

Red Mud Liquid Media Recycling

Subjects: Biochemical Research Methods

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Definition

Bauxite residue, known as red mud, is a by-product of alumina production using the Bayer process. Currently, its total global storage amounts to over 4.6 billion tons, including about 600 million tons in Russia. The total global storage of red mud occupies large areas, leading to environmental damage and increasing environmental risks. Moreover, it contains a significant amount of sodium, which is easily soluble in subsoil water; therefore, a sustainable approach for comprehensive recycling of red mud is necessary. The bauxite residue contains valuable elements, such as aluminum, titanium, and scandium, which can be recovered using liquid media.

1. Background

The main industrial approach used for alumina production is the Bayer method, which is based on the selective dissolution of bauxite ore components by alkaline solution. This method generates a large amount of waste called red mud. Red mud is the insoluble portion of the ore that is dumped into landfills.

By various estimates, production of 1 ton of alumina generates from 0.9 to 1.5 tons of red mud ^{[1][2]}. Currently, red mud landfills occupy large areas, which leads to environmental damage and increases environmental risks.

According to ^[3], more than 4.6 billion tons of this waste had been accumulated globally by 2018, including about 600 million tons in Russia ^[4]. Moreover, global alumina production also generates more than 175.5 million tons of red mud annually ^[5]. Consequently, development of cost-effective technologies for red mud processing is a crucial environmental, scientific, and technical task.

At present, only about 15% of the annually generated red mud is recycled ^[6]. The storage of the main part of red mud in special sludge dumps results in misuse of large land areas, and necessitates special dump protection and maintenance. These areas could be used for other purposes, e.g., for agriculture. The maintenance of sludge dumps and the construction of new dumps require significant material, financial, and human resources. In addition, the storage of red mud is potentially dangerous due to the possibility of release to the environment of compounds containing sodium, chromium, arsenic, and other toxic components ^[7].

Numerous approaches for red mud processing are currently known. The Scopus search engine finds over 5800 documents for the queries of “red mud” and “bauxite residue”. Furthermore, many review articles reporting different red mud applications, have been published. Among these, a wide range of reviews considers recovery of valuable elements from red mud by pyrometallurgical, hydrometallurgical, and complex methods ^{[6][8][9][10][11][12][13][14]}, including those focused on the chemistry of these processes ^[15], in addition to application in construction materials ^[16], road material ^[17], catalyst ^[18], coagulant and adsorbent ^[19], geotechnical engineering applications ^{[20][21]}, etc.

Several articles describe a complex influence of red mud storage and recycling on environment and socio-technological development, in addition to methods of reducing their negative impact ^{[3][22][23]}. Other research papers aim to discuss all developed methods for red mud usage and storage management ^{[24][25]}. Articles have discussed storage and processing of red mud with a focus on different regions ^{[2][26][27][28]}.

However, there are still no cost-effective integrated technologies for comprehensive recycling of red mud applied on a large industrial scale.

Red mud has a complex chemical and mineralogical composition and contains up to 60% Fe₂O₃, up to 25% Al₂O₃, and up to 12% TiO₂. In addition, it can contain up to 1700 mg/kg of rare-earth elements (REEs), including up to 120 g/t Sc, 80 ppm Ga, 150 ppm Y, 350 ppm Zr, and about 60 ppm U and 30 ppm Th [29]. In our previous work [30], we reviewed the pyrometallurgical methods of red mud processing, mainly for iron recovery. In this work, we consider the hydrometallurgical, solvometallurgical, and complex methods of selective recovery of aluminum, titanium, and sodium, and rare and rare-earth elements from red mud, including the economic viability and environmental impact of these processes, with emphasis on using alkaline or acid solutions, in addition to ionic liquids, bacterial cultures, and microorganisms.

2. Red Mud Processing Using Alkaline Solutions

Red mud can contain a significant amount of unextracted alumina, which is partly alkali soluble and partly in the form of complex sodium aluminosilicates such as sodalite and cancrinite [31][32]. The treatment of red mud by alkaline solutions enables extraction of a part of such alumina, in addition to sodium, and can be comparatively easily integrated into the main technological cycle of aluminum plants. Table 1 demonstrates the main trends of red mud processing using leaching of aluminum and sodium by alkaline solutions.

Table 1. Methods of red mud processing using alkaline solutions.

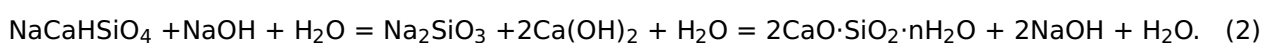
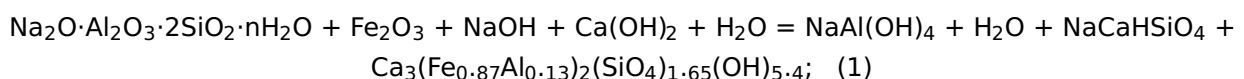
Methods of Red Mud Processing Using Alkaline Solutions	Merits	Demerits
Leaching at atmospheric pressure	- simple equipment; - low processing costs.	- low extraction degree of Al ₂ O ₃ (≤70%); - demand of additional reagent (lime).
Hydro-chemical process	- high extraction degree of Al ₂ O ₃ (>85%) and Na ₂ O (>95%).	- complicated equipment; - use of elevated temperature and pressure; - demand of additional reagent (lime).
Sintering process	- almost full extraction degree of Al ₂ O ₃ (>99%).	- high energy costs of sintering stage at 900–1000 °C; - demand of additional reagents (soda, earth alkali oxides).

