed. The entire process does not use any technologies, which are not applied in alumina production (sorption, extraction, multiple-stage hydrolysis, etc.), therefore, it can be integrated into the Bayer process, as all intermediate products and tailings are recycled into the main process. Moreover, resulting mutual neutralization of some streams allows obtaining a high-grade REM concentrate. Scandium oxide can be produced with minimal operational costs and high total recovery of scandium. The additional advantage of this process lies in reducing the carbon footprint of alumina production due to the use of flue gases containing up to 8 vol.% CO_2, as well as alkali neutralization in the bauxite residue.

Keywords: Scandium oxide, Bauxite residue, Yttrium, Thorium, REM, Neutralization, Carbon footprint.

1. Scandium, Yttrium, REMs, etc. in Bauxites from the North of Russia and their Behaviour in the Bayer Process

RUSAL's Bogoslovsky Alumina Refinery (BAZ refinery) processes ≈ 85:15 mixture of diasporic bauxites from the North Urals deposit (SUBR bauxite) and boehmitic bauxites from the Middle-

Timan deposit (STBR bauxite) at a digestion temperature of 230÷235 °C and residence time of ≈ 2 hours and high caustic soda concentration.

Under such severe digestion conditions almost all bauxite rock-forming minerals decompose (including boehmite, diaspore, kaolinite, chamosite, al-goetite, anatase, rutile, pyrite, calcite, zircon, etc.). The only mineral that is not altered is hematite, which contains approx. 30 % of scandium that could not be extracted by using sodium bicarbonate digestion. Bauxite residue (BR) contains the following phases:

- sodium hydroalumosilicate (DSP) of sulfate-cancrinite type with general formula $Na_6Ca[AlSiO_4]_6(SO_4)\times1.7H_2O$;
- calcium hydrogarnet (HG) represented by formula $Ca_3(Al,Fe)_2[SiO_4]_{1.4}\times(OH)_{9.2}$;
- perovskite with the formula $CaTiO_3$.

Scandium and a number of other impurities demonstrate the following behaviour.

1.1 Scandium

Due to specific conditions of the bauxite formation in the North of the European Russia, scandium is present in boehmite and diaspore, which act as so-called geochemical traps. Over 50 % of scandium is isomorphically bonded in the structure of two polymorphic aluminium oxyhydroxides, i.e. diaspore and boehmite (γ- и α-AlO(OH)) [1].

Some references discuss several polymorphic modifications of scandium oxyhydroxide, including γ-ScO(OH) and α-ScO(OH), which are similar to boehmite and diaspore [2] (see Table 1).

Table 1. Structural characteristics of Sc, Y, Al and Fe hydroxides, oxyhydroxides and oxides.

#	Formula/mineral phase	Crystal system	Unit cell parameters, Å		
			a	b	c
1	$Sc(OH)_3$	hexagonal	5.84	5.84	3.45
2	$Sc(OH)_3$	cubic	7.88	7.88	7.88
3	γ-ScO(OH)	rhombic	4.02	13.04	3.24
4	ScO(OH)	tetragonal	5.23	5.23	5.05
5	α-ScO(OH)	rhombic	4.76	10.30	3.21
6	$Sc_2O_3\cdot0.2H_2O$	cubic	9.82	9.82	9.82
7	$Sc_2O_3\cdot1.3H_2O$	cubic	9.82	9.82	9.82
8	Sc_2O_3	monoclinic	13.36	3.22	8.06
9	Sc_2O_3	hexagonal	3.39	3.39	5.66
10	Sc_2O_3	cubic	9.79	9.79	9.79
11	$Y(OH)_3$	hexagonal	6.26	6.26	3.54
12	YO(OH)	monoclinic	4.28	3.63	6.05
13	α-$Y(OH)_3$	monoclinic	6.25	6.01	15.40
14	Y_2O_3	hexagonal	3.66	3.66	5.92
15	Y_2O_3	monoclinic	14.12	3.52	8.69
16	Y_2O_3	rhombic	5.71	3.20	12.16
17	Y_2O_3	cubic	5.26	5.26	5.26
18	$Al(OH)_3$ (gibbsite)	monoclinic	8.54	5.07	9.72
19	$Al(OH)_3$ (bayerite)	monoclinic	5.06	8.67	4.71
20	γ-AlO(OH) (boehmite)	rhombic	3.09	12.24	2.86
21	α-AlO(OH) (diaspore)	rhombic	4.40	9.39	2.83
22	γ-FeO(OH) (lepidocrocite)	rhombic	3.86	12.50	3.06
23	α-FeO(OH) (goethite)	rhombic	4.61	9.96	3.02
24	γ-Fe_2O_3 (maghemite)	cubic	8.32	8.32	8.32
25	α-Fe_2O_3 (hematite)	rhombic	4.91	4.91	13.26

Restricted isomorphism between goethite and diaspore FeO(OH) - AlO(OH) is well studied. Isomorphous substitution of Al to Fe in al-goetite is equal to up to 34 mol. %. Isomorphous substitution of Fe to Al in ferric diaspore does not exceed 5 mol. % [3]. Therefore, it can be suggested that restricted isomorphism occurs between scandium and aluminium in diaspore and boehmite. Scandium oxyhydroxide is supposed to enter the structure of boehmite and diaspore during the metasomatic changes of these bauxites. In course of time SUBR bauxites underwent a number of alterations, i.e. chloritization, siderite generation, deferrization, pyritization, calcitization, etc. [4] One of these processes resulted in scandium embedding boehmite and diaspore structure. SUBR, STBR, and SOBR bauxites have only one common metasomatic process, i.e. chloritization (transformation of kaolinite to form chamosite (type $(Mg,Fe^{+2})Al[Si_3AlO_{10}](OH)_6{\times}nH_2O$)). It is suggested, therefore, that scandium embedding into aluminium oxyhydroxides is associated with this very process. In other bauxite regions with fewer alteration processes, boehmite and diaspore did not accumulate scandium in such geochemical traps. Consequently, it is concluded that scandium embedded into the structure of alumina-bearing minerals is a typical feature of SUBR and STBR bauxites.

In the Bayer process at a pH of >> 14, boehmite and diaspore are digested and scandium dissolves; however, due to the large amount of sodium aluminate in the liquor, scandium demonstrates low solubility and precipitates mainly in form of scandium oxyhydroxide ScO(OH) on the surface of the bauxite residue (BR) [5].

