Ion Flotation of Ytterbium 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 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 study of ytterbium ions removal from aqueous standard test solutions by the adsorptive bubble method—ion flotation—was conducted. The experiments showed that by using the ion flotation method, the maximum removal of ytterbium (III) was achieved at pH = 8.30. It was shown that ytterbium (+3) distribution coefficients as a function of aqueous phase pH value in the process of ion flotation with sodium dodecyl sulphate were derived. The comparison of values of removal pH with those of hydrate formation pH allowed to conclude that ytterbium float as basic dihydroxyytterbium dodecyl sulphate $\text{Yb(OH)}_2\text{(C}_{12}\text{H}_{25}\text{OSO}_3)$. 

Keywords: contamination in environmental media; ion flotation; rare-earth elements; removal

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 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 physicochemical properties in order to prevent them from entering the environment and living organisms with disposal of hazardous waste containing REE [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 lanthanum and cerium. The choice of such a material was due to the fact that lanthanum and cerium 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, and 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 [7–11].

This paper studies the possibility of lanthanide ion removal from diluted aqueous solutions (as exemplified by yttrium ions) by the ion flotation method using SDS as the...
collector agent [12]. Russia has no less than 20% of the world’s REE reserves, but the volume of extraction of raw materials is approximately 2% of the world’s extraction volume [13–17].

To identify the process mechanisms of metal cation removal and separation by the ion flotation method, it is necessary to know how to know the pH of metal hydroxo complexes formation and the 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 \(\Delta_f G_{298}^0\) and hydration enthalpy \(\Delta_{hydr} H\) of Ln\(^{3+}\) \(_{aq}\) cations [18].

| Element | \(-\Delta_f G_{298}^0\) (Ln\(^{3+}\) \(_{aq}\)), kJ/mol | \(-\Delta_{hydr} H\) (Ln\(^{3+}\) \(_{aq}\)), 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 low REE content and complex chemical and mineralogical composition. The processing of such raw materials is unprofitable [19–27]. Furthermore, ore mined at the Kola peninsula (a fairly developed Arctic region in Russia) is used for production of up to 25 concentrates that are different in terms of their composition and properties [28].

According to data [21], the ion flotation method was used for removal of rare-earth and radioactive metal cations from residential wastewaters. Additionally, this method was used for removal of oil admixtures and petroleum contained in the system from wastewaters [22]. The removal ratio of ion flotation when removing metal cations from the solutions of lean technogenic raw materials achieved 100% [29–32].

The main aim is to show experimentally the possibility of extraction by ion flotation of ytterbium cations from dilute aqueous solutions and with thermodynamic calculations to confirm the shape of the extracted complex considered REE.

### 2. Materials and Methods

#### 2.1. Process Procedure

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 the mining industry [18,19]. It was assumed that the decrease of REE toxicity, and the risk of damaging the environment, is presumed. In [18,19,21], the ion flotation method was offered for REE removal from apatite sulphuric acid processing products.

Ion flotation was conducted on a flotation machine (Figure 1) [30]. Two hundred milliliters of ytterbium nitrate solution with a concentration of 0.001 mol/L and dry SDS were added to the cuvette. The process continued no more than 5 min. The formed froth was broken by 5 mL of sulphuric acid solution with a concentration of 1 mol/L. The resulting froth pulp and the solution that remained in the cuvette were analyzed for REE content by using a method from [33] and for dodecyl sulphate ion content by the potentiometer method [30].
**2.2. Equipment**

This paper studied the distribution of Yb$^{3+}$ ions in solutions formed by standardized test solutions containing Yb$^{3+}$ ions and a surfactant—sodium dodecyl sulphate (SDS). A flotation machine for ion flotation of lanthanide ions is shown in Figure 1. The critical concentration for micelle formation (CCM) of NaDS is $8 \times 10^{-3}$ mol·kg$^{-1}$ at 20 °C [29].

