



STUDY OF IRON STRIPPING FROM DEHPA SOLUTIONS DURING THE PROCESS OF RARE EARTH METALS EXTRACTION FROM PHOSPHORIC ACID

Cheremisina O. V., Sergeev V. V., Fedorov A. T., Alferova D. A. and Lukyantseva E. S
Saint Petersburg Mining University, Liniya V. O., St. Petersburg, Russia
E-Mail: bers10@bk.ru

ABSTRACT

During the processing of apatite concentrate, the distribution of REM in solutions of phosphoric acid (15-20%) and solid industrial waste - phosphogypsum (85-80%) occurs. Therein the larger half of more valuable heavy subgroup of REM, including Y, Yb, Er and Dy compounds, are dissolved in the phosphoric acid solutions. Complex composition of the apatite concentrate processing products and low concentration of heavy REM subgroup relatively to metal impurities and light REM inhibits REM extraction and separation process, and, probable, is responsible for low extractant capacity for individual compounds of REM. Iron (3+) ions have a significant impact on rare-earth metals extraction process. This impact is caused by the competitive participation of these ions in the extraction process, which, with account of their much higher concentration in EPA solutions, compared with rare-earth ions, leads to decrease in the extractant capacity for REM. Therefore, the study of the purification of the extract from iron ions (3+) is a relevant problem.

Keywords: rare earths, phosphoric acid, D2EHPA, solvent extraction, iron stripping.

INTRODUCTION

Taking into account the resource potential of the Khibiny group of apatite deposits, increasing the depth of processing of these ores for the rare-earth metals (REM) extracting purposes is a strategic task. On the other hand, apatite concentrate is characterized by a low REM content (0, 4-1%), so that the lanthanides contained in the apatite composition were not extracted for the economic reasons. During the processing of apatite concentrate, the distribution of REM in solutions of phosphoric acid (15-20%) and solid industrial waste - phosphogypsum (85-80%) occurs [1]. Therein the larger half of more valuable heavy subgroup of REM, including Y, Yb, Er and Dy compounds, are dissolved in the phosphoric acid solutions. Due to similarity of lanthanides' chemical properties, extraction processes is widely used for individual REM recovery.

Rare earth metals recovery from products of apatite concentrate processing is carried out in strongly acidic solutions, what predetermines the use, mainly, acidic organophosphorus and neutral extractants.

In the acidic organophosphorus systems REM extraction was investigated with using tributyl phosphate (TBP), Cyanex 272, Cyanex 302, Cyanex 923, di-2-ethylhexyl phosphoric acid (D2EHPA), dibutyl phosphoric acid (DBPA) and diamyl phosphoric acid (DAPA)[3, 4-6]. The highest extraction performance was obtained using D2EHPA [3, 7], which dissolved in the organic inert non-polar diluent.

Complex composition of the apatite concentrate processing products and low concentration of heavy REM subgroup relatively to metal impurities (Table-1) and light REM (Table-2) inhibits REM extraction and separation process, and, probable, is responsible for low extractant capacity for individual compounds of REM.

Iron (3+) ions have a significant impact on rare-earth metals extraction process. This impact is caused by the competitive participation of these ions in the extraction process, which, with account of their much higher concentration in EPA solutions, compared with rare-earth ions, leads to decrease in the extractant capacity for REM. Therefore, the study of the purification of the extract from iron ions (3+) is a relevant problem.

Thus, the purification of the D2EHPA solution from iron using various reagents was investigated by Maryam Akhlaghi *et al* in [8]. The authors found that iron extraction improved even at low concentrations of the modifying additives, while the best conditions were achieved when using a buffer solution of oxalic acid and ammonium oxalate as a re-extractant, thus, the degree of iron extraction was 75%. The effect of TBP on the reextraction process was also investigated. The results of this study showed that with an increase in the concentration of tributyl phosphate (from 2% to 6%) in D2EHPA, the degree of iron extraction from the organic phase is increased.