Simulation of the pressure digestion of hematite with hydroxides of scandium, yttrium, zirconium, titanium, REMs under the conditions of BAZ refinery showed that 99 % of scandium precipitates on the surface of hematite, mainly in form of γ-ScO(OH), and $Y_3ScFe_4O_{12}$ forms [6]. In the Bayer process yttrium predominantly precipitates in form of $Y(OH)_3$, that is why no solid solutions were detected between ScO(OH) and YO(OH).

Scandium dissolves only within the following two pH ranges:

- in acidic medium from a pH of << 0 up to a pH of ≤ 4.5;
- in alkaline medium comprising a mixture of soda and sodium bicarbonate from a pH of ≥ 7.5 to a pH of ≤ 12.

In the sulfuric acid medium at a pH ranging from 4.5 to 7.5 and depending on the cationic composition of the liquor, scandium can form two compounds. At a high sodium content and at a low sodium content scandium forms double salt $Na_2SO_4{\times}Sc_2(SO_4)_3{\times}5H_2O$ and basic scandium sulfate $Sc(OH)SO_4$ respectively.

1.2 Yttrium

At BAZ refinery the bauxite residue from processing SUBR bauxite contains 2.8÷3.3 more yttrium as compared with Sc_2O_3, i.e. the amount of yttrium is 330÷450 ppm (in terms of metal).

Yttrium adjoins scandium in Group three of the Periodic table; therefore, they possess similar chemical properties and form similar phases (see Table 1). Geochemistry of yttrium in SUBR and STBR bauxites is not well studied, but it can be assumed that yttrium is also associated with zircon, boehmite, diaspore, apatite, and hematite. It is demonstrated that yttrium and scandium are present in metamict (amorphized) grains of zircon $ZrSiO_4$, where yttrium content measures up to 16 % [7].

As it has been mentioned, during the pressure digestion in the Bayer process yttrium forms mainly oxyhydroxide YO(OH) and complex oxide $Y_3ScFe_4O_{12}$. Incomplete extraction of scandium during the sodium bicarbonate digestion can be attributed to the presence of this complex oxide.

1.3 Copper

Copper in the BR from processing SUBR bauxite is associated with sulfide mineral composition of this bauxite, in which it is represented by following two minerals:

- up to 3 % of pyrite (FeS_2), which comprises copper in form of an isomorphic impurity;
- occasional grains of chalcopyrite $CuFeS_2$ [3].

During the pressure digestion chalcopyrite and pyrite decompose and in strong caustic alkali copper forms insoluble copper hydroxide $Cu(OH)_2$ that remains in the BR solids. During the washing copper hydroxide partially reacts with soda in the wash water to form copper carbonate $Cu_2CO_3(OH)_2$. Both compounds are soluble in the sodium bicarbonate digestion at a pH of 9.5±0.5, therefore, copper and scandium dissolve into the product liquor. When Sc-containing product liquor is digested with an alkaline aluminate solution, copper reacts to form $Cu(OH)_2$ or $Cu_2CO_3(OH)_2$ and precipitates with primary Sc-containing aluminium hydroxide.

1.4 Zirconium

Zirconium is present in bauxites in form of zircon $ZrSiO_4$, which binds up to 15 % of scandium, as well as yttrium. During the pressure digestion almost all zircon decomposes excluding large strong crystals. Resulting hydrated zirconium oxide $ZrO_2 \times nH_2O$ is not soluble in caustic alkali and, consequently, sorbed on the BR particles. Scandium and yttrium, which are released from zircon, are also sorped on the BR surface.

1.5 Thorium and other REMs

Rare-earth metals adjoin scandium in Group three of the Periodic table, therefore they demonstrate similar chemical properties. During the pressure digestion almost all REMs are disposed with the bauxite residue. The bauxite residue from processing SUBR and STBR bauxites contains a high amount of middle (from samarium to lutecium) REMs. They are the most valuable REMs but their extraction is not viable due to their low content in BR.

Thorium is associated with zircon in the bauxites and during the pressure digestion it goes to the BR in form of hydrate.

1.6 Hafnium

Hafnium in the bauxite is bonded with zircon in the amount of ≥ 2 %. Titanium, zirconium and hafnium adjoin each other in Group four of the Periodic table, therefore, hafnium can isomorphically enter the structure of two polymorphic titanium oxides (low temperature anatase and high temperature rutile). All three minerals decompose when they are pressure digested. During the digestion titanium reacts with calcium to form stable phases of perovskite $CaTiO_4$ and hydrokassite. Hafnium forms $Hf(OH)_4$, which does not dissolve in the caustic solution and sorbed on the BR surface.

During the pressure digestion of SUBR and STBR bauxites, most of Sc, Y, Zr, Ti, Hf, Cu, Th, and other REMs are digested from the minerals and under strong caustic conditions transform into hydrated forms, which are removed from the process with the bauxite residue.

With due consideration of the behavior and form of scandium, yttrium, REMs and others in the bauxite residue, it is suggested, therefore, that this group is co-precipitated as complex oxides and hydroxides that affects their behavior during the sodium bicarbonate digestion.

2. Sodium Bicarbonate Digestion of Scandium, Yttrium and Other Impurities from Bauxite Residue

2.1 Breaking Down and Activation of Bauxite Residue

Up to 70 % of scandium in the bauxite residue can be extracted using the sodium bicarbonate digestion at a pH of 8.5 ÷ 9.5. Scandium extraction at the pilot facility at the Urals refinery (UAZ pilot unit) amounted to ~ 25±10 % [8]. Incomplete recovery of scandium can be attributed to the following reasons:

- bauxite residue from the last washing stage is characterized by the cross-linked structure [9]. Said cross-linked structure is generated during the BR thickening and washing when exposed to 2−3 synthetic flocculants. In the Bayer process flocculants are added at the thickening and washing stages to improve the separation of the pregnant liquor and bauxite residue. Bauxite residue represents a well-ordered structure due to differences of zeta potentials of different minerals and phases. When affected by flocculant long linear molecules the main phases (DSP, hematite, calcium hydrogarnet, perovskite, chamosite, etc.) flocculate and form a three-dimensional structure with hematite at the lattice points [9]. Therefore, to improve scandium extraction, said cross-linked structure needs to be broken to allow the reaction of the sodium bicarbonate solution with scandium oxyhydrate sorbed on the BR surface;
- fresh bauxite residue is a material amenable to contact hardening, i.e. under compression of several kg/cm^2, 1−3 µm DSP particles form water-stable structures, which are hard to disperse [9]. Contact hardening occurs when bauxite residue is filtered using a filter-press at a pressure of 2÷4 atm. Filter pressing generates a strong water-resistant cake, which poorly reacts in the sodium bicarbonate solution;
- scandium oxyhydroxide has an induction period for activation with further formation of soluble scandium carbonate ($Na_3Sc(CO_3)_3$);
- along with ScO(OH) some other phases are present, which do not react in the sodium bicarbonate solution;
- secondary losses of scandium during the sodium bicarbonate digestion occur due to hydrolytic polymerization of scandium compounds and their precipitation in carbonate solutions in the presence of proton of carbonic acid and aluminium [10]. Alumina in the sodium bicarbonate solution occurs due to the partial break down of hydrogarnets and DSP during the gassing with CO_2 [11].

