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# Destruction of mineral components of red mud during hydrothermal extraction of scandium

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**Abstract.** The technology of scandium extraction from red mud of bauxite processing by hydrochemical method has been developed, including preliminary treatment of red mud with alkaline solution for aluminum extraction, subsequent thermochemical transformation in sodium hydrogen carbonate solution and repulping in solution containing a mixture of sodium carbonate and sodium hydrogen carbonate and sorption extraction of scandium from carbonization solution. As a result of pretreatment of red mud with alkaline solution, with the addition of CaO at the rate of obtaining the ratio of $CaO:SiO_2$= 1:1 in the pulp at a temperature of 240-260°C extraction of aluminum obtained in the solution more than 80%. To increase the degree of extraction of scandium, thermochemical transformation of the phase composition of red mud by treatment with sodium hydrogen carbonate solution at a temperature of 260°C, duration of 6 hours and the ratio L:S = 10. Extraction of scandium from red mud is carried out by pulp repulping method with soda-hydrocarbonate recycling solution containing $Na_2O_{tot}$ = 65 g/dm$^3$ at $NaHCO_3/Na_2CO_3$ ratio~ 2 with solution gassing with carbon dioxide to reach pH≤9 at temperature 80°C and duration 3 hours. According to the developed technology the degree of scandium extraction from red mud amounted to 86.5%. The efficiency of the technology is associated with the destruction of mineral components of red mud as a result of two-stage transformation of the phase composition, its recrystallization and release of the difficult-to-discover part of scandium. The analysis of existing technologies of sorption extraction of scandium from sulfuric acid leaching solutions was carried out, which showed that the best selectivity for scandium is possessed by ion-exchange resins synthesized by phosphorylation of copolymers of styrene and divinylbenzene. When using phosphorus-containing amphoteric ionite Lewatit TP 260, the degree of scandium extraction from the carbonization solution was 98%.

**Keywords:** *red mud, scandium, alkaline solution, thermochemical transformation, destruction, repulsion, sodium carbonate, sodium hydrogen carbonate.*

## 1. Introduction

Scandium, one of the most expensive metals ($5.1 per 1 g of metal in 2023) with a limited volume of production could increase the economic efficiency of bauxite processing. The unique properties of scandium create the prerequisites for highly effective specific application of this metal and its compounds in a wide variety of industries, such as shipbuilding, aerospace, aircraft, 3D-printing and others. In recent years, the demand for scandium has increased dramatically as the prospects for its use have expanded. The demand for scandium oxide is predicted to increase up to 300 t/year [1].

It is known that up to 70% of the total world reserves of scandium are concentrated in bauxite ores and their processing wastes - red mud (RM) [2,3,4] and various technologies have been developed for its extraction using leaching by acid and salt solutions or preliminary concentration by enrichment or pyrometallurgy [5-10].

The methods [11,12,13] include leaching of RM with solutions of sodium carbonate or sodium hydrogen carbonate or their mixture. The disadvantages of these methods are low extraction of scandium. The maximum $Sc_2O_3$ recovery of 30.1÷30.5% was obtained in the method [11] which includes slime repulsion in soda-hydrocarbonate circulating solution with carbon dioxide gasification of the solution to achieve pH≤9 and carbonization leaching with soda-hydrocarbonate solution containing $Na_2O_{total}$ = 65-75 g/dm$^3$ at temperature of 60-100°C.

The low degree of scandium recovery can be explained by the fact that the red mud contains several forms of scandium: easily extractable scandium, sorbed or deposited on the surface; difficult to extract, located in the crystal lattice, mostly iron-bearing minerals and chemically bound in compounds with aluminum, calcium, iron, etc. [14]. At scandium leaching from red mud by solutions of sodium carbonate and sodium hydrocarbonate mainly scandium is extracted which is sorbed on the surface of red mud and forms water-soluble complexes with carbonate and hydrocarbonate [3]. It is required to develop new effective technologies to extract scandium from hard-to-extract and chemically bound forms, which may be associated with the need for preliminary transformation of the initial phase composition of RM.

The aim of the conducted research was to increase the degree of extraction of scandium from red mud.

## 2. Materials and methods

X-ray fluorescence analysis was performed on a Venus 200 spectrometer with wave dispersion (PANalyical B.V., Holland).

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Chemical analysis of the samples was performed on an optical emission spectrometer with inductively coupled plasma (Optima 8300 DV, Perkinelmer, Waltham, MA, USA). The random error component was 2.0%.

X-ray phase analysis was performed using a D8 Advance (Bruker, Billerica, Massachusetts, USA) with Cu KA radiation obtained at 40 kV and 40 mA.

Thermal analysis was performed using the STA 449 F3 Jupiter synchronous thermal analysis instrument.

RM was treated with an alkaline solution containing 240-260 g/l $Na_2O_{caust}$ with added CaO; at a 1:1 $CaO:SiO_2$ ratio in the pulp and a temperature of 240-260°C, more than 80% of aluminium passed into the solution. Scandium remained in the sludge, which had the following composition (mass %): 7.33 $Na_2O$; 7.6$Al_2O_3$; 19.6 $SiO_2$; 21.3 CaO; 22.9 $Fe_2O_3$; 0.0095 $Sc_2O_3$; 21.26 p.p.p.

Thermochemical transformation of sludge was carried out in a solution containing 40-120 g/dm$^3$ $NaHCO_3$, ratio L:S = 3-10, temperatures 120-260°C and duration 30-300 minutes. The maximum content in the solution of sodium hydrogen carbonate 120 g/dm$^3$ is justified by the solubility limit.

The repulpation process was performed in a soda-hydrocarbonate circulating solution containing $Na_2O_{tot} = 65$ g/dm$^3$ at a ratio of $NaHCO_3/Na_2CO_3 \sim 2$ with carbon dioxide gassing until pH≤9 was reached at a temperature of 80°C, an L:S ratio of 1:1 and a duration of 3 hours.

The flow rate of the process solution and eluent through the ion exchange resin was controlled using a Hei-FLOW Precision peristaltic pump.

The equilibrium static exchange capacity (SEC) of the resin was determined by changing the produced solution containing 0.05 g/dm$^3$ $Sc_2O_3$. Solutions of sodium carbonate (analytical grade) were used as the eluent.

## 3. Results and discussion

As a feedstock for studies was used RM from the processing of bauxite Krasnogorskoye deposit in the Pavlodar aluminum smelter JSC «Aluminium of Kazakhstan» with composition, wt %: 15.0 $Na_2O$; 19.47 $Al_2O_3$; 1.3 CaO; 11.19 $SiO_2$; 26.95 $Fe_2O_3$; 0.01 $Sc_2O_3$.

