Evaluation of Main Factors for Improvement of the Scandium Leaching Process from Russian Bauxite Residue (Red Mud) in Carbonate Media

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ABSTRACT: The carbonate leaching of scandium from the landfilled bauxite residue (red mud) of the Bogoslovsky Aluminum Plant (Russia) and samples of red mud (RM) after alkaline pretreatment has been investigated. The results of kinetic studies allowing to compare and evaluate the effectiveness of different conditions and intensification factors in the process of scandium leaching from RM in carbonate/bicarbonate media are presented. It was determined that for 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) leaching solution ultrasonic treatment under gas (CO\(_2\)) carbonation conditions in the pH range of 9.5–10.0 allows reducing the scandium leaching time by two times and reaching 40–45% scandium extraction. Leaching of RM in carbonate/bicarbonate media is accompanied by secondary processes (adsorption, hydrolysis, and coprecipitation) leading to a decrease in scandium extraction. The obtained results allow improving understanding of scandium chemical behavior in complex aqueous carbonate/bicarbonate systems and can be used for the optimization of the alternative carbonate process for scandium extraction from RM.

1. INTRODUCTION

The long-term storage of bauxite residue or red mud (RM), a waste product from alumina production, poses a significant threat to the environment. In addition, this material is not currently used on an industrial scale. The main obstacles to the direct reuse of RM are heavy metal content, radioactivity, alkalinity/high sodium content, high hazard class, high moisture content, and transportation costs.\(^1\) At the same time, RM is an interesting potential source of iron (Fe), aluminium (Al), titanium (Ti), zirconium (Zr), yttrium (Y), lanthanides (Ln), scandium (Sc), gallium (Ga), and some other valuable metals. Extraction of only Fe and/or Al from RM cannot make the process economically profitable. Only complex reprocessing of RM in a single integrated system with obtaining the maximum amount of marketable products, including the expensive Sc and other rare-earth elements (REEs), will reliably make the process cost-effective and minimize the generated waste.\(^2\)\(^-\)\(^3\)

Mineral and organic acids\(^4\)\(^-\)\(^11\) have been suggested for Sc and REEs recovery from different types of RM and their processing products.\(^12\) The use of mineral acid solutions provides a relatively easy decomposition of RM because of the high content of Fe/Al/calcium (Ca)/Ti-containing mineral phases with which Sc is chemically associated.\(^13\)\(^-\)\(^15\) This allows achieving high values of extraction yields of the most valuable components and critical metals such as REEs from RM. Alternative approaches and lixiviants for extraction of Sc and other REEs from RM are also known. These options may include the use of ionic liquids,\(^16\) bioleaching processes,\(^17\)\(^,\)\(^18\) and also carbonation (sometimes called “carbonization”) leaching processes with using gaseous carbon dioxide (CO\(_2\)) and carbonate reagents (NaHCO\(_3\) and/or Na\(_2\)CO\(_3\)).\(^19\)\(^-\)\(^32\) Such approaches may solve some of the problems associated with the use of concentrated mineral acid solutions, for example, the high corrosive activity of mineral acids, and the formation of multicomponent salt solutions, which are difficult to recycle and utilize.

Under the condition of carbonate/bicarbonate leaching of RM, selective extraction of Sc occurs, as well as Y, Ln, Zr, and Hf which belong to the group of so-called less common elements (LCEs). However, Fe/Al/silicon (Si)-containing mineral phases are inert in carbonate media and almost completely remain in the insoluble residue after carbonate leaching of RM.\(^19\)\(^-\)\(^22\) The fundamental possibility of extracting...
some part of Sc and other valuable metals from RM formed at Russian aluminum plants contributed to the development of carbonate approaches. Currently, such approaches using the carbonation method for Sc extraction have shown the possibility of their use for samples of the Russian RM. At the same time, mineralogical compositions of differently sourced RM suspensions may differ, and this can significantly affect the efficiency of the processing method or make it not applicable for specific types of RM. Both individual stages and an integrated approach to RM processing in carbonate media are being considered and researched currently in Russia.19–32

At present, various options have been developed for the carbonation of mineral slurries and industrial wastes including RM, with the participation of CO3(g).33–34 Carbonation of the RM slurry is carried out to decrease its alkalinity by neutralization with NaOH, Na2CO3, and NaAl(OH)3 (the content of which varies from 1 to 6% expressed as Na2O).35,36 with the conversion of sodium to NaHCO3. This process reduces the pH of the RM suspension from 12–13 to <8.5 and decreases its toxicity to the environment and humans.37–42 Carbonation of RM using CO2(g) makes the subsequent disposal process safer.38–45

During the carbonate leaching of RM, a part of NaHCO3 is converted to Na2CO3, which reduces Sc extraction because of its lower solubility in Na2CO3 solutions. Additional treatment of the RM slurry by CO2(g) increases the content of NaHCO3, which contributes to an increase in Sc extraction.20 Carbonation allows intensifying to some extent the leaching of some LCEs from RM in carbonate media. CO2(g) is a widely available and relatively inexpensive reagent, in particular, for other industrial sources for carbonation. The use of CO2(g), which have been developed by various alumina production companies.40,41 Much attention has been paid to the study of the carbonation mechanisms of RM with CO2(g).42 Preliminary neutralization of the alkalinity of RM with carbonic acid (H2CO3) formed when dissolving CO2 in water allows reducing the consumption of mineral acid during subsequent acid leaching conditions of or chemically bound to sodium hydroaluminosilicate or calcium hydrogranates contained in RM, which break down partially or completely under the carbonation process conditions.28 The major part of Sc included in the lattice of hematite, goethite, and zircon13, as well as Sc associated in mineral particles located in pores and cracks of large iron oxide particles, is not extracted under carbonate leaching conditions because of the stability of these mineral phases in carbonate/bicarbonate media.28 Therefore, all such factors as the mineral composition of the original bauxite ore, the form of Sc location in mineral phases, its distribution, and content, as well as the Bayer process conditions, will affect the feasibility and effectiveness of the subsequent reprocessing in carbonate media and extraction of Sc from each specific type of RM. For RM samples of RUSAL aluminum plants, the content of so-called “easily leachable” Sc-containing phases (Al-containing compounds and secondary phases) can reach up to 60% (of the total content in original RM).62–64

Second, Sc extraction from RM during leaching in carbonate media can also be complicated as a result of secondary processes, such as (i) hydrolysis of Sc carbonate complexes; (ii) coprecipitation of Sc with dawsonite or calcium carbonates; and (iii) adsorption of Sc on the surface of mineral particles.28

One of the most important tasks while improving the reprocessing of RM in carbonate media is to increase the extraction of Sc. In this regard, additional measures for intensification of the leaching process and stabilization of Sc in carbonate solutions are needed. To increase the extraction of Sc from RM into carbonate solutions, physical methods of intensification, such as ultrasonic treatment (UT), can be used.29,63,64 The options for enhancing Sc extraction processes using microwave55 or vibrocavitation treatment65,66 and mechanical activation69,64 are also described.