To increase Sc extraction and limit the above-described effects, the process of BR activation has been created. At BR activation at the pilot facility of Bogoslovsk alumina refinery (BAZ pilot unit) some optimal parameters were determined, including the following:

- Liquid/solids in the filtered bauxite residue and recycled sodium bicarbonate solution;
- High-velocity propeller agitator in the BR dispenser.
- Concentrations in the recycled solution in terms of Na_2CO_3 and $NaHCO_3$, including an optimal pH value;
- Activation temperature;
- Conditions of gassing the slurry with the flue gasses to provide for maximum absorption of CO_2, including temperature of bubbled gas, blower design;
- Activation time under the optimal conditions, etc.

The BR activation is accompanied with the processes, which result in formation of scandium soluble form by the following reaction:

$$ScO(OH) + 3NaHCO_3 = Na_3Sc(CO_3)_3 + H_2O \quad (1)$$

Activation is an extensive process with one cycle duration of > 12 hours. It does not require any additional reagents. The main consumable is electric power needed for air blowers to supply flue gases to the activators, pressure reactors and agitators. The BR activation is mainly limited by the temperature of the process, as scandium shall transform into soluble carbonate form, but scandium dissolution shall be prevented to avoid scandium secondary losses due to scandium hydrolytic polymerization in the presence of a proton of carbon acid and aluminium. Activation is a simple process solution, which allows improving scandium extraction by 70−80 % using sodium bicarbonate digestion at the BAZ pilot unit as compared with the results at the UAZ pilot unit. BR activation enabled reducing the specific amount of the bauxite residue required to produce 1 kg of scandium oxide product from ~ 25 t/kg to ~ 14 t/kg Sc_2O_3.

2.2 Behaviour of Impurities during Activation and Sodium Bicarbonate Digestion of Bauxite Residue

All impurities in liquids and solids were analyzed using a number of methods [12, 13] in the RUSAL's laboratory, which is equipped with the necessary equipment, including the following:

- ICP AS (Inductively Coupled Plasma Atomic Emission Spectrometer Optima 8000 Perkin Elmer, the USA; Inductively Coupled Plasma Atomic Emission Spectrometer Agilent 5110 VDV ICS-OES, Agilent, the USA);
- ICP MS (Inductively Coupled Mass Spectrometer iCAP Qc, Thermo Scientific, the USA);
- XRF (X-Ray Fluorescent Spectrometer Zetium 2.4 kW Malvern Panalytical B.V., the Netherlands);
- XRD (X-Ray Diffractometer X`PertPRO MPD, Malvern Panalytical B.V., the Netherlands).

Measurement procedures and quality control samples were developed to analyze bauxite residue, semi-products and end products. Said procedures and samples have been certified by The D.I. Mendeleev All-Russian Institute for Metrology (VNIIM). Table 2 presents the results of BR composition analyses after the activation and sodium-bicarbonate digestion at the BAZ pilot unit. The data are given for 22 digestion cycles. All impurities in liquids and solids are analyzed using various methods and the balance is calculated.

Table 2. Extraction of scandium, yttrium, thorium, zirconium, titanium from the bauxite residue at the BAZ pilot unit (April−September 2022).

Sample description and the date	Content, wt. %						Dissolution, %				
	Sc_2O_3	ZrO_2	TiO_2	P_2O_5	Y	Th	Sc_2O_3	Y_2O_3	Th	ZrO_2	TiO_2
Raw BR, April 2022	0.016	0.063	3.79	1	0.04	0.006	-	-	-	-	-
BR after processing, dd. 29.04.22	0.007	0.044	2.84	0.616	0.025	0.004	51.14	45.34	30.30	27.42	22.79
BR after processing, dd.03.05.22	0.0075	0.035	2.85	0.683	0.025	0.003	48.30	45.34	45.45	40.40	22.55
BR after processing, dd.08.05.22	0.007	0.044	2.94	0.729	0.025	0.005	51.14	45.34	15.15	27.42	20.39
BR after processing 8 dd. 09.05.22	0.0072	0.037	2.88	0.711	0.025	0.004	50.00	45.34	30.30	37.52	21.83
BR after processing, dd. 11.05.22	0.008	0.047	3.04	0.707	0.027	0.004	45.45	39.30	30.30	23.09	17.99
BR after processing, dd. 14.05.22	0.008	0.052	2.97	0.731	0.028	0.005	45.45	36.27	15.15	15.87	19.67
BR after processing, dd. 17.05.22	0.0074	0.05	2.87	0.694	0.026	0.004	48.86	42.32	30.30	18.76	22.07
BR after processing, dd. 22.05.22	0.0069	0.039	2.94	0.763	0.028	0.005	51.70	36.27	15.15	34.63	20.39
BR after processing, dd. 23.05.22	0.0065	0.045	2.9	0.754	0.028	0.004	53.98	36.27	30.30	25.97	21.35
Raw BR, June 2022	0.017	0.096	4.37	1.121	0.044	0.008	-	-	-	-	-
BR after processing, dd. 02.07.22	0.0084	0.046	2.42	0.613	0.025	0.004	47.35	57.43	45.45	37.88	25.80
BR after processing, dd. 04.07.22	0.0099	0.056	3.13	0.744	0.03	0.005	37.88	42.32	34.09	38.83	18.93
BR after processing, dd. 05.07.22	0.0097	0.055	3.46	0.783	0.031	0.005	38.83	39.30	34.09	37.88	28.71
BR after processing, dd. 09.07.22	0.011	0.056	2.99	0.788	0.03	0.005	37.88	42.32	34.09	42.61	36.61

