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NEW METHOD FOR REMOVAL OF RADIOACTIVE PARTICLES FROM WASTE WATER AFTER DECONTAMINATION

Nowa metoda usuwania radioaktywnych zanieczyszczeń z roztworów poakcyjnych

Streszczenie

Atak terrorystyczny z użyciem substancji radioaktywnych wymaga podjęcia odpowiednich działań zmierzających do dekontaminacji skażonych powierzchni. Istotą działania jest mechaniczne usuniecie substancji radioaktywnych z użyciem wodnych roztworów związków powierzchniowo czynnych, co jednak skutkuje postawianiem dużych objętości radioaktywnych ścieków (roztworów poakcyjnych). Rozwiązaniem problemu może być zastosowanie szybkiej i efektywnej metody wydzielania substancji promieniotwórczych z roztworów wodnych, tj. flotacji jonowej. W pracy przedstawiono wyniki badań wydzielania radioizotopów Ba-133, Sr-85 i Cs-137 z rozcieńczonych, zasolonych $NaNO_3$ $(1.0 \cdot 10^{-3}$ M) roztworów wodnych z użyciem nowej grupy związków makrocyklicznych, tj. jonizowanych eterów lariatowych o stężeniu $1 \cdot 10^{-5}$ M w obecności niejonowego roztworu spieniacza – Tritonu X-100 $(1 \cdot 10^{-5}$ M). Stężenie każdego radioizotopu w mieszaninie wynosiło $1 \cdot 10^{-5}$ M i założenia odpowiadało składem radioaktywnym ściekom po dekontaminacji obiektów po ataku bombą radiologiczną. Na bazie uzyskanych wyników zaproponowano zastosowanie „modułu flotacyjnego", który umożliwiłby szybkie usuwanie zanieczyszczeń promieniotwórczych z roztworów poakcyjnych, a przez to zasadniczą redukcje objętości ścieków radioaktywnych.

Summary

A terrorist attack 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 ($< NaNO_3$ $1.0 \cdot 10^{-3}$ mol/L) aqueous solutions. Effect of the structure of proton-ionizable lariat ethers on removal of Ba-133, Sr-85 and Cs-137 in ion flotation process from dilute aqueous solutions has been studied. The initial volume of each feed solution was 100 ml and the initial concentration of Ba-133, Sr-85 and Cs-137 in floated solution was $1.0 \cdot 10^{-5}$ M. According to results of experiments, "the ion flotation module can be proposed". From practical point of view the application of this module can significant reduce amount of radioactive waste water and cost of decontamination process.

Słowa kluczowe: flotacja jonowa, Cs-137, Sr-85, Ba-133, jonizowalny eter lariatowy;
Key words: ions flotation, Cs-137, Sr-85, Ba-133, proton-ionizable crown ether;

Introduction

Current threats include the proliferation of CBRN (chemical, biological, radiological and nuclear) weapons are known to have been highlighted the most challenges task for the National System of Crisis Emergency. Furthermore, a wide range of Toxic Industrial Materials **(TIM)** including various insecticides, industrial chemicals and potent toxins may be relatively easy to produce or otherwise acquire. TIM is a generic term for toxic chemical, biological and radioactive substances in solid, liquid, aerosolized, or gaseous form created for industrial, commercial, medical, or domestic purposes. One of TIM is Toxic Industrial Radiological **(TIR)** and its possible sources are: civil nuclear production, research, recycling and storage facilities, waste containment sites, industrial and medical sources, materials and sources in transit, stolen or smuggled nuclear weapons grade material [1]. Sealed medical and industrial sources, such as cobalt-60, cesium-137, strontium-90, and iridium-192, could be targets for terrorists. Recently, the threat of radiation event as a result of terrorist activity has arisen, and a "radiological bomb" seems to be excellent "psychological" weapon to cause the ensuing panic and psychological distress. The attack can be prepared with using radiological dispersal devices (RDD), which can spread or disperse radioactive materials to produce contamination hazards over vital area. Terrorists and other adversaries deploying RDDs will likely choose delivery means which maximize the dispersion of radioactive particles. These can include

explosive dissemination, direct spraying or scattering, or dispersal of solid or liquid aerosols downwind. Fire and smoke can also be used to disperse radioactive material. Terrorist may also attempt to attack a nuclear installation (such as a power plant or waste respiratory in an effort to disperse radioactive material. In the worst-case scenario, terrorists may manage to obtain a nuclear weapon for detonation.

