Environment Protection Engineering

Vol. 3 1977 No. 1–2

WŁADYSŁAW WALKOWIAK, WITOLD CHAREWICZ*

THE APPLICATION OF ADSORPTIVE BUBBLE SEPARATION METHODS TO WASTEWATER TREATMENT AND RECOVERY OF TRACE ELEMENTS

Research on application of the adsorptive bubble separation methods to wastewater treatment and rare elements metallurgy is presented. Radioactive wastewater decontamination by foam separation and precipitate flotation is discussed in particular. The uranium and other metals recovery from mine drainage and from the seawater by ion and precipitate flotation is also presented. Moreover, the results on perrhenate, molybdate and chloraurate anions flotation from industrial effluents and hydrometallurgical leach solution are shown with a prospective technical and economical effectiveness up to the full scale operation.

1. INTRODUCTION

Besides the well known ore flotation, adsorptive bubble separation methods are relatively new and prospective. They comprise flotation of ions, colloids, and precipitates from an aqueous solution. The main advantage of these methods over the ion exchange or liquid extraction is their simplicity and applicability to extremely diluted aqueous solutions. The process, based on the adsorption of chemical compounds on gas/water and solid/water interfaces, is realized by the introduction of gas bubbles to the real or colloidal aqueous solution containing a chosen ionogenic surfactant. The surfactant interacts with ions or particles from solution and thus binds them on gas water interface atop the gas bubbles. Resultant foam is enriched in the chemical compounds, and after destruction forms a concentrated suspension (foamate).

The adsorptive bubble separation methods have been detailed in several reviews [2, 4, 7, 15, 30, 32, 33, 39, 43, 44, 46, 48]. Since about twenty years where increasing scientific interest of these methods was observed, some nomenclature problems arose. Several different and not always rational classifications were suggested [17, 30, 33, 42, 46], although two basic groups of ion separation processes are easily distinguished:

---

* Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław Technical University, Wrocław, Poland.

- adsorptive bubble separation of homogeneous system, e. g. foam fractionation, and bubble fractionation,
- adsorptive bubble separation of heterogeneous system, e. g. precipitate flotation, colloid flotation, and colloidal carrier flotation.

The basic difference between these two groups of separation processes is the mechanism of the surfactant action. For a homogeneous system it is like the regular chemical stoichiometric reaction whereas for a heterogeneous system, surfactant adsorbs on the solid particles surface and acts similarly to the collector of ore flotation.

Water pollution control and the chemical metallurgy of rare and precious elements would provide the prospective application field for the adsorptive buble segregation processes. In particular, the effective removal of trace amounts of extremely toxic and radioactive pollutants as well as the recovery of metals from the industrial effluents are of major interest.

2. SEPARATION OF RADIOACTIVE FISSION PRODUCTS BY FOAM FRACTIONATION

Foam fractionation has been applied in the USA and France to the decontamination of radioactive wastes of medium level activity [1, 11, 12, 13]. These solutions, which are usually acidic, contain large amounts of sodium nitrate (0.1–1.0 M) because of neutralization with caustic soda. The concentration of calcium and magnesium ions varies from 100 to 200 g per m^3. The principal radioisotopes present are: ^{90}Sr, ^{137}Cs, and ^{144}Ce.

Due to the chemical composition of wastes, a search was conducted for the surfactant of a great affinity to strontium, caesium, and cerium ions at high concentration of sodium nitrate [1]. Several commercial surface-active agents were tested. The most effective separation of caesium was obtained with sodium tetraphenylboron as the complexing agent and the sodium salt of dodecylbenzyldiethylenetriaminetetraacetic acid (DBDTTA) as the principal foaming agent. The latter agent is also one of the best surfactants for strontium and caesium. Cations such as Sr^{2+} can be removed due to the formation of stable complexes with anionic surfactant under certain conditions. At $pH > 6$, Sr^{2+} forms a complex with DBDTTA, however when the pH is below 4, most of this surfactant is undissociated. In general, the activity governs the competition between the acid form and the metal form of the anionic surfactants. Calcium ions also interfere with the foam fractionation process of strontium and caesium. For example, at the Ca^{2+} concentration increasing from 4 to 80 g/m^3 the decontamination factor of strontium decreases from 183 to 1.6 with DBDTTA as the surfactant. Thus, it is necessary to reduce the concentration of calcium ions by chemical pretreatment of the wastewaters based on the precipitation of calcium oxalate or carbonate.

The application of the foam fractionation to decontamination of a real wastewaters was not very encouraging. This was not because of the low decontamination factors, but because of the great chemical and hydrodynamic interferences observed [11]. The most likely successful application of the foam fractionation is the processing of wastewaters, which at many atomic energy installations have a composition similar to the drinking water of slightly impaired quality. The objective of foam separation project at Oak Ridge National Laboratory (ORNL) was the wastewater processing of the composition shown in table 1 [11].

Table 1

Composition of ORNL process wastewater [11]

Component	Concentration
HCO_3^-	100 g/m^3
Ca^{2+}	27 g/m^3
Mg^{2+}	7 g/m^3
Na^+	1.5 g/m^3
Cl^-	1.5 g/m^3
pH	7.7
^{137}Cs	168 μCi/m^3
^{90}Sr	139 μCi/m^3
^{89}Sr	9.4 μCi/m^3
Rare earths (primary ^{90}Y)	36 μCi/m^3
^{60}Co	18 μCi/m^3

The wastewater contained only ^{30}Sr at the concentration exceeding the maximum permissible concentration for disposal to the environment. Several commercial surfactants were tested using caesium and strontium as check variables. Judged on the basis of performance and economical considerations, dodecylbenzenesulphonate (DBS) was the best surfactant tested, and this surfactant was used in most of the succeeding experiments as well as in the pilot plant test.

Preliminary chemical treatment necessitated by the presence of calcium which interferes with strontium removal during foam separation, was based on adding sufficient sodium carbonate and sodium hydroxide to the water for the residual concentration of 0.0005 M of each. Then slowly stirred, suspensed-bed sludge column was used to remove the resulting calcium carbonate and magnesium hydroxide precipitate.

Applying this procedure and adding Fe^{3+} (a few g/m^3) as a coagulant the reduction of the residual hardness of the water to 5 g/m^3 or less was achieved. At this concentration, calcium does not interfere with the removal of strontium by foam fractionation. In order to improve the removal of caesium, which is not extensively separated by foam fractionation, about 60 g of baked grundite clay was added per 1 m^3 of treated water. The overall flow sheet summarizing the two-step process for strontium removal from radioactive wastewater is shown in fig. 1. The Sr^{2+} decontamination factor across the foam column exceeded 200 with the removal of about 75% of the remaining ruthenium and 80–85% of ^{144}Ce. Pilot plant studies were also conducted with processing rates of 1.13 m^3/hr and 0.45 m^3/hr.

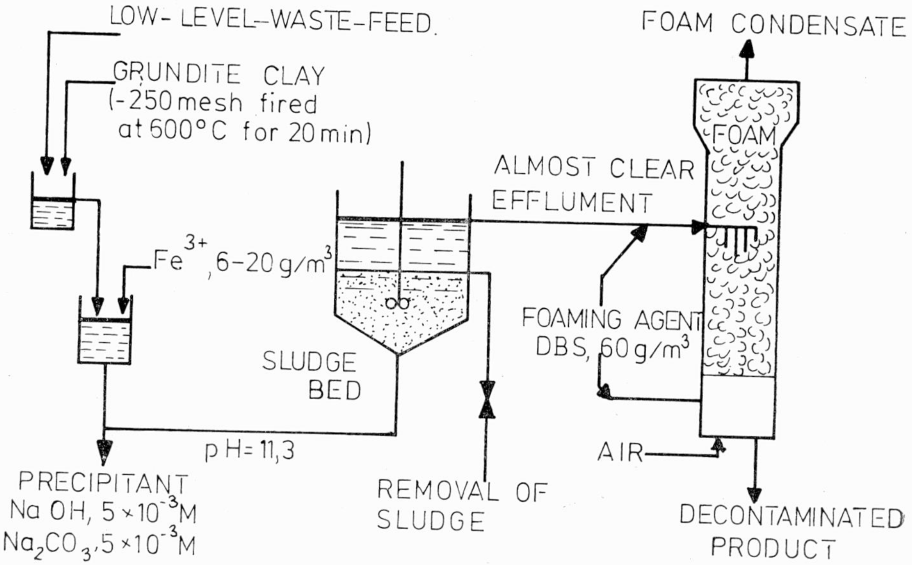

Fig. 1. Flowsheet of the two-step process for removing strontium [11]

Rys. 1. Schemat dwuetapowego procesu usuwania strontu

3. SEPARATION OF FISION PRODUCTS BY PRECIPITATE AND COLLOIDAL CARRIER FLOTATION

The results of the caesium removal by foam fractionation technique show that caesium removal is rather poor and does not warrant further application. Consequently, the allied technique of precipitate flotation was then tested and found more satisfactory [14, 24, 25]. In this method, a suitable precipitate that could be floated readily must be formed in situ with the Cs ions. Its function is to occlude the Cs^+ ions and let remove them from the solution by subsequent flotation of the precipitate. According to the literature [14, 24, 25, 36] many di- and tri-valent metal derivatives of the ferrocyanides have been prepared and most of them were found to be excellent sorbents for caesium ions under both static and dynamic conditions. The ferrocyanides of Zn and Cu have been reported to be the best for use in Cs^+ adsorption [14].

