THERMODYNAMIC JUSTIFICATION OF THE EXTRACTION OF RARE-EARTH METALS DURING THE CARBONATE CONVERSION OF SECONDARY PHOSPHATE RAW MATERIALS

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ABSTRACT

Currently, complex compounds of lanthanide carbonates remain poorly understood, but this information is of no small importance for research in various fields of science. Processing of dumps of phosphogypsum to produce new marketable products and reducing their total amount is achievable by the carbonate conversion method. At the moment, the average level of beneficial use of phosphogypsum - waste processing apatite or phosphorite raw materials is not more than 2.0%. Moreover, the content in phosphogypsum of valuable components, for example, compounds of rare-earth metals, is comparable with the mass fraction of REE oxides in ores of natural deposits. Targeted extraction of rare earth metals from phosphogypsum will not lead to an improvement in the environmental situation, since the volume of the blade and its composition changes little. To reduce the amount of dump phosphogypsum can lead to its processing on a number of other commercial products. Of particular interest are methods for the conversion of phosphogypsum to produce ammonium or sodium sulfate and commercial calcium carbonate. Mathematical modelling showed the fundamental possibility of such an approach with the extraction of REEs in the form of carbonate complexes in solution by the reaction $LnPO_{4(s)} + 2CO_{3(l)}^{2-} \rightarrow Ln(CO_3)_{2(l)}^- + PO_{4(l)}^{3-}$, for which $\Delta_r G$ is from 150 to 300 kJ / mol. The presence of rare-earth metals in the chalk obtained by carbonate processing indicates kinetic difficulties in the dissolution of rare-earth phosphates. It should be noted that for both light lanthanides and heavy lanthanides, the degree of extraction into solution is consistent with the Gibbs energy changes calculated in this work. A lower value of Gibbs energy corresponds to a larger value of the degree of extraction (dependences for Nd and Eu); comparable Gibbs energies for holmium and europium lead to a small difference in the degree of extraction into solution for these elements. For heavy REM, there is a greater, compared with light, extraction into the solution, which can be explained by both thermodynamic and kinetic factors and requires separate experimental and theoretical studies.

Keywords: phosphogypsum, utilization, building materials, agriculture, rare earth elements, conversion, modelling.

INTRODUCTION

Rare earth metals are becoming an increasingly valuable material in world industry. Their use in high-tech industries and their use in the military-industrial complex makes it clear that these elements, both now and in the future, will play an important role in the development of the global economy. All the reserves of rare-earth metals in Russia are concentrated in the deposits of complex ores, where the rare-earth raw materials are associated components (Savelyeva I.L. 2011).

The state balance of reserves takes into account about 17 deposits containing rare earth metals. Geographically accessible deposits located in regions with a well-developed infrastructure are developed to produce phosphoric acid or fertilizers, titanium concentrates, titanium compounds, zirconium (Table-1). Compounds of rare and rare-earth metals either represent by-products, such as during loparite processing, or are not currently produced and accumulate in dumps, for example phosphogypsum obtained from processing apatite or phosphorite raw materials (Kaplunov D.R. *et al* 2011), (Sarychev G.A. 2012), (Evenchika S.D. *et al* 1990).

Table-1. Balance deposits containing rare and rare earth metals.

Deposit	Owner	Total ore reserve	REM content
Tantalum, niobium Production			
Zashikhinsky	CJSC «Technoinvest Alliance»	33,5 million tons	335 thousand tons (1 %)
Katuginskoe	ZAO «Katugino»	200 million tons	665 thousand tons (0,2-0,4%)
Titanium, zirconium production			
Lovozero	LLC «Lovozero GOK»	400 million tons	4376 thousand tons (1,1%)
Lukoyanovskoe	JSC «Atomredmetzoloto»	35 million tons	175 thousand tons (0,5-1%)
Tugan	JSC «TGOK Ilmenite»	216 million tons	900 thousand tons (0,3-0,5%)
Kovdor	JSC «Kovdor GOK»	500 million tons	1,5 million tons (0,3-0,4%)
Phosphoric acid and phosphate fertilizers			
Seligdar		1300 million tons	4410 thousand tons (0,3%)
Khibiny	OJSC «Apatit»	2034 million tons	12,6 million tons (0,3-0,4%)
Oleniy ruchey	CJSC «North-West Phosphorus Company»	271 million tons	0,3-0,4%
Partomchorr	CJSC «North-West Phosphorus Company»	700 million tons	0,3-0,4%
Phosphogyps	Phosphate Fertilizer Companies	> 120 million tons	1,08 million tons (0,1-0,8%)

