

Małgorzata ULEWICZ*, Władysław WALKOWIAK**

FLOTATION OF ZINC(II) AND CADMIUM(II) IONS FROM DILUTE AQUEOUS SOLUTIONS IN THE PRESENCES OF INORGANIC LIGANDS

Received March 15, 2002; reviewed and accepted May 15, 2002

An experimental investigation is presented on competitive flotation of zinc(II) and cadmium(II) ions from dilute aqueous solutions with sodium dodecylbenzenesulfonate (DBSNa) as the anionic surfactant and hexadecylpyridinium chloride (CPCI) as the cationic surfactant. The effect of inorganic ligands, i.e. cyanides, thiocyanides, sulfates, thiosulfates, nitrates, and perchlorates on the selectivity of cadmium(II) over zinc(II) is established. Separation of Cd(II) and Zn(II) ions by DBSNa is not occurred. The separation of Cd(II)/Zn(II) by CPCI in presence of inorganic ligands at concentration range from 0.01 M to 1.0 M increases in the sequence: $CN^- \leq SCN^- < SO_4^{2-} < S_2O_3^{2-}$.

Key words: zinc(II), cadmium(II), inorganic ligands, ion flotation

INTRODUCTION

Zinc(II) and cadmium(II) ions are removed from dilute aqueous solutions applying physicochemical methods such as solvent extraction, ion flotation, sorption, liquid membranes and ionic exchange. Ion flotation is an effective and simple process of metal ions concentration and separation from dilute aqueous solutions ($C_{Me} \leq 1.0 \cdot 10^{-4} M$), which involves the use of the ionic surfactant (collector) and the subsequent passage of gas bubbles through the aqueous solution.

The ion flotation selectivity for metal ions has been presented in several papers. Foam separation of Cd(II) ions by sodium dodecylsulfate and sodium dodecanoate from aqueous solutions was investigated by Jurkiewicz (1984-85). The presence of electrolytes in the solutions have a negative influence on cadmium(II) foam removal. Jurkiewicz (1985) also investigated separation of thiocyanate and iodide complexes of

* Department of Chemistry, Technical University of Czestochowa,
42-200 Czestochowa, Armii Krajowej 19 Street, e-mail: ulewicz@mim.pcz.czest.pl

**Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University
of Technology, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27 Street,
e-mail: Walkowiak@ichn.ch.pwr.wroc.pl

cadmium(II) from acidic aqueous solutions using hexadecyltrimethylammonium bromide (CTMABr). In the presence of acids, the zinc thiocyanate complex removal increases in the presence of following acids: perchloric < iodide < nitric < sulfuric < phosphoric < acetic. Jurkiewicz (1990) conducted the separation of zinc(II) and cadmium(II) ions with CTMABr in the presence of chloride, bromide, iodide and thiocyanate ions. For anionic surfactants (sodium dodecylbenzenesulfonate and sodium dodecylsulfonate) Walkowiak (1991) found the following foam separation selectivity sequences toward cations: $Mn^{2+} < Zn^{2+} < Co^{2+} < Fe^{3+} < Cr^{3+}$, and $Ag^+ < Cd^{2+} < In^{3+}$. The good correlation between selectivity sequences of studied metal ions with anionic surfactant and the ionic potentials of those cations was discovered. The flotation selective of zinc(II), cadmium(II), mercury(II), and gold(III) ions using hexadecyltrimethylammonium chloride in the presence of chlorides and cyanides was also investigated by Walkowiak et al. (1976, 1979, 1992). Selectivity order of foam fractionation was as follows: $Au(CN)_4^- > Hg(CN)_4^{2-} > Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$ (Walkowiak and Grieves 1976). The effect of inorganic ligands, i.e. thiosulfates, thiocyanates, and cyanides on the selectivity of ion flotation of Zn(II) and Ag(I) was investigated by Charewicz et al. (1999). The influence of zinc(II) and cadmium(II) ions concentrations on the effectiveness of flotation removal with potassium oleate was studied by Sinkova (1998). Zinc(II) and cadmium(II) ions are removed effectively from aqueous solution using this surfactant. Also, Scorcelli et al. (1999) was studied the removal of cadmium(II) using sodium dodecylsulfate as a collector. The best removal (99 %) was achieved for the concentration ratio of a metal cations to collector equal to 1:3. Preliminary research of cadmium(II) over zinc(II) ions separation by hexadecyltrimethylammonium chloride was conducted by Kozłowski et al. (2000). Recently Ulewicz et al. (2001) investigated separation of cadmium(II) over zinc(II) ions by hexadecyltrimethylammonium chloride in the presence of halides in the aqueous solutions. In the presence of halides in the aqueous solutions the separation of Cd(II) over Zn(II) ions by DBSNa was not occurred, whereas selective separation of Cd(II)/Zn(II) by CPCI in presence of halides at concentration range of 0.001 M to 1.0 M increases in the sequence: $F^- < Cl^- < Br^- < I^-$.