The experiments were carried out on caesium removal by precipitate flotation at various concentrations and ratios of the precipitating agents (figure 2). It is interesting to note that, at a Cu^{2+} concentrations below its equivalent value, removals are virtually nil, whilst at this value and above, removal suddenly reaches the maximum value. The necessity of certain stoichiometric excess of Cu^{2+} ions is clearly demonstrated and from the fig. 2 the copper concentration of $11.81 \cdot 10^{-5}$ M was chosen as an optimum. By varying the pH for each run with either NaOH or HNO_3 results were obtained as in fig. 3, which shows

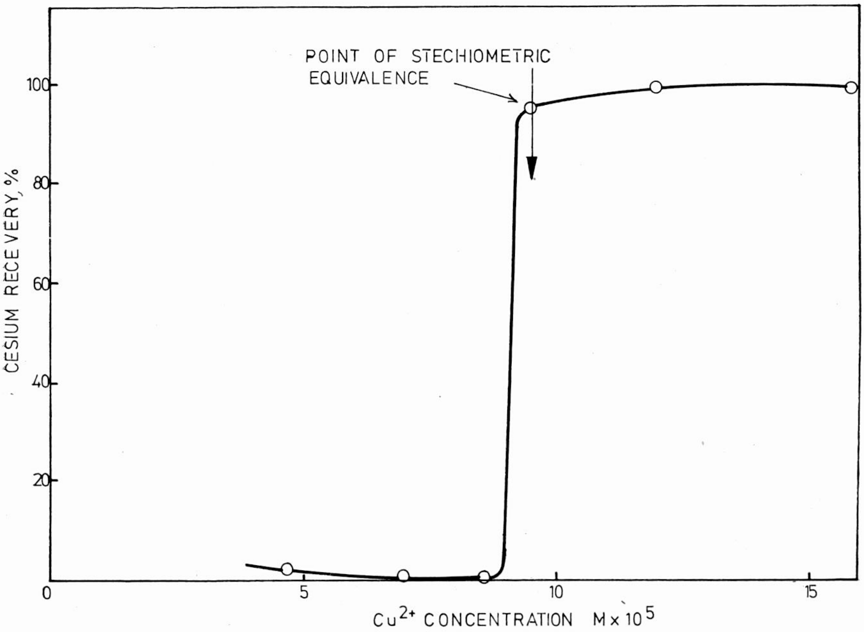

Fig. 2. Variation of copper concentration with caesium removal α-SPA used as surfactant [14]

Rys. 2. Wpływ stężenia miedzi na procent usunięcia cezu

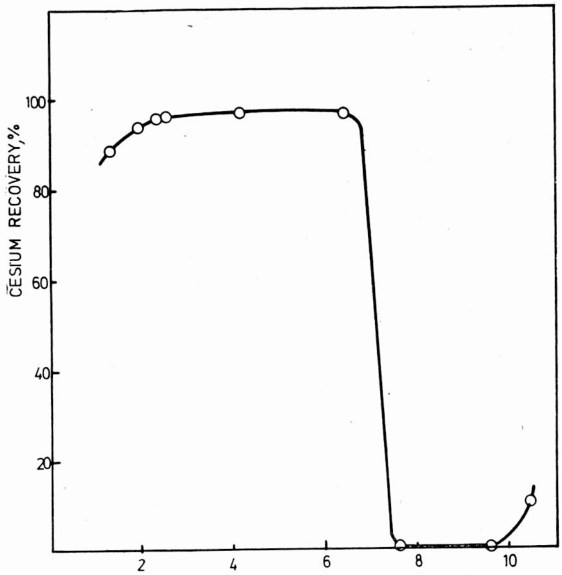

Fig. 3. Variation of caesium removal with pH. α-SPA used as surfactant [14]

Rys. 3. Wpływ pH na procent usunięcia cezu a plateau for the efficient use of α-sulphopalmitic acid (α-SPA) at pH range from 2.5 to 6.0. At pH changed from 6.0 to about 9.5 the caesium removal drops completely. For this pH range the precipitated copper ferrocyanide with occluded Cs ions loses its positive character and therefore cannot be floated by an anionic surfactant.

On the basis of determined flotabilities [26–28, 36] the long-lived fission products are classified into three groups, according to the table 2. ^{137}Cs belongs to the first group and is selectively removed at pH 4.0–5.5 by cupric ferrocyanide as the coprecipitant and with the octadecylamine acetate (ODAA) as the surfactant. The mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr is selectively removed at pH 6.0–8.0 or pH 10.5–11.5 by $Fe(OH)_3$ or $Co(OH)_2$ as the coprecipitant and with the sodium oleate (NaOl) as the surfactant. ^{90}Sr belongs to the third group and is selectively removed at pH 9.0–10.5, by ferric hydroxide as the coprecipitant, with the sodium oleate as the surfactant and with the cupric nitrate as the activator. ^{90}Sr is also removed at pH 9.0–10.5 with octadecylamine acetate as the surfactant.

Table 2

Classification of the long-lived fission products based on their flotabilities [36]

Class	Nuclide	Coprecipitant	Surfactant	Activator	pH
1	^{137}Cs	Cupric ferrocyanide	ODAA	—	3.0– 5.5
2	^{144}Ce ^{106}Ru ^{95}Zr	Cobalt hydroxide	NaOl	—	10.5–11.5
		Ferric hydroxide	NaOl	—	6.0– 8.0
3	^{90}Sr	Ferric hydroxide	NaOl ODAA	cupric. nitrate —	9.5–10.5 9.5–10.5

The experimental procedure was as follows: 100 cm^3 of original wastewater was put in 300 cm^3 beaker, and then coprecipitant and the pH regulating agent were added. The mixture was stirred rapidly for 10 minutes, the surfactant was added and stirred again for 5 min. Thereafter the frother was added and the pH was measured. The waste solution pre-treated in such a way was fed into the flotation cell and resultant froth was colected for 1 min.

According to the fission products classification (table 2) the following experimental procedure was applied (fig. 4).

1. At the first stage (fig. 4) the mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr was selectively removed at pH 6.0–8.0 by 30 g/m^3 of ferric hydroxide as the coprecipitant and 20 g/m^3 of sodium oleate as the surfactant.

2. At the second stage ^{90}Sr was selectively removed at pH 9.5–10.5 by 60 g/m^3 ferric hydroxide as the coprecipitant, 20 g/m^3 of cupric hydroxide as the activator and 20 g/m^3 of sodium oleate as the surfactant.

