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SEPARATION OF HO³⁺ IN STATIC MAGNETIC FIELD

The rare earths elements (REE) belong to the group of critical metals and they are achieving more and more interest due to their special properties. However, there occur some problems connected with their production. The most difficult phase is separation of REE. It includes a necessity to intensify currently applied processes and looking for new solutions.

The present work introduces an idea to use differences in physical properties of the REE ions to get them separated. In the experimental part of the work some efforts were undertaken to analyse results presenting changes of holmium ions concentration under an influence of the magnetic field gradient. There was determined the gradient of magnetic field and concentration of Ho^{3+} ions depending on initial concentration of the solution and time. A simulation of changing the concentration of holmium ions in the solution under an influence of the magnetic field gradient was performed to compare the mathematical model with the obtained results.

Keywords: rare earth metals, REE, recycling, separation, magnetic field

1. Introduction

The rare earths elements (REE) belong to the group of metals which, due to their special properties, are wider and wider applied in new technologies, among others, in motorisation, electronic, aviation and space industries [1].

The largest producer of the rare earths metals and their compounds is China. Currently, this country features the highest world stock (39-42 %), and the highest production of REE (more than 90%) [2]. Therefore, prices of the metals are strongly dependant on the policy of the country. It creates a necessity to intensify presently known methods of the rare earths metals production, mainly from secondary sources that are accessible in many countries including Poland [1].

Recycling is a good solution to the problem connected with storage of waste like electronic one, used fluorescent lamps [3,4], power plant ashes and phosphorus slags [5]. The materials are often hazardous to the environment. Moreover, recovery of metals is generally much more profitable than production from primary sources.

Currently, the rare earths metals are obtained, among others, through hydrometallurgical processes which are often complicated and time-consuming, and as a result, highly expensive. The most difficult phase is separation of the REE ions into individual metals.

Commonly applied methods rely on subtle differences in chemical properties of individual ions. They include methods like: fractional crystallization, fractional precipitation, ion exchange chromatography, solvent liquid-liquid extraction [6,7]. All the methods are used in the processes of obtaining the rare earths metals from primary sources and their recovery from secondary sources.

The producers' requirements concerning application of metals of the highest purity generate necessity to intensify and modernize the methods of recovery and separation that are currently applied. New solutions will contribute to lowering prices of the metals and increasing their accessibility. Limitation of processes based on ion liquids will positively affect the natural environment.

The REE ions can be divided into para- and diamagnetic ones depending on the atomic number and most ions at the third degree of oxidation feature strong paramagnetic properties.

Electron configuration as the lanthanide elements f-electron is as follows: $4f^{1\text{-}14}5d^{0,1}6s^2$. The phenomenon of paramagnetism is connected with occurrence of unpaired electrons on valence shell 4f, therefore ions of lanthanum, lutetium, scandium and yttrium of closed shells are diamagnetic. Moreover, magnetic moment depends on the resultant spin moment and resultant orbital moment of the unpaired electrons 4f.
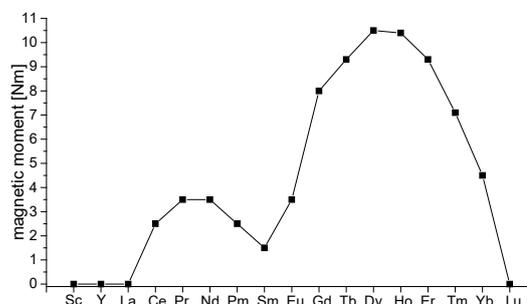

Fig. 1. Magnetic moment of REE³⁺ ions [8]

The present work suggests application of physical

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properties of the rare earths ions (magnetic moment, Fig. 1) in order to intensify processes of their separation in aqueous solutions.

The first works analysing possibilities of the REE ions separations in a heterogeneous magnetic field were undertaken in the 50s in 20th century by Noddack et al. [8-10], however, due to technical limitations it was not possible to continue studies over the issue. Separation of ions in a magnetic field is known in the group of transition metals, whereas enrichment of areas of liquid with the REE ions was determined mainly for individual elements.