Methods of Red Mud Processing Using Alkaline Solutions	Merits	Demerits
Reduction roasting with alkalis followed by leaching at atmospheric pressure	<ul style="list-style-type: none"> - iron extraction as pig iron, iron concentrate or iron powder; - high extraction degree of Al₂O₃ and Na₂O. 	<ul style="list-style-type: none"> - use of high roasting temperatures (1100–1400 °C); - demand of reducing agent.
Reduction smelting followed by autoclave leaching	<ul style="list-style-type: none"> - high extraction degree of iron and aluminum. 	<ul style="list-style-type: none"> - use of high smelting temperatures (>1400 °C); - use of elevated leaching temperature and pressure; - demand of additional reagent (lime, carbonaceous reducing agent).

2.1. Hydro-Chemical Process

Baica et al. [33] studied the effect of leaching conditions on the solubility of the aluminum compounds contained in red mud using NaOH solutions at atmospheric pressure. Statistical processing using the Taguchi method showed that the most important parameters are solid-to-liquid (S/L) ratio in the leaching slurry and interaction temperature. The second important set of parameters that affects the aluminum recovery comprises NaOH concentration, time, and temperature. NaOH concentration of 10 M (400 g/L), temperature of 80 °C, duration of 4 h, and stirring speed of 800 rpm were the optimal leaching parameters for the recovery of 67.3% Al.

To convert aluminum from hardly soluble compounds into highly soluble ones, the Bayer process is used, namely, the autoclave leaching of red mud by alkaline solution with the addition of calcium oxide. The process can be described by the following reactions [34]:



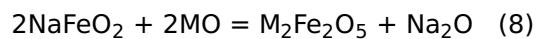
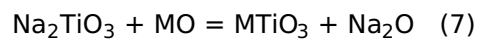
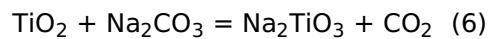
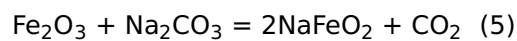
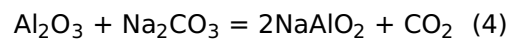
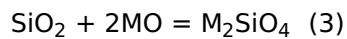
The experiments of red mud autoclave leaching by 40–60% NaOH solution in the temperature range of 170–210 °C with lime milk addition has shown the possibility of the recovery of 87.5% and 96.4% for Al₂O₃ and Na₂O, respectively [34]. The best results were obtained by leaching for 3.5 h with a 100/25 ratio of red mud/calcium oxide in a 45% NaOH solution at temperature of 200 °C and pressure of 0.8 MPa. An

increase in temperature up to 250 °C led to a decrease in the leaching time to 1 h with a dosage of $\text{CaO/SiO}_2 = 0.3$, and resulted in over 70% Al_2O_3 recovery in the solution and <1% of remaining Na_2O in the residue [35]. It was also shown [1] that an elevated content of iron oxides in red mud increases the dissolution degree of sodium.

The aluminum recovery degree and the filtration rate of the leached red mud slurry can be improved by adding fly ash from coal-fired power plants. Liu et al. [36] carried out high-temperature leaching at 260 °C using a strong alkaline solution containing 530 g/L Na_2O with varying chemical composition of the ash and the ash:red mud ratio at molar ratios of $\text{Na}_2\text{O/Al}_2\text{O}_3 = 30$, $\text{CaO/SiO}_2 = 1.05$, and $\text{S/L} = 1/8$. The optimal ratio of the ash:red mud equal to 1:1 led to 91.7% alumina recovery, whereas recovery was 72.14% without additives. In addition, filtration time dropped from more than 240 s to 80 s using the optimal ash:red mud ratio. The chemical composition change of the ash by variation of $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio had a minimal effect on the recovery degree of alumina. However, a decrease in the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio significantly increased filtration time.

2.2. Sintering Process

To improve aluminum recovery, many authors proposed sintering red mud with Na_2CO_3 and materials containing divalent earth alkali oxides (CaO , MgO , BaO) for conversion of aluminum from sodium aluminosilicates that are insoluble in alkaline solutions into water-soluble sodium aluminate NaAlO_2 , and for fixing silicon into barely soluble silicates (M_2SiO_4 , where M is a divalent alkaline earth metal). The sintering process can be described according to the following reactions (3)–(8) [37]:



This method can be combined simultaneously with carbothermic reduction of iron to obtain cast iron at the temperature range of 1300–1450 °C [38][39] or an iron-containing concentrate at the range of 1000–1200 °C [40][41].

Hodge et al. [42] studied the kinetics of sodium monoaluminate formation in the process of red mud sintering with soda and calcium carbonate at 1000 °C. Peak formation of sodium monoaluminate occurred after 5 min of sintering, and then its content in the sample decreased with an increase in sintering time. Leaching of the obtained sinter by a solution containing 5 g/L NaOH and 5 g/L Na_2CO_3 at 80 °C for 30 min dissolved 64% of sodium and 55% of aluminum.

Wai et al. [43] investigated the effect of CaO , MgO , and BaO addition on the aluminum and sodium recovery from red mud after sintering with Na_2CO_3 . The mixtures of red mud, 25% of soda, and various additives in the amount of 20% were sintered at 900 °C for 2 h and then leached in 0.1 M NaOH solution. It was revealed that BaO has the greatest effect on dissolution of aluminum and sodium; their maximum recovery degree reached 75.2% and 94%, respectively. The rise of temperature and duration of soda sintering of red mud with BaO up to 1000 °C and up to 4 h, respectively, achieved 99.5% aluminum

recovery in the solution [44].

Gao et al. [40] considered the reduction roasting process of red mud with the addition of MgO and Na₂CO₃ followed by magnetic separation of iron and subsequent leaching of aluminum by alkaline solution. It was shown that the optimal roasting conditions, which are a MgO/SiO₂ ratio of 1.5, temperature of 1200 °C, and duration of 90 min, lead to an iron recovery degree of 92%. The leaching of the magnetic separation tailings by 3% NaOH solution at 90 °C for 20 min resulted in recovery of over 70% of aluminum.