To extract scandium from RM the technology was used, which includes the extraction of $Sc_2O_3$ by sludge repulsion in a soda-hydrocarbonate recycled solution with carbon dioxide gasification of the solution to achieve pH≤9 and carbonization leaching with a soda-hydrocarbonate solution [11-13].

The phase composition of the initial RM is shown in Figure 1.

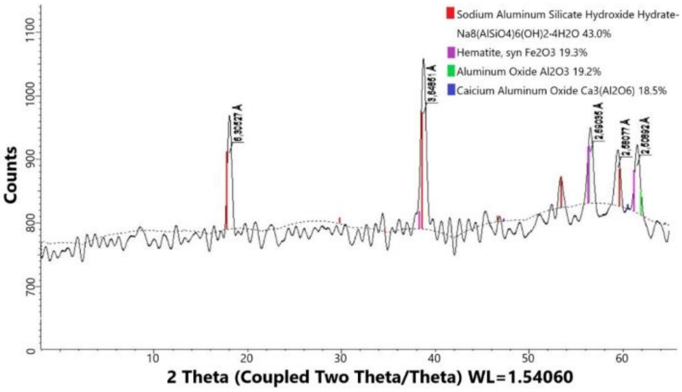

*Figure 1. X-ray radiograph of the original red mud*

To increase the extraction of scandium the technology was developed consisting of the following stages (Figure 2):

– red mud pre-treatment with an alkaline solution for aluminum extraction;

– thermochemical transformation of sludge after alkaline treatment in a solution of sodium hydrogen carbonate;

– repulping of sludge after pretreatment in a solution containing a mixture of sodium carbonate and sodium hydrogen carbonate to extract scandium.

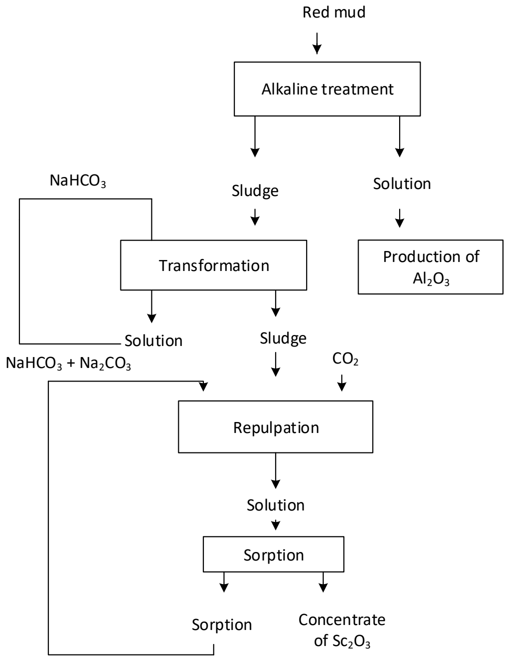

***Figure 2. Technological scheme of scandium extraction from RM***

As a result of RM processing, the phase composition of the sludge is shown in Figure 3.

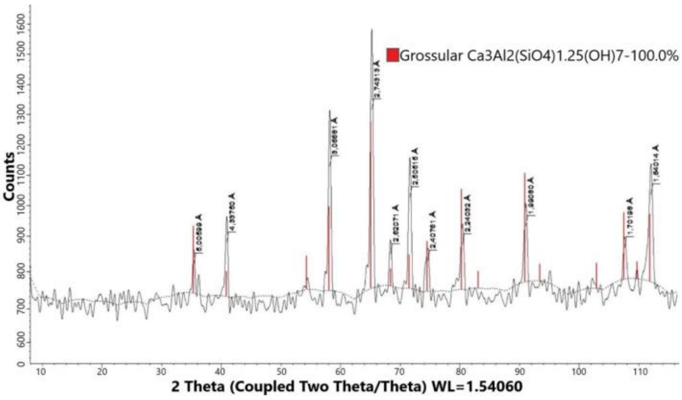

***Figure 3. X-ray radiograph of red mud after treatment with alkaline solution***

Chemical composition of sludge, wt %: 7.33 $Na_2O$; 7.6 $Al_2O_3$; 19.6 $SiO_2$; 21.3 CaO; 22.9 $Fe_2O_3$; 0.0095 $Sc_2O_3$; 21.26 s.l. As a result of the treatment, more than 80% of the aluminum passed into solution. After treatment, scandium remained in the sludge.

To determine the conditions of maximum transformation of the sludge phase composition we carried out research at temperature 120 ÷ 260°C, the ratio L:S in the sludge is 3 ÷ 10 and duration of 1 ÷ 6 hours. The concentration of sodium bicarbonate solution is conditioned by its solubility limit.

Determination of the influence of thermochemical transformation of sludge was carried out at duration of 1 hour and ratio in slurry L:S = 10 (Tables 1,2).

***Table 1. Influence of temperature on phase composition of sludge***

| Name of phase | Formula | Composition, % | | | | |
|---|---|---|---|---|---|---|
| | | Holding temperature, °C | | | | |
| | | 120 | 150 | 180 | 220 | 260 |
| Andradite | $Ca_3Fe_2(SiO_4)_3$ | 29.6 | 26 | 24.5 | 17 | - |
| Aragonite | $CaCO_3$ | 19.6 | 17.8 | 14.8 | 14,1 | - |
| Cancrinite | $Na_6Ca_2[(CO_3)_2\|Al_6Si_6O_{24}]\cdot 2H_2O$ | 16.7 | 15.6 | 14.4 | 13.2 | 12.1 |
| Calcite | $CaCO_3$ | - | - | - | 15.0 | 45.0 |
| Sodium Iron Silicon Oxide | $Na_{0.765}(Fe_{0.785}Si_{0.215})O_2$ | 13.2 | 12.8 | 13.3 | 8.5 | - |
| Morimotoite | $Ca_3(TiFe^{2+})(SiO_4)_3$ | 12.9 | 14.3 | 15.6 | 13.7 | 16.8 |
| Hematite | $Fe_2O_3$ | 9.1 | 8.5 | 9.3 | 9.2 | 9.5 |

***Table 2. Effect of temperature on the chemical composition of sludge***

| Composition, % | Holding temperature, °C | | | | |
|---|---|---|---|---|---|
| | 120 | 150 | 180 | 220 | 260 |
| $Na_2O$ | 5.05 | 5.42 | 6.001 | 6.63 | 7.61 |
| $Al_2O_3$ | 7.11 | 7.27 | 7.98 | 7.74 | 7.6 |
| $SiO_2$ | 15.66 | 15.4 | 15.29 | 15.179 | 15.1 |
| CaO | 14.27 | 14.174 | 14.94 | 14.47 | 14.1 |
| $Sc_2O_3$ | 0.0133 | 0.0133 | 0.0132 | 0.0134 | 0.0135 |
| $Fe_2O_3$ | 36.23 | 36.55 | 36.49 | 35.97 | 36.38 |

It follows from the obtained results that the following transformation of phases takes place with increasing exposure temperature in sodium hydrogen carbonate solution:

– the content of aragonite, cancrinite, androdite and sodium iron-siliceous oxide decreases (androdite and sodium iron-siliceous oxide phases disappear at 260ºC);

– the content of morimotoite phase increases;

– starting from temperature 220ºC the calcite phase is formed;

– the red mud chemical composition practically does not depend on the curing temperature, only the $Na_2O$ content increases.

