

Separation of rare earth elements by zone recrystallization

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Abstract. The separation of holmium and cerium by zone recrystallization using a mixture of $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ was investigated. It is shown that holmium is enriched at the end of the crystal that the recrystallization zone moves to, while cerium is concentrated in the primary solidification zone. The possible reasons for the experimentally observed distribution of hydrated ions of cerium and holmium along the length of the ingot are discussed. Also the coefficients of enrichment and separation are calculated.

1. Introduction

The demand for rare earth elements (REEs) and also scandium and yttrium is ever increasing due to their wide range of applications, such as in radio electronics, instrumentation, nuclear engineering, mechanical engineering, chemical industry and metallurgy [1-12]. For this reason, there is a steady increase worldwide in the consumption and production of REEs. In order to reduce the cost of processing raw materials both the traditional and new technological schemes for processing monazite and other minerals which contain the REEs are developing now [13]. The separation of REEs individually has also always attracted the attention of researchers [14, 15].

The processes of ion exchange and extraction are the main methods in modern industry for separation of REEs into individual components. However, these methods have some disadvantages. If we use liquid extraction, it is necessary to consider the mutual solubility of the organic and aqueous phases. In this case we will lose the extracting agent, the cost of which is comparable with REEs. The method of the ion exchange provides low separation coefficients of REEs, and therefore this method may be just additional in the technological scheme of the extraction separation of REEs. For these reasons, there is today a search for new methods for separating REEs [16].

Zone recrystallization, often called zone melting, is widely used for purification of the different substances, to obtain them in single-crystal form, and also for separating those elements with similar properties [17].

The literature contains information on the distribution of REEs in melts of NH_4NO_3 , NH_4SCN , MgCl_2 and BaCl_2 in which it is shown that the ratio of the concentrations of REEs of the yttrium and cerium group in the zone recrystallization varies slightly [18-20].

Here we report our investigations into the process of separating the chlorides of REEs by using zone recrystallization of their chloride hexahydrates. This choice was influenced by two factors. The first one is the full melting of REEs chloride hexahydrates at low temperatures. Secondly, compounds also contain water molecules, which can affect the distribution of the REEs during the process of zone recrystallization.



In this way, the aim of this work was to investigate the possibility of separating REEs by using zone recrystallization of their chloride hexahydrates.

2. Experimental

2.1 Reagents

$\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ (analytical grade) and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ (analytical grade) were used. Their mixture was prepared by melting in the percentage ratio of $\text{CeCl}_3 \cdot 6\text{H}_2\text{O} : \text{HoCl}_3 \cdot 6\text{H}_2\text{O} = 59.5:40.5$.

2.2 Instrumentation

Investigations were conducted on samples with a length of 90 mm and a diameter of 10 mm. For preparing samples, the chloride hexahydrates of REEs were heated until they melted. After that, part of the melt was placed into a glass tube, which was sealed at one end.

All experiments were carried out on the installation, which has five heating elements and five cooling elements (Figure 1). Nichrome wire was used as the heating element. The temperature of the melt zone was equal to 160 ± 1 °C. The length of the melt of the ingot was from 1 to 1.5 cm.

The main part of the installation was a platform with the heating elements placed at equal distance in the form of a ring, the inner diameter of which corresponds to the outer diameter of the glass tube. Power supply GW INSTEK PSH -10100 was used for regulating the temperature of the heating elements. Temperature was measured by using a chromel-alumel thermocouple. Between the heating elements the cooling elements were installed, which were cooled by tap water. The temperature of cooling elements was equal to $+23 \pm 1$ °C.

