Complex alkaline-carbonate-chloride processing of red mud with the recovery of scandium, REEs, titanium, aluminum and iron

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Abstract. At the moment, the world has accumulated about 4 billion tons of red mud (RM) and their number is constantly increasing every year by another 120-150 million tons. These large-tonnage industrial highly alkaline alumina production wastes can be considered as a potential secondary polymetallic raw materials and a source of valuable metals such as iron, aluminum, titanium, zirconium, and especially the most expensive and critically important metals such as scandium, yttrium, lanthanum and lanthanides, which may be contained in some RM in economically significant quantities. The extraction of these metals during the processing of the RM of Russian alumina enterprises may be important for the development of the domestic rare earth elements industry and may allow solving the problem of providing Russia's raw material base in them.

To solve the problem of recycling process of RM, a complex technological approach is needed with the transformation of all components into products used in various types of industry. Only the complex processing of RM can significantly reduce the formation of secondary waste and proceed to the gradual elimination of extensive sludge ponds. Economically justified use of RM is possible only if all valuable components, including iron and aluminum, are extracted from them at the same time. The development of efficient processes for the utilizing or processing of RM is an urgent task and is important for the massively use of alumina production waste, increasing profitability and transition to the concept of zero waste.

The D.I. Mendeleev University of Chemical Technology of Russia carry out systematic research on the development and optimization of key stages of the technology of complex processing of RM, including the processes of extraction of scandium, REEs and other metals from RM in carbonate solutions. An important task for improving the carbonate-alkali technology is to increase the extraction of scandium, REEs, titanium and other valuable components from the RM and to reduce their losses during processing. The solution of this complex technological problem can be achieved only with systematic study and carefully development of the chemical bases of carbonate leaching processes, identification of the main factors affecting the increase in the extraction of scandium and REEs, as well as the elimination of adverse factors leading to loss of valuable metals. It is important to select and optimize the conditions and modes of the used processes, as well as to develop a variant of a hybrid scheme of pyro- and hydrometallurgical processes that allow the extraction of iron and aluminum, as well as to increase the effectiveness and complexity of recycling process of RM.

The main goal of the present work was to increase the extraction of scandium, REEs, aluminum, titanium and zirconium at the initial stages of complex processing of red mud in alkaline, carbonate and carbonate-chloride media, as well as the development of the extraction of scandium, REEs, titanium and zirconium from the slag of reducing iron by melting in acidic media.

The main tasks were: to determine the main factors that affected on the extraction of aluminum, scandium, REEs, titanium and zirconium from RM in alkaline, carbonate and carbonate-chloride media; to study the influence of the main factors on the kinetic characteristics of the leaching processes of aluminum, scandium, REEs, titanium and zirconium from RM with

alkaline, carbonate and carbonate-chloride solutions; to identify and optimize conditions for increasing the extraction of aluminum, scandium, REEs, titanium and zirconium from RM in alkaline, carbonate and carbonate-chloride media; to determine the phase and chemical composition of obtained slag after reducing melting of iron concentrates, obtained during the processing of RM in alkaline-carbonate-chloride media; to determine the main factors of defining the extraction of scandium, REE, titanium and other less-common elements (LCEs) from the slag of reducing iron by melting into solutions of sulfuric, nitric and hydrochloric acids; to develop conditions for acidic processing of the slag of reducing iron by melting with the extraction of scandium, REE, titanium and other LCEs.

Scientific novelty.

1. It has been established that during carbonation of RM with carbon dioxide, proceeds partial or complete destruction of cancrinite and calcium hydrogranate with the formation of nordstrandite and the releasing of isomorphically substituted and chemically bounded of scandium from the solid phase of these minerals into a carbonate solution.

2. The applicability of the Yander equation for the mathematical description of the kinetic curves of carbonate: in two–phase solid-liquid systems, and carbonation: in three–phase solid – liquid - CO_2 gas systems, scandium leaching from RM. The reaction rate constants and apparent activation energies of scandium leaching from RM in the following systems are calculated and tabulated: RM – $Na_2CO_3(NaHCO_3)$ – H_2O and RM – $Na_2CO_3(NaHCO_3)$ – CO_2 – H_2O, including during ultrasonic and mechanical pulp processing.

3. The formation of mixed hetero-poly-nuclear compounds of aluminum with scandium, and by the example of yttrium and ytterbium with REEs, in the processes of polycondensation of their oxycarbonate compounds, forming secondary precipitates during leaching of RM by carbonation, has been proved by the methods of X-ray fluorescence and FTIR spectroscopy.

