Determination of the mutual entrainment of the extractant and the aqueous phase in the extraction of rare-earth elements from the technological phosphoric acid solution

D Lutskiy, O Cheremisina, M Ponomareva and A Ignatovich

Department of Physical Chemistry, Saint Petersburg Mining University, 21 line, Saint-Petersburg, 2199106, Russian Federation

Abstract. The data on the distribution of orthophosphoric acid in the system di-(2-ethylhexyl) phosphoric acid (D2EHPA) – H₃PO₄ – H₂O was obtained. The mutual losses of the extractant and the aqueous phase in the extraction of rare-earth elements occur from phosphoric acid using D2EHPA. The quantitative characteristics of redistribution between the aqueous and organic phases was determined. The composition of solvates in extracts was established at different equilibrium concentrations of orthophosphoric acid in the aqueous phase. The obtained data allow us to make changes in the technological process, which will allow us to obtain cleaner REEs after extraction and reduce the concentration of extractant in water effluents.

1. Introduction

The Khibiny group of apatite ores of the Murmansk region contains about 0.4% rare earth metals (REM). The main part of apatite is processed by sulfuric acid extraction to phosphoric acid (EPA), from which phosphate fertilizers are obtained. The method involves treating crushed apatite with sulfuric acid to produce production EPA and phosphogypsum with precipitation of calcium sulfate dihydrate.

During production of EPA, rare-earth metals are converted by 10–15% into a solution of a phosphoric acid extract, the rest of them remain in the solid phase of phosphogypsum. Further processing of phosphogypsum with obtaining soluble salts, for example, nitrate solutions, is a complex multi-process with a significant consumption of reagents. On the other hand, EPA is almost ready-to-use raw materials that do not require pre-treatment (grinding, dissolving, enrichment), which causes its potential economic attractiveness. The total production capacity of only two plants of PhosAgro OJSC for the receipt of EPA is 80 m³·h⁻¹ with a content of rare-earth metals about 0.1% by weight. Thus, the development of an associated method for extracting and separating a group of rare-earth metals from phosphate solutions is an important task.

For the associated extraction of rare-earth metals from strongly acidic solutions, it was decided to use liquid-phase extraction processes.

The advantages of extraction processes include the simplicity of performing multiple repetitions of operations without increasing the consumption of heat or reagents. Extraction processes are extremely effective when either high purification is necessary, or when metals have properties that are so close that a single precipitation or crystallization operation does not give the necessary degree of separation [1-3].
In phosphate systems, the extraction of rare-earth metals was studied using Cyanex 272, Cyanex 302, di-2-ethylhexyl phosphoric (D2EHPA), di-butyl phosphoric (DBPA) and di-amyl phosphoric (DAPA) acids [4]. The highest extraction rates were obtained using D2EHPA [4].

D2EHPA has a higher REE capacity than solid sorbents. The circulation of the extractant in the production cycle occurs much faster than the circulation of the sorbent. Extraction is characterized by high selectivity and purity of separation, the ability to work with small amounts of the substance without carriers, the absence of contamination of the product. Processes that occur only in liquid phases are easier to control and easier to automate [5].

In the extraction technology of rare-earth elements (REE) using di-(2-ethylhexyl) phosphoric acid (D2EHPA) orthophosphoric acid is present in the technological schemes. The extraction of REEs depends on its distribution and the mechanism of extraction in the D2EHPA – H2O heterophase system; for this reason, the study of the extraction process of phosphoric acid by D2EHPA is an important task.

The disadvantages of extraction technologies include the loss of the extractant in the aqueous phase, the formation in some cases of hardly separated emulsions and sometimes the third phases, the danger of fires due to the presence of significant amounts of flammable diluents such as kerosene.

In the process of mixing the organic and aqueous phases, the formation of both direct and inverse emulsions is also possible. During the experiments, qualitative differences were observed in the behavior of the system when a direct and inverse emulsion occurred; in particular, the separation time in the latter case can be more than an order of magnitude greater than the values recorded for the same systems during the formation of a direct emulsion. The type of emulsion obtained may depend on several factors: the order of phase mixing, the presence of an emulsifier, the emulsification technique, the ratio of the volume of liquids. By creating certain conditions in a dispersed system, it is possible to achieve the desired type of emulsion. The most technologically advanced method of controlling the type of emulsion is to vary the volumes of the organic and aqueous phases.

