

Technology to Produce Scandium Oxide from Sintering Red Mud

Alexander Suss¹, Natalia Kuznetsova², Andrey Knyzev², Sergey Pishchalnikov³,
Elena Malukova⁴ and Andrey Panov⁵

1. Department Director

2. Chief Researcher

3. Project Manager

4. Manager

5. Director R&D Alumina

RUSAL Engineering and Technology Center, Saint Petersburg, Russia

Corresponding author: aleksandr.suss@rusal.com

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Abstract

The paper describes further development of RUSAL's technology to produce scandium oxide from red mud using the residue of the RUSAL Krasnoturyinsk alumina refinery. RUSAL Krasnoturyinsk and RUSAL Kamensk-Uralsky refineries process local boehmite-diasporic bauxites that are characterized by a high content of calcite and pyrite. To balance the sulphates and carbonates in the process, the refineries use sintering areas where low-quality bauxite is processed. In the course of development of the technology to extract scandium oxide from sintering red mud, the transformation of scandium-containing bauxite minerals (boehmite, diasporite, hematite, chamosite, goethite, zircon, apatite, etc.) during the sintering process and the formation of new scandium phases were studied. When the sinter is digested, scandium also forms new phases. Up to 400 kt of sintering red mud having Sc_2O_3 content of 140 ± 10 ppm are disposed in the bauxite residue disposal area (BRDA) annually, i.e. more than 55 tonnes of Sc_2O_3 are placed annually to the disposal area. The behaviour of scandium, thorium, hafnium, copper, REMs, and other impurities was studied during the soda-bicarbonate digestion of sintering red muds. The possibility to significantly simplify the equipment and process is shown as compared with soda-bicarbonate digestion of the Bayer red mud. Additionally, the possibility of reducing operating costs is presented. Processing sintering red mud allows increasing the concentration of scandium in the solutions after digestion and in a Sc-containing concentrate. Moreover, soda-bicarbonate digestion also enables to extract alumina and alkali from sintering red mud and return them to alumina production. Thus, RUSAL's technology for producing scandium oxide from red mud further evolved resulting in minimal Capex and Opex for its implementation.

Keywords: Sintering red mud, Scandium oxide, Soda- bicarbonate digestion.

1. Introduction

RUSAL established pilot facilities for producing scandium oxide from the Bayer red mud (Bayer RM) at two alumina refineries, i.e. RUSAL Krasnoturyinsk (BAZ refinery) and RUSAL Kamensk-Uralsky (UAZ refinery). The Bayer RM is generated from processing boehmitic and diasporic bauxites from two deposits located in the north of European Russia, i.e. North Urals (SUBR) and Middle Timan (STBR) bauxites by the Bayer method. Red mud from these bauxites contains on average 140–180 ppm Sc_2O_3 . Non-pressure sodium bicarbonate digestion is used to extract scandium from the Bayer RM. Sodium bicarbonate (NaHCO_3) is obtained by absorption of carbon dioxide (CO_2) from flue gases with partial conversion of soda into sodium bicarbonate. Sodium bicarbonate digestion of scandium from the Bayer RM allows reducing carbon footprint of alumina production, as well as the hazard class of production wastes.

Testing two pilot facilities for producing scandium from the Bayer RM revealed a number of issues, which affect capital expenses and performance indicators of the process, namely as follows:

