Kinetics of carbonation of light lanthanides

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Abstract. The article provides the problem of extracting rare earth metals from technogenic raw materials. The analysis showed that there is no effective technology. It is required to consider the thermodynamic and kinetic parameters of the carbonization process. The process of carbonization of sediments of light lanthanides is considered. The work determines the effect of temperature and degree of mixing on the extraction process. The activation energy of the process was calculated. The equation for the dependence of the reaction rate on temperature is given. It was shown that the process of carbonization of light lanthanides proceeds in the diffusion region.

1. Introduction

Rare earth metals represent great potential for the development of modern technologies, particularly for the production of materials for high-tech consumption areas. So, rare earth elements are used for the synthesis of block oxide catalysts for the CO conversion [1], for the production of phosphors on the basis of rare earth metals (REM) [2, 3], for the production of neodymium magnets, which constitute power units of hybrid and electric cars [4], as well as samarium-cobalt magnets are used in the defense and space industries [5].

With an increase in the rate of production, the amount of REM-containing wastes increases significantly, while traditional sources are depleted. Therefore, the most urgent task is to involve technogenic raw materials in the production process as an alternative source of valuable components, thus reducing the amount of emissions of harmful substances, thereby improving the environmental performance.

As a result, methods for processing waste products and industrial waste are being developed. They include extraction [6], sorption and biosorption [7, 8], methods for extracting rare earth metals, as well as methods of acid and bioleaching [9].

In addition to the considered secondary sources of rare earth metals, waste from alumina production - red mud, as well as waste from the production of extraction phosphoric acid - phosphogypsum have a great potential. The rare earth metals present in them are contained in the form of insoluble precipitates in oxide, carbonate, hydroxide and phosphate forms [10].

Red mud (RM) is formed during the processing of bauxite ores by the Bayer method and poses a serious threat to the environment due to the high alkali content, from about 2 to 10 wt. % in terms of Na₂O [11]. Annually, more than 120 million tons of red mud accumulate all over the world resulting from the alumina production. RM is stored in tailings as a solid residue [12].

Existing red mud processing technologies include pyrometallurgical and hydrometallurgical methods. The developed pyrometallurgical technologies, considering methods of low-temperature
reduction at 1050-1200 °C and methods of reduction smelting, make it possible to extract iron from red mud, the content of which varies from 20 to 60 wt. % in terms of Fe₂O₃ [13]. The authors of the work raise the issue of processing red mud, which is so relevant in Russia [14]. They propose a scheme for producing alumina, cast iron and cement. The resulting slags can be used to obtain alumina, titanium, rare earth metals (REM), as well as to obtain building materials [15]. The article [16] describes the main possible ways of using red mud. A detailed technological scheme and marketable products based on red mud were proposed. However, the existing pyrometallurgical technologies do not permit the use of the RM itself due to the high alkali content. As a result, such a process must be accompanied by a stage of alkali removal, which leads to an increase in the cost of processing. There is a developed domestic technology for extracting scandium and other valuable components from red mud, in which the process is intensified by using carbon dioxide [17], however, the efficiency of this process for the extraction of rare earth metals has yet to be assessed.

Phosphogypsum is 80 % CaSO₄·2H₂O waste, which is formed during the production of extraction phosphoric acid from apatite concentrate. All over the world, up to 280 Mt of phosphogypsum are produced annually, most of which is sent to dumps without pretreatment and is not implanted anywhere in the future. This waste is a safe secondary source of lanthanides, since the total radioactive background is not exceeded. The content of rare earth metals in phosphogypsum is in the range of 0.4 - 0.6%. The co-extraction of rare earth metals during the complex processing of phosphogypsum or phosphohydrate, for example, by liquid conversion, is a fundamentally possible and promising method due to the simultaneous formation of several important products: phosphomel, which is widely used in construction and synthesis of slaked lime, and calcium sulfate (sodium, ammonium) which is used in agriculture as a fertilizer [18].