Taking into account many important factors described above, scandium recovery from RM (RUSAL) during the carbonate leaching process can vary in a wide range, from 6 to 50–55%. Table 1 shows the main published Sc leaching techniques and methods from Russian RM (RUSAL) in carbonate media.

Based on the results of systematic studies published earlier,20,23,26–29,47,59,64 it can be said that some points have not been investigated in sufficient detail. More detailed research is required for a better understanding of the chemical behavior of Sc in complex heterogeneous systems formed under conditions of RM leaching in carbonate and carbonate—


Table 1. Different Methods for Scandium Leaching from Russian RM in Carbonate Media

| conditions | original RM | Sc leaching yield, % | ref |
|------------|-------------|----------------------|-----|
| direct leaching: 5−12% Na₂CO₃ or NaHCO₃ or mixtures thereof; ≤50 °C; ≥ 2 h; S/L = 1/2.5−5.0, three recycling steps of the carbonate solution. | sintering dust of electric filters (1) or RM (2) (RUSAL), Russia. Sc content—(1) 52 mg kg⁻¹; (2) 81 mg kg⁻¹. | 59—123 | 19 |
| direct leaching: 30−100 g L⁻¹ Na₂CO₃ and 50−100 g L⁻¹ NaHCO₃; S/L = 1/(2−5), 50−60 °C, bubbling with the CO₂(g)−air mixture (10−17% vol) CO₂(g), 10 recycling steps of the carbonate solution. | landfilled RM (RUSAL), Russia. Sc content—81 mg kg⁻¹. | 136—139 | 21 |
| direct leaching: 100−150 g dm⁻³ Na₂CO₃; 60 °C; S/L = 1/3−5; precarbonation with bubbling of gases from bauxite ore sintering or calcination furnaces (10% vol) CO₂(g), seven recycling steps of the carbonate solution. | RM (RUSAL), Russia. Sc content—72 mg kg⁻¹. | 136—15.8 | 22 |
| direct leaching: 5% NaHCO₃; 45 °C; cavitation treatment. | RM, Bogoslovsky Aluminum Smelter (RUSAL), Russia. Sc content—110 mg kg⁻¹. | 15—17 | 68 |
| RIP (resin-in-pulp)-process: 35−40 °C; S/L = 1/3.0−4.0, bubbling of CO₂(g) (balloon), the mass ratio of resin to RM = 1/50−150 g dm⁻³, 40 °C, 8 h, and ion exchange resin: KFP-12 cationite and/or ampholite ANKF-80. | RM (RUSAL), Russia. | 15—20 | 47 (pp 242−243) |
| direct leaching: (1) without treatment; (2) preliminary mechanical activation (≥7 min); (3) cavitation treatment (5 min, amplitude 60 μm). | | | |
| vibrocavitation pretreatment (peripheral speed 20−40 m s⁻¹ and agitation time 45−60 min); direct leaching: 100−150 g dm⁻³ NaHCO₃; 55−65 °C; 4−6 h, bubbling of the CO₂(g)−air mixture, recycling of carbonate solutions after Sc recovery. | RM (RUSAL), Russia. | (1) 18.3 | 64 |
| RIP process: 20 g L⁻¹ NaHCO₃ | | (2) 16.7 | |
| direct leaching: (1) 125 g dm⁻³ NaHCO₃ one step; (2) 85−100 g dm⁻³ NaHCO₃ and 20.0−45.0 g dm⁻³ Na₂CO₃ one step; (3) 90.0 g dm⁻³ NaHCO₃ and 35.0 g dm⁻³ Na₂CO₃; 5−7 recycling steps of carbonate solution; (4) 125 g dm⁻³ NaHCO₃ overpressure of gases from bauxite ore sintering or calcination furnaces (8.0−17.0% vol) CO₂(g) equal to 6 atm; vibrocavitation treatment, 60 °C; 8 h; general conditions of direct leaching: 50−60 °C; 95% (vol %) CO₂(g) overpressure—30−60 atm; vibrocavitation treatment (peripheral speed 30−40 m/s and agitation time 4−8 h. | Landfilled RM, Bogoslovsky Aluminum Smelter (RUSAL), Russia. Sc content—65 mg kg⁻¹. | (1) 18.5 | 67 |
| direct leaching: 125 g L⁻¹ NaHCO₃, 60 °C; S/L = 1/4; CO₂(g) overpressure: (1) 4.0 atm; (2) 6.0 atm. | RM (RUSAL), Russia. | (2) 26.0 | |
| repulpation mixing: NaHCO₃−Na₂CO₃ mixture solution (110/45−100/50 g dm⁻³), 80−85 °C; ≥3 h; S/L = 4.5−S/1, one step, bubbling of the CO₂(g)−air mixture to pH ≤ 9. | | (3) 19.0−19.5 | |
| direct leaching: 60−70 g (Na₂O) L⁻¹ (NaHCO₃−Na₂CO₃ mixture with ratio ~1.5 + 2); 180 min; 80−85 °C; S/L ≥ 3.5. | | (4) 20.5 | 23 |
| direct leaching: (1) pH = 8.8−9.2, 60 °C; L/S = 3/1, 60 min, CO₂(g) overpressure 10.0 atm; (2) additional mechanical activation; (3) additional mechanical activation and UR. | | | |
| repulpation mixing: NaHCO₃−Na₂CO₃ mixture (40−80 g dm⁻³ Na₂O), wherein Na₂O (in the form of NaHCO₃) content makes from 50 to 100% of Na₂O (total); 40−90 °C; S/L = 1/2.5−5.0; bubbling of the CO₂(g)−air mixture. RIP process: continuous countercurrent mode; the mass ratio of resin to RM = 1/20−120; 1−8 h (for each step); ion exchange resin: Lewatit TR-260 Monopolus (Na⁺ form). | RM, Middle-Timian bauxite mine), Ural Aluminum Smelter (RUSAL), Russia. Sc content—90 mg kg⁻¹. | (1) 22.5 | 26.5 |
| direct leaching: (1) sodium bicarbonate digestion; (2) bicarbonate−RIP digestion. | | | |
bicarbonate media, as well as key parameters of Sc extraction in such systems.

The objective of this research is to evaluate and identify the main factors for improvement of Sc extraction from landfilled bauxite residue (red mud) of Bogoslovsky Aluminum Plant (Russia) during its hydrochemical reprocessing in carbonate and carbonate−bicarbonate solutions under various conditions of the process such as agitation or ultrasonication time, type and concentration of carbonate reagents, temperature, and pH value.

