A Novel Process of Heap Leaching Extraction of Sc, Zr, Ti, Al, Na from Bauxite Residue with Carbon Footprint Reduction

Alexander Kozyrev[1], Alexander Suss[2], Nataliya Kutkova[3],
Tatiyana Gabrielyan[4], Alexander Damaskin[5] and Andrey Panov[6]
1. Chief Researcher
2. Department Director
3. Engineer
4. Engineer
5. Senior Researcher
6. Director R&D Alumina
RUSAL Engineering and Technology Center, Saint Petersburg, Russia
Corresponding author: Aleksandr.Suss@rusal.com

Abstract

A novel process of valuable elements extraction from bauxite residue (BR) with a sodium hydrocarbonate solution using cold "heap" leaching (HL) has been proposed and evaluated in this study. Recovery of Sc, Zr, Ti, Al, Na using the HL process from BR from 2 Russian refineries was studied. Heap leaching provides for extraction of ~ 30 % of scandium from BR. At optimum process conditions, Sc_2O_3 content in the product solution amounted to 5–20 mg/dm^3 and ZrO_2 content amounted up to 0.25 g/dm^3. The obtained concentration of Sc_2O_3 in the solution is higher as compared with "hot" sodium bicarbonate leaching of bauxite residue. With the established technology Sc-concentrate, as well as zirconium, titanium, aluminum are extracted from Sc-containing solution. After Sc, Zr, Ti, and Al have been precipitated the recirculated solution is treated with CO_2 containing exhaust gas of the refinery to convert part of soda to sodium bicarbonate preparing these liquors to be returned to the head of the process to heap leaching. Aluminum removed from BR as pseudoboehmite (AlOOH) or gibbsite-bayerite $Al(OH)_3$ is returned to alumina production or used as special grade products.

Gravity filtration of the sodium bicarbonate ($NaHCO_3$) solution through a BR layer promotes several processes, i.e. caustic alkali sorbed on BR surface is converted to liquid phase sodium carbonate; sodium aluminate is washed from the residue. Alkali from BR and alkali used to obtain Sc-concentrate promote the HL process. Part of tricalcium hydroaluminates (TCA) and hydrogarnets (HG) from bauxite residue react with sodium bicarbonate to form calcium hydrocarboaluminates and low-temperature calcium carbonates thus binding CO_2. Part of alkali in desilication products (DSP) is replaced with CO_2, and DSP partially decomposes. In HL process bauxite residue binds a significant amount of the refinery emitted carbon dioxide thus reducing carbon footprint of alumina production. After completion of heap leaching both liquid and solid phases of bauxite residue have almost neutral pH values and therefore are of lower hazard class.

Keywords: Bauxite residue, Heap (cold) leaching, Carbon dioxide, Sodium bicarbonate, Carbon footprint.

1. Introduction

Bauxites from the deposits located in the north of European Russia, i.e. North Urals (SUBR), Middle-, South-, and North-Timan (STBR), North Onega (SOBR) bauxites, are characterized by high scandium content (60–350 ppm Sc_2O_3equiv.). Explored reserves of these bauxites amount to > 1.5 Gt thus containing a significant part of the world's supply of available scandium. Due to the mineral and geochemical features of these bauxites a major part of scandium is present in boehmite and diaspore as well as in chamosite, zircon $ZrSiO_4$, and pyrite FeS_2, while a lesser amount occurs in iron-containing minerals (hematite Fe_2O_3 and goethite FeOOH) [1].

The RUSAL Kamensk Uralsky and RUSAL Krasnoturyinsk refineries (UAZ and BAZ respectively) produce alumina from a mixture of boehmitic and diasporic bauxites (SUBR and STBR bauxites) using a parallel combined Bayer-sintering process. Scandium is leached from boehmite, diaspore, zircon, and pyrite at a high temperature (≈ 230 °C) and sorbed on the surface of the bauxite residue (BR) in the form of $Sc(OH)_3$ or ScOOH. Scandium oxide concentration increases in UAZ and BAZ residues by two or more times compared with bauxite. Sc_2O_3 content increases to 140÷160 ppm (UAZ) and 180÷210 ppm (BAZ). Moreover, ≥ 60 % of scandium in these BRs are present in the form that can be easily leached with alkaline solution at a pH of ≤ 9 [1].

The results of pilot tests at the Urals refinery (UAZ pilot plant) proved the possibility of leaching up to 35 % scandium with a sodium bicarbonate solution (consisting of the mixture of Na_2CO_3 and $NaHCO_3$) at the atmospheric pressure [2, 3].