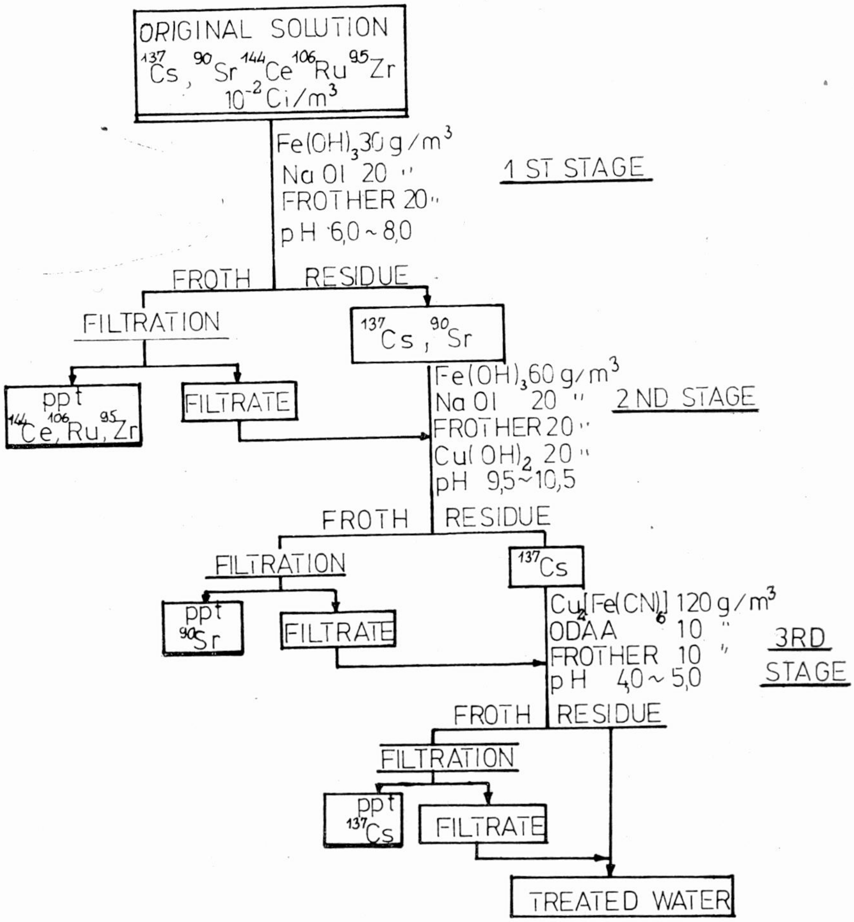

Fig. 4. Procedure for the preferential precipitate flotation of the long-lived fission products [36]

Rys. 4. Schemat flotacji osadów trwałych produktów rozszczepienia

3. At the third stage, ^{137}Cs was selectively removed at pH 5.0–6.0 using 20 g/m^3 of cupric ferrocyanide as the coprecipitant and 10 g/m^3 of octadecylamine acetate as the surfactant.

The experimental results on the selective removal of the mixed fission product, according to the order collection from fig. 4 are shown in fig. 5. Curve (*I*) from fig. 5 shows gamma-ray spectrum of the original solution. The curve illustrates ^{144}Ce, ^{106}Ru–^{106}Rh, ^{137}Cs and ^{95}Zr–^{95}Nb photopeaks at channel numbers 15, 59, 75 and 89, respectively. Curve (*II*) gives the gamma-ray spectrum of the treated water from the first stage; the ^{144}Ce and ^{106}Ru–^{106}Rh photopeaks considerably disappear. By the quantitative analysis of long-lived fission products, it was confirmed that 98% of ^{144}Ce, 98% of ^{106}Ru and 99% of ^{95}Zr were selectively removed at the first stage precipitate flotation, while 98% of ^{137}Cs and ^{90}Sr remained in the treated water.

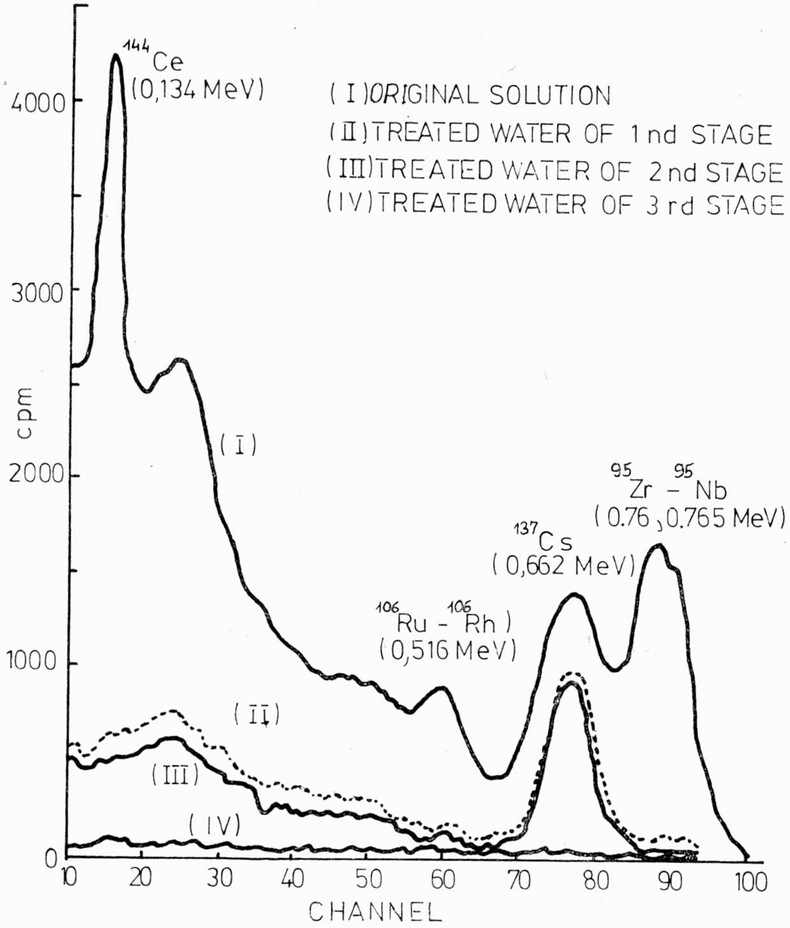

Fig. 5. Gamma-ray spectra of the original solution and the treated water [36]

Rys. 5. Gamma spectrum roztworu oryginalnego i przerabianego

Curve (*III*) gives the gamma-ray spectrum of treated water from the second stage. In comparison with the curve (*II*) the heights of all photopeaks decrease slighly. From the results of the quantitative analyses, it was recognized that only 2% of ^{137}Cs, 1% of ^{144}Ce, and 1% of ^{106}Ru were removed, but ^{90}Sr removal reaches 87% at the second stage precipitate flotation. Curve (*IV*) shows the gamma-ray spectrum of the treated water from the third stage, where flotation was carried at pH 5.0 for the recovery of ^{137}Cs. The ^{137}Cs photopeak disappears. From the quantitative analyses 95% of ^{137}Cs and 7% of ^{90}Sr removal in the third stage precipitate flotation were found. The total flotation efficiency for each nuclide is as follows: 99% for ^{137}Cs, ^{144}Ce, ^{106}Ru, and ^{95}Zr, 96% for ^{90}Sr. This study confirmed that the mixed long-lived fission products could be selectively removed by the preferential precipitate flotation of three stages. It is also conceivable that the preferential precipitate flotation represents a new economical secure method for the wastewater treatment from the chemical processing of used nuclear fuel. Also OGŁAZA and SIEMIASZKO [37], applying $Cu_2Fe(CN)_6$ as the coprecipitant, removed ^{90}Sr and ^{137}Cs isotopes from the wastewater.

Another approach to this problem has been presented by PUSHKAREV and co-workers [38–40, 45]. Their research was concerned with the separation of radioisotopes like ^{106}Ru, ^{144}Ce, ^{95}Zr, ^{90}Y and ^{90}Sr at the concentration of 5–15 mCi/m^3 by the ferric hydroxide as a colloidal coprecipitant and gelatin as a surfactant for colloidal carrier flotation. The conditions chosen for selective removing were as follows:

^{90}Y — at a $pH \geqslant 6$ with 96–99% removal;
^{95}Zr at a $pH \geqslant 2.3$ with removal equal to 96–99%;
^{144}Ce can be removed at a $pH \geqslant 6.5$ (99%);
^{106}Ru can be recovered with 90% efficiency at pH 5;
the best ^{98}Sr removal was achieved at pH 10.0 (97%).

4. SEPARATION OF TRACE-METAL IONS FROM SEAWATER BY ADSORPTIVE COLLOID FLOTATION

Adsorptive colloid flotation technique can be applied for the separation of trace-metal ions from seawater. The first study concerns the recovery of molybdenium from seawater [18, 21]. Under the best chosen conditions molybdate is flotated quantitatively and reproducibly in less than five minutes as an easity removable froth by positively charged iron (III) hydroxide collector an anionic surfactant (sodium dodecylsulphate) and the air bubbles. The attraction of molybdate ion to the colloidal collector is presumably of electrostatic and chemical nature. With an anionic surfactant and at low pH, the positively charged surfaces of the molybdenum-enriched ferric hydroxide particles attract the surfactant anions.