2. RESULTS AND DISCUSSION

2.1. Carbonation of RM. Both CO₂(g) and chemical reagents NaHCO₃ or Na₂CO₃ are used in the RM carbonation processes. On a laboratory scale, carbonation using CO₂(g) from the gas cylinder is carried out by saturation (during barbotage) of the alkaline suspension of RM slurry or under conditions of elevated pressure in an autoclave. On an industrial scale, various flue gases containing CO₂(g) have been proposed for carbonation. Carbonic acid (H₂CO₃), which is formed by pushing CO₂(g) through a layer of RM suspension, reacts with its main components, thus lowering the pH of the RM suspension. During neutralization of NaOH in RM by CO₂(g), Na₂CO₃ and NaHCO₃ are formed, which are suitable reagents for leaching not only Sc, but also Y, Ln, Zr, Hf, and Ti from some mineral phases of RM. The concentration of carbonate salts in the solution after carbonation directly depends on the content of residual alkali in RM and on the amount of CO₂(g) supplied to the system. The NaOH content in the freshly generated flows and stocks of the RM suspension is higher compared with landfilled residue, so its carbonation requires a higher consumption (amount) of CO₂(g). As a result, the concentration of Na₂CO₃/NaHCO₃ in the slurry liquid phase achieved during the carbonation of the freshly generated RM is higher. On the one hand, the increase of carbonate content contributes to the increased extraction of Sc and other valuable components from RM. On the other hand, when recycled in a technological cycle to the stage of leaching of carbonate solutions, the accumulation of Na₂CO₃/NaHCO₃ in them will go faster. To reduce sodium losses and prevent its accumulation in recycled solutions, excess sodium must be removed from the system.

During carbonation of the aqueous suspension of the RM sample at CO₂(g) flow rate (Q) equal to 0.9 L min⁻¹, the value of Sc extraction (α(Sc)) did not exceed 0.05% (Table 2).

| carbonation conditions | t, °C | [Sc], mg L⁻¹ | α(Sc), % |
|-----------------------|------|--------------|---------|
| barbotage CO₂(g)−H₂O | 20   | 0.0040       | 0.046   |
| p(CO₂(g)) = 1 atm−H₂O |      | 0.0043       | 0.050   |
| p(CO₂(g)) = 5 atm−H₂O |      | 0.0043       | 0.050   |
| p(CO₂(g)) = 10 atm−H₂O |     | 0.0086       | 0.100   |
| p(CO₂(g)) = 10 atm−H₂O | 50   | 0.0086       | 0.100   |
| 0.1 mol L⁻¹ NaHCO₃−H₂O | 20   | 0.0098       | 0.11    |
| 0.25 mol L⁻¹ NaHCO₃−H₂O |     | 0.100        | 1.10    |
| 0.5 mol L⁻¹ NaHCO₃−H₂O |     | 0.170        | 1.98    |
| 0.75 mol L⁻¹ NaHCO₃−H₂O |     | 0.196        | 2.20    |
| 1.0 mol L⁻¹ NaHCO₃−H₂O |     | 0.200        | 2.32    |

Table 2. Extraction of Sc by Carbonation of the RM Suspension Sample at L/S = 10
neutralized with the formation of NaHCO$_3$. Under such conditions, NaOH in the solution was completely decreased to 6.9 and did not change any further (Figure 1b).

Hydroaluminosilicates (DSP) such as sodalite ($[\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}]$) which are present in RM, causes their hydrolysis with the formation of NaOH. However, these processes, which can be expressed by the chemical reactions shown in eqs 2 and 3, apparently occur at relatively low rates under normal conditions.

\[
2\text{NaAlO}_2 + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{NaOH} \tag{1}
\]

\[
[q\text{NaAlO}_2 \cdot p\text{H}_2\text{O}] + q\text{Na}^+ + q\text{AlO}_2^- + [\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}] 
\]

\[
3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}) + 2\text{H}_2\text{O} 
\rightleftharpoons 2\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 7\text{H}_2\text{O} + \text{NaOH} \tag{3}
\]

During 20 min of CO$_2$ barbotage at liquid-to-solid (L/S) ratio equal to 10 and 20 $^\circ$C, the pH value of the liquid phase decreased to 6.9 and did not change any further (Figure 1b). Under such conditions, NaOH in the solution was completely neutralized with the formation of NaHCO$_3$. If the CO$_2$ overpressure ($p(\text{CO}_2(g))$) was increased from 1 to 10 atm when the carbonation of RM was performed in a steel autoclave, a slight increase in Sc extraction into the liquid phase (from 0.05 to 0.1%) was observed (Table 2). A low degree of Sc extraction under these conditions is due to the low concentration of the leaching reagent and Sc complexing agent (NaHCO$_3$) and due to reduction of pH to 7–8 resulting in low-soluble Sc compounds, as well as Sc coprecipitation with Al in the form of dawsonite (NaAlCO$_3$(OH)$_2$)$_2$.

Neutralization of the RM suspension in the presence of CO$_2(g)$ occurs in accordance with the chemical reaction eqs 4–8:

\[
\text{NaAl(OH)}_4 + \text{CO}_2 \rightleftharpoons \text{NaAlCO}_3(\text{OH})_2 + \text{H}_2\text{O} \tag{4}
\]

\[
\text{NaOH} + \text{CO}_2 \rightleftharpoons \text{NaHCO}_3 \tag{5}
\]

\[
\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{NaHCO}_3 \tag{6}
\]

\[
3\text{Ca(OH)}_2 \cdot 2\text{Al(OH)}_3 + 3\text{CO}_2 
\rightleftharpoons 3\text{CaCO}_3 + \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O} \tag{7}
\]

\[
\text{Na}_2[\text{AlSiO}_4]_6 \cdot 2\text{NaOH} + 2\text{CO}_2 
\rightleftharpoons \text{Na}_2[\text{AlSiO}_4]_6 + 2\text{NaHCO}_3 \tag{8}
\]

Under carbonation conditions, permutite, sodium calcium silicates, for example, Na$_2$CaSiO$_4$, and tricalcium aluminate hexahydrate (TCA) can also undergo decomposition:

\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{CO}_2 
\rightleftharpoons \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \tag{9}
\]

\[
\text{Na}_2\text{CaSiO}_4 + 2\text{CO}_2 + \text{nH}_2\text{O} 
\rightleftharpoons \text{CaCO}_3 + \text{SiO}_2 \cdot \text{nH}_2\text{O} + \text{Na}_2\text{CO}_3 \tag{10}
\]

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + \text{nCO}_2 
\rightleftharpoons \text{nCaCO}_3 + \frac{n}{3}(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) + \frac{3-n}{3}(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}) + \text{nH}_2\text{O} \tag{11}
\]

As noted above, in aqueous media the hydrolysis and hydration of some mineral components of RM occur, which leads to a change in its chemical and mineralogical composition. Solubility and stability in aqueous solutions of most of the phases in the composition of RM are determined by the acidity of the medium, that is, the pH value of the solution. A rapid pH decrease in the aqueous phase of the RM suspension (Figure 1) is due to the neutralization of only a part of the alkaline material in RM (NaOH, Na$_2$CO$_3$, and sodium aluminate). Other alkaline components in the solid phase of the slurry (some mineral alkaline phases), under normal conditions, interact slowly with H$_2$CO$_3$. The time needed for the neutralization of the aqueous phase of the suspension is not enough for its complete interaction with H$_2$CO$_3$ and neutralization. In the absence of CO$_2(g)$, the pH of the aqueous phase of the RM suspension soon rises again as an additional alkaline material is leached from the RM as a result of the gradual decomposition of alkaline mineral phases. In the lack or absence of CO$_2(g)$, as a result of binding to calcite (in accordance with reaction 11), a transformation of NaHCO$_3$ to Na$_2$CO$_3$ occurs and its partial caustification to NaOH. In this case, the pH of the liquid phase of the RM suspension can exceed 12–13. This is why in the absence of CO$_2(g)$ during carbonate leaching of RM a spontaneous pH increase of the aqueous phase usually occurs, which leads to a decrease of Sc extraction because its solubility in alkaline solutions is essentially lower as compared with bicarbonate ones. In the area of high pH values, the OH$^-$ ions completely replace the CO$_3^{2-}$ ions in the carbonate complexes of Sc, as a result of which secondary precipitates are formed, including Sc(OH)$_3$ or ScO(OH)$_2$.