With sodium bicarbonate leaching (SBL) a significant part of zirconium and some titanium are leached from BR with scandium. If added to the aluminium alloy in a specific amount with scandium, zirconium and titanium serve as alloying elements for production of Al-Sc alloys. The addition of zirconium and titanium allows reducing specific consumption of scandium while maintaining the properties of Al-Sc alloy.

RUSAL Engineering and Technology Center has developed a method for direct production of Sc-containing smelter grade alumina from a Sc-containing sodium bicarbonate solution [4]. Use of Sc-containing alumina comprising a specific amount of Zr and Ti enables to directly produce Al-Sc alloys excluding the following stages: 1) deep purification of scandium concentrate from impurities; 2) producing Al-Sc2% master alloy. RUSAL’s technology reduces scandium losses and decreases the production cost of Al-Sc alloys.

To treat the larger residue volumes and to enable the in-situ treatment of BR disposal areas, it was decided to develop the technology of so-called cold heap leaching to extract Sc, Zr, and Ti from the bauxite residue. Cold heap leaching is widely applied in gold and uranium industries. The present paper discusses the results obtained.

2. Experimental - Cold Heap Leaching Tests

Aprox. 450±25 g (on a dry basis) samples of bauxite residue from different alumina refineries were placed into gravity columns (with an inner diameter of Ø 45 mm) (Figure 1). In all tests the BR layer was ≈ 350±3 mm. Then the BR samples were processed as follows:

- aprox. 450±25 g (on a dry basis) sample of the bauxite residue was reslurried using 1 dm^3 of cold water;
- the obtained BR slurry was placed into the gravity column;
- the flow rate of the water passing through the BR layer reduced to ~ 0.5÷0.1 cm^3/h after 4–5 hours that is typical for the formed but not compacted BR layer in the BRDA (hydraulic conductivity $K \approx n \times 10^{-5} \div n \times 10^{-6}$ cm/s). Yield differences depend on the specifics of phase and mineral composition and particle size distribution of BRs from different alumina refineries;
- when the BR layer in the gravity columns is formed, sodium bicarbonate solutions of following compositions are introduced into the columns;
- the composition of the sodium bicarbonate solution used for heap leaching was specified by a sum of ΣNa_2O_{total} in Na_2CO_3 and $NaHCO_3$ as well as a pH value. Na_2O_{total}

concentration in the solutions amounted to 10, 20 and 60 g/dm^3. The proportion of Na_2O in the form of sodium carbonate to Na_2O in the form of sodium bicarbonate changed within a large range. pH of the solutions varied from 8.5 to 9.5 (pH value for 1.0 M Na_2CO_3solution at an ambient temperature amounts to ≈ 12, and pH value for 1.0 M solution of sodium bicarbonate solution amounts to ≈ 8.4);

- the HL tests were carried out at an ambient temperature of the bauxite residue and solution, said temperature varied from + 15 to + 26 °C;
- above the BR surface a layer of the sodium bicarbonate solution of a specific composition was maintained. The fluid column ranged from 3 to 1 cm. To prevent evaporation the gravity columns were covered by the lids.

Figure 1 shows a lab unit for simulating the dynamics of cold (heap) leaching of scandium, titanium, zirconium, aluminum, and sodium from the bauxite residue.

Figure 1. Laboratory test unit of BR cold heap leaching.

Table 1 shows the compositions of the initial BR samples that were used for heap leaching.

The production rate of a Sc-containing product solution (infiltrate) in the column (after passing through the BR layer) was a variable value and varied within the range of 0.1–2.0 cm^3/h. It was resolved to take samples of the product solution (PS) when the volume of the said solution amounted to 50 cm^3 (further below this volume is called standard volume and shown in the graphs, as it allows to quantify how the process takes place during the time). Actually, PS samples in the amount of 50 cm^3 that had been obtained over the period of 1.5–20 days were analyzed, but in average, 50 cm^3 of product solution were obtained within 6–8 days. At such a rate, 1 m^2 of disposed BR shall yield approx. 0.2 dm^3/h of the product solution.

Table 1. Chemical composition of the initial bauxite residue from BAZ and UAZ (Russia).

Sample	Content, mass. %													
	Sc_2O_3	ZrO_2	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	V_2O_5	Cr_2O_3	MnO
BAZ	0.019	0.028	6.3	10.7	47.3	4.3	1.2	13.4	1.0	2.0	<0.15	0.11	0.05	0.24
UAZ	0.015	0.10	10.7	14.1	41.8	4.3	0.76	11.9	0.86	4.5	<0.15	0.1	0.06	0.34

3. Results and Discussion

Heap leaching process can be provisionally divided into 3 stages as follows:

- Stage of reaching the production conditions when pH value in the liquid phase reduces to ≤ 10 (Preparation stage);
- Production stage;

- Stage of leaching completion with displacement (squeezing) of the sodium bicarbonate solution from the BR layer.