Yang et al. worked over magnetic separation of paramagnetic ions of transition metals (Mn^{2+}, Cu^{2+}) [11]. As a result of the researches it was found out that the most efficient separation was obtained in a solution of the highest concentration of manganese (1 M $MnSO_4$), where the concentration change reached 5 mM after the period of about 1000 s. Moreover, it was observed that the process can take place only in a certain type of a magnetic field, namely, the field gradient is necessary to realise the process.

Pulko et al. conducted separation of Dy^{3+} ions in a magnetic field as the REE group ion of the highest value of the magnetic moment [12]. The experiments involved applying solutions of concentrations 0.1, 0.5 and 1 M obtained by dissolving $DyCl_3$ salt in distilled water. A neodymium magnet placed above the quartz cuvette had an influence on changes of ions concentrations in the upper part of the measuring vessel. After more than 2000 s a change of concentration by 6 mM was obtained.

2. Experimental

During realization of the research work some aqueous solutions of holmium (III) were used. The element was chosen due to its high value of the magnetic moment from among the REE ions at +3 degree of oxidation. Moreover, the solution of the metal ions is colourful which enables a possibility to analyse it with the spectrophotometric method UV-Vis. The solutions were prepared by dissolving 2.7 g $HoCl_3$ (Sigma Aldrich) with addition of 2 cm^3 HCl 35-38 % analytical purity (POCH S.A.) and supplementing with distilled water to the volume of 10 cm^3. The pH value of the obtained solution was 1, and subsequent solutions were obtained by dilution to the desired concentration of Ho^{3+} ions so the ratio of the amount of Ho^{3+} ions to Cl^- was always the same. All the experiments were conducted in room temperature.

Obtaining the gradient of paramagnetic ions can occur only when the applied magnetic field is non-homogeneous in the solution volume. The magnetic field can be obtained through electromagnets or permanent magnets. In this case it was decided to use permanent neodymium magnets (Ne-Fe-B).

The solutions were placed in quartz cuvettes of 4.5 cm^3 volume (dimensions: 10x10x45 mm) designed for the spectrophotometric analysis UV-Vis. The cuvettes were put into the magnetic field generated by permanent neodymium magnets of dimensions: diameter – 22 mm, height – 10 mm.

The measurement system containing the magnets and the cuvette with solution was placed directly in the spectrophotometer UV-Vis Jasco V-760. The ions concentration in the lower part of the cuvette located closer to the magnets surface (Fig. 2a) was examined. Such a solution allowed the measurement directly during conducting the experiments. The system was chosen because the unwanted vibrations of the cuvette and thus mixing of the solution could be eliminated.

The magnetic field gradient in the analysed system was defined with the use of the Maxwell SV software [13] (Fig. 2b).
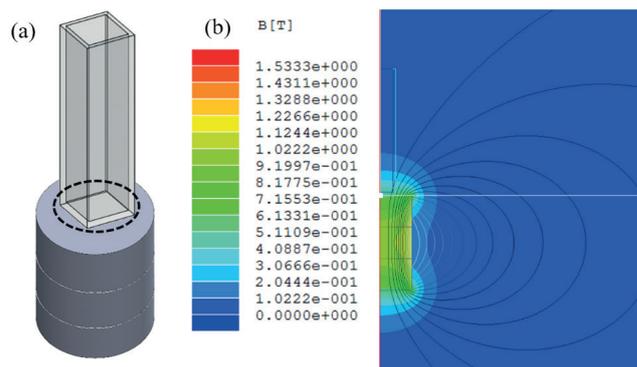

Fig. 2. a) Location of the stationary magnets in relation to the examined solutions and part of solution for analysis in spectrophotometer UV-Vis, b) the intensity of magnetic field depending on the distance from the magnets