This paper concerns the selective removal of zinc(II) and cadmium(II) ions from dilute aqueous solutions ($c_{Me} = 1.0 \cdot 10^{-5}$ M) in competitive ion flotation in the presence of inorganic ligands such as cyanides, thiocyanides, sulfates, thiosulfates, nitrates, and perchlorates. The Zn(II) and Cd(II) flotation for anionic complexes from aqueous solutions by hexadecylpyridinium chloride as a cationic surfactant was applied. The competitive ion flotation of Zn^{2+} and Cd^{2+} by sodium dodecylbenzenesulfonate was also studied.

EXPERIMENTAL

The apparatus and procedure were as described in recently published paper (Ulewicz et al., 2001). Experiments were performed at an ambient temperature (20 ± 2 °C) and at a constant gas (nitrogen) flow rate of 12 ml/minute through a sintered

glass sparger of 20-30 μm , nominal porosity. The concentration of zinc(II) and cadmium(II) was $1.0 \cdot 10^{-5} \text{ M}$. All ligands, i.e. CN^- , SCN^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, NO_3^- , and ClO_4^- , were investigated in range of the concentrations of $5.0 \cdot 10^{-5} \div 1.0 \text{ M}$. Reagent grade inorganic chemicals, i.e. NaCN , NaSCN , NaNO_3 , NaClO_4 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, ZnSO_4 , CdSO_4 , NaOH and H_2SO_4 were obtained from POCh (Gliwice, Poland). Typical ionic surfactants were applied, i.e. sodium dodecylbenzenesulfonate (DBSNa, BHD reagent) as an anionic surfactant, and hexadecylpyridinium chloride (CPCI, Loba-Chemie reagent) as a cationic surfactant. Both surfactants were purified by recrystallization from ethanol. The concentration of surfactants in the aqueous solutions was $2.0 \cdot 10^{-4} \text{ M}$. The gamma radioactive isotopes used, i.e., Zn-65 and Cd-115m, were from the Atomic Energy Institute „POLATOM” (Świerk, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration (9.2 MBq/mg for Zn-65 and 2.26 MBq/mg for Cd-115m).

The efficiency and rate of flotation, i.e. the flotation degree ($M = 1 - c_f/c_i$) and the first order rate constant (k, min^{-1}) were calculated from experimental curves of c/c_i vs. time (where c_i , c , and c_f are the initial, actual, and final concentration of floated ion). The selectivity coefficient (S) was also used such as in previous paper (Ulewicz et al., 2001).

