

Physicochemical  
Problems  
of Mineral Processing  
43 (2009)

**Instructions for preparation of manuscripts**

It is recommended that the following guidelines be followed by the authors of the manuscripts:

- Original papers dealing with the principles of mineral processing and papers on technological aspects of mineral processing will be published in the journal which appears once a year
- The manuscript should be sent to the Editor for reviewing before February 15 each year
- The manuscript should be written in English. For publishing in other languages an approval of the editor is necessary
- Contributors whose first language is not the language of the manuscript are urged to have their manuscript competently edited prior to submission.
- The manuscript should not exceed 10 pages
- Two copies of the final manuscript along with an electronic version should be submitted for publication before April 15
- There is a 80 USD fee for printing the paper. No fee is required for the authors participating in the Annual Symposium on Physicochemical Problems on Mineral Processing
- Manuscripts and all correspondence regarding the symposium and journal should be sent to the editor.

**Address of the Editorial Office**

Wrocław University of Technology  
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland  
Institute of Mining Engineering  
Laboratory of Mineral Processing

**Location of the Editorial Office:**

pl. Teatralny 2, Wrocław, Poland  
phone: (071) 320 68 79, (071) 320 68 78  
fax: (071) 344 81 23

pawel.nowak <ncnowak@cyf-kr.edu.pl>

jan.drzymala@pwr.wroc.pl

andrzej.luszczkiewicz@pwr.wroc.pl

zygmunt.sadowski@pwr.wroc.pl

<http://www.ig.pwr.wroc.pl/minproc>

**Physicochemical Problems  
of Mineral Processing  
43 (2009)**

[www.ig.pwr.wroc.pl/minproc](http://www.ig.pwr.wroc.pl/minproc)

**Pawel Nowak** guest editor  
Institute of Catalysis and  
Surface Chemistry  
Polish Academy of Sciences, Kraków

WROCLAW 2009

*Editors of the journal*

Jan Drzymala-chief editor  
Andrzej Łuszczkiewicz  
Zygmunt Sadowski  
Paweł Nowak

*Editorial Board*

Ashraf Amer, Wiesław Blaschke, Marian Brożek, Stanisław Chibowski, Witold Charewicz, Tomasz Chmielewski, Beata Cwalina, Janusz Girczys, Andrzej Heim, Jan Hupka, Andrzej Krysztalkiewicz, Janusz Laskowski, Kazimierz Małysa, Paweł Nowak, Andrzej Pomianowski (honorary chairman), Stanisława Sanak-Rydlowska, Jerzy Sablik, Kazimierz Sztaba (chairman), Barbara Tora

*Reviewers*

Beata Cwalina, Tomasz Chmielewski, Jan Drzymala, Kazimierz Małysa, Władysława Mulak, Paweł Nowak, Wojciech Simka, Kazimierz Sztaba, Maria Zembala

*Technical assistance*

Danuta Szyszka

*The papers published in the Physicochemical Problems of Mineral Processing journal are abstracted in Chemical Abstracts, Thomson Reuters (Science Citation Index Expanded, Materials Science Citation Index, Journal Citation Reports), Coal Abstracts, Google Scholar and other sources*

*This publication was supported in different forms by:*

Komitet Górnictwa PAN  
(Sekcja Wykorzystania Surowców Naturalnych)  
Akademia Górniczo-Hutnicza w Krakowie  
Politechnika Śląska w Gliwicach  
Politechnika Wroclawska

ISSN 1643-1049

OFICyna WYDAWNICZA POLITECHNIKI WROCLAWSKIEJ  
WYBRZEŻE WYSPIAŃSKIEGO 27, 50-370 WROCLAW, POLAND

## CONTENTS

T. Chmielewski, J. Wódka, Ł. Iwachów, Ammonia pressure leaching for Lubin shale middling .....	5
P. Górka, A. Zaleska, A. Suska, J. Hupka, Photocatalytic activity and surface properties of carbon-doped titanium dioxide .....	21
E. Grządka, S. Chibowski, Influence of a kind of electrolyte and its ionic strength on the adsorption and zeta potential of the system: polyacrylic acid/MnO <sub>2</sub> /electrolyte solution .....	31
M. Krzan, K. Małyś, Influence of solution pH and electrolyte presence on bubble velocity in anionic surfactant solutions .....	43
L. Kushakova, A. Muszer, Optimisation of roasting of arsenic-carbon refractory gold ores for cyanide leaching.....	59
P. Maciejewski, M. Żuber, M. Ulewicz, K. Sobianowska, Removal of radioisotopes from waste water after “dirty bomb” decontamination.....	65
M. Markiewicz, J. Hupka, M. Joskowska, Ch. Jungnickel, Potential application of ionic liquids in aluminium production – economical and ecological assessment .....	73
E. Zarudzka, Pre-flotation leaching of Polish carbonate copper ore .....	85