In case of the processing of technogenic deposits, a number of economic reasons can also be cited: deposits are available because they are located in areas with developed infrastructure, do not require preliminary preparation (crushing, grinding), and they allow to obtain a fairly wide range of useful products. The processing of tailings and dumps in the chemical industry is becoming a paramount task all over the world, since their accumulations have reached certain critical values.

All of the above applies to phosphogypsum - large-capacity waste production of phosphoric acid by the sulfuric acid method. According to the NIUIF in Russia, at least 12 phosphate fertilizer plants operate using sulfuric acid technology. In the dumps of each plant, 10-12 million phosphogypsum accumulated, the amount of which continues to increase annually by 0.81 million tons. A similar situation exists at phosphorus fertilizer plants in Poland, the Republic of South Africa, Ukraine, Belarus, and Uzbekistan (Kulczyckaa J. *et al* 2016), (Mulopo J. *et al* 2012). In addition, phosphogypsum dumps significantly affect the biosphere. So, for example, soils within a radius of 2 km from the dumps of phosphogypsum are contaminated with elements that make up the waste (Szlauer B *et al* 1990).

At present, the global average level of useful use of this industrial waste is not more than 4% and only Japan processes its gypsum waste almost completely, which, however, may be associated with small volumes of generation of this type of waste.

The mass fraction of REM oxides in phosphogypsum is less than in bastnesite ores or in the ores of the Bayan Obo deposit in China (these deposits are fairly unique in terms of REM content), but in principle it is comparable with the mass fraction of REM oxides in not so rich deposits (Table-2)

Table-2. Balance deposits containing rare and rare earth metals.

Raw materials	Mass fraction of Ln_2O_3, %
Phosphogypsum	0,1 - 0,8
Scrub Oaks (USA)	1,4
Mountain Pass (USA)	7 - 10
Bayan Obo (China)	3 - 5,4
Loparite ores of the Kola Peninsula	0,3 - 0,8
Afrikanda, Kola Peninsula	0,4 - 2
Chuktukonskoe deposite	2,0

The general scheme for processing phosphogypsum in order to extract REM from it consists in partial decomposition of phosphogypsum using, most often, diluted sulfuric acid and isolating the sum of REM from the resulting solution by extraction, sorption or precipitation methods (Ibrahim T.M.M. *et al* 2007), (Binnemans K. *et al* 2007), (Lokshin E.P. *et al* 2002), (Kolokolnikov V.A. *et al* 2009), (Hesham M.K. *et al* 2015).

Processing of dumps of phosphogypsum only with the aim of obtaining REM compounds will not lead to an improvement in the environmental situation, since the volume of the blade, and its basic composition, does not change much. A significant decrease in the quantity of

dump phosphogypsum can be caused by its processing into a number of other commercial products.

Of particular interest are methods for the conversion of phosphogypsum to produce ammonium sulphate or sodium. The technological scheme for the conversion of phosphogypsum is quite simple and involves the treatment of phosphogypsum with solutions of sodium or ammonium carbonates to produce synthetic calcium carbonate and magnesium sulphate (ammonium). In this case, rare-earth metals remain in the carbonate residue (Akhmetov A.S. *et* al 1986), (Kosynkin V.D. *et al* 2012), (Lutskiy D.S. *et al* 2018), (Anton A. Pavlovich *et al* 2019), (Sizyakov V.M. *et al* 2012).

The aim of this study is a thermodynamic assessment of the possibility of associated extraction of the amount of rare earth metals during the carbonate conversion of phosphogypsum in the form of soluble carbonate complexes.
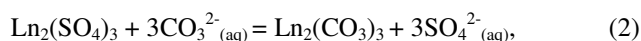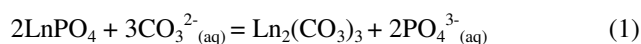
EXPERIMENTAL PART

The Gibbs energies of the formation of lanthanide phosphates, sulphates and carbonates, as well as the Gibbs energies of the formation of anions of acid residues in aqueous solutions were borrowed from literature (Glushko V.P. 2004).

