

# Separation of similar elements and isotopes separation in non-stationary conditions

A.A. Kopyrin<sup>a</sup>, M.A. Afonin<sup>a,\*</sup>, T. Todd<sup>b</sup>

<sup>a</sup> Saint-Petersburg Institute of Technology, 26 Moskovsky av., 190013 Saint-Petersburg, Russia

<sup>b</sup> Idaho National Laboratory, Idaho Falls, ID 83415, USA

Received 29 June 2006; received in revised form 10 April 2007; accepted 11 April 2007

Available online 21 April 2007

## Abstract

The new separation extraction method was created based on oscillatory extraction/stripping process in two extractors coupled by bulk liquid membrane (LM). The experimental set-up to investigate the kinetics of non-stationary processes was built in Saint Petersburg State Institute of Technology at Rare Earth Department. To induce the oscillatory extraction–stripping process the cyclic Belousov–Zhabotinsky (BZ) reaction or cyclic electrochemical oxidation–reduction was used. The experimental evidences of cerium and neodymium isotopes separation were obtained. The separation of <sup>142</sup>Ce and <sup>140</sup>Ce isotopes between aqueous phases of two extractors coupled by bulk LM in the experiments with cyclic chemical oxidation/reduction with enrichment factor about 2.5% was observed. In the same conditions the separation of the Nd isotopes (heavy isotopes of Nd: <sup>144</sup>Nd, <sup>145</sup>Nd, <sup>146</sup>Nd, <sup>148</sup>Nd and <sup>150</sup>Nd from the light isotope: <sup>143</sup>Nd) in the same experiment with enrichment factor about 0.7–1.4% was observed.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Rare earth; Kinetics; Isotope separation

## 1. Introduction

The possibility to increase the elements separation by oscillatory non-equilibrium methods of extraction was shown in [1–3]. In the last few years, the attention of experts has been directed to a membrane extraction processes in which stages of extraction and stripping are going on simultaneously in a system that consisted of three liquid phases. This high performance and economic process provides complete, and in some cases selective extraction of target compounds from water solutions, sewage and biological liquids, and also a significant concentrating effect of the resulting solution in comparison with traditional solvent extraction [4].

## 2. Experimental

The principal scheme of the experimental set-up is shown on the Fig. 1. To induce the extraction/stripping process the BZ reaction was used. Two extractors were coupled by loop of bulk LM (0.25 M TBP (Fig. 2) or 0.5 M TBP (Fig. 3)

in tetradecane). In aqueous phases in both extractors the solutions of 0.039 M Nd(NO<sub>3</sub>)<sub>3</sub> and 0.039 M Pr(NO<sub>3</sub>)<sub>3</sub>, 0.1 M Ce(NO<sub>3</sub>)<sub>3</sub> in 6 M NaNO<sub>3</sub> in presence of 0.35 M potassium bromate and 0.35 M malonic acid were used. Continuous flow stirred tank reactor (CSTR) mode of operation was investigated. In this mode the reagents were continuously fed (flow rate of aqueous phases was 0.9 ml/min) to the aqueous phase of extractors and the aqueous phases were continuously pumped from the extractors with the same flow rate. During all experiment the equal volume of aqueous phases in both reactors was maintained equal to 60 ml, total volume of organic phase was equal to 60 ml, the ratio of organic phase to aqueous phase was 1:2. Every 5–7 min the aqueous samples (5–7 ml) have been taken from both extractors to measure metals concentration. The UV–vis spectra of the LM had been measured on-line by diode-array spectrophotometer SF-2000-01 every 7–10 s. The red/ox potential in both extractors was measured during all experiment with frequency 20 Hz. The composition of cerium isotopes was measured using MI-1201 apparatus by thermo ionizing mass-spectrometry method (TIMS). The concentrations of HNO<sub>3</sub> in the extractors were different (on the Figs. 2 and 3. 0.1 M HNO<sub>3</sub>, left extractor; 0.3 M HNO<sub>3</sub>, right extractor) to maintain different frequencies of oscillatory reactions in the extractors. Organic phase was continuously fed from the left extractor to the right extractor and back with constant flow rate: flow rate = 6 ml/min on the Fig. 2, and flow rate = 9 ml/min on the Fig. 3.