4. It has been shown that the introduction of chloride anions, or complex-ones such as EDTA and 8-oxyquinoline, into leaching carbonate solutions increases the degree of extraction of scandium, medium-heavy REEs, titanium, aluminum, gallium from RM, and also stabilizes carbonate solutions of these elements, preventing secondary precipitation.

5. By the methods of XRD, SEM-EDS and ICP-MS, it was found that the composition of the slag obtained in the process of reducing of iron by melting from RM includes nepheline $Na_{7.11}(Al_{7.2}Si_{8.8}O_{32})$; hercynite $(Fe_{0.807}Al_{0.193})(Al_{1.807}Fe_{0.193})O_4$; rutile TiO_2; kirshteinite $CaFeSiO_4$; perovskite $CaTiO_3$ and the mineral phase of the composition $Ca_{8.688}Na_{0.625}(Al_6O_{18})$. The isomorphic substitution of aluminum and iron with scandium, gallium and REEs in hercenite, kirshteinite and the phase of the composition $Ca_{8.688}Na_{0.625}(Al_6O_{18})$, and titanium with zirconium and hafnium in rutile and perovskite.

6. The physic-chemical bases of acidic processing of slag obtained in the process of reducing of the iron-containing part by melting of the RM with the extraction of scandium, REEs, aluminum, titanium and other REs have been developed.

The theoretical and practical significance of the work. A method has been developed for carbonation leaching of scandium and REEs from RM, which prevents the formation of secondary precipitation due to hetero-poly-nuclear compounds of scandium and REEs with aluminum, allowing more than 40-45% of scandium and more than 60% of medium-heavy REEs to be extracted into carbonate solutions in one stage. Conditions for increasing the content of scandium in the rough scandium concentrate extracted from carbonate solutions from 1.5–2% to 10-15% have been developed. A process of carbonate-chloride leaching of aluminum, scandium, REEs, titanium and other LCEs from RM has been developed, which makes it possible to increase their extraction into productive solutions by 30-40% and the stability of such solutions for further processing. The stages of acidic processing of the slag of the reducing of the iron-containing part by melting of the RM with the extraction of more than 85% of scandium, up to 70% of the amount of REEs, more than 90% of zirconium, up to 60% of hafnium, more than 65% of gallium and up to 20% of titanium into solutions of sulfuric or hydrochloric acids have been developed. On the basis of the conducted studies, the stage of carbonation leaching of scandium, REEs, titanium and other LCEs from RM has been optimized. Due to optimization, the extraction of scandium was increased by 10-15%, REE by 20-30% in one stage, the scandium content in the rough scandium concentrate by 10-12%, the iron content in the iron-containing part of the RM by 5-10%. The final stages of the complex processing of RM after the reduction melting of the iron-containing concentrate obtained after the extraction of aluminum, scandium, REEs, titanium and other LCEs in alkaline carbonate media, acidic processing of slag with the extraction of scandium, REEs, zirconium, hafnium, gallium and titanium from it have been developed. The total extraction of valuable components from RM according to the proposed complex technology reaches: scandium - more than 90%, yttrium - more than 70%, REEs of the heavy group - 60-95%, REEs of the medium group - 60-75%, REEs of the light group - 35-55%, iron more than 92%, titanium ~50%, zirconium - 80-90%, aluminum ~40%.

Defense Provisions.

1. Results of optimization of conditions and development of methods for intensifying the processes of extraction of scandium, REEs, titanium and aluminum from RM in alkaline, carbonate and carbonate-chloride media in two-phase liquid-solid systems and three-phase liquid-solid-CO_2 gas systems;

2. Results of mathematical processing of kinetic curves of scandium leaching from RM in carbonate, carbonate-bicarbonate, carbonate-chloride media and data on kinetic parameters of the process;

3. Data on the compositions of metallurgical slag of reducing of iron-containing concentrate by melting and hydrolytic polymerization products obtained by carbonization with gas of carbonate-alkaline solutions containing aluminum, scandium, yttrium, and ytterbium;

4. Scientific substantiation and development of an acidic method for the extraction of scandium, REEs and titanium from metallurgical slag of reducing iron concentrates by melting;

5. Modernization of the integrated processing scheme of the RM of Bogoslovsky Aluminum Plant to increase the depth and complexity of processing with the extraction of scandium, REEs, titanium, iron and aluminum.