Table 1. Stability constants of zinc(II) and cadmium(II) for complexes with inorganic ligands (Stability constants, 1982). Ionic strength $I = 0.1 \text{ M}$

System		$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
$\text{S}_2\text{O}_3^{2-}$	Zn(II)	0.96	1.94	3.30	-
	Cd(II)	2.74	4.65	6.95	7.12
SO_4^{2-}	Zn(II)	0.89	1.23	1.66	1.67
	Cd(II)	0.95	1.55	1.76	2.30
SCN^-	Zn(II)	0.71	1.00	1.20	1.50
	Cd(II)	1.16	1.49	1.63	1.65
CN^- $\text{pK}_a = 9.21$	Zn(II)	-	10.64	15.74	19.98
	Cd(II)	5.62	10.80	15.70	19.20
NO_3^-	Zn(II)	-0.20	-0.64	-	-
	Cd(II)	-0.05	-0.80	-	-
ClO_4^-	Zn(II)	1.70	-	-	-
	Cd(II)	-	-	-	-

The total concentration of metal in aqueous solutions can be described by an equation (1), whereas the ratio of formed metal complexes was calculated by an equation (2). In Table 1 are given values of the stability constants of inorganic complexes for Zn(II) and Cd(II).

$$c_M = [M] + [ML] + [ML_2] + \dots + [ML_n] \quad (1)$$

$$\alpha_n = \frac{\beta_n [L]^n}{1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n} \quad (2)$$

where [L] - concentration of ligand which is not complexed by a metal,
 β_n - overall stability constants of metal complex.

RESULTS AND DISCUSSION

The flotations of zinc(II) and cadmium(II) ions with sodium dodecylbenzenesulfonate from aqueous solutions containing single metal ions at the concentrations of metals equal to $1.0 \cdot 10^{-5}$ and $2.0 \cdot 10^{-5}$ M were described in previous papers (Ulewicz et. al 2001). The flotation removal and rate of Zn^{2+} and Cd^{2+} cations with DBSNa as the anionic surfactant was comparable. Also the removal of Zn^{2+} and Cd^{2+} cations with DBSNa in the presence of halides was comparable. The differences in the removal of Zn(II) and Cd(II) ions from solutions containing halides with CPCl were observed. In the this paper the influence of inorganic ligands, i.e. CN^- , SCN^- , SO_4^{2-} , $S_2O_3^{2-}$, NO_3^- , and ClO_4^- on the separation of zinc(II) and cadmium(II) ions was examined.

It was found that the removal of zinc(II) and cadmium(II) ions decreases with increasing of ligands concentration in aqueous solutions using anionic collector, i.e. DBSNa (Fig.1).

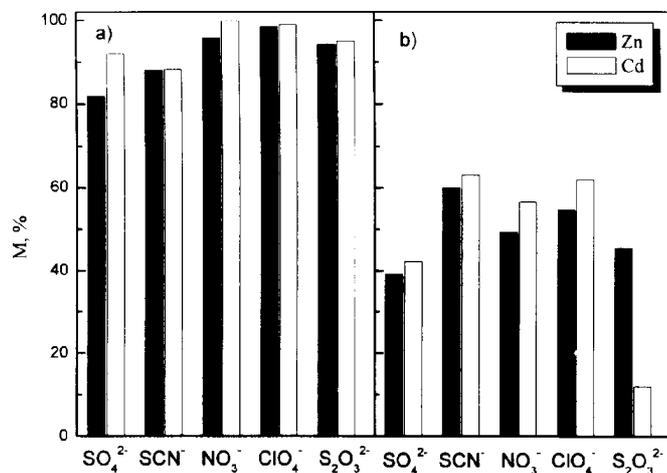


Fig. 1. The flotation degree of Zn(II) and Cd(II) ions from aqueous solutions in the presence of the inorganic ligands at concentration of $1.0 \cdot 10^{-4}$ M (a) and $1.0 \cdot 10^{-2}$ M (b) by $2.0 \cdot 10^{-4}$ M DBSNa

The separation of Zn(II) and Cd(II) in thiocyanides, sulfates, nitrates, and perchlorates media aqueous solution with DBSNa does not occurred, since the removal of both metals was comparable. Only in the presence of thiosulfates at higher concentration (0.01 M) of $S_2O_3^{2-}$ ions, the removal of Zn(II) was observed as much

higher than Cd(II) ions. The selectivity coefficients of Zn(II)/Cd(II) for concentration of $S_2O_3^{2-}$ equal to 0.001, 0.01, and 0.1 M were: 2.5; 3.8 and 9.7, respectively. In the presence of CN^- removal of Zn(II) and Cd(II) ions is not occurred.