### 2.1. Mass-spectroscopy measuring of samples

Measuring was conducted on mass spectrometer MI1201 with usage three-tape (Re) thermo ionic source. The isotope separation factor  $\alpha$  and

\* Corresponding author. Tel.: +7 8123627813; fax: +7 8127127791.

E-mail address: afonin1@lti-gti.ru (M.A. Afonin).

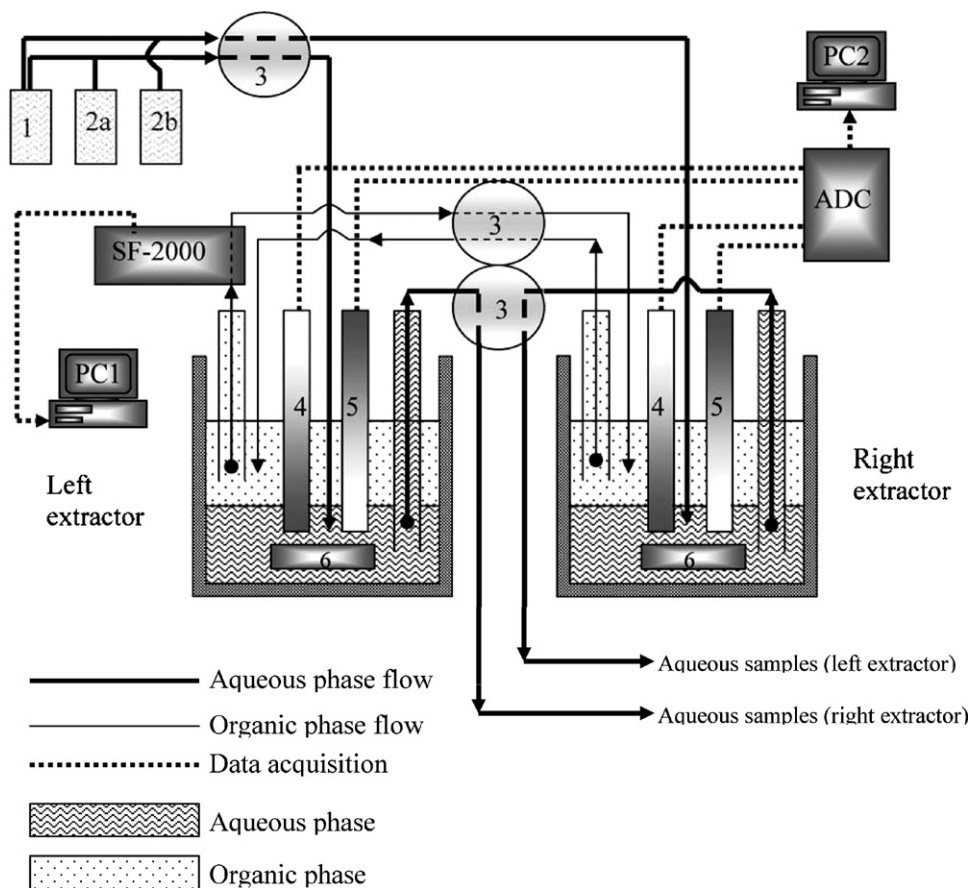


Fig. 1. The principal scheme of CSTR with LM set-up 1, 2a, 2b: vessels with initial solutions, 3: peristaltic pump, 4: Pt electrode, 5: reference electrode, 6: magnetic stirrer, ADC: analogue-digital converter, PC1 and PC2: personal computers, SF2000: spectrophotometer.

enrichment factor  $\varepsilon$  are calculated on the basis of the measurements average values of ratios  $^{142}\text{Ce}/^{140}\text{Ce}$  in different measurement conditions (scale mode a or b). The isotope separation factor  $\alpha$  was determined as follows:  $\alpha = (^{142}\text{Ce}/^{140}\text{Ce})_{\text{R}} / (^{142}\text{Ce}/^{140}\text{Ce})_{\text{L}}$ , where  $(^{142}\text{Ce}/^{140}\text{Ce})_{\text{R}}$  and  $(^{142}\text{Ce}/^{140}\text{Ce})_{\text{L}}$  the average ratios of isotopes in the series of samples R (aqueous phase of the right extractor) and L (aqueous phase of the left extractor), accordingly. The enrichment factor  $\varepsilon$  was determined as  $\varepsilon = (\alpha - 1)/\alpha$ . Errors of the obtained factors are given for the confidence interval 0.68 ( $1\sigma$ ).