3.1 Preparation Stage

This stage is characterized by a presence of several kinds of alkalis and sodium aluminate in the BRs, namely as follows:

- incorporated into the liquid phase (of a pond liquor);
- sorbed on the surface of BR particles as solvation shells and immobilized inside the bauxite residue having so-called “network” structure [5]. “Network” structure of the bauxite residue is attributed to the use of synthetic flocculants for thickening and washing in the alumina production that flocculate the BR phases and minerals, which have different surface charges (zeta potential);
- chemically bonded into desilication products (DSP) that have a zeolite structure. In zeolites (DSP) alkali is incorporated into the crystalline structure as well as additional anionic groups that are characterized by higher mobility.

When the sodium bicarbonate solution is supplied on the BR layer, the displacement of alkaline pond liquor begins. This process can be clearly seen by presence of 0.8÷3.5 g/dm^3 of dissolved Al_2O_3 in the filtrate and pH value of > 11.5. Reaching the production conditions with the BR layer of 0.5 m might take up to 3 months. This stage is required if the alumina production uses back end wash thickeners, which yield the bauxite residue with L : S = 2 : 1 (by weight). If deep cone thickeners are used in the process or if bauxite residue is filtered (e.g. using filter-presses or vacuum drum filters), then L : S in the BR will be less than 1. Such bauxite residue can be reslurried with a sodium bicarbonate solution to start directly with the production stage.

As the sodium bicarbonate solution is passing through the BR layer caustic alkali carbonation begins as well as hydrolysis of dissolved sodium aluminate as per the following reactions:

$$NaOH + NaHCO_3 = Na_2CO_3 + H_2O \tag{1}$$

$$NaAlO_2aq + NaHCO_3 = Al(OH)_3 + Na_2CO_3 \tag{2}$$

During the carbonation the solvation shells around the phases and minerals of the bauxite residue with a high zeta potential break and sodium carbonate dissolves into the liquid. For this reason alkali concentration in the filtrate increases by 20–70 % as comparted with the sodium carbonate solution fed to heap leaching. Evaporation of the water from the surface also promotes the increase of alkali concentration in the bauxite residue.

Due to the carbonation of caustic alkali, hydrolysis of sodium aluminate, and formation of sodium bicarbonate the pH value gradually decreases. Leaching of scandium that is sorbed on the BR surface starts only when pH in the liquid phase decreases below ~ 10.

3.2 Production Stage

When pH in the product solution decreases below ~ 10.2 scandium that is sorbed on the BR surface starts to dissolve. Scandium solubility directly depends on the concentration of the leaching solution. In terms of industry scandium content in the product solution shall be no less than 4.5 ÷ 5 mg/dm^3 (calculated as Sc_2O_3). Said values can be achieved if the concentration of the initial leaching solution is 60 g/dm^3 equiv. Na_2O_{total} (Figures 2 and 3).

