Solvent sublation as a method of lanthanides recovery from weak solutions

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Abstract. Currently, the increase of effectiveness of (lanthanides (REE)) recovery from solutions by hydrometallurgical methods by integrated processing of weak raw materials is topical. The article examines the possibility of REE recovery by the example of solutions, containing ions of rare-earth elements – Erbium, by solvent sublation method (SS). Process regularities in liquid-phase systems were deduced from experiments. A polycomponent system includes \( \text{Er}^{3+} \) and \( \text{NaDS} \) (collector) cations. It was discovered that REE cations recovery from weak aqueous solution during solvent sublation is in direct relationship to medium pH. Here isooctyl alcohol \( \text{C}_8\text{H}_{17} \text{OH} \) acts as "traps" and is called a surfactant.

1. Introduction

Nowadays as technologies are developing rapidly, economy should be profitable to its maximum. Hence, the economic rationality criterion, which is objective and universal in nature, makes it possible to assess the status of organization at the current time and in the future adequately [1, 2]. It is also vital to pay attention to creating a functional and interoperable space that will meet the primary and daily needs in the sphere of construction and architecture [3].

On the whole in the above-mentioned approaches the works on green flotation using biosurfactants for mineral separation and removal techniques of Cr(VI) toxic ion from aqueous solution are appropriate [4, 5]. Of special significance are novel nanocollectors for the removal of nickel ions from synthetic wastewater using ion flotation [6]. The effectiveness of bubble-particle attachment, detachment and collection efficiencies in a mechanical flotation cell depended on speed impellor has been proved. This speed impellor is also effective while conducting sulfidization of silver-polymetallic ore for decreasing loss of silver in mill tailings [7, 8].

Also, Pivovarova pays special attention to developed expert information system when assessing environmental risks for complexly structured and uncertain source data. Meanwhile, author I.V. Goman and I.S. Oblova consider that the concepts of environmental ethics and environmental responsibility have direct relation to the performance of companies [9, 10]. I.V. Goman, E.A. Varlakova consider communication in this respect to be a crucial skill [11].

To decrease losses of target component one improves different processes such as catalytic conversion ones [12, 13], liquid extraction ones [14], mechanism of deformation of various liquids [15], sorption processes [16]. Lightweight materials are valued in terms of ecology not only in the spheres of industry but also in construction [17, 18].

Not only green production but also utilization of different wastes is critical such as utilization of carbide slag and flooded phosphate rock [19, 20]. The article of M.A. Pashkevich and T.A. Petrova has
suggested that recycling based on the roasting of the ore beneficiation tailings depends on the temperature regimes and the exposure time [21].

For enterprises the important step is developing a network of monitoring of air [22, 23], water quality management in the area of mining and processing plants [24].

Authors of this paper concentrated their attention on the study of the process of rare-earth elements’ removal on the example of erbium (III).

It’s common knowledge that REEs have peculiar properties and are used in all industries: in the manufacture of laser materials, mechanical engineering, metallurgy, in aviation and space technology, instrument making, medicine [25, 26]. In heavy industry REE are used for manufacturing special-property alloys to enhance their many useful properties: mechanical, strength, plastic, corrosive.

Individual REE are of extrinsic value. REE individualization and specialization in production and consumption is a steady trend in modern technology. The most stable demand is forecasted for individual lanthanides. The improvement of technology for removal and separation of REE with the receipt of individual components is a modern trend in science and technology [27, 28].

From literature sources it’s known that lanthanum, cerium, and yttrium compounds are necessary for the production of specialty glasses and catalysts, besides such metals as holmium and erbium are actual for nuclear power engineering. The multipurpose use of mineral stock is the most important resource-saving trend today. The increase of recovery effectiveness of similar (in terms of properties) REE becomes an actual problem. Other methods of adsorptive bubble separation don't reach maximum separation coefficients and recovery rates of REE [29, 30]. Therefore, solvent sublation studying is not only of scientific importance but also of commercial value [31, 32].

The article considers a solvent sublation method (a method of surface separation), in which ascending gas bubbles carry over components adsorbed on these bubbles between two immiscible phases. Along with foam separation, solvent sublation is qualified as a adsorptive bubble separation method [33, 34]. This method is characterized by high selectivity and specificity. To recover trace quantities of REE, the minimum amount of expensive surfactants is required. In this method surfactants are carrier agents for the recovered substance (colligant) [35].

2. Erbium recovery during solvent sublation

Solvent sublation took place in a laboratory column. Concentration of metal ions in standard test solutions of chemically pure erbium nitrates was $1 \cdot 10^{-3}$ mol·l$^{-1}$. Solution volume was 0.1 l. Sodium dodecyl sulphate with a general formula of $C_{12}H_{25}OSO_3Na$ (NaDS) and concentration of $3 \cdot 10^{-3}$ M (DS$^-$ - dodecyl sulphate ion) was used as a surfactant [36, 37].