Determination of the effect of the duration of on the thermochemical transformation of sludge was carried out at a temperature of 260ºC with the ratio in the sludge L:S = 10 (Tables 3,4).

As the duration of exposure in sodium hydrogen carbonate solution increases, the following phase transformation occurs:

– the content of the cancrinite phase decreases;

– the content of calcite phase increases;

***Table 3. Influence of time on phase composition of sludge***

| Name of phase | Formula | Composition, % | | | |
|---|---|---|---|---|---|
| | | Duration, hour | | | |
| | | 1 | 2 | 4 | 6 |
| Cancrinite | $Na_6Ca_2[(CO_3)_2\|Al_6Si_6O_{24}]\cdot 2H_2O$ | 14.9 | 13.6 | 12.7 | 11.2 |
| Calcite | $CaCO_3$ | 55.1 | 57.3 | 58.6 | 60 |
| Morimo-toite | $Ca_3(TiFe^{2+})(SiO_4)_3$ | 18.1 | 18.8 | 19.1 | 18.6 |
| Hematite | $Fe_2O_3$ | 10 | 10.5 | 10.7 | 10.2 |

***Table 4. Effect of time on the chemical composition of sludge***

| Composition, % | Duration, hour | | | |
|---|---|---|---|---|
| | 1 | 2 | 4 | 6 |
| $Na_2O$ | 6.52 | 6.97 | 6.84 | 7.49 |
| $Al_2O_3$ | 755 | 7.75 | 7.69 | 7.38 |
| $SiO_2$ | 15.23 | 15.47 | 15.31 | 15.3 |
| CaO | 14.15 | 14.74 | 14.68 | 14.2 |
| $Sc_2O_3$ | 0.0132 | 0.0131 | 0.0134 | 0.0135 |
| $Fe_2O_3$ | 36.96 | 36.65 | 35.29 | 36.29 |

Determination of the effect of L:S ratio in the sodium bicarbonate slurry and sludge on the thermochemical transformation was carried out at a temperature of 260ºC and duration of 6 hours (Tables 5,6).

***Table 5. Influence of L:S ratio in sodium bicarbonate solution on phase composition of sludge***

| Name of phase | Formula | Composition, % | | |
|---|---|---|---|---|
| | | L:S | | |
| | | 3:1 | 5:1 | 8:1 |
| Cancrinite | $Na_6Ca_2[(CO_3)_2\|Al_6Si_6O_{24}]\cdot 2H_2O$ | 20 | 19.1 | 16.9 |
| Calcite | $CaCO_3$ | 40.9 | 44.9 | 53.5 |
| Morimotoite | $Ca_3(TiFe^{2+})(SiO_4)_3$ | 24.9 | 22.2 | 18.6 |
| Hematite | $Fe_2O_3$ | 14.3 | 13.8 | 11 |

***Table 6. Influence of L:S ratio in sodium bicarbonate solution on chemical composition of sludge***

| Composition, % | Composition, % | | |
|---|---|---|---|
| | L:S | | |
| | 3:1 | 5:1 | 8:1 |
| $Na_2O$ | 6.88 | 6.73 | 7.5 |
| $Al_2O_3$ | 7.59 | 7.41 | 7.58 |
| $SiO_2$ | 15.94 | 15.58 | 15.3 |
| CaO | 14.45 | 14.67 | 14.18 |
| $Sc_2O_3$ | 0.0132 | 0.0133 | 0.0135 |
| $Fe_2O_3$ | 36.28 | 35.56 | 36.34 |

As the L:S ratio in the pulp increases, the following phase transformation occurs:

– the content of the cancrinite phase decreases;

– the content of calcite phase increases;

– the content of morimotoite phase increases;

As a result of the analysis of the results obtained, it follows that for the maximum transformation of the phase composition of the sludge should be held in a solution of sodium bicarbonate at 260ºC, at duration of 6 hours and the ratio L:S = 10. The X-ray phase analysis of sludge after thermochemical transformation is shown in Figure 4.

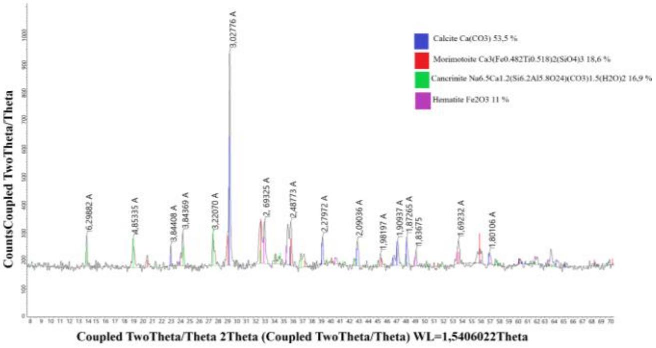

***Figure 4. X-ray radiograph of red mud after thermochemical transformation in sodium bicarbonate solution***

At thermochemical transformation of RM in sodium hydrogen carbonate solution there is disappearance of andradite phase, reduction of cancrinite and alkaline iron silicate with formation of new phases - calcite and morimotoite.

Thus, as a result of leaching of RM in alkaline solution with addition of active form of calcium oxide and thermochemical transformation there was a two-stage change in the initial phase composition.

The scheme of two-stage transformation of RM as a result of alkaline pretreatment and thermochemical transformation in sodium hydrogen carbonate solution can be presented as follows:

sodium aluminosilicate ($Na_8(AlSiO_4)6(OH)_2{\cdot}4H_2O$) + CaO => aluminum hydrogarnet ($Ca_3Al_2(SiO_4)_{1.25}(OH)_7$) => cancrinite ($Na_6Ca_2[(CO_3)_2|Al_6Si_6O_{24}]\text{-}2H_2O$) + morimotoite ($Ca_3(TiFe^{2+})(SiO_4)_3$) + $CaCO_3$

After thermochemical transformation we extracted scandium from RM by the known method [6] by repulsion of the sludge in soda-hydrocarbonate recycled solution containing $Na_2O_{total}$ = 65 g/dm$^3$ at a $NaHCO^3/Na_2CO_3$ ratio of 2 with the solution gasification with carbon dioxide to achieve pH≤9 at 80 $^oC$ and duration of 3 hours.