This technique was also applied successfully to the separation of uranium, as the stable uranyl carbonate ion, $UO_2(CO_3)_3^{4-}$ [19]. At pH equal to 6.7 the uranium to the concentration range 2.9–3.3 kg/m^3 is adsorbed effectively on the positively charged ferric hydroxide. In the presense of sodium dodecylsulphate added to the seawater, colloidal particles of $Fe(OH)_3$ enriched by adsorption with uranium are floated within 2–3 minutes. Thorium (IV) hydroxide was found to be more efficient adsorbent of uranium [22, 23, 34]. With the sodium dodecanoate and thorium (IV) hydroxide recovery of uranium from seawater by flotation was improved from 82 to ca 91%. It may be explained on the basis of the Paneth-Fajans-Hahn rule, according to which, the effectiveness of the adsorbing colloid depends on the solubility of the adsorbing anion-precipitate cation compound. The uranium tricarbonate anion forms with Th(IV) a compound which is of lower solubility than ferric uranium carbonate. It appears that the solubility of such compounds is an important factor in the process of cooprecipitation-flotation of trace elements.

Colloid flotation was next extended to the separation of trace cations of zinc (II) and copper (II) from seawater by the use of negatively charged ferric hydroxide at pH 7.6 and with a cationic surfactant, dodecylamine [20]. Statistical studies on test series show a mean metal recovery of 94.0% with a relative standard deviation of 6.1% for zinc and of 95.0% with a relative standard deviaton of 6.1% for copper. Cationic surfactants, like hexadecylammonium chloride and docedylpyridium chloride were also tested, however without success. The results were obtained for basic solutions. This is ascribed to the fact that a cationic amine will lose its proton in alkaline solution and hence its cation properties disappear as a result of the reversion to the uncharged form. More recent work has applied the flotation technique to such heavy metal pollutants as cadmium and mercury [47]. The results obtained are summarized in table 3. Although these studies have been confirmed to laboratory scale, there is potential perhaps for the separation of various trace metals from seawater of economical importance such as uranium [23].

Table 3

Summary of results of the trace metal ions separation by colloid flotation [23]

Metal	Ionic species	Surfactant	pH	Ionic concentration in seawater, mg/m^3	Recovery per cent
Molybdenum	MoO_4^{2-}	sodium dodecylsulphate	4.0	11.4	95.3
Uranium	$UO_2(CO_3)_3^{4-}$	sodium dodecylsulphate	5.7	3,2	82.0 and 91.0
Zinc	Zn^{2+}	Dodecylamine	7.6	3.2	94.0
Copper	Cu^{2+}	Dodecylamine	7.6	0.8	93.0

5. RECOVERY OF URANIUM AND OTHER METALS FROM THE MINE WATERS

Rabrenovic has studied [41] uranium ion flotation from the low grade uranium ore leach solution. The leaching process was accomplished with sulphuric acid, so that uranium in the solution is being presented as uranylsulphate complex anion. The leach solution contents ranged: 0.475–2.10 kg/m^3 of U, 3.15–6.46 kg/m^3 of Fe, 0.45–2.02 kg/m^3 of Mg, 0.029–0.11 kg/m^3 of As, 0.001–0.057 kg/m^3 of Cu, 0.087–0.500 kg/m^3 of Zn and 0.30–0.71 kg/m^3 of SiO_2. The pH value of the solutions ranged from 1.0 to 2.3. Several surfactants like primary and tertiary amines, and different fatty acids of the plant and animal origin have been tested, as well as their acetates of various commercial names such as: Armeen, Duomeen, Armac, Flotigam. The best results 76–90% of uranium recovery were obtained with Armeens 12 D and C, and Flotigam PA, and SA. The process, however, was considerably slow: 30–40 minutes. To improve the process, and especially to rise its rate, liquid ion exchangers were introduced as activators. Triooctylamine (TOA) and triisooctylamine (TiOA) in combination with various precipitate collectors were tested. Several comparable results are given in fig. 6. The results show possibility not only to improve the process to the practically complete recovery of uranium up to 97 and 99%, but also to increase the process rate.

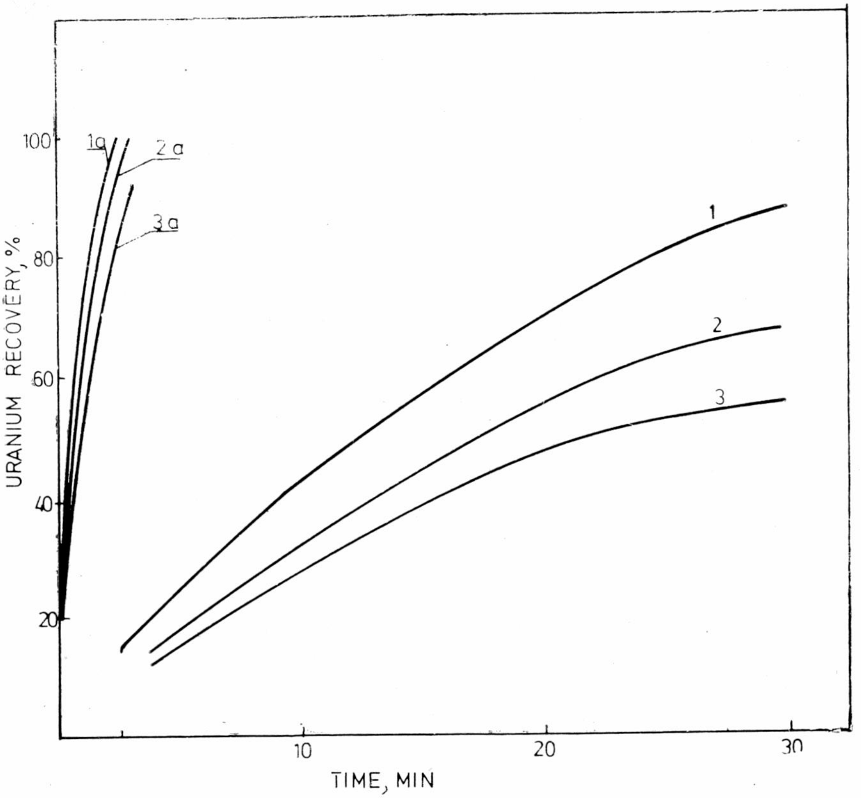

Fig. 6. Comparable results of the uranium ion flotation without (1, 2, 3) and with (1a, 2a, 3a) ion exchangers [41]

1 – Armeens 12D, 1a – Armeens 12D+TOA or TiOA,

2 – Flotigam PA, 2a – Flotigam PA+TOA or TiOA,

3 – Armacs C, 3a – Armacs C+TOA or TiOA.

Rys. 6. Porównawcze wyniki flotacji jonowej bez (1, 2, 3) i z (1a, 2,a 3a,) wymieniaczami jonowymi

JUDE and FRATILA [16] investigated uranium recovery from mine water by ion flotation, test on uranium compounds was carried out with mine carbonate water, and at the varied flow rates, depending on the atmospheric conditions. Concentration ranges of the different component of water studied were: U, 0.002–0.005 kg/m^3; Cl, 0.0128–0.183 kg/m^3; Na_2CO_3, 0.0412–0.0557 kg/m^3; Ca, 0.036–0.040 kg/m^3; Mg, 0.040–0.090 kg/m^3; SO_4^{2-}, 0.054–0.097 kg/m^3; Mo 0.001 kg/m^3 and pH 6.5–7.0. Uranium was present as uranyl tricarbonate ($UO_2(CO_3)_3^{4-}$). Talamine acetate and Aerofloat 31 were used as collecting reagents during flotation tests under the following constant working conditions: flotation with talamine acetate — flotation time 20 min.; reagent consumtion 1.5 kg/m^3; for flotation with Aerofloat 31 — flotation time 25 min.; reagent consumption 0.8 kg/m^3. The three-stage flowsheet of flotation tests (fig. 7) in mechanical cells with self aeration with

