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SEPARATION OF ZINC AND CADMIUM IONS FROM AQUEOUS CHLORIDE SOLUTIONS BY ION FLOTATION AND LIQUID MEMBRANES

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An experimental investigation is presented on zinc(II) and cadmium(II) ions separation from aqueous chloride solutions, containing equimolar mixture of both metals ions, by ion flotation (IF) and polymer inclusion membrane (PIM) processes. The IF experiments from dilute aqueous chloride solutions ($c_{Me} = 1 \cdot 10^{-5}$ M) with an anionic surfactant (sodium dodecylbenzene sulfonate) and a cationic surfactant (cetylpyridinium chloride) are shown. With a cationic surfactant, the flotation separation of Cd/Zn grows with Cl^- concentration increase. In addition, a selective transport of Zn(II) and Cd(II) from aqueous chloride source phase ($c_{Me} = 1 \cdot 10^{-3}$ M) through PIM containing cellulose triacetate (support), o-nitrophenyl pentyl ether (plasticizer) and tri-n-octylamine (ion carrier) is shown. The transport selectivity of Cd/Zn is decreasing with HCl concentration increase in source phase. In both studied separation methods zinc(II) and cadmium(II) are removed from an aqueous chloride solution in the form of $ZnCl_3^- + ZnCl_4^{2-}$ and $CdCl_3^- + CdCl_4^{2-}$, respectively. Results are discussed in terms of the stability of chloride complex species for zinc(II) and cadmium(II).

Key words: ion flotation, polymer inclusion membranes, zinc, cadmium

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INTRODUCTION

Selective separation of heavy metal ions from industrial and waste aqueous solutions is frequently required in hydrometallurgical processes (Davies 1987). In such technological processes, as CLEAR (Ochs et al. 1983) or EZINEX (Diaz et al. 1995) chloride solutions are used as aqueous leaching liquors and as the result those solutions contain zinc and cadmium chloride complexes. There are several methods of metal ions separation from aqueous solutions, i.e. solvent extraction, ion exchange, sorption, flotation methods, and liquid membranes (Davies 1987).

An effective and simple method of metal ions concentration and separation from dilute aqueous solutions ($c_{Me} \leq 1 \cdot 10^{-4}$ M) is an ion flotation, which involves the removal of surface inactive ions from aqueous solutions by the introduction of an ionic surfactant (called collector) and the subsequent passage of gas bubbles through the solution (Lemlich 1972). The selectivity of cationic surfactants for anions has been established in several ion flotation experiments including oxyanions of Re(VI), Mo(VI), W(VI), Cr(VI), and V(V) (Grieves and Charewicz 1974), cyanide metal complexes of Zn(II), Cd(II), Hg(II), Pd(II), and Pt(IV) (Walkowiak et al. 1976; Walkowiak 1992). Removal of zinc (II) in the presence of chlorides by ion flotation with cationic collector was also investigated by Jurkiewicz (Jurkiewicz 1990) as well as by Hualing and Zhide (Hualing and Zhide 1989).

The use of liquid membranes containing ion carriers offers as an alternative to solvent extraction for selective separation and concentration of metal ions from source aqueous phase, in which the concentration of metal ionic species is $> 1 \cdot 10^{-4}$ M. A variety of types of liquid membranes exists, i.e. bulk (BLM), emulsion (ELM) and supported (SLM) membranes (Bartsch and Way 1996). Moderate success in metal ion species separations with SLM was achieved using a porous polymer film, such Celgard or Accurel, and an organic solution of an ion carrier. On the other hand, a common problem for this system is loss of the carrier and membrane solvent to the contacting aqueous phases, which limits the long-term integrity of the membranes. Recently, a new type of membrane system, called polymer inclusion membranes (PIMs), has been developed which provides metal ion transport with high selectivity, as well as easy setup and operation (Sugiura et al. 1987). Casting cellulose triacetate from a solution to form a thin film forms the PIMs. The casting solution also contains a membrane plasticizer and an ion-exchange carrier. Since these membranes do not utilize an organic solvent to maintain this phase separation, PIMs are simpler to use than SLMs, and do not suffer from loss of the organic solvent. There are few papers, which deals with cadmium(II) removal and cadmium(II) over zinc(II) separation by supported liquid membranes. Breembroek et al. (1998) has reported on cadmium extraction through a flat sheet and hollow fiber supported liquid membranes using tertiary amines as ion carriers. Also Urtiga and Ortiz (1999) studied cadmium removal

from aqueous phosphoric acid by SLM. The separation of cadmium(II) from zinc(II) chloride media by a supported liquid membrane using quaternary ammonium salts as ion carriers was reported by Danesi et al. (1983) and Hoh et al. (1990). The only two papers on removal of cadmium(II) from chloride aqueous solutions by polymer inclusion membranes were published by Hayashita (1996).