Chemical composition of red mud after repulsion in soda-hydrocarbonate solution, wt %: 8.5 NaO; 8.89 $Al_2O_3$; 17.85 $SiO_2$; 16.49 CaO; 42.3 $Fe_2O_3$; 0.0013 $Sc_2O_3$; 5.96 other products.

Scandium extraction as a result of repulping into carbonization solution was 86.5 %, which can be attributed to recrystallization of sludge and release of hard to-recover part of scandium.

To choose an effective sorbent for selective extraction of scandium from carbonization solutions the analysis of existing methods was carried out.

The best sorption selectivity of sulfuric acid solutions for scandium is exhibited by the ion-exchange resins KRF-5, KRF-8 and KRF-12, which are synthesized by phosphorization of copolymers of styrene and divinylbenzene [15].

Techniques have been developed for the sorption of scandium from sulfuric acid solutions by the macroporous complexing phosphorus-containing ampholyte AFI-22, as well as for the sorption of rare earth elements (REEs) with the cation exchanger KU-2-8n, and have been tested on a semi-industrial scale [16, 17]. The extraction of scandium at the sorption stage was 52.5% [16].

The ampholyte AFI-22 sorbed scandium from clarified sulfuric acid solutions to realize extraction from the combined eluate [18]. The scandium content in the commercial eluate obtained by desorption with 15% sodium carbonate solution from iron-purified ionite was only 43-65 mg/dm$^3$.

Scandium was concentrated from complex circulating solutions of underground and heap leaching of uranium containing approximately 1 mg/dm$^3$ scandium by using a macroporous strong acid cation exchanger based on styrene and divinylbenzene (Purolite S957, Purolite Co. (USA) and Purolite Ltd. (UK)); this approach is distinguished by good kinetic properties and a high scandium working exchange capacity (WEC) of 688 mg/dm$^3$ due to the grafted phosphoric $H_2PO_3$ and sulfonic$-SO_3H$ functional groups [19].

Red mud (RM) from alumina production can serve as a raw material for the production of scandium. For example, the content of scandium in mother solutions of sulfuric, nitric, or hydrochloric acid leaching of Australian bauxite waste sludge can reach 54 mg/dm$^3$ [20]. When using traditional hydrometallurgical methods for brine processing based on aqueous solutions of mineral acids, the extraction of scandium, depending on the technological conditions, is at least 80-95% [21-26].

For the sorption of scandium from sulfuric acid leaching solutions of RM with various phosphorus-containing resins, Lewatit TP 260 and Purolite D 5041 ion exchangers have the highest sorption capacity [27].

According to a reported method [28], titanium is isolated from RM sulfuric acid leaching solution by two separate sorption steps. First, sorption is performed with a weakly basic polyethylenepolyamine anion exchanger that has been previously converted into the sulfate form; then, scandium is isolated from the sorption filtrate with a phosphorus-containing ion exchanger. The extraction of titanium in this case is over 99.9%, and that of scandium is in the range of 96-99%.

For the sorption extraction of scandium from the mother liquor of hydrochloric acid leaching of RM, the sulfonic cation exchanger Dowex 50W-X was proposed. The recoveries of scandium, yttrium, and ytterbium into the sorbent phase were 80, 90, and 70%, respectively [29].

By comparing the sorption of scandium from acidic sulfate-chloride solutions, it has been established that the impregnated materials I-D2EGFK and I-EGFK containing di-2-ethylhexylphosphoric acid and ethylhexylphosphoric acid in hypercrosslinked polystyrene (MN-202) are superior in kinetic properties to the ion exchangers Lewatit TP 260 and Purolite S957 and corresponding solid extractants containing organophosphorus (TBP, diisooctylmethylphosphonate) [30].

In general, acid leaching of RM is very problematic since many salt-forming elements are dissolved together with scandium. Leaching with sulfuric acid, which is characterized by low cost and wide availability, can lead to gypsum pulp if the permissible concentration at low temperature is exceeded and increases the viscosity, which slows the process. The highly corrosive nature of nitric and hydrochloric acids necessitates the use of expensive acid-resistant equipment.

Recently, a new, more environmentally friendly, and less costly method of processing sludge with carbonation solutions has been developed; this method passes flue gases from alumina sintering furnaces through bottom sludge water enriched with $Na_2CO_3$ [31, 32].

It is impossible to directly achieve complete scandium extraction and selectivity from carbonation slurry by sorption due to clogging of the sorbent pores by fine mechanical suspensions. The large loss of ion exchangers, especially the fine-grained fractions with low selectivity, leads to the production of concentrates heavily contaminated with impurities [33-37].

A method of obtaining scandium concentrate with a mass fraction of at least 15% $Sc_2O_3$ from the primary filtered solution of RM carbonation pulp was developed; this method is suitable for the commercial production of high-purity (over 99 wt.%) scandium oxide and is based on the sorption concentration of scandium by the ampholyte Lewatit TP 260 with the production of enriched carbonate eluate [38]. This method is unsuitable for implementation on an industrial scale since the sorption processing of scandium-poor primary RM carbonation leaching solutions requires a large volume of solution to saturate the ion exchanger, and the duration and low productivity are not compatible with commercial scandium production.

In the conducted work we investigated the possibility of increasing the efficiency of scandium sorption extraction using Lewatit TP 260 ampholyte from carbonization solutions of RM sludge after four-fold repulping to increase the concentration of scandium in the solution. As a result of repulping, a solution containing 0.05 g/dm$^3$ $Sc_2O_3$ was obtained. Extraction of scandium in the repulping solution amounted to 86.5%. The residual content of scandium in the slurry amounted to 0.0002%.

The sorption properties of the phosphorus-containing amphoteric ion exchanger Lewatit TP 260 (Lanxess Deutschland GmbH, Germany), containing only one amino group in its structure, which gives it weakly basic properties, were studied. This ionite is characterized by high selectivity for the extraction of anionic scandium carbonate complexes, which form strong coordination compounds with the phosphonic groups in the sorbent.

Notably, Lewatit TP 260 ampholyte in H+ form is superior to the phosphorus-containing strongly acidic ampholyte Purolite S 957 in terms of kinetic properties in sulfuric acid solutions of scandium sulfate [39].

The macromesh amphoteric ion exchanger Lewatit TP 260 has a developed surface, and due to its porosity and monodisperse distribution of uniform-diameter granules, it is capable of ion exchange in both the swollen and non-swollen state.

The macro mesh structure ensures that the active groups of the ampholyte are available to participate in the sorption process.

The monodisperse distribution of granules significantly increases the phase interface in the «ion-exchange resin – solution» system and increases the kinetics and degree of ion exchange in the processes of sorption and desorption, respectively [40].

The high chemical and thermal stability of the ion exchanger, indirectly indicating the strength of polymer cross-linking, is another important indicator of its performance (Table 7).