P. Maciejewski\*, M. Żuber\*, M. Ulewicz\*\*, K. Sobianowska\*\*\*

## REMOVAL OF RADIOISOTOPES FROM WASTE WATER AFTER “DIRTY BOMB” DECONTAMINATION

*Received November 13, 2008; reviewed; accepted December 10, 2008*

An adequate response to terrorist event of any magnitude requires the effective coordination of many organizations. A terrorist event involves the release and dispersion of radioactive material among civilian population or over vital area causes a permanent radioactive contamination, which should be removed in decontamination process. Finally, after this procedure, a large amount of radioactive waste water is made, which should be collected and stored in a special nuclear waste stockpile. We present results of experimental work, which was focused on removal of radioactive substances from waste water from decontamination process after using “dirty bomb”. The ion flotation process was used to remove radioisotopes from slightly salty ( $<1.0 \cdot 10^{-3}$  mol/dm<sup>3</sup>) aqueous solutions. Multistage ion flotation and fractionation of concentrate from the ion flotation process using appropriate lariat ethers as collectors allowed separation of radioisotopes, which might have a practical usage for the decontamination of radioactive waste aqueous solutions.

*key words: ions flotation, Cs-137, Sr-85, Ba-133, Co-60, Pb-212, proton-ionizable crown ether*

### INTRODUCTION

The threat of radiation event as a result of terrorist activity has recently arisen, and a “dirty bomb” seems to be excellent “psychological” weapon to cause the ensuing panic and psychological distress. In the “dirty bomb” conventional explosives are linked to a radioactive source with the intention of dispersing radioactive particles.

---

\* The Tadeusz Kosciuszko Land Forces Military Academy, ul. Czajkowskiego 109, 51-150 Wrocław, Pawel.Maciejewski@tedc.nato.int

\*\* Czestochowa University of Technology, ul. J.H. Dąbrowskiego 69, 42-200 Częstochowa

\*\*\* Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław

Sealed medical and industrial sources, such as cobalt-60, cesium-137, strontium-90, and iridium-192, could be targets for terrorists (Tintinalli, 2004). A terrorist event involves the release and dispersion of radioactive material among civilian population or over vital area causes a permanent radioactive contamination, which should be removed in decontamination process. Finally, after this procedure, a large amount of radioactive waste water is made, which should be collected and stored in a special nuclear waste stockpile. The ion flotation process seems to be excellent for this task as that it is a simple and effective method for removal and separation of metals ions from dilute aqueous solutions ( $c < 1.0 \cdot 10^{-4} \text{ mol/dm}^3$ ). In this process, an ionic surface active compound (collector) is introduced to the aqueous solution to transport non-surface active colligend of the opposite charge from a bulk aqueous solution to the interface of solution and vapour. Counter ions must be co-adsorbed to neutralize the charge. If a sufficiently large aqueous solution/gas interface is provided by sparging gas through the solution, the colligend ions can be concentrated and removed along with the collector in a foam phase. The most important fact is that the radioactive substances are collected in a separate container.

We now present results of experimental work, which was focused on removal of radioactive substances from waste water from decontamination process after using “dirty bomb” in the ion flotation process.

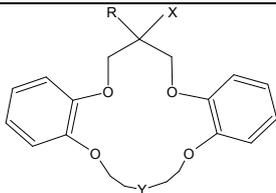
## MACROCYCLIC COMPOUNDS IN ION FLOTATION