In determining the Gibbs energy of the formation of yttrium and lanthanide carbonate complexes, the data obtained in the analysis and systematization of data (Johannesson K.H. *et al* 1996), (Luo Y.R. et al 2004), (Lee J.H. *et al* 1993), (Cantrell K.J. *et al* 1987) on the equilibrium compositions and thermodynamic characteristics of systems Ln^{3+}_{aq} - $CO_3^{2-}_{(aq)}$ - $[Ln(CO_3)_2]^-_{aq}$ are taken as the basis.

THE RESULTS AND DISCUSSION

The main form of the existence of lanthanides in phosphogypsum is phosphates of trivalent metals. However, given the specifics of obtaining phosgogypsum in the processing of apatite raw materials, their existence in the form of sulphates is also possible (Köhler S.J. *et al* 2005). In the carbonate conversion of phosphogypsum, it can be assumed that reactions of formation of lanthanide carbonates occur and they precipitate with calcium carbonate.

$$2LnPO_4 + 3CO_3^{2-}_{(aq)} = Ln_2(CO_3)_3 + 2PO_4^{3-}_{(aq)} \tag{1}$$

$$Ln_2(SO_4)_3 + 3CO_3^{2-}_{(aq)} = Ln_2(CO_3)_3 + 3SO_4^{2-}_{(aq)}, \tag{2}$$

An estimate of the Gibbs energy change in the reactions of formation of rare-earth carbonates is shown in Figure-1.
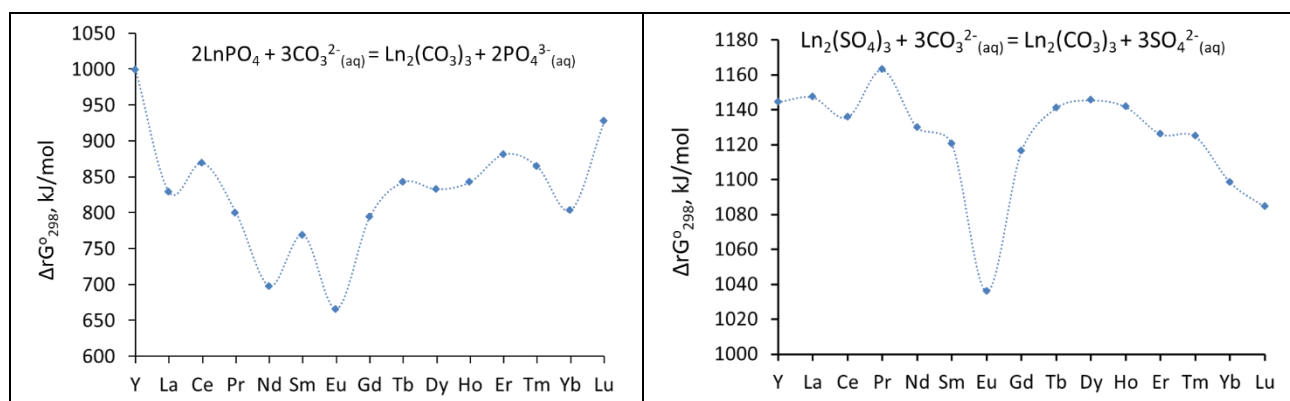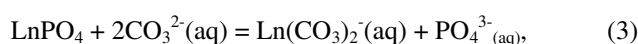

Figure-1. Change in Gibbs energy under the assumption of the formation of rare-earth carbonates from their sulphates and/or phosphates.
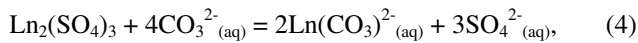
The purely positive value of the Gibbs energy indicates the fundamental impossibility of the formation of rare-earth carbonates from their phosphates and, especially, sulphates from exchange reactions. It is known (Siziakova E.V. *et al* 2017) that scandium is capable of forming soluble carbonate complexes of the composition $[Sc(CO_3)_2]^-$ and $[ScCO_3]^+$, the strength of which is comparable to the strength of similar sulphate complexes. The possibility of dissolution of rare-earth carbonates under the action of an excess of ammonium or potassium carbonate has also been shown (Siziakova E.V. *et al* 2019).