***Table 7. Physical and chemical properties of the ampholyte Lewatit TP 260***

| Swelling, V beats units ml/g | SEC by 0.1 n NaOH, g-eq/kg | Chemical resistance in 5 N NaOH, % | Temperature resistance in water (50 h. kip.), % |
|---|---|---|---|
| 3.4 | 5.7 | 99.7 | 100 |

The absorption properties of the ampholyte Lewatit TP 260 in static mode at S:L = 1:500 and a temperature of 220°C for 8 hours were analysed. The results showed that the degree of extraction (E) of scandium by the resin effectively increases with increasing scandium content in the produced RM carbonation leaching solutions due to salting out into the sorbent phase (water) by titanates and sodium carbonate zircon titanates, which are prone to solvation (Figure 5).

In this case, the completeness of scandium extraction, estimated by the distribution coefficient in the resin phase *D* (which expresses the ratio of the concentration of sorbed scandium in the resin phase to its content in the initial solution), improves as the temperature rises to a certain limit (Figure 6).

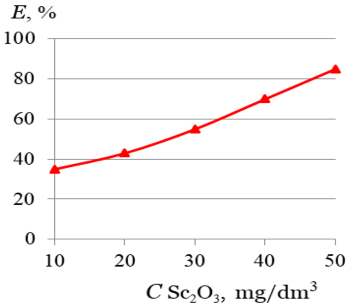

***Figure 5. Sorption of scandium by the ampholyte Lewatit TP 260 depending on its content in circulating solutions***

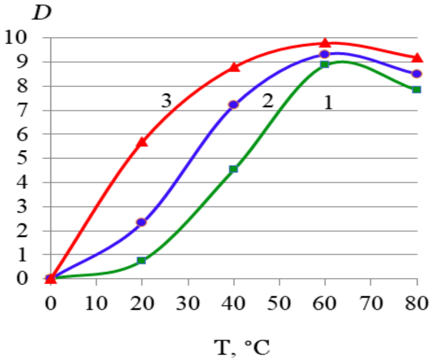

***Figure 6. Temperature dependence of scandium sorption: Content of $Sc_2O_3$ in produced solutions, mg/dm$^3$: 1–23; 2–34; 3–50***

The decrease in the value of the distribution coefficient of scandium into the resin phase at a solution temperature above 70°C is explained by the initial thermal decomposition of sodium bicarbonate and an increase in the concentration of sodium carbonate in solution:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \uparrow \quad (4)$$

The scandium sorption removal isotherm with maximum saturation of the resin was generated by applying produced RM repulpation solution with a temperature of 60°C in static mode. The results indicated that the sorption exchange capacity (SEC) of Lewatit TP 260 ampholyte for scandium was 2.53 g/dm$^3$ (Figure 7).

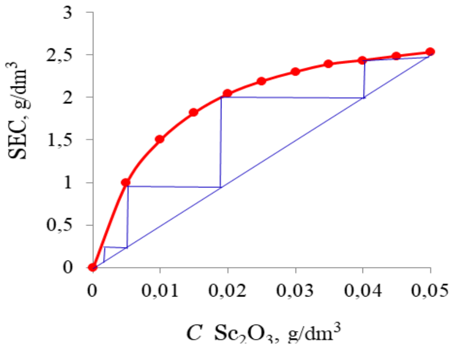

***Figure 7. Scandium sorption isotherm***

The initial section of the sorption isotherm, which reflects the equilibrium state in the ion exchanger–solution system, has a convex shape. This shape indicates a high driving force of the process, determined by a constant decrease in the scandium content in the sorption filtrate and an increase in the scandium concentration gradient in the resin phase.

A straight working line was drawn on the sorption isotherm at an inclined angle to the abscissa, as were horizontal and vertical segments of the lines intersecting the isotherm curve. It was found that to achieve the complete extraction of scandium ions while maximizing the working capacity of the resin, 4 theoretical stages of sorption are required.

The graphically calculated number of theoretical sorption stages is consistent with the number of devices in the technological chain. Using this minimum number can ensure a trace residual content of scandium in the sorption filtrate when sorption is carried out in countercurrent mode due to the constant shift in the equilibrium state of the system established at each sorption stage (i.e., in each device).

By selecting technological conditions for the sorption of scandium in dynamic mode, the optimal permissible linear feed rate of the produced RM repulpation solution with 0.05 g/dm$^3$ $Sc_2O_3$ and a temperature of 60°C through the ion exchanger was determined. At this value, the dynamic exchange capacity (DEC) of the Lewatit TP 260 resin before the first breakthrough of $Sc_2O_3$ reached 0.84 g/dm$^3$, which is almost 17 times higher than the concentration of $Sc_2O_3$ in the initial solution.

The optimal linear feed rate at a volume ratio of produced RM repulpation solution (Vp) to sorbent (Vs) of 40÷50 ensures the extraction of at least 98% of scandium and maximizes the working exchange capacity (WEC) of the resin. The maximum WEC corresponds to the full dynamic exchange capacity (FDEC) within a 6-hour equilibrium sorption process (Figure 8, Table 8).

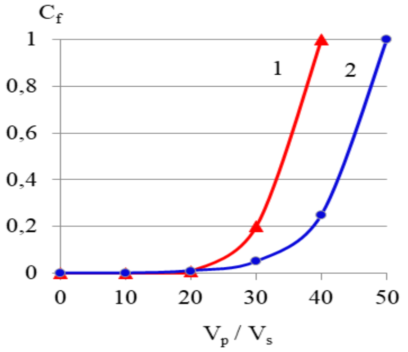

***Figure 8. Scandium sorption output curves. Linear feed rate of produced MRM repulpation solution through the resin, m/h: 1−2.0; 2−2.5; $C_f$−residual content of $Sc_2O_3$ in sorption filtrate, mg/dm$^3$***

***Table 8. Scandium sorption technological conditions and Lewatit TP 260 resin capacity***

| Produced MRM repulpation solution | | | | SEC, g/dm$^3$ | DEC (before break-through), g/dm$^3$ | FDEC, g/dm$^3$ | WEC, g/dm$^3$ | *E*, % |
|---|---|---|---|---|---|---|---|---|
| *WITH* $Sc_2O_3$, g/dm$^3$ | T °C | Linear feed rate, ml/min | Vp/Vs | | | | | |
| 0.05 | 60 | 2.0 ÷ 2.5 | 40 ÷ 50 | 2.53 | 0.84 | 3.33 | 3.17 | 98 |

Judging by the efficiency of sorption extraction, the mechanism of interaction of scandium ions with ampholyte suggests that the only possible or predominant form of the target metal in the produced RM repulpation solution can be expressed by the equivalent exchange reaction of hydroxide ions on the phosphoric group of the resin for monocharged scandium bicarbonate ions:

$$RPO[OH]2 + 2[Sc(CO3)2]^{-} \rightarrow RPO[Sc(CO3)2]2 + 2[OH]^{-} \qquad (1)$$

where R is the high-molecular-weight hydrocarbon radical of the ampholyte matrix and PO[OH]2 is the ampholyte functional phosphoric group in OH- form.