The people have been concerned with radiation injuries for the last 50 years, but the threat has been centred around nuclear power plant accidents and using a nuclear weapon in a war setting. However, with today's widespread use of radiation technology in medicine, research, industry, power production, there is a growing potential for radiation injures. According to U.S. Department of Energy, the Radiation Emergency Assistance Center/Training Site (REACTS) 426 radiation accidents have been recorded worldwide a total of 133,811 victims; 3063 had significant exposure and there were 134 fatalities since 1944. The 1986 Chernobyl accident accounted for 116,500 individuals and 28 acute fatalities [2]. There have also been some limited attacks on nuclear power facilities worldwide; numerous unsubstantiated threats to trigger a nuclear explosive device; and at least one reported case of the use of radiological materials-albeit in a very limited manner (the placing of a medical cesium capsule by Chechen rebels in a Moscow park in 1995) by terrorists [3].

The chemical rescue groups are responsible for decontamination and they must have the radioactive contamination of people or vital area cleaned. Decontamination is the process of making personnel, objects or areas safe by removing radioactive material to below personnel health effects. 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.

Authors present results of experimental work, which was focused on removal of radioactive substances from waste water from decontamination process after using "radiological bomb" in the ion flotation process. In the experiments, models of radioactive waste water were studied, containing Cs-137, Sr-85, Ba-133 (single radioisotope in the aqueous solution). The composition of aqueous solution is know to be the most important factor in ion flotation process. Therefore, the addition of foreign cations, concentration of lariat ethers and non-ionic foaming agent as well as an impact of pH on ion flotation process were studied.

I. Methods for removal of ions from water solution – quick review

In the decontamination process of radioactive contamination, there will be made a large amount of radioactive waste water. The radioactive substances are known, to be in solution in different forms, but the most challenging is to remove ionic form. From practical point of view, the process of removal radioactive particles from waste water should be fast and simple. There is a lot of physicochemical methods of the mixtures separation and removal of radioactive substances, but the ion flotation process seems to be the most appropriates for this task.

The ion flotation process is a simple and an effective method for removal and separation of metals ions from dilute aqueous solutions (c < 1.0 10^{-4} mol/L). In this process, an ionic surface active compound (collector) is introduced to the aqueous solution to transport non-surface active colligent 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 rate and efficiency of the ion flotation process separation is a function of many factors, but the most important is the composition of aqueous solution from which ions are floated [4-11]. Flotation of ions has been known since the early sixties [12]. Unfortunately, the selectivity of a regular ionizable surfactant towards cations and/or anions is limited and might be roughly attributed to the hydration/ionization/complexation behavior of an individual ion. On the other hand, serious environmental hazards originating from liquid radioactive wastes [13] and certain industrial effluents containing traces of extremely dangerous ionic species substantiate the search for other, efficient and specific separation techniques. This is the reason why inclusion compounds having a cage, such as crown ethers, calixarenes or cryptands, and their derivatives have been investigated for many systems of metal ions selective removal in recent years. Since the discovery of the first crown ether in 1967 by Pedersen [14], 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 [15-18]. The recent advances of the crown ethers chemistry have been reviewed [19-21]. There are only few papers which deal with application of macrocycles in the ion flotation process. Koide et al. [25] used phosphate ethers of C-undecylcalix resorcinarenes for uranium flotation from seawater and calix[4]arenes derivatives for alkali metal cations flotation [26]. Schulz and Warr [27] applied cryptand 222, and 18-crown-6
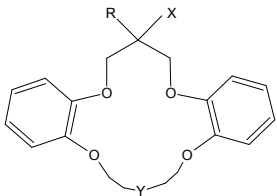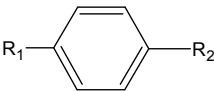
together with anionic surfactant, i.e. bis (2,2')-ethylhexylsulfosuccinate (AOT) for alkali metal cations separation. Another approach to application of macrocycles for flotation of metal cations was done by Charewicz et al. [28]. They used the macrocycles proton-ionizable lariat ethers with sulphonic, phosphate and carboxylic acid groups for flotation of Sr^{2+} and Cs^+ cations. Ulewicz et al. [29-30] used proton-ionizable lariat ethers with foaming agent for flotation of Zn(II) and Cd(II) ions from aqueous solutions. Maciejewski et al. studied selective removal of Cs^+, Sr^{2+} and Ba^{2+} cations with proton-ionizable lariat ethers in the ion flotation process.