In general, the application of the alkaline methods enables the selective recovery of alumina and sodium from red mud without significant iron dissolution. Despite using a higher temperature and pressure, direct alkaline leaching leads to incomplete dissolution of alumina phases in red mud, so the application of this method for aluminum extraction from red is unpromising. The use of the sintering method with simultaneous iron reduction allows two types of products to be obtained, but this method also has some disadvantages. In particular, the aluminum recovery degree is low due to incomplete conversion of aluminum into water-soluble aluminates with the application of CaO and MgO as additives, whereas the use of BaO considerably increases the processing cost.

3. Red Mud Processing Using Acid Solutions

In recent years, many authors [8][12] have made efforts to find an optimal technology for selective acid recovery of REEs from red mud. The processes of direct leaching of valuable elements from red mud by the most common acids, such as H₂SO₄, HCl, HNO₃, and H₃PO₄, and their mixtures, have been widely studied. It has become apparent that sulfuric acid has a sufficiently high selectivity for scandium and titanium; the use of hydrochloric acid leaching leads to efficient recovery of aluminum, iron, and REEs.

3.1. Direct Acid Digestion

Karimi et al. [45] studied the efficiency of red mud dissolution in hydrochloric, nitric, sulfuric, and phosphoric acids, and in their mixtures, in the presence and in the absence of hydrofluoric acid. The experiments were carried out at 85 °C, stirring time of 120 min, and liquid-to-solid ratio of 20 mL/g. The dissolution efficiency of red mud in three N acid solutions was 79.35% for HCl, 46.21% for H₂SO₄, 79.70% for HNO₃, and 41.33% for H₃PO₄. The highest dissolution degree of red mud was 80.37%, which was obtained by leaching using the mixture of HCl:HNO₃ 1:1 in the presence of 3 wt.% of HF. This research showed that a single acid alone cannot fully decompose red mud at atmospheric conditions. Accordingly, direct acid leaching only enables extraction of some elements from red mud.

Reid et al. [46] compared application of different acids for leaching of REEs from Canadian red mud at atmospheric pressure. HCl, HNO₃, and H₂SO₄ were used at various leaching conditions in the ranges of acid concentration from 0.5 to 3 M and temperature from 25 to 90 °C for 30 min. Systematic experiments have indicated that nitric acid is the most effective for REE recovery. However, taking into account the cost, practical consideration of the process with application of volatile reagent, and its efficiency, 1.5 M H₂SO₄ at 90 °C was chosen as the best leaching condition. The maximum recovery of Ce, La, Nd, and Sc was at the S/L ratio of 1/15. Microwave pretreatment tests of red mud to increase the recovery of REEs showed that the pretreatment leads to the formation of cracks and pores in the particles, which enables the leaching agent to diffuse into the interior of the particle, and therefore facilitates the dissolution of REEs. As a result, the recovery degrees of Sc and Nd were increased from 40.0% to 64.2%, and from 54.3% to 78.7%, respectively.

Lim and Shon [47] investigated the influence of ultrasonic waves on the process of sulfuric acid leaching of titanium from red mud. The recovery degrees of iron, aluminum, and titanium increased with an increase in ultrasonic power output, leaching temperature, and acid concentration, but decreased with an increase in S/L ratio. The recovery rates of iron, aluminum, and titanium were 48.22%, 72.94%, and 88.95%, respectively, using the following optimal conditions: ultrasonic power of 150 W, H₂SO₄ concentration of 6

M, leaching at temperature of 70 °C for 2 h at an S/L ratio of 2/100. The significant S/L ratio was used to prevent silica gel formation. The REE behavior was outside the scope of the research.

Ochsenkuehn-Petropoulou et al. [48] also found that the application of sulfuric acid for selective recovery of scandium is more appropriate compared with hydrochloric and nitric acids, and with aqua regia. Experiments conducted under wide ranges of temperature and concentration showed that leaching by 2 M H₂SO₄ at 80 °C for 60 min with an S/L ratio of 1/20 was optimal, and resulted in Sc recovery of about 50%. High pressure acid leaching at 220 °C, in addition to acid concentration rise, led to a significant increase in iron dissolution. High-temperature conditions contributed to the optimal selectivity of scandium recovery with respect to iron and excluded the formation of silica gel, which substantially hinders the separation of the target solution from the residue.

Xie et al. [49] studied the effect of red mud particle size on the recovery of aluminum and iron by hydrochloric acid leaching at varying acid concentrations, S/L ratios, and durations. The optimal leaching conditions, which led to dissolution of 96.7% Al and 95.1% Fe, for red mud with a particle size of 150 microns were as follows: temperature of 80 °C, duration of 150 min, HCl concentration of 10 M, and S/L ratio of 1/8.

Zhao et al. [50] investigated leaching of bauxite reaction residue (BRR) by hydrochloric acid. It was found that direct acid leaching at optimal conditions, namely acid concentration of 8 M, L/S 5:1, leaching temperature of 85 °C, and leaching time of 3 h, can pass into solution only 44.15% Al, 38% Fe, 42%Ca, and 12% Ti. After removal of 81.21% Si from BRR by 3 M NaOH solution at 75 °C for 2 h and a 5:1 L/S ratio, the aluminum leaching rate only increased by 5.05%. Preliminary mechanical activation treatment for 10 h also led to only 46% Al being passed into solution. To increase aluminum dissolution efficiency, high-pressure acid leaching was used. After 10 h milling pretreatment and high-pressure red mud leaching at 210 °C, dissolution degrees of Al, Ca, Fe, and Ti were 84.23%, 73%, 43% and 15%, respectively. A study on kinetics of high-pressure aluminum dissolution determined that the apparent activation energy of the process was 20.82 kJ/mol, which corresponds to a liquid diffusion rate-controlling process. It showed that a liquid poly-aluminum chloride solution for water treatment can be prepared from the obtained solution. The developed process can be used for red mud treatment after the removal of iron.