According to Pearson (Pearson R.G. 1988), all the rare-earth elements belong to the class of "hard" acids and form the most durable and stable Ln^{3+} complexes with "hard" bases, which include carbonate, phosphate, and sulphate anions. The formation of complexes of lanthanides with inorganic oxygen-containing anions is facilitated by the formation of high-energy Ln-O bonds. The composition of phosphate complexes is described by the formula $[Ln(H_xPO_4)_y]^{3-y(3-x)}$,, where x and y take the values 1 or 2 (Johannesson K.H. *et al* 1996).

The presence of an ion hydrophosphate in the complex excludes its formation in alkaline media, which are inevitable during the carbonate conversion of phosphogypsum. The possibility of the formation of soluble carbonate complexes of yttrium and lanthanides by reactions:

$$LnPO_4 + 2CO_3^{2-}(aq) = Ln(CO_3)_2^-(aq) + PO_4^{3-}_{(aq)}, \tag{3}$$

$$Ln_2(SO_4)_3 + 4CO_3^{2-}{}_{(aq)} = 2Ln(CO_3)^{2-}{}_{(aq)} + 3SO_4^{2-}{}_{(aq)}, \qquad (4)$$

for which the calculation of the Gibbs energy change should indicate the possibility of dissolution of rare-earth phosphates and / or sulfates with the formation of soluble carbonate complexes.

To calculate the direction of the process, information on the Gibbs energies of the formation of rare-earth carbonate complexes is needed, which are absent in the widespread databases, for example, in (Glushko V.P. 2004).

Gibbs energies of formation of yttrium and lanthanide carbonate complexes were calculated on the basis of published data on the equilibrium constants of reactions (Luo Y.R. *et al* 2004):

$$Ln^{3+}{}_{aq} + nHCO_3^-{}_{aq} = [Ln(CO_3)_n]^{3-2n}{}_{aq} + nH^+{}_{aq}, \text{ where } n = 1 \text{ or } 2. \qquad (5)$$
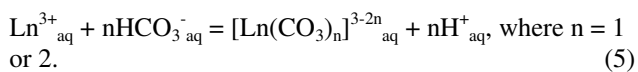
and according to the data on the stability constants of complexes of the composition $[Ln(CO_3)_n]^{3-2n}{}_{aq}$, obtained by studying extraction equilibria with tributyl phosphate in carbonate media and by the results of potentiometric studies (Luo Y.R. *et al* 2004), (Lee J.H. *et al* 1993).

Data on the stability constants from various sources were systematized, reduced to the same conditions (ionic strength of the solution, temperature) and compiled to the average value. The calculation results are shown in Figure-2.
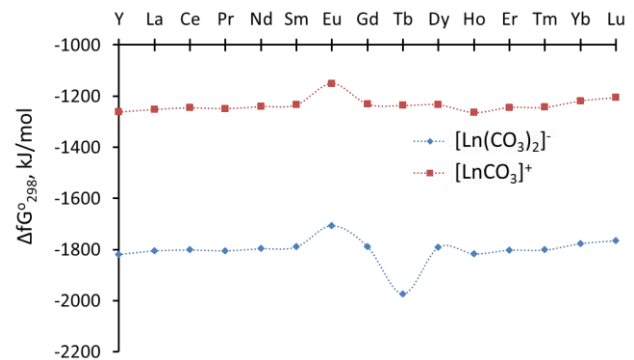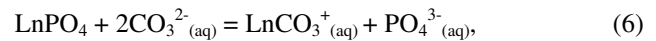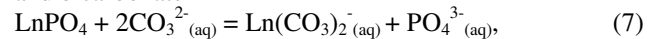

Figure-2. Gibbs energies of formation of yttrium and lanthanide carbonate complexes.

The lower value of the Gibbs energy for the formation of carbonate complexes of the composition $Ln(CO_3)_2^-$ indicates their greater stability compared to monocarbonate complexes.