3. Results and discussion

The first step was to create a calibration curve to determine the molar absorption coefficient of Ho^{3+} ions which is a characteristic value for a given ion and is essential for concentration assessment. Measurements were done for solutions of known concentrations of the analysed ions, and next the values of absorbance maximum in the highest peaks of the obtained curves depending on the concentrations were determined (Fig. 3 a and b). The direction coefficient of the obtained function of absorbance maximum from concentration is a searched value of the molar absorption coefficient (Fig. 4).
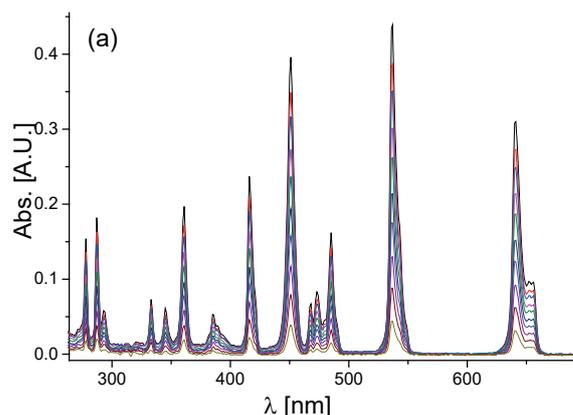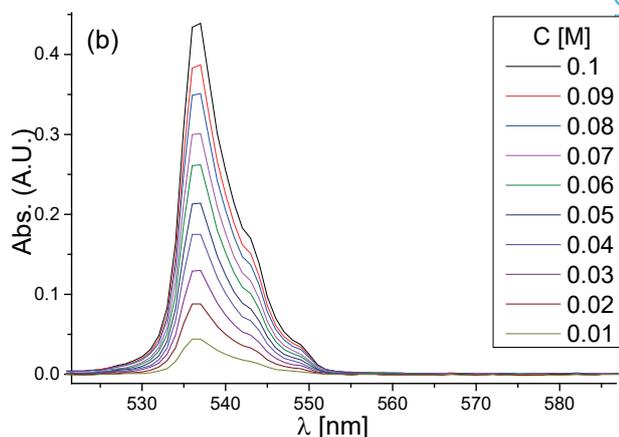
Fig. 3. (a) UV-Vis curves of Ho³⁺ ions; (b) change of height of peaks in maximum (wavelength 537 mm)
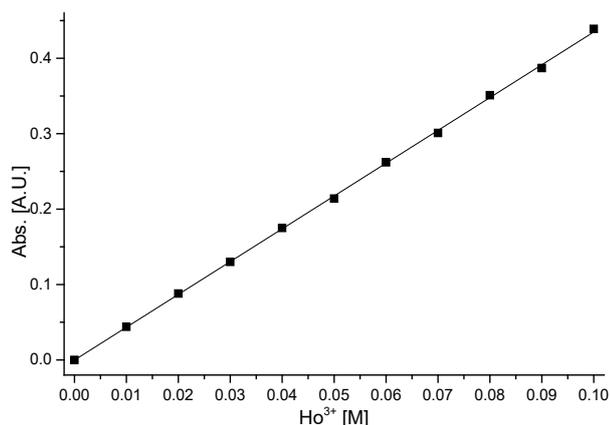

Fig. 4. Determination of molar absorbance coefficient of Ho³⁺ ions using graphical method

The performed measurements led to determining the value of the holmium molar coefficient at 4.35 ± 0.03 [dm³·mol⁻¹·cm⁻¹].

Efficiency of the method was analysed by measurement of the Ho³⁺ions concentration in the time function. The measurement was done for the solution in the lower part of the cuvette. The point of reference in the initial time (t=0) was accepted as 100%. The change of Ho³⁺ ions concentration was defined through the relation:

$$\Delta C = (C_t/C_0) \cdot 100\% \tag{1}$$

where ΔC – change of concentration, C_0 – ions concentration in the initial time, C_t – concentration after a certain time.

On the basis of the Lambert-Beer Law the concentration of ions was determined depending on the absorbance in the maximum of the highest peak:

$$C = A_\lambda /(\varepsilon_\lambda \cdot l) \tag{2}$$

where A_λ is a value of absorbance in the peak maximum (for $\lambda = 537$ nm), ε_λ – molar absorption coefficient of holmium ions, determined in the first part of the experimental work, l – thickness of the absorption layer (10 mm).

The measurements of the change in concentration of Ho³⁺ ions took place within 120 minutes. Fig. 5 presents kinetic curves showing a percentage change of Ho³⁺ ions concentration in the time function.

