Principles of rational processing of red mud with the use of carboxylic acids

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Due to the known limitations of economic nature, the global production complex continues to focus on the most accessible technologies of alumina production, leading to the accumulation of solid waste (red mud), which has created the well-known problem of their processing, and its scale and importance continue to grow in connection with the steady increase in the world volume of aluminum production and consumption. The priority of rational use of natural resources allows us to speak about the preference of principles of deep and waste-free processing of mineral raw materials, which are fully applicable to the processing of red mud, as accumulated raw materials of technogenic origin. At the same time, the key point of this approach becomes the hierarchical division of components into groups of technological products, taking into account the processes that ensure this selective-group division. In this regard, the use of carboxylic acids is of notable interest, as they have a known selectivity to the main components of red mud, which allows to separate low-soluble components (iron and silicon compounds) from light and rare-earth metals with minimum consumption rates. An experimental study has shown that flow-through leaching of thermochemically prepared red mud using formic acid provides high and acceptable recoveries of sodium, calcium, scandium, and rare earth metals. This makes it affordable to use the cheapest method of apparatus-free leaching when implementing this approach on an industrial scale. Experimentally determined the differences in the sequence of elution of sodium, calcium, aluminum and rare-earth metals formates during flow leaching, which creates favorable conditions for concentrating components and separate processing of sampled solutions. The regime parameters of the process that provides complete precipitation of aluminum, scandium and rare earth metals during the neutralization of formate solution with milk of lime, resulting in the necessary prerequisites for further concentration of rare earth metals to obtain technologically significant product are determined.

Key words: alumina production, red mud, complex processing, selective extraction, light and rare earth metals, carboxylic acids, formates.

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Introduction

Currently, the technological operations of complex bauxite processing, recycling and the use of alumina sludge have come a long historical way, including the development of rational principles for their implementation, but which have notable limitations due to economic, logistical and other reasons [1—11]. At the same time, some of these solutions are quite well known and have been implemented at the factory scale, which allows complete or partial separation of the main components of bauxite (Al_2O_3, Fe_2O_3, SiO) in the reduction electrofusion, selective milling of bauxite and a number of other processes with obtaining the end product [1—8]. Due to the known limitations of economic nature, the global production complex continues to focus on the most accessible technologies of alumina production, leading to the accumulation of solid waste (red mud), which has created the well-known problem of their processing, and its scale and importance continue to grow in connection with the steady increase in the world volume of aluminum production and consumption [12—16]. This allows us to

formulate the basic principles and ways of chemical-metallurgical processing of red mud, including:

— collective use of red mud components in metallurgy of ferrous metals, production of portland cement, geopolymers, composite and other materials [7, 8, 16—28];

— selective extraction and separation of red mud components to produce high value materials and products [29—31];

— deep processing of red mud based on the principles of selective group separation of components to produce ferrous, non-ferrous and rare metals [6, 32—34].

At the state level the priority of rational use of natural resources was approved by the Decree of the President of the Russian Federation in 2011, which allows to speak about preference of principles of deep and waste-free processing of mineral raw materials, which are fully applicable to the use of red mud as accumulated raw materials of anthropogenic origin. At the same time, the key point of this approach becomes the hierarchical division of components into groups of technological products, taking into account the processes that provide such selec-

tive-group separation. This principle is well known in the practice of non-ferrous metals production and as applied to the processing of aluminum-containing raw materials is implemented in technological systems with a high concentration of an alkaline component, which allows to separate the main amount of silicon and iron, coming with the raw material, in the form of low-soluble compounds from aluminum, which has high solubility in alkaline solutions [3, 35, 36]. This makes an alkaline medium poorly suited for the subsequent separation of components in the sludge of alumina production, despite known attempts to use it for the extraction of aluminum and alkali metals [2–5, 10, 14]. Acid technology has a great variety and capabilities, but it also has a number of disadvantages associated with iron separation, acid regeneration, and the complex and multi-threaded nature of the process [6, 30–34]. In this regard, the use of carboxylic acids is of notable interest, as they have a known selectivity to the main components of red mud, which allows to separate low-soluble components (iron and silicon compounds) from light and rare-earth metals with minimum consumption rates [37]. Thus, the actual task of the experimental study is to determine the indicators of separation and isolation into independent products of the key components of red mud when using carboxylic acids, which allows us to outline the contours of the appropriate technological process.

