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Ion exchange on resins with temperature-responsive selectivity IV. Influence of solution and column parameters on efficiency of reagentless separation of copper and zinc using thermo-induced concentration waves technique

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Abstract

The effect of solution and column parameters such as pH, ratio of metal ions and the height of resin bed on formation of the thermo-induced concentration waves (TICW) in the course of the thermostripping process of Cu^{2+} and Zn^{2+} ions from iminodiacetic resin Lewatit TP-207 has been studied. The formation of TICW is attributed by both different diffusivities of metal ions and the presence of the third (H^+) ion in the system. This effect makes it possible to carry out a reagentless separation of metal ions by using either the metal depletion or metal concentration mode of operation. The efficiency of the TICW-based separation process by using the metal depletion mode appears to be the higher the lower relative concentration of metal ion under removal (slower diffusing ionic species). The mathematical model proposed allows for qualitative and quantitative description of thermostripping processes in a wide range of pH and solution compositions. The physical model of the TICW process proposed makes it possible to account for the influence of different process parameters and generalise the applicability of the TICW separation technique to the binary mixtures of any metal ions with different diffusivities. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Concentration waves, thermo-induced; Thermostripping; Copper; Zinc

1. Introduction

Multicomponent ion-exchange (IE) systems, such as IE in soils [1–3], chromatographic IE separations [4–6], deionization and softening of water [7–9], recovery of mineral components from sea water [10,11], or other hydromineral sources [12–14], and others attract the attention of scientists and engineers due to their great theoretical and practical importance. At the same time, these systems are far less thoroughly investigated than simple binary ones, although during the last years intensive studies of IE equilibrium [1,11], kinetics [15,16] and dynamics

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[17–20] in these systems have been carried out. Most of the models proposed to describe the IE equilibrium in multicomponent systems can be classified as electrostatic retention models [21], as they are mainly based on the Gouy–Chapman–Stern theory for the double electric layer [21–27]. Moreover, all models proposed describe the IE separation only under isothermal conditions.

The dual-temperature IE separation techniques including parametric pumping [28–31], thermal ion-exchange fractionation [32,33] and similar dual-temperature IE processes [10–13,34–37] constitute a group of ecologically clean fractionation techniques applicable for the separation of multicomponent ionic mixtures [38], due to the possibility to design reagentless (and wasteless as a result) IE separation processes [39,40]. On the other hand, the lack of information about equilibrium, dynamics and kinetics in multicomponent IE systems at different temperatures still limits their wide application. In the previous communications of this series we reported the results obtained by studying the equilibrium [41], kinetics and dynamics [42], and conditions of metal complex formation in the resin phase [43] at different temperatures in IE systems involving chelating resins and mixtures of transition metal ions such as, Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} at different pH. The formation of concentration waves during a dual-temperature thermostripping cycle was observed for the first time and both mathematical and physical models describing this phenomenon were developed [42]. The present work is addressed to (1) the further development of the model proposed in our previous communication [42] to describe reagentless separation of Cu^{2+} and Zn^{2+} ions by the dual-temperature IE technique, (2) determination of the influence of system parameters (Cu/Zn ratio, pH and resin bed height) on the efficiency of dual-temperature IE separation, and (3) evaluation of validity of predictions made by using the physical and the mathematical models proposed in a wide range of experimental conditions.

2. Experimental section

2.1. Reagents and apparatus

Zinc sulphate, copper sulphate and sulphuric acid of p.a. grade were from Panreac (Barcelona, Spain).

Iminodiacetic (IDA) ion exchanger, Lewatit TP-207, was kindly supplied by Bayer Hispania Industrial, S.A. (Barcelona, Spain). Doubly-distilled water was used in all experiments. Prior to experiments, all solutions were degassed by using an ultrasonic bath (Branson 1200, Danbury, CT, USA) and a vacuum pump. The ratio of Zn^{2+} to Cu^{2+} in stock solution, the pH of this solution and the amount of resin was varied in the different series of experiments as shown in Table 1. The concentrations of metal ions were determined by the ICP technique using the ARL Model 3410 spectrometer (Valencia, CA, USA) provided with minitorch. The emission lines used for the spectrochemical analysis were 324.754 nm for Cu^{2+} and 206.200 nm for Zn^{2+}. The uncertainty of metal ions determination was <1.5%. The pH was controlled using a Crison pH meter 507 (Barcelona, Spain) supplied with a combined glass electrode. A glass column of 1.1 cm I.D. connected with a thermostat (Selecta Ultraterm 6000383, Barcelona, Spain) was used in all experiments carried out. The construction of the column permitted a simultaneous thermostatic conditioning of both the resin and the entering solution phases.