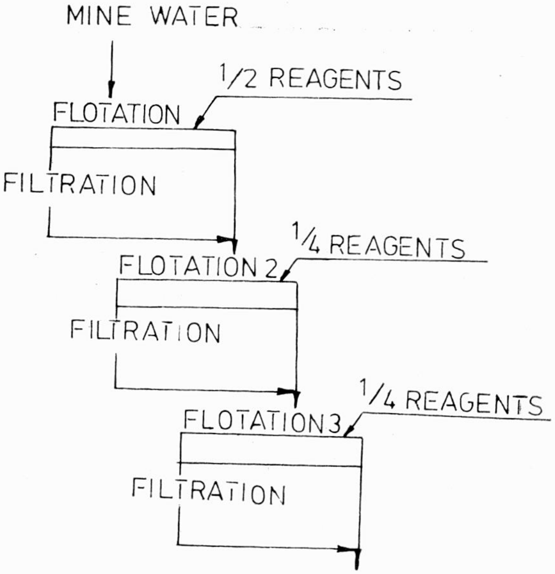

Fig. 7. Three-stage flotation flowsheet of uranium recovery from mine water [16]
Rys. 7. Trzystopniowy schemat flotacji jonowej uranu z wód kopalnianych

fractional reagents dosing was considered to be the most attractive. With richer solutions (0.005 kg/m^3) of uranium and flotation with Aerofloat 31 metal recoveries of 93% were obtained, the ratio of the uranium content in the initial solution to that in final waste, i. e. the decontamination ratio was 16.7. Under similar conditions with talamine acetate, metal recoveries of 90.8% were obtained and the decontamination ratio was 11.0. With smaller contents (3.5 g/m^3) of uranium in the initial solution the uranium compounds were recovered almost completely after the second stage of flotation. The resultant flotation concentrate comprises a liquid and solid phase, and reaches about 10–15% by volume of the initial solution. The uranium is distributed virtually completely in the solid phase. Flotation concentrate was filtered and the liquid phase was reintroduced into the circuit. Other compounds, e. g. molybdenum were floated together with the uranium. In addition to the mentioned data, which represent the technological results obtainable by flotation with mechanical stirring and self-aeration, some tests were also carried out in flotation columns on mine waters that were either clear solutions or contained, at most, 1-2 kg/m^3 of solid phase. These waters do not require strong stirring and are amenable to column operations. In comparison with the normal flotation cell, columns are much cheaper and their use may lead to considerable saving in operational cost. The uranium recovery was equal to that for flotation cells.

BIKERMAN and co-workers [3] conducted basic experiments on the feasibility of foam fractionation for the treatment of acid coal mine drainage and the removal of iron, calcium manganese and magnesium. Experiments were conducted with synthetic and real acid mine waters. The composition of the synthetic water was: 0.997 kg $FeSO_4 \cdot 7H_2O$, 0.344 kg $CaSO_4 \cdot 2H_2O$, 0.186 kg $Al_2(SO_4)_3 \cdot 18H_2O$, 0.246 kg $MgSO_4 \cdot 7H_2O$, and 0.024 kg $MnSO_4 \cdot H_2O$ dissolved in 1 m^3 of 0.005 M H_2SO_4, and was similar to the composition of common and actual acid mine drainage. The few experiments performed on artifical sodium dodecylsulphate as a surfactant have indicated that the accumulation of iron, calcium and magnesium in foamate is feasible in complex solutions. The production of persistent foams was greatly reduced when the complex solutions were used. Further addition of gelation agent improved foam production and persistence. A sample of natural mine drainage was subjected to foaming for 24 hours. Before the foaming was started, significant oxidation, and precipitation of ferric hydroxide had occurred as evidenced by red precipitate in the sampling containers. Thus, these experiments are explained by colloidal iron and the well known scavenging properties of ferric hydroxide for other soluble metal ions. Table 4 illustrates the material balance for major metallic constituent, e. g. ferrous iron at an effective rate of 26.7 m^3/day. This balance can be scaled up linearly for 267 m^3/day. Operating costs for 26.7 m^3/day and 267 m^3/day foam separation were estimated in the range of 1.91–5.82 \$/m^3. The key to reducing operating costs is reuse of surfactant. The capital estimated cost for complete plants ranges \$ $4.13–6.46 \times 10^5$ and \$ $1.53–1.70 \times 10^6$ for 26.7 m^3/day and 267 m^3/day capacities, respectively.

Table 4

Chemical costs estimate of foam separation for the treatment of acidic coal mine waters [3]

	Material balance for pilot-plant	Additional suction foaming for reduction of surfacant loss
Water volume, m^3	150	—
Fe removal, kg	44.5	—
NaOH used for surfactant regeneration, kg	95.1	—
Surfactant loss, kg	100	21.1
NaOH cost, \$	10.50	10.50
Surfactant cost, \$	66.00	13.90
Total chemical cost, \$	76.50	24.40
Total chemical cost per 1 m^3, \$	0.51	0.16

6. RARE METALS RECOVERY BY FOAM SEPARATION

The development of the chemical metallurgy, particularly hydrometallurgy and more recent biometallurgy opens a new prospect for application of adsorptive bubble separation methods. Several papers of CHAREWICZ and co-workers [5, 8, 9, 10] discussed flotation of ions originated from rare metals, such as rhenium, molybdenum, gold and vanadium. One of these problems was the rhenium recovery from the waste acidic solution and dusts of copper smelter [5, 8]. During the original smelting process of copper concentrate about 50 to 60% of rhenium goes to the converter dust and gases. To process the converter gas for sulphuric acid production this gas is washed by circulating solution of the sulphuric acid at the concentration of about 50%, and average rhenium concentration up to 0.25 kg/m^3. That solution must be periodically withdrawn from the process and then neutralized before release to the wastewaters. For the perrhenate ion experiments, the acid waste solution of the composition: Re — 0.145 kg/m^3, Mo — 0.050 kg/m^3, Cu — 4.6 kg/m^3, Pb — 4.2 kg/m^3 and H_2SO_4 — 51.4%, was taken. On the basis of the previous studies [5] it was confirmed that respective dilution of the circulating acid solution could provide selective separation of perrhenate anions by flotation with a cationic surfactant leaving cations and molybdenum in the residual solution. Thus the feed solution was diluted with water and the resulting lead sulphate was separated, then diluted and clear solution was subjected to flotation with the quaternary ammonium surfactant, dimethylbenzyldodecylammonium bromide. Fig. 8 illustrates the laboratory-scale results. The best separation factor for rhenium is achieved at sulphuric acid concentration of 0.17 M which corresponds to the forty-fold dilution of the original industrial solution. The rhenium recovery drops at the higher H_2SO_4 concentration. Although surfactant was used in about thirty-fold weight excess, its losses were estimated as equal to 10%. About 90% of surfactant can be recovered from the foamate and then reused. The flotation concentrate (foamate) processing was successfully studied by means of coacervation as well as the ion exchange techniques. The rhenium recovery process by selective flotation of perrhenate anions is shown in fig. 9. The process gives the rhenium recovery as $KReO_4$ up to 95% and surfactant recovery up to 85%. The only loss of perrhenate occurs at the barium sulphonate stage. The above process was patented and tested on a pilot-plant with the flotation column of the capacity 2 m^3. The test confirmed previous results and gave rhenium recovery of 95% at sulphuric acid content in solution from 0.10 to 0.20 M with the Re versus Mo separation from 500 to 600, and volume reduction up to 1000.

Another example of the search for an application of ion flotation in the hydrometallurgy of rare and elements is the work on flotation of chloroaurate anions from anodic slime leach solution [10]. The anodic slime from copper electrorafinery contains a substantial amount of silver, and some other elements, like selenium, tellurium, gold, and platinides [6]. A hydrometallurgical processing of this slime is based on the leaching it by nitric acid for extraction of silver, copper and iron. All gold remains in the residual solid phase and can be

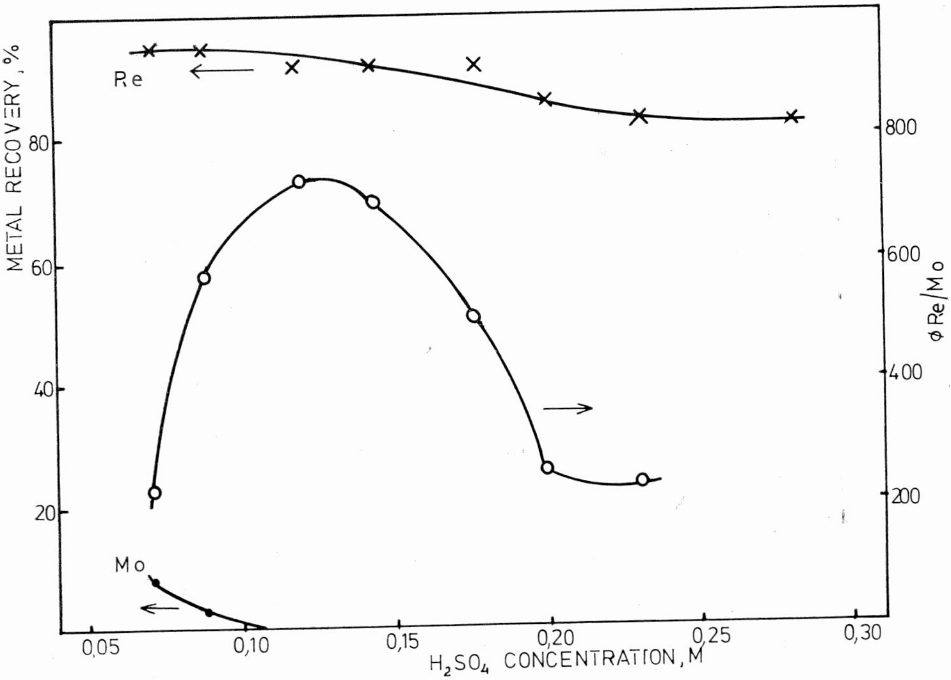

Fig. 8. Laboratory-scale results on the selective flotation of perrhenates from the acidic circulating solution of copper smelter [5]