The complex hydrochloric acid leaching process developed by Orbite aluminate Inc. [51] allows extraction of more than 90% of valuable elements from red mud, including REEs. The process consists of several stages. The initial stage is high-pressure acid leaching of red mud at 150–170 °C with dissolution of almost all elements except Si and Ti, followed by HCl gas treatment of leached solution for AlCl₃·6H₂O precipitation. The roasting of the obtained AlCl₃·6H₂O at 900–950 °C allows production of Al₂O₃; the off-gas can be returned to the precipitation stage. After Al removal, the solution heats up to 180 °C for Fe₂O₃ formation after Mg recovery by precipitation and calcination. To recover REEs from the solution, solvent extraction was proposed.

A statistical analysis of experimental data [52] indicated that concentration of the sulfuric acid solution used, in addition to the process temperature, have the greatest influence on titanium leaching efficiency from red mud. In addition, two-factor conditions—acid concentration and temperature, or acid concentration and S/L ratio—were also statistically significant; thus, the leaching efficiency can be considered to be dependent not only on one, but on several process parameters. The "best" model of the parameters with recovery of 64.5% Ti was obtained for the leaching by 6 N H₂SO₄ for 4 h at a temperature of 60 °C, S/L ratio of 5%, and fixed stirring speed of 700 rpm. The use of concentrated sulfuric acid solution resulted in dissolution of 46% Fe and 37% Al in addition to titanium. The main phases of the insoluble residue were anhydrite (CaSO₄), bassanite (CaSO₄·0.5H₂O), and various hydrated aluminum sulfates, whereas, taking into account experimental conditions, the existence of unreacted gibbsite (Al(OH)₃) and diaspore (AlO(OH)) in the sulfate residue appears to be doubtful.

Lymperopoulou et al. [53] investigated leaching of iron and scandium from red mud by sulfuric acid using a statistical analysis of the obtained data using the Taguchi method. In the experiments the following ranges of the parameters were used: acid concentration of 1–6 M, S/L ratio of 10–30%, temperature of 25–85 °C, and leaching time of 1–7 h. The analysis indicated that the most important factors were S/L ratio and temperature for scandium recovery, and mainly temperature for iron recovery. The optimized leaching conditions for Sc recovery were as follows: 6M H₂SO₄, 85 °C, 30% S/L ratio, 4 h; the conditions for Fe recovery were as follows: 2M H₂SO₄, 25 °C, 10% S/L ratio, 1 h.

Alkan et al. [54] derived a more efficient application of sulfuric acid for leaching compared with hydrochloric acid or their mixture in terms of titanium recovery from red mud. After 2 h red mud treatment by 4 M H₂SO₄ solution at 70 °C and S/L ratio of 1/50, the recovery of titanium was 67.3%, which was the highest among all used lixiviants. The application of 4 M HCl and a combination of the two acids in the ratio of HCl to H₂SO₄ of 1:3 led to titanium recovery degrees of 59.8% and 56.4%, respectively, which were slightly lower.

Shoppert and Loginova [55] suggested a method of sequential processing of red mud by diluted solutions of hydrochloric and sulfuric acids to obtain a titanium-containing concentrate. In the first stage, Ca, Na, Al, Si and K were removed from red mud by the treatment using HCl solution of pH = 3 at 25 °C for 1 h. In the second stage, the residue enriched in titanium and iron was leached by H₂SO₄ solution. The optimal conditions for the separation of iron from titanium were determined by factorial design. Dissolution of iron with titanium recovery up to 6% was carried out using H₂SO₄ solution of 80 g/L at an S/L ratio of 1/20 and 50 °C for 90 min. The insoluble perovskite residue contained 46.7% titanium.

It is known that silicon dioxide polymerization with the formation of silica gel significantly impedes the filtration rate of the leachates, and this effect is particularly profound with the use of 1–3 M H₂SO₄ solutions [56]. Alkan et al. [57] studied a silicagel formation rate in the process of direct sulfuric acid leaching of red mud, in addition to slags obtained by its reduction smelting at 1500–1550 °C in the presence of the fluxes, silicon oxide, or lime. Acidic slag contained 1.4% Fe₂O₃, 15.3% CaO, and 38% SiO₂; basic slag included 1.4% Fe₂O₃, 43.2% CaO, and 7.6% SiO₂. In all cases, the leaching by 2.5 M H₂SO₄ solution at 75 °C and S/L ratio of 1/10 for 1 h formed a stable silica gel, and for acid slag at the highest rate. The preliminary sulfating of dry red mud or slags by 97% H₂SO₄ at 75 °C followed by water leaching contributed to a significant suppression of silica gel formation. The treatment of acidic slag by this method showed that it is possible to achieve the most efficient recovery of about 70% Sc with a simultaneous insignificant dissolution of Ti (<10%) and Si (<3%).

Alkan et al. [58] proposed an application of a mixture of sulfuric acid and hydrogen peroxide to increase the efficiency and selectivity of titanium and scandium recovery. A parametric study demonstrated that H₂O₂ addition suppresses silica gel formation, decreases iron dissolution, increases titanium recovery degree due to the formation of soluble titanium peroxosulfate, and negligibly affects solubility of other red mud components. The leaching by the mixture of 2.5 M H₂O₂ and 2.5 M H₂SO₄ at 90 °C and an S/L ratio of 1/10 for 30 min resulted in the recovery of 68% Sc and 91% Ti; the yield of Fe and Al in the sulfuric acid solution was 23% and 43%, respectively.

