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Behaviour of cerium (III) phosphate in a carbonate-alkaline medium

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Abstract

The article investigates the behaviour of rare earth metals in carbonate-alkaline systems. The results of experimental studies on rare earth element extraction from phosphogypsum, a large-tonnage industrial waste forming in production of phosphoric acid are presented. Using the liquid phase leaching method, it was possible to extract more than 53 % of rare earth elements from old phosphogypsum and more than 69 % from fresh phosphogypsum due to solid phase treatment with a 4 mol/l potassium carbonate solution at temperature 90 °C. The behaviour of model cerium (III) phosphate in a carbonate-alkaline medium is characterized: a solubility isotherm is obtained as well as the dependences of the degree of cerium extraction into solution on temperature, carbonate ion concentration, interphase ratio, stirring intensity, and pH. The ability of soluble rare earth element complexes to precipitate over time was established, which was confirmed using cerium and neodymium as an example. Within 240 h after the end of the experiment, approximately 25 % of cerium and 17 % of neodymium were precipitated from the liquid phase. A similar property was recorded in representatives of the light group and was not noted in elements of the heavy group. The ability to self-precipitate in future can serve as a basis for developing an alternative approach to separating rare earth metals into groups after extraction in a carbonate ion medium. Also, based on the analysis of experimental data, the mechanism of cerium (III) phosphate dissolution in a carbonate-alkaline medium was characterized. An assumption was made that rare earth metal phosphates dissolve sequentially passing into an insoluble carbonate and then into a soluble carbonate complex.

Keywords

rare earth metals; lanthanoids; cerium; carbonate leaching; phosphogypsum; complexation; precipitation

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Introduction

Rare earth metals (REM) are a group consisting of 15 lanthanoids, scandium and yttrium [1, 2]. These metals are widely used in catalysis, defence industry, manufacturing of magnets, batteries, superconductors, etc. [3-5]. REM are strategic metals, and a promising trend for their production is processing of REM-containing technogenic raw materials [6, 7].

Natural apatite is used as a raw material for producing phosphoric acid and phosphorus fertilizers, however, during its beneficiation and processing, the waste forms: refinement tailings and phosphogypsum (PG) [8, 9]. REM found in apatite pass into target products and waste as impurities, with 20-30 % of REM migrating into refinement tailings, 10-15 % into H_3PO_4 and 60-70 % into phosphogypsum [10-12]. Thus, PG is a by-product of phosphoric acid production technology and contains approximately 0.5-0.6 % REM (mainly light ones). Considering that more than 6 billion tons of such waste accumulated in the world, it can be regarded as an accessible source of REM [13]. It is noteworthy that the predominant REM phases in GF are monazite (PO_4^{3-}) and gypsum (SO_4^{2-}) containing rare earth elements in the oxidation state +3 [14]. Among the possible phases, phosphate form of REM is less soluble and less extractable than the other ones; therefore, in order to develop the REM extraction technology, it is necessary to proceed from its properties [15].

A method of acid leaching of rare earth elements from phosphogypsum is known [16]. Most recent studies focus on their extraction by treatment with citric or sulfuric acids. This approach allows achieving a high extraction degree (over 90 %), but requires the use of autoclaves, since the process occurs at elevated temperatures (at least 250 °C) and reagent concentrations (2 mol/l H_2SO_4) [17, 18]. In case of using sulfuric acid for leaching REM, the reaction equation has the following form:

$$2\mathrm{REMPO}_{4_{(s)}} + 3\mathrm{H_2SO}_{4_{(l)}} \rightarrow \mathrm{REM_2(SO_4)}_{3_{(l)}} + 2\mathrm{H_3PO}_{4_{(l)}}.$$

Among the disadvantages of this method are its non-environmentally friendly nature (the impact of acid solutions on the environment) and the impossibility to extract calcium as the main component of phosphogypsum (conversion of calcium into a valuable product is excluded) [19, 20].