II. Experimental Section

Reagents. The aqueous solutions were prepared with doubly distilled water of 5 μS/m conductivity at 25 °C. Analytical grade inorganic compounds: $NaNO_3$, HNO_3, NaOH, $NH_3 \cdot H_2O$, (POCh Gliwice, Poland), $CsNO_3$ (Fluka), $Sr(NO_3)_2$, $Ba(NO_3)_2$ (Aldrich), Triton X-100 (nonionic foaming agent, Merck). As the collectors 4 lariat ethers with cavity DB-16-C-5 and four different acidic groups, i.e. sulfonamide, sulfonic, carboxylic and phosphonic 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 and Sr-85 were purchased from the Atomic Energy Institute (Swierk/Otwock, Poland), Ba-133 from Institute of Nuclear Chemistry and Technology (Warsaw, Poland).

Table 1.

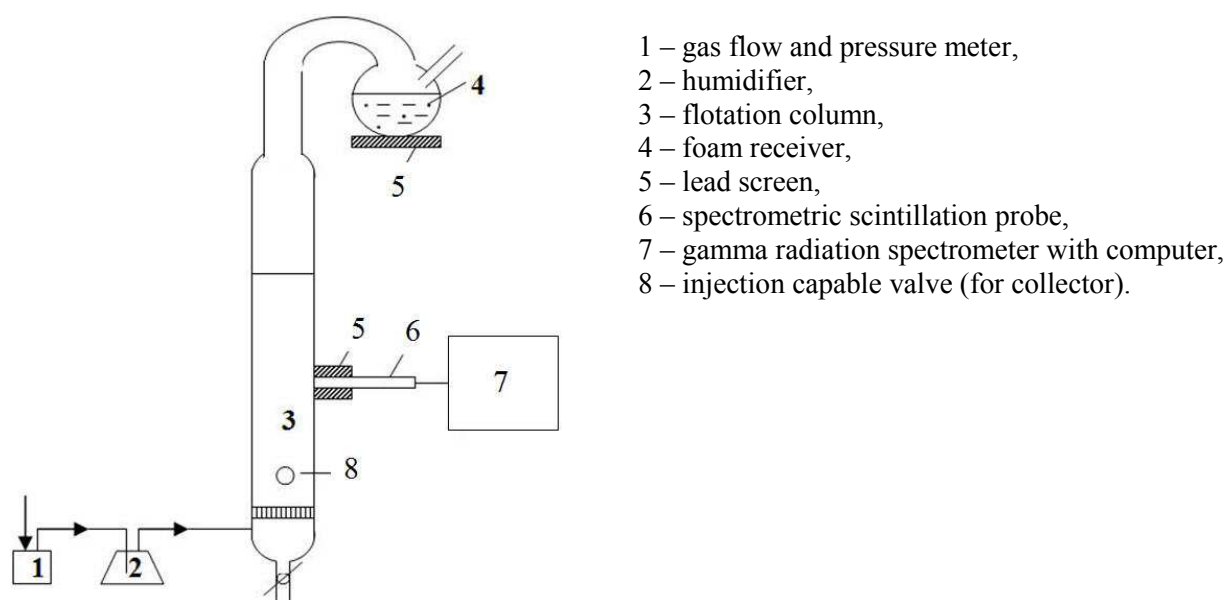### List of lariat ethers and nonionic foaming agent

Structure	Crown	R	X	No. ether
	DB16C5	$-C_{10}H_{21}$	$-OCH_2CONHSO_2CF_3$	**1**
			$-O(CH_2)_3SO_3Na$	**2**
			$-OCH_2COOH$	**3**
			$-OCH_2PO(OH)(OC_2H_5)$	**4**
	$R_1 = -C_8H_{17}$ $R_2 = -O(CH_2CH_2O)_{10}H$	Triton X-100		**5**