The partial separation of studied metals occurs when a cationic collector, i.e. CPCI, was applied. Flotation kinetics curves of Zn(II) and Cd(II) for competitive ion flotation of those metals from 0.1 M (a) and 1.0 M (b) $S_2O_3^{2-}$ aqueous solutions with CPCI is presented in Fig. 2. As can be seen from this figure cadmium(II) is floated much higher than zinc(II) ions. The removal of Zn(II) and Cd(II) ions increases with increase of thiosulfates ions concentration. The selectivity coefficients of Cd(II)/Zn(II) for concentration of $S_2O_3^{2-}$ equal to 0.10 and 1.0 M were 1.4 and 4.2, respectively.

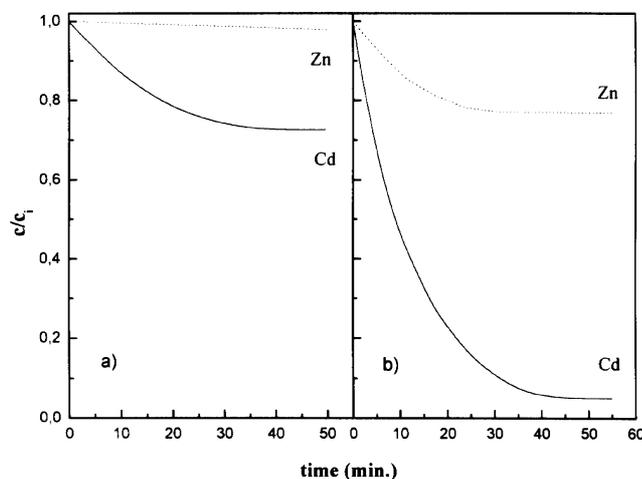


Fig. 2. Kinetic curves of the Zn(II) and Cd(II) ions from aqueous solutions containing 0.10 M (a) and 1.0 M (b) $S_2O_3^{2-}$ by CPCI, $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5} M$, $[CPCI] = 2.0 \cdot 10^{-4} M$, $pH = 4.0$

Flotation of Zn(II) and Cd(II) ions from aqueous solutions containing NO_3^- , or ClO_4^- with cationic collector does not occur. The maximal percent removal of Zn(II) and Cd(II) ions in presence of cyanides, thiocyanides, sulfate, and thiosulfates ions are shown in Fig. 3. In this figure, the calculated formation percent of metal complexes for cyanides, thiocyanides, sulfate, thiosulfates, is also shown. Using this collector it is possible to remove Zn(II) and Cd(II), which are existing as anionic forms in aqueous solutions. The differences of predominance range for anionic forms of Zn(II) and Cd(II) allow to separate cadmium(II) over zinc(II). With the increase of ligand concentration, the removal of Cd(II) and Zn(II) ions increase. The flotation degree of Cd(II) and Zn(II) is comparable for the inorganic complex anions of the investigated metals.

The selectivity coefficients of cadmium(II) over zinc(II) in presence of investigated ligands are shown in Fig. 4. The selectivity coefficients for Cd/Zn by CPCI in inorganic media aqueous solutions at the concentration range from 0.01 to 1.0 M increase in the following sequence: $CN^- \leq SCN^- < SO_4^{2-} < S_2O_3^{2-}$, respectively.