2.1.1. Procedure

Thermostripping experiments were carried out under dynamic conditions by using the following procedure: after equilibration of the resin with the

Table 1
Main parameters of the systems studied

Study	Cu:Zn ratio [Cu]+[Zn] = 0.156 M	pH	H_{RB}, cm
Influence of Cu:Zn ratio	1:4	1.9	3.2
	1:8.5	1.9	3.2
	1:19	1.9	3.2
	1:39	1.9	3.2
	1:80	1.9	3.2
Influence of pH	1:19	1.9	3.2
	1:19	2.5	3.2
	1:19	3.0	3.2
	1:19	3.5	3.2
Influence of resin bed height	1:80	3.5	2.2
	1:80	3.5	3.2
	1:80	3.5	6.4

stock solution at 333 K, the excess of the equilibrium solution was removed from the column by the use of a vacuum pump. Then, the column was cooled up to 293 K and the feed solution of the same composition was passed through the column and collected in portions followed by determination of Zn^{2+}, Cu^{2+} and H^+ concentration in each eluate sample. After equilibration of the system at 293 K, the metals were stripped from the resin with 1 M H_2SO_4 solution to determine both the capacity of the resin and the separation factor, α, the value of which was calculated as follows:

$$\alpha_{Zn}^{Cu} = \frac{q_{Cu}[Zn]_0}{q_{Zn}[Cu]_0} \qquad (1)$$

where q_{Cu} and q_{Zn} are the partial resin capacities towards Cu and Zn, respectively, and $[Zn]_0$ and $[Cu]_0$ are the initial concentration of both metals in the stock solution.

All thermostripping cycles (both 'conventional' and sequential) were carried out by using the procedure described in detail elsewhere [42]. Experiments on the separation of Cu and Zn in sequential

thermostripping cycles were carried out as follows: the stock solution used in the first cycle had a Cu:Zn ratio of 1:80 and pH of 3.5. After equilibration of the resin with this solution (at 333 K) and carrying out the first thermostripping (at 293 K), the second stock solution was prepared so that it's composition corresponded to the medium composition (in terms of metal concentrations and pH) of the first 300 ml of the eluate collected in the previous (first) cycle. The same procedure was followed when carrying out the third cycle.

3. Results

3.1. Effect of Cu:Zn ratio

The relative concentration–volume histories obtained in thermostripping cycles by using stock solutions with different Zn/Cu ratios at pH = 1.9 are shown in Fig. 1. The ratio of relative metal ion concentrations in each eluate sample, R_{Zn-Cu}, was calculated as follows:
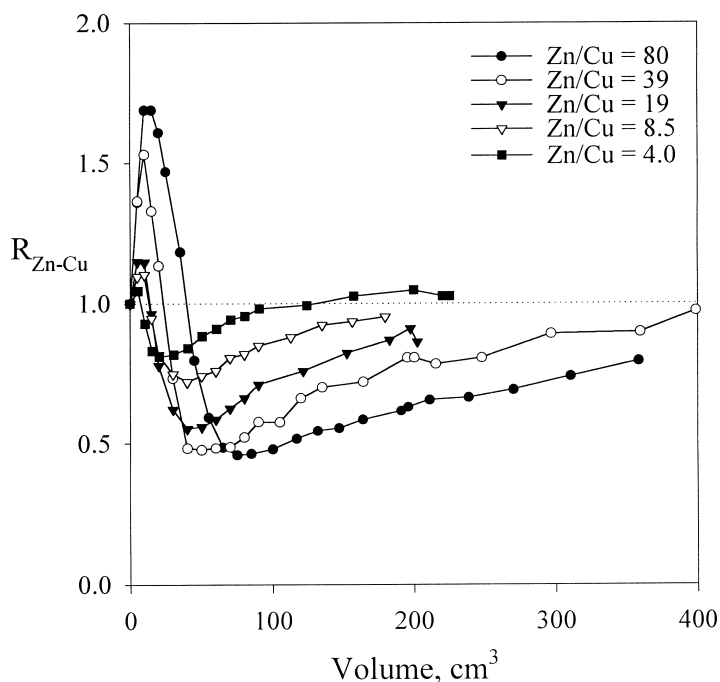

Fig. 1. Relative concentration–volume histories obtained in thermostripping cycles by using stock solutions with different Cu:Zn ratios. Conditions: $[Zn^{2+}] + [Cu^{2+}] = 0.156$ h; pH = 1.9; $H_{RB} = 3.2$ cm; $T_1 = 293$ K; $T_2 = 333$ K.

$$R_{Zn-Cu} = \frac{[Zn]}{[Zn]_0} \frac{[Cu]_0}{[Cu]} \qquad (2)$$

where [Zn] and [Cu] are the concentrations of zinc and copper in each sample collected, and $[Zn]_0$ and $[Cu]_0$ are the same as in Eq. (1). As seen from Fig. 1, the thermostripping process in all systems studied leads to formation of concentration waves in the column. The first portions of the stripping solution in all cases are characterised by higher R_{Zn-Cu} values ($R_{Zn