The desorption of scandium from a saturated ion exchanger in static and dynamic modes can be analysed to optimize the temperature, concentration, volume and linear rate of desorbent transmission to ensure efficient scandium elution.

The results in Figure 10 show that scandium is almost completely desorbed, with a rate of up to 99-99.8%, by 300-320 g/dm$^3$ $Na_2CO_3$ solution at a temperature of 40-45°C (Figure 9).

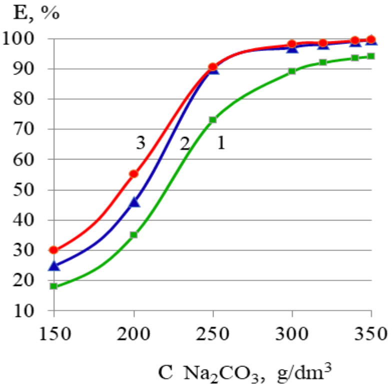

***Figure 9. Desorption of scandium as a function of eluent concentration. Scandium-enriched ampholyte: 1−static mode; 2, 3−dynamic mode***

At a linear desorbent flow rate in the range of 0.25-0.3 m/h in an equal volume ratio with a dynamically saturated sorbent, an eluate with over 3.3 g/dm$^3$ $Sc_2O_3$ was obtained (Figure 10).

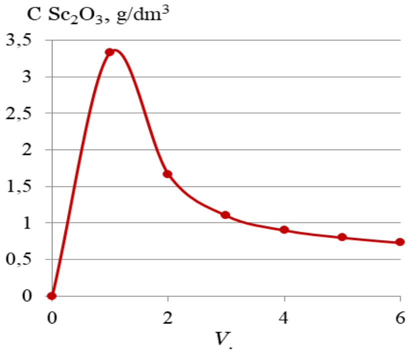

***Figure 10. Dependence of the scandium concentration in the eluate on the volume of the carbonate desorbent solution passed through the saturated ion exchanger***

The ease of elution of scandium during the regeneration of saturated ampholyte with a strong solution of sodium carbonate is explained by the conversion of well-sorbed monocharged scandium bicarbonate anions, which have a high affinity for the phosphoric group of the ion exchanger [40], into a coordinative saturated polycharged tri- and tetracarbonate form not retained by the resin:

$$RPO[Sc(CO_3)_2]_2 + 2[CO_3)]^{2-} \rightarrow 2[Sc(CO_3)_3]^{3-} + RPO \qquad (2)$$

$$RPO[Sc(CO_3)_2]_2 + 4[CO_3)]^{2-} \rightarrow 2[Sc(CO_3)_4]^{5-} + RPO \qquad (3)$$

Thus, by optimization of technologically acceptable conditions the possibility of complex processing of complex in composition multi-turn solutions of carbonization leaching of alumina production with obtaining commercial scandium regenerate, selective sorption concentration by high-capacity Lewatit TP 260 ampholyte and desorption by sodium carbonate solution has been established for the first time.

## 4. Conclusions

The technology of scandium extraction from bauxite processing RM by hydrochemical method was developed, including preliminary treatment of RM with alkaline solution for aluminum extraction, subsequent thermochemical transformation in sodium bicarbonate solution and repulping in solution containing a mixture of sodium carbonate and sodium bicarbonate with scandium extraction. The recovery rate of scandium from RM was 86.5%.

At leaching of RM in alkaline solution with addition of calcium oxide, the contained sodium aluminosilicate undergoes destruction with formation of aluminum hydrogranate and transfer of 80% of aluminum into solution.

During thermochemical treatment in sodium bicarbonate solution, aluminum hydrogranate degrades to form cancrinite and calcite (aragonite).

A phosphorus-containing amphoteric ionite Lewatit TP 260 was selected for selective extraction of scandium from carbonization solution of five-fold repulping with the content of 0.05 g/dm$^3$ $Sc_2O_3$. In static mode it was found that the sorption exchange capacity of the ionite for scandium is 2.53 g/dm$^3$.

The optimal linear feed rate of the produced sludge repulpation solution per unit volume of sorbent at a ratio of 40÷50 extracted at least 98% of scandium and maximized the working exchange capacity of the resin; under these conditions, the dynamic exchange capacity of the resin before the first breakthrough of $Sc_2O_3$ reached 0.84 g/dm$^3$.

The desorption of scandium with 300-320 g/dm$^3$ $Na_2CO_3$ solution at a temperature of 40-45°C from a saturated ion exchanger in static and dynamic modes was analysed to optimize the temperature, concentration, volume and linear velocity of the desorbent, and the corresponding scandium elution efficiency reached 99-99.8%.

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## References

[1] A confidential report prepared by CM Group. (2018). 10-year outlook for the global scandium market to 2028. *Retrieved from:* https://www.cmgroup.net/app/uploads/2019/02/Scandium_22Oct2018_TOC.pdf

[2] Lavrenchuk, V.N., Stryapkov, A.V. & Kokovin, E.N. (2004). Scandium in bauxites and clays. *Kamensk-Uralsky: Kamensk-Uralskaya tipografiya*

[3] Petrakova, O.V., Panov, A.V., Gorbachev, S.N., Klimentenok, G.N., Perestoronin, A.V., Vishnyakov, S.E. & Anashkin, V.S. (2015). Improved efficiency of red mud processing through scandium oxide recovery. *Light Metals*, 93-96. https://doi.org/10.1007/978-3-319-48248-4_17

[4] Yatsenko, S.P., Sabirzyanov, N.A., Pasechnik, L.A., Pyagay, I.N. & Skachkov, V.M. (2012). Hydro chemical reprocessing of alumina industry mud. *Ecology and Industry of Russia*, (11), 10-13. https://doi.org/10.18412/1816-0395-2012-11-10-13

[5] Anashkin, V.S., Bukharov, A.N., Girshin, G.L., Efimov, A.Y. & Sivakov, D.A. (2013). *Method of processing red mud of alumina production*. Patent §RF 2480412, IPC C01F7/02, C22D59/00, B03C1/00, B03B7/00. Patent holder Limited Liability Company Research and Production Company «Skanteh» (RU)

[6] Bogomazov, V.A., Senyuta, A.S. (2015). *Method of acid processing of red mud*. Application No. 2013151918/02. Applicant and patent holder Limited Liability Company «United Company RUSAL Engineering and Technology Center» (RU)