- Scandium is distributed in the Bayer RM at a ratio of ~ 30:70 between iron minerals (hematite, goethite, chamosite of type $(\text{Mg,Fe}^{+2})\text{Al}[\text{Si}_3\text{AlO}_{10}](\text{OH})_6 \times n\text{H}_2\text{O}$) and scandium digested from boehmite and diaspore. 70 % of scandium extracted from alumina-containing materials form the phases, which are sorbed on red mud particles. Depending on the matrix substrate, scandium forms various phases. Thus, scandium is sorbed on hematite and goethite as oxyhydroxide $\gamma\text{-ScO}(\text{OH})$ and a more “solid” tertiary oxide with yttrium and iron $\text{Y}_3\text{ScFe}_4\text{O}_{12}$; scandium is sorbed on the DSP as a silicate having eringait structure $\text{Ca}_3\text{Sc}_2(\text{Si}_3\text{O}_{12})$; scandium is sorbed on alumino-iron-calcium hydrogarnet as davisite CaAlScSiO_6 . Davisite and tertiary oxide with yttrium and iron prevail in the Bayer RM. Sodium bicarbonate digestion extracts only part of scandium, which is sorbed on the Bayer RM surface. Scandium contained in the crystal lattice of iron-containing minerals is not recovered [1];
- Preparation of the finely-dispersed Bayer RM (containing over 60 % of $\leq 10 \mu\text{m}$ particles) for sodium bicarbonate digestion followed by separating the mud and Sc-containing product solution requires use of high-rate batch-operated filter presses. Filter presses are expensive to manufacture and operate; said factor affects the Capex and Opex of scandium production;
- Sodium bicarbonate digestion of the Bayer RM yields the Sc-containing liquor with relatively low scandium content, i.e. 8–15 mg $\text{Sc}_2\text{O}_3 / \text{dm}^3$.
- Concentrating scandium from the Sc-containing product solution to obtain primary scandium concentrate proved to be ineffective. Primary scandium concentrate is obtained for the pregnant liquor from the main alumina process thus increasing the cash cost of Sc_2O_3 production.

To overcome said challenges, as well as to reduce Capex and Opex of scandium production, RUSAL decided to produce scandium from the sintering red mud (sintering RM). The sintering RM is available at the UAZ and BAZ refineries as SUBR and STBR bauxites are characterized by a high content of calcium carbonate in form of magnesium calcite (4–16 %) and sulphide sulphur S^{2-} in form of pyrite (FeS_2), chalcopyrite (CuFeS_2), sphalerite (ZnS). To obtain sulphate and carbonate balances the UAZ and BAZ refineries use sintering to causticize the recycled soda and remove sulphate as soda-sulphate mixture. Soda produced at RUSAL’s Achinsk alumina refinery is added to the process to compensate the alkali losses.

The previous tests on scandium extraction from a mixture of the Bayer RM and sintering RM by heap leaching showed that this process occurs even on the BRDA at low temperatures [2].

A 1.2 m column setup was designed and 3D-printed to test main processes of counter-current leaching and select the conditions for the reaction zones (see Figure 1). Operation of the column allowed to define 3 distinct zones as described further.