Materials used and research methodology

Earlier studies have shown a high efficiency of formation of formates of light and rare-earth metals at low-temperature (110 °C) treatment of red mud with concentrated formic acid (85%), which determines the possibility of subsequent leaching of soluble formates in a flow-through mode, as the most economical in terms of apparatus design [37]. Because of this, for laboratory realization the method of preliminarily prepared red mud leaching in a column-type unit with upper feed of distilled water and final solution withdrawal in the lower part of the unit was chosen. A sample of red sludge from the Ural aluminum smelter was used as a feedstock with the following composition, %: $Fe_2O_3 - 41.8$; $Al_2O_3 - 14.1$; $CaO - 11.9$; $Na_2O - 5.5$; $\sum(REM)_{ox} - 0.23$, content of rare earth metals in terms of oxides; $Sc_2O_3 - 0.014$. The chemical composition of initial materials and products was determined by inductively coupled plasma atomic emission spectrometry on an Optima 8000 spectrometer, as well as by X-ray fluorescence analysis using a ARL 9800 spectrometer. A Sartorius MA30 analyzer was used to measure humidity, and the acidity of solutions was determined using a HANNA HI 83141 portable pH meter with thermocompensation function. As an instrumental base for hydrometallurgical operations (neutralization, repulsion, dissolution of sediments, etc.) "AutoLAB" of HEL company (Great Britain) reactor systems with the reactor working volume from 0.4 to 2.0 liters were used. Regardless of the reactor volume, they are equipped with mechanical stirring, condensate

return and temperature maintenance with an accuracy of at least ±0.1 degrees, when using an "A350 HE" (Julabo, Germany) oil circulating thermostat. The reactor control system consists of a personal computer, WinISO software and interface cards assembled in a separate module.

Results and discussion

Flow-through leaching of red mud sample after its thermochemical treatment with formic acid was performed in a glass reaction column at room temperature and constant rate of distilled water supply at 0.03 m^3/m^2h. Analysis of the composition of the solution sampled at the bottom of the column allows us to plot the output concentration dependences of dissolution and elution of metals (Figs. 1, 2), as well as to estimate their recovery rates, for example, for scandium and rare-earth metals, as one of the most sought-after and expensive components of red mud, Fig. 3. The calculation of metal recovery was based both on the results of the current solution composition
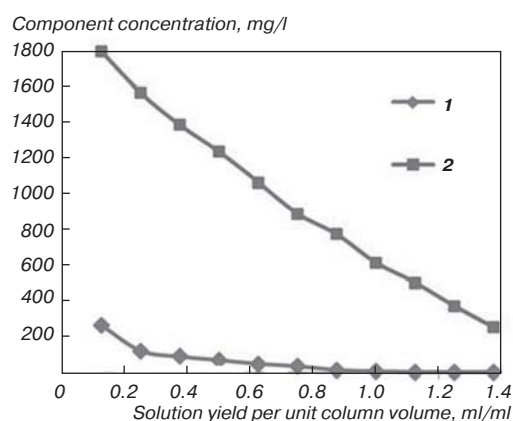