Some authors [59][60] have attempted to combine pyro- and hydrometallurgical methods aimed to reduce and remove iron in metallic form from the process, because, due to significant iron content compared to REEs both in red mud and in leached solutions, it is the main hindering factor for the separation and subsequent processing of the solutions. However, leaching of the slags from reduction smelting, which can be essentially considered REE preconcentrates, is complicated. To increase the solubility of the slags, their composition can be adjusted during the smelting process depending on the composition of red mud and the lixiviant used.

Yagmurlu et al. [59] tested six slag samples for selective recovery of REEs that were obtained by reduction smelting of red mud with fluxes, lime, or silica, at different rates of cooling rates, water quenching, or

slow cooling. [Table 2](#) demonstrates the chemical composition of red mud and the slags.

Table 2. Chemical composition of red mud and the slag samples from reduction smelting analyzed by [59], wt.%. (reproduced from Ref. [59]).

Sample	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	TiO ₂	Sc (mg/kg)
Bauxite residue	43.5	24	10.2	5.5	5.6	120
Basic slag	1.8	38.3	43.2	7.6	7.6	170
Neutral slag	1.5	39.8	29.9	22.0	7.4	170
Acidic slag	1.2	36.8	15.3	38	7.3	170

A kinetic study of REE leaching from different slags using the mixture of 2.5 M H₂SO₄ and 2.5 M H₂O₂ was carried out at 75 °C and S/L ratio of 1/10. It showed that both slag composition and cooling rate affect REE recovery. The best results were found for the quenched basic slag with recovery of 97% Sc and 95% Ti in solution without the formation of silica gel. Scandium phosphate concentrate with 85% total scandium recovery from red mud was precipitated from the obtained solution by a three-stage treatment using a solution of ammonia and ammonium hydrogen phosphate (NH₄)₂HPO₄.

Rivera et al. [60] studied high-pressure acid leaching of REEs by HCl and H₂SO₄ at elevated temperatures from the slags obtained by reduction smelting of red mud. Six types of slags were obtained using the different fluxes, lime or silica, and the cooling rate, water quenching, or slow cooling. [Table 3](#) presents the chemical compositions of red mud and the slag samples.

Table 3. Chemical composition of red mud and the slag samples * from reduction smelting analyzed by [60], where slag I was obtained by 20% CaO addition, and slags II and III were obtained by CaO and SiO₂ addition, respectively, wt.%. (reproduced from Ref. [60]).

Element	Bauxite Residue	Slag I.FC	Slag I.SC	Slag II.FC	Slag II.SC	Slag III.FC	Slag III.SC
Al	9.6	20.2	20.0	16.9	17.8	19.3	19.1
Ca	6.1	27.2	27.1	17.7	15.9	16.9	16.3
Si	3.4	4.6	4.7	11.8	12.3	10.4	10.1
Ti	3.5	5.2	5.5	6.1	5.4	5.5	5.2
Na	2.1	1.8	0.9	2.2	2.0	2.1	2.3
Fe	32.7	1.5	2.5	2.0	2.4	2.5	3.7

* FC: Fast cooling; SC: Slow cooling; Slag I, II and III produced with mixture I, II and III, respectively.

After leaching of the slowly cooled slag III by 3 N H₂SO₄ solution at 150 °C, selective recovery of above 95% Sc occurred due to the formation of double sulfates [40], whereas the recovery of other REEs was about 20%. In addition, leaching of the quenched slag II by 3 N HCl solution at 120 °C led to the recovery of over 90% Y, La, and Nd, and of 80% Sc. The dissolution degree of Ti and Si under the optimal conditions was up to 5%, and over 60% Fe and 90% Al passed into solution. A cost-benefit evaluation of the high-pressure acid leaching process is required.

Acid leaching can be used in combination with physical beneficiation methods of raw materials, such as hydrocyclone processing followed by drying [61]. This treatment increased the contents in the separated fraction of La by 19%, Ce by 23%, and Sc by 7%, and decreased Fe content by 22%. It also contributed to

minimizing total recovery of iron and increased leaching degree of REEs. Leaching of fine hydrocyclone beneficiated fraction by 2 M H₂SO₄ solution at 95–100 °C, pH = 4 and S/L ratio of 1/10 for 2 h increased Sc recovery by 15%, La by 16%, and Ce by 9% compared with original red mud, whereas Fe content in the solution was decreased from 4.9% to 2.2%.

Guo et al. [62] proposed the preliminary calcination process of a mixture of red mud and fly ash from coal-fired power plants in the presence of sodium carbonate in the temperature range of 600–900 °C for 2 h followed by acid leaching. Leaching of the calcine, which was obtained by roasting at 850 °C the mixture of 100 g of the ash and 106.4 g of red mud, by 6 M HCl solution and boiling for 2 h led, to the dissolution of above 90% of alumina.

Kashcheev et al. [63] suggested an improved sulfuric acid method for red mud processing using ammonium sulfate as a leaching agent. A comparative assessment of leaching characteristics of ammonium sulfate and sulfuric acid showed that they are equal in terms of their efficiency of the dissolution of sodium, calcium, iron, and aluminum. In the first stage, the boiling treatment by 8.45% (NH₄)₂SO₄ solution at S/L ratio of 1/14 for 30 min extracted 95% Na and no more than 13–17% Al and Fe, thereby decreasing red mud weight by 23%. In the second stage, when the reagent concentration was increased to 58.7% and the volume of the solution to the S/L ratio was 1/30, boiling for 60 min led to dissolution of 77.2% Al, 78.6% Ca, 60.25% Fe, 95.7% La, 71.0% Sc, and 86.5% Y. Then, hydroxides of aluminum, iron, and alkaline-earth metals with an admixture of REEs were precipitated by sequential neutralization to obtain a solution of ammonium and alkali metal sulfates. In the final residue, titanium and silicon compounds, in addition to calcium sulfate, were concentrated. It is the authors' opinion that the advantage of this technology compared with sulfuric acid leaching is a lower cost of ammonium sulfate, which is used as a lixiviant. Other important advantages are the possibility of obtaining a neutralizing reagent, ammonia, during the regeneration of ammonium hydrosulfate, in addition to environmental compatibility, high productivity due to better filtration characteristics of the solutions, etc.