The $\text{Er}^{3+}$ ions content in organic phase was calculated from concentration difference in original and equilibrium aqueous phases:

$$C_{\text{org}} = (C_{\text{orig}} - C_{\text{aq}})$$

where $C_{\text{orig}}$ and $C_{\text{aq}}$ are the molarity of metal ions in organic and aqueous (equilibrium) phases respectively, mol·l$^{-1}$; $C_{\text{orig}}$ is the initial molarity of erbium ions in the aqueous phase, mol·l$^{-1}$.

The $\text{Er}^{3+}$ cation molarity was determined by a photometric method with an arsenazo III indicator [38], dodecyl sulphate ion concentration – by potentiometric titration with cetyltrimethylammonium chloride solution with $2 \cdot 10^{-3}$ M concentration and ion-selective electrode, containing silver chloride (ЭВЛ-1МЗ), immersed in NaDS and NaCl solutions, and a DS$^-$ ion sensitive membrane.

The membrane was made in the ionometry laboratory of the SPbMU chemistry department [39, 40]. Solution pH varied from 4.85 to 9.05 and fixed by nitric acid solution or sodium hydroxide.

Table 1 shows solution concentration values as a function of pH in nitrate mediums.

| t, min. | C, M           |
|--------|----------------|
| pH=4.85 | pH=6.20       |
| pH=7.05 | pH=8.0        |
| pH=9.05 |                |

Table 1. Erbium (III) cations molarity in a liquid-phase system.
Figure 1 shows experimental results as a function of solvent sublation process time.

Table 2 shows experimental results for the removal process efficiency and distribution coefficients of Er$^{3+}$ during solvent sublation.

Distribution coefficient ($K_p$) was determined depending on the relation between the concentration of Er$^{3+}$ in organic and aqueous equilibrium phases:

$$K_p = \frac{[Ln^{3+}]_{org}}{[Ln^{3+}]_{aq}}$$

where $[Ln^{3+}]$ is the REE ions (Er$^{3+}$) molarity in organic and aqueous phases, respectively. $K_p$ in this case the value depends on distribution conditions and does not depend on the volume of phases.

Table 2. Erbium (III) recovery ratio $\alpha$ and distribution coefficient $K_p$, $t = 120$ minutes and $C_0 = 1 \cdot 10^{-3}$ mol/l (initial molarity).

| pH   | C org$\cdot 10^{-3}$ | Kp   | $\alpha$, % |
|------|----------------------|------|-------------|
| 4.85 | 6.9                  | 9.3  | 18.9        |
| 6.2  | 5.0                  | 6.2  | 13.5        |
| 7.05 | 40.2                 | 1761.1 | 97.8    |
| 8.00 | 40.4                 | 2961.8 | 98.7    |
| 9.05 | 37.0                 | 377.1 | 90.4     |

$C_0$ – initial (input) molarity of Erbium (III) cations.
Er$^{3+}$ cations recovery ratio is determined by using the formula (3):

$$\alpha = \frac{C_0 - C_{aq(\text{equilibrium})}}{C_0} \cdot 100\% \quad (3)$$

For erbium (III) cations the maximum of $K_p = 2961.8$ is observed at pH 8.0, over pH range of 4.0-6.0 not exceeding 9.3. pH of beginning of the removal is 6.2. At pH > 6.2 the distribution coefficient increases up to the value exceeding 1760 at pH 7.05. At pH from 7.05 to 8.0 $K_p$ increases upwards in nitrate medium and reaches 2961.8. During erbium (III) cations solvent sublation in acid medium the recovery practically doesn’t take place. The maximum value of distribution coefficient is reached at pH 8.0.

From table 2 data it appears that the recovery ($\alpha$, %) of Er$^{3+}$ cations is most effective at medium pH 8.0. Besides, in practice, the dependence of recovery ratio in the studied process is similar to the behaviour of the dependence of recovery ratio in solutions, containing erbium cations and sodium dodecyl sulphate in solvent sublation.

3. Conclusion
As a result of the experimental study of Er$^{3+}$ removal from weak solutions containing surfactants, it was discovered that the Er$^{3+}$ recovery directly depends on the medium pH. During the experimental study it was made more accurate that the Er$^{3+}$ recovery reaches the maximum value at pH = 8.0 that conforms with the obtained results for distribution coefficients and the recovery ratio value $\alpha = 98.7\%$, at that, the distribution coefficient value has a maximum value of 2961.8.

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