Sample description and the date	Content, wt. %						Dissolution, %				
	Sc_2O_3	ZrO_2	TiO_2	P_2O_5	Y	Th	Sc_2O_3	Y_2O_3	Th	ZrO_2	TiO_2
BR after processing, dd. 11.07.22	0.0089	0.051	2.61	0.702	0.029	0.004	42.61	45.34	45.45	32.20	23.92
Raw BR, July 2022	0.017	0.062	4.25	1.21	0.044	0.0065	-				
BR after processing, dd. 25.07.22	0.01	0.056	3.15	0.805	0.034	0.0049	37.43	30.23	22.38	8.80	23.53
BR after processing, dd. 06.08.22	0.01	0.043	3.47	0.881	0.037	0.0039	37.43	21.16	36.36	27.86	16.68
BR after processing, dd. 09.08.22	0.0095	0.04	3.41	0.889	0.031	0.0044	40.11	39.30	29.37	32.26	17.97
BR after processing, dd. 09.08.22	0.0085	0.041	3.42	0.912	0.031	0.005	45.45	39.30	20.98	30.79	17.75
Raw BR, August 2022	0.017	0.062	4.25	1.21	0.044	0.0065	-	-	-		
BR after processing, dd. 28.08.22	0.01	0.06	3.33	0.825	0.031	0.004	37.43	39.30	34.97	2.93	19.68
BR after processing, dd. 03.09.22	0.009	0.05	3.39	0.913	0.035	0.004	42.78	27.20	34.97	-11.73	18.40
BR after processing, dd. 07.09.22	0.009	0.06	3.31	0.886	0.032	0.004	42.78	36.27	34.97	90.91	20.11
BR after processing, dd. 11.09.22	0.01	0.07	3.37	0.918	0.034	0.005	37.43	30.23	20.98	90.91	18.82

Sc, Y, Zr, Ti, Th extraction showed a high correlation coefficient, i.e. the conditions of the BR activation and sodium bicarbonate digestion are optimal to digest all these elements. It can be suggested that the form of these elements in the BR is the same as the form of scandium, i.e. they are sorbed on the BR particles and well soluble in the sodium bicarbonate solution at a pH of $\approx 8.5 \div 9.5$.

The correlation coefficient of > 80 % proves that during the pressure digestion Zr, Y, Sc hydroxides are not just sorbed on the BR surface but presumably form solid liquids, i.e. zirconium with yttrium and/or scandium.

During the sodium bicarbonate digestion of the activated BR, Sc_2O_3 content in the product liquors amounts to $15 \div 18$ mg/dm^3 per one cycle, which is rather good. However, the content of unwanted and harmful impurities in much higher.

3. Scandium Precipitation in Form of Sc-containing Aluminium Hydroxide

Previously, at the UAZ pilot unit the following processes were used to precipitate scandium from the Sc-containing product liquor obtained from the sodium bicarbonate digestion [8]:

- two-stage hydrolysis;
- scandium sorption on an ion-exchange resin.

Two-stage hydrolysis of the sodium bicarbonate solution is rather tricky, as system $Na_2CO_3 - NaHCO_3 - H_2O$ serves as a buffer. Under actual production conditions, hydrolysis of a hot solution at a target pH is hard to control, is an extensive process and requires expenses for heating and cooling of the solutions, etc. Due to these reasons two-stage hydrolysis was abandoned.

Sorption-desorption of scandium on a resin. High selectivity of a resin enables to sorb scandium from the sodium bicarbonate solution to obtain a stripping with a high content of scandium and remove most unwanted and harmful impurities. Three years of using sorption at the UAZ pilot unit showed the following challenges of the sorption process:

- mechanical break-down of the resin due to the desorption of a hot strong soda solution;
- decrease of the sorption capacity of the resin due to its poisoning with iron compounds, etc. Regeneration of the resin with oxalic acid restores the sorption capacity but promotes the resin break-down;
- purification of rich scandium concentrate ($Sc_2O_3 \approx 30$ %) to produce 2N or 3N scandium oxide requires almost the same operations as the purification of the concentrate with a low scandium content;

- high consumption and cost of phosphate ion exchange resins deteriorate economic performance of this process of scandium production.

Scandium precipitation using reagents is discussed in reference [14]. Scandium was precipitated at a higher pH in the sodium bicarbonate solution due to reactive carbonization with various reagents, including sodium zincate, sodium aluminate, milk of lime, etc. Scandium precipitation in form of Sc-containing aluminium hydroxide using an alkaline aluminate liquor was selected, as scandium precipitation with the milk of lime is effective, but it results in generation of additional solid wastes and complicates the purification process [15].

At BAZ refinery the alkaline aluminate liquor goes to the scandium production facility and then alumina and soda are returned to the main process.

When the Sc-containing product liquor is mixed with the alkaline aluminate liquor the reaction (2) of reverse causticization and decomposition of sodium aluminate occurs:

$$NaAlO_2 + NaHCO_3 + H_2O = Al(OH)_3\downarrow + Na_2CO_3 \tag{2}$$

Stirring process results in precipitation of a mixture of fine amorphized bayerite and gibbsite, which captures scandium, yttrium, zirconium, titanium, etc. ≥ 95 % of scandium precipitates at the concentration coefficient of > 500. Scandium traces, which remain in the solution ($Sc_2O_3 \leq 1$ mg/dm^3, are not lost because the soda filtrate is fed to the process to activate a fresh batch of the bauxite residue.

Table 3 presents the compositions of primary Sc-containing aluminium hydroxides obtained at the BAZ pilot unit. Samples were produced from mixtures of Sc-containing product solutions containing ≈ 15±3 mg/dm^3 of Sc_2O_3.

Table 3. Chemical composition of primary Sc-containing aluminium hydroxide samples obtained at the BAZ pilot unit (April−October 2022).