Rys. 8. Wyniki laboratoryjnych badań flotacji nadrenianów z kwaśnego roztworu obiegowego

extracted by leaching with the mixture of nitric and hydrochloric acids:

$$Au+4H^{+}+NO_3^{-}+4Cl^{-} \rightleftharpoons AuCl_4^{-}+NO+2H_2O.$$

Chloroaurate anions can be recovered by flotation with a cationic surfactant. It was confirmed that gold was completely removed with dimethylhexadecylammonium chloride (HPCl) as the surfactant [10]. Silver which exists in the leach solution at a considerably lower concentration is removed up to 20% for DEHAHCL and up to 33% for HPCl (fig. 10), most probably because of its chloride complexation leading to Ag $(CN)^{-}$ anions.

The first commercial application of molybdate ion flotation was reported in the Soviet Union [31],where the ion flotation was selected, because it is particularly significant from the point of view of this metal utilization, often present in small quantities in industrial solutions and effluents, as well as because of technological considerations on wastewater treatment. Particularly as a raw material for commercial molybdenum recovery by ion flotation, waste solution from calcium molybdenum processing was selected. This solution had pH value of 8–9 and contained: Mo, 0.1–1 kg/m^3; Cl$^-$, 0.3–3 kg/m^3; SO_4^{2-}, 1.5–4.5 kg/m^3; HCO_3^-, 1–2 kg/m^3; CO_3^{2-}, 0.02–0.04 kg/m^3 and impurities of Fe, Al, SiO_2. For many years substantial amounts of molybdenum have been lost with discharged waste solutions polluting the environment.

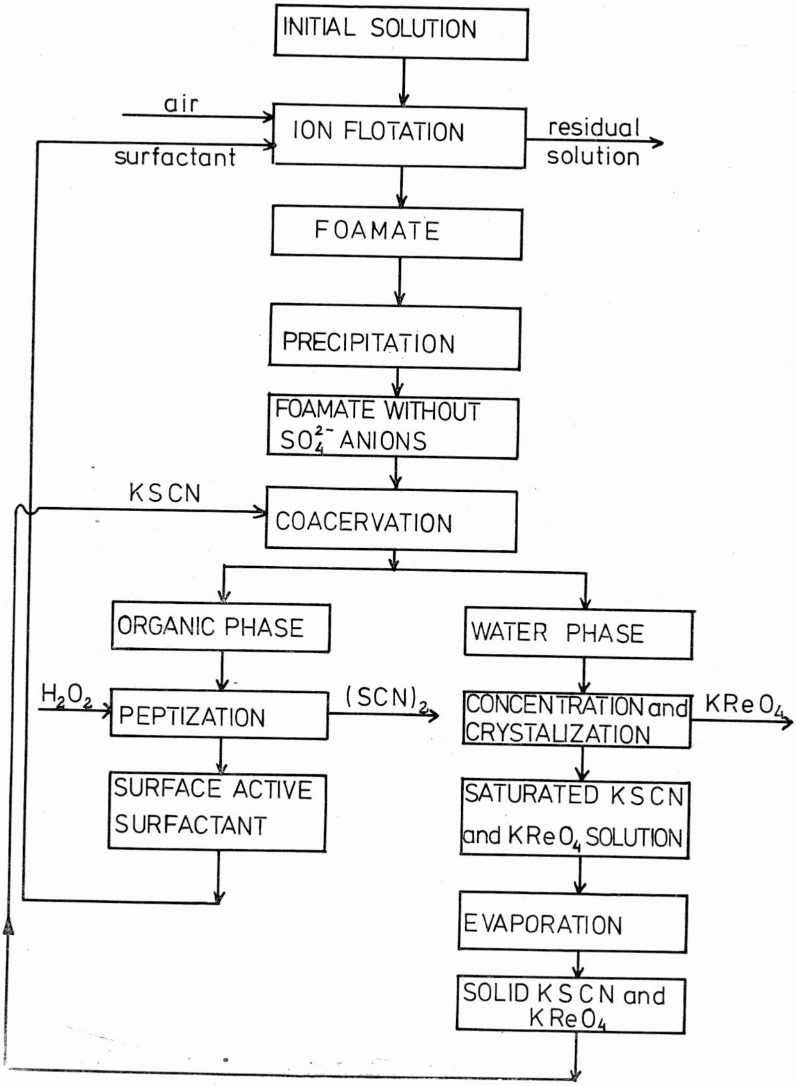

Fig. 9. The flowsheet of rhenium recovery process from the circulating acid solution of copper smelter by ion flotation [5]

Rys. 9. Schemat procesu otrzymywania nadrenianu potasowego z kwaśnych roztworów obiegowych metodą flotacji jonowej

Laboratory scale research indicated that purified ANP (amino paraffine chlorhydrate) reagent added to the sample of industrial wastewaters at a concentration of 40–60 kg/m^3, the consumption rate of 3.0–3.5 kg/kg of Mo and pH value 3.6–3.9 provide the recovery of 90–95% of Mo within 2–3 minutes. The flowsheet of commercial scale plant is given

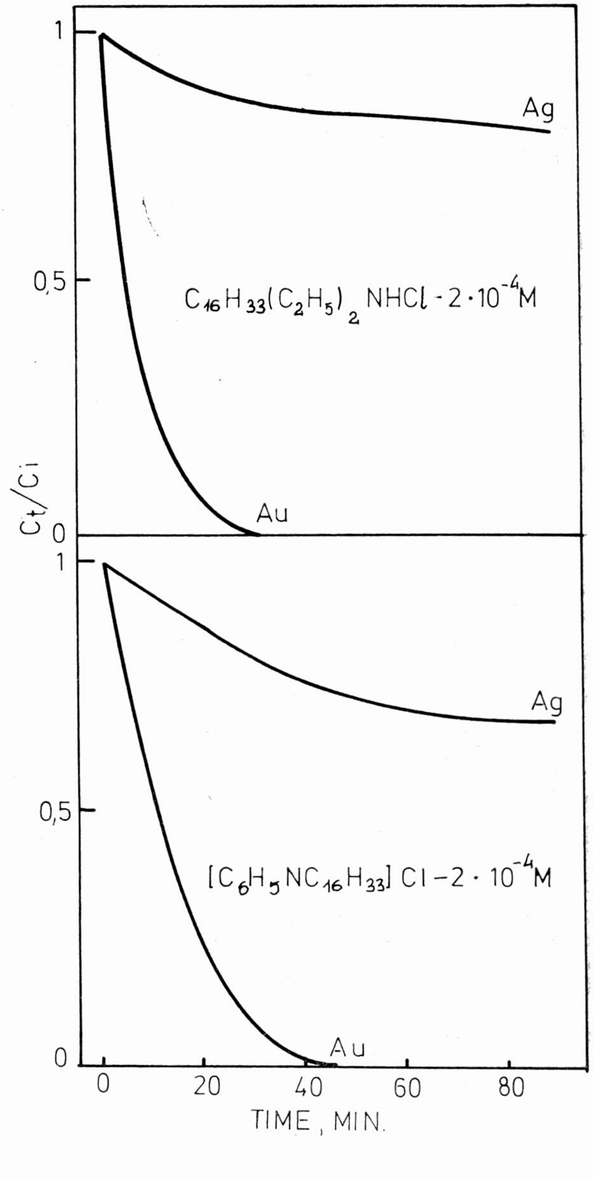

Fig. 10. Flotation of gold and silver from diluted leach solution of anodic slime residual (initial Ag concentration — $4.4\cdot10^{-8}$ M, initial Au concentration — $6.3\cdot10^{-6}$ M) [10]

Rys. 10. Flotacja złota i srebra z rozcieńczonych roztworów potrawiennych (stężenie początkowe Ag — $4.4\cdot10^{-8}$ mol/m^6, Au — $6.3\cdot10^{-6}$ mol/m^3)

in fig. 11. The process comprises acidification of feed solution, ion flotation of molybdenum with purfied ANP reagent and roasting of froth product. Eventual collector regeneration is also included. Operation of the commercial unit, started up in September 1972, proved the high efficiency of the process. The recovery o molybdenum from the initial solution into the commercial product amounts to 90–95%, the enrichment ratio is about 2,000, the economic effect exceeds Rbl 16 per kg of molybdenum recovered.