Present work deals with the separation of zinc(II) and cadmium(II) metal ionic species from chloride aqueous solutions containing equimolar mixture of both metals by ion flotation ($c_{Me} = 1 \cdot 10^{-5}$ M) and polymer inclusion membranes ($c_{Me} = 1 \cdot 10^{-3}$ M).

EXPERIMENTAL

Ion flotation

The ion flotation experiments were carried out in a glass column 45.7 cm in high and 2.4 cm in diameter. Nitrogen gas was saturated with water and the flow rate was maintained at 12 cm³/min. through a sintered sparger of 20–30 μm nominal porosity. The volume of each initial aqueous solution, prior to ion flotation, was 100 cm³, and the temperature was maintained at 22 ± 2 °C.

The initial aqueous solutions were prepared with double distilled water and the salts ZnCl₂, CdCl₂, NaCl, HCl (all from POCh Gliwice, reagents of analytical grade). The surfactants, i.e. sodium dodecylbenzene sulfonate (DDBSNa) and cetylpyridinium chloride (CPCl), as analytical reagent grade, were utilized as 0.05 M standard solutions in water. The surfactants concentrations in the initial solutions were kept constant at 2.0 · 10⁻⁴ M throughout this investigation. The gamma radioactive isotopes, i.e. Zn-65 and Cd-115m, were in the form of chloride acidic solution (0.1 M HCl). They were of sufficiently low specific activity to neglect the effect of carrier concentration (Zn-65: 9.2 GBq/g, Cd-115m: 2.2 GBq/g). These isotopes were from the Atomic Energy Institute (Świerk).

The time dependence of zinc(II) and cadmium(II) concentrations in the bulk solution (*c*) was recorded continuously during each ion flotation run by means of radioactive analytical tracer, and gamma radiation spectrometry, following a procedure described previously (Walkowiak and Ulewicz 1999). A single channel, gamma radiation spectrometer was applied as the detector of radioactive intensity of specific energy. The *c* versus time curves enabled the calculation of the percent removal (*M*):

$$M = [1 - (c_r/c_i)] \cdot 100\% \quad (1)$$

where c_i is the initial metal concentration, c_r is the metal concentration in residual solution after foam ceased. Also selectivity coefficients (S) of Cd(II) over Zn(II) was calculated:

$$S_{\text{Cd(II)/Zn(II)}} = M_{\text{Cd(II)}}/M_{\text{Zn(II)}} \quad (2)$$

Polymer inclusion membranes

A solution of cellulose triacetate (as the support), tri-*n*-octylamine (as the ion carrier), and *o*-nitrophenyl pentyl ether (as the plasticizer) in dichloromethane was prepared. A portion of this organic solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a plate glass with cellulose triacetate - dichloromethane glue. Dichloromethane, as the organic solvent, was allowed to evaporate overnight and the resultant polymer inclusion membrane was separated from the glass plate by immersion in water. The membrane was stored in water. Content of membrane (in weight percents) was: CTA - 41%, *o*-nitrophenyl pentyl ether - 37%, and TOA - 22%. The concentration of TOA was 1.28 M based on plasticizer.

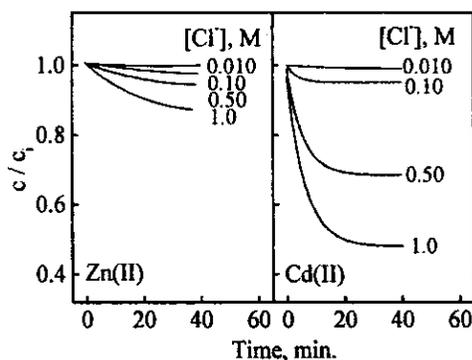


Fig. 1. Rate curves of zinc(II) and cadmium(II) concentration vs. time from aqueous solution containing equimolar mixture of both metals ($c_{Me} = 1.0 \cdot 10^{-3}$ M) in presence of chlorides with DBSNA ($c_{surf.} = 2.0 \cdot 10^{-4}$ M)

Transport experiments were conducted in a permeation cell in which the membrane film (at surface area of 4.9 cm^2) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm^3 each), were mechanically stirred at 600 rpm. The receiving phase was 0.10 M aqueous solution of ammonium acetate. The PIM transport experiments were carried out at the same temperature as IF

runs. Small samples (0.1 cm^3 each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc and cadmium concentrations by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam).