Thus, the objective of this study is to determine the factors affecting the process of extracting iron from REM-loaded extracts based on D2EHPA, as well as identifying ways to increase the capacity of organic extractant for rare-earth metals during the recovery and separation of REM by extraction methods in the course of processing of phosphoric acid production solutions.

MATERIALS AND METHODS

The subjects of the present study were model and industrial solutions of WPA obtained during the treatment of apatite's using the sulfuric acid method by the precipitation of calcium sulfate dihydrate under the conditions of Balkovo branch of AO Apatit. WPA solutions composition is presented in Table-1.



Model test solutions of phosphoric acid was prepared by mixing distilled water, 6M solution of sulfuric acid and concentrated (85%) phosphoric acid. To achieve the

required concentration of rare-earth metals in model solutions, nitrates of the corresponding metals were used (grade “chemically pure”).

Table-1. Composition of WPA solutions (The weight content, %).

Ln	P ₂ O ₅	SO ₃	F	Al ₂ O ₃	CaO	Fe ₂ O ₃	SiO ₂
0,07-0,1	26-28	1,2-1,8	1,4-1,5	0,1-0,4	0,3-0,8	0,3-0,4	0,8-1,1

Table-2. Relative composition of REM oxides (Ln₂O₃) in WPA solutions.

REM oxide	Composition, rel. %	REM oxide	Composition, rel. %	REM oxide	Composition, rel. %
La ₂ O ₃	15,07	Sm ₂ O ₃	3,175	Dy ₂ O ₃	1,92
Ce ₂ O ₃	37,54	Eu ₂ O ₃	0,96	Ho ₂ O ₃	0,335
Pr ₂ O ₃	4,67	Gd ₂ O ₃	3,51	Y ₂ O ₃	12,51
Nd ₂ O ₃	18,335	Tb ₂ O ₃	0,425	Er ₂ O ₃	0,88
				Yb ₂ O ₃	0,51

Di-2-ethylhexylphosphoric “D” grade with a D2EHPA concentration of at least 60% was used as the extractant and “pure” grade kerosene with an at least 95% mass fraction of saturated hydrocarbons was used as an inert diluent.

For stripping, oxalic acid solutions were used, which were obtained by dissolving oxalic acid of the “chemically pure” grade in the appropriate volume of water.

An experimental study of extraction and re-extraction was carried out in two different types of reactors[^] the first reactor- Automated HEL, equipped with a submersible mixer, was used for mixtures with a total volume of up to 1 l; the second, the Parallel Automated HEL, equipped with a magnetic stirrer, was used to simultaneously conduct several experiments on extraction and re-extraction over mixtures of up to 200 ml.

During experiment, all process parameters the temperature, the required duration of contact of the phases, the stirring speed were set and kept constant. The concentration of individual REM determined by the X-ray fluorescent spectrometer PANalytical Epsilon 3.

RESULTS AND DISCUSSIONS

Study of cooperative stripping of iron and erbium from model D2EHPA

To study the effect of oxalic acid concentration on the stripping of rare-earth metals and iron, model solution of the organic phase containing 0.0015 M iron and 0.003 M erbium was used. Stripping was carried out under following conditions: phase ratio of 1: 1, a stirring speed of 450 rpm and a contact time of 15 minutes. The results of the study are presented in Table-3 and in Figure-1.

Table-3. Results of the study of iron and erbium cooperative stripping from model D2EHPA.

C _{H2C2O4} , M	E, %	
	Iron	Erbium
0,125	3,60%	0,00%
0,25	12,33%	0,00%
0,5	29,60%	0,00%
0,75	35,87%	0,00%
1	37,40%	1,68%