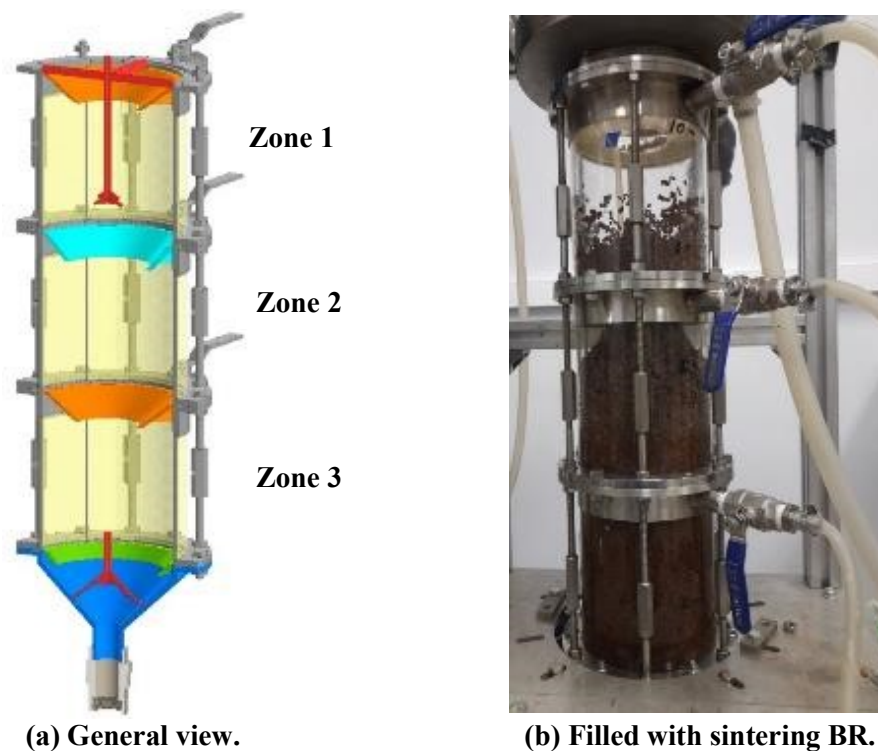


Figure 1. Laboratory column setup.

The obtained data were used to design and build two large-scale pilot facilities at the BAZ refinery to produce Sc-containing concentrate from the sintering RM. 3 m pilot facilities were used to test and approve all process operations, as well as to produce primary Sc-containing concentrate in the amount required for the next purification steps up to Sc_2O_3 product. Based on the obtained parameters, the construction of the commercial-scale production facility began. Further, the paper discusses the results of the physical simulation of scandium production from sintering red mud that provided insights into the chemical behaviour of all involved processes.

2. Scandium Behaviour during Processing the Bauxites to Produce Alumina Using Sintering followed by Sinter Digestion with a Weak Soda Solution in APC-layer Complex

When alkaline mixtures comprising high-carbonate SUBR bauxite, recycled and fresh soda, and limestone are sintered at 1150 °C, all Sc-containing materials broke up. X-ray diffraction analysis (XRD) was used to determine two newly formed Sc-containing crystalline phases:

- Predominantly CaSc_2O_4 ;
- Subordinate amount of ScFeO_3 .

It was considered that scandium can associate with sodium ferrite or aluminoferrite (NaFeO_2 and $\text{Na}(\text{Al,Fe})\text{O}_2$) during the sintering. However, this consideration was not confirmed.

At the BAZ refinery, alkaline sinters were digested using the automated process complex (APC-layer complex). When the sinter is digested using a soda solution with a concentration of $\sim 8 \text{ g/dm}^3$ as $\text{Na}_2\text{O}_{\text{carbonate}}$ in the APC-layer complex, scandium does not pass into the pregnant liquor. Regardless of scandium content in the sinter, as per the ICP AS results the pregnant liquor contains only traces of scandium ($\leq 0.5 \text{ ppm Sc}_2\text{O}_3$).

X-ray diffraction analysis of the sintering RM showed that digestion in the APC-layer complex does not decompose CaSc_2O_4 , which remains in the mud, but decreases the amount of ScFeO_3

and presumably leads to formation of γ -ScO(OH). It is not possible to assess this process numerically as after two stages of digestion all iron in the sinter in form of sodium ferrite or alumoferrite $\text{Na}(\text{Al,Fe})_2\text{O}_2$ convert into X-ray amorphous ferrihydrites ($\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$), which cause a very high background in the XRD patterns.

In fact, the APC-layer complex produced the sintering RM, which contains 120–140 ppm Sc_2O_3 in form of three crystalline phases, i.e. CaSc_2O_4 , ScFeO_3 and γ -ScO(OH). These phases demonstrate different reaction properties in the sodium bicarbonate digestion.

3. Change of Sintering RM during the Sodium Bicarbonate Digestion and Behaviour of Scandium and Other Impurities

Sintering red mud demonstrates the following properties:

- Particle size of the sintering RM is from 1 to 6 mm, the average value of 2–2.5 mm (see Figure 2). Fraction < 1 mm amounts to $\sim 20 \pm 2\%$ and is easily separated with the vibration screen thus partially dewatering the mud. Coarse material is characterized by high permeability, therefore, scandium can be easily digested from the material using the sodium bicarbonate solution in the column setup via countercurrent sodium bicarbonate solution and sintering RM. Thus, sodium bicarbonate digestion can be carried out in a column setup similar to the APC-layer complex;



Initial sintering RM from the APC-layer complex.



