Article

THE REMOVAL OF RARE-EARTH METALS FROM WATER-SALT SYSTEMS – AN INNOVATIVE ASPECT OF THE MODERN INDUSTRY

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Abstract: Considering the ever-increasing role of rare-earth elements (REE) in the modern hi-tech field, their effective use has a tremendous significance, although the production process is inevitably linked to the large volumes of industrial ammonia effluents and heavy metal wastes. In the process of metallurgical separation of metals, the emission of large volumes of noxious gases and radioactive substances is inevitable. Lean technogenic raw material processing is sensible under the condition of the development of non-waste technology. The lack of competent regulations governing the disposal of waste containing REE has an impact on adjacent territories, accumulating in water bodies and, as a result, in the human body. Such an impact cannot pass without a trace, however, the ambiguity of opinions in the scientific community regarding the toxic effects of REE on living organisms determines the relevance of a more detailed study of this issue. The paper presents experimental and theoretical results of studies of ion flotation in the aqueous solutions containing ytterbium cations and a surfactant as a collector - sodium dodecyl sulphate (NaDS).

Keywords: contamination in environmental media 1, ion flotation 2, rare-earth elements 3, removal 4.

1. Introduction

The development of REE mineral deposits provokes the leakage of pollutants that pose a danger to human life and health, and severely damages the environment. The rectification of pollution consequences and environmental rehabilitation of territories is topical in the present-day world for the REE mining and production areas [1]. Among the relevant areas of detailed study of the effect of REE on living organisms, the following can be distinguished: the widespread and active use of REE in industry necessitates the study of their physico-chemical properties in order to dispose of hazardous waste containing REE to prevent them from entering the environment and living organisms [2-5]. In particular, to conduct ecological and geochemical zoning and allocation of territories with the presence of anomalies (the presence of REE), Tomsk Polytechnic University conducted studies of the ratio of La and Ce. The choice of such a material was due to the fact that La and Ce are light REE, and it is they that accumulate in organ tissues and blood plasma, while heavy REE are concentrated mainly in the skeleton. According to the assumptions put forward, toxic elements enter the human body through drinking water, are absorbed into the blood from the gastrointestinal tract and then enter the thyroid gland. Part of the REE is able to linger in the lungs, which can lead to the development of chronic nonspecific inflammatory phenomena such as bronchitis, bronchiolitis, alveolitis, pneumonia [6]. The presence of polar points of view on the effects of REE on the human body serves as the basis for studying this area [7-9].

The paper studies the possibility of lanthanide ions removal from diluted aqueous solutions (as exemplified by yttrium ions) by ion flotation method using NaDS as collector agent [12]. Russia has not less than 20% of world REE reserves, but the volume of extraction of raw materials is approximately 2% of world extraction volume [13-17].

To identify the process mechanisms of metal cations removal and separation by ion flotation method, one should know the pH of metal hydroxo complexes formation and pH of hydrate formation, calculated based on the Gibbs energies of hydroxo complexes and metal hydroxides formation (Table 1). The pH value of Yb(OH)²⁺ hydroxo complexes formation can be calculated based on the expression for instability constants [18].
Table 1. Thermodynamic quantities – Gibbs energy of formation of hydrated ions \(\Delta_f G_{\text{hydr}}^0\) and hydration enthalpy \(\Delta_{\text{hydr}} H\) of Ln\(^{3+}\) cations [19]

| Element | \(-\Delta_f G_{\text{hydr}}^0\) \((\text{Ln}^{3+}\text{aq})\), kJ/mol | \(-\Delta_{\text{hydr}} H\) \((\text{Ln}^{3+}\text{aq})\), kJ/mol |
|---------|-------------------------------------------------|-------------------------------------------------|
| Tb      | 664.18                                          | 3570                                            |
| Dy      | 660.92                                          | 3600                                            |
| Ho      | 685.89                                          | 3650                                            |
| Er      | 670.93                                          | 3680                                            |
| Tm      | 670.08                                          | 3700                                            |
| Yb      | 644.43                                          | 3710                                            |
| Lu      | 631.45                                          | 3750                                            |

A special feature of Russian raw material sources is the REE low content and complex chemical and mineralogical composition. The processing of such raw materials in unprofitable [20-28]. Besides, ore mined at Kola peninsular (a fairly developed Arctic Region in Russia) are used for production of up to 25 concentrates that are different in terms of their composition and properties [29].

The main aim – experimental and thermodynamic study of the possibility of selective REE removal (by the example of Yb\(^{3+}\)) by an adsorptive bubble separation technique.