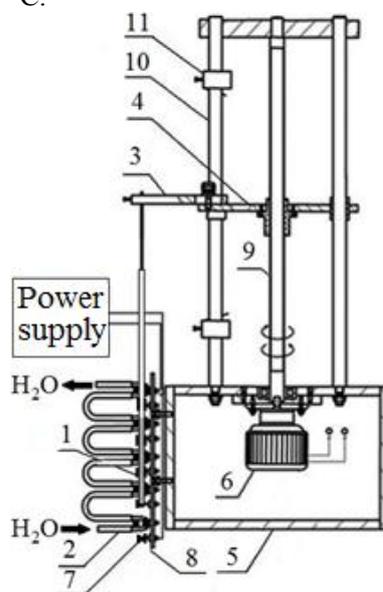


Figure 1. Installation for zone recrystallization (1 – mixture of REEs; 2 – cooling element; 3 – rod; 4 – carriage; 5 – housing; 6 – stepper motor; 7 – heating element; 8 – platform; 9 – shaft; 10 – guides; 11 – sensor).

The glass tube with the mixture of REEs was placed on the platform and fixed by using the rod on the carriage. The speed of the tube was 3 cm/hour. Our process was finished when the number of zone processes was equal to 40. After this, the glass tube was cut into samples, 10 mm in length. Samples were removed, weighed and dissolved in distilled water. In the obtained solutions we determined the content of cerium and holmium; these solutions were also investigated by spectrophotometry. Quantitative analysis was carried out using an atomic-emission spectrometer iCAP 6300 with

inductively coupled plasma. The electronic absorption spectra of solutions were obtained by using a spectrophotometer Evolution 600 in quartz cuvettes 10 mm thick.

3. Results and discussion

Figure 2 shows both the electronic absorption spectra of soluble samples of the REE mixture, which were obtained after the process of zone crystallization, and the spectra of the original sample

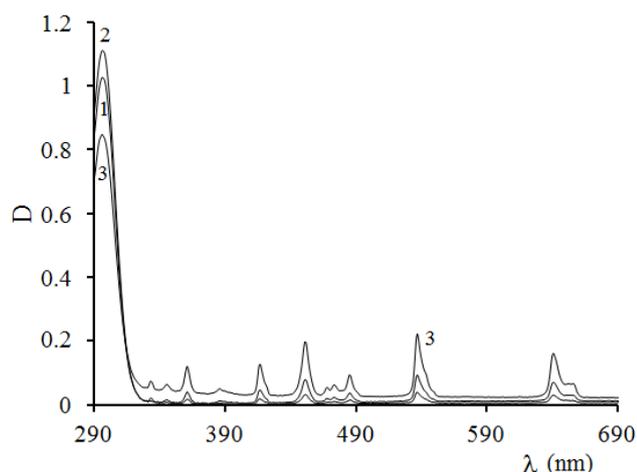


Figure 2. The electronic absorption spectra of solutions of cerium and holmium chlorides mixture: 1 – the original; 2 – the sample which was obtained on the 2 cm length of the ingot; 3 – the sample which was obtained on the 8 cm length of the ingot.

The maximum in the electronic absorption spectra at 296 nm belongs to the absorption by the aqua complexes of cerium chloride, all the rest belong to the aqua complexes of holmium chloride [21]. As we can see from the figure, the maximums related to the ions of cerium are increased in the initial crystallization zone of the samples, and the maximums related to the holmium ions are reduced. This means that the concentration of cerium ions is increased in the initial crystallization zone of the sample, while holmium moves with the melt zone and concentrates at the edge of the sample.

From the data that were obtained by atomic-emission analysis, the distribution of cerium and holmium on the length of the ingot after the process of zone recrystallization of chloride hexahydrates was plotted in Figure 3.

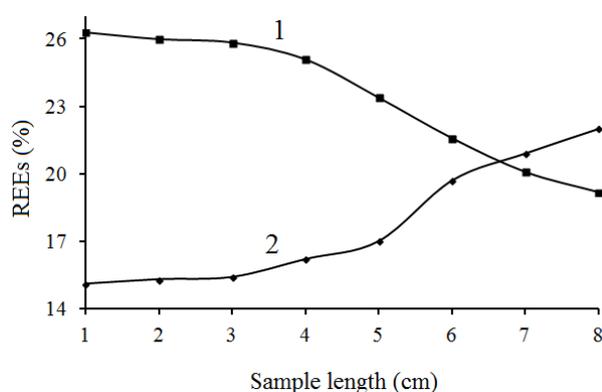


Figure 3. Distribution of cerium (1) and holmium (2) on the length of the ingot after the process of zone recrystallization

The results confirm that cerium, which is lighter, was concentrated in the initial zone of recrystallization, while the heavier holmium was concentrated in the end zone of the ingot. In addition, we can say that 40 recrystallization zones are insufficient for a full distribution of REEs in the sample.