Under conditions of carbonic acid treatment at ambient temperature, we did not observe significant changes in the mineralogical composition of RM. It was found that under the carbonate conditions there was a slight change in the...
The intense broadband within 3400–3600 cm⁻¹ with maxima at 3601, 3550, and 3358 cm⁻¹ and a weak band at 1630 cm⁻¹ in the FTIR spectrum of the original RM sample (Figure 3) refer to OH⁻ valence and bending vibrations of free and bound water. The bands at 3601, 3530, and 3358 cm⁻¹ registered within the 3400–3600 cm⁻¹ area of the FTIR spectrum can also be attributed to OH groups in Fe (goethite–FeO(OH) and alumogoethite) and Al (cancrinite, gibbsite–γ-Al(OH)₃ or kaolinite–Al[(OH)₂SiO₃]₃) compounds. In the FTIR spectra of these compounds, the absorption bands are in superposition with each other. The stretching and bending vibrations of tetrahedral SiO₄²⁻ groups appear as a high-intensity band at about 1000 cm⁻¹ and a low-intensity band at 1392 cm⁻¹. The bands at 683–656 and 1110–964 cm⁻¹ can also correspond to the vibrations of the aluminosilicate framework. The vibrations along with the Fe–O and Al–O bonds are manifested by bands at 463 and 561 cm⁻¹. The bands at 1630, 816, 565, and 540 cm⁻¹ can also be attributed to the gibbsite. The bands at 1630, 1110, 816, 540, and 434 cm⁻¹ can be attributed to kaolinite. The bands at 1630, 1487, 1392, 1000, 756, 679, 463, and 434 cm⁻¹ correspond to DSP absorption. The bands at 617, 540, and 463 cm⁻¹ can be attributed to hematite (α–Fe₂O₃).

Thus, during carbonation of the RM suspension, there is practically no dissolution of the main mineral phases containing Fe, Al, Ti, and Si. Neutralization of the RM suspension with weak carbonic acid can only proceed to pH ~7, while the above major metals begin to dissolve at pH < 6. Alkali and alkaline-earth elements (Na, K, Ca, and Mg) dissolve into the liquid phase of the RM suspension during carbonation. The main amounts of Ca and Mg were deposited from the solution in the form of insoluble carbonate compounds. Thus, the enriched sodium solution can be recycled to the Bayer process.

2.2. Leaching of Scandium from RM with Aqueous Solutions of NaHCO₃. Leaching of RM by solutions of NaHCO₃ without CO₂(g) proceeds with an increase in Sc extraction when compared with Na₂CO₃. By increasing the medium temperature from 20 to 70 °C during leaching with 1.0 mol L⁻¹ NaHCO₃, the value of α(Sc) is increased from 0.1 to 2.3% in 120 min at L/S = 10 and 20°C. The increase in concentration in the solution of NaHCO₃– CO₃²⁻, being strong complexing agents for Sc, results in the formation of Na[n₁–n₃]Sc(CO₃)₃ compounds stable in carbonate solutions with the increase in solubility of Sc₂O₃ and Sc(OH)₃⁻. Increasing the medium temperature from 20 to 70 °C during leaching with 1.0 mol L⁻¹ NaHCO₃ solution (pH = 9.84) improves the Sc extraction from 2.3 to 19.8%, in 120 min (Figure 4) which agrees with the literature data. Although we noted that in the range of NaHCO₃ concentrations of 0.1–0.5 mol L⁻¹ the maximum extraction was achieved at 50 °C, a further increase in temperature did not contribute to an increase in the Sc extraction and even slightly lowered it. When using concentrated NaHCO₃ solutions, Zr and Hf are also leached from RM, and their extraction can reach 90%. With a further increase in the leaching time (τ), the concentration of Sc in the solution does not increase significantly.
not change. Increasing the temperature above 70 °C in these systems leads to lower α(Sc) because of the decomposition of Sc carbonate complexes with the formation of poorly soluble basic carbonate Sc(OH)(CO₃)₂⁻.

After carbonation using aqueous solutions of NaHCO₃, like in the case of CO₂(g), there is a decrease in the intensity of the main reflexes of calcite, laumontite, DSP, and hematite just as in the case of carbonation with CO₂(g) (Figure 5). Also, the appearance of new reflexes 2θ = 20.35°, 2θ = 28.90°, and 2θ = 32.39° was observed and attributed to calcium aluminosilicate, the exact composition of which we were unable to determine using the JCPDS–ICDD PDF–2010 database. This compound is one of the decomposition products of calcium hydrogarnet (HG) by the formula 3CaO·(Al₂Fe₂)O₃·n(Si, Ti)O₁₂·(6−2n)H₂O in the RM under carbonation conditions. In addition, the increase of TiO₂ reflex intensity was detected, which also indicates the destruction of HG which contains Ti. Calcite and its low-temperature forms (aragonite and vaterite), dawsonite, and alkaline sodium hydrosilicate are also products of HG decomposition.

In addition, during carbonation with NaHCO₃, the decomposition of hydrated calcium aluminate occurs. The decrease in the intensity of calcium carbonate reflexes may be related to its transformation into more soluble calcium bicarbonate.

### 2.3. Leaching of Scandium from RM with Aqueous Solutions of Na₂CO₃

The carbonation of RM in 1.0 mol L⁻¹ Na₂CO₃ solutions (pH = 10.27) without CO₂(g), as well as in the case of 1.0 mol L⁻¹ NaHCO₃, proceeds with the increase of Sc extraction into the solution compared with the methods not using reagents. However, the increase in α(Sc) is not as significant as in the case of 1.0 mol L⁻¹ NaHCO₃ (pH = 9.84). Increasing the medium temperature from 20 to 70 °C increases the value of α(Sc) from 1.8 to 8.1% (Figure 6).