Processed sintering RM from sodium bicarbonate digestion.

Figure 2. Sintering RM from the BAZ refinery.

- Real density of the sintering RM amounts to $\rho = 2.9 \pm 0.05 \text{ g/cm}^3$, but its porosity amounts to $\sim 60\%$. Therefore, bulk weight of the compacted mud is equal to $0.95\text{--}1 \text{ g/cm}^3$. Low bulk weight and high strength of mud structure keep it from deformation in the column setup and do not influence the porosity of the mud and/or generation of a large amount of fine fractions removed from the setup with the solutions;
- Analysis of scandium content in the fractions of the sintering RM showed that scandium distribution by mud fractions is relatively equal, however, in $+ 2$ mm fractions it is higher by ~ 3 to 5% ;
- At the BAZ refinery the disposed sintering RM contains over 40 t of Sc_2O_3 . Current global production of Sc_2O_3 amounts to $\sim 80 \text{ t/y}$. Consequently, producing scandium from the sintering RM allows meeting RUSAL's in-house needs and provides for the growth of Al-Sc master alloys and alloys market.

Therefore, RUSAL's experience of digesting the coarse material in column countercurrent digesters, as well as the properties of the sintering RM after the column APC-layer complex

provided for the development of the continuous countercurrent moving bed column (CMB column) to produce Sc-containing product solution with the maximum content of scandium.

4. Physical Simulation of Sodium Bicarbonate Digestion in the CMB Column

The chemical processes taking place in the CMB column are illustrated in Figure 3 and can be divided into three zones earlier indicated in Figure 1, as follows.

Zone 1. Low temperature causticization and obtaining the sodium alkaline solution. The sintering RM from classification and sodium bicarbonate solution from zone 3 react with TCA, dicalcium silicate and the products of degradation thereof, calcium hydroxide to form calcium carbonates (mainly calcite with low-temperature aragonite and vaterite impurities), sodium aluminate and caustic alkali by reactions (1)–(5):



In fact, the sodium bicarbonate solution promotes low temperature causticization of the sintering RM where calcium carbonate becomes the main phase (up to 60 % as shown in Tables 1 and 2) and a greater part of alumina from TCA and other phases goes into the sodium bicarbonate solution. Additional digestion of alumina from the sintering RM due to low temperature causticization enables to return ≥ 1 t of Al_2O_3 per 1 kg of Sc_2O_3 to alumina process in form of aluminium hydrate and dawsonite. Besides, producing 1 kg of scandium oxide, ≥ 1.1 t of CO_2 is bound with the mud.

Table 1. Estimated quantitative phase composition of the sintering RM before and after sodium bicarbonate digestion.

Description	Crystalline phases*	Calcite 3.03 Å	Zeolite 3.66 Å	Dawsonite 5.70 Å	$\text{Ca}_3\text{AlFeSiO}_4(\text{OH})_8$ 2.78 Å	$\text{Ca}_3\text{Al}_2\text{O}_6$ 2.70 Å	$\text{Ca}_2\text{Fe}_2\text{O}_5$ 2.67 Å
Sintering RM after APC-layer	CaCO_3 – calcite, aragonite $\text{Ca}_3\text{AlFeSiO}_4(\text{OH})_8$ $\text{Ca}_3\text{Al}_2\text{O}_6$, $\text{Ca}_2\text{Fe}_2\text{O}_5$	7	-	-	5	18	9
Sintering RM after sodium bicarbonate digestion	CaCO_3 , calcite $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2\times 4\text{H}_2\text{O}$, zeolite group $\text{NaAlCO}_3(\text{OH})_2$ - dawsonite	58	5	3	-	-	-

* The remaining phases are represented by X-ray amorphous ferrihydrites, etc.