Fig. 1. Scandium and rare-earth metal elution rates during flow-through leaching of thermochemically treated red mud by metal concentrations in the solution according to the legend, mg/l: 1 – Sc_2O_3; 2 – $\sum(REM)_{ox}$
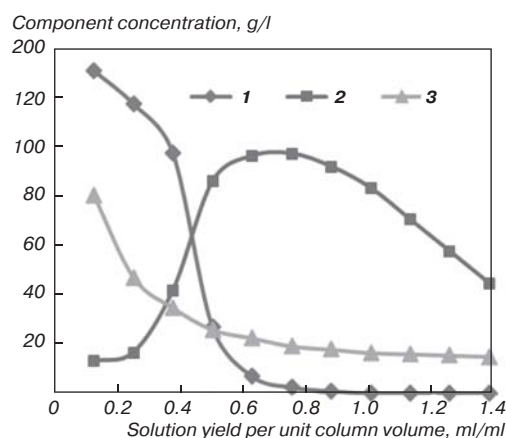

Fig. 2. Elution rates of sodium, calcium and aluminum in terms of oxides during flow-through leaching of red mud, thermochemically treated, by their concentration in the solution according to the legend, g/l: 1 – Na_2O; 2 – CaO; 3 – Al_2O_3
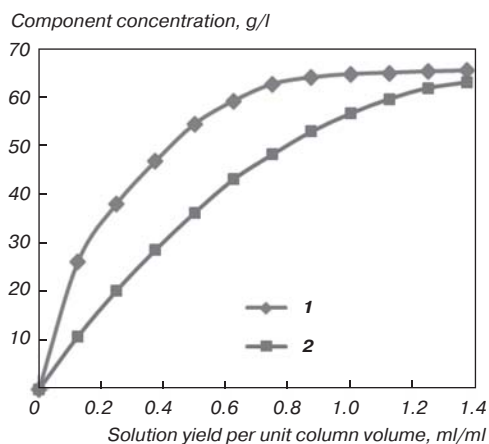
Fig. 3. Elution rates of scandium and rare-earth metals during flow-through leaching of red mud, thermochemically treated, by their recovery in the solution according to the legend, %:
$1 - Sc_2O_3$; $2 - \Sigma(REM)_{ox}$

and volume and on the chemical composition of the red mud sample at the end of the flow-through leaching:

$$\varepsilon_{me,i} = ([Me_{ox}]_i \cdot \Sigma V_i)/(Me_{ox})^{in} \cdot (m_{r.m})^f;$$

$$\varepsilon_{me,f} = [(Me_{ox})^{in} \cdot (m_{r.m})^{in} - (Me_{ox})^f \cdot (m_{r.m})^f]/(Me_{ox})^{in} \cdot (m_{r.m})^{in},$$

$\varepsilon_{Me,i}$ and $\varepsilon_{Me,f}$ — metal recovery into solution of the i-volume and final solid phase recovery, respectively; $[Me_{ox}]_i$ — metal concentration converted to oxide in the i-volume of solution; $(Me_{ox})^{in}$, $(Me_{ox})^f$ — initial and final metal content in terms of metal oxide in the initial and final sample of red mud, respectively; $(m_{r.m})^{in}$, $(m_{r.m})^f$ — initial and final mass of red mud, respectively; ΣV_i — total volume of the formate solution obtained at the moment of indicators measurement.

At the end of the flow-through leaching, the content of the main monitored elements in the spent red mud was, %: $Fe_2O_3 - 62.3$; $Al_2O_3 - 14.9$; $CaO - 3.2$; $Na_2O - 0.3$; $\Sigma(REM)_{ox} - 0.13$; $Sc_2O_3 - 0.0075$. This makes it possible to determine the extraction rates of the corresponding elements in the formate solution, which according to the results of laboratory experiments reach the following values, %: $Sc_2O_3 - 65\%$, $Al_2O_3 - 31.5\%$, $Na_2O - 96.0\%$, $CaO - 82.5\%$ и $\Sigma(REM)_{ox} - 63\%$. At the same time, the difference in kinetics and sequence of leaching of the corresponding components, allows to propose selection of the first 35-40% of the total volume of the product solution, which provides concentration of the most valuable components and convenience of their further processing. Then there is an opportunity to concentrate mainly calcium formate in the subsequent volume of the production solution, which is of interest for its extraction as a final product.