No.	Content, wt. %								
	Al_2O_3	Sc_2O_3	ZrO_2	TiO_2	Fe_2O_3	SiO_2	P_2O_5	CaO	MgO
1	36.34	0.94	6.8	6.48	2.49	3.36	0.003	1.08	0.29
2	31.68	1.3	8.0	5.88	2.52	3.0	0.008	0.83	0.23
3	22.3	1.30	9.04	13.43	2.43	4.95	< 0.1	0.98	0.26
4	6.8	1.40	8.06	9.24	2.59	2.49	< 0.1	0.67	0.55
5	8.7	1.70	8.81	12.42	3.11	2.95	< 0.1	1.01	0.33
6	17.7	1.73	10.71	11.56	3.35	3.93	< 0.1	1.19	0.48
7	5.3	1.80	9.02	38.3	4.41	2.99	< 0.1	2.07	0.7
8	15.5	1.82	9.20	9.34	2.35	6.84	< 0.1	0.77	0.29
9	14.14	3.1	15.5	2.2	9.24	5.65	NA	6.4	1.53
10	9.7	3.60	24.30	13.13	3.25	7.54	< 0.1	2.79	0.9

No.	Content, wt. %										
	Na_2O	K_2O	Cu	Cr_2O_3	SO_3	Y	Th	Hf	Yb	Ce	Sr
1	6.26	0.45	ND	0.004	0.21	0.525	0.138	ND	ND	ND	ND
2	10.43	0.67	ND	0.001	0.27	0.399	0.162	ND	ND	ND	ND
3	11.2	0.94	0.16	< 0.01	0.91	0.78	0.20	0.31	0.24	0.23	0.5
4	27.8	2.39	0.16	< 0.01	1.78	0.89	0.21	0.22	0.19	-	-
5	23.3	1.65	0.03	< 0.01	1.12	0.90	0.23	0.33	0.18	0.2	0.11
6	13.9	1.09	0.29	< 0.01	0.84	1.13	0.27	0.31	0.31	-	0.1
7	8.6	0.72	0.4	< 0.01	0.55	1.88	0.22	0.22	0.2		0.1
8	18.7	1.22	ND	< 0.01	1.08	0.87	0.27	ND	ND	ND	ND
9	15.2	0.06	ND	NA	NA	0.49	0.018	ND	ND	ND	ND
10	5.8	0.46	0.42	< 0.01	0.78	1.82	0.57	0.6	0.36	0.29	-

Note: * NA stands for “not available”, ND stands for “not determined”.

XRD analysis showed that the main crystalline phase of primary Sc-containing aluminium hydroxide is represented by gibbsite and bayerite.

Soda is represented in primary Sc-containing aluminium hydroxides by the following water-soluble forms:

- unhydrous sodium carbonate Na_2CO_3;
- thermonatrite $Na_2CO_3 \times H_2O$;
- sodium carbonate heptahydrate $Na_2CO_3 \times 7H_2O$;
- traces of dawsonite $NaAlCO_3(OH)_2$;
- traces of compound sodium and scandium carbonate $Na(Sc(CO_3)_4)_2H_2O$.

The presence of alkali increases the specific consumption of sulfuric acid for further step of selective sulfuric acid leaching of scandium. Therefore, the conditions of Sc-containing aluminium hydroxide washing with water were determined. This operation enables to reduce the alkali content in Sc-containing aluminium hydroxide by 1.5÷2 times. The soda solution from washing ($Na_2CO_3 \sim 25$ g/dm^3) is returned to the decomposition of the Sc-containing product solution.

XRD analysis of primary Sc-containing aluminium hydroxide does not detect any phases containing titanium, zirconium, yttrium and other REMs, i.e. they are X-ray amorphous.

4. Selective Leaching of Scandium from Sc-containing Aluminium Hydroxide

Primary Sc-containing aluminium hydroxides from the BAZ pilot unit have a multicomponent composition. The amounts and ratios of the elements vary widely. A substantial amount of tests were carried out to determine the purification parameters and develop a process flow sheet, which should satisfy the following conditions:

- stable production of 2N scandium oxide ($Sc_2O_3 \geq 99$ wt. % in calcined samples) regardless of the impurity composition in the raw Sc-containing aluminium hydroxide;
- effective removal of all impurities with minimum process operations and their compatibility with alumina production process;
- minimal losses of scandium oxide to achieve high total recovery, including due to return of Sc-containing solutions and solids to the upstream purification processes or head of the process;
- minimum expenses for the reagents and their reuse or return to alumina process to avoid additional wastes.

Technically, purification uses only industrial grade sulfuric acid (72 %), which is low-cost and available in the Urals region. The BAZ refinery has a storage for sulfuric acid as it is used for chemical cleaning of the equipment. Sodium sulfate, which is generated from purification of Sc-containing aluminium hydroxide, is returned to alumina production. Said sulfate represents an insignificant part of sodium sulfate, which is generated during SUBR pyritized bauxite digestion containing up to 1 wt. % of sulfur. As per the current technology at the BAZ refinery Na_2SO_4 is removed from the process using sulfate evaporation in form of soda-sulfate mixture, which contains 90÷95 % of berkeite $Na_2CO_3 \times 2Na_2SO_4$. Said mixture is sold to outside detergent producers, etc.

The laboratory performed extensive work to determine the conditions of the selective leaching of scandium from Sc-containing aluminium hydroxide enabling to extract ≥ 90 % of scandium at a minimum consumption of sulfuric acid.

The following parameters of selective leaching were varied: a pH value, liquid/solids, temperature, and residence time.

Selective sulfuric acid leaching of Sc-containing aluminium hydroxide at a pH of < 1 generates aluminium sulfates and reduces the filtration rate to < 0.01 $m^3/m^2/h$; and at a pH of ≥ 2.6 scandium extraction decreases to 65 %.

XRD analysis of the insoluble cake from selective leaching showed that it is composed of a mixture of two polymorphic phases (gibbsite and bayerite $Al(OH)_3$). Under the optimal conditions of selective leaching, scandium extraction amounts to ~ 92 %. Filtration rate of insoluble precipitate on a Nutsche filter was acceptable (0.2÷0.3 $m^3/m^2/h$).

Selective sulfuric acid leaching allows removing a number of impurities, i.e. the resulting insoluble cake contains as follows:

- \> 98 % of iron;
- \> 99 % of titanium;
- \> 95 % of zirconium;
- \> 85 % of silica;
- \> 70 % of alumina.

However, selective sulfuric acid leaching does not remove yttrium, thorium, hafnium and other REMs. That is why further steps of purification have been introduced in the technology.