The obtained sodium bicarbonate solution contains ~ 30 g/dm³ $\text{Na}_2\text{O}_{\text{caustic}}$, up to 15 g/dm³ $\text{NaAl}(\text{OH})_4$ and has a pH of ~ 13 . The sodium alkaline solution is removed from the CMB column, filtered and used for hydrolytic precipitating the Sc-containing product solution to produce primary Sc-containing concentrate (see Figure 3).

Table 2. Changes in the composition of the sintering RM from the APC-layer using the sodium bicarbonate digestion.

Description	Chemical composition, wt. %										
	Sc ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	CO ₂	ZrO ₂	Y ₂ O ₃	ThO ₂	CuO
Sintering RM after APC-layer (from classification)	0.023	20.85	30.93	6.81	48.64	9.4	6.69	0.188	0.0495	0.0205	0.0355
Sintering RM after sodium bicarbonate digestion at the pilot facility at the BAZ refinery	0.014	14.61	26.21	5.55	40.29	16.59	36.26	0.113	0.0397	0.0182	0.0310
The amount in the Sc-containing product solution, %	39.1	29.93		18.5	17.17			40.1	19.72	11.2	12.72

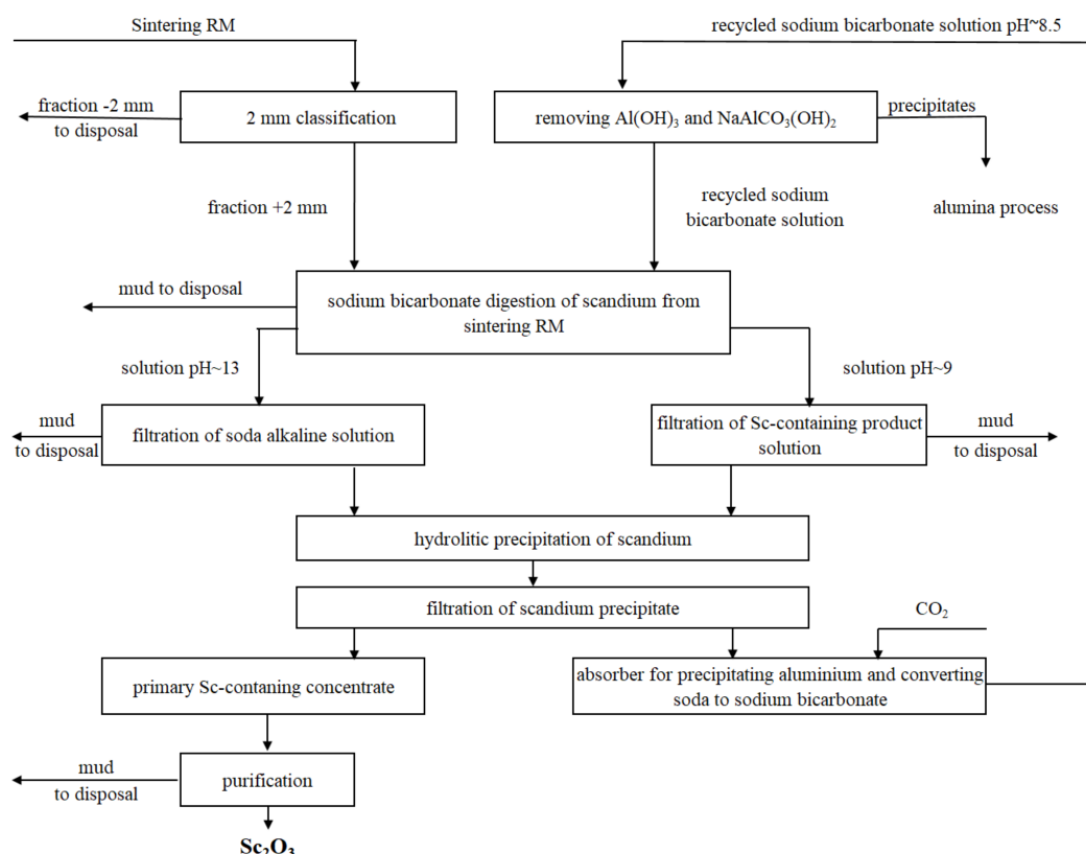


Figure 3. PFD of digesting the sintering RM to obtain the primary Sc-containing concentrate, hydrate-dawsonite precipitate and recycled sodium bicarbonate solution.

The sodium bicarbonate solution that is bypassed from zone 3 to zone 1 contains 5–8 mg/dm³ of dissolved scandium oxide. In zone 1 this scandium reacts with sodium aluminate to form double oxide AlScO₃ and is sorbed on the surface of the sintered RM. Furthermore, this double oxide is again digested in zone 3.

Zone 2. Producing Sc-containing product solution. After low temperature causticization the sintering RM moves from upper zone 1 of the CMB column to the upper part of zone 2. Part of sodium bicarbonate solution goes from zone 3 to the upper part of zone 2. The causticized sintering RM reacts with the sodium bicarbonate solution to activate scandium oxyhydroxide sorbed on the mud surface in form of oxyhydroxide ScO(OH) and to digest thereof to obtain the Sc-containing product solution containing ~ 30 mg/dm³ of Sc₂O₃ and a pH of ~ 9.5–10 in the