The results of calculating the change in Gibbs energy under the assumption of the dissolution of rare-earth phosphates with the formation of monocarbonate.

$$LnPO_4 + 2CO_3^{2-}{}_{(aq)} = LnCO_3^+{}_{(aq)} + PO_4^{3-}{}_{(aq)}, \qquad (6)$$

and bicarbonate

$$LnPO_4 + 2CO_3^{2-}{}_{(aq)} = Ln(CO_3)_2^-{}_{(aq)} + PO_4^{3-}{}_{(aq)}, \qquad (7)$$

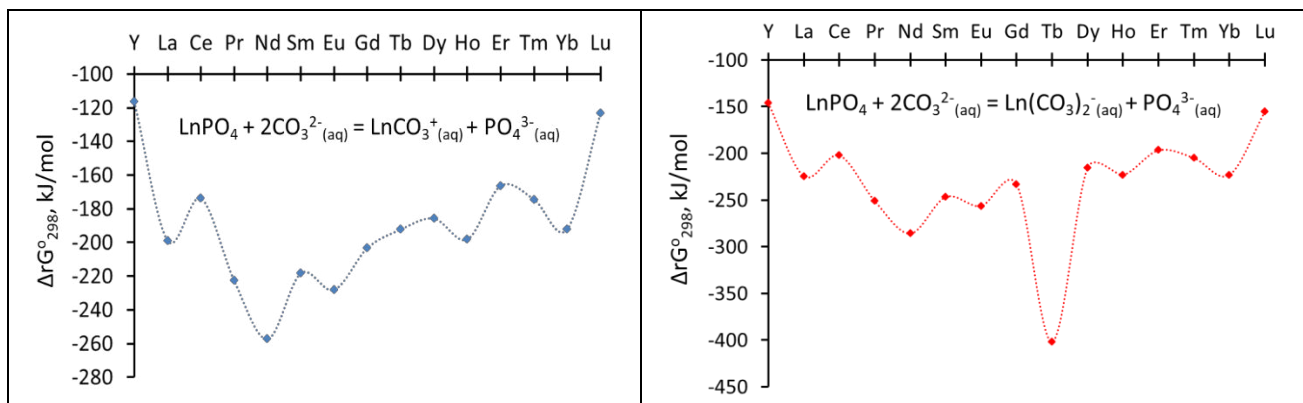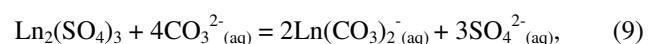complexes of yttrium and lanthanides are shown in Figure-3.

Figure-3. Change in Gibbs energy of reactions of formation of carbonate complexes upon dissolution of lanthanide phosphate in a carbonate medium.

Negative values of Gibbs energy indicate spontaneous dissolution of rare-earth phosphates with the formation of both mono- and bicarbonate complexes. Therefore, there is the possibility of the associated extraction of yttrium of other lanthanides during the carbonate conversion of phosphogypsum. Under the assumption of the existence of lanthanide sulphates in the composition of phosphogypsum, the change in Gibbs energy of dissolution of rare-earth sulphates with the formation of monocarbonate

$$Ln_2(SO_4)_3 + CO_3^{2-}{}_{(aq)} = 2LnCO_3^+{}_{(aq)} + 3SO_4^{2-}{}_{(aq)}, \qquad (8)$$

and bicarbonate

$$Ln_2(SO_4)_3 + 4CO_3^{2-}{}_{(aq)} = 2Ln(CO_3)_2^-{}_{(aq)} + 3SO_4^{2-}{}_{(aq)}, \qquad (9)$$