Another method for extracting REM involves treating phosphates of rare earth elements (III) with alkali [21, 22]:

$$\mathrm{REMPO}_{4_{(s)}} + 3\mathrm{NaOH}_{(l)} \rightarrow \mathrm{REM(OH)}_{3_{(s)}} + \mathrm{Na_3PO}_{4_{(l)}}. \tag{1}$$

It is proposed to use sodium hydroxide solution with concentration 50-70 % at temperature 150 °C [16]. Reaction (1) is accompanied by formation of solid REM (III) hydroxide which is unstable and can transform into REM oxide (especially typical for cerium) [23]. Thus, the separation of solid mixture of products is a task for solving which the additional technological operations are required [24].

The behaviour of lanthanoids in REM (III) – $\mathrm{CO_3^{2-}}$ – H_2O system was investigated [25, 26]. Based on the analysis of published data, carbonate ions can act as a ligand and form soluble complex compounds [27]:

$$\mathrm{REMPO}_{4_{(s)}} + n\mathrm{CO}_{3\,(l)}^{2-} \rightarrow \mathrm{REM(CO_3)}_{n\,(l)}^{3-2n} + \mathrm{PO}_{4\,(l)}^{3-}. \tag{2}$$

The mechanism of reaction (2) is poorly understood. Although n can take values from 1 to 4, carbonate complexes with n = 1; 2 are considered to be more stable [28, 29]. Moreover, due to the hydrolysis process, the forming $\mathrm{OH^-}$ and $\mathrm{HCO_3^-}$ can also be ligands. Approach (2) seems to be most suitable for processing phosphogypsum, since gypsum ($CaSO_4 \cdot nH_2O$) at temperature 50-90 °C for 4-6 h also reacts with carbonate ion to form valuable calcium carbonate [30-32].

Thus, the aim of this study is an attempt to characterize the dissolution mechanism of REE (III) phosphates in a carbonate-alkaline medium using cerium as the most widespread REM in GF and to propose further separation of rare earth elements from carbonate complexes.

Methods

Synthetic cerium (III) phosphate, which was previously obtained by mixing the solutions of cerium nitrate (0.2 mol/l), and phosphoric acid (0.2 mol/l): was used as the starting material containing REM:

$$\mathrm{Ce(NO_3)}_{3_{(l)}} + \mathrm{H_3PO}_{4_{(l)}} \rightarrow \mathrm{CePO}_{4_{(s)}} + 3\mathrm{HNO}_{3_{(l)}}.$$

Cerium (III) phosphate precipitation was carried out at stirring for 30 min with priming. After washing and drying, the average particle size of the precipitate was determined using “Microsizer 201” analyser: from 30 to 60 μm. Phosphates of other rare earth elements were obtained by a similar procedure.

In addition to synthetic lanthanoid precipitates, samples of fresh and old phosphogypsum from the Kingisepp dumps (Russian Federation) were used for the studies. Fresh phosphogypsum was obtained directly from production, and old phosphogypsum was stored at the landfill for at least one year. According to mass spectrometric analysis, the following REM were found in the samples: Ce, Dy, Er, La, Nd, Pr, and Y. The results of analysis are presented in Table 1.

Table 1

Results of mass spectrometric analysis of phosphogypsum samples, wt.%

PG	SO_3	CaO	P_2O_5	K_2O	REM_2O_3	Na_2O	SrO	Fe_2O_3	Al_2O_3	MgO	BaO
Old	54.84	41.39	1.73	0.77	0.32	0.28	0.22	0.19	0.18	0.02	0.01
Fresh	54.40	41.01	2.49	0.80	0.33	0.38	0.20	0.19	0.10	0.07	0.01

All experimental studies presented in the article were conducted using potassium carbonate as a leaching agent.

The solubility of cerium (III) phosphate in carbonate-alkaline systems was studied at temperature 25-90 °C, potassium carbonate concentration 1-4.5 mol/l, interphase ratio 10-3,000 ml/g, and stirring intensity 50-1,200 rpm. Thus, the solubility isotherm of cerium (III) phosphate at 90 °C was experimentally obtained as well as the dependences of the extraction degree into solution on time at different concentrations of carbonate ion, temperatures, L:S ratios, and stirring intensity. Each experiment was performed in the HEL Automate Reactor System at least twice. REM content in solutions was determined by trilonometric titration in the presence of arsenazo (III) indicator. The degree of REM extraction into solution was calculated from the formula

$$E(\text{REM}) = \frac{C(\text{TB})V(\text{TB})V(L)M(\text{REM PO}_4)}{m(\text{REM PO}_4)V(\text{A})} \cdot 100\,\%,$$

where C(TB) is concentration of Trilon B, M; V(TB), volume of Trilon B, ml; $V(L)$, volume of liquid phase after the experiment, l; M(REM PO_4), molar mass of REM phosphate, g/mol; m(REM PO_4), mass of REM phosphate sample weight, g; V(A), volume of aliquot, ml.