Ion Flotation Procedure. The flotation experiments were carried out in ambient temperature (20 ± 2°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 μm nominal porosity (Fig. 1). The initial volume of each feed solution was 100 mL. Concentrations of Cs^+, Sr^{2+} and Ba^{2+} in aqueous solutions were $1.0 \cdot 10^{-5}$ mol/L. The floated cations concentration in the bulk solution (c) versus time was recorded continuously during the ion flotation experiments by means of radioactive analytical tracers (Cs-137, Sr-85, Ba-133) and gamma radiation spectrometry following a procedure described by Ulewicz et al. [29]. The single channel gamma radiation spectrometer was used as the detector of radiation intensity of specific energy. The maximal percent removal (W) was calculated by the equation:

$$W = (1 - c_r/c_i) \cdot 100\% \quad (1)$$

where: c_i - initial metal ion concentration and c_r - metal ion concentration in the residual solution after foam cease.

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).

Fig. 1. Scheme of ion flotation apparatus

1. Results and discussion

1.1. Parameters influencing Cs-137, Sr-85 and Ba-133 flotation removal

First, results of Cs-137, Sr-85, Ba-133 flotation with four lariat ethers possessing DB-16-C-5 cavity, decyl liphofilic group and a different acidic groups, i.e. sulfonamide (**1**), sulfonic **2**, carboxylic **3** and phosphonic **4** are presented. All flotation experiments were performed

from dilute aqueous solutions containing a single metal cation in the presence of nonionic foaming agent Triton X-100 **5**. All radioisotopes in aqueous solution were in cationic form.

Effect of pH. The important factor which influences flotation ability of proton-ionizable lariat ethers is the pH of aqueous solution. The pH of the aqueous solution was in the range of 4.0 - 10.0 and was measured after each experiment. Generally, for all lariat ethers, removal of mentioned cations increases with increasing pH, excluding crown ether with sulfonic group **2**. The maximal removal of metals ions depends upon the aqueous solution's pH for carboxylic crown ether **3** and it increases linearly with increasing pH. The percent removal for **4** is high and increases with increasing pH up to 5.0 and then remains constant (Fig. 2). The results for **1** are similar to the results for **4**. On the other hand, the maximal removal for sulfonic crown ether **2** is independent from the pH of aqueous solution (over 97%).
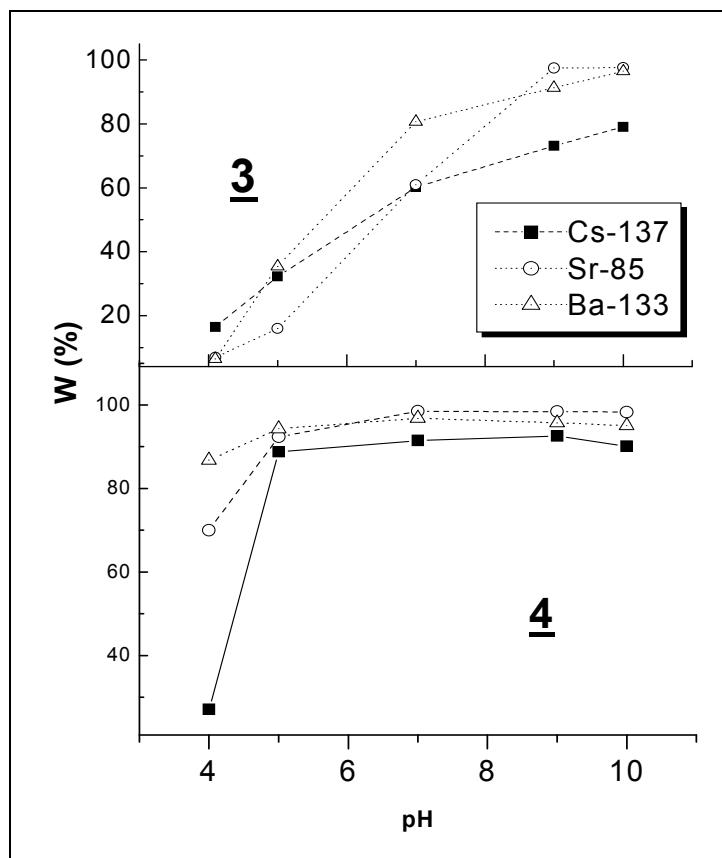
Fig. 2. The maximal percent removal of Cs-137, Sr-85, Ba-133 in ion flotation process with **3**, and **4** crown ethers in the presence of nonionic foaming agent (**5**); $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, $[\underline{3}, \underline{4}] = 5 \cdot 10^{-5}$ mol/L, $[\underline{5}] = 2 \cdot 10^{-5}$ mol/L