The main method of hydrometallurgical processing of ores is leaching of solid residues of production with mineral acids or alkaline solutions. The use of acids in ores opening is impractical from the point of view of material and energy costs. Other important aspects which have a negative impact on the environment are the formation of toxic gases during leaching and the acidification of the soil.

Since red mud is characterized with high alkali content, and its pH is in the range from 10 to 12.5 pH units [19], it is advisable to consider the method of carbonate-alkaline leaching of insoluble rare earth compounds.

Despite the fact that phosphogypsum has a weak acid medium with pH≈5, the use of the acidic leaching method is ineffective in comparison with the alkaline method, since the process indicators are not high enough, and there is also a dissolution of the present impurities, which complicates the further process of extracting rare earth metals, as well as their separation.

The analysis of thermodynamic data of carbonate-alkaline leaching of rare earth metals from their carbonates and hydroxides showed that this method is promising and is accompanied by rather high process parameters, namely the degree of extraction of rare earth metals into solution [20].

To select the optimal technological parameters of the process, it is necessary to study the kinetics of the process of dissolution of rare-earth metals precipitates in carbonate-alkaline solutions. The study of the dissolution rate, that is, the kinetics of the process, is reduced to determining the rate-limiting step of the process, which can be in the diffusion, mixed or kinetic regions, and determining the order of the reaction.

This study is aimed to determine the rate-controlling step of the carbonation process. This requires the determination of the activation energy. If its values are less than 40 kJ, the process takes place in the diffusion region, if the value of the activation energy is more than 60 kJ, the process is in the kinetic one. It is also necessary to show graphically the effect of the pulp stirring intensity on the degree of extraction of rare earth metals into the solution during leaching of their sediments.

2. Materials and methods
Sediments of rare earth metals belonging to the cerium group (light lanthanides), namely, cerium and neodymium sediments, were selected as objects of study. This choice is due to the high content of these elements in red mud and phosphogypsum. The experiment was carried out for neodymium and cerium
phosphates and carbonates. According to the obtained data of X-ray phase analysis, cerium can be found only in phosphate and carbonate forms, hydroxide form transforms into cerium dioxide.

The study of the kinetics of the carbonization process consisted of the following stages:

1. Carrying out an experiment on the HEL Auto-MATE Reactor System according to the process parameters presented in tables 1 and 2.

To determine the influence of the pulp stirring intensity, the experiment was carried out in accordance with the process parameters indicated in table 1.

### Table 1. Determination of mixing intensity influence.

| Process parameter       | LnPO₄ | Ln₂(CO₃)₃ |
|-------------------------|-------|-----------|
|                         | Nd³⁺  | Ce³⁺      | Nd³⁺  | Ce³⁺      |
| Concentration of CO₃²⁻ in solution, mol/l | 2     | 4         | 1     | 1.5       |
| Mixing intensity, rpm (variable parameter) | From 50 to 1500 | From 50 to 1200 | From 100 to 1000 |
| Temperature, K          | 90    |           | 20    |           |
| Mixing time, min        | 120   | 60        | 10    |           |
| l:s ratio               | 2100  |           | 2100  |           |

The effect of temperature on the degree of extraction of rare earth metals from the insoluble precipitates into solution was determined for different temperatures. The parameters of the experiments are shown in table 2.

### Table 2. Determination of temperature influence.

| Process parameter       | LnPO₄ | Ln₂(CO₃)₃ |
|-------------------------|-------|-----------|
|                         | Nd³⁺  | Ce³⁺      | Nd³⁺  | Ce³⁺      |
| Concentration of CO₃²⁻ in solution, mol/l | 2     | 1         | 1.5   |           |
| Mixing intensity, rpm   | 650   |           | 1000  |           |
| Temperature, K          | 1st temperature: 50 | 1st temperature: 20 |
|                         | 2nd temperature: 70 | 2nd temperature: 30 |
|                         | 3rd temperature: 90 | 3rd temperature: 40 |
| Mixing time, min (variable parameter) | From 60 to 510 | From 30 to 480 | From 2 to 40 |
| l:s ratio               | 2100  |           | 2100  |           |