The extraction of valuable elements from red mud by direct acid leaching is a well-studied method. The use of sulfuric and hydrochloric acids as leaching agents is most promising for industrial application due to their wide application and low cost. Nevertheless, these methods have several disadvantages, such as high dissolution of iron, silica gel formation, the need for the use of a high temperature, leaching duration, acid concentration, and pressure or preliminary roasting to increase the recovery degree. A significant interest for industrial application exists in the Orbite process [51], which allows extraction of valuable elements from red mud with the acquisition of high-grade alumina. However, using high pressure avoids the formation of silica gel and leads to the high dissolution of iron, which is the main hindering factor for the subsequent extraction of REEs from the solutions. Although dissolution of iron can be decreased by the use of a mixture of sulfuric acid and hydrogen peroxide [58], its concentration in the solution remains too high, so the most promising means of decreasing iron content in the solution is preliminary extraction by pyrometallurgical methods. Using ammonium sulfate as a leaching agent for the extraction of valuable elements from red mud is a new and prospective but poorly studied method.

3.2. Scandium Recovery by Sulfation Method

Scandium is among the most important rare-earth elements in red mud because its price is about 90% of the total price of all REEs contained in this waste. Red mud contains scandium and other REEs in various mineral forms. Scandium is mainly present as an impurity of hematite or goethite that substitutes Fe³⁺ and Al³⁺ [64]. A portion of scandium is in silicon-rich minerals such as quartz or zeolite. Unlike other REEs, individual scandium mineral particles have not been detected. Particles containing REEs also consist of titanium and iron, therefore, they are called REE ferrotitanates [65]. The REE distribution varies significantly depending on the origin of red mud. For example, in Greek red mud, 65% of scandium is present in an easily extractable form on the surface of red mud particles, but Russian red mud from Ural aluminum plants contains a smaller amount of scandium in chamosite.

One of the most widely studied and simple acid methods for the recovery of REEs, particularly scandium, from red mud is the sulfation method, which is the roasting of red mud with concentrated sulfuric acid at an S/L ratio close to 1 to convert scandium minerals into water-soluble sulfates followed by water leaching [66]. This method makes it possible to recover scandium selectively without silica gel formation. The advantage of this method is the possibility to process and reuse some products that are formed during thermal decomposition of the acid and during the roasting, namely SO_2 , SO_3 , $\text{NaFe}(\text{SO}_4)_2$, and $\text{NaAl}(\text{SO}_4)_2$, as raw materials for regeneration of sulfuric acid [67].

Meng et al. [68] studied the process of red mud sulfation by the treatment of its aqueous emulsion using concentrated H_2SO_4 at an S/L ratio of 2/1 followed by heating in a muffle furnace up to the required temperature and holding for 30 min. As a result, metal oxides in red mud were converted into highly soluble sulfates, and silicon was polymerized and transformed into an insoluble macromolecular form of silicic acid. An increase in roasting temperature led to the decomposition of titanium, iron (III), and aluminum sulfates into corresponding oxides. The maximum recovery degree of scandium sulfate from red mud was 96.5%, which was obtained by the leaching of the sample roasted at 750 °C for 60 min. An increase in the roasting temperature up to 850 °C led to a decrease in the solubility of scandium sulfate to about 90% due to its partial decomposition to hardly soluble oxide. However, it contributed to significantly better scandium selective recovery due to lower dissolution of titanium, iron (III), and aluminum, which also dissociated during the roasting from sulfates into oxides, but at lower temperatures of 544 °C, 683 °C, and 716.6 °C, respectively.

Liu et al. [69] showed that sodium can have an inhibitory effect on the release of SO_2 or SO_3 from metal sulfates during the roasting of red mud with concentrated sulfuric acid, and an excess of the acid over 1 mL/g has no growth effect on Sc and Na leaching. The optimal treatment conditions were chosen as follows: roasting temperature of 750 °C, roasting duration of 40 min, liquid-to-solid ratio of 10 mL/g, leaching temperature of 65 °C, leaching time of 30 min, and stirring speed of 250 rpm. The roasting and leaching under these conditions extracted over 95% Na and about 60% Sc in the presence of the obtained solution of 7% Al, 29% Ca, and 3% Si, in addition to Fe, Ti^{4+} , and Ga^{3+} in inconsequential amounts.

Roasting of the mixture of Chinese red mud and sulfuric acid with S/L ratio of 1 g/mL at 750 °C for 40 min and subsequent water leaching at 50 °C for 30 min contributed to the dissolution of about 53% Sc, 30.3% Ca, and 8.9% Al, in addition to less than 1.0% Fe and 0.3% Si. A roasting temperature rise up to 760 °C led to a drop in recovery degree of Sc to 49.5%, Fe to 0.1%, Si to 0.2%, Ca to 27.0%, and Al to 1.6%. According to the authors [66], scandium after roasting was in the form of complex sulfate $\text{Na}_3\text{Sc}(\text{SO}_4)_3$.