2. Materials and Methods

According to literature data, an increase of process effectiveness because of valuable components extraction from production wastes is possible when using the ion flotation method in mining industry [18, 20]. At that, the decrease of REE toxicity, and the risk of damaging the environment, is presumed. In papers [18,20,22] the ion flotation method is proposed for REE removal fromapatite sulphuric acid processing products.

2.1. Ion flotation

According to data [22] the ion flotation method is used for removal of rare-earth and radioactive metal cations from residential wastewaters. Besides, this method can be used for removal from wastewaters of oil admixtures and petroleum contained in the system [23]. The removal ratio of ion flotation when removing metal cations from the solutions of lean technogenic raw materials processing reaches 100% [30-33].

2.2. Process procedure

The ion flotation was conducted on the flotation machine (figure 1) [31]. 200 ml of ytterbium nitrate solution with the concentration of 0.001 mol/l and dry NaDS were added to the cuvette. The process continued no more than 5 minutes. The formed froth was broken by 5 ml of sulphuric acid solution with the concentration of 1 mol·l\(^{-1}\). The resulting froth pulp and the solution that remained in the cuvette were analysed for REE content by using method [34] and for dodecyl sulphate ion content by potentiometer method [31].

2.3. Equipment

This paper studies the distribution of Yb\(^{3+}\) ions in solutions formed by standardised test solutions containing Yb\(^{3+}\) ions and a surfactant - sodium dodecyl sulphate (NaDS). A flotation machine for ion flotation of lanthanide ions is shown in fig. 1. Critical concentration for micelle formation (CCM) of NaDS is \(8 \times 10^{-3} \text{ mol·kg}^{-1}\) at 20°C [30].
3. Experimental and theoretical results

The results of ion flotation study of the solutions, containing Yb³⁺ and DS⁻, are shown in table 2. The ytterbium cations distribution coefficient between water and organic phases was determined by the formula: 

\[ K_{\text{distribution}} = \frac{C_{\text{org}}}{C_{\text{aq}}} \]

Table 2. The results of the experimental study of ion flotation in Yb³⁺ solutions.

| pH    | [Yb³⁺]₉₄·10⁴ mol/l | [Yb³⁺]ₒᵣ·10³ mol/l | Distribution coefficient |
|-------|---------------------|---------------------|-------------------------|
| 1.86  | 6.59                | 1.56                | 2.3                     |
| 3.00  | 3.40                | 2.03                | 5.9                     |
| 3.50  | 3.43                | 2.33                | 6.8                     |
| 4.01  | 2.62                | 2.37                | 9.1                     |
| 4.60  | 2.73                | 2.24                | 8.2                     |
| 5.03  | 2.23                | 2.21                | 9.5                     |
| 5.50  | 2.69                | 2.48                | 9.2                     |
| 6.00  | 1.79                | 2.46                | 13.8                    |
| 6.40  | 0.25                | 2.40                | 95.4                    |
| 7.06  | 0.07                | 1.85                | 281.3                   |
| 7.38  | 0.05                | 1.96                | 365.3                   |
| 8.30  | 0.06                | 2.27                | 403.7                   |
| 9.10  | 0.06                | 2.03                | 318.4                   |

From the experimental data shown in the table, one can conclude that the Yb³⁺ removal doesn’t practically take place in acidic mediums. With the increase of pH value from 4.01 to 5.50, the distribution coefficient value is just over 9.0. Not surprisingly that in this pH range neutral and basic ytterbium dodecyl sulphates Yb(C₁₂H₂₅OSO₃)₃ and Yb(OH)(C₁₂H₂₅OSO₃)₂ float. From the resulting experimental data, it’s clear that at pH exceeding 6.00 the distribution coefficient increases rapidly. This value is lower than the pH value of hydrate formation that was previously determined by us. Consequently, in the pH range satisfying the maximum removal, ytterbium floats in the hydroxide form with the admixture of neutral and basic dodecyl sulphate.

4. Discussion
According to the literature data, in the process of ion flotation of metal cations, the increase in removal occurs in the pH range of hydrate formation [30,31], that is the metal cations passing into froth as hydroxides is observed. In a number of papers [1,15,18] it was discovered that to identify the mechanism of metal cations removal by ion flotation one should know the pH of metal hydroxo complexes and pH of hydrate formation. The pH value of Yb(OH)$^{2+}$ hydroxo complexes formation is calculated based on the expression for instability constant.