Secondary precipitate forming in the course of experiment at interphase ratio 100 ml/g was sent for Raman scattering spectroscopy (Raman spectra) for identification after filtration, washing and drying.

Based on the results presented in Table 1, both PG samples contain 0.3 wt.% REM (in terms of oxides), therefore, the experiments were also performed on concomitant extraction of REM into solution during calcium sulfate conversion. Based on the properties of model REM precipitates, leaching should be carried out at temperature 90 °C, L:S ratio 2,000 ml/g, stirring rate 650 rpm, and potassium carbonate concentration 4 mol/l for three hours. Upon completion of leaching, the solid phase was separated from the solution and, after washing and drying, was sent for mass spectrometric analysis.

Discussion of results

Solubility isotherm of cerium (III) phosphate (Fig.1) was obtained at 90 °C, L:S = 2,100 ml/g, and 650 rpm and is presented as a functional dependence of the extraction degree on the potassium carbonate concentration. Investigations were carried out in a wide range of potassium carbonate concentrations. It was found that in the range 1-2.5 mol/l the solution acquired a yellow colour, and at concentration above 3 mol/l – an orange colour. This fact can indicate a change in the shape of the complex ion from $CeCO_3^+$ to $Ce(CO_3)_2^-$, which is theoretically possible.

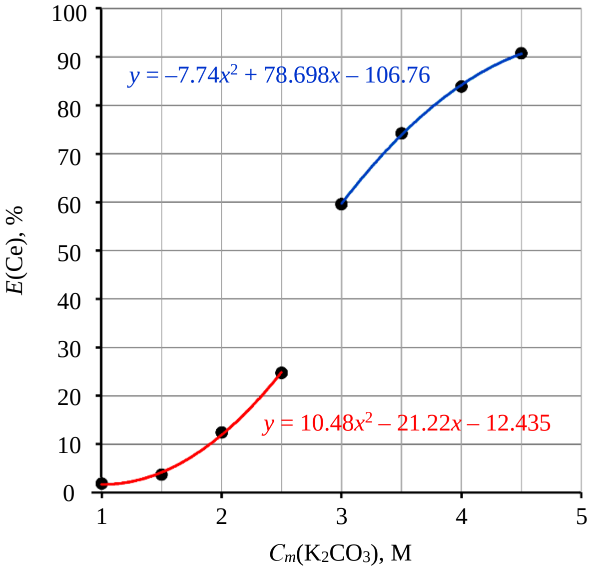

Fig.1. Cerium (III) phosphate solubility isotherm

The obtained isotherm is, probably, characterized by the presence of three intervals: the first one is 1-2.5 mol/l; the second one, 2.5-3 mol/l; and the third one, 3-4.5 mol/l. The first and the third intervals are described in Table 2.

Table 2

Characteristic of cerium (III) phosphate solubility isotherm

C (K_2CO_3), mol/l	Ionic strength, mol/kg	E, %	Equation	Possible soluble form
1.0-2.5	3.0-7.5	1.9-24.7	$y = 10.48x^2 - 21.22x + 12.435$	$CeCO^{+}_{3(l)}$
3.0-4.5	9.0-13.5	59.6-90.8	$y = -7.74x^2 + 78.698x - 106.76$	$Ce(CO_3)^{-}_{2(l)}$

Solubility of phosphates is due to complexation process occurring under the influence of carbonate ion. In case of cerium (III) phosphate, the interphase ratio (Fig.2) and the concentration of carbonate ion (Fig.3) are the factors that have a significant effect on the dissolution process.