For the determination of the separation coefficient we compared the initial concentrations of REEs with their concentrations after the process of zone recrystallization. The values of the separation and enrichment coefficients for both elements were calculated. The obtained data are presented in Table 1.

The values of the enrichment coefficients were calculated for the extreme zones of the ingot after zone recrystallization using the following formula:

$$\beta = \frac{x_e}{1-x_e} \cdot \frac{1-x_0}{x_0}, \quad (1)$$

where x_e – the contents of the element after the process of zone recrystallization in the maximum enriched zone, %;

x_0 – the initial contents of the element, %.

$$\beta_{Ho} = \frac{x_e}{1-x_e} \cdot \frac{1-x_0}{x_0} = \frac{22}{78} \cdot \frac{82.3}{17.7} = 1.311;$$

$$\beta_{Ce} = \frac{x_e}{1-x_e} \cdot \frac{1-x_0}{x_0} = \frac{26.3}{73.7} \cdot \frac{76.4}{23.6} = 1.155.$$

The separation coefficients (α) were found from the following relation:

$$lg\alpha = \frac{lg\beta}{n-1}, \quad (2)$$

where n – the number of passes of the zone.

$$lg\alpha_{Ho} = \frac{lg\beta}{n-1} = \frac{0.118}{39} = 0.0030;$$

$$\alpha_{Ho} = 10^{0.0030} = 1.007.$$

$$lg\alpha_{Ce} = \frac{lg\beta}{n-1} = \frac{0.063}{39} = 0.0016;$$

$$\alpha_{Ce} = 10^{0.0016} = 1.004.$$

Table 1. The coefficients of separation and enrichment of cerium and holmium after the process of zone recrystallization.

Characteristics of the process of zone recrystallization	REEs	
	Ho	Ce
Coefficient of enrichment (β)	1.311	1.155
Coefficient of separation (α)	1.007	1.004

It is known that when the impurity increases the melting point, the concentration of this impurity will decrease upon crystallization in the liquid phase. Conversely when the impurity decreases the melting point, upon crystallization we will observe the reverse effect [17]. According to the data in [22, 23], the melting point of $CeCl_3 \cdot 6H_2O$ is 403 K, and that of $HoCl_3 \cdot 6H_2O$ is 437 K. Thus, changes in the concentrations of cerium and holmium during the process of zone recrystallization of the chloride hexahydrates cannot be explained by the difference in their melting temperatures. It is known that the solubility of the light lanthanide chlorides is higher than that of the heavy ones, and therefore the cerium ions should be concentrated in the region of the melt [22-24]. However, the experimental results show the inverse movement of REEs in the sample.

Burton, Prim and Slichter obtained the formula for the effective distribution coefficient [25]:

$$K = \frac{1}{1 + \left[\left(\frac{1}{K_0} \right) - 1 \right] e^{-f\delta/D}}, \quad (3)$$

where K_0 – the equilibrium distribution coefficient, f – the crystal growth rate, δ – the thickness of the diffusion layer in front of the crystallization front, D – the diffusion coefficient.

From this equation we can conclude that differences between the effective distribution coefficient K and the equilibrium distribution coefficient K_0 will be more significant if the value of the diffusion coefficient D is higher and the thickness of the diffusion layer in front of the crystallization front is smaller. The chlorides of light REEs have a large diffusion coefficient and, correspondingly, a large

mobility. For this reason they should move with the melting zone, but this fact also does not correspond with the observed experimental data.

Apparently, these results may be explained only by assuming that the distribution of REEs by the recrystallization process is superimposed by ion solvation (hydration), which can inhibit the diffusion of the hydrated cerium ions and thus contribute to the cerium–holmium separation.