column. The obtained Sc-containing product solution is removed from the CMB column, filtered and used to produce the primary Sc-containing concentrate by hydrolytic method (see Figure 3).

Zone 3. Activation and extraction of scandium from the solid phases. The causticized sintering RM goes down the CMB column and get from the lower part of zone 2 to the upper part of zone 3, in which the recycled sodium bicarbonate solution is supplied from the bottom (see Figure 3). In this zone scandium is activated and digested from double oxides ScAlO_3 and ScFeO_3 , which are harder to digest. A larger part of a weak Sc-containing solution obtained in zone 3 (Sc_2O_3 content of 5–8 mg/dm^3) goes to zone 2 where the Sc-containing product solution is obtained (Sc_2O_3 content of 25–30 mg/dm^3). A smaller part of the weak Sc-containing solution is removed from the upper part of zone 3 and bypassed to zone 1 for low temperature causticization of the classified sintering RM and obtaining the sodium bicarbonate solution (see Figure 3). Depending on the rate of leaching the extraction of Sc from the sintering RM makes $57 \pm 15 \%$.

During the sodium bicarbonate digestion a significant amount of yttrium, medium-weight REMs, hafnium, etc. dissolves with scandium into the product solution.

5. Obtaining the Primary Sc-Containing Concentrate

As a result of sodium bicarbonate digestion of the sintered RM in the CBM column, two solutions are obtained:

- Sc-containing product solution, containing $\sim 30 \text{ mg}/\text{dm}^3 \text{ Sc}_2\text{O}_3$, as well as yttrium, medium-weight REMs, zirconium, titanium, hafnium, etc. and at a pH of ~ 9.5 – 10 ;
- Sodium bicarbonate solution contains $\sim 30 \text{ g}/\text{dm}^3 \text{ Na}_2\text{O}_{\text{caustic}}$, up to $15 \text{ g}/\text{dm}^3 \text{ NaAl(OH)}_4$ and a pH of ~ 13 .

Under the specified conditions of mixing these solutions (pH, temperature, residence time, mixing rate, etc.) primary Sc-containing concentrate with Sc_2O_3 content of $\geq 4 \text{ wt.}\%$ (on dry basis) is produced (see Table 3).

Table 3. Chemical composition of primary Sc-containing concentrate.