2. Experimental part

Extraction of phosphoric acid D2EHPA was carried out in separating funnels per 100 ml at a temperature of 25,0 ± 0,5 °С. The mixture was mechanically stirred for an hour, and then centrifuged, after which the aqueous and organic phases were separated. The duration of the extraction experiments was selected using the results of the kinetics of extraction processes with the participation of aqueous solutions of rare-earth metals and mixtures of D2EHPA/diluent presented in the works [6-7], as well as on the basis of our own preliminary experiments on the establishment of equilibrium in the systems under study. The concentration of phosphoric acid in the aqueous phase before and after extraction was determined by two independent methods:

- photometric method based on the interaction of phosphate ions in an acidic environment with ammonium molybdate and the formation of phosphorus-molybdenum heteroalicyclic, which is then reduced by ascorbic acid in the presence of antimony-tartaric acid potassium-colored complex or colored in yellow the color of the vanadomolybdophosphate complex formed by phosphate ions in an acidic medium in the presence of vanadium (V) and molybdenum (VI).
- X-ray fluorescence method for the determination of the phosphorus content in the solution using the Epsilon 3 X-ray fluorescence spectrometer of Malvern Panalytical company.

To check the formation of emulsions during the contact of the D2EHPA solution with a volume fraction of 40% in kerosene with a solution of phosphoric acid with a molar concentration of 4.5 mol·dm\(^{-3}\), a series of experiments were carried out without centrifugation. The organic and aqueous phases were separated in a separating funnel for 20 minutes, after which the formation of direct and inverse emulsions was visually estimated from the turbidity of the phases. The phases were further separated and the change in volume of the phases was measured.

The infrared spectra of the extracts were recorded on a Nicolet 6700 Fourier transform infrared spectrometer using a ZnSe crystal using the method of impaired total internal reflection in the interval 4000 – 630 cm\(^{-1}\).
3. Results and discussion
The mutual entrainment of the aqueous and organic phases was studied. The frequency of formation of emulsions is presented in table 1.

**Table 1.** Frequency of formation of emulsions upon contact of D2EHPA solution with a volume fraction of 40% in kerosene with a solution of phosphoric acid with a molar concentration of 4.5 mol‧dm⁻³ at different ratios of phase volumes ("dir. em." - direct emulsion, "rev. em." - reverse emulsion).

| № | V_{org}:V_{aq} | 2:1          | 1:1          | 1:2          | 1:4          |
|---|----------------|--------------|--------------|--------------|--------------|
| 1 | rev. em.       | rev. em.     | dir. em.     | dir. em.     |              |
| 2 | rev. em.       | dir. em.     | rev. em.     | dir. em.     |              |
| 3 | rev. em.       | rev. em.     | dir. em.     | dir. em.     |              |

The type of emulsion formed was determined by the turbidity of one of the phases. In the case of a direct emulsion, the turbidity of the aqueous phase was observed, for an inverse emulsion, the organic phase was observed. An analysis of the statistics obtained allows us to conclude that a substantial predominance of the cases of formation of a direct emulsion in the system under consideration is observed if the volume of the aqueous phase exceeds the volume of the organic phase by no less than 2 times, which can be used to increase the efficiency of the separation process due to an increase in its speed and a decrease in extractant loss.

Experiments were carried out to determine the mutual entrainment of the aqueous phase with the extractant and the extractant with the aqueous phase upon contact of the D2EHPA solution with a volume fraction of 40% in kerosene with a solution of phosphoric acid.

The organic solution released from the emulsion was not transparent, which indicates the formation of a stable microemulsion of the extractant with an aqueous solution. The magnitude of the ash is estimated by the difference in the volume of the phases and is presented in table 2.