Individual experiments were held at room temperature. Due to the use of permanent magnets instead of the electromagnet, cooling system was not used, so it can be concluded that the temperature is constant.
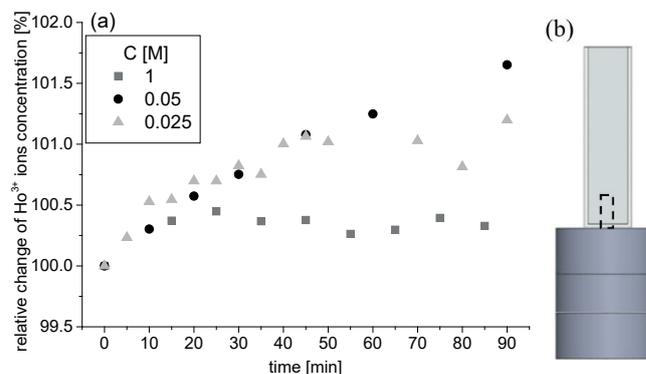

Fig. 5 (a) Change of Ho³⁺ ions concentration in time in solution of concentration 1, 0.05 and 0.025 M; (b) scheme of experimental set with selected part for measurement of concentration

The conducted experiments resulted in obtaining a local concentration of the solutions. The concentration increase was from 0.5 to 2 % depending on initial concentration of the solution (Fig. 5).

A change of concentration in the lower part of the solution proceeds until plateau is achieved both for diluted and concentrated solutions. The plateau was connected with settling a dynamic balance inside the solution between attracting the ions by the magnetic field and diffusion. In case of solutions of higher concentration, plateau is achieved faster, after about 25 min, but enrichment is lower in comparison to diluted solutions where plateau is achieved after two times longer period of time (50 min), on average.

The research work included the use of both concentrated (1 M) and diluted (0.05 and 0.025 M) solutions. However, it should be emphasized that industrial processes take place in diluted solutions. Concentration of the ions depends on the applied input material and technology.

4. Theory section

Additionally, a simulation of changing the concentration of holmium ions in the cuvette axis of symmetry in the analysed solutions was performed. The calculations included values of the magnetic field concentration obtained through the Maxwell SV software.

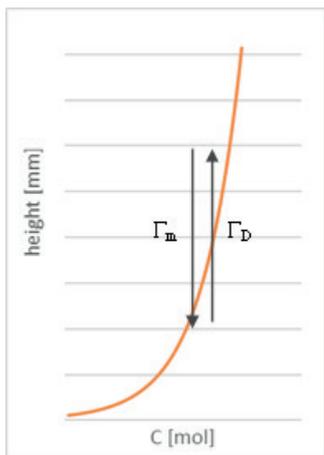The calculations were performed for holmium ions in the state of plasma.

Fig. 6. Schematic change of concentration of ions along height of cuvette

The basis for the calculation of the concentration of the ion in magnetic field is the equation of atomic flux acting on the ions: generated by magnetic field and diffusion.

$$\bar{\Gamma}_m + \bar{\Gamma}_D = 0 \qquad (3)$$

The first flux is generated by magnetic field:

$$\bar{\Gamma}_m = n_i < \bar{v} > \qquad (4)$$

where: $\bar{\Gamma}_m$ – atomic flux generated by magnetic field, n_i – number of ions, $< \bar{v} >$ – velocity component of the incoming atoms normal to the magnet

$$< \bar{v} > = \frac{\mu \cdot \bar{F}}{q} \qquad (5)$$

μ – magnetic mobility [kg·s^{-1}], $\bar{F}$ – magnetic force, k – Boltzmann's constant k = 1.38064852·10^{-23} m^2·kg·s^{-2}·K^{-1}, q – electrical charge of particles

During movement of ions generated by magnetic field, gradient of concentration is increasing. Due to the change of concentration, its gradient is a driving force of diffusion.

$$\bar{\Gamma}_D = -D \nabla n_i \qquad (6)$$

$\bar{\Gamma}_D$ – atomic flux generated by diffusion, D – diffusion constant

Comparing the transport of ions generated by the magnetic field and diffusion is replaced by the following relationship:

$$D \nabla n_i = n_i \frac{\mu \cdot \bar{F}}{q} \qquad (7)$$

Using Einstein's relationship defining the diffusion constant can be determined:

$$D = \frac{\mu \cdot k_B \cdot T}{q} \rightarrow \frac{\mu}{q \cdot D} = \frac{1}{k_B \cdot T} \qquad (8)$$