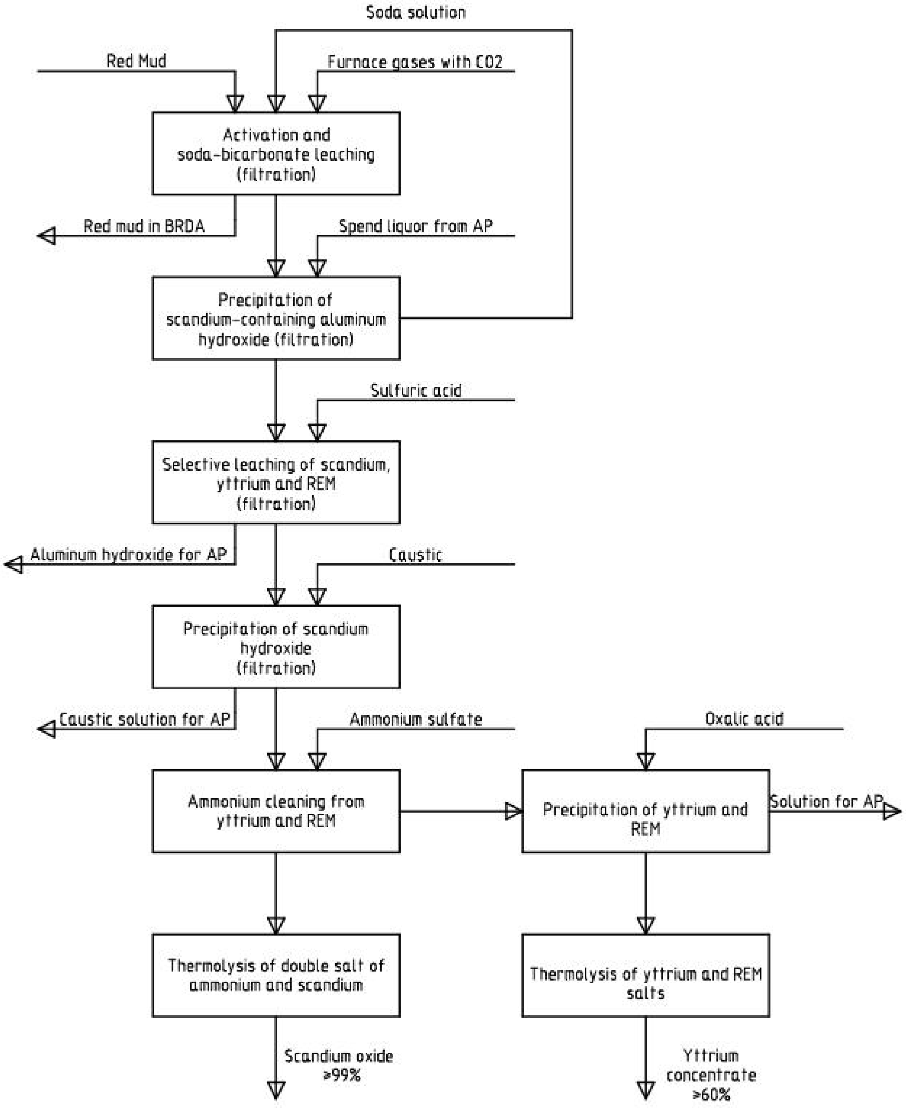


Figure 1. – Principle flow sheet of scandium oxide production from bauxite residue.

5. Precipitating Scandium Hydroxide with Alkali

For further scandium concentrating and removing a number of impurities, including calcium, aluminium, etc., scandium precipitation with caustic at a pH of > 13 was introduced.

Scandium precipitates with caustic alkali without losses and allows removing a number of impurities while increasing Sc_2O_3 content up to ~ 15 % in a calcined product. The caustic solution from filtration is used to decompose a Sc-containing product solution.

6. Ammonium Purification to Remove Yttrium and Other REMs

References [16 and 17] suggest a method of separating scandium from yttrium and other REMs with ammonium salts due to different solubility of $ScNH_4(SO_4)_2$ and sulfates of yttrium and other REMs. The method comprises precipitating scandium from a sulfuric acid solution with ammonium sulfate at a temperature of + 40÷95 °C. The resulting Sc-containing precipitate is separated and washed, and yttrium and other REMs remain in the spent solution.

It was found that said method required some improvement. The laboratory conducted extensive testing of ammonium purification of scandium hydroxide to show that one-stage ammonium purification does not reduce the content of yttrium, zirconium, thorium, calcium and other impurities to the acceptable level, which is required to produce 2N scandium. Two-stage purification shall be performed. The following parameters affect removing impurities from scandium:

- concentration of sulfuric acid and ammonium sulfate and the ratio thereof;
- liquid/solids and mixing efficiency;
- temperature profile of generation and aging of scandium precipitate;
- reaction time, etc.

XRD analysis of scandium precipitate proved that ammonium treatment yields a mixture containing several salt, i.e. ~ 90 % crystalline hydrate of double salt of ammonium sulfate and scandium $ScNH_4(SO_4)_2 \times 2H_2O$ and ~ 10 % scandium sulfate $Sc_2(SO_4)_3$ and other Sc-containing phases.

These salts dissolve under different conditions that should be considered at further purification stages.

Reduction of ammonium sulfate specific consumption. Yttrium and REMs are removed from the ammonium solution from the second stage of ammonium purification using the oxalate solution from the next purification stage. The obtained purified solution is supplied to the first stage of ammonium purification. This method reduces the specific consumption of ammonium sulfate and allows obtaining Yttrium and REMs concentrate.

Use of ammonium sulfate for purification does not produce any significant impact on the cash cost of production of scandium oxide, as NH_4SO_4 is produced as a fertilizer and is not a rare or high-priced reagent. Upon two-stage ammonium purification Sc-containing precipitate is filtered, squeezed on a Nutsche filter, washed with water and supplied to convert scandium into scandium oxalate.

7. Precipitating and Calcining Scandium Oxalate to Produce Scandium Oxide Product

It is recognized that scandium oxalates are characterized by a number of crystalline hydrates (including 18-, 10-, 6-, 5-, 4,- 3- and 2- aqua hydrates), however only dihydrate $Sc_2[C_2O_4]_3 \times 2H_2O$ is stable. Therefore, scandium oxalate, which is dried at a temperature of + 105 °C to a constant weight, represents mainly a dihydrate.

Due to the presence of several scandium and ammonium sulfates in the precipitate from the ammonium purification, the conditions of producing and calcining scandium oxalate required improvement, including as follows:

- conditions of dissolving ammonium and scandium sulfates (including the composition of the solution, temperature, time, liquid\solids);
- concentration and dosage of oxalic acid solution, as well as process stoichiometry;
- conditions of precipitating scandium in form of scandium oxalate $Sc_2(C_2O_4)_3$ (including the composition of the solution, temperature, time, liquid\solids);
- condition of filtering and washing the obtained precipitate (including temperature, water consumption for washing);

- conditions of calcining scandium oxalate to obtain scandium oxide (temperature and time of calcination, heating profiles, etc.).