Since the discovery of the first crown ether in 1967 by Pedersen the, i.e. dibenzo-18-crown-6, the macrocyclic compounds hold great interest and potential. They have applied successfully for many metal ion separations in solvent extraction, transport across liquid membranes, and ion-exchange systems (Bond et al., 1999; Bartsch, Way, 1996; Nghiem et al., 2006; Ulewicz et al., 2006). The recent advances of the crown ethers chemistry have been reviewed (Ludwig; 2000; Alexandratos, Stine, 2004; Robak et al., 2006; Maciejewski et al., 2008). There are only few papers which deal with application of macrocycles in the ion flotation process. Koide et al. (1996) used phosphate ethers of C-undecylcalix(4)resorcinarenes for uranium flotation from seawater and calyx(4)arenes derivatives for alkali metal cations flotation (1993). Schulz and Warr (1998) applied cryptand 222, and 18-crown-6 together with anionic surfactant, i.e. bis (2,2')-ethylhexylsulfosuccinate (AOT) for alkali metal cations separation. Another approach to application of macrocycles for flotation of metal cations was done by Charewicz et al. (2001). They used the macrocycles proton-ionizable lariat ethers with sulphonic, phosphate and carboxylic acid groups for flotation of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  cations. Ulewicz et al. (2003, 2006) used proton-ionizable lariat ethers with foaming agent for flotation of Zn(II) and Cd(II) ions from aqueous solutions. Maciejewski and Walkowiak (2004) studied selective removal of Cs(I), Sr(II) and Ba(II) cations with proton-ionizable lariat ethers in the ion flotation process.

## EXPERIMENTAL SECTION

**Reagents.** The aqueous solutions were prepared with doubly distilled water of 5  $\mu\text{S/m}$  conductivity at 25 °C. Analytical grade inorganic compounds:  $\text{NaNO}_3$ ,  $\text{HNO}_3$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , were obtained from POCh (Gliwice, Poland). The nonionic foaming agent - octylphenylodecyl (ethylene glycol) ether (Triton X-100) was from Merck. As the collectors 6 lariat ethers possessing cavities from DB-16-C-5 to DB-22-C-7 and different acidic groups, i.e. sulphonamide and sulfonic were used (from prof. Bartsch, R.A., Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, USA, see Tab.1). The lariat ethers were added as ethanol solutions. The gamma-radioactive isotopes, i.e. Cs-137, Sr-85 and Co-60 were purchased from the Atomic Energy Institute (Swierk/Otwock, Poland), Ba-133 and Pb-212 from Institute of Nuclear Chemistry and Technology (Warsaw, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration.

**Table 1.** List of lariat ethers and nonionic foaming agent

Structure	Crown	R	X	No. ether
	DB16C5	$-\text{C}_{10}\text{H}_{21}$	$-\text{OCH}_2\text{CONHSO}_2\text{CF}_3$	<u>1</u>
			$-\text{O}(\text{CH}_2)_3\text{SO}_3\text{Na}$	<u>2</u>
	DB19C6	$-\text{C}_{10}\text{H}_{21}$	$-\text{OCH}_2\text{CONHSO}_2\text{CF}_3$	<u>3</u>
	DB22C7	$-\text{C}_7\text{H}_{15}$	$-\text{O}(\text{CH}_2)_3\text{SO}_3\text{Na}$	<u>4</u>
		$-\text{C}_4\text{H}_9$	$-\text{OCH}_2\text{CONHSO}_2\text{CF}_3$	<u>5</u>
	$-\text{C}_{10}\text{H}_{21}$	$-\text{OCH}_2\text{CONHSO}_2\text{CF}_3$	<u>6</u>	
	$\text{R}_1 = -\text{C}_8\text{H}_{17}$ $\text{R}_2 = -\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$	Triton X-100 (eter oktylofenylodekaetylenoglikolowy)		<u>7</u>

**Ion Flotation Procedure.** The flotation experiments have been carried out in ambient temperature ( $20 \pm 2^\circ\text{C}$ ) in a glass column 45.7 cm in height and 2.4 cm in diameter. The argon gas was saturated with water, and the flow rate was maintained at 12 mL/min through a sintered glass sparger of 20–30  $\mu\text{m}$  nominal porosity. The initial volume of each feed solution was 100 mL and contained aqueous solutions of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes (at  $1.0 \cdot 10^{-8}$  mol/dm<sup>3</sup> concentration), and  $\text{NaNO}_3$  as the source of foreign cations (at  $1.0 \cdot 10^{-3}$  mol/dm<sup>3</sup> concentration). The single and multi channel, gamma radiation spectrometers were used as the detectors of radiation intensity of specific energy.

The percent of decontamination was calculated by the equation:

$$D = (1 - A_r / A_i) \cdot 100\% \quad (1)$$

where  $A_i$ ,  $A_r$  – initial and residual gamma radiation intensity of solution,  $Bq/dm^3$ .