[7] Sokolova, Yu.V., Bogatyreva, E.V. (2016). *Method of scandium extraction from red mud of alumina production.* Patent RF §2581327, IPC C22B59/00, C22B3/08. Patent holder Federal State Autonomous Educational Institution of Higher Education «National Research Technological University «MISIS» (RU)

[8] Anashkin, V.S., Bukharov, A.N., Girshin, G.L., Efimov, A.Yu. & Sivakov, D.A. (2013). *Method of obtaining scandium-containing concentrate from red mud*. Patent §RF 2484164, IPC C22B59/00, C22B3/08, C22B3/24. Patent holder Limited Liability Company «Research and Production Company «Skanteh» (RU)

[9] Rychkov, V.N., Kirillov, S.V., Kirillov, E.V., Bunkov, G.M. et al. (2016). *Method of extraction of scandium and rare-earth elements from red mud*. Russian patent §2603418, IPC C22B59/00, C22B3/24. Patent holder Limited Liability Company RUSAL Engineering and Technology Center (RU)

[10] Stepanov, S.I., Maung Maung, Aung, Boyarintsev, A.V., Gozian, A.V. & Chekmarev, A.M. (2017). On complex processing of red sludge. *Actual issues of production and use of REM and REM-2017: Proceedings of the International Scientific and Practical Conference.* M.: JSC Institute GINTSVETSMET

[11] Yatsenko, S.P., Pyagay, I.N. (2009). Carbonization of red mud with scandium extraction. *Chemical Technology, 10*(4), 231-237

[12] Suss, A.G., Kuznetsova, N.V., Kozyrev, A.V., Gorbachev, S.N. & Panov, A.V. (2017). Features of scandium behavior during soda-bicarbonate leaching of red mud. *IX International Congress «Non-Ferrous Metals and Minerals – 2017»*, Krasnoyarsk. https://doi.org/10.1007/978-3-319-72284-9_22

[13] Kozyrev, A.B., Petrakova, O.V., Gorbachev, S.N., Suss, A.G., Perestoronina, M.A., Vishnyakov, S.E. & Panov, A.V. (2017). Results of pilot tests of technology for scandium oxide production from red mud of UC RUSAL alumina production. *XXV Conference «Siberian Aluminium»*, St. Petersburg

[14] Suss, A., Kuznetsova, N.V., Kozyrev, A., Panov, A. & Gorbachev, S. (2017). Specific Features of Scandium Behavior during Sodium Bicarbonate Digestion of Red Mud. *Proceedings of 35th International ICSOBA Conference*, Hamburg, Germany. https://doi.org/10.1007/978-3-319-72284-9_22

[15] Chibisov, V.N., Egert, A.V. & Komissarova, L.N. (1985). *Method for stripping scandium from alkyl phosphoric acids.* Certificate of authorship USSR §1341914

[16] Akimova, I.D., Babkin, A.S., Ivanov, A.G. & Vorontsova, O.M. (2017). Geotechnology of uranium (Russian experience). M.: KDU

[17] Logvinenko, I.A., Volkov, N.I. et al. (2005). *Underground and heap leaching of uranium, gold and other metals*. M.: Ore and metals, V.1., Uranus

[18] Laverov, N.P., Abdulmanov, I.G., Brovin, K.G. & etc. (1998). *Underground leaching of polyelement ores*. M.: Acad. bugle Sciences

[19] Sokolova, Yu.V., Pirozhenko, K.Yu. (2015). Sorption of scandium from sulfuric acid solutions using industrial grade

phosphorus-containing ion exchangers. *Sorption and chromatographic processes, 15*(4), 563-570

[20] Ochsenkühn-Petropulu, M., Lyberopulu, Th., Ochsenkühn, K.M. et al. (1996). Recovery of lanthanides and yttrium from red mud by selective leaching. *Analytica Chimica Acta, 319*(1-2), 249-254. https://doi.org/10.1016/0003-2670(95)00486-6

[21] Kudryavsky, Yu.P., Anashkin, V.S., Kazantsev, V.P., Trapeznikov, Yu.F., Smirnov, A.L. & Strelkov, V.V. (2003). *Method for processing scandium-containing solutions.* Patent RF §2196184

[22] Ochsenkühn-Petropulu, M., Lyberopulu, Th. & Parissakis, G. (1995). Selective separation and determination of scandium from yttrium and lanthanides in red mud by a combined ion exchange/solvent extraction method. *Analytica Chimica Acta,* (315), 231-237. https://doi.org/10.1016/0003-2670(95)00309-N

[23] PiaePyo, Aung, Troshkina, I.D., Veselova, O.A., Davidovich, Yu.A., Tsyurupa, M.P. & Davankov, V.A. (2017). Sorption of scandium by hypercrosslinked polystyrene impregnates containing organophosphorus acids. *Sorption and chromatographic processes, 17*(1), 45-53

[24] Yatsenko, S.P., Sabirzyanov, N.A., Pasechnik, L.A., Rubinshtein, G.M., Diev, V.N. & Skryabneva, L.M. (2005). *Method for obtaining scandium oxide from red mud.* Patent RU §2247788

[25] Pyagay, I.N., Yatsenko, S.P., Pasechnik, L.A., Ibragimov, T.S., Kim, V.A. & Skryabneva, L.M. (2013). *Method for producing scandium oxide from red mud.* Patent RU §2483131

[26] Pyagai, I.N., Kozhevnikov, V.L., Pasechnik, L.A. & Skachkov, V.M. (2016). Processing of waste sludge from alumina production with the extraction of scandium concentrate. *Zapiski Gornogo instituta, (218),* 225-232

[27] Sabirzyanov, N.A., Yatsenko, S.P. (2006). *Hydrometallurgical methods of complex processing of bauxites.* Yekaterinburg: Ural Branch of the Russian Academy of Sciences

[28] Yatsenko, S.P., Sabirzyanov, N.A., Pasechnik, L.A., Rubinshtein, G.M., Diev, V.N. & Skryabneva, L.M. (2005). *Method for producing scandium oxide from red mud.* Patent RU §2247788

[29] Pyagai, I.N., Yatsenko, S.P. & Pasechnik, L.A. (2013). *Method for producing scandium oxide from red mud.* Patent RU §2483131

[30] Diev, V.N., Sabirzyanov, N.A., Skryabneva, L.M., Yatsenko, S.P., Anashkin, V.S., Aminov, S.N., Zavadsky, K.F., Sysoev, A.V. & Ustich, E.P. (2003). *Method for extracting scandium during processing of bauxites for alumina.* Patent RU §2201988

[31] Anashkin, V.S., Vishnyakov, S.E., Panov, A.V., Petrakova, O.V. & Gorbachev, S.N. (2015). *Method for producing scandium concentrate from red mud.* Patent RU §2562183