When increasing the Na₂CO₃ concentration from 1.0 mol L⁻¹ (pH = 10.27) to 2.0 mol L⁻¹ (pH = 10.43), the Sc extraction into the solution improves significantly, also the growth of α(Sc) with increasing temperature is observed (Figure 7). At the same time, as the temperature rises to 90 °C, an extremum in the kinetic curve is observed, associated with a decrease in Sc concentration in the carbonate solution as a result of decomposition of its carbonate complexes in the solution and the formation of poorly soluble compounds. Previously, it was found that increasing the Na₂CO₃ concentration to more than 1.5 mol L⁻¹ at temperatures above 70 °C results in a decrease in α(Sc). This was attributed to alkaline hydrolysis of [Sc(CO₃)₃]⁻(2n−3)⁻ (where n ≥ 2) resulting in the partial or complete substitution of the carbonate ion in Sc compounds with a hydroxyl group to form poorly soluble Sc(OH)CO₃·nH₂O compounds, where n = 2−5 as well as Sc(OH)₃. The presence of a significant amount of Na₂CO₃ and/or NaOH introduced into the carbonate solution with the RM suspension in the absence of CO₂(g) leads to lower extraction of Sc from RM. Only at optimal amounts of Na₂CO₃ and NaHCO₃ in the carbonate solution, formation of soluble carbonate complexes contributing to Sc extraction improvement can be ensured. The required adjustment of the carbonate solution medium in the process of RM leaching can be achieved in the presence of CO₂(g). After carbonation using aqueous solutions of Na₂CO₃, as in the cases of CO₂(g) and NaHCO₃, there is a decrease in the intensity of reflexes of the main phases of Sc: calcite, laumontite, DSP, and hematite (Figure 8).

Thus, in the absence of CO₂(g), the maximum Sc extraction is observed when using 1.0 mol L⁻¹ NaHCO₃ solution. In this system, conditions are reached (pH = 9.84) under which the solubility of Sc₂O₃ or Sc(OH)₃ increases because of the formation of stable carbonate complexes in accordance with the following chemical equations:

$$\text{Sc}_2\text{O}_3(s) + 6\text{NaHCO}_3(aq) \rightleftharpoons 3\text{Na}_2\text{CO}_3(aq) + 3\text{H}_2\text{O} + \text{CO}_2(g)$$

(Figure 5. XRD patterns of the original RM sample (1) and samples after carbonation with NaHCO₃ aqueous solutions without CO₂(g) at L/S = 10 and 70 °C. [NaHCO₃], mol L⁻¹: (2) 0.1; (3) 0.5; and (4) 1.0.

Figure 6. Scandium leaching from RM with 1.0 mol L⁻¹ Na₂CO₃ at L/S = 10.

Figure 7. Scandium leaching from RM with 2.0 mol L⁻¹ Na₂CO₃ at L/S = 10.

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solution. As shown earlier, during CO2(g) barbotage through a
and, accordingly, a decrease in the pH of the carbonate
In the presence of CO2(g), at the initial stage, the reaction of
by changing the CO2(g)
control the pH level and maintain the pH at the required level
lower solubility. In the process of carbonation, it is possible to
decrease in Sc extraction into the carbonate solution due to its
determination are observed. At pH values exceeding 10, there is a
coprecipitation of Sc take place. To ensure maximum Sc
extraction from RM in Na2CO3 solutions, the process must be
preparation and washing with water, Sc extraction in the
association with its interaction with NaOH (Figure 10).
2.4. Leaching of Scandium from RM after Alkaline
Pretreatment. To prevent the formation of dawsonite and
co precipitation of Sc with it in the processes of carbonate RM
leaching, it is necessary to prevent the release of Al into the
carbonate solution together with Sc.27 In the absence of Al, the
saturation of Sc carbonate solutions by CO2(g) does not result
in the formation of secondary precipitates.27 To remove some
of the soluble forms of Al from RM, two consecutive stages of
alkaline pretreatment of RM were carried out with aqueous 4.0
mol L−1 NaOH solution at 100 °C for 120 min. This treatment
practically does not leach Sc, while some portion (15–20%) of
Al is released into the alkaline solution.87 The concentration of
Al in carbonate solutions was 2.0–2.2 g L−1. XRD data of the
pretreated and washed RM sample indicate a decrease in the
intensity of the reflexes of calcium carbonate which is
associated with its interaction with NaOH (Figure 10).
In the case of leaching RM samples after alkaline
pretreatment and washing with water, Sc extraction in the
absence of CO2(g) was increased using 2.0 mol L−1 Na2CO3
solution (Figure 11a) at L/S = 10 and 70 °C. The Sc
extraction increased from 13 to 40–45% in one step at L/S = 5 and 70 °C under
such conditions.

![Figure 8](image-url) XRD pattern of the RM sample after carbonation with 2.0 mol L−1 Na2CO3 aqueous solutions without CO2(g).

\[
SC_2(CO_3)_3(aq) + (n - 3)Na_2CO_3(aq) \rightarrow 2Na_{(2a-3)}[Sc(CO_3)_n](aq)
\] (13)

In systems with Na2CO3, the direct reaction between Sc2O3
and Na2CO3 in carbonate-alkaline solutions does not occur.47
A small excess of H2CO3 is required to dissolve Sc2O3, which
can be provided by slurry saturation or by dissolution in
bicarbonate solution. As a result of several factors:
lowering pH of the solution, hydrolysis of Sc carbonate
complexes, and Sc coprecipitation with Al in the form of
dawsonite.27 When the solution’s pH falls to 9, more intensive
decomposition of HG occurs, resulting in the formation of new
solid phases: dawsonite, calcite, aragonite, and vaterite, which
capture Sc from the carbonate solution. At the same time, Sc in
the composition of HG is also coprecipitated.62

As a result of leaching a part of Al from RM into the
carbonate solution, during barbotage CO2(g) associated with a
pH decrease, the formation of low-soluble dawsonite and
coprecipitation of Sc take place. To ensure maximum Sc
extraction from RM in Na2CO3 solutions, the process must be
carried out within the pH range of 9.5–10.0 (Figure 9). At pH
values, less than 9.5, dawsonite formation and Sc coprecipitation
are observed. At pH values exceeding 10, there is a
decrease in Sc extraction into the carbonate solution due to its
lower solubility. In the process of carbonation, it is possible to
control the pH level and maintain the pH at the required level
by changing the CO2(g) flow rate and the time of its feeding into the RM suspension. It was found that, to ensure the
optimal pH value for leaching with 2.0 mol L−1 Na2CO3
aqueous solutions, it is enough to barbotage CO2(g) at Q = 0.9
L min−1 during the first 15–20 min of the leaching process.
The time of CO2(g) barbotage (carbonation) needed to
establish and maintain a constant pH value of ∼9.5 to 10 was
20 min.

The results of studies on the leaching of RM with 2.0 mol
L−1 Na2CO3 solutions at CO2(g) barbotage during the first 20
min of leaching showed an increase in the Sc extraction from
13–15 to 40–45% in one step at L/S = 5 and 70 °C under
such conditions.