Considering the possibility of hydrolysis of rare earth metal cations and aluminum during the neutralization of the formate solution, the complete-

ness of precipitation of the corresponding hydroxides depending on the acidity of the medium was investigated. The choice of the alkaline component was primarily determined by factors that exclude the transition of additional impurities into sediment or their accumulation in solution, as well as the availability and low cost of the reagent. In this regard, preference was given to calcium hydroxide, which was injected into the solution in the form of milk of lime with a calcium oxide concentration of 200 g/l. Neutralization of the formate solution was carried out at 50 °C to a given pH value at the mechanical agitation mode of the solution followed by an exposure of one hour, which ensures the approach of the system to an equilibrium state with the maximum yield of sediment and the formation of its preferred structure, taking into account recrystallization processes, **Table 1**. These results suggest that the best precipitation conditions for aluminum, scandium and other rare earth metals achieved at pH = 6.5, as further introduction of lime milk does not affect their precipitation, eliminates the formation of soluble calcium formate and leads to an accumulation of calcium hydroxide in the precipitate. The precipitate isolated at pH = 6.5 and filtered on a vacuum filter had the following chemical composition, %: $Sc_2O_3 - 0.16$; $\Sigma(REM)_{ox} - 1.72$; $Al_2O_3 - 54.8$; $CaO - 1.7$; $Na_2O_T - 2.15$; $K_2O <0.15$; $MgO <0.02$; $Fe_2O_3 - 0.01$. The filtrate obtained is an aqueous solution of sodium and calcium formates with relatively low content of impurity components, g/l: $Na_2O - 93.2$; $CaO - 94.0$; $Al_2O_3 - 0.4$; $MgO - 0.11$; $SiO_2 <0.02$; Since the main component of the precipitate is aluminum hydroxide, its separation from rare-earth and alkali earth metals is not difficult and can be realized by selective extraction in a solution of caustic alkali. This process was carried out in a solution with a concentration of caustic in terms of $Na_2O_k = 250$ g/l, which provides solutions close in composition to the factory flows and their involvement in the technological process of alumina production. Taking into account the high chemical activity of freshly precipitated aluminum hydroxide, its dissolution was carried out at atmospheric pressure and temperature of 90 °C, followed by separation of the products by vacuum filtration. The resulting precipitate can be rightfully considered as a concentrate of rare earth metals, due to the following

Table 1

Indicators of precipitation of the components of the formate solution when it is neutralized with milk of lime

No.	pH of the formate solution	Composition of the formate solution in terms of oxides, g/l				
		Sc_2O_3	$\Sigma(REM)_{ox}$	Al_2O_3	CaO	Na_2O_T
1	3.8	0.14	1.5	48.3	40.1	93.2
2	5.0	0.12	1.28	34.2	53.4	85.5
3	5.5	0.02	0.31	3.3	89.5	64.3
4	6.0	<0.01	0.15	0.1	90.8	62.1
5	6.5	<0.01	0.01	<0.1	91.1	61.9
6	7.0	<0.01	0.01	<0.1	93.1	61.7

Red mud

85% HCOOH

Thermal threatment

H$_2$O

Flow-through leaching

Waste red mud

Metallurgy, construction industry

Formate solution

Ca(OH)$_2$

Neutralization

Aluminum hydroxide precipitate (Sc, REM)