Effect of Collector Concentration. In the experiments lariat ethers: **1**, **2**, **3**, **4** were used at concentration 1.0 - 5.0 $\cdot 10^{-5}$ mol/L and in the presence of nonionic foaming agent (**5**) in the optimal values of aqueous solutions pH appropriate for the lariat ether. The lariat ethers were

added as ethanol solutions. All experiments were conducted from a single metal cation solution. The initial concentration of lariat ethers possess a strong influence on floated radioisotopes removal. The fastest and practically complete flotation of Sr-85 and Ba-133 is observed at $3.0 \cdot 10^{-5}$ mol/L initial collector concentration. The maximal removal of metals depended upon initial concentration of crown ether, for Sr-85 especially (Fig. 3). In all experiments there is a small amount of foam (< 1 g), which means that the enrichment ratio of metals in foam is high.

Finally, the correlation between the flotation efficiency of metal cations (W) and pH as well as crown ether concentration (c) was found for carboxylic crown ether derivative (**3**) as follow:

$$W = (15.724 \pm 1.044) \cdot pH + (7.356 \pm 2.203) \cdot c - (87.923 \pm 16.062)$$

$$r^2 = 0.961, \text{ s.d.} = 1.326, F = 136, N = 20,$$

where: c – the initial concentration of ether **3**, s.d. - standard deviation, F - Fischer-Sedecor test function (F-statistic), N- represents the number of experimental data.

From the statistical point of view, the obtained correlation is significant. It is also important that the deviation of experimental points from the correlation is lower than ± 3 s.d. According to this equation, efficiency of flotation (*W*) increases with pH value as well as with initial concentration of lariat ether.
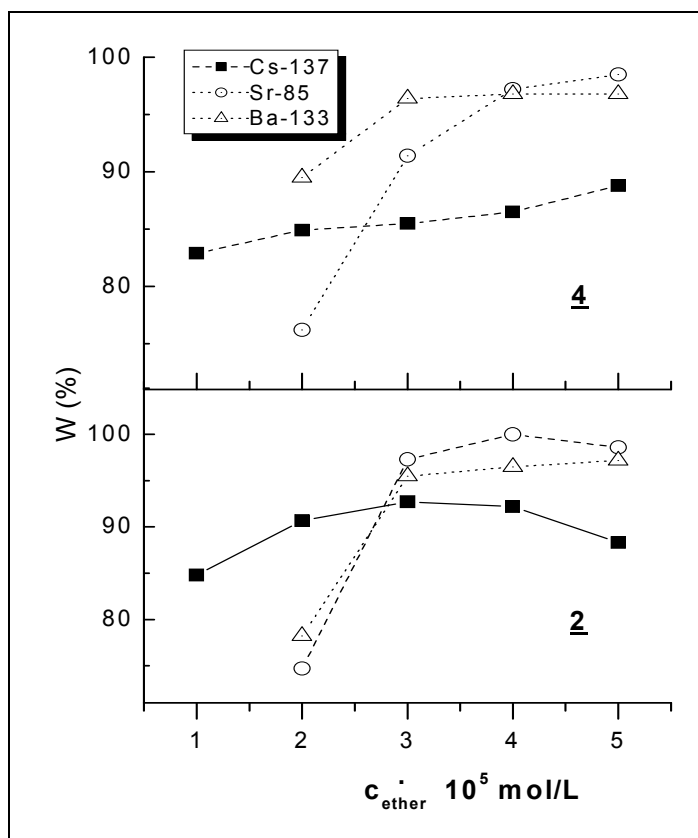
Fig. 3. The maximal percent removal of Cs-137, Sr-85, Ba-133 with crown ethers **4** and **2**; $[M^{2+}] = [M^{+}] = 1 \cdot 10^{-5}$ mol/L, $[\underline{5}] = 2 \cdot 10^{-5}$ mol/L, at pH aqueous solution 4.0 for **2** and 7.0 for **4**

Influence of Foaming Agent Concentration. The preliminary experiments revealed that the lariat ethers with sulfonamide **1** and carboxylic **3** groups exhibited insufficient foaming ability, so that they had to be used simultaneously with the foaming agent. On the other hand, crown ethers with sulfonic **2** and phosphonic **4** groups independently possess a sufficient foaming ability itself and they behave like the regular ion flotation collectors.