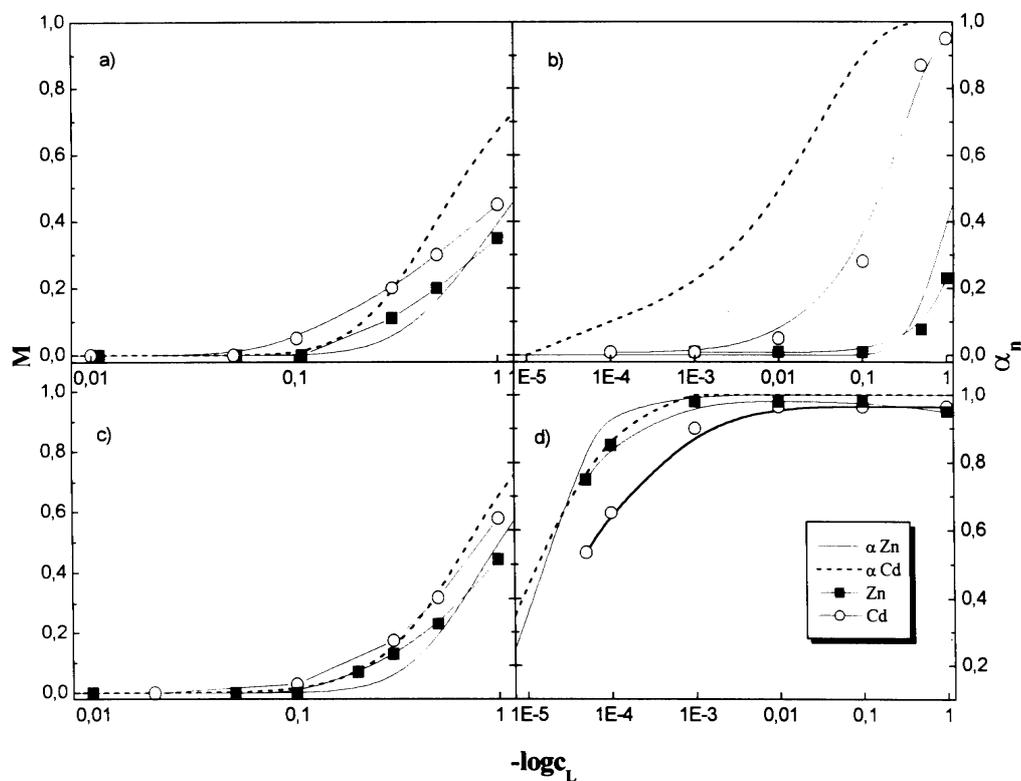


Fig. 3. Influence of analytical concentration of sulfates (a), thiosulfates (b), thiocyanates (c), and cyanides (d) on removal of Zn(II) and Cd(II) ions with CPCl, and molar fractions of anionic metal complexes, pH = 4.0 (for CN⁻ pH=11.0)

Separation of Cd(II) and Zn(II) ions with CPCl is the best in the presence of thiosulfates (Table 2). As can be seen from this table the kinetic rate constants for cadmium(II) are higher than for zinc(II). The rate constant ratios of Cd(II)/Zn(II) for SO₄²⁻, SCN⁻, and S₂O₃²⁻ are equal: 1.2; 1.1 and 5.3, respectively.

Table 2. Rate constant of Zn(II) and Cd(II) by CPCl in presence of inorganic ligands at concentration of 0.5 M

Lignads	k [min ⁻¹] Zn(II)	r^2 determination coefficients	k [min ⁻¹] Cd(II)	r^2 determination coefficients
SO ₄ ²⁻	0.137	0.9916	0.168	0.9909
S ₂ O ₃ ²⁻	0.069	0.9941	0.369	0.9875
SCN ⁻	0.172	0.9829	0.184	0.9934