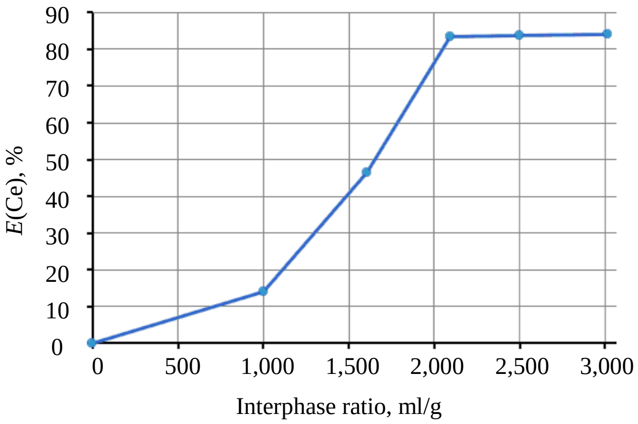

Fig.2. Effect of interphase ratio on the degree of cerium extraction into solution

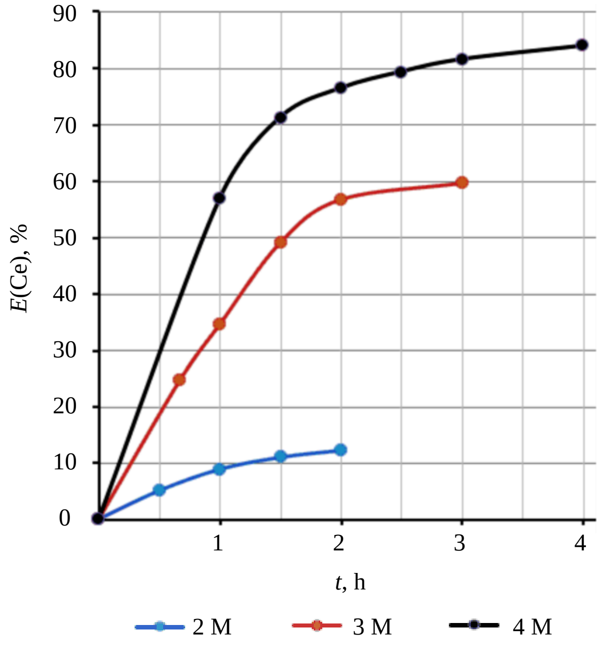

Fig.3. Dependence of degree of cerium extraction into solution on stirring time at different concentrations of carbonate ion

According to the solubility isotherm, the maximum degree of cerium extraction at temperature 90 °C corresponds to potassium carbonate concentration 4.5 M and is 90.8 %. Thus, the following resulting reactions are possible for cerium (III) phosphate:

C (K_2CO_3) = 1-2.5 mol/l; T = 50-90 °C;
L:S = 2,100 ml/g;

$$CePO_{4(s)} + CO^{2-}_{3\ (l)} \rightarrow CeCO^{+}_{3(l)} + PO^{3-}_{4\ (l)};$$

C (K_2CO_3) > 3 mol/l; T = 50-90 °C;
L:S = 2,100 ml/g;

$$CePO_{4(s)} + 2CO^{2-}_{3\ (l)} \rightarrow Ce(CO_3)^{-}_{2(l)} + PO^{3-}_{4\ (l)};$$

C (K_2CO_3) = 2.5-3 mol/l; T = 50-90 °C;
L:S = 2,100 ml/g – both reactions can occur.

The effect of L:S ratio was investigated at 90 °C and potassium carbonate concentration 4 M at stirring for two hours. According to the data obtained, it affects the degree of extraction, so that a significant excess of potassium carbonate solution is necessary to increase the solubility.

An increase in carbonate ion concentration naturally leads to an increasing degree of cerium extraction. A long time is required to achieve the state close to equilibrium, which can point to a possible diffusion limitations (caused, in particular, by pulp viscosity). A growing extraction degree with increasing concentration indirectly indicates the formation of an anionic complex in the form of an ion pair.

It was ascertained that temperature also affects the dissolution process. Figure 4 shows three kinetic curves obtained in the temperature range 50-90 °C at initial potassium carbonate concentration equal to 2 M. It was experimentally determined that at least 4 h of stirring are required to achieve the equilibrium state, and the dependencies have a similar appearance. With growing temperature, the extraction degree and the rate of the process increase from 50 to 90 °C, as indicated by a decrease in time required for attaining the equilibrium state.