It is well known that the solvation of ions in the solution is determined by the nature and ratio of different types of interactions in solution – the ion–ion, ion–molecular and intermolecular interactions [26]. For ionic systems, the solvation contributions can be estimated by considering the following processes:

1. The process of the formation of a cavity in a solvent (the contribution of interactions that depend on the size of the ion);
2. The process of the transition of uncharged particles, which are isoelectronic with respect to the ion, into a cavity;
3. The process of the redistribution of the electron density between the ion and solvent molecules (the contribution from other interactions that depend on the ion charge).

Apparently, the greatest contribution to the suppression of diffusion of the cerium ions is due to their interaction with the water molecules, i.e. the chemical hydration of the components, and to the fact that cerium has a smaller ion own size than the holmium ion. The value of the hydration shell will depend on the density of the ion charge on this surface. Therefore, ions that have a larger size also have a smaller hydration shell [27].

The molecule of H₂O is an electrodonor and has the donor–acceptor interaction with both ions of cerium and ions of holmium through the cation–solvent mechanism. If we have a low content of water molecules, the most part of these molecules will be coordinated by the cerium ion, which has the ability to have a large hydration shell. This fact will lead to a decrease in the diffusion of the hydrated ions of cerium and will also lead to an increase in the diffusion of the hydrated ions of holmium. This was confirmed experimentally.

According to this fact we can conclude that after the process of zone recrystallization the molecules of water will concentrate in the initial zone of crystallization. In our the next work we will determine the behaviour of the water molecules during the process of zone recrystallization of the chloride hexahydrates of REEs. We will find the optimal conditions for the separation of REEs by using the process of zone recrystallization. In addition we will conduct an experimental investigation of the process of separation of different multi-component mixtures of REEs.

4. Conclusions

For separation of salts REEs was applied the method of zone recrystallization. Also was studied the distribution of hexahydrates chlorides of cerium–holmium during the process of zone recrystallization. The coefficients of enrichment and separation were calculated. Results show that process of zone recrystallization can be used for separation of hexahydrates chlorides of REEs. If the salts of REEs will use as working substances which have low melting points (90–165 °C) it will allow obtain the individual high purity REEs with two advantages: expensive organic compounds will not use (the extractants and ion exchangers); the amount of water and water-organic waste will decrease. The both of these advantages will reduce the cost of REEs. Also the method of zone recrystallization can be used for effective separation of mixtures REEs.

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References

- [1] Gschneidner K A and Pecharsky V K 2006 Rare Earths and Magnetic Refrigeration *Journal of Rare Earths* **24** 641