![Figure 9](image-url) Influence of the pH value on leaching of Sc from RM with
2.0 mol L−1 Na2CO3 at L/S = 5 and 20 °C. pH correction by
barbotage of CO2(g).

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and Na2CO3 in carbonate-alkaline solutions does not occur.47
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In the case of leaching RM samples after alkaline
pretreatment and washing with water, Sc extraction in the
absence of CO2(g) was increased using 2.0 mol L−1 Na2CO3
solution (Figure 11a) at L/S = 10 and 70 °C. The Sc
extraction increased from 13–15 to 27% in one leaching step,
and in two steps, the total Sc extraction was about 48%. Under

![Figure 10](image-url) XRD pattern of the RM sample after two steps of alkaline pretreatment with 4.0 mol L−1 NaOH at 100 °C for 120 min.
such conditions, the extraction of not only Sc but also Y and Ln from RM increases. At the same time, for 1.0 mol L\(^{-1}\) NaHCO\(_3\) solution the contrary effect was observed (Figure 11b). Scandium extraction under other equal conditions decreased from 19.8 to \(\sim\)11%.

### 2.5. Leaching of Scandium from RM in Carbonate Media with Ultrasonic Assistance

One of the options to increase the completeness and selectivity of recovery of valuable components, that is, to improve the efficiency of the reprocessing technospheric stocks and minerals, is UT. During UT refinement and erosion (accumulation of defects and appearance of small cracks), renewal of the reaction surface of RM particles (cleaning from blocking layers of insoluble minerals or reaction products formed in carbonate media) takes place, which leads to an increase in Sc release into the solution. UT decreases diffusive resistance in the diffusive processes, which are the limiting stage in the carbonate leaching of RM, and intensifies the mass transfer processes in the system. In addition, during UT intensive emulsification and activation of chemical reactions take place.\(^{88}\)

At continuous UT of the RM suspension in the process of leaching with 1.0 and 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solutions without CO\(_2\)(g), the values of \(\alpha(\text{Sc})\) achieved within the same time interval were somewhat lower than those under similar conditions without UT. In addition, the kinetic curves (Figure 12) show a gradual decrease in Sc extraction, which becomes more pronounced as the temperature increases.

![Figure 11. Scandium leaching from RM after alkaline pretreatment. Leaching conditions: L/S = 10, 70 °C. (a) 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\); (b) 1.0 mol L\(^{-1}\) NaHCO\(_3\).](image1)

The decrease of Sc extraction in the process of soda leaching is related to the decomposition of HG and formation of NaOH or sodium aluminate, accompanied by an increase of pH of the carbonate solution. This leads to a decrease in the Sc concentration in the solution and its extraction yield. UT significantly accelerates these processes, so their effect on the leaching of Sc is much stronger compared with conventional conditions in equal time intervals. Prolonged (more than 60 min) UT also results in refinement of the solid phase of RM\(^{89}\) mainly due to decomposition of large agglomerates of particles as well as the clay fraction of RM. This leads to an increase in the surface area of reacting particles and the release of fine mineral particles based on Fe, Ti, and other metals in which Sc and other REEs are usually concentrated.\(^{85,86,90-92}\) In the process of UT (during 60 min), a slight increase in the proportion of fine fraction (1–7 \(\mu\)m) of particles occurs, as well as a decrease in the proportion of the 8–12 \(\mu\)m fraction (Figure 13).

![Figure 13. Granulometric analysis of RM samples: (a) original RM; (b) RM after leaching of Sc with 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solution at UT, L/S = 10, and 70 °C in 60 min.](image2)

Carbonation of CO\(_2\)(g) at UT significantly accelerates the process of Sc leaching from RM with 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solutions. The time to achieve equivalent values of \(\alpha(\text{Sc})\) at UT is reduced by \(\sim\)2 times from 240 to 120–140 min (Figure 14). It should be noted that UT not only intensifies the process of Sc extraction from RM but also accelerates the processes resulting in the formation of low-soluble forms of Sc (hydrolysis) or its coprecipitation with Al in the form of dawsonite\(^{27,62}\) or calcium carbonate.\(^{62}\) This leads to its lower concentration in carbonate solutions (Figure 14, curve 1). A similar situation is observed during continuous barbotage by CO\(_2\)(g) with/without UT (Figure 14, curve 5). At the same time, CO\(_2\)(g) barbotage for only the first 20 min \((Q = 0.9 \text{ L} \text{ min}^{-1})\) allows adjusting the pH to 9.8–10, which makes it...

![Figure 12. Scandium leaching from RM at UT with 1.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solution (a) and 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solution (b) L/S = 10.](image3)

![Figure 14. Scandium leaching from RM with 2.0 mol L\(^{-1}\) Na\(_2\)CO\(_3\) solution at L/S = 10 and 70 °C (1–5). 1—UT, without barbotage CO\(_2\)(g); 2—without UT and without barbotage CO\(_2\)(g); 3—without UT, barbotage CO\(_2\)(g) only for an initial 20 min; 4—UT, barbotage CO\(_2\)(g) only for initial 20 min; 5—without UT, barbotage CO\(_2\)(g) during the whole process; 6—without UT, barbotage CO\(_2\)(g) only for initial 20 min, 90 °C.](image4)
possible to achieve high values of $\alpha(\text{Sc})$ at 40–45% in one leaching step. Under such conditions, stabilization of Sc in the carbonate–bicarbonate solution is achieved and secondary processes affecting Sc extraction do not occur.

In the case of the three-step counterflow mode of the leaching process under these conditions, scandium extraction can reach 50–60 ± 5%. Such values are comparable and even higher than the results presented in the literature when the resin-in-pulp technique and methods of mechanical intensification or their combination (see Table 1) for scandium leaching are used.\textsuperscript{29,62,63,70} The extraction of scandium from RM (RUSAL) in carbonate media is limited by the content of so-called “easily leached” Sc-containing phases, the proportion of which in RM (RUSAL) can account for up to 60% of the total scandium content.\textsuperscript{62} Increasing the extraction of scandium and other valuable metals from RM (RUSAL) requires the development of a complex approach with the combination of pyro- and hydrometallurgical methods, including optimized leaching processes in carbonate media.

When hot carbonate solutions are cooled after leaching at UT in the presence of CO$_2$(g), a mixture of Na$_2$CO$_3$·7H$_2$O and Na$_2$CO$_3$·H$_2$O hydrates crystallizes in a few hours (Figure S1 in the Supporting Information). As a result, part of Sc is captured by the precipitate, and its concentration in the carbonate solution decreases.

3. CONCLUSIONS

The obtained results of laboratory leaching experiments for samples of landfilled RM (Bogoslovsky Aluminum Plant, Russia) show that the degree of scandium extraction varies significantly and depends on the agitation or ultrasonication time, type and concentration of carbonate reagents, temperature, and pH value (including the gas carbonation mode in the presence of carbon dioxide).