**3. Experimental and Theoretical Results**

The results of ion flotation study of the solutions containing Yb$^{3+}$ and DS$^{-}$ are shown in Table 2. Ytterbium cation distribution coefficients between water and organic phases was determined by the formula: $K_{distribution} = C_{org}/C_{aq}$.

Table 2. The results of the experimental study of ion flotation in Yb$^{3+}$ solutions.

| pH  | $[\text{Yb}^{3+}]_{aq} \times 10^4$ mol/L | $[\text{Yb}^{3+}]_{org} \times 10^5$ 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, we could conclude that Yb$^{3+}$ removal did not practically take place in acidic mediums. With the increase of pH value from 4.01 to 5.50, the distribution coefficient value was just over 9.0. Not surprisingly, in this pH range, neutral and basic ytterbium dodecyl sulphates Yb(C$_{12}$H$_{25}$OSO$_3$)$_2$ and Yb(OH)(C$_{12}$H$_{25}$OSO$_3$)$_2$ float. From the resulting experimental data, it was clear that at pH exceeding 6.00, the distribution coefficient increased rapidly. This value was 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 [29,30], that is, metal cations are observed passing into froth as hydroxides. In a number of studies [1,15,18] it was discovered that to identify the mechanism of metal cation removal by ion flotation, the pH of metal hydroxo complexes and pH of hydrate formation need to be known. 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)

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 [34] $-$1268.59 ± 3.77 kJ/mol and in the handbook [35], agreed poorly. In the database [36], this value is missing. The Gibbs energy values of Yb(OH)$^{2+}$ formation $-$832.62 ± 3.77 kJ/mol in the database [34] and $-$836.29 in [36] agreed satisfactorily; however, they were at odds with the pH of hydrate formation. Calculated by the value [34], pH$_{\text{compl}}$ 7.7 was notably higher than pH$_{\text{hydr}}$, which was 6.40, while the formation of hydroxo complexes should precede hydroxide sedimentation and take place at lower pH values. Because of inconsistency of values available in the literature data, an 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.

Table 3. Thermodynamic characteristics of ytterbium hydroxo compounds.

| Compound   | $\Delta G_{298}^0$ (kJ mol$^{-1}$) | $\Delta G_{298}^0$ (L (K mol$^{-1}$)) | $L$ (K$_{u.2}$) | pH$_{\text{hydr}}$ (pH$_{\text{compl}}$) |
|------------|----------------------------------|-------------------------------------|-----------------|-------------------------------------|
| Yb(OH)$_3$ | $-1266.74 \pm 3.90$              | $-149.81 \pm 2.57$                | $(5.66 \pm 4.50) \times 10^{-27}$ | 6.56                                |
| Yb(OH)$^{2+}$ | $-849.17 \pm 3.03$              | $-47.39 \pm 0.77$                | $(4.99 \pm 1.33) \times 10^{-9}$  | 5.47                                |
| Yb(OH)$_2^{2+}$ | $-1050.47 \pm 3.22$             | $-43.95 \pm 1.35$                | $(1.61 \pm 0.45) \times 10^{-8}$  | 6.08                                |

1. Up to 60 mL of titrant—a linear drop of specific electrical conductivity was observed, accompanied with a pH rise because of the nitric acid neutralization by alkali. This section was 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—weak linear growth of specific electrical conductivity was observed, which showed the binding of added hydroxyl anions into a poorly dissociated compound with sodium nitrate accumulation in the solution. Since the formation of hydroxides was not observed (optical density of solutions did not change), this part handled the formation of hydroxo complexes. By the quantity of milliequivalents of alkali spent in this part, we defined that the process flows until the formation of Yb(OH)$_2^{+}$ monohydroxo complex. pH = 5.50, conforming to the beginning of this part of the titration curve, was taken as the 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 was observed at 67–68 mL, conditioned by high equivalent conductivity of the added hydroxyl anions. Next, from 68 to 74 mL of titrant, there was an almost horizontal part of the titration curve, attributed to Yb(OH)$_2^{+}$ dihydroxo complexes formation. pH = 6.00 conformed 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 was observed. This part of the titration curve corresponded to hydroxide sedimentation in accordance with the reaction: Yb(OH)$_2^{+}$ + OH$^{-}$ = Yb(OH)$_3$. 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:

$$L = \left[ Yb^{3+} \right] \left( 10^{pH_{hydr} - 14} \right)^3 \cdot \gamma_\pm$$

where ytterbium cation concentration considering aliquot dilution during the titration up to the volume of 85 mL was $1.46 \times 10^{-4}$ mol·kg$^{-1}$ in the experiment. 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 achieved. The medium ion activity coefficient of ytterbium nitrate was taken equal to the activity coefficient of lanthanum chloride under this ionic strength—0.81 [19]. The Gibbs energy of hydroxide formation was calculated according to the equation:

$$\Delta fG^0{Yb(OH)_3} = \Delta fG^0{Yb^{3+} + OH^-} + 3\Delta fG^0{OH^-} + RT \ln L$$

The standard Gibbs energy value of ytterbium ion formation in an aqueous solution was accepted according to the database [34] as $-644.88 \pm 2.93$ kJ/mol. The resulting values are shown in Table 3. At the same place, the Gibbs energy values of ytterbium $\Delta fG^0_{298}$ hydroxide dissolution and Gibbs energies of complex formation $\Delta_{compl}G^0_{298}$ over ytterbium $\Delta_{compl}G^0_{298}$ hydroxide dissolution and Gibbs energies of complex formation $\Delta_{compl}G^0_{298}$ over the following stages:

$$Yb^{3+} + OH^- \leftrightarrow Yb(OH)^{2+}$$
$$Yb(OH)^{2+} + OH^- \leftrightarrow Yb(OH)_2^{+}$$
$$Yb(OH)_2^{+} + OH^- \leftrightarrow Yb(OH)_3$$

The obtained Gibbs energy value of ytterbium hydroxide formation agreed well with the database [34], where the value of $-1268.59 \pm 3.77$ kJ/mol is specified. The Gibbs energy value of ytterbium monohydroxo complex formation differed significantly from the values of $-832.62 \pm 3.77$ kJ/mol and $-836.29$ kJ/mol specified in the databases [34–37]. We calculated the Yb(OH)$_2^{+}$ hydroxo complex instability constant according to data from [34]. The gotten value of $3.96 \times 10^{-6}$ corresponded to the pH of complex formation onset that...
was 7.7. However, according to our data, this value was significantly higher than the pH of hydrate formation, which is contradictory. Data for ytterbium Yb(OH)$_2^{2+}$ dihydroxocomplex formation was obtained for the first time.

5. Conclusions

The conductometric titration method was used to determine Gibbs energy values of ytterbium (3+) hydroxide, mono- and dihydroxocomplexes formation, which were $-1266.74 \pm 3.90 \text{kJ} \cdot \text{mol}^{-1}$, $-849.17 \pm 3.03 \text{kJ} \cdot \text{mol}^{-1}$ and $-1050.47 \pm 3.22 \text{kJ} \cdot \text{mol}^{-1}$, respectively. Data for ytterbium Yb(OH)$_2^{2+}$ dihydroxocomplex formation was obtained for the first time. Interesting experimental results were obtained—using the ion flotation method, the maximum removal of ytterbium (III) was achieved at pH = 8.30. Ytterbium (3+) distribution coefficients as a function of aqueous phase pH value in the process of ion flotation with sodium dodecyl sulphate were derived. The comparison of values of removal pH with those of hydrate formation pH allowed to conclude that ytterbium floats as basic dihydroxyytterbium dodecyl sulphate 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 No 2735017 C1, 27 October 2020.

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