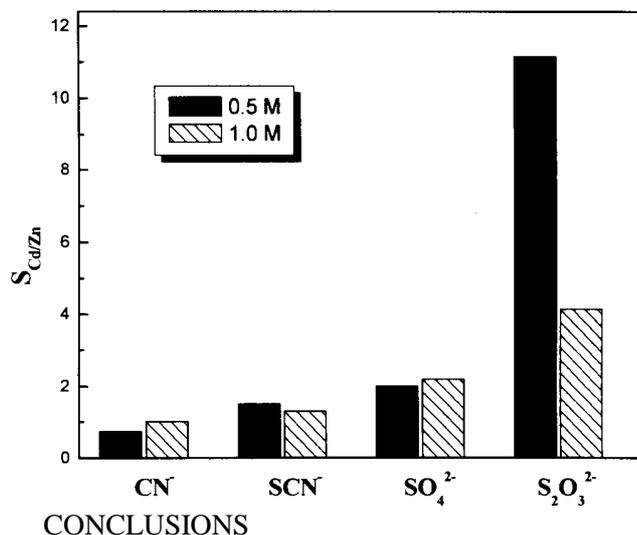


Fig. 4. Selectivity coefficients ($S_{Cd/Zn}$) vs. concentration of ligands, $[CPCI] = 2.0 \cdot 10^{-4}$ M, $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, pH = 4.0 (for CN^- pH=11.0)

CONCLUSIONS

Separation of Cd(II) and Zn(II) ions using anionic collector, i.e. DBSNa from aqueous solutions in the presence of inorganic ligands at the concentrations range of $5.0 \cdot 10^{-5} \div 1.0$ M with the exception of $S_2O_3^{2-}$, was not observed since the removal of both metals is comparable. This is caused by the fact, that zinc(II) and cadmium(II) form cation complexes which possess comparable values of stability constants. In the presence of thiosulfates the removal of Zn(II) is much higher than Cd(II) ions by DBSNa. The high selectivity coefficient of Zn(II)/Cd(II), i.e. 9.7, was obtained for concentration of $S_2O_3^{2-}$ equal 0.1 M.

The cadmium(II) over zinc(II) selectivity was observed in the presence of thiosulfates ligands when cationic surfactant, i.e. hexadecylpyridinium chloride, was applied. The selectivity coefficients for Cd(II)/Zn(II) increase in the following order of ligands: $CN^- \leq SCN^- < SO_4^{2-} < S_2O_3^{2-}$. The values of Cd(II)/Zn(II) selectivity coefficients at $S_2O_3^{2-}$ concentration equal to 0.10, 0.05, and 1.0 M were 1.4, 11.2, and 4.2, respectively.

ACKNOWLEDGMENT

Financial support of this work was provided by Polish Science Foundation Grants 4 T09B 107 22.

REFERENCES

- CHAREWICZ W. A., HOLOWIECKA B. A., WALKOWIAK W., (1999), *Selective flotation of zinc(II) and silver (I) ions from dilute aqueous solutions*, Sep. Sci. Technol., Vol. 34, No 12, 2447-2460.
- CHAREWICZ W., NIEMIEC J., (1969), *Flotation of anions using cationic surfactants, I. Flotation of molybdates*, Nukleonika, Vol. 14, 17-27.
- GRIVES R. B., WALKOWIAK W., BHATTACHARYYA D., (1979), *Foam fractionation selectivity sequence of quaternary ammonium surfactant for simple and complex anions: A review*, In: *Recent development in Separation Science*, CRC Press Inc., Florida, 5, 55-65.