Simultaneous thermal analysis of obtained scandium oxalate showed that scandium oxalate dihydrate is stable within a temperature range from + 200 °C to ~ 230 °C, then dehydration occurs up to reaching a temperature of 320÷380 °C. Thermal dissociation of anhydrous scandium oxalate is characterized by a complex nature, as due to CO disproportionation or decomposition of carbon-oxygen polymers free carbon is formed. These polymers occur due to combining oxygen and carbon radicals from breaking bonds with C_2O_4-group. In the air, free carbon burns at a temperature range of + 460÷680 °C. The resulting pattern is quite complicated, as thermal decomposition of dehydrated scandium is accompanied with endothermic effects that is obvious when measurements are performed in vacuum. However, in the air they overlap with exothermic CO and C oxidation. Therefore, it is widely noted that patches of carbon remain on scandium oxyde after calcination of scandium oxalate in a thick bed (H > 20 mm) even at a temperature of ~ 800 °C. Moreover, it is recognized that intermediate products of oxalate decomposition (i.e. monox dicarbonate $Sc_2O\times(CO_3)_2$; diox carbonate $Sc_2O_2\times CO_3$) are generated during the thermal decomposition of scandium, yttrium and REM oxalates.

Thermal dissociation of said intermediate forms to obtain scandium oxide might take much time. Simplified aggregated reaction of scandium oxalate thermal decomposition is suggested as follows:

$$Sc_2(C_2O_4)_3 \rightarrow Sc_2O_3 + 3CO\uparrow + 3CO_2\uparrow \tag{3}$$

This reaction should end by a temperature of + 600 °C by formation of amorphous metastable form.

Crystallization of scandium oxide at a temperature of + 600 °C. At a temperature above 600÷700 °C scandium, yttrium, REM oxalates undergo exothermic processes associated with crystallization of fine-crystalline oxides [18] and transfer of metastable C-form into B-form [19]. Calcination produces 2N scandium oxide (see Table 4).

Form of scandium oxide extraction. It can be believed that the extraction form and surface morphology of obtained scandium oxide is affected by the composition of salt/salts, which were subjected to thermal decomposition.

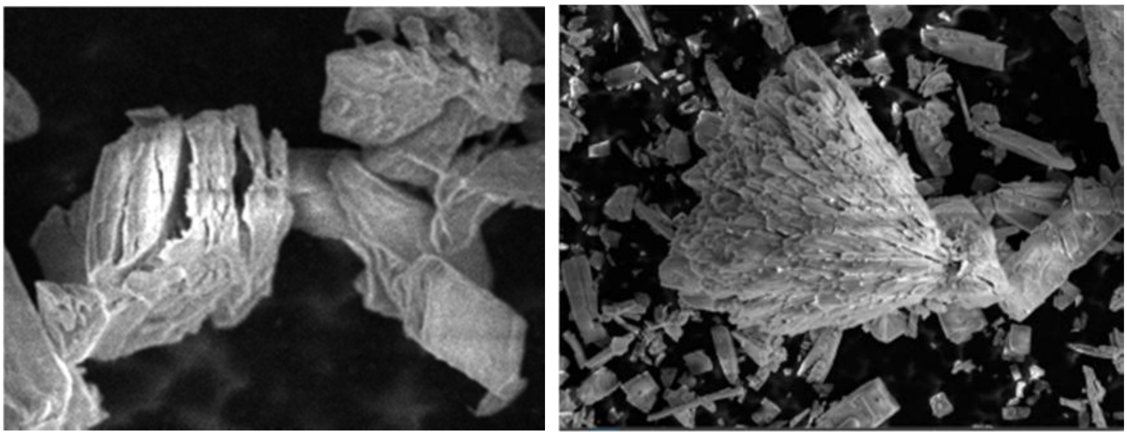
Table 4. Chemical composition of scandium oxide obtained from ammonium purification and calcination, wt. %.

Sc_2O_3	ZrO_2	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
99.0	0.019	0.10	0.16	0.028	0.0021	0.13	0.003	0.013	0.12

Y_2O_3	CuO	HfO_2	Th	La	Ce	Pr	Nd	Sm	Eu
0.24	<0.002	<0.0020	0.01	0.0032	0.091	0.0049	0.033	0.020	0.0062

Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U
0.018	0.0064	0.052	0.013	0.038	0.0059	0.041	0.0048	0.00001

Thermal decomposition of scandium oxalate salts comprising a mixture of hexa- and octa-aqua scandium oxalate $C_6O_{12}Sc_2\cdot 6\div 8H_2O$ and scandium hydroxide $Sc(OH)_3$) produces scandium oxide, which is characterized by prismatic crystals layered along one axis (Figure 2 a).



a) scandium oxide obtained from acid alkaline purification at the BAZ pilot unit: prismatic crystals layering occurs along one axis

b) scandium oxide obtained from ammonium purification: radial fibrous, needle-like crystals

Figure 2. Forms of scandium oxide.

Thermal decomposition of a sample containing mainly a mixture of hexa-aqua scandium oxide crystalline hydrate $C_6O_{12}Sc_2{\cdot}6H_2O$, double ammonium sulfate and scandium sulfate $NH_4Sc_3(SO_4)_2(OH)_6$ and scandium oxyhydroxide ScO(OH) impurity produces scandium oxide, which is characterized by radial fibrous and needle-like precipitates (Figure 2 b).

Table 5. Specific surfaces and densities of scandium oxide by various manufacturers.

Description	Specific surface m^2/g	Density g/cm^3	Average particle size, µm
Manufacturer 1 (Russia)	79.7	3.55	9.9
Manufacturer 2 (Russia)	11.9	3.80	11.4
Manufacturer 3 (China)	27.4	3.75	11.5
Acid alkaline purification at BAZ pilot unit (RUSAL, Russia)	9.3	3.83÷3.84	11.6
Ammonium purification at BAZ pilot unit (RUSAL, Russia)	20.4	3.67÷3.68	29

It is concluded that properties of scandium oxide from different manufacturers differ to a significant degree (Table 5).

8. Neutralization of Tailings of Ammonium Purification and Oxalate Precipitation of Scandium to Produce High Grade Yttrium Concentrate

Spent solutions from precipitating scandium with ammonium sulfate and precipitating scandium in form of scandium oxalate shall be neutralized, as oxalate should not be returned into alumina production.

An ammonium solution from the first stage of ammonium purification is treated with an oxalate solution (from the next purification stage) to remove yttrium and REMs. The yttrium concentrate contains > 60 % of yttrium (calculated as Y_2O_3), as well as > 15 % of REMs (see Table 6).

Table 6. Chemical composition of Y concentrate calcined at a temperature of + 1100 °C.