According to the experimental results, the titration curve was plotted as shown in figure 2.

![Figure 2](image-url)

**Figure 2.** Specific electrical conductivity of Yb(NO)$_3$ solution and pH as a function of NaOH solution volume in the course of conductometric titration.

The Gibbs energy values of Yb(OH)$_3$ formation, specified in the database under the editorship of V.P. Glushko [35] – 1268.59±3.77 kJ/mol and in the handbook [36], agree poorly. In the database [37] this value is missing. The Gibbs energy values of Yb(OH)$^{2+}$ formation – 832.62±3.77 kJ/mol in the database [35] and – 836.29 in [37] agree satisfactory, however they are at odds with the pH of hydrate formation. Calculated by the value [35] pH$_{compl}$ 7.7 is notably higher than pH$_{hydr}$ that is 6.40, while the formation of hydroxo complexes should precede the hydroxide sedimentation and take place at lower pH values. Because of inconsistency of values available in the literature data, the evaluation of pH of complex formation and hydrate formation by conductometric titration method was attempted. Titration results were reproduced three times to confirm their reliability. The calculated values are shown in table 3. The following areas on the conductometric titration curves are marked out.

1. Up to 60 ml of titrant – a linear drop of specific electrical conductivity is observed, accompanied with the pH rise because of the nitric acid neutralization by alkali. This section is not mandatory but can be added to the manuscript if the discussion is unusually long or complex.
2. From 62 to 67 ml of titrant – a weak linear growth of specific electrical conductivity is observed, which shows the binding of added hydroxyl anions into a poorly dissociated compound with sodium nitrate accumulation in the solution. Since the formation of hydroxides wasn’t observed (optical density of solutions didn’t change), this part handles the formation of hydroxo complexes. By the quantity of milliequivalents of alkali spent in this part, one can determine that the process flows until the formation of Yb(OH)$^{2+}$ monohydroxo complex. pH$_{compl}$ = 5.50, conforming to the beginning of this part of the titration curve, was taken as pH of complex formation over the first stage of pH$_{compl}$.
3. Upon the completion of complex formation over the first stage, a surge on the relationship of specific electrical conductivity as a function of titrant volume is observed at 67-68 ml, conditioned by high equivalent conductivity of the added hydroxyl anions. Next, from 68 to 74 ml of titrant – there’s an almost horizontal part of the titration curve, attribute to Yb(OH)$_3$ dihydroxo complexes formation. The pH= 6.00 conforms to the beginning of complex formation over the second stage.
4. At the titrant volume of 74-75 ml a new electrical conductivity surge with a transition
to a horizontal part of the titration curve at the titrant volume of 75-86 ml is observed. This part of the titration curve corresponds to the hydroxide sedimentation in accordance with the reaction:

\[ \text{Yb(OH)}^n + \text{OH}^- = \text{Yb(OH)}^m \]

The latter was observed visually and confirmed by an increase in the optical density of solutions. The pH value of hydrate formation was 6.50.

5. Further on the titration curve, the near-linear growth of specific electrical conductivity because of excess alkali was observed.

The solubility product of ytterbium hydroxide was calculated according to the formula:

\[
L = \left[ \text{Yb}^{3+} \right] \left[ \text{OH}^{−} \right] \cdot \gamma^{\pm} \quad (1)
\]

where ytterbium cation concentration considering aliquot dilution during the titration up to the volume of 85 ml was in the experiment \(1.46 \times 10^{-3}\) mol·kg\(^{−1}\). Ionic strength was calculated considering nitric acid, added to establish an initial pH value of 3.07, and alkali, added during the titration. The value of \(3.64 \times 10^{-3}\) mol·kg\(^{−1}\) was got. The medium ion activity coefficient of ytterbium nitrate was taken equal to the activity coefficient of Lanthanum chloride under this ionic strength - 0.81 [38].

The Gibbs energy of hydroxide formation was calculated according to the equation:

\[
\Delta_r G_{298}^0 \{\text{Yb(OH)}^n\} = \Delta_f G_{298}^0 \{\text{Yb}^{3+}\} + 3 \Delta_f G_{298}^0 \{\text{OH}^{−}\} + RT \ln L \quad (2)
\]

The standard Gibbs energy value of ytterbium ion formation in an aqueous solution was accepted according to the database [35] as \(−644.88±2.93\) kJ/mol.