Effect of Alkali Metal Cations. The practical meaning of the studied separation process depends strongly on its resistibility against the ionic strength of a feed solution. Therefore, we have studied the effect of alkali metal nitrate (Na^+) on the efficiency and rate of Cs-137, Sr-85, Ba-133 flotation with sulfonic **2** and carboxylic **3** lariat ether derivatives. The addition of $NaNO_3$ as the source of foreign cations depressed the removal of Cs-137, Sr-85, Ba-133 remarkably and when the concentration of $NaNO_3$ was higher than $1.0 \cdot 10^{-3}$ mol/L the removal of all floated cations was very low. Up to 100-fold molar excess of added salts over the floated cations do not depress flotation of the studied cations with **3** and **2** lariat ethers as collectors. Past 100, however, the higher excess of added salts strongly decreases the flotation of metal ions.

We also found a correlation between alkali metal concentrations and the maximal percent removal (W) for Cs-137, Sr-85, Ba-133 flotation with crown ether **2** in the presence of Na$^+$ nitrates and with **3** crown ether for Cs-137 flotation in the presence of NaNO$_3$:

$$W = -(687.53 \pm 23.20)\, c_{salt}^{0.5} + const$$

where: c_{salt} – the initial concentration of the appropriate alkali metal nitrate

Ether No.	Floated cation	Cations presence	Const value
2	Sr-85, Ba-133	Na$^+$	100.58 ± 1.32
2	Cs-137	Na$^+$	77.20 ± 3.92
3	Cs-137	Na$^+$	81.38 ± 1.32

$r^2 = 0.985$, s.d. $= 1.983$, F $= 972$, N $= 49$

Conclusions

Proton-ionizable crown ethers with sufficient surface activity and water solubility seem to be the new generation of collectors for flotation of Cs-137, Sr-85, Ba-133 radioisotopes (cations) from dilute aqueous solutions. Sulfonamide and carboxylic lariat ether derivatives exhibit insufficient foaming ability, so they have to be used together with a nonionizable foaming agent. On the other hand, lariat ethers with sulfonic and phosphonic acidic groups behave like a regular ion flotation collector and have a sufficient foaming ability. The use of lariat ethers as collectors for flotation of metal cations allow practically complete removal of Cs-137, Sr-85, Ba-133 radioisotopes even at the stoichiometric lariat ethers concentration to floated cations. The addition of nonionic foaming agents (Triton X-100) does not significantly affect the efficiency of radioisotopes flotation with the lariat ethers.

The acidic group character of lariat ethers determines range of pH, resulting on various effectivity on ion flotation. The maximal removal of metals depends upon the pH of the aqueous solution and particularly for crown ether carboxylic derivative, which increases linearly with pH increase. The percent removal for sulfonamide and phosphonic derivative ethers increases with increasing pH up to 5.0 and then remains constant. On the other hand, the maximal removal for sulfonic derivatives ether are independent from the pH of the aqueous solution. Because of different acidity strengths of acidic groups tested, lariat ethers could be used in ion flotation process at pH as follows: for carboxylic derivatives > 9.0,

sulfonamide and phosphonic derivatives > 5.0, and for sulfonic lariat ether derivatives from 4.0 to 10.0.

The addition of $NaNO_3$ as the source of foreign cations depresses the removal of Cs-137, Sr-85, Ba-133 remarkably. When the concentration of alkali metal nitrates was higher than $1.0 \cdot 10^{-3}$ mol/L the removal of all floated radioisotopes was very low.