Iron and erbium cooperative stripping

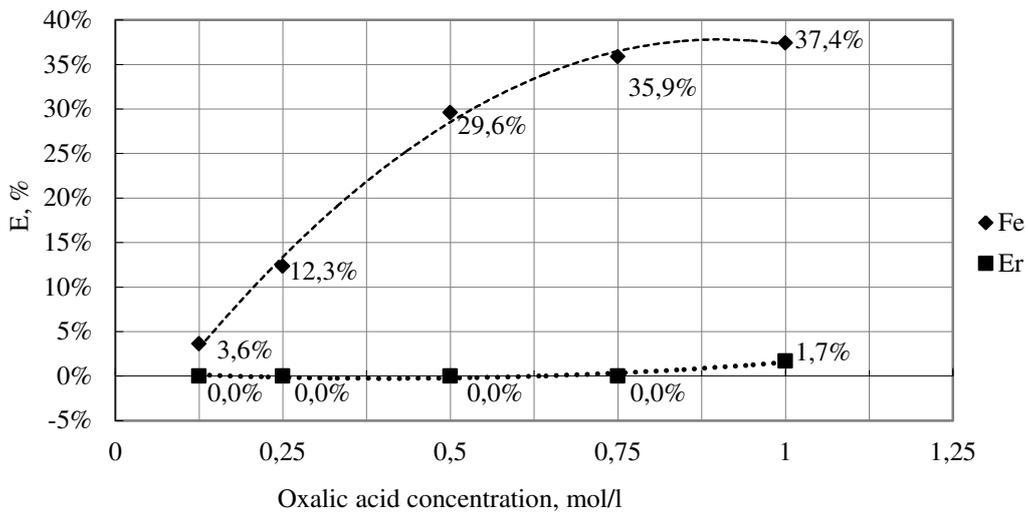


Figure-1. Results of the study of iron and erbium cooperative stripping from model D2EHPA.

The phase ratio effect on the iron stripping was studied using a 1M solution of H₂C₂O₄, a stirring speed of 450 rpm and a contact time of 15 minutes. The results of the study are presented in Table-4 and in Figure-2.

Table-4. Results of the study of phase ratio effect on the iron stripping.

V _{aq} /V _{org}	E, %
4	32,41%
3	47,96%
2	44,23%
1	37,40%
0,5	36,44%
0,25	23,19%

Phase ratio effect on the iron stripping

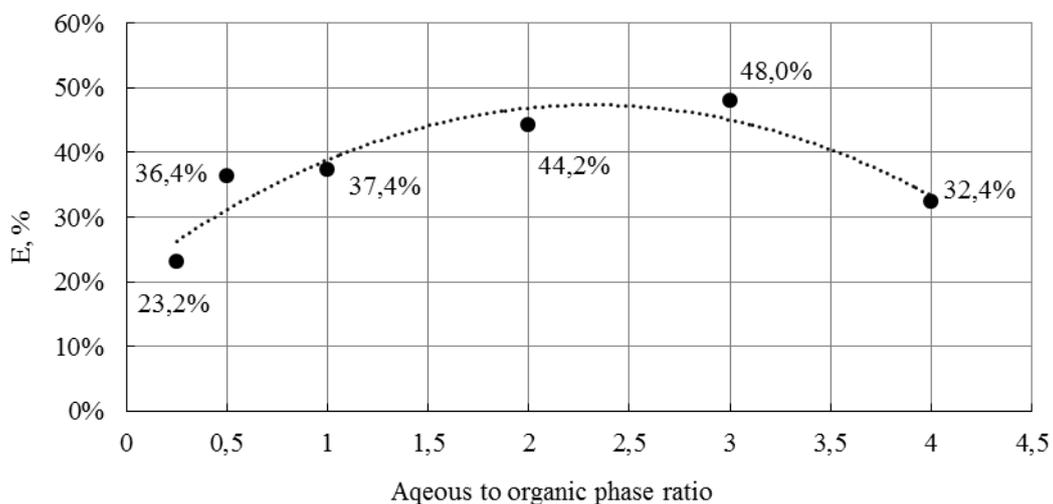


Figure-2. Results of the study of phase ratio effect on the iron stripping.



The stirring speed effect on the iron stripping was studied a 0,5M solution of $H_2C_2O_4$, with a 1:1 phase ratio and a contact time of 10 minutes. The results of the study are presented in Table 5 and in Figure-3. A further increase (more than 500 rpm) in the speed of mixing leads to the formation of a stable emulsion, so the optimum mixing rate is 400-500 rpm.