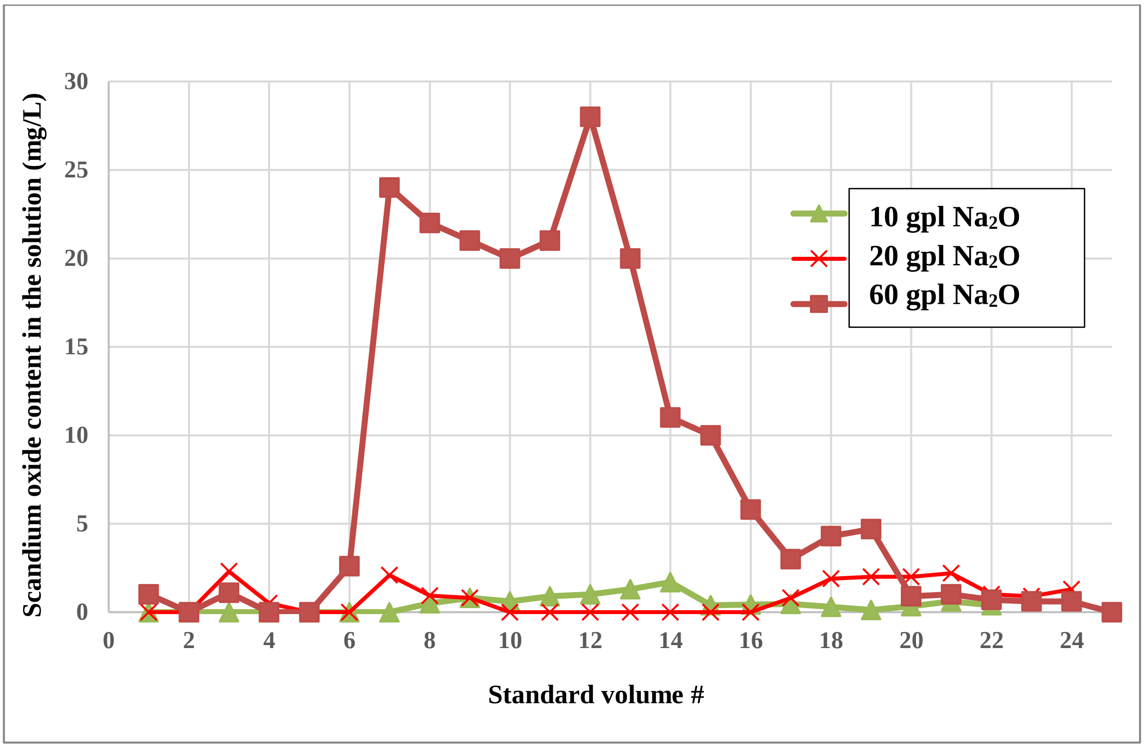

Figure 2. Impact of the concentration in the solution on Sc_2O_3 extraction from BAZ BR.

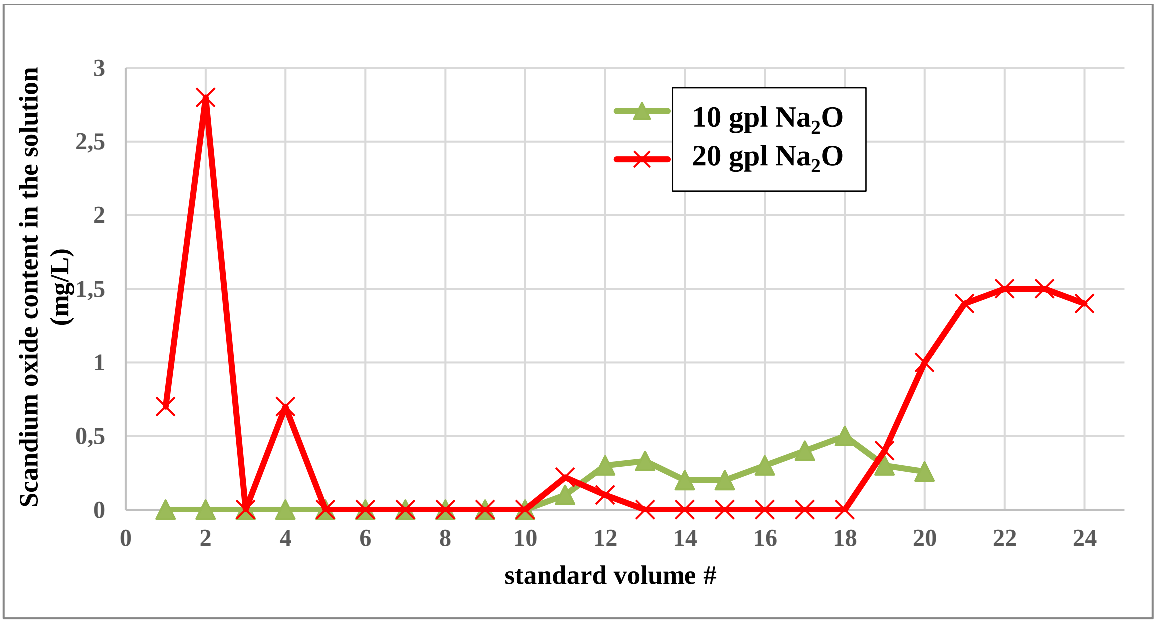

Figure 3. Impact of the concentration in the solution on Sc_2O_3 extraction from UAZ BR.

Along with scandium, zirconium and titanium start to dissolve into the filtrate (Figure 4).