The inorganic chemicals, their purity, and producer were the same as in ion flotation experiments. The organic chemicals, i.e. cellulose triacetate (Fluka), tri-n-octylamine (Serva), o-nitrophenyl pentyl ether (Fluka), and dichloromethane (POCH) were of analytical reagent grade. The percent removal and selectivity coefficients were calculated according to equations (1) and (2) in which c_i and c_r are the initial and residual metal concentrations in the aqueous source phase.

RESULTS AND DISCUSSION

First, the competitive ion flotations were studied to determine the chloride ions influence on flotation kinetic of both metals using an anionic (Fig. 1) and a cationic (Fig. 2) surfactant.

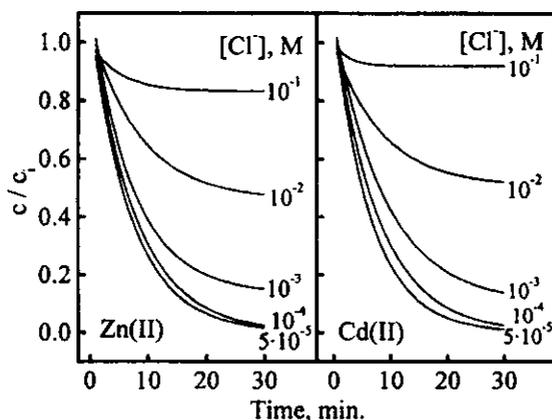


Fig. 2. Rate curves for competitive ion flotation of zinc(II) and cadmium(II) ($c_{Me} = 1.0 \cdot 10^{-5} \text{ M}$) in presence of chlorides with CPCl ($c_{surf.} = 2.0 \cdot 10^{-4} \text{ M}$)

According to Fig. 1, with the increase of chlorides concentration rate and removal of both floated ions, i.e. zinc(II) and cadmium(II), decrease. At concentration of chloride ions equal to 0.10 M , percent removal of zinc and cadmium reaches 17% , and 10% , respectively. Contrary influence of chloride concentration on competitive ion flotation of zinc and cadmium is observed using a cationic surfactant, i.e. CPCl

(Fig. 2). In this case both flotation rate and percent removal of Zn(II) and Cd(II) increase with Cl^- concentration increase and partial separation of cadmium over zinc is observed (Fig. 3).

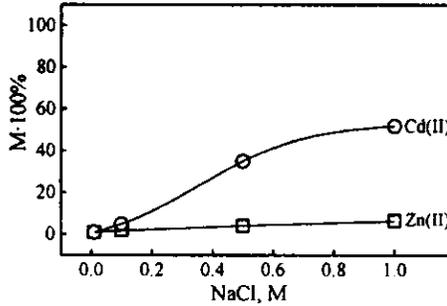


Fig. 3. Percent removal of zinc(II) and cadmium(II) in competitive ion flotation from aqueous solutions containing equimolar mixture of both metals vs. chlorides concentration. Conditions as in Fig. 2

The percent removal of cadmium(II) grows much faster than zinc(II) with chloride concentration increase.

Next, the competitive transport of zinc(II) and cadmium(II) ions from aqueous source phase ($c_{Me} = 1.0 \cdot 10^{-3}$ M) containing chlorides through polymer inclusion membranes into receiving aqueous phase was investigated. The kinetics of zinc(II) and cadmium(II) ions transport through PIM from aqueous source phase containing equimolar mixture of both metals is shown in Fig. 4.

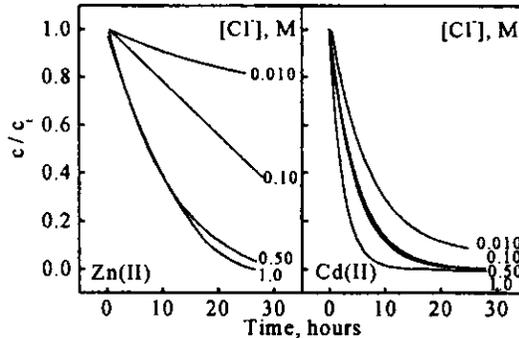


Fig. 4. Kinetics of zinc(II) and cadmium(II) transport through PIM from source aqueous phase ($c_{Me} = 1.0 \cdot 10^{-3}$ M) at different HCl concentrations

Comparison of both processes kinetics, i.e. IF and PIM (Figs. 2 and 4) shows that transport through polymer inclusion membranes is much slower than ion flotation of adequate metals, and it takes from 5 to 30 hours to remove more than 90 % of cadmium from source aqueous phase. Similarly to IF, in case of PIM transport of cadmium(II) goes faster than zinc(II). The dependence of percent removal of zinc(II) and cadmium(II) ions from a source aqueous phase as a function of HCl concentration for PIM is presented in Fig. 5.