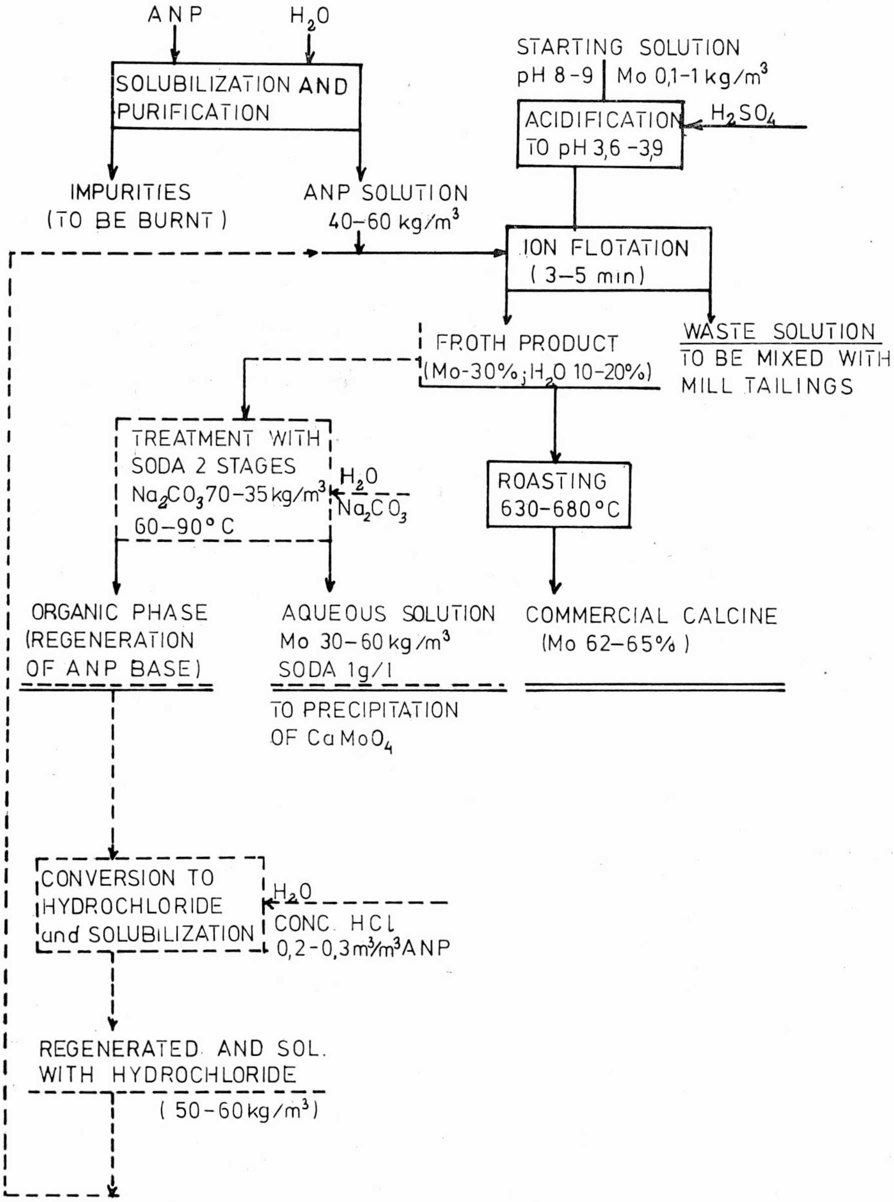

Fig. 11. Flowsheet of a commercial-scale plant for ionic flotation of molybdenum [31]

Rys. 11. Schemat przemysłowej instalacji do flotacji jonowej molibdenu

FINAL REMARKS

The work presented in the paper confirms an increasing scientific and technological interest in the application of adsorptive bubble separation methods to wastewater treatment and rare metals recovery. At first the attention was put on the decontamination of the radioactive wastewaters and subsequently on the rare and precious metals recovery from different industrial effluents and also from the leach solutions. The recoveries, enrichment ratios and volume reductions are relatively high. The precipitate or colloid flotation processes rates are relatively higher than for foam separation. The major advantages of these separation methods are: their simplicity, high rates and possibility of processing reasonably higher volumes of wastewaters at a given technological unit as compared to ion exchange, solvent extraction or sorption. The main disadvantage seems to be in the cost of adequate surfactants and consequently success of the simple and economical methods is connected with the reuse of surfactants. It seems that further development of these new separation techniques in the environmental pollution control and chemical metallurgy depends on the basic research studies. The studies should aim at synthesis of new highly selective surfactants, as well as their selective action during the flotation and at the new effective methods of surfactant regeneration.

METODY ADSORPCJI NA PĘCHERZYKACH GAZU I ICH ZASTOSOWANIE DO OCHRONY WÓD I ODZYSKU PIERWIASTKÓW RZADKICH

Dokonano przeglądu prac dotyczących zastosowań metod adsorpcji na pęcherzykach gazów w ochronie wód przed zanieczyszczeniem i metalurgii pierwiastków rzadkich. W szczególności omówiono dekontaminację radioaktywnych wód za pomocą flotacji jonów i osadów. Przedstawiono również prace dotyczące odzysku uranu i innych metali z wód kopalnianych i z wody morskiej za pomocą flotacji jonów i osadów. Ponadto pokazano wyniki flotacji anionów nadrenianowych, molibdenianowych i chlorozłocianowych z odpadowych roztworów i ścieków przemysłowych oraz z roztworów po hydrometalurgicznym ługowaniu. Podkreślono techniczną i ekonomiczną efektywność tych operacji w skali przemysłowej.

ADSORPTION AN GASBLASEN – ANWENDUNG IM GEWÄSSERSCHUTZ UND ZUR RÜCKGEWINNUNG SELTENER ELEMENTE

Der Beitrag gibt einen Überblick über bisher bekannte Arbeiten im Bereich der Adsorption an Gasblasen. Im einzelnen wird die Dekontaminierung radioaktiver Wässer mittels der Ionen-und Feststoff-Flotation erläutert. Weiterhin wird über Versuche zur Rückgewinnung von Uran und anderer Metalle aus Gruben- und Meerwasser mit Hilfe des erwähnten Flotationsverfahrens berichtet. Flotationsergebnisse von Perrhenat-, Molybdat- und Chloroaurat-Anionen aus industriellen Abfallaugen und aus Extraktionslaugen der Hydrometallurgie werden dargelegt. Hingewiesen wird auf die technische und ökonomische Effektivität dieses Verfahrens bei Einsatz im technischen Maßstab.

МЕТОДЫ АДСОРБЦИИ НА ПУЗЫРКАХ ГАЗА И ИХ ПРИМЕНЕНИЕ ДЛЯ ОЧИСТКИ ВОД И ВЫДЕЛЕНИЯ РЕДКИХ ЭЛЕМЕНТОВ

Выполнен обзор последних работ по использованию метода адсорбции на пузырках газа в очистке вод и металлургии редких элементов. В частности, обсуждается обеззараживание вод с помощью флотации ионов и осадков. Рассмотрены современные работы по выделению урана и других металлов из рудничных и морских вод с помощью этого метода. Кроме того, представлены результаты флотации перренатных, молибдатных и аурихлоридных анионов из промышленных сбросных вод, а также из растворов после гидрометаллургического выщелачивания. Отмечена техническая и экономическая эффективность этих операций в промышленных масштабах.

REFERENCES

[1] Arod J., *Separation of surfactant and metallic ions by foaming: Studies in France*, [In:] *Adsorptive bubble separation technique*, Interscience, New York 1972.

[2] Baarson R. L., Ray C. L., *Precipitate flotation: A new metal extraction and concentration technique*, The American Institute of Mining, Metallurg. Petrol. Engrs, Symposium on unit processing in hydrometallurgy, Dallas, Texas, February 24–28, 1963.

[3] Bikerman J. J., Hanson P. J., Rose S. H., *Treatment of acid mine drainage by foam fractionation*, Water Pollution Control Research Series, FWQA No 14010, Washington 1970.

[4] Charewicz W., *Selective ion flotation* (In Polish), Papers of Inst. Inorg. Chem. and Metallurgy, of Rare Elements Wrocław Tech. Univer., No 34, Monographs No 10, Wrocław 1975.