The ion flotation process allows the efficient decontamination of slightly salty aqueous solutions containing Sr-85, Ba-133 and Cs-137 radioisotopes. The ion flotation process can be realized in period or continuous system. It is fast method, with final removal reached in just 30 minutes, which might have a practical usage for the decontamination of radioactive waste aqueous solutions, e.g. after decontamination. According to results of experiments, the ion flotation module can be proposed (Fig. 4). From practical point of view the application of this module can significant reduce amount of radioactive waste water and cost of decontamination process.
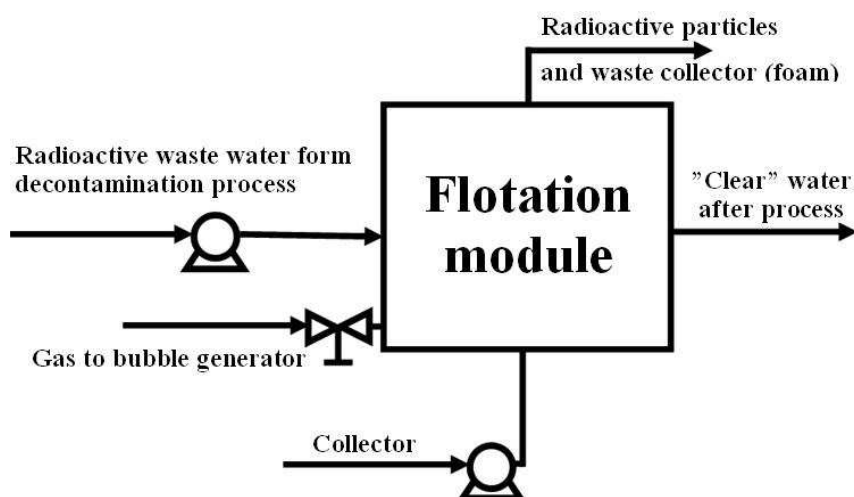
Fig. 4. Scheme of ion flotation module

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NOWA METODA USUWANIA RADIOAKTYWNYCH ZANIECZYSZCZEŃ Z ROZTWORÓW POAKCYJNYCH

Słowa kluczowe: flotacja jonowa, Cs-137, Sr-85, Ba-133, jonizowalny eter lariatowy

Streszczenie

Atak terrorystyczny z użyciem substancji radioaktywnych wymaga podjęcia odpowiednich działań zmierzających do dekontaminacji skażonych powierzchni. Istotą działania jest mechaniczne usuniecie substancji radioaktywnych z użyciem wodnych roztworów związków powierzchniowo czynnych, co jednak skutkuje postawianiem dużych objętości radioaktywnych ścieków (roztworów poakcyjnych). Rozwiązaniem problemu może być zastosowanie szybkiej i efektywnej metody wydzielania substancji promieniotwórczych z roztworów wodnych, tj. flotacji jonowej. W pracy przedstawiono wyniki badań wydzielania radioizotopów Ba-133, Sr-85 i Cs-137 z rozcieńczonych, zasolonych $NaNO_3$ ($1.0 \cdot 10^{-3}$ M) roztworów wodnych z użyciem nowej grupy związków makrocyklicznych, tj. jonizowanych eterów lariatowych o stężeniu $1 \cdot 10^{-5}$ M w obecności niejonowego roztworu spieniacza – Tritonu X-100 ($1 \cdot 10^{-5}$ M). Stężenie każdego radioizotopu w mieszaninie wynosiło $1 \cdot 10^{-5}$ M i założenia odpowiadało składem radioaktywnym ściekom po dekontaminacji obiektów po ataku bombą radiologiczną. Na bazie uzyskanych wyników zaproponowano zastosowanie „modułu flotacyjnego", który umożliwiłby szybkie usuwanie zanieczyszczeń promieniotwórczych z roztworów poakcyjnych, a przez to zasadniczą redukcje objętości ścieków radioaktywnych.

New method for removal of radioactive particles from waste water after decontamination

Key words: ions flotation, Cs-137, Sr-85, Ba-133, proton-ionizable crown ether

Abstract

A terrorist attack 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 ($< NaNO_3$ $1.0 \cdot 10^{-3}$ mol/L) aqueous solutions. Effect of the structure of proton-ionizable lariat ethers on removal of Ba-133, Sr-85 and Cs-137 in ion flotation process from dilute aqueous solutions has been studied. The initial volume of each feed solution was 100 ml and the initial concentration of Ba-133, Sr-85 and Cs-137 in floated solution was $1.0 \cdot 10^{-5}$ M. According to results of experiments, "the ion flotation module can be proposed". From practical point of view the application of this module can significant reduce amount of radioactive waste water and cost of decontamination process.