T – temperature [K]

while the strength of the magnetic field is determined by:

$$\bar{F} = \bar{m} \cdot \nabla \bar{B} \qquad (9)$$

$\bar{m}$ – magnetic moment, $\bar{B}$ – magnetic field

and:

$$\frac{\nabla n_i}{n_i} = \frac{\mu}{q \cdot D} \cdot \bar{F} = \bar{F} \cdot \frac{1}{k_B \cdot T} = \frac{\bar{B}}{B} \cdot m \cdot \nabla B \cdot \frac{1}{k_B \cdot T} \qquad (10)$$

$$\frac{d}{dx} [\ln(n_i)] = \frac{m}{k_B \cdot T \cdot B} \nabla (\frac{1}{2} B^2) \qquad (11)$$

$$\ln(n_i) = \int \frac{m}{k_B \cdot T \cdot B} \nabla \left(\frac{1}{2} B^2\right) dx + C \qquad (12)$$

The calculation obtained the following relationship:

$$n_i(x) = n_\infty \exp[\frac{m}{-kT} \int \frac{1}{B} \nabla \left(\frac{1}{2} B^2\right) dx] \qquad (13)$$

$n_i(x)$ – function of number of ions in height of cuvette [-], $n\infty$ – the number of ions at an infinite distance [-], m – magnetic moment of holmium ions m = 11.2 N·m, k – Boltzmann's constant k = 1.38064852·10^{-23} m^2·kg·s^{-2}·K^{-1}, T – temperature T = 298 K, B – magnetic field [T]

Using the finite element method (trapezoidal method) concentration of holmium ions along the axis of symmetry of cuvettes was calculated.

The conducted calculations resulted in obtaining distribution of holmium ions concentration and enrichment along the cuvette height in its axis of symmetry.
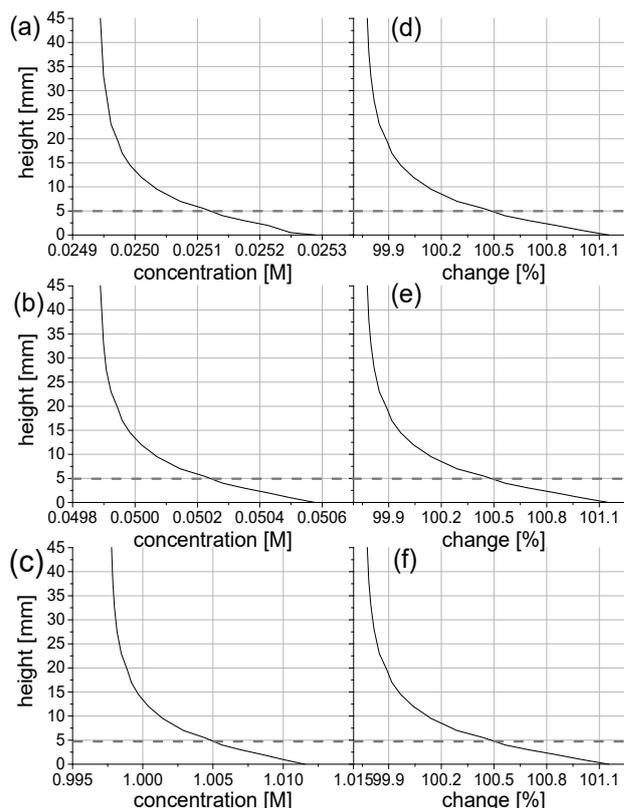

Fig. 7. Concentration of Ho^{3+} ions along axis of symetry of cuvettes for the solution of the initial concentration (a) 0.025 M, (b) 0.050 M, (c) 1 M; change of concentration along axis of symetry of cuvettes for the solution of the initial concentration (d) 0.025 M (e) 0.050 M, (f) 1 M

The above presented diagrams (Fig. 7) show that the concentration change is the same for all cases regardless of the initial concentration. The highest concentration was found

in the layer of liquid placed the closest to the magnets surface where the field gradient was the highest.