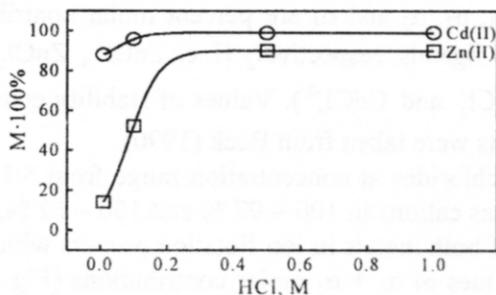


Fig. 5. Percent removal of zinc(II) and cadmium(II) ions from source aqueous phase containing equimolar mixture of both metals ($c_{Me} = 1,0 \cdot 10^{-3}$ M) vs. HCl concentration in source phase

Fig. 5 shows that the percent removal of both metals is increasing with HCl concentration increase and at acid concentration ≥ 0.5 M remains stable. This causes that separation of Cd/Zn coefficient is the highest for low concentrations of chlorides, i.e. 0.010 M.

To compare the separation of cadmium(II) over zinc(II) in ion flotation and in polymer inclusion membrane processes the bar plots of Cd/Zn separation coefficients are presented in Fig.6.

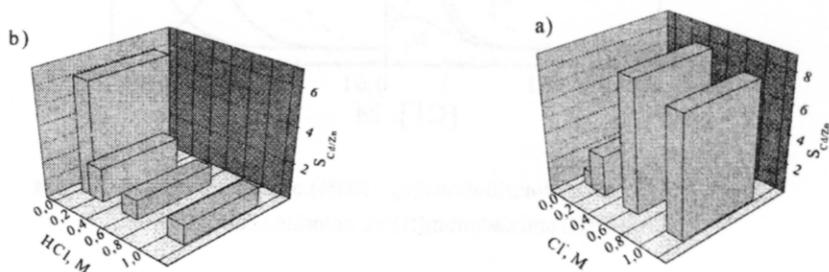


Fig. 6. Bar plots of Cd/Zn separation coefficients vs. chloride concentration in ion flotation (a), and polymer inclusion membrane (b) processes (conditions as in Figs. 3 and 5, respectively)

As it comes from this figure dependence of separation coefficients of Cd/Zn versus Cl^- concentration for both processes is different. For ion flotation, values $S_{\text{Cd/Zn}}$ are growing with Cl^- concentration increase while those coefficients values for polymer inclusion membranes are decreasing with HCl concentration increase. To explain IF and PIM experimental results, the contributions of formed complex species of zinc(II) and cadmium(II) in aqueous chloride solution are needed. The percent molar contributions of chloride complex species for those metals versus Cl^- concentration are presented in Fig. 7. α_0 is the percent molar contribution of uncomplexed cations (i.e. Zn^{2+} and Cd^{2+}); α_1 , α_2 , α_3 and α_4 are percent molar contributions of complexed ions with 1, 2, 3, and 4 ligands, respectively (i. e. ZnCl^+ , ZnCl_2 , ZnCl_3^- and ZnCl_4^{2-} or CdCl^+ , CdCl_2 , CdCl_3^- and CdCl_4^{2-}). Values of stability constants for Zn(II) + Cl^- and Cd(II) + Cl^- systems were taken from Beck (1990).

In the presence of chlorides at concentration range from $5 \cdot 10^{-5}$ to 0.10 M zinc(II) and cadmium(II) exist as cations in 100 – 97 % and 100 – 62 %, respectively (Fig. 7). But percent removal of both metals in ion flotation process with an anionic surfactant is much lower than values of $\alpha_0 + \alpha_1$ molar contributions (Fig. 1). This is caused by interfering influence of sodium cations. Percent removal of zinc(II) in IF process with a cationic surfactant remains very low in the whole range of Cl^- concentration (Fig. 3).

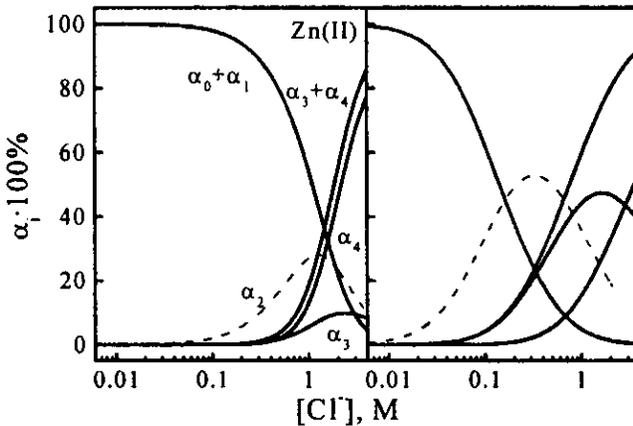


Fig. 7. Percent molar contributions ($\alpha_n \cdot 100\%$) of chloride complex species for zinc(II) and cadmium(II) vs. chloride concentrations