**Table 2.** The quantity of aqueous phase losses with the extractant upon contact of D2EHPA with phosphoric acid solutions.

| The volume ratio of organic and aqueous phases, V_{org}:V_{aq} | Aqueous phase losses with the extractant D2EHPA with a volume fraction of 40% in kerosene, % |
|-------------------------------------------------------------|--------------------------------------------------------------------------------------|
|                                                             | Molar concentration of phosphoric acid in the aqueous phase                           |
|                                                             | 8,0 mol‧dm⁻³ | 4,5 mol‧dm⁻³ | 3,0 mol‧dm⁻³ | 1,0 mol‧dm⁻³ |
| 2:1                                                         | 0,4          | 0,3          | 0,2          | 0,2          |
| 1:1                                                         | 0,9          | 0,8          | 0,8          | 0,7          |
| 1:4                                                         | 2,8          | 2,8          | 2,8          | 2,8          |

The aqueous solution after separation was transparent with a volume ratio of organic and aqueous phases, V_{org}:V_{aq} - 1:1 and 2:1. With an increase in the volume of the aqueous phase, turbidity and the formation of a stable microemulsion of the extractant with an aqueous solution were observed.

Confirmation of the transfer of the extractant into the aqueous phase was confirmed by an increase in the optical density of the aqueous phase after extraction compared with the initial samples of phosphoric acid in the near UV region at a wavelength of 340 nm.
Quantitatively, losses of the extractant with the aqueous phase were determined from changes in the volumes of the phases and changes in the concentration of phosphorus in the aqueous and organic phases, recorded by photometric and X-ray fluorescence analysis.

**Table 3.** The quantity of extractant losses with the aqueous phase upon contact of D2EHPA with phosphoric acid solutions.

| Molar concentration of phosphoric acid in the aqueous phase | Extractive agent losses (D2EHPA with a volume fraction of 40 % in kerosene) with a solution of phosphoric acid, % |
|-------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| 8,0 mol·dm$^{-3}$                                          | 4,5 mol·dm$^{-3}$                                                                                 | 3,0 mol·dm$^{-3}$                                                                                 | 1,0 mol·dm$^{-3}$                                                                                 |
| 2:1                                                        | 0,005                                                                                           | 0,005                                                                                           | 0,005                                                                                           | 0,007                                                                                           |
| 1:1                                                        | 0,040                                                                                           | 0,040                                                                                           | 0,040                                                                                           | 0,050                                                                                           |
| 1:4                                                        | 0,140                                                                                           | 0,160                                                                                           | 0,170                                                                                           | 0,220                                                                                           |

The value of the entrainment of the aqueous phase with the extractant at a volume ratio of 2:1 phase is at a technologically acceptable level. However, increasing the phase ratio leads to an undesirable increase in the value of the ash. As possible measures to counteract the ablation can serve as additional settling tanks at the outlet of the organic phase from the extreme stages of the extraction units, separators for separating microemulsions or using highly efficient centrifugal extractors from the point of view of emulsion separation.

Sufficiently high rates of phase separation from the emulsion formed when D2EHPA is mixed with aqueous solutions will allow for a countercurrent process in an extractor of the mixer-settling type. However, it is necessary to take into account the entrainment of the aqueous phase with the organic phase in all operations of processing the initial solution.

IR spectra of the extracts after the interaction of concentrated D2EHPA with solutions of phosphoric acid and the initial extractant are shown in figure 1.

On all spectra (figure 1), there are characteristic for aliphatic compounds bands of stretching and deformation vibrations of the methyl and methylene groups (2950–2855, 1460, 1380 cm$^{-1}$) [8].