In order to compare values of the obtained enrichment there were selected values of changes in holmium ions concentration in a point 5 mm away from the magnet surface – it is a similar area in which the solution was analysed with the UV-Vis method. The results of the obtained enrichment after the longest time – 90 min were selected from the experimental part.

TABLE 1

Local enrichment of holmium ions

C_0 [M]	enrichment [%]	
	calculated	experimental
0.025	0.441	1.199
0.05	0.441	1.652
1	0.441	0.328

While comparing the obtained results, it can be stated that in case of theoretical calculations, the initial concentration of the solution does not influence the value of enrichment. Whereas, the results obtained in the experimental part allowed to achieve more effective concentration and the highest increase of holmium ions concentration was obtained for concentration of 0.05 M, and the lowest for 1 M.

The difference is likely to result from the density and viscosity differences of holmium solutions which were not taken into account in the mathematical model. Moreover, the difference between the size of a simple ion and the complex one was not defined.

5. Conclusions

The present work includes preliminary results of tests performed to analyse an influence of the magnetic field on transportation of the REE ions within the volume of solutions. The innovative character of the research relies on separation of the REE ions using their physical, not chemical properties. The rare earths metals ions are divided into para- and diamagnetic ones.

The solutions of holmium(III) were used in the work due to their very strong magnetic properties featured by their ions in comparison to other rare earths metals. The magnetic field was generated by a set of neodymium magnets.

There are differences between results obtained in concentrated and dilutes solutions. Namely, in high concentrated solution (1 M) local concentration increased to 100.5 % compared to initial concentration, plateau was achieved after about 25 min. In lower concentration solutions value of local enrichment reached about 2 % after longer time – about 50 minutes.

The results obtained during the experimental phase were compared with the calculations of changes in holmium ions in the cuvette volume under an influence of the magnetic field gradient. The enrichment values obtained through calculations and experiments do not fully overlap.

The calculations presented the same enrichment values along the cuvette axis, regardless of the initial concentration of the solution.

The calculations did not take into account the ions sizes. The complex ion of holmium features higher volume than an ion in a form of simple salt, therefore it is necessary to apply stronger magnetic field for efficient separation of ions.

The calculations were performed assuming that holmium ions are placed in the plasma environment. However, the realised calculations do not allow to approximate how the magnetic field gradient influences the ions transportation.

REFERENCES

[1] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, S. J Clean Prod **51**, 1-22 (2013).

[2] S. Massari, M. Ruberti, Resour Policy **38**, 36-34, (2013).

[3] C. Tunsu, M. Petranikova, C. Ekberg, T. Retegan, Sep Purif Technol (2016), DOI: http://dx.doi.org/10.1016/j.seppur.2016.01.048 (in press).

[4] K. Binnemans, P.T. Jones, J Rare Earth, **32** (3), 195-200 (2014)

[5] Z. Karshigina, Z. Abisheva, Y. Bochevskaya, A. Akcil, E. Sargelova, S. Trasatti, Miner Eng **77**, 159–166 (2015).

[6] P.K. Parhi, K.H. Park, C.W. Nam, J.T. Park, J Rare Earth **33** (2), 207-213 (2015).

[7] N. Panda, N. Devi, S. Mishra, J Rare Earth **30** (8), 794-797, (2012).

[8] W. Noddack, I. Noddack, E. Wicht, Z Elektrochem **62**, 77-85 (1958).

[9] W. Noddack, I. Noddack, E. Wicht, Z Elektrochem **56**, 893-895 (1952).

[10] I. Noddack, E. Wicht, Chem Tech-Leipzig **7**, 3-5 (1955).

[11] X. Yang, K. Tschulik, M. Uhlemann, S. Odenbach, K. Eckert, Ieee T Magn **50** (11), 4600804 (2014).

[12] B. Pulko, X. Yang, Z. Lei, S. Odenbach, K. Eckert, Appl Phys Lett **105**, 232407 (2014).

[13] http://maxwell-sv.software.informer.com/