Table-5. The results of the study of stirring speed influence on the process of iron stripping.

V_{aq}/V_{org}	E, %
200	6,04%
350	14,50%
500	15,99%
650	43,42%

Stirring speed influence on the process of iron stripping

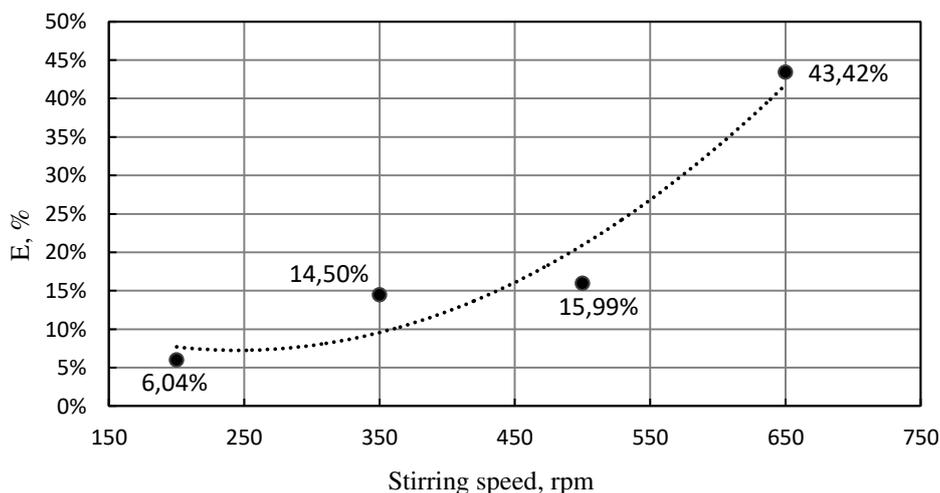


Figure-3. The results of the study of stirring speed influence on the process of iron stripping.

The study of the increasing extractant capacity due to removal of iron impurities

In the course of work on the purification of the extract from iron using oxalic acid, it was suggested that the capacity of the extractant could be increased by adding an additional stage of purification of the organic phase from iron after each stage of extraction.

For the study of changes in the capacity of the extractant for rare-earth metals, an industrial solution of EPA was used as a source of iron and rare-earth metals. An experiment was carried out on the extraction (15 stages) of rare-earth metals from EPA without purification

from iron. As a result of this experiment; a control extract of the composition indicated in Table 6 was obtained. Then, the experiment was repeated with the addition of iron reextraction stage after each extraction stage. Oxalic acid with concentration of 0.5 M was used as a stripping solution. Both processes were carried out at a temperature of 21 °C, at a stirring speed of 400 revolutions per minute for 10 minutes. Extraction was carried out at a volume ratio of the organic to aqueous phase - 1:10, reextraction of iron - 1: 4. The results of the study are presented in Table-6.

Table-6. Study of the extractant capacity.

Stage	Iron stripping	Concentration, mmol/l			
		Fe/Org	Y/Org	Yb/Org	Er/Org
15	Not conducted	8,06	3,62	0,71	0,45
15	After each stage except	6,65	6,57	1,27	1,14
18	After each stage except 18	9,63	7,43	1,57	1,14
15	After each stage + 8 stages of iron stripping	0,33	6,74	1,27	-

As a result, by adding an additional stage of purification of the organic phase from iron after 15 pairs

of stages of extraction and re-extraction, it was possible to increase the capacity of the extractant for yttrium by 1.81



times, for ytterbium by 1.78 times and by erbium by 2.53 times; after 18 pairs - for yttrium by 2.05 times, for ytterbium by 2.2 and for erbium by 2.53 times.

CONCLUSIONS

The obtained results show that with the stripping of iron (3+) with oxalic acid from extracts based on REM-loaded D2EHPA solutions, the rare-earth metals are preserved in the organic phase. This makes it possible to purify the extract from iron during the extraction process, as well as after it, in order to increase the content of rare-earth metals in the extract due to the released fraction of the capacity of the extractant occupied by iron.