Phase	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	V_2O_5
Washed primary Sc concentrate	1.76	0.24	4.84	6.41	0.233	2.01	2.89	0.76	0.01	0.055

Table 3 cont'd.

MnO	Ce	Nd	Gd	Yb	SO_3	Sc_2O_3	ZrO_2	Y_2O_3	Cr_2O_3	CuO	HfO_2
0.056	3.50	0.163	0.047	0.475	0.62	4.0	25.60	4.90	0.001	0.07	0.51

The spent liquor that is obtained after scandium hydrolytic precipitation is used in the absorber:

- Recycled sodium bicarbonate solution, which is supplied to the head of the process;
- Hydrate dawsonite slurry comprising the mixture of Al(OH)_3 and dawsonite $\text{NaAlCO}_3(\text{OH})_2$, which is returned to alumina process. Dawsonite decomposes at a temperature of $> 600 \text{ }^\circ\text{C}$ to form sodium aluminate NaAlO_2 .

Hydrolysis of two solutions obtained in the CMB column allows scandium concentrating without sorption or extraction. Cost of producing 1 kg of scandium oxide (in form of primary Sc-containing concentrate amounts to $\approx 100 \text{ USD}/\text{kg}$).

6. Purification of Primary Sc-containing Concentrate.

To produce scandium oxide with Sc₂O₃ content of ≥ 99 wt.% (in the calcined product) RUSAL ETC has developed and applied the sulfate ammonium process, which is presented in [3].

The method of purification of primary Sc-containing concentrate to obtain scandium oxide is based on the following:

- Ability of scandium to dissolve in the solutions of sulfuric acid and alkalis within a narrow ranges of pH values to form complex compounds (of [ScOH]²⁻ type) and within a different narrow ranges of pH values to form insoluble compounds, i.e. carbonate complexes (of [Sc(CO₃)₄]⁵⁻ type) with carbonate ions (CO₃²⁻, HCO₃⁻), acid sulfates ScOHSO₄ or double sulfates with ammonium NH₄Sc(SO₄)₂, oxalates Sc₂(C₂O₄)₃;
- Ability of scandium to precipitate in the neutral medium in form of hydroxides and oxyhydroxides Sc(OH)₃, ScO(OH) and/or basic scandium sulfate Sc₂(C₂O₄)₃;
- Ability of scandium to precipitate in the highly acid medium in form of double salt of and ammonium sulfate and scandium of lower solubility as compared with yttrium and REM. The latter is attributed to the fact that in terms of chemical properties scandium is more like light REM and yttrium is more like medium-weight REMs;
- Low solubility of scandium oxalate Sc₂(C₂O₄)₃, which is formed in the reaction (ion exchange) ScOHSO₄ or NH₄Sc(SO₄)₂ with oxalic acid solution H₂C₂O₄;
- Thermolysis scandium oxalate at a temperature of > 900 °C to remove carbon from oxalate in form of carbon monoxide and obtain scandium oxide of the required quality.

The purification of primary Sc-containing concentrate produced from the sintering RM differs from purification of primary Sc-containing concentrate produced from the Bayer RM in lower transition of zirconium and titanium and a higher transition of REM and yttrium. Therefore, neutralization of ammonium and oxalate tailings yields a by-product, i.e. the concentrate containing ≥ 50 % Y₂O₃ and 30 % medium-weight REMs and hafnium (in a calcined product). This concentrate is also a valuable product.

7. Conclusion

Replacing the Bayer red mud with the sintering red mud enables to reduce Opex and Capex of producing scandium of 2N purity including the following:

- No use of expensive filtration equipment;
- Switching over from batch to continuous sodium bicarbonate digestion;
- Return of ≥ 1 t of Al₂O₃ per 1 kg of scandium oxide;
- No use of sorption and extraction as well as scandium concentrating without use of expensive consumables.

Two years of operation of the large pilot facility at the BAZ refinery have validated all process stages and enabled to commence the construction of the commercial-scale production facility.

The presented process is protected by the patents.

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