NaOH

Ca *and* Na *formate solution*

Dissolution

Polyhydric crystallization

Aluminate solution

Sc, REM *concentrate*

Na *formate solution*

Ca formate precipitate

To *alumina production*

Processing into target products

Chemical production
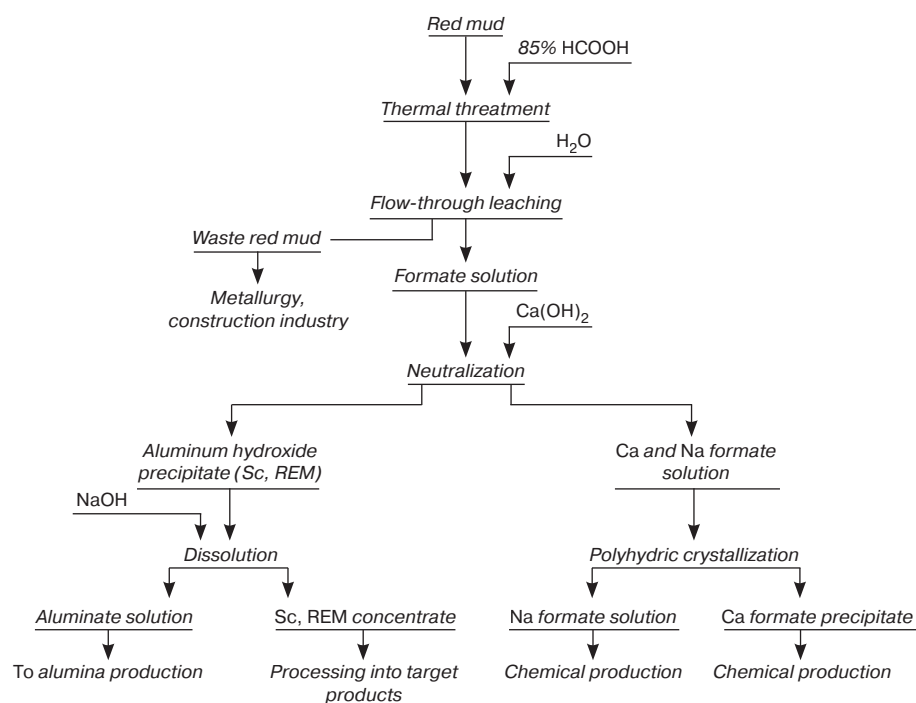
Chemical production

Fig. 4. Basic technological scheme of selective-group processing of red mud of alumina production using formic acid at the stage of thermochemical preparation of raw materials

chemical composition on a wet weight, %: Sc$_2$O$_3$ − 3.5; $\sum$(REM)$_{ox}$ − 38.2; Al$_2$O$_3$ − 7.8; CaO − 1.3; Na$_2$O$_T$ − 2.4.

The solution of sodium and calcium formates formed at the stage of aluminum hydroxide precipitation is a valuable chemical raw material, and the separation of the solution components is provided by differences in their solubility and can be realized in the process of polythermal evaporation. In exploratory studies, it was found that deep calcium formate extraction with limited sodium co-precipitation is possible up to solution concentration at 190 g/l for Na$_2$O content. This allowed to carry out quantitative separation of components to produce calcium formate precipitate containing 38.2 % CaO with Na$_2$O content of 5.15 % in wet sediment. At the same time the residual CaO content in the sodium formate solution is 6.9 g/l. A similar technique is fully applicable to the second part of the formate solution formed during the flow-through leaching of red mud, but requires fine-tuning of the technological regimes of formate precipitation, taking into account the preferential content of calcium formate in this solution.

The considered technological operations of red mud complex processing, of course, need additional clarification and optimization of the regime, which does not prevent the formation of basic technological principles for selective-group processing of red mud using formic acid, and possibly other organic acids, **Fig. 4**.

Conclusion

1. It has been shown that flow-through leaching of pretreated red mud using formic acid provides high and acceptable recovery rates of sodium, calcium, scandium and rare earth metals, which makes it affordable to use the cheapest method of apparatus-free leaching when implementing this approach on an industrial scale.

2. Experimentally determined the differences in the sequence of elution of sodium, calcium, aluminum and rare-earth metals formates during flow leaching, which creates favorable conditions for concentrating components and separate processing of sampled solutions.

3. The regime indicators of the process that provides complete precipitation of aluminum, scandium and rare earth metals during the neutralization of formate solution with milk of lime, resulting in the necessary prerequisites for further concentration of rare earth metals to obtain technologically significant product are determined.

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