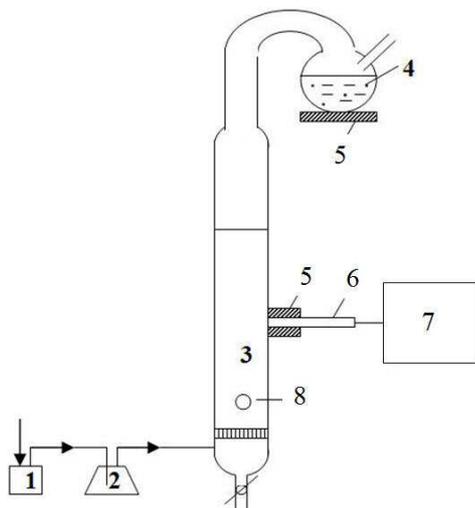


Fig. 1. Scheme of ion flotation apparatus  
 1 – gas flow and pressure meter,  
 2 – humidifier,  
 3 – flotation column,  
 4 – foam receiver,  
 5 – lead screen,  
 6 – spectrometric scintillation probe,  
 7 – gamma radiation spectrometer with computer,  
 8 – injection capable valve (for collector).

## RESULTS AND DISCUSSION

### RADIATION RESISTANCE OF LARIAT ETHERS

An important parameter for flotation of metal ions from radioactive waste aqueous solutions is a radiation resistance of lariat ethers. The radiation resistance of two lariat ethers (1, 2) using Cs-137 source was measured. The lariat ethers after exposition (dose from 0.1 to 10 Gy) were examined for Cs-137 ( $1.0 \cdot 10^{-8} \text{ mol/dm}^3$ ). The percent decontamination of Cs-137 for 1 and 2 after exposition is at the same level as before radiation, so the lariat ethers have enough radiation resistance and can be used for ion flotation of radioactive cations.

### SELECTIVE FLOTATION OF CS-137, SR-90, BA-133, CO-60 AND PB-212 RADIOISOTOPES

The ion flotation process was applied for selective removal of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes, which could be consider as radioactive waste water from decontamination. The aqueous solutions contained Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes (at  $1.0 \cdot 10^{-8} \text{ mol/dm}^3$  concentration) and  $\text{NaNO}_3$  as the source of foreign cations (at  $1.0 \cdot 10^{-3} \text{ mol/dm}^3$  concentration).

The preliminary flotation experiments with the addition of  $\text{NaNO}_3$  as the source of foreign cations indicated reduction of all radioisotopes removal. When the concentration of  $\text{NaNO}_3$  was higher than  $1.0 \cdot 10^{-3} \text{ mol/dm}^3$ , the removal of radioisotopes was very low. The experiments were performed also at the various initial concentrations of lariat ethers and pH values.

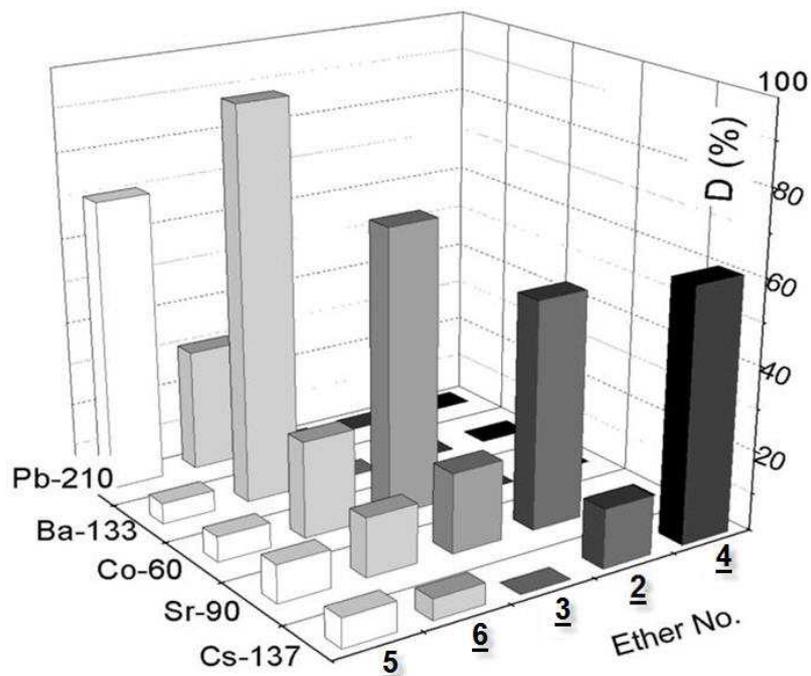


Fig. 2. The selective flotation of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 with lariat ethers: 5, 6, 3, 2 and 4 at  $1.0 \cdot 10^{-8} \text{ mol/dm}^3$  initial concentration and in the presence of nonionic foaming agent 7 from aqueous solutions containing  $\text{NaNO}_3$  ( $1.0 \cdot 10^{-3} \text{ mol/dm}^3$ ),  $[\text{Lariat ether}] = [\text{7}] = 1.0 \cdot 10^{-5} \text{ mol/dm}^3$