- JURKIEWICZ K. (1984-85), *Study on the separation of Cd from solutions by foam separation. I. Foam separation of cadmium cations*, Sep. Sci. Technol., Vol. 19, 1039-1050.
- JURKIEWICZ K. (1985), *Study on the separation of Cd from solutions by foam separation. III. Foam separation of complex cadmium anions*, Sep. Sci. Technol., Vol. 20, 179–192.
- JURKIEWICZ K. (1990), *The removal of zinc from solutions by foam separation. I. Foam separation of complex zinc anions*, Int. J. Miner. Process., Vol. 28, 173 – 187.
- KOZŁOWSKI C., ULEWICZ M., WALKOWIAK W., (2000), *Separation of zinc and cadmium ions from chlorides by ion flotation and liquid membranes*, Physicochemical Problems of Mineral Processing, No. 34, 141-151.
- SCORZELLI I. B., FRAGOMENI A. L., TOREM M. L., (1999), *Removal of cadmium from a liquid effluent by ion flotation*, Minerals Engineering, Vol. 12, 905-917.
- SINKOVA L. A. (1998), *Influence of zinc and cadmium ions concentration on effectiveness of flotation removal from aqueous solutions with potassium oleate*, Ukr. Kim. Zhurn. Vol. 64 , 94-99.
- Stability Constants of Metal-Ion Complex; Part A: Inorganic Ligands, Pergamon Press, New York, 1982.
- ULEWICZ M., WALKOWIAK W., KOZŁOWSKI C (2001), *Selective flotation of zinc(II) and cadmium(II) ions from aqueous solutions in the presence of halides*, Physicochemical Problems of Mineral Processing, 35, 21-29.
- ULEWICZ M., (2001), *Flotation of ions from aqueous solutions in hydrometallurgical process of removal and separation of cadmium and zinc*, Doctoral dissertation, Technical University of Częstochowa.
- WALKOWIAK W. (1991), *Mechanism of selective ion flotation. 1. Selective flotation of transmission metal cations*. Sep. Sci. Technol., Vol. 26, 559 – 568.
- WALKOWIAK W., (1992), *Mechanism of selective ion flotation technology*”, In: *Innovation in flotation technology*, Edited by P. Mavros, K. A. Matis, NATO ASI Series, Kluwer Academic Publishers, London, Vol. 208, 455-473.
- WALKOWIAK W., BHATTACHARYYA D., GRIEVES R. B., (1976), *Selective foam fractionation of chloride complex of Zn(II), Cd(II), Hg(II), and Au(III)*, Anal. Chem., Vol. 48, 975-979.
- WALKOWIAK W., GRIEVES R. B. (1976), *Foam fractionation of cyanide complex of zinc(II), cadmium(II), mercury(II), and gold(III)*, J. Inorg. Nucl. Chem., Vol. 38, 1351-1356.
- WALKOWIAK W., ULEWICZ M., (1999), *Kinetics studies of ions flotation*, Physicochemical Problems of Mineral Processing, No. 33, 201-214.

Ulewicz M., Walkowiak W., *Flotacja jonów Zn(II) i Cd(II) z rozcieńczonych roztworów wodnych w obecności ligandów nieorganicznych*, Fizykochemiczne Problemy Mineralurgii, 36, (2002) 225-232 (w jęz. ang.)

Przy użyciu kolektora kationowego – chlorku heksylopirydyniowego (CPCI) oraz kolektora anionowego - dodecylobenzenosulfonianu sodu (DBSNa) wydzielano oraz rozdzielano jony cynku(II) i kadmu(II) odpowiednio w postaci kationowych i anionowych form kompleksowych z wybranymi ligandami nieorganicznymi z roztworów wodnych zawierających równomolową mieszaninę obu metali. Rozdzielenie jonów Zn(II) i Cd(II) przy użyciu kolektora anionowego w obecności jonów SCN^- , SO_4^{2-} , NO_3^- i ClO_4^- nie jest możliwe ponieważ cynk(II) i kadm(II) tworzą kationowe formy kompleksowe o podobnych wartościach stałych trwałości. Przy użyciu tego kolektora jedynie w obecności $\text{S}_2\text{O}_3^{2-}$ obserwowano separację jonów Zn(II)/Cd(II). Współczynniki selektywności Zn(II)/Cd(II) przy stężeniu $\text{S}_2\text{O}_3^{2-}$ równym 0,001; 0,01 i 0,1 M wynoszą odpowiednio: 2,5; 3,8 i 9,7. Natomiast przy użyciu kolektora kationowego, tj. chlorku heksylopirydyniowego, obserwowano separację jonów kadmu(II) od cynku(II). Separacja badanych jonów metali przy użyciu CPCI w obecności ligandów nieorganicznych w zakresie ich stężeń 0,1 ÷ 1,0 M wzrasta w szeregu: $\text{CN}^- \leq \text{SCN}^- < \text{SO}_4^{2-} < \text{S}_2\text{O}_3^{2-}$. Współczynniki selektywności Cd(II)/Zn(II) przy stężeniu $\text{S}_2\text{O}_3^{2-}$ równym 0,1; 0,5 i 1,0 M wynoszą odpowiednio: 1,4; 11,2 i 4,2.