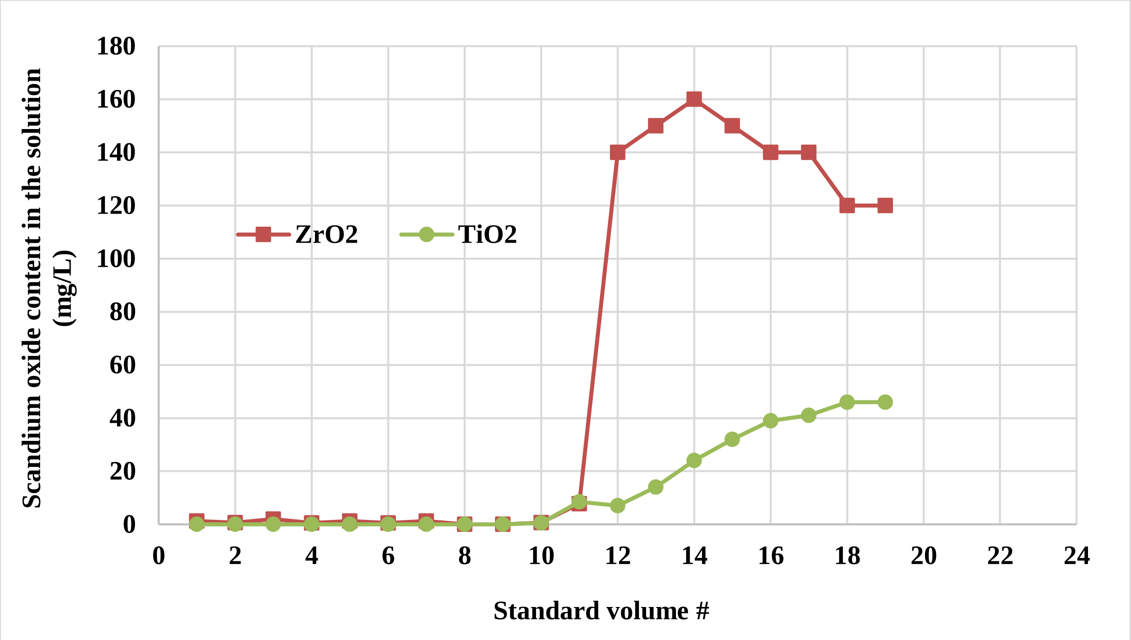

Figure 4. Kinetics of extraction of zirconium and titanium in the course of heap leaching of the bauxite residue from BAZ.

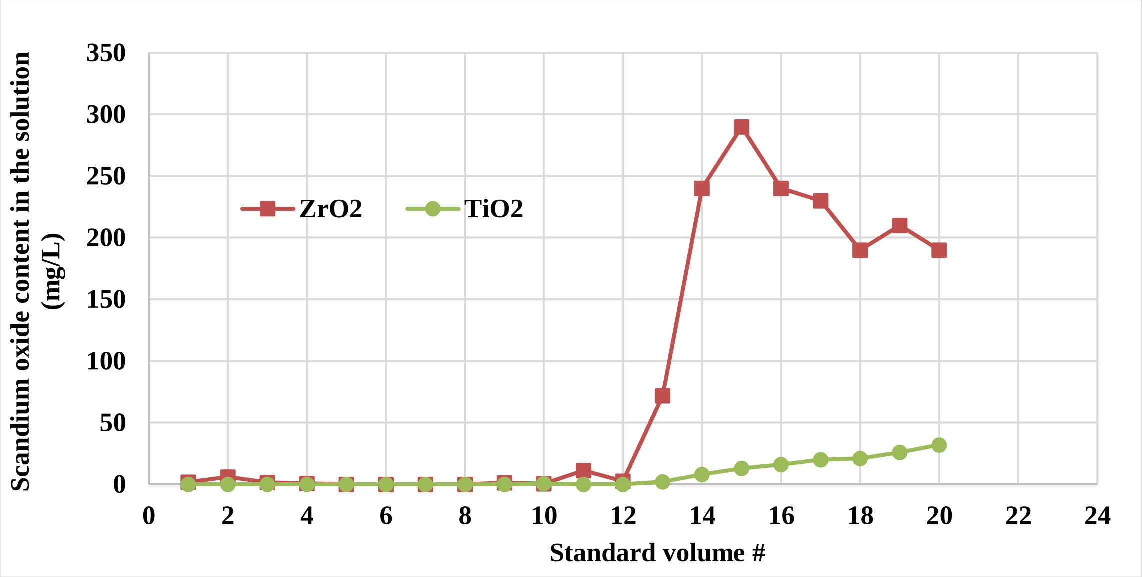

Figure 5. Kinetics of extraction of zirconium and titanium in the course of heap leaching of the bauxite residue from UAZ.

Production stage, when the product solution contains much scandium, can last for 6 months or longer (for 0.5 m BR layer). The calculated results show that 1 hectare of stacked bauxite residue (S = 10 000 m^2) will yield 80–100 kg Sc_2O_3 per a year.