[32] Pasechnik, L.A., Pyagai, I.N. & Yatsenko, S.P. (2009). Carbonization technology for extracting scandium from alumina production sludge. *Non-ferrous metallurgy, (1),* 2-46

[33] Ivanov-Emin, B.N., Egorova, A.M., Romanyuk, V.I. & Siforova, E.N. (1970). Formation constants of anionic hydroxocomplexes of some elements of group III of the periodic system. *ZhNKh, (5),* 1224-1228

[34] Cox, M. (2008). *Liquid-Liquid Extraction and Liquid Membranes in the Perspective of the Twenty-First Century. In book: Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials*. CRC Press: Taylor & Francis. https://doi.org/10.1201/9781420014112.ch1

[35] Kirov, S.S., Khairullina, R.T., Alexandrov, P.V., Suss, A.G. (2017). Sedimentation of Sc-concentrate from solutions of carbonate-bicarbonate leaching with lime milk followed by sulfuric acid refining of Ca-Sc-precipitates. *Tsvetnye metally, (1),* 46-52. https://doi.org/10.17580/tsm.2017.01.08

[36] Rychkov, V.N., Kirillov, E.V., Kirillov, S.V., Bunkov, G.M. & Titova, S.M. (2017). Scandium Recovery from Red Mud by Carbonate Assist. *International Conference with Elements of School for Young Scientists on Recycling and Utilization of Technogenic Formation*

[37] Boboev, I.R., Aleksandrov, P.V. & Imideev, V.A. (2017). *Method for extracting scandium from red mud.* Patent RU §2630183

[38] Anashkin, V.S., Kudryavsky, Yu.P., Kazentsev, V.P., Trapeznikov, Yu.F., Yatsenko, S.P. & Diev, V.N. (2001). *Method for extracting scandium from solutions of processing of technogenic raw materials.* Patent RU §2176680

[39] Sokolova, Yu.V., Pirozhenko, K.Yu. (2015). Sorption of scandium from sulfuric acid solutions using industrial grade phosphorus-containing ion exchangers. *Sorption and chromatographic processes, 15*(4), 563-570

[40] Nesterov, Yu.V. (2007). *Ionites and ion exchange. Sorption technology in the extraction of uranium and other metals by underground leaching.* M.: OAO Atomredmetzoloto

# Скандийдің гидротермиялық экстракциясы кезінде қызыл шламның минералды компоненттерін жою

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**Аңдатпа.** Қызыл шламнан бокситтерді гидрохимиялық әдіспен қайта өңдеудің скандийді алу технологиясы әзірленді, ол қызыл шламды алюминийді алу үшін сілтілі ерітіндімен алдын ала өңдеуді, натрий бикарбонаты ерітіндісіндегі термохимиялық трансформацияны және құрамында карбонат пен натрий бикарбонаты қоспасы бар ерітіндідегі репульпацияны және карбонизация ерітіндісінен скандийді сорбциялық алуды қамтиды. Қызыл шламды алдын ала өңдеу 240-260°C температурада CaO:SiO$_2$ = 1:1 қатынасын алу есебінен CaO қосылған сілтілі ерітіндіде жүргізіледі. Өңдеу нәтижесінде алюминийдің 80%-дан астамы ерітіндіге өтеді. Қызыл шламның бастапқы құрамының максималды фазалық өзгеруіне қол жеткізу үшін термохимиялық белсендірудің оңтайлы шарттары анықталды – натрий гидрокарбонатының ерітіндісінде 260°C температурада, ұзақтығы 6 сағат және С:Қ = 10 қатынасында ұстау. Қызыл шламнан скандийді алу құрамында Na$_2$O$_{жалпы}$ = 65 г/дм$^3$ бар NaHCO3/Na2CO3 ~ 2 қатынасында 80°C температурада және 3 сағат ұзақтықта рн≤9 жеткенше көмірқышқыл газымен репульпациялау айналымды ерітіндімен өткізілді. Скандийдің қызыл шламнан алыну деңгейі 86.5% құрады. Технологияның тиімділігі фазалық құрамның екі сатылы трансформациясы қиын бөлігінің жойылуы мен ашылуы, оның қайта кристалдануына байланысты. Стирол мен дивинилбензол сополимерлерін фосфорлау арқылы синтезделген ион алмасу шайырлары скандийдің ең жақсы селективтілігін көрсетті. Құрамында фосфор бар амфотерлі ионит lewatit TP 260 қолданған кезде скандийдің карбонизациялық ерітіндіден алыну деңгейі 98% құрады.

***Негізгі сөздер:*** *қызыл шлам, скандий, сілтілі ерітінді, термохимиялық трансформация, деструкция, репульпация, натрий карбонаты, натрий гидрокарбонаты*.

# Деструкция минеральных компонентов красного шлама при гидротермальном извлечении скандия

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**Аннотация.** Разработана технология извлечения скандия из красного шлама переработки бокситов гидрохимическим методом, включающая предварительную обработку красного шлама щелочным раствором для извлечения алюминия, последующую термохимическую трансформацию в растворе гидрокарбоната натрия и репульпацию в растворе, содержащем смесь карбоната и гидрокарбоната натрия и сорбционное извлечение скандия из карбонизационного раствора. В результате предварительной обработки красного шлама щелочным раствором, с добавлением CaO из расчета получения в пульпе соотношения $CaO:SiO_2 = 1:1$ при температуре 240-260°С получено извлечение алюминия в растворе более 80%. Для повышения степени извлечения скандия проводят термохимическую трансформацию фазового состава красного шлама путем обработки раствором гидрокарбоната натрия при температуре 260°С, продолжительности 6 часов и отношении Ж:Т = 10. Извлечение скандия из красного шлама осуществляют методом репульпации пульпы содо-гидрокарбонатном оборотном раствором, содержащем $Na_2O_{общ} = 65$г/дм$^3$ при соотношении $NaHCO_3/Na_2CO_3 \sim 2$ с газацией раствора углекислым газом до достижения $pH \leq 9$ при температуре 80°С и продолжительности 3 часа. По разработанной технологии степень извлечения скандия из красного шлама составила 86.5%. Эффективность технологии связана с деструкцией минеральных компонентов красного шлама в результате двухстадийной трансформации фазового состава, его перекристаллизацией и освобождением трудновскрываемой части скандия. Проведен анализ существующих технологий сорбционного извлечения скандия из сернокислых растворов выщелачивания, который показал, что наилучшей селективностью по скандию обладают ионообменные смолы, синтезированные фосфорированием сополимеров стирола и дивинилбензола. При использовании фосфорсодержащего амфотерного ионита Lewatit TP 260 степень извлечения скандия из карбонизационного раствора составила 98%.

***Ключевые слова:*** *красный шлам, скандий, щелочной раствор, термохимическая трансформация, деструкция, репульпация, карбонат натрия, гидрокарбонат натрия*.

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