The resulting values are shown in table 3. At the same place, the Gibbs energy values of ytterbium hydroxide dissolution and Gibbs energies of complex formation \(\Delta_{\text{compl}} G_{298}^0\) over the following stages:

\[
\text{Yb}^{3+} + \text{OH}^- \leftrightarrow \text{Yb(OH)}^2^+ \quad (3)
\]

\[
\text{Yb(OH)}^2^+ + \text{OH}^- \leftrightarrow \text{Yb(OH)}_3^+ \quad (4)
\]

\[
\text{Yb(OH)}_3^+ + \text{OH}^- \leftrightarrow \text{Yb(OH)}_4^3^+ \quad (5)
\]

Table 3. Thermodynamic characteristics of ytterbium hydroxo compounds.

| Compound | \(\Delta_f G_{298}^0\), kJ·mol\(^{−1}\) | \(\Delta_{\text{compl}} G_{298}^0\), kJ·mol\(^{−1}\) | \(L\) (K-v) | \(pH_{\text{hydr}}\) (pH_{\text{compl}}) |
|----------|-----------------|------------------|-----------|-----------------|
| Yb(OH)_3  | −1266.74±3.90 | −149.81±2.57      | (5.66±4.50)·10\(^{-27}\)  | 6.56            |
| Yb(OH)_2^+ | −849.17±3.03 | −47.39±0.77       | (4.99±1.33)·10\(^{-4}\)  | 5.47            |
| Yb(OH)_3^+ | −1050.47±3.22 | −43.95±1.35       | (1.61±0.45)·10\(^{-4}\)  | 6.08            |

The obtained Gibbs energy value of ytterbium hydroxide formation agrees well with the database [35], where the value of \(−1268.59±3.77\) kJ/mol is specified. The Gibbs energy value of ytterbium monohydroxo complex formation differs significantly from the values of \(−832.62±3.77\) kJ/mol and \(−836.29\) kJ/mol, specified in the databases [35-38]. We calculated the Yb(OH)_2^+ hydroxo complex instability constant according to data [35]. The got value of 3.96·10\(^{-8}\) corresponding to the pH of complex formation onset that is 7.7. However, according to our data, this value is significantly higher than the pH of hydrate formation, which is contradictory. Data for ytterbium Yb(OH)_3^+ dihydroxo complex formation was obtained for the first time.

5. Conclusions

1. The study of ytterbium ions removal from aqueous standard test solutions by adsorptive bubble method - ion flotation, was conducted.

2. The experiments showed that when using the ion flotation method, the maximum
removal of ytterbium (III) was achieved at pH=8.30.

3. To determine Gibbs energy values of ytterbium (3+) hydroxide, mono- and dihydroxo complexes formation, that are $-1266.74\pm3.90 \text{ kJ} \cdot \text{mol}^{-1}$, $-849.17\pm3.03 \text{ kJ} \cdot \text{mol}^{-1}$ and $-1050.47\pm3.22 \text{ kJ} \cdot \text{mol}^{-1}$ respectively, the conductometric titration method was used.

4. Ytterbium (3+) distribution coefficients as a function of aqueous phase $\text{pH}$ value in the process of ion flotation with sodium dodecyl sulphate were derived. The comparison of values of $\text{pH}$ of removal with $\text{pH}$ of hydrate formation allows to conclude that ytterbium floats as basic dihydroxyytterbium dodecyl sulphate $\text{Yb(OH)}_2(C_{12}H_{25}OSO_3)$.

6. Patents

Lobacheva O.L., Dzhevaga N.V. Method of separation of holmium (III) and cerium (III) by anionic surfactant from an aqueous solution of their nitrates. RU № 2735017 C1, 27.10.2020

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References

1. Dzhevaga, N., Lobacheva, O. Reduction in technogenic burden on the environment by flotation recovery of rare earth elements from diluted industrial solutions (2021) Journal of Applied Sciences 11(16),7452.

2. Narkovich, D. V., Baranovskaya, N. V., Koval, E. V., & Korogod, N. P. (2016). Influence of technogenesis on forming element composition of children’s hair. Bulletin of the Tomsk Polytechnic University, Geo Assets Engineering, 327(8), 116-128.

3. Carneiro, M.F.H., Moresco, M., Chagas, G.R., Oliveira Souza, V.C., Rhoden, C., Barbosa, F., Jr., Assessment of trace elements in scalp hair of a young urban population in Brazil (2011) Biological Trace Element Research, 143 (2), pp. 815-824.