[5] Charewicz W., *The use of ion flotation to rhenium separation from some industrial solutions* (In Polish), Papers of Inorg. Chem. and Metallurgy of Rare Elements of Wrocław Tech. Univer., Studies and Research No 4, 71–88, 1971.

[6] Charewicz W. et al., *A balance of hydrometallurgical anodic slime treatment technology* (in Polish), Papers of Inst. of Inorg. Chem. and Metallurgy of Rare Elements, Wrocław Tech. Univ., Conferences No 6, 227–237, 1976.

[7] Charewicz W., Niemiec J., *Ion flotation* (In Polish), Wiadomości Chem. **20** (11), 693–709, 1966.

[8] Charewicz W., Torbiński R., Walkowiak W., *A method for rhenium recovery from copper smelters, dusts, growths and solutions*, Polish Patent No 72692, 1974.

[9] Charewicz W., Walkowiak W., *Physico-chemical processes of separation of metals from leach solutions* (In Polish), Fizykochemiczne problemy przeróbki kopalin **8**, 191–(222), Wrocław 1974.

[10] Charewicz W., Walkowiak W., *Ion flotation of gold from the acidic leach solutions* (In Polish), Fizykochemiczne problemy przeróbki kopalin **6**, 49–55, Gliwice 1972.

[11] Davies Jr. W., Haas P. A., *Separation of surfactants and metallic ions by foaming: Studies at Radiation Applications Inc., and Oak Ridge National Laboratory*, U. S. A., Chapter 19 [In:] *Adsorptive Bubble Separation Technique*, Interscience, New York 1972.

[12] Davies S. B., Sebba F., *Removal of trace amounts of strontium from aqueous solutions by ion flotation. I. Batch experiments*, J. Appl. Chem. **16** (10), 293–297, 1966.

[13] Davies S. B., Sebba F., *Removal of trace amounts of strontium from aqueous solutions by ion flotation. II. Continuous scale operation*, J. Appl. Chem. **16** (10), 297–300, 1966.

[14] Davies S. B., Sebba F., *The removal of radioactive ceasium contaminants from simple aqueous solutions*, J. Appl. Chem. **17** (2), 40–43, 1967.

[15] Eldib I. A., *Foam and emulsion fractionation*, [In:] *Advances in petroleum chemistry and refining*, Vol. 7, Interscience, New York 1963.

[16] Jude E., Fratila J., *Recovery of uranium compounds in mine water by ion flotation*, 10th Intern. Mineral Processing Congress, London 1973.

[17] Karger B. L., Grieves R. B., Lemlich R., Rubin A. J., Sebba F., *Nomenclature: Recomendations for adsorptive bubble separation methods*, Separation Science **2**(3), 401–404, 1967.

[18] Kim Y. S., Zeitlin H., *Separation of molybdenum from seawater by adsorbing colloid flotation*, Separation Science **6** (12), 505–513, 1971.

[19] Kim Y. S., Zeitlin H., *Separation of uranium from seawater by adsorbing colloid flotation*, Anal. Chem. **43** (11), 1390–1493, 1971.

[20] Kim Y. S., Zeitlin H., *The separation of zinc and copper from seawater by adsorbing colloid flotation*, Separation Science **7** (1), 1–12, 1972.

[21] Kim Y. S., Zeitlin H., *The role of iron (III) hydroxide as a collector of molybdenum from seawater*, Anal. Chim. Acta **46** (1), 1–8, 1969.

[22] Kim Y. S., Zeitlin H., *Thorium hydroxide as a collector of molybdenum from seawater*, Anal. Chim. Acta **51** (3), 516–519, 1970.

[23] Kim Y. S., Zeitlin H., *Separation of trace metal ions from seawater by adsorptive colloid flotation*, Chem. Commun. **13**, 672, 1971.

[24] Koyanaka Y., *Treatment of radioactive waste regenerant of ion exchange resins by preferential flotation method*, Journal of Nucl. Science and Technology **6** (10), 607–608, 1967.

[25] Koyanaka Y., *Studies on separation of fission product by flotation method — separation of* ^{137}Cs, Radioisotopes (Tokyo) **15** (2), 77–82, 1966.

[26] Koyanaka Y., *Studies on removal of fission product by flotation method-removal of* ^{144}Ce, Technical Report of Res. Reactor Inst. Kyoto Univ. No 19, 1966. Trans. Kernforschungszentrum Karlsruhe, No 232, 1967.

[27] Koyanaka Y., *Studies on removal of fission product by flotation method-removal of* ^{106}Ru, Technical Report of Res. Reactor Inst. Kyoto Univ. No 21, 1966, Trans. Kernforschungszentrum Karlsruhe, No 233, 1967.

[28] Koyanaka Y., *Studies on removal of fission product by flotation method-removal of* ^{95}Zr–^{95}Nb, Technical Report of Res. Reactor Inst. Kyoto Univ. No 24, 1966, Trans. Kernforschungszentrum Karlsruhe, No 234, 1967.

[29] Koyanaka Y., Trutsui T., *Treatment of the radioactive sludge producted by precipitate flotation method*, Ann. Repts. of Res. Reactor Inst. Kyoto Univ. **3**, 147–152, 1970.

[30] Kuzkin S. F., Golman A. M., *Flotation of ions and particles*, Nedra, Moscow 1971.

[31] Larkovin N. B., Golman A. M., Kuznetsova E. N., Gorodetsky M. I., Meder L. I., Plasca N. E., Nikolayeva T. I., *Ionic flotation of molybdenum: the theory and experience of a commercial scale operation*, 11th Intern. Mineral Processing Congress, Cagliari, Italy, April 21–26, 1975.

[32] Lemlich R., *Principles of foam fractionation*, [In:], *Progress in separation and purification*, Interscience, 1–56, New York 1968.

[33] Lemlich R., ed., *Adsorptive bubble separation technique*, Academic Press, New York 1972.

[34] Leung G., Kim Y. S., Zeitlin H., *An improved separation and determination of uranium in seawater*, Anal. Chim. Acta **60** (1), 229–232, 1972.

[35] Matsuzaki C., Zeitlin H., *The separation of collectors used as coprecipitants of trace elements in seawater by adsorption colloid flotation*, Separation Science **8** (2), 185–197, 1973.

[36] Mukai S., Tsutsui T., Koyanaka Y., *Application of the flotation method for the treatment of the waste solution in the chemical processing of used nuclear fuel-selective removal of mixed fission products*, Nippon Genshiryoku Gakkaishi **11** (4), 198–213, 1969.

[37] Ogłaza J., Siemiaszko A., *Applicability studies on ion flotation for decontamination of water* (in Polish), Nukleonika **11** (6), 421–427, 1966.

[38] Pushkarev V. V., *Enrichment of radioactive isotope solutions by the foaming method with colloidal ferric hydroxide as the function of pH*, Radiokhimiya **8** (4), 431–436, 1966.

[39] Pushkarev V. V., Egorov I. V., Krustalev B. V., *Decontamination of wastewaters by the foaming method*, Atomizdat, Moscow 1969.

[40] Pushkarev V. V., Skrylev L. D., Bagniecov W. F., *Removal of radioactive caesium by mixed ferrocyanides of heavy metals*, Zh. Prikl. Khim. **33** (1), 81–85, 1960.

[41] Rabrenovic R., *Ionic flotation of uranium from diluted solutions*, Rudy **18** (3), 138–141, 1970.

[42] Robertson G. H., Vermeullen T., *Foam fractionation of rare-earth elements*, Lavrence Radiation Laboratory, Univ. of Calif., Report UCRR-19525, Berkeley 1969.

[43] Rubin R., Gaden E. L., *Foam Separation*, [In:] *New chemical engineering separation technique*, Interscience, New York 1962.

[44] Sebba F., *Ion flotation*, Elsevier, Amsterdam 1962.

[45] Skrylev L. D., Pusharev V. V., *On the enrichment of radioactive cesium solutions by the foaming method*, Koll. Zh. **24**(6), 738–741, 1962.

[46] Somasundaran P., *Foam separation methods*, Sepn. Purif. Methods **1**(1), 117–198, 1972.

[47] Voyce D., Zeitlin H., *The separation of mercury from sea water by adsorption colloid flotation and analysis by flameless atomic absorption*. Anal. Chim. Acta **69**(1), 27–34, 1974.

[48] Walkowiak W., Charewicz W., *New ion flotation methods* (in Polish) Wiadomości Chem. **25**, 6, 419–433, 1971.