### 3. Results and discussion

The results of the experiment with 0.25 M TBP in tetradecane and flow rate of LM equal to 6 ml/min are shown in the Table 1. Left extractor was enriched by  $^{140}\text{Ce}$  isotope and right extractor was enriched by  $^{142}\text{Ce}$  isotope. The results of the experiment with 0.5 M TBP in tetradecane and flow rate of LM equal to 9 ml/min are shown in the Table 2. Left extractor was enriched by  $^{142}\text{Ce}$  isotope and right extractor was enriched by  $^{140}\text{Ce}$

isotope. The same investigations were made for Nd isotopes separation. The results of the experiment with 0.25 M TBP in tetradecane and flow rate of LM equal to 6 ml/min are shown in the Table 3. In this case  $\alpha$  was calculated by the following formulae  $\alpha = (^{144}\text{Nd}/^{143}\text{Nd})_{\text{R}} / (^{144}\text{Nd}/^{143}\text{Nd})_{\text{L}}$  (the average ratio of heavy (Nd) isotope to  $^{143}\text{Nd}$  isotope in the series of sample R – aqueous phase of the right extractor to the same average ratio in the series of sample L – aqueous phase of the left extractor). Left extractor was enriched by heavy isotopes of Nd ( $^{144}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{146}\text{Nd}$ ,  $^{148}\text{Nd}$ ,  $^{150}\text{Nd}$ ) isotope and right extractor was enriched by light  $^{143}\text{Nd}$  isotope.

The possible basic reasons of isotope separation results are following. The difference on isotopes' properties in the kinetic of extraction and complexation in aqueous phase and the difference of oxidation/reduction potential of different isotopes are the main reasons of isotopes separation. The electron binding energy of  $^{142}\text{Ce}$  must be higher than the electron binding energy

Table 1  
Separation factor  $\alpha$  and isotope enrichment factor  $\varepsilon$  for  $^{142}\text{Ce}/^{140}\text{Ce}$  isotope separation for the experiment with 0.25 M TBP in tetradecane and flow rate of LM equal to 6 ml/min

Scales ratio	$\alpha$	$\varepsilon$
15V/15V	$1.0256 \pm 0.0100$	$0.0250 \pm 0.0003$
15V/5V	$1.0121 \pm 0.0100$	$0.0120 \pm 0.0001$

Table 2  
Separation factor  $\alpha$  and isotope enrichment factor  $\varepsilon$  for  $^{142}\text{Ce}/^{140}\text{Ce}$  isotope separation for the experiment with 0.5 M TBP in tetradecane and flow rate of LM equal to 9 ml/min

Scales ratio	$\alpha$	$\varepsilon$
15V/15V	$0.9775 \pm 0.0110$	$-0.0230 \pm 0.0002$
15V/5V	$0.9823 \pm 0.0065$	$-0.0180 \pm 0.0001$