The effect of stirring rate on solubility was investigated under the following conditions: 90 °C; 4 M K_2CO_3; L:S = = 2,100 ml/g; *t* = 1 h. From the dependence in Fig.5 it follows that stirring significantly affects solubility to a value 650 rpm. Consequently, the process of cerium (III) phosphate dissolution is limited by diffusion.

Solid phase was analysed by Raman scattering spectroscopy (Fig.6) to determine the nature of precipitate and its components after treatment with potassium carbonate solution. The experiment was conducted for three hours with 4 M K_2CO_3 solution at temperature 90 °C, stirring rate 650 rpm, and L:S ratio 100 ml/g. After leaching, the precipitate was repeatedly washed to remove potassium carbonate. The analysis results were interpreted using the RRUFF database and publications [33, 34].

Spectral peaks of phosphate and carbonate anions are particularly prominent among the others indicating a possibility of cerium (III) carbonate formation as a secondary precipitate. It can be presumed that conversion of cerium phosphate to carbonate is the first stage of the overall dissolution process:

$$2CePO_{4_{(т)}} + 3CO_3^{2-}{}_{(ж)} \rightarrow$$
$$\rightarrow Ce_2(CO_3)_{3_{(т)}} + 2PO_4^{3-}{}_{(ж)}.$$

The results of investigating the kinetics of REM (III) carbonates dissolution process in carbonate-alkaline systems were presented