- [2] Chen Y, Jin L, Fang D, Song Y and Ye R 2015 Effect of calcium, samarium addition on microstructure and mechanical properties of AZ61 magnesium alloy *Journal of Rare Earths* **33** 86
- [3] Wong P S, Wan M H, Hussin R, Lintang H O and Endud S 2014 Structural and luminescence studies of europium ions in lithium aluminium borophosphate glasses *Journal of Rare Earths* **32** 585
- [4] Miao Y, Yaohui L, Jiaan L and Song Y 2014 Corrosion and mechanical properties of AM50 magnesium alloy after being modified by 1 wt.% rare earth element gadolinium *Journal of Rare Earths* **32** 558
- [5] Janos P, Kuran P, Kormunda M, Stengl V, Grygar T M, Dosek M, Stastny M, Ederer J, Pilarova V and Vrtoch L 2014 Cerium dioxide as a new reactive sorbent for fast degradation of parathion methyl and some other organophosphates *Journal of Rare Earths* **32** 360
- [6] Balachandran G 2014 Extraction of Rare Earths for Advanced Applications *Treatise on Process Metallurgy* **3** 1291
- [7] Visseaux M and Bonnet F 2011 Borohydride complex of rare earths, and their applications in various organic transformations *Coordination Chemistry Reviews* **255** 374
- [8] Guanming Q, Xikum L, Tai Q., Haitao Z, Honghao Y and Ruiting M 2007 Application of Rare Earths in Advanced Ceramic Materials *Journal of Rare Earths* **25** 281
- [9] Cao X 2007 Application of rare earths in thermal barrier coating materials *Journal of Materials Science and Technology* **23** 15
- [10] Goonan T G 2011 *Rare earth elements – End use and recyclability* (Virginia: U.S. Geological Survey)
- [11] Srinivasan R, Yogamalar N R, Elanchezhyan J, Joseyphus R J and Bose A C 2010 Structural and optical properties of europium doped yttrium oxide nanoparticles for phosphor applications *Journal of Alloys and Compounds* **496** 472
- [12] Ahmad H, Thambiratnam K, Paul M C, Zulkifli A Z, Ghani Z A and Harun S W 2012 Fabrication and application of zirconia-erbium doped fibers *Optical materials express* **2** 1690
- [13] Egorov N B, Djyachenko A N, Akimov D V, Kiselyov A D, Obmuch K V and Chalov S A 2014 Influence of adding ammonium bifluoride when leaching monazite using sulphur acid *Procedia Chemistry* **10** 168
- [14] Karve M and Vaidya B 2008 Selective Separation of Scandium (III) and Yttrium (III) from other Rare Earth Elements using Cyanex302 as an Extractant *Separation Science and Technology* **43** 1111
- [15] Kim J S, Kuman N, Lee J Y, Kantam M L and Reddy B R 2012 Separation and recovery of Light Rare-Earths from Chloride solutions using Organophosphorus based Extractants *Separation Science and technology* **47** 1644
- [16] Liao Ch, Wu Sh, Cheng F, Wang S, Liu Y, Zhang B and Yan C 2013 Clean separation technologies of rare earth resources in China *Journal of Rare Earths* **31** 331
- [17] Pfann W G 1967 *Zone melting* (New York: John Wiley & Sons)
- [18] Valtsev K V, Avvakumov K V and Pyref M F 1961 Distribution of lanthanides in the melt of ammonium nitrate during the process of zone recrystallization *Bulletin of Siberian Branch of the USSR Academy of Sciences* **6** 71
- [19] Valtsev K V, Oziashvili E D and Solovev L K 1962 The process of zone recrystallization of compounds of rare-earth elements from some of molten salts *Bulletin of Siberian Branch of the USSR Academy of Sciences* **2** 53
- [20] Valtsev K V, Avvakumov K V, Pyrev M F and Kravchenko L Ch 1963 Separation of lanthanides in ammonium nitrate using the process of zone recrystallization *Bulletin of Siberian Branch of the USSR Academy of Sciences* **3** 152
- [21] Ryabchikov D I and Pyabuchin V A 1966 *Analytical chemistry of rare earth elements and yttrium* (Moscow: Nauka)

- [22] Mioduski T, Guminski C and Zeng D 2009 IUPAC-NIST Solubility Data Series 87 Rare Earth Metal Chlorides in Water and Aqueous Systems Part 2 Light Lanthanides (Ce–Eu) *Journal of Physical and Chemical Reference Data* **2** 441
- [23] Mioduski T, Guminski C and Zeng D 2009 IUPAC-NIST Solubility Data Series 87 Rare Earth Metal Chlorides in Water and Aqueous Systems Part 3 Heavy Lanthanides (Gd–Lu) *Journal of Physical and Chemical Reference Data* **4** 925
- [24] Mioduski T, Guminski C and Zeng D 2008 IUPAC-NIST Solubility Data Series 87 Rare Earth Metal Chlorides in Water and Aqueous Systems Part 1 Scandium Group (Sc, Y, La) *Journal of Physical and Chemical Reference Data* **4** 1765
- [25] Wilson L 1978 On interpreting a quantity in the Burton, Prim and Slitchter equation as a diffusion boundary layer thickness *Journal of Crystal Growth* **44** 274
- [26] Krestov G A, Novoselov N P, Perelygin I S, Kolker A M, Safonova L P, Ovchinnikova V D and Trostin V N 1987 *Ion solvation* (Moscow: Nauka)
- [27] Turaev N S and Gerin I I 2006 *Chemistry and technology of uranium* (Moscow: Ore and Metals)