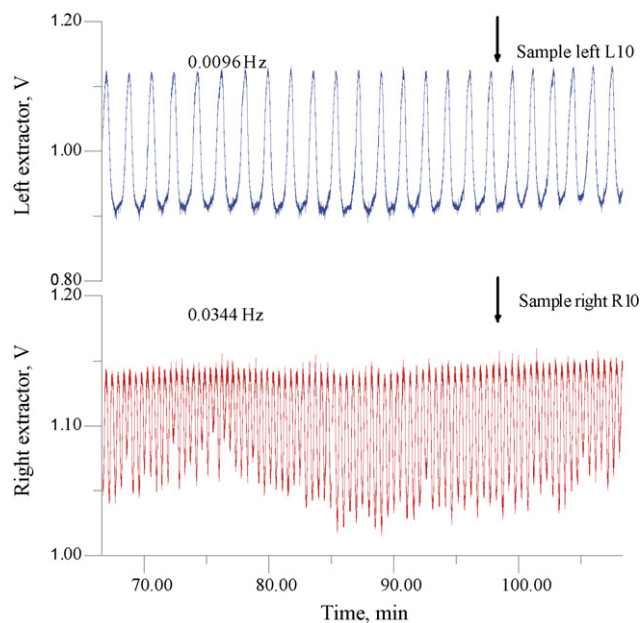


Fig. 2. Temporal red/ox potential dependencies in oscillatory extraction system with bulk LM. Composition of the solutions: Aqueous phase in the left and in the right extractors: 0.039 M  $\text{Nd}(\text{NO}_3)_3$ , 0.039 M  $\text{Pr}(\text{NO}_3)_3$ , 0.1 M  $\text{Ce}(\text{NO}_3)_3$ , 0.35 M  $\text{KBrO}_3$ , 0.35 M malonic acid, 6 M  $\text{NaNO}_3$ , 0.05 M  $\text{HNO}_3$ : left extractor, 0.15 M  $\text{HNO}_3$ : right extractor. LM (organic phase): 0.25 M TBP in tetradecane. LM flow rate = 6 ml/min. red/ox frequencies: left extractor, 0.0096 Hz; right extractor, 0.0344 Hz. The samples have been taken from the aqueous phases in the time shown on the figure by arrows.

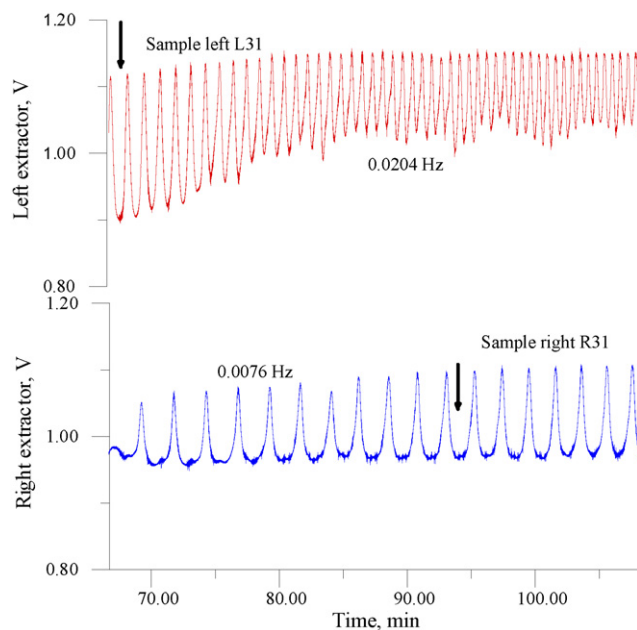


Fig. 3. Temporal red/ox potential dependencies in oscillatory extraction system with bulk LM. Composition of the solutions: Aqueous phase in the left and in the right extractors: 0.039 M  $\text{Nd}(\text{NO}_3)_3$ , 0.039 M  $\text{Pr}(\text{NO}_3)_3$ , 0.1 M  $\text{Ce}(\text{NO}_3)_3$ , 0.35 M  $\text{KBrO}_3$ , 0.35 M malonic acid, 6 M  $\text{NaNO}_3$ , 0.05 M  $\text{HNO}_3$ : left extractor, 0.15 M  $\text{HNO}_3$ : right extractor. LM (organic phase): 0.5 M TBP in tetradecane. LM flow rate = 9 ml/min. red/ox frequencies: left extractor: 0.0076 Hz, right extractor: 0.0204 Hz. The samples have been taken from the aqueous phases in the time shown on the figure by arrows.

of  $^{140}\text{Ce}$  because the Rydberg coefficient  $R_i$  depends on effective mass of atom as follows:

$$R_i = \frac{2\pi^2 m_e e^4}{(1 + (m_e/M_i))ch^3},$$

where  $m_e$  is the electron mass,  $e$  the electron charge,  $M_i$  the nucleus mass,  $c$  the light speed,  $h$  the Planck's constant. The binding energy is in proportion to  $R_i$ . The higher the isotope mass the higher the binding energy. The isotope with higher mass will be reduced more easily than light isotope and it will be oxidized less easily than the light isotope.