![Figure 1. IR spectra of extracts of di- (2-ethylhexyl) phosphoric acid after extraction of orthophosphoric acid: 1 - $V_{org}$:$V_{aq}$ = 1:1, pure $H_3PO_4$; 2 - $V_{org}$:$V_{aq}$ = 1:1, C($H_3PO_4$) = 12,6 M; 3 - $V_{org}$:$V_{aq}$ = 1:1, C($H_3PO_4$) = 8,5 M; 4 - $V_{org}$:$V_{aq}$ = 1:1, C($H_3PO_4$) = 4,25 M; 5 - pure di- (2-ethylhexyl) phosphoric acid. For clarity, spectra are arbitrarily shifted along the vertical axis.](image-url)
The spectra of the extracts slightly differ from the spectra of the initial acid; however, after the contact of the extractant with concentrated phosphoric acid, the characteristic lines at wavelengths of 1113, 1155, 1223 cm\(^{-1}\) shifted to values of 1007, 1156, 1211 cm\(^{-1}\) and became much wider and more intense than the pure D2EHPA, which indicates the chemical interaction of D2EHPA and phosphoric acid by the solvation mechanism with the transfer of the latter into the organic phase.

At all concentrations of \(\text{H}_3\text{PO}_4\), the spectra of all extracts show a complex band with \(\nu_{\text{max}}\) 1000 cm\(^{-1}\), belonging to the deformation oscillation of the P–O–Alk group [9].

Oscillation of the phosphoryl group P = O, having \(\nu_{\text{max}}\) at 1275 cm\(^{-1}\) [8], [9], does not appear as an individual band (figure 2). However, the absorption in this region in the extracts is substantially greater than in the spectra of pure D2EHPA. Apparently, the P = O band is superimposed on the phosphoric acid ester bands [9] (figure 1).

4. Conclusions
The quantitative characteristics of the mutual redistribution of matter between the aqueous and organic phases are determined. The value of the extractant entrainment with the aqueous phase at a volume ratio of 2:1 phase is at a technologically acceptable level and does not exceed 0.007 % by volume. However, increasing the volume of the aqueous phase leads to an undesirable increase in the value of entrainment. Based on the IR spectra of the extracts, it can be concluded that the extraction of phosphoric acid D2EHPA proceeds by the solvation mechanism exclusively in the zone of high concentrations. Thus, we can assume that part of the phosphoric acid enters the organic phase in the form of solvate complexes of the composition, \([\text{S}_m] \cdot \text{nH}_3\text{PO}_4\), where S is the extractant molecule.

Acknowledgements
This work was financially supported by the Russian Science Foundation (project № 19-19-00377 «Technological principles of extraction and selection of strategically significant rare earth elements from products of apatite processing» dated 04.22.2019).

References
[1] Lobacheva O L and Dzhevaga N V 2017 Rare-Earth Elements Recovery on the Example of Europium (III) from lean Technogenic Raw Material. Journal of Ecological Engineering 18 (6) 122-6
[2] Cheremisina O V, Fedorov A T et al 2019 Study of iron stripping from D2EHPA solutions during the process of rare metals extraction from phosphoric acid ARPN Journal of Engineering and Applied Science 8(1) 1591–5
[3] Martynova E S, Bazhin V Yu and Kharazov V G 2019 Increasing the level of control and management of arc steel-smelting furnaces. IOP Conference Series: MSE 537 1-6
[4] Radhika S, Kumar B N et al 2010 Liquid-liquid extraction and separation possibilities of heavy and light rare-earths from phosphoric acid solutions with acidic organophosphorus reagents Separation and Purification Technology 75(3) 295-302
[5] Voropanova L A and Pukova V P 2018 Extraction of copper, cobalt and nickel ions from aqueous solutions by the extractant of the Cyanex 272 Journal of Mining Institute 233 498–505
[6] Danesi P R and Vandegrift G F 1981 Kinetics and mechanism of the interfacial mass transfer of europium (3+) and americium (3+) in the system bis(2-ethylhexyl) phosphate-n-dodecanesodium chloride-hydrochloric acid-water J. Phys. Chem. 85(24) 3646–51
[7] Geist A, Nitsch A W and Kim J 1999 On the kinetics of rare-earth extraction into D2EHPA Chem. Eng. Sci. 54(12) 1903–7
[8] Kazitsyna L A and Kupletskaya N B 1966 Application of UV, IR and NMR spectroscopy in organic chemistry (Moscow: Publishing House "High School")
[9] Bellamy L 1963 Infrared spectra of complex molecules (Moscow: Publishing House of Foreign Literature)