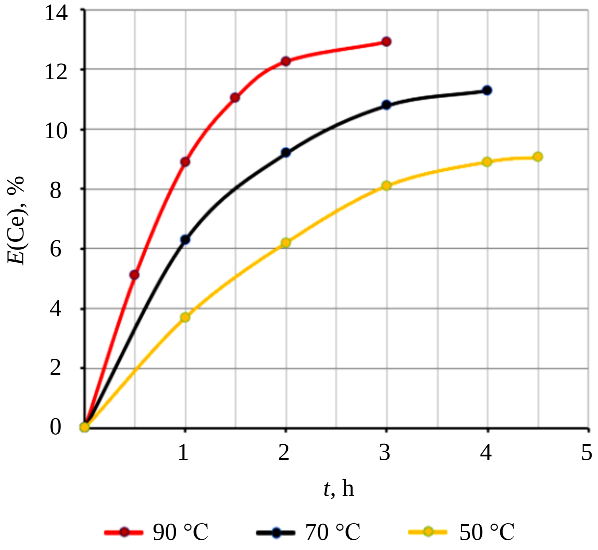

Fig.4. Temperature effect on degree of cerium extraction into solution

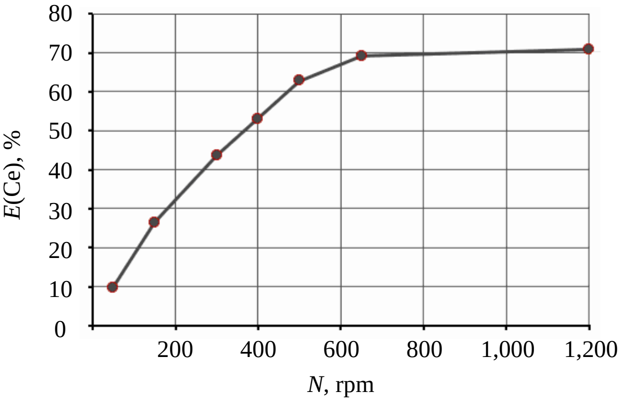

Fig.5. Effect of stirring rate on degree of cerium extraction into solution

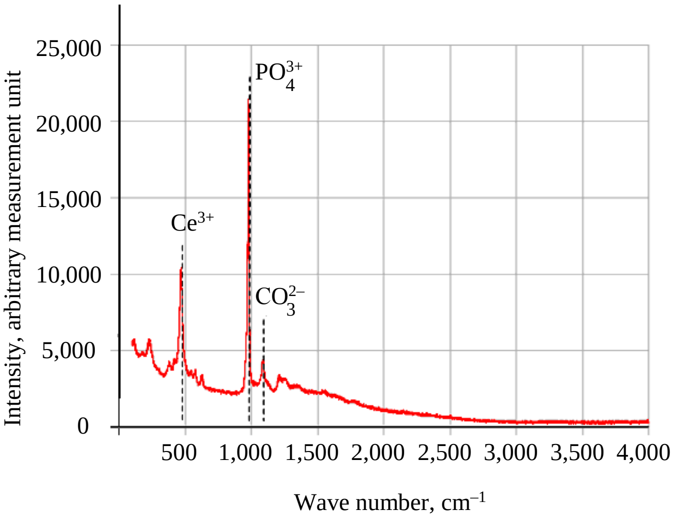

Fig.6. Raman scattering spectroscopy of secondary cerium precipitate

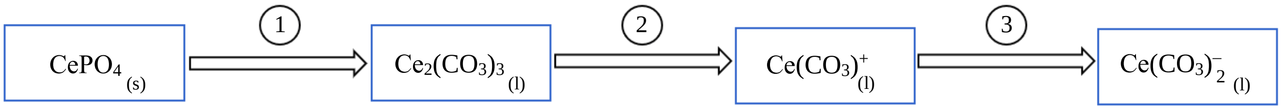

Fig.7. Possible dissolution mechanism of cerium (III) phosphate

in [35]. It is noteworthy that dissolution of carbonates occurs faster than dissolution of phosphates. Therefore, it can be presumed that the process of phosphate reprecipitation is the longest stage. The mechanism of REM phosphates dissolution can be described by three successive stages – reprecipitation and two stages of complexation (Fig.7).

Another factor affecting the degree of cerium extraction into solution is pH level. The effect is similar to that described in article [36]: addition of both acid and alkali to a mixture of cerium (III) phosphate and potassium carbonate solution in both cases leads to a decreasing solubility. Probably, along with carbonate anion, hydroxide anion and bicarbonate anion act as ligands which form less stable complexes. Considering the ability of REM (III) phosphates to transform into REM (III) carbonates a combined addition of OH^- and CO_3^{2-} can cause formation of REM (III) hydroxycarbonates. Thus, to achieve high solubility values, only the addition of carbonate solution without additional reagents is required.

It was found that some solutions containing REM carbonate complexes become turbid over time and form a precipitate. Similar behaviour was recorded for some representatives of light REM, while heavy REM complexes did not form a precipitate. Thus, self-precipitation of REM from lye can be used as a method for further separation of a mixture of rare earth elements into individual components or groups. Among rare earth elements, cerium can be characterized as more capable of self-precipitation of metal from carbonate complexes: 24.7 % of its complexes were destroyed after 240 hours of settling, while in the case of neodymium only 17.1 % precipitated.

Carbonate leaching method was used in processing technogenic waste, in particular phosphogypsum. The investigations indicate a possibility of extracting rare earth metals from PG into solution. The degree of REM extraction from samples of old and fresh phosphogypsum differs. As a result of experiments conducted for three hours at temperature 90 °C and potassium carbonate solution concentration 4 M, it was possible to extract 53.6 % REM from samples of old PG and 69.6 % REM from fresh PG. Difference in extraction degree is caused by differences in morphology of PG powders, as indicated by their difference in colour (a sample of old PG is dark grey, a sample of fresh PG is light grey). Such a difference can be caused by phase changes while in the dump.

Conclusion

A presumptive mechanism of cerium phosphate dissolution in a carbonate-alkaline medium (as one of the most common representatives of REM in phosphogypsum) was determined. Cerium (III) phosphate is successively converted into cerium (III) carbonate and then passes into a soluble carbonate complex. It was ascertained that the degree of REM extraction is affected by many factors: temperature, carbonate ion concentration, L:S ratio, stirring rate, and pH level. Parameters at which the maximum solubility of synthetic cerium phosphate is experimentally achieved were established for the conversion of technogenic phosphogypsum samples.

Thus, the method of carbonate-alkaline conversion can be used for processing phosphogypsum, resulting in formation of calcium carbonate, potassium sulphate, and carbonate complexes of rare earth metals. This approach is complex, unlike the previously developed acid methods, since it is simultaneously possible to extract a significant amount of REM into solution: it was possible to extract 53.6-69.6 % of total REM from different phosphogypsum samples.

A promising trend for further research is separation of rare earth elements in carbonate-alkaline systems, which is technically possible, since some lanthanoids can self-precipitate, in particular, representatives of the light REM group.

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