The maximum extraction of scandium in one leaching step equal to ~20% in the absence of gas carbonation was observed when 1.0 mol L$^{-1}$ NaHCO$_3$ solution at 70 ºC for 120 min agitation time was used, in comparison with 8.1% for 1.0 mol L$^{-1}$ Na$_2$CO$_3$ at 70 ºC and 17.4% for 2.0 mol L$^{-1}$ Na$_2$CO$_3$ at 90 ºC.

Alkaline pretreatment of RM with NaOH solutions allows not only recovery of an additional 15–20% of Al but also can have positive effects on the subsequent extraction of scandium with 2.0 mol L$^{-1}$ Na$_2$CO$_3$ (extraction yield of scandium in the absence of CO$_2$(gas) in one leaching step increases from 13–15 to 27%).

Using the gas carbonation in the presence of carbon dioxide (i.e., when reached an optimum pH value in carbonate solution), scandium extraction from RM in carbonate media can be significantly increased. However, in studied carbonate systems, an excess of CO$_2$(gas) leads to the formation of insoluble dawsonite and calcium carbonate with which scandium coprecipitates. To retain scandium in carbonate–bicarbonate solutions, it is necessary to maintain the pH within the range of 9.5–10 which is optimal. In this pH region, scandium extraction from RM was 40–45% when used 2.0 mol L$^{-1}$ Na$_2$CO$_3$ as the initial solution at 70 ºC. The rate of the scandium leaching process from RM in carbonate media increases by two times (from 240 to 120–140 min) under UT but is accompanied by acceleration of secondary processes (hydrolysis and coprecipitation), as a result of which scandium passes back from the carbonate solution into the secondary precipitates. The processes of hydrolysis and coprecipitation, as well as scandium adsorption on the surface of mineral phases of RM, are the main reasons for the secondary loss of scandium during carbonate leaching.

The obtained results and their comparison made it possible at this stage of the study to determine the most suitable conditions and factors for achieving maximum extraction of scandium (40–45%) from landfilled RM samples during one step of direct carbonate leaching: (i) initial leaching solution—2.0 mol L$^{-1}$ Na$_2$CO$_3$; (ii) temperature—70 ºC; (iii) time of leaching without ultrasonication (only agitation)—240 min or 120 min with ultrasonic assistance; (iv) pH value of the liquid phase in the RM suspension ∼9.5 to 10 (required of CO$_2$(gas) carbonation). These conditions can be used for the design of the most appropriate stages of carbonate leaching of scandium from the RM of Bogoslovsky Aluminum Plant (Russia). At the same time for other types of RM (Greek/German/Hungarian), these selected conditions may not be as effective or even not be valid because of the difference in the crystal structure.

The use of carbonate reagents (NaHCO$_3$ and/or Na$_2$CO$_3$) and CO$_2$(gas) can be a valid alternative approach (with the comparison of the mineral acid used and other lixiviants) for recovery of scandium and other REEs from RM in the case of scandium secondary loss reduction, as well as optimization of conditions and modes of the process. For improving and confirming the efficiency of carbonate systems and enhancing scandium extraction from RM, it is necessary to develop techniques for stabilizing scandium in carbonate media and multistage countercurrent leaching process modes (including the use of recycled carbonate solutions), as well as carry out additional studies using different types of RM.

The stage of carbonate leaching of scandium should be considered only as part of the complex technology for reprocessing of RM. Under complex technology, which includes a combination of pyro- and hydrometallurgical methods, it is assumed that the total recovery of scandium and other REEs may be enhanced.

4. EXPERIMENTAL SECTION

4.1. Raw Material Characterization. The raw material used for this research was represented by air-dried (moisture content was not higher than 0.5 wt %) landfilled RM of the Bogoslovsky Aluminum Smelter (RUSAL), which was obtained during reprocessing of bauxites from the Middle-Timan (Urals, Russia) by the combined Bayer sintering process. The major components in the RM sample used are Fe, Al, Si, Ca, Na, and Ti, whose contents (expressed as oxides) are shown in Table 3.

Table 3. Major Chemical Components (Expressed as Oxides) in the Original RM Sample

| compound | Fe$_2$O$_3$ | Al$_2$O$_3$ | SiO$_2$ | CaO | Na$_2$O | TiO$_2$ |
|----------|------------|------------|--------|-----|--------|--------|
| wt %     | 42.1       | 12.7       | 9.4    | 7.8 | 4.8    | 4.3    |

Apart from the major elements, RM contains microcomponents, which include LCEs. The content of LCEs in the RM sample is shown in Table 4, where it can be seen that the content of light REEs is higher than that of heavy REEs. The RM sample also contains significant quantities of such trace elements as Sc (86 mg kg$^{-1}$) and Ga (51 mg kg$^{-1}$). The total concentration of LCEs (not including Ti) in the RM sample was about 2.9 wt %, including about 0.14 wt % of REEs...
and about 0.01 wt % of radioactive elements (Th$^{228}$, U$^{238}$, and U$^{235}$).

Red mud is a conglomerate of a large number of different minerals, as a result of which the XRD patterns are characterized by a complex set of reflexes that can be superimposed. By the XRD method, the following principal minerals and compounds were detected: hematite with an overlay of peaks of perovskite and titanium dioxide, as well as diaspor, calcite, laumontite, sodium aluminosilicate hydrate of cancrinite type, and mineral phases of calcium sodium aluminum oxide and calcium aluminum oxide silicate hydrate (Figure 15). These data correlate with the data from literature sources.$^{93,94}$

The morphological structure of the samples was analyzed using scanning electron microscopy (SEM) images (Figure 16, 1–3), and the microchemical composition was determined by the energy-dispersive X-ray spectroscopy (EDX) method (Figure 16, 4–15). SEM micrographs show that the original RM is a very fine and roughly crystallized material. These results are in line with the analysis of particle sizes (Figure 18).

The main elements detected by the EDX method in the original RM sample were Fe, Al, Si, Na, Ca, and Ti. Analysis and comparison of the selected points demonstrate a great level of inhomogeneity of each point. Content of Fe in seven points of RM varied from 1 to 40%, Al from 2.5 to 16.7%, Si from 2 to 16.7%, Na from 1.8 to 11%, Ca from 0.7 to 27.6%, and Ti from 0.2 to 3.3% (Figure 17 and Table 5).

In the original RM, 90% of particles are smaller than 10 μm, 80% of particles are smaller than 5 μm, and 50% of particles are smaller than 2 μm (Figure 18).

The chemicals used for the leaching of RM samples are Na$_2$CO$_3$, NaHCO$_3$, NaOH (chemically pure), and technical gas cylinder carbon dioxide.

4.2. Methodologies. 4.2.1. Leaching of RM Samples.

Leaching of RM without UT was carried out in a three-neck round-bottom glass flask with a volume from 250 to 1000 mL placed in a thermostat bath for maintaining a constant temperature of 20–90 ± 0.1 °C, with L/S equal to 5–10 (Figure 19a). Leaching time established based on preliminary kinetic tests was 120 min, while the CO$_2$(g) bubbling (gas carbonation) time for achieving and maintaining the constant value of pH = 9.6–9.8 ± 0.2 was 20 min. The volumetric flow rate of CO$_2$(g) was set using a gas flowmeter (LZM-15Z visiofloat).