Y_2O_3	Sc_2O_3	ZrO_2	ThO_2	Yb_2O_3	Nd_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Lu_2O_3	HfO_2	UO_2
63.6	0.49	0.29	0.049	6.48	1.31	0.080	0.92	0.169	0.626	0.220	1.187	0.365	3.948	1.420	5.592	0.936	1.228	0.0008	0.00001

Due to small production capacities this yttrium concentrate is currently of no commercial value, but upon scaling-up of the production it has the potential of becoming a marketable product.

9. Conclusions

Boehmite and diaspore in the SUBR and STBR bauxites are characterized by a high content of scandium. When these bauxites are processed by the Bayer process scandium is sorbed on the surface of bauxite residue, mainly in form of γ-ScO(OH) and can be easily extracted by a sodium bicarbonate solution. Therefore, this bauxite residue can be considered one of the largest sources of scandium. Additionally, along with scandium a lot of elements with similar chemical properties go into the bauxite residue, i.e. yttrium, hafnium, REMs, etc.

RUSAL Engineering and Technology Center is mastering a technology for extracting scandium oxide from the bauxite residue to produce 2N scandium oxide product at a large-scale pilot facility at Bogoslovsk alumina refinery. Trial batches of scandium oxide have been obtained using the novel technology that are used for production of Al-Sc alloys and Al-Sc master alloys at the facilities of RUSAL Engineering and Technology Center. Scaling-up of the BAZ pilot facility will enable to launch the full-scale production of scandium oxide.

The advantage of the novel technology lies in reducing carbon footprint of the main alumina production process due to the use of kiln flue gases containing up to 8 vol.% CO2, that also results in the BR neutralization.

A reliable and reproducible process have been developed for removing zirconium, titanium, copper, yttrium, thorium and other REMs from scandium by extraction of double salt of scandium sulfate and ammonium sulfate ScNH4(SO4)2. Ammonium purification does not increase or generate any additional tailings. Moreover, neutralization of resulting spent solutions enables to obtain one more product, i.e. 60 % yttrium concentrate containing ~ 15 % of medium REMs.

10. Acknowledgment

The authors are grateful for the assistance in preparation of this paper to the following specialists of “RUSAL ETC” LLC: Natalya Kutkova, Tayana Gabrielyan, Tatyana Golovanova, Yuliya Chernyshova, Darya Ionkina, Tatyana Mukina, Natalya Maksimenko, Irina Paromova, Anna Damaskina, Olga Kholomeeva, Edgaras Urbonavichyus, Elena Malyukova.

11. References

1. Lev Bykhovsky et al., *Scandium in Russia: Prospects of processing and production development*, Moscow, VIMS, 2007, 45 pages.
2. Osvald Knop and Jean M. Hartley, Refinement of the crystal structure of scandium oxide, *Canadian Journal of Chemistry*, Vol. 46, (1968), 1446-1450.
3. Naum S. Malts and Alexander G. Suss, Aluminium and chromium containing goethites: composition, properties, behavior in soda aluminate liquors in presence of silicon, titanium and calcium compounds, *Light Metals*, 1992, 1343-1347.
4. S.I. Beneslavsky, *Bauxite mineralogy*, 2nd Edition, Moscow, Nedra, 1974, 168 pages.
5. Alexander Suss et al., Specific Features of Scandium Behavior during Sodium Becarbonate Digestion of Red Mud, *Light Metals*, 2018, 165-174.
6. E.L. Dukhovskaya, Y.G. Saksonov and A.G. Titova, Oxygen parameters of some compounds with garnet structure, Izv. Akad. Nauk SSSR*, Neorg. Mater.*, No. 9, (1973), 809-813.

7. L.E. Mordberg, C.J. Stanley and K. Germann, Mineralogy and geochemistry of trace elements in bauxites: the Devonian Schugorsk deposit, *Mineralogical Magazine*, Vol. 65(1), (2001), 81–101.
8. Aleksandr Kozyrev et al., Industrial Trials Results of Scandium Oxide Recovery from Red Mud at UC RUSAL Alumina Refineries, *Proceedings of 37th International Conference of ICSOBA and XXV International Conference "Aluminium Siberia"*, 16 – 20 September 2019, Krasnoyarsk, Russia, *TRAVAUX* 48, 497-508.
9. V.I. Korneev, A.G. Suss and A.I. Tsekhovoy, *Bauxite residue – properties, storage, utilization*, Moscow, Metallurgiya, 1991, 144 pages.
10. Maung Maung Aung, *Extraction of scandium from bauxite residue of alumina production*, PhD Thesis, Dmitry Mendeleev University of Chemical Technology of Russia, Moscow, Russia, 2019.
11. Aleksandr Suss et al., Comparison of Lime and Carbon Dioxide Methods of Bauxite Residue Neutralization", *Proceedings of 38th International ICSOBA Conference*, Virtual Conference, 16 – 18 November, 2020, *TRAVAUX 49*, 427-440.
12. Tatyana Golovanova et al., Quantitative Chemical Analysis of Red Mud and Products of its Processing to Scandium, Zirconium and REE Oxides by ICP AES, *Proceedings of 34th International ICSOBA Conference*, Quebec, Canada, 03 – 06 October 2016, *TRAVAUX 45,* 241-246.
13. Tatyana Golovanova et al., Specifics of Sample Preparation and Mass Spectrometry Analysis of Trace Impurities in Alumina and Aluminium", *Proceedings of 35th International ICSOBA Conference*, Hamburg, Germany, 02 – 05 October 2017, *TRAVAUX 46*, 301-306.
14. N.A. Sabirzyanov and S.P. Yatsenko, *Hydrochemical methods of complex processing of bauxites*, Yekaterinburg, UrO RAN, 2006, 386 pages.
15. S.P. Jatsenko et al., Method for preparation of scandium oxide from red mud, *RU Patent* 2,247,788, filed June 24, 2003, granted March 10, 2005.
16. Vladimir P. Volkov, Method for separation of scandium and rare-earth elements, *RU Patent* 2,079,431, filed July 14, 1994, granted May 20, 1997.
17. Igor N. Pyagay, *Extraction of scandium and other metals from red mud of alumina production with absorption of toxic gases from kilns*, PhD Thesis, Saint Petersburg Mining University, Saint Petersburg, Russia, 2016.
18. Blum S.L., Maguere E.A. Bull. Amer. Ceram. Soc., 1960, v. 39, p. 310.
19. Shear E.S. Brit. Ceram. Soc., 1962, v. 61, p. 225.