When the concentration in a sodium bicarbonate solution is 60 g/dm^3 (Na_2O_{total} equiv.) then Na_2O_{total} content increases significantly in the product solution. It is associated with a number of reactions of BR phases with sodium bicarbonate [6, 7], including the following:

- tricalcium hydroaluminate (TCA) and calcium hydrogarnet (HG) react with sodium bicarbonate to form calcite and other low-temperature carbonates (vaterite, aragonite) and X-ray amorphous aluminum hydroxide by the following reaction:

$$3CaO.Al_2O_3.6H_2O + 6NaHCO_3 = 6Al(OH)_3 + 3CaCO_3 + 3Na_2CO_3 + 6H_2O \quad (3)$$

- additionally, a two-stage process occurs, i.e. calcium hydrocarboaluminate reacts with sodium bicarbonate to form various calcium carbonates (calcite, vaterite, aragonite) and bayerite (possibly, pseudoboehmite):

$$Ca_4Al_2(OH)_{12}CO_35H_2O + 3CO_2 = 4CaCO_3 + 2Al(OH)_3 + 8H_2O \quad (4)$$

$$2Ca_4Al_2(OH)_{12}CO_3 \cdot 5H_2O + 18NaHCO_3 = 8CaCO_3 + 8Al(OH)_3 + 10Na_2CO_3 + 19H_2O \quad (5)$$

Moreover, XRD analysis showed that the said process generates some portlandite $Ca(OH)_2$.

- TCA reacts with CO_2 and portlandite in the aqueous solution to form calcium hydrocarboaluminate:

$$Ca_3Al_2(OH)_{12} + CO_2 + Ca(OH)_2 = Ca_4Al_2(OH)_{12}CO_35H_2O \quad (6)$$

- two processes occur when bicarbonate reacts with DSP: 1) partial replacement of NaOH bonded into DSP crystalline structure as an additional anionic group with CO_2 and 2) partial DSP decomposition (from 5 to ~ 8 %).

All these reactions result in partial BR de-alkalisation and fixation of carbon dioxide into the insoluble products.

The solutions from the heap leaching were analyzed for REM (Rare Earth Metals) using ICP-MS. The results show that only the following elements are extracted in significant quantities:

- yttrium from 0.1 to 3.3 mg/dm^3 expressed as yttrium metal;
- thorium from 0.8 to 0.01 mg/dm^3 expressed as thorium metal;
- ytterbium from 1.05 to 0.3 mg/dm^3 expressed as ytterbium metal.

All remaining REMs in the product solution amount to no more than 5.1 mg/dm^3.

3.3 Stage of Completion of Valuable Components Leaching

This stage is limited due to the need to return the sodium bicarbonate solution to the process. The best option is to replace the alkaline solution with the process water when the heap leaching is completed. Then the spent bauxite residue is replaced with a new batch of fresh BR.

4. Heap Leaching Process

Figure 6 shows the process block flow diagram of CO_2 absorption during the heap leaching of scandium and other impurities from the bauxite residue.

Currently, the conditions of sodium bicarbonate production by gassing with the exhaust gas from sintering (~ 5 vol.% CO_2) are being fine-tuned at the pilot unit at the BAZ refinery . This reaction goes at low temperatures as follows:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 \quad (7)$$