In the Figure 2, there are results for competitive flotation of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes with appropriate proton-ionizable lariat ethers from dilute, slightly salty ( $[\text{NaNO}_3] = 1.0 \cdot 10^{-3} \text{ mol/dm}^3$ ) aqueous solutions. The studied cations have different ionic radius and ionic potential, which allow separation of mentioned cations from dilute aqueous solutions with using 5 lariat ethers possessing DB-16-C-5 cavity and different lipophilic (from butyl to decyl) and acidic groups, i.e. sulfonamide (i.e. 1, 3, 5, 6) and sulfonic (2, 4) (Ulewicz et. al., 2006a). As it can be seen in this Figure, five stages of ion flotation and concentrate fractionation of the ion flotation process with appropriate lariat ethers as collectors (i.e. 5, 6, 3, 2, 4) allow separation of radioisotopes in the order: Pb-212 > Ba-133 > Sr-85 > Co-60 > Cs-137. A multistage ion flotation means that in one experiment the same feed solution is floated with using a proper collector in a correct sequence. Each stage was started with injec-

tion of a new portion of collector ( $<1.0 \cdot 10^{-5}$  mol/dm<sup>3</sup>) which was injected through valve 8 (see Figure 1) and the stage was finished when it was stopped floating. One stage took about 5 minutes and there was a small amount of foam ( $<0,5$  g), which means that the enrichment ratio of radioisotope in foam is high. The competitive ion flotation of radioisotopes was fast and after 30 minutes final removal was reached, which might have a practical usage for the decontamination of radioactive, slightly salty ( $<1.0 \cdot 10^{-3}$  mol/dm<sup>3</sup>), waste aqueous solutions.

## CONCLUSIONS

Proton-ionizable crown ethers with sufficient surface activity and water solubility seem to be the new generation of collectors for flotation of Cs<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup> cations from dilute aqueous solutions.

The lariat ethers have enough radiation resistance so they can be used for ion flotation of radioactive isotopes.

The ion flotation process allows the efficient decontamination of slightly salty ( $<1.0 \cdot 10^{-3}$  mol/dm<sup>3</sup>) aqueous solutions containing Co-60, Sr-85, Ba-133, Cs-137 and Pb-212 isotopes. Multistage ion flotation and fractionation of concentrate from the ion flotation process using appropriate lariat ethers as collectors allowed us to separate radioisotopes with selectivity decreasing in the order: Pb-212 > Ba-133 > Sr-85 > Co-60 > Cs-137. The competitive ion flotation of radioisotopes is fast, with final removal reached in just 30 minutes, which might have a practical usage for the decontamination of radioactive waste aqueous solutions.

## REFERENCES

- ALEXANDRATOS, S.D., STINE, CH.L. (2004) *Synthesis of ion-selective polymer-supported crown ethers: a review*, Reactive & Functional Polymers, Vol. 60, pp.3–16.
- BARTSCH, R. A., WAY, J. D., (eds.) (1996) *Chemical Separations with Liquid Membranes*, ACS Symposium Series 642, Washington, DC.
- BOND, H., DIETZ, M.L., ROGERS, R.D. (eds.) (1999) *Metal-Ion Separation and Preconcentration, Progress and Opportunities*, ACS Symposium Series 716, Washington, DC.
- CHAREWICZ, W., GRABOWSKA J., BARTSCH, R.A. (2001) *Flotation of Co(II), Sr(II), and Cs(I) cations with proton-ionizable lariat ethers*, Sep. Sci. Technol., Vol. 36, pp.1479–1494.
- KOIDE, Y., OKA, T., IMAMURA, A., SHOENJI, H., YAMADA, K. (1993) *The selective flotation of cesium ion with resorcinol type calyx(4)arenes with alkyl side chains*, Bull. Chem. Soc. Jpn., Vol. 66, pp. 2137–2132.
- KOIDE, Y., TERASAKI, H., SATO, S., SHOENJI, H., YAMADA, K. (1996) *Flotation of uranium from sea water with phosphate ethers of C-undecylcalix(4)resorcinarene*, Bull. Chem. Soc. Jpn., Vol. 69, pp. 785–790.
- LUDWIG, R. (2000) *Foam separation*, Fresenius J. Anal. Chem., Vol. 367, pp. 103–128.
- MACIEJEWSKI, P., WALKOWIAK, W. (2004) *Selective removal of cesium(I), strontium(II) and barium(II) cations with proton-ionizable lariat ethers in the ion flotation process*, Physicochemical