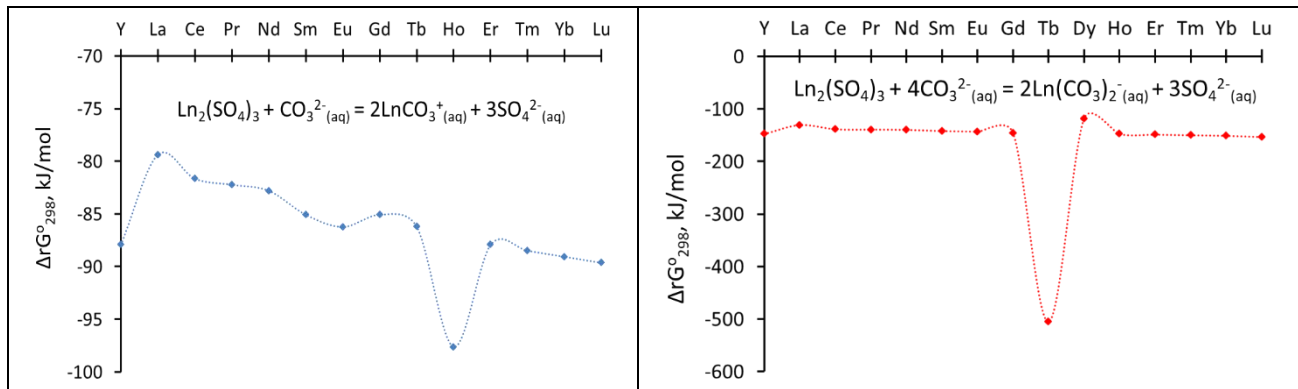complexes of yttrium and lanthanides are shown in Figure-4.

Figure-4. Change in Gibbs energy of reactions of dissolution of lanthanide sulfate in a carbonate medium.

The results of experimental testing of the obtained theoretical results are shown in Figure-5, but which presents the solubility isotherm of lanthanide phosphates, which are classified as light (cerium) rare-earth metals and in the group of heavy (yttrium) elements.
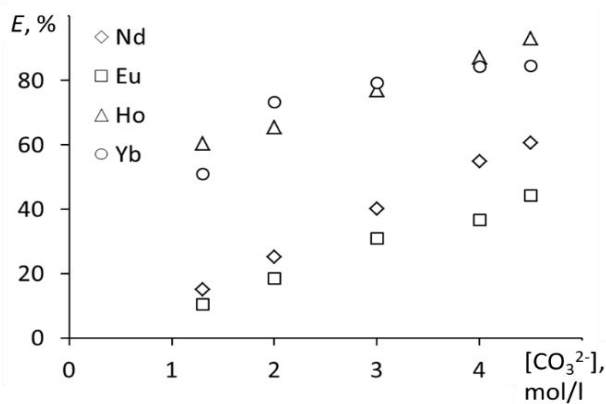

Figure-5. Dependences of the degree of extraction of light (Nd, Eu) and heavy (Ho, Yb) lanthanides into the solution on the carbonate concentration in the solution.

It should be noted that for both light lanthanides and heavy lanthanides, the degree of extraction into solution is consistent with the calculated value of the Gibbs energy change. A lower value of Gibbs energy corresponds to a larger value of the degree of extraction (dependences for Nd and Eu); comparable Gibbs energies for holmium and europium lead to a small difference in the degree of extraction into solution for these elements. For heavy rare-earth metals, there is a greater, compared to light, extraction into solution, which can be explained by both thermodynamic and kinetic factors and requires separate experimental and theoretical studies.

CONCLUSIONS
a) Currently, the average level of beneficial use of phosphogypsum - waste processing apatite or phosphorite raw materials is not more than 2.0%.

b) The content in phosphogypsum of valuable components, for example, compounds of rare-earth metals, is comparable with the mass fraction of REE oxides in ores of natural deposits.

c) The targeted extraction of rare-earth metals from phosphogypsum will not lead to an improvement in the environmental situation, because the volume of the blade and its composition does not change much.

d) To reduce the amount of dump phosphogypsum can lead to its processing on a number of other commercial products. Of particular interest are methods for the conversion of phosphogypsum to produce ammonium or sodium sulphate and technical calcium carbonate

e) Mathematical modelling showed the fundamental possibility of such an approach with the extraction of REEs in the form of carbonate complexes in solution by the reaction $LnPO_{4(s)} + 2CO_3^{2-}_{(l)} \rightarrow Ln(CO_3)_{2(l)}^- + PO_{4(l)}^{3-}$, for which $\Delta_r G$ is from 150 to 300 kJ/mol. The fact that REMs remain during carbonate processing as part of the chalk indicates kinetic difficulties in the dissolution of REM phosphates.

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