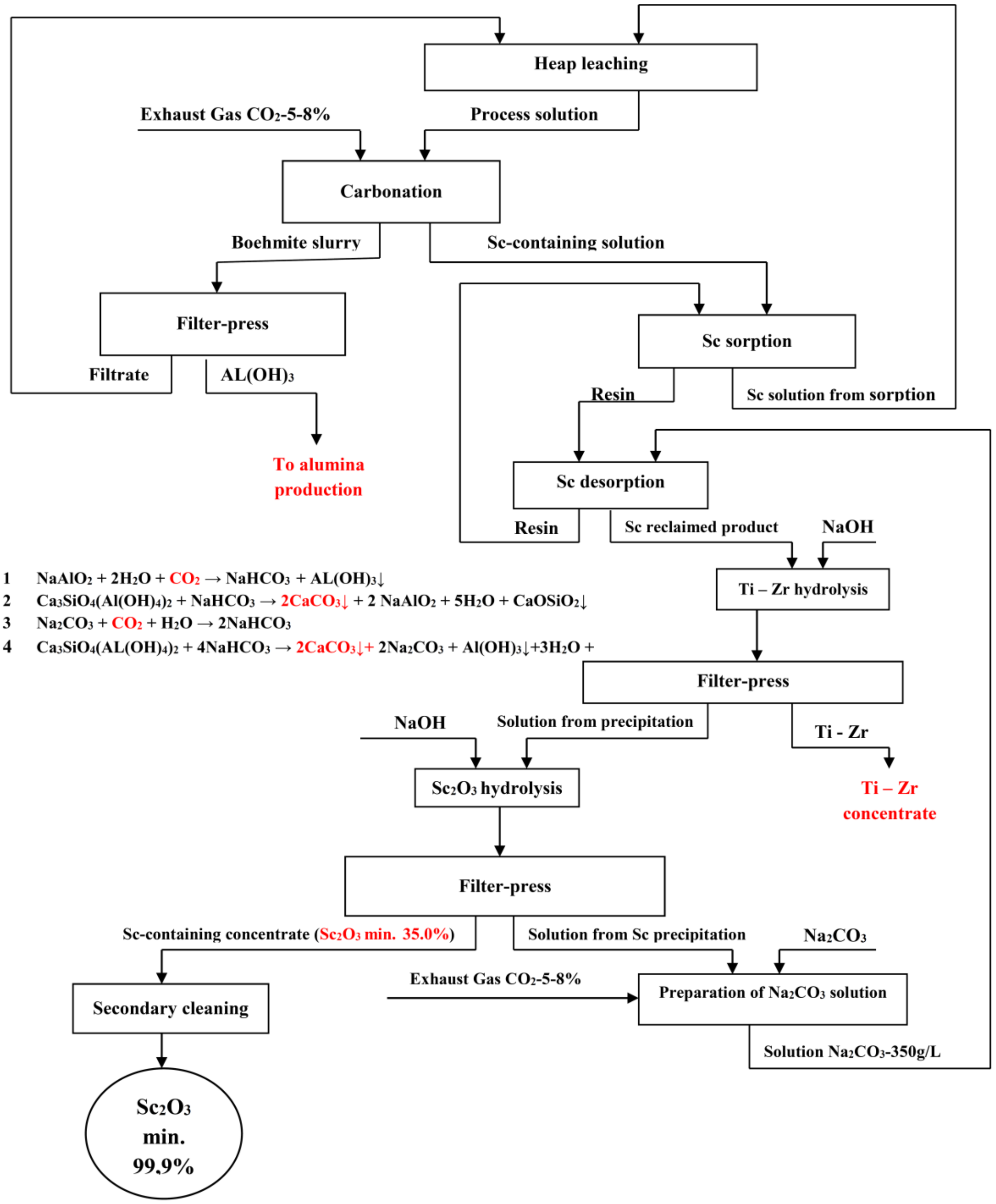

Figure 6. Process flow diagram of CO_2 absorption during the heap leaching of the bauxite residue.

4.1 Layout of Heap Leaching Process

It is expedient to arrange a cyclic process of heap leaching as follows:

- supplying the bauxite residue from the last washer with L : S ≈ 2÷1.5 : 1 (by weight) to the prepared leach cell to build up ~ 0.5 m layer (Figure 7);
- removing the pond liquor via the drainage, generating the layer with L : S ≈ 0.5 : 1 (by weight);
- supplying the process leaching solution with a pH of ≤ 9 on the BR layer via the sprinkler system;

- reaching the production conditions when a pH value in the liquid phase reduces to ≤ 10. At this stage Al & Sc-containing solution with pH of ≥ 10.4 is pumped to carbonation (Figure 6);
- production stage. The solution with a pH of ≤ 10.2 and Sc_2O_3 content of more than 2 mg/dm^3 is pumped to Ti-Zr hydrolysis (Figure 6);
- extracting the scandium-zirconium concentrate from the product solution;
- carbonation of the spent (recirculated) solution with exhaust gas from sintering containing CO_2 to reduce a pH value from ≥ 11.5 to ≤ 9 and supplying the obtained solution to the BR layer.