This correlates with low percent molar contribution of Zn(II) anionic forms (i.e. $\alpha_3 + \alpha_4$) which reaches 18 % at 1.0 M NaCl (Fig. 7). On the other hand cadmium(II) percent removal grows with Cl^- concentration increase and reaches 55 % at 1.0 M

NaCl (Fig. 3). This is in accordance with increase of percent molar contributions of anionic forms of Cd(II) up to 59 % at 1.0 M NaCl.

In case of polymer inclusion membranes the separation coefficients of Cd/Zn decrease with hydrochloric concentration increase. In addition, affinity of $\text{CdCl}_3^- + \text{CdCl}_4^{2-}$ anions to CPCI is higher than $\text{ZnCl}_3^- + \text{ZnCl}_4^{2-}$ anions to the cationic surfactant.

In case of polymeric inclusion membrane transport, which is significantly slower process (in comparison with IF), the main factor influencing the Cd/Zn separation is ratio of molar contributions of anionic forms for both metals. As it comes from Fig. 7, the mentioned ratio decreases with HCl concentration increase. Consequently the separation factor of Cd/Zn, which depends mainly on complexation reactions on source phase / membrane boundary, is decreasing with increase of hydrochloric acid concentration.

CONCLUSION

Zinc(II) and cadmium(II) can be effectively separated from aqueous chloride solutions in hydrometallurgical processes of ion flotation and polymer inclusion membranes. Ion flotation with a cationic surfactant (CPCI) allow to separate cadmium(II) from zinc(II) from dilute aqueous solutions ($c_{\text{Me}} = 1 \cdot 10^{-5}$ M) with separation coefficient increasing with Cl^- concentration increase. Competitive transport of zinc(II) and cadmium(II) from an aqueous chloride source phase ($c_{\text{Me}} = 1 \cdot 10^{-3}$ M) through polymer inclusion membranes containing tri-n-octylamine as ion carrier into aqueous ammonium acetate solutions also enables separation of cadmium over zinc. The selectivity coefficient of Cd/Zn for PIM decreases with HCl concentration increase in source phase. In both studied separation methods zinc(II) and cadmium(II) are removed from an aqueous chloride solutions in the form of $\text{ZnCl}_3^- + \text{ZnCl}_4^{2-}$ and $\text{CdCl}_3^- + \text{CdCl}_4^{2-}$, respectively. Results are discussed in terms of the chloride complex species stability for zinc(II) and cadmium(II).

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Kozłowski C., Ulewicz M., Walkowiak W., Rozdział jonów cynku i kadmu z roztworów chlorkowych w hydrometalurgicznych procesach flotacji jonowej i ciekłych membran *Fizykochemiczne Problemy Mineralurgii*, 34, 141-151 (w jęz. angielskim)

Zbadano selektywność procesu wydzielania jonów cynku(II) i kadmu(II) z wodnych roztworów chlorkowych zawierających równomolową mieszaninę jonów obu metali za pomocą flotacji jonowej (IF) i polimerycznych membran inkluzyjnych (PIM). Pokazano wyniki IF z rozcieńczonych roztworów wodnych ($c_{Me}=1,0 \cdot 10^{-3}$ M) za pomocą kolektora anionowego (dodecylobenzenosulfonian sodu) i kationowego (chlorek cetylopirydyniowy). Wykazano, że dla kolektora kationowego ze wzrostem stężenia chlorków selektywność flotacji Cd/Zn wzrasta. W pracy prezentowane są również wyniki transportu Zn(II) i Cd(II) z wodnej fazy zasilającej ($c_{Me}=1,0 \cdot 10^{-3}$ M) przez PIM zbudowaną z trójoctanu celulozy (nośnik), eteru o-nitrofenylopropylowego (pastyfikator) i tri-n-oktyloaminy (przenośnik jonów). Selektywność transportu przez PIM malała wraz ze wzrostem stężenia HCl w fazie zasilającej. Wyniki przedyskutowano w świetle zakresów trwałości poszczególnych form jonów kompleksowych Zn(II) i Cd(II). W obu procesach tj. IF i PIM wydzielane jony cynku i kadmu występowały w formie anionów tj. $ZnCl_3^- + ZnCl_4^{2-}$ oraz $CdCl_3^- + CdCl_4^{2-}$.