Analysis of isotopic separation could be performed on this step of investigation qualitatively. The main difference between experimental conditions of the experiments presented on the Fig. 2 and on the Fig. 3 is the relationship between red/ox frequencies in aqueous phases in the left and in the right extractors.

Sample R10 (Fig. 2) had been taken from aqueous phase of right extractor where the red/ox potential frequency was higher than in the left extractor. In the sample R10 there is enrichment of cerium composition by  $\text{Ce}^{142}$  isotope.

Sample L31 (Fig. 3) had been taken from aqueous phase of left extractor where the red/ox potential frequency was higher than in the right extractor. In the sample L31 there is also enrichment of cerium composition by  $\text{Ce}^{142}$  isotope.

As a very preliminary hypothesis we can suggest that the heaviest isotope of Ce preferentially stays in the media with higher red/ox potential frequency. This hypothesis should be checked in further investigation. The possible basis for the Nd isotope separation is the following: During BZ reaction the concentration of "free" TBP in organic phase is changing periodically because the ratio of cerium 4 to the cerium 3 in the aqueous and in organic phases is changing. Because of TBP concentration

Table 3  
Separation factor  $\alpha$  and isotope enrichment factor  $\varepsilon$  for Nd isotopes separation for the experiment with 0.25 M TBP in tetradecane and flow rate of LM equal to 6 ml/min

$\frac{\alpha_{R10/L10}}{\varepsilon_{R10/L10}}$	143	144	145	146	148	150
143	1	0.986 ± .005	0.990 ± .0035	0.991 ± .005	0.989 ± .004	0.993 ± .004
144	-0.014, -1.4%	1	1.003 ± .005	1.005 ± .005	1.004 ± .0055	1.009 ± .006
145	-0.010, -1.0%	0.003, 0.3%	1	1.001 ± .005	1.000 ± .0035	1.003 ± .004
146	-0.009, -0.9%	0.005, 0.5%	0.001, 0.1%	1	0.997 ± .0055	1.003 ± .006
148	-0.011, -1.1%	0.004, 0.4%	0	-0.003, 0.3%	1	1.003 ± .004
150	-0.007, -0.7%	0.009, 0.9%	0.003, 0.3%	0.003, 0.3%	0.003, 0.3%	1

changing the partition coefficients of metals (including isotopes of Nd) is changing. Unlike cerium, all isotopes of which are even-even nuclides (zero spin) the isotopes of neodymium 143, 145 have the spin  $7/2\hbar$ , i.e. these nuclides differ from even–even isotopes of this element. Therefore for neodymium the chemical properties modifications depend not only on the factor of weight, but also they depend on differences in structure of the electronic shells caused by the big difference in nuclear spins. The average concentration of light isotope in organic phase should be higher or lower than the average concentration of heavy isotope depending on the conditions. Because of the different frequencies of red–ox potentials in the left and in the right extractors the average concentrations of isotopes should be different in organic phase of both extractors. Liquid membrane is transporting organic phase from left extractor to the right extractor and back. The extraction/stripping process repeats continuously. The isotope composition of the aqueous phases in the left in the right extractor should be different also. The mathematical simulation of three-phase extraction system showed that changing of the concentration of extractant could change the direction of

enrichment and changing the flow rate of liquid membrane could change the magnitude of isotope separation factor  $\alpha$  [5].

### Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under grant RC0-20000-SC14 and RUC2-20011-ST-04 administered by the Civilian Research and Development Foundation.

### References

- [1] M.A. Afonin, et al., *J. Alloys Compd.* 374 (2004) 426.
- [2] M.A. Afonin, E.V. Komarov, *Doklady AN SSSR* 307 (1989) 388 (In Russian).
- [3] A.A. Kopyrin, A.A. Baulin, M.A. Afonin, *Radiochemistry* 47 (4) (2005) 387–391.
- [4] S.U. Ivakhno, E.V. Urtov, *Itogi Nauki I tekhniki. Ser. Neorg. Khimija* 18 (1990) 176 (in Russian).
- [5] A.A. Kopyrin, M.A. Afonin, A.A. Baulin, Recent Advances in Actinide Science. The Proceedings of the Eighth Actinides Conference, Actinides 2005, University of Manchester, UK on 4–8 July 2005, 2005, pp. 572–574.