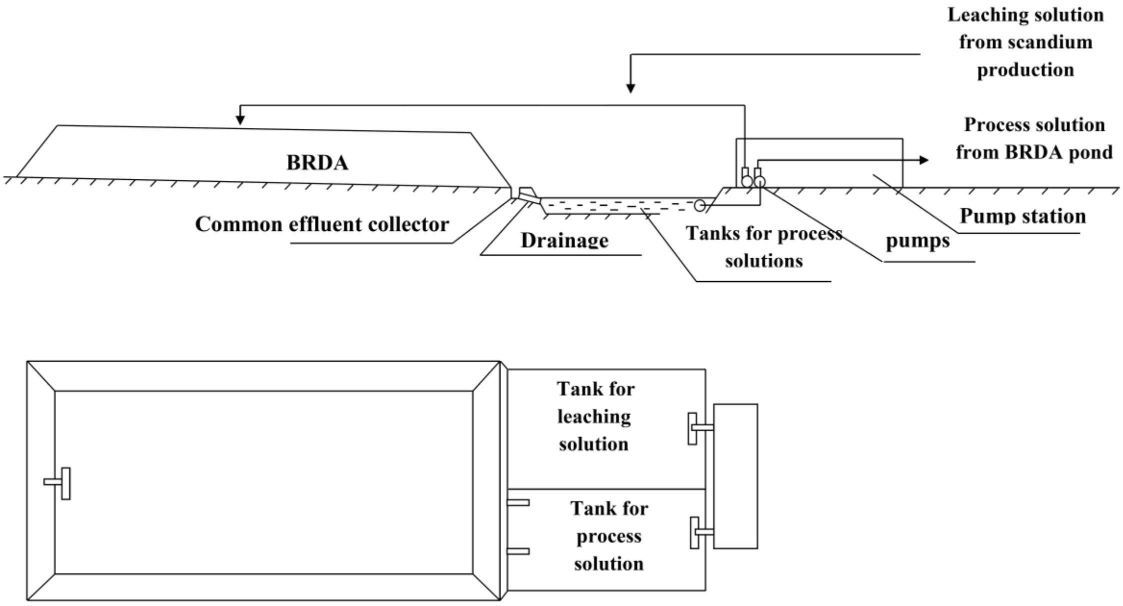

Figure 7. Layout drawing of cold heap leaching of scandium, zirconium, and titanium from bauxite residue. (Font size within the Figure is suggested to increase_ Reviewer - Done)

- stage of process completion. When Sc_2O_3 content in the product solution decreases below 2 mg/dm^3 the supply of the sodium bicarbonate solution shall be stopped and process water shall be fed to the cell to replace (squeeze) the sodium bicarbonate solution;
- removing the spent bauxite residue and supplying a new batch of bauxite residue.

To ensure a balanced operation of the facility a minimum of five cells shall be installed operating in a phase-shifted mode.

5. Conclusions

A new technology of heap leaching allowing to extract valuable components from bauxite residue and to reduce alumina refinery CO_2 emissions is proposed in this study.

Extraction of scandium from the bauxite residue amounts to 35 %. Zirconium extraction can reach up to > 90 %. Extraction of titanium amounts to 6–8 %.

To provide for the viability of the heap leaching the following properties of the leaching solution shall be maintained: Na_2O_{total} content of ≥ 60 g/dm^3, with a pH value in the output product solution of no more than 10.2. Under these conditions a high content of Sc_2O_3, i.e. ≥ 5 mg/dm^3 in the product solution can be maintained over a long period of time (6 months or more).

The area of a heap leach cell of 1 hectare will yield minimum 80–100 kg Sc_2O_3 per a year. As the concentration of Na_2O in the leaching solution increases due to replacement of the alkali and self-evaporation from the surface, scandium production will increase.

The process allows to extract alkali both from solid and liquid phases of stored BR and also to bind CO_2 with BR solid phase providing sustainable solution for disposal of treated bauxite residue in alumina refining.

6. Acknowledgements

The authors would like to acknowledge Tatyana Golovanova, Tatyana Mukina, Yulia Maksimova, Yulia Chernyshova, and Irina Paromova – employees of the Engineering and Technology Department of LLC RUSAL ETC in St. Petersburg, who made a great contribution to this work.

7. References

1. Alexander Suss et al., Specific features of scandium behavior during sodium bicarbonate digestion of red mud, *Proceedings of the 35th International Conference ICSOBA Conference and Exhibition*, 2–5 October 2017, Hamburg, Germany, *TRAVAUX 46*, 491-503.
2. Olga Petrakova et al., Improved Technology of Scandium Recovery from Solutions of Bauxite Residue Carbonation Leaching, *Light Metals*, 2019, 1407-1413.
3. Alexander Suss et al., Refining Technology of Scandium Concentrate Obtained from Bauxite Residue, *Light Metals,* 2019, 1403-1406.
4. Aleksandr Kozyrev, Viktor Mann, Olga Petrakova, Aleksandr Suss and Andrey Panov, Scandium-containing alumina and methods of production thereof, Patent Application RF 2020134635 filed October 22, 2020.
5. Valentin Korneev, Alexander Suss and Alexander Tsekhovoy, *Red muds: properties, stacking, utilization*, M. Metallurgiya, 1991, 144 pages.
6. Aleksandr Suss, Alexander Damaskin, Andrey Panov and Martin Fennell, Comparison of Lime and Carbon Dioxide Methods of Bauxite Residue Neutralization, *Proceedings of the 38th International Conference Virtual ICSOBA-2020*, 16–18 November 2020, *TRAVAUX 49*, 427-439.
7. Sameer Khaitan, David A. Dzombak, and Gregory V. Lowry, Mechanisms of Neutralization of Bauxite Residue by Carbon Dioxide, *Journal of Environmental Engineering,* Vol. 135, No. 6, 2009, 433-438.