4. Popov, V. K., Pasechnik, E. Y., Protsenko, P. I., & Goncharov, O. Y. (2018). Rare earth element content in groundwater of tomsk water intake. Bulletin of the Tomsk Polytechnic University, Geo Assets Engineering, 329(6), 97-105.

5. Zabrecky, J.M.; Liu, X.-M.; Wu, Q.; Cao, C. Evidence of Anthropogenic Gadolinium in Triangle Area Waters, North Carolina, USA. Water 2021, 13, 1895. https://doi.org/10.3390/w13141895

6. Ge, Q.; Xue, Z.G.; Chu, F. Rare Earth Element Distributions in Continental Shelf Sediment, Northern South China Sea. Water 2020, 12, 3540. https://doi.org/10.3390/w12123540.

7. Liu, Y.; Li, C.; Omar, R.B.; Shi, X.; Zhang, H.; Faiz, N.N. Sediment Sources and Dispersion on the Western Sunda Shelf, Malay Peninsula, Southern South China Sea. Water 2021, 13, 2823. https://doi.org/10.3390/w13202823

8. Litvinova, T. Yttrium and lanthanides metallurgy (2012), Saint Petersburg, 185 p.

9. Cheremisina, O.V., Volkova, O., Litvinova, T.E. Influence of anion nature on acid leaching of silicate minerals and solvent extraction of rare and rare-earth elements (2020) Chemie der Erde, 80 (3), paper № 125507. DOI: 10.1016/j.chemer.2019.04.003

10. F. Sebba Ion flotation. // M. Metallurgy. 1965. 170 p.

11. Matveeva, V., Danilov, A., Pashkevich, M. Treatment of multi-tonnage manganese-containing waste water using vermiculite (2018) Journal of Ecological Engineering, 19 (1), pp. 156-162. DOI: 10.12911/22998993/79416

12. Strizhenok A.V., Ivanov A.V. (2021) Monitoring of Air Pollution in the Area Affected by the Storage of Primary Oil Refining Waste Journal of Ecological Engineering 22(1) 60–67 DOI: 10.12911/22998993/128873

13. Lutsik, D., Litvinova, T., Ignatovich, A., Fialkovskiy, I. Complex processing of phosphogypsum - A way of recycling dumps with reception of commodity production of wide application (2018) Journal of Ecological Engineering, 19 (2), pp. 221-225. DOI: 10.12911/22998993/83562
16. Goman, I.V., Oblova, I.S. Analysis of companies' corporate social responsibility as a way to develop environmental ethics for students specialising in oil and gas activity (2018) International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, 18 (5.4), pp. 11-18. DOI: 10.5593/sgem2018/5.4/S22.002

17. Machevariani, M.M., Alekseenko, A.V., Bech, J. Complex characteristic of zircon from granitoids of the Verkhneurmiysky Massif (Amur region) (2021) Minerals, 11 (1), № 86, pp. 1-31. DOI: 10.3390/min11010086

18. Lobacheva O.L, Dzhvaga N.V., Danilov A.S. Understanding the regularities of recovering non-ferrous and rare earth metals from standard test solutions by flotation and solvent sublation

19. Non-ferrous metals. 2020 No. 10 pp. 14–19. DOI: 10.17580/tsm.2020.10.02

20. Database of chemicals and compounds: «Chemical Database Schemix» http://www.schemix.ru/downloads.aspx

21. Lobacheva, O., Dzhvaga, N. Rare-earth elements recovery on the example of Europium (III) from lean technogenic raw materials (2017) Journal of Ecological Engineering, 18 (6), pp. 122-126. DOI: 10.12911/22998993/76827

22. Kola Peninsula in solving problems of national arctic materials science (2019) IOP Conference Series: Materials Science and Engineering, 696 (1), статья № 012019. DOI: 10.1088/1757-899X/696/1/012019.

23. Grieves R.B., Charewicz W.R. Ion and colloid flotation of Ni, Co and Pt // Separation Science. 1975. Vol.10. N 1. P.77-92.

24. S.B. Savin / Arsenazo III. M.: Atomizdat. 1966. 265 p.

25. Thermal constants of substances. Handbook. Ed. V.P. Glushko/M.: USSR Academy of Sciences. Vol. 1978. 358 p.

26. Lidin R.A., Andreeva A.A., Molochko A.V. // Handbook. Constants of inorganic substances. Ed. "Dvora", M. 2006.

27. HSC Chemistry OutoKumpu Research OY (ver. 4.1.), Pori, Finland.

28. Ravdel A.A., Ponomareva A.M. / Guide of physics.-chemical quantities.2003,240 p.