The optimal parameters for the extraction of iron, in particular the concentration of oxalic acid and the ratio of the volumes of the aqueous and organic phases, are determined. The obtained dependency of the degree of reextraction from the stirring speed is questionable and requires clarification. Also, it is required to study the effect of temperature on the reextraction process.

The conditions for increasing the capacity of the extractant on the D2EHPA basis on REM (in particular, on Y, Yb and Er) are determined. It was established that the adding an additional step of purification from iron with oxalic acid after each stage of extraction leads to an increase in the capacity of the extractant up to 2.5 times, depending on the quantity steps of extraction and the specific REM.

REFERENCES

- [1] Cheremisina O.V., Sergeev V.V., Chirkst D.E., Litvinova T.E. 2015. Thermodynamic investigation into extraction of cerium (III) by tributyl phosphate from phosphoric acid solutions / Russian Journal of Non-Ferrous Metals. 56(6): 615-621.
- [2] Jorjani E., Shahbazi M. 2016. The production of rare earth elements group via tributyl phosphate extraction and precipitation stripping using oxalic acid / Arabian Journal of Chemistry. 9(Supplement 2): S1532-S1539.
- [3] Cheremisina O.V. 2015. Extraction of rare-earth metals with di-(2-ethylhexyl) phosphoric acid from phosphoric acid solutions / Zapiski Gornogo Instituta. 214: 39-50.
- [4] L. Wang *et al.* 2010. Recovery of rare earths from wet-process phosphoric acid / Hydrometallurgy. 101: 41-47.
- [5] K. S. Dhruva *et al.* 2010. Simultaneous recovery of yttrium and uranium using D2EHPA-TBP and DNPPA-TOPO from phosphoric acid / Biennial Symposium on Emerging Trends in Separation Science and Technology. - Kalpakkam. (4): 583.
- [6] De Carvalho Gomes *et al.* 2017. The Influence of Lactic Acid Concentration on the Separation of Light Rare Earth Elements by Continuous Liquid-Liquid Extraction with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester / Metallurgical and Materials Transactions B. 49(1): 460-465.
- [7] Yun C, Lee C., Lee G., Jo S., Sung S. 2016. Modeling and simulation of multicomponent solvent extraction processes to purify rare earth metals / Hydrometallurgy. 159: 40-45.
- [8] Maryam Akhlaghi, Fereshteh Rashchi. 2010. Ehsan Vahidi Stripping of FE (III) from D2EHPA using different reagents / XXV International Mineral Processing Congress. 1: 460-465.
- [9] Sizyakov V.M., Vlasov A.A., Bazhin V. Yu. 2016. Strategy tasks of the Russian metallurgical complex / Tsvetnye Metally. 2016(1): 32-37.
- [10] Mosisa E., Yu Bazhin V., Savchenkov S. 2016. Review on nano particle reinforced aluminum metal matrix composites / Research Journal of Applied Sciences. 11(5): 188-196.
- [11] Cheremisina O.V., Ponomareva M.A., Chirkst D.E., Lobacheva O.L., Shul'gin I.A. 2014. Sorptive separation of yttrium and cerium on a weakly basic anionite / Russian Journal of Physical Chemistry A. 89(1): 119-124.
- [12] Chirkst D.E., Litvinova T.E., Cheremisina O.V., Ivanov M.V., Mironenkova N.A. 2003. Isotherm of Strontium Sorption on Clay / Russian Journal of Applied Chemistry. 76(5): 727-730.
- [13] Cheremisina O., Lutsky D., Fedorov A. 2017. Comparison of extraction methods for extraction of iron, aluminum, manganese and titanium using carboxylic acids and natural vegetable oils from water-salt systems / International Multidisciplinary Scientific Geo Conference Surveying Geology and Mining Ecology Management, SGEM. 17(11): 803-810.