Experiments with UT were performed with the usage of an ultrasonic horn waveguide (diameter of 50/30 mm) connected to an ultrasonic wave generator and the control panel of the Bulava-P UZAP-3/22-OP unit manufactured by Ultrasonic

![Figure 15. XRD pattern of the original RM sample.](image1)

![Figure 16. SEM micrographs with different magnifications (1–3) and EDX elemental mapping of the original RM sample (5–15).](image2)

![Figure 17. EDX of the original RM sample with different magnifications.](image3)

![Table 4. Content of Selected LCE Composition of the Original RM Sample, mg kg$^{-1}$](table1)
Technologies Center, Russia (Figure 19b). Ultrasonication was performed at a frequency of 22 ± 1.65 kHz and an intensity of 10 W cm\(^{-2}\) (100% of unit power) in stationary mode. In all experiments, the depth of waveguide immersion in RM slurry was maintained at the fixed level of 5 cm, because this parameter affects the obtained results. The cylindrical jacketed cell was closed with a cover to prevent water evaporation at prolonged UT. To prevent RM suspension overheating as a result of absorption of ultrasonic energy, a glass cell with a water (as coolant) jacket was used. After loading all reagents into the reactor, the supply of CO\(_2\) (g) at \(Q(\text{CO}_2) = 0.9\ \text{L min}^{-1}\) (for all tests, when required) was activated. The process of leaching was performed in the mode: agitation using a magnetic stirrer and/or UT (when required). At certain intervals, portions of RM suspension were withdrawn and filtered on a ceramic filter (Schott glass filter) under vacuum \((P = -0.7\) to 0.9 bar) created by a water jet pump. After this, the content of Sc in mother liquor was being determined.

4.3. XRD Patterns. The phase composition of RM powders was determined by XRD. Diffraction patterns were recorded using D2 PHASER (Bruker, Germany), with radiation of Cu\(K\alpha\), a filter of Ni, with graphite monochromator \((\lambda = 1.54178\ \text{Å})\), in pipe mode (Cu) of 10 mA, 30 kV, with 2\(\theta\) (theta) angle value range from 10 to 70\(^\circ\), increment of 0.02\(^\circ\), a slit of 0.6 mm, point exposure of 1.5 s, and discriminator per energy values of 0.17–0.23 keV. Identification of spectrum and calculation of phase composition were performed with the help of the ICDD PDF-2 minerals library with the usage of specialized software TOPAS/EVA.

4.4. Electron Microscopy. A microscopic study of the sample was performed with a Vega3 scanning (raster) electron microscope (manufactured by Tescan, Czech Republic) with a lanthanum hexaboride (LaB\(_6\)) cathode and in high-vacuum mode.

4.5. FTIR Spectroscopy. FTIR spectra were obtained on an FT-IR Nicolet 380 Spectrometer (Thermo Fisher Scientific Inc., United States) using Omnic software.

### Table 5. Chemical Composition of the Original RM Sample by the EDX Method

|   | O  | Na | Mg | Al | Si | P  | S  | Cl | K  | Ca | Ti | Mn | Fe | total |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|-------|
| 1 | 55.2 | 1.9 | 7.5 | 16.7 | 16.7 | 0.7 | 0.2 | 1.0 | 100 |
| 2 | 31.2 | 1.8 | 0.2 | 2.5 | 2.0 | 0.3 | 0.1 | 27.6 | 19 | 0.5 | 31.9 | 100 |
| 3 | 52.0 | 11.0 | 0.9 | 12.0 | 10.5 | 1.4 | 0.1 | 1.5 | 0.8 | 0.3 | 9.2 | 100 |
| 4 | 27.8 | 2.3 | 0.5 | 8.8 | 9.0 | 0.2 | 0.8 | 2.8 | 3.9 | 3.3 | 0.8 | 40.0 | 100 |
| 5 | 43.9 | 5.2 | 0.7 | 7.2 | 5.1 | 0.1 | 0.5 | 0.2 | 2.7 | 2.1 | 1.4 | 30.9 | 100 |
| 6 | 51.5 | 7.7 | 8.4 | 6.1 | 0.7 | 0.1 | 0.1 | 2.1 | 1.7 | 0.4 | 21.2 | 100 |
| 7—area  | 47.5 | 6.6 | 0.6 | 8.6 | 6.3 | 0.2 | 0.7 | 0.2 | 2.7 | 2.1 | 0.4 | 24.2 | 100 |
| min. | 27.8 | 1.8 | 0.2 | 2.5 | 2.0 | 0.3 | 0.1 | 0.1 | 0.7 | 0.2 | 0.3 | 1.0 | 100 |
| max. | 55.2 | 11.0 | 7.5 | 16.7 | 16.7 | 0.2 | 1.0 | 28.6 | 3.3 | 1.4 | 40.0 | 100 |

**Figure 18.** Cumulative particle size distribution of the original RM sample.

**Figure 19.** Schematic diagram of the experimental units for RM leaching without (a) and with (b) UT. 1—thermostat; 2—three-neck round-bottom glass flask; 3—stirrer motor; 4—electronic controller; 5—reflux condenser; 6—gas flowmeter; 7—cylindrical jacketed cell; 8—magnetic stirrer; 9—waveguide; 10—transducer; 11—ultrasound generator control panel.
4.5.1. Granulometric Analysis. To determine the granulometric composition of powders, a NanoTec Laser Particle Sizer Analysette 22 (manufactured by Fritsch, Germany) was used. The range of measurable particle sizes is from 10 nm to 2000 μm. To ensure maximum resolution, measurements were performed with seven positions of measuring cell during dispersion of the studied sample in water medium with exposure to ultrasound with a frequency of 36 kHz and with a power of 70 W.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04580.
Additional XRD and mineralogical composition data (PDF)

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Author Contributions
All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by H.Y.A., A.V.B., and P.I.I. The first draft of the manuscript was written by A.V.B., and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript. Conceptualization: S.I.S.; Methodology: S.I.S. and A.V.B.; Formal analysis and investigation: H.Y.A., A.V.B., and V.G.G.; Writing—original draft preparation: A.V.B. and H.Y.A.; Writing—review and editing: S.I.S., V.G.G., and A.A.S.; Funding acquisition: S.I.S.; Resources and supervision: S.I.S.

Notes
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ABBREVIATIONS
RM, red mud
LCEs, less common elements
REEs, rare-earth elements
XRD, X-ray diffraction
SEM, scanning electron microscopy
EDX, energy-dispersive x-ray
JCPDS—ICDD, Joint committee on power diffraction standards—International Centre for Diffraction Data
FTIR, Fourier-transform infrared
tca, tricalcium aluminate hexahydrate
dsp, sodium hydroaluminosilicate
Hg, calcium hydrogarnet
UT, ultrasonic treatment

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