- Problems of Mineral Processing, 38, 139–146.
- MACIEJEWSKI, P., ROBAK, W., ULEWICZ, M., SOBIANOWSKA, K. (2008) *Zastosowanie związków makrocyklicznych do usuwania toksycznych kationów metali z roztworów wodnych w procesie flotacji jonowej*, Zeszyty naukowe WSOWŁąd, 1(147), 113–125.
- NGHIEM, L.D., MORNANE, P., POTTER, I.D., PERERA, J.M., CATTALL, R.W., KOLEV, S.D. (2006) *Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs)*, J. Membrane Sci., Vol. 281, pp.7–41.
- PEDERSEN, C.J., 1967, *Cyclic polyethers and their complex with metal salts*, J. Am. Chem. Soc., Vol. 89, pp. 7017–7036.
- ROBAK, W., APOSTOLUK, W., MACIEJEWSKI, P. (2006), *Analysis of liquid-liquid distribution constants of nonionizable crown ethers and their derivatives*, Anal. Chim. Acta, Vol. 569, pp.119–131.
- SCHULZ, C., WARR, G.G. (1998) *Comparison of variables in ion and precipitate flotation*, Ind. Eng. Chem. Res., Vol. 37, pp.2807–2809.
- TINTINALLI, J.E. (2004) *Emergency medicine*, 6. Edition McGraw-Hill, New York.
- ULEWICZ, M., WALKOWIAK, W., BARTSCH, R.A. (2006a) *Ion flotation of zinc(II) and cadmium(II) with proton-ionizable lariat ethers. Effect of cavity size*, Sep. Purif. Technol., Vol. 48, pp. 264–269.
- ULEWICZ, M., LESINSKA, U., BOCHENSKA, M., WALKOWIAK, W. (2006b) *Facilitated transport of Zn(II), Cd(II) and Pb(II) ions through polymer inclusion membranes with calyx(4)-crown-6 derivatives*, Sep. Purif. Technol.
- ULEWICZ, M., WALKOWIAK, W., JANG, Y., KIM, J.S., BARTSCH, R.A. (2003) *Ion flotation of cadmium(II) and zinc(II) in the presence of proton-ionizable lariat ethers*, Anal.Chem., Vol. 75, pp. 2276–2279.

**Maciejewski P., Zuber M., Ulewicz M., Sobianowska K., 2008, Usuwanie radioizotopów z roztworów ściekowych z dekontaminacji po użyciu broni radiologicznej**, Physicochemical Problems of Mineral Processing, 43 (2009), 65–72 (w jęz. ang)

Zbadano selektywne wydzielanie radioizotopów: Pb-212, Ba-133, Sr-85, Co-60 i Cs-137, z rozcieńczonych, zasolonych  $\text{NaNO}_3$  ( $1.0 \cdot 10^{-3}$  M) roztworów wodnych z użyciem nowej grupy związków makrocyklicznych, tj. jonizowanych eterów lariatowych o stężeniu  $1 \cdot 10^{-5}$  M w obecności spieniacza niejonowego Tritonu X-100 ( $1 \cdot 10^{-5}$  M). Stężenie każdego radioizotopu w mieszaninie wynosiło  $1 \cdot 10^{-8}$  M i założenia odpowiadało składem radioaktywnym ściekom po dekontaminacji obiektów po ataku bombą radiologiczną. Zastosowanie frakcjonowania koncentratu podczas flotacji radioaktywnych, zasolonych  $\text{NaNO}_3$  ( $1.0 \cdot 10^{-3}$  M) roztworów wodnych z użyciem odpowiedniej sekwencji jonizowalnych eterów lariatowych ( $1 \cdot 10^{-5}$  M) umożliwiła efektywne i selektywne usunięcie radioizotopów z roztworu wodnego. Zbadano również odporność radiacyjną kolektorów, która okazała się wysoka ( $< 10$  Gy), co pozwala na wielokrotne użycie kolektora w procesie flotacji jonowej. Omawiana metoda może być użyta do dekontaminacji toksycznych (radioaktywnych) roztworów wodnych.

słowa kluczowe: flotacja jonowa, Cs-137, Sr-85, Ba-133, Co-60, Pb-212, jonizowalny eter lariatowy