2. Determination of the content of Ln³⁺ in the solution after leaching by photometric and trilometric methods of analysis in the presence of Arsenazo III indicator;

3. Mathematical processing of the obtained experimental data.

### 3. Results and discussion

To find the Arrhenius constant, it is necessary to obtain experimentally the dependences of the degree of extraction into a solution of Ln³⁺ (E) on time (τ) at different temperatures (50 °C, 70 °C, 90 °C for cerium and neodymium phosphates and 20 °C, 30 °C, 40 °C for cerium and neodymium carbonates) with the subsequent drawing of the tangent to the sections of the curves, where the highest speed of the process is observed (figure 1). Let us consider the determination of the activation energy by the example of cerium carbonate.
Figure 1. Effect of temperature on the degree of extraction of Ce$^{3+}$ ions into solution.

The rate constant is determined by the tangent of the slope of the curves for Ce$_2$(CO$_3$)$_3$: $k_1$=3.125, $k_2$=4.75, $k_3$=8.0. The obtained values of the reaction rate constants are presented in table 3.

| Carbonation rate constants. | Ce carbonate | Nd carbonate | Ce phosphate | Nd phosphate |
|----------------------------|-------------|--------------|--------------|-------------|
| ln(k) | 1/T | ln(k) | 1/T | ln(k) | 1/T | ln(k) | 1/T |
| 1.1394 | 0.0034 | 1.0986 | 0.0034 | 1.3558 | 0.0031 | 2.1861 | 0.0028 |
| 1.5581 | 0.0033 | 1.1787 | 0.0033 | 1.8563 | 0.0029 | 1.2947 | 0.0029 |
| 2.0794 | 0.0032 | 1.3218 | 0.0032 | 2.3979 | 0.0028 | 0.4700 | 0.0031 |

The determination of the apparent activation energy of the carbonization process of Ln$^{3+}$ sediments is carried out by establishing a functional dependence of the form lnk=f(1/T) (figures 2, 3).

Figure 2. Dependence lnk=f(1/T) for carbonates.
Figure 3. Dependence lnk=f(1/T) for phosphates.

The calculation of the apparent activation energy was made according to the formula (1):

\[ E_a = \tan\alpha \cdot R \]  

(1)

The values of the apparent activation energy for the carbonization of neodymium and cerium carbonates were 8.48 kJ/mol and 35.78 kJ/mol, respectively. The values of the apparent activation energy for the carbonization of neodymium and cerium phosphate were 41.74 kJ/mol and 25.35 kJ/mol, respectively.

The effect of stirring intensity (n) on solubility (E) is shown in figure 4.

Figure 4. Effect of stirring on the carbonation process.

It can be seen that up to 600 rpm there is a significant effect of mixing intensity on carbonation. In the area of higher rotation values there is no significant increase in the recovery. Thus, two conclusions can be drawn: 1) in the technology of extracting rare earth metals from technogenic raw materials, the number of revolutions in the reactor should not exceed 600; 2) the obtained values of the activation energy indicate the occurrence of the process of carbonization of carbonates and phosphates of neodymium and cerium at the junction of the diffusion and transition regions.
4. Conclusion

The process of extracting lanthanide ions from carbonates and phosphates is similar. The differences lie in different activation energies. The results achieved are summarized below.

- Light lanthanides begin to dissolve when exposed to several factors: temperature, mixing.
- The more intense the impact, the better the carbonation process is.
- The dissolution of carbonates and phosphates of light lanthanides begins when the energy barrier is reached - the activation energy.
- Phosphates and carbonates of light lanthanides dissolve intensively until a mixing degree of 600 rpm is reached, then an increase in the degree of mixing is irrational.
- The combination of data on the effect of temperature and mixing intensity indicates that the carbonization process takes place in the diffusion and transition regions.

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