Narayanan et al. [70] indicated that scandium and other REEs can be easily separated by a precipitation from the sulfate leaching solution obtained by red mud processing. Sulfation was carried out by the treatment of red mud using 80% H_2SO_4 at 120 °C for 14 h, followed by calcination at 700 °C for 1 h. Mixtures of REE oxides were sequentially precipitated from the leached sulfate solution by the addition of sodium hydroxide at pH = 8; scandium was deposited as scandium oxalate by the addition of oxalic acid followed by calcination at 800 °C for 1 h to obtain a pure oxide. The recovery degree of scandium by this method was 75%.

Alkan et al. [57] extracted scandium from the slags that were obtained by reduction smelting of red mud with the addition of lime and silica. Slags with a weight of 13 g were mixed with 5, 10, and 15 mL of concentrated sulfuric acid (97% H_2SO_4) and 5 mL of deionized water, then the samples were held at 75 °C for 1 h in a furnace. After the treatment of the silicic slag, about 70% Sc, less than 10% Ti, and 3% Si passed into solution without silica gel formation.

Rivera et al. [52] investigated REE recovery from red mud by a multistage treatment using hydrochloric and sulfuric acids, followed by water leaching. The recovery of Si, Al, Fe, Sc, Y, La, and Nd into the solution was studied depending on the amount of acid and number of treatment cycles. Sulfating with 95-

97% sulfuric acid for 24 h with H_2SO_4 consumption of 412 g/kg of red mud and subsequent water leaching of the roasted sample for 24 h at 25 °C and S/L ratio of 1/5 led to dissolution of 2.5% Si, 30% Al, 22% Ti, 3% Fe, 22% Sc, 12% Y, 11% La, and 11% Nd. Treatment by 37% HCl with following water leaching under the same conditions caused the dissolution of the main macrocomponents to decrease slightly, but dissolution of REE increased; thus, 28% Al, 2% Ti, 3% Fe, 29% Sc, 44% Y, 25% La, and 28% Nd passed into solution at HCl consumption of 788 g/kg. A 4–9-fold increase in recovery degree of the components following a decrease in water consumption by 50–60% was achieved by five treatment cycles. Taking into account the price of scandium oxide for December 2017, the preliminary evaluation showed that the estimated profit margin of the technology with multistage leaching by HCl is 531 USD per tonne of red mud, whereas for leaching by H_2SO_4 , profit is 563 USD per tonne of red mud.

The use of sulfation roasting and water leaching leads to selective extraction of more than 60% Sc from red mud without a significant dissolution of iron, titanium, and silica gel formation [69]. This method can be applied only for the extraction of Sc and has industrial potential due to high scandium prices. However, due to the large amount of accumulated red mud and low Sc content in it, this method can be used only as a part of a complex treatment of red mud with extraction of major valuable elements such as Fe, Al, and Ti.

Generally, it should be noted that an application of acid methods is a promising approach for red mud processing, and enables extraction of almost all elements, including small amounts of scandium and other REEs. The main disadvantages of these methods are the need for acid-resistant equipment and low selectivity. This necessitates development of multistage technologies that are difficult to practically implement.

4. Red Mud Processing by Organic Solvents

The application of organic media for the treatment of raw materials and the recovery of valuable components can avoid the formation of a significant amount of processing solutions and spent liquor, which also need to be utilized for the mitigation of environmental impacts. Recently, non-aggressive hydrocarbons with low toxicity, and their mixtures, have been synthesized and introduced into industry. These hydrocarbons are attractive due to their use as promising extraction media and sorption materials. The application of such leaching agents makes it possible to use cheaper equipment, thereby reducing the loss of the extractant by evaporation or hydrolysis in contact with aqueous solutions.

4.1. Organic Acid Leaching

Yang et al. [71] proposed applying a mixture of oxalic and sulfuric acids for selective recovery of iron from red mud. To reduce the loss of more expensive oxalic acid before leaching, red mud was neutralized by diluted hydrochloric acid of 3 mol/L at a liquid-to-solid ratio of 2 mL/g for 1 h at room temperature. As a result of pretreatment, the loss of $\text{H}_2\text{C}_2\text{O}_4$ with leached residue decreased from about 17% to less than 1%. Leaching of iron was carried out using the mixture of pretreated mud/ $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ at the mass ratio of 3/3/2 and S/L ratio of 1/16 g/mL. The treatment at 95 °C for 1.5 h led to the recovery of 94.15% Fe and 21.12% Al, and no more than 0.69% Fe remained in the residue. The treatment of the leached solution with the addition of iron scrap as a reducing agent at 50 °C for 60 min led to the precipitation of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The precipitated iron oxalate was treated by 9 M H_2SO_4 solution at S/L ratio of 1/5 g/mL at 50 °C for 20 min to obtain $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and for $\text{H}_2\text{C}_2\text{O}_4$ regeneration. In another paper [72], after oxalic acid leaching, the same authors carried out the precipitation of iron as iron hydroxide by neutralization of the solution to pH = 3.5 using CaCO_3 addition. To selectively dissolve iron from the precipitate, leaching by the aqueous solution containing 1 M HCl and 200 g/L of CaCl_2 at S/L ratio of 1/4 g/mL was used. The following reprecipitation of $\text{Fe}(\text{OH})_3$ at pH = 3.52 and the calcination at 750 °C for 3 h resulted in the acquisition of Fe_2O_3 of 98.44% purity. Oxalic acid and, in part, the solution of HCl- CaCl_2 were regenerated, and the remaining part of calcium was precipitated as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ of 99.31% purity.

Yu et al. [73] precipitated iron in the form of poorly soluble β - $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by ultraviolet irradiation without any reagent addition from iron (III) oxalate solution obtained by the leaching of red mud by 1 M $\text{C}_2\text{H}_2\text{O}_4$ at 75 °C for 2 h. As a result, the residual iron content in the solution decreased to 1 g/L, and the oxalate solution after filtration was regenerated for the leaching of red mud.

Ujaczki et al. [74] studied selective recovery of gallium by the leaching of red mud using 1–2 M solutions of HCl, HNO_3 and H_2SO_4 , in addition to 1 M $\text{C}_2\text{H}_2\text{O}_4$. The degree of gallium recovery from the suspension of 100 g of red mud in 1 L of the solution after the treatment at 60 °C for 24 h varied depending on the type of acid, and was 34.8% for HCl, 27.9% for HNO_3 , 28.6% for H_2SO_4 , and 42.0%, the highest value, for $\text{C}_2\text{H}_2\text{O}_4$. Oxalic acid leaching was investigated by varying the concentration of the acid from 0.05 to 3 M, treatment duration from 1 to 24 h, temperature from 22 to 80 °C, and concentration of the suspension from 10 to 200 g/L. The best results with the recovery of about 80% Ga was obtained using 2.5 M oxalic acid at 80 °C and an S/L ratio of 10 g/L for 21.7 h.

In the method [75], solutions of formic and acetic acids, and their mixtures, were used to extract aluminum and REEs from red mud. Leaching was carried out in a reactor with a stirrer at 80 °C using gradual addition of raw materials and continuous pH monitoring. The red mud addition was terminated upon reaching the specified acidity of the suspension in the range of $\text{pH} = 1.6$ – 4.0 , but the leaching was continued for 1 h thereafter, and then held at a fixed temperature for an additional 1 h. Analysis of the acid leachates obtained after separation and extraction showed that an increase in pH from 1.6 to 3.8 led to a decrease in the aluminum recovery from 71.5% to 67.5% and scandium recovery from 74.4% to 70.2%, whereas the application of acetic acid resulted in a decrease in the recovery from 65% to 61.4% for Al, and from 67.7% to 63.9% for Sc. For the mixture of the acids of 1:1 ratio, the recovery degree of aluminum and scandium dropped from 67.6% to 63.8% and from 70.3% to 66.4%, respectively.

Atalay Kalsen et al. [76] compared the solubility of red mud components, namely Fe, Al, Ca, Si, Na, and Ti, in hydrochloric and citric acids depending on acid concentration, temperature, and leaching time. It was shown that the temperature was the most significant factor of the leaching process by hydrochloric acid, whereas the leaching process by citric acid depended on the temperature to a lesser degree. Leaching by 8 M HCl solution for 5 h at 100 °C caused almost full recovery of calcium and iron, in addition to the dissolution of over 60% Ti and 80% Al. The use of citric acid under the same conditions enabled recovery of 50% Ca and 60% Al with a simultaneous low dissolution of the remaining elements without any studies of the REEs' behavior.

Gu et al. [77] leached over 46% of lithium from red mud, which was previously neutralized by 0.5 mol/L oxalic acid, using 25% solution of acetic acid at 85 °C for 60 min. The increase in acetic acid concentration above 25% and temperature led to the decrease in the percentage of metals dissolved, such as Al and Fe, and precipitation of a part of the released metal including lithium. Nevertheless, the leaching efficiencies of lithium were developed up to 60.27%, which is higher than those of sodium under neutralizing red mud using 0.01 mol/L hydrochloric acid.

The most important lixiviant among the investigated organic acids is oxalic acid, which enables selective dissolution of Fe [71][72][73] and Ga [74] from red mud. This method can be used as an alternative approach to iron recovery instead of pyrometallurgical methods.

4.2. Leaching by Ionic Liquids

Ionic liquids are salts that consist of an organic cation and an inorganic anion, the melting point of which is lower than the boiling point of water. They also have been used as alternative solvents for the recovery of valuable components from mineral raw materials [78][79].

Davris et al. [80] considered leaching of REEs from red mud by betainium bis(trifluoromethylsulfonyl)imide [HBet][Tf_2N], which is hydrophobic ionic liquid. The leaching was carried out at atmospheric pressure with the addition of water, and under autoclave conditions. After the leaching, the dissolved elements were

desorbed by hydrochloric acid solution using stirring at room temperature for 30 min. Then, the purified organic media was reused. The studied factors influencing the recovery of elements were the amount of water, temperature, rate and duration of mixing, and pulp density. The optimal leaching conditions, namely aqueous solution of 40% at 150 °C with stirring at 400 rpm for 4 h, resulted in the recovery of 45% Sc, 30% Al, and below 3% Fe, and negligible dissolution of Ti and Si. Temperature had the greatest impact on Sc recovery.

Bonomi et al. [81] investigated direct leaching of red mud by 1-ethyl-3-methylimidazolium hydrogen sulfate [Emim][HSO₄]. The experiments were carried out in a 50 mL mini-reactor with a stirrer and a steam condenser at the temperatures of 150, 175, and 200 °C. To reduce the viscosity and facilitate the process, dimethyl sulfoxide was added during vacuum filtration, and the obtained solutions were treated by 65% HNO₃. The experiments showed that the temperature and duration of the leaching had the greatest influence on the recovery of Sc and Ti in the solution. A stirring speed of 200 rpm and temperature of 200 °C for 12 h at an S/L ratio of 1/20 led to the recovery of 80% Sc, 90% Ti, 98% Fe, 38% Al, and 42% Na. The analyses of the leach residue using scanning and transmission electron microscopes indicated that undissolved scandium is mainly associated with ZrSiO₄.

Thus, the use of hydrophilic ionic liquids, especially [Emim][HSO₄], as the solvents for the recovery of valuable components from red mud, is more favorable than the use of hydrophobic ionic liquids, due to their low cost and high degree of scandium and titanium recovery [82]. However, due to the high solubility of iron in hydrophilic ionic liquids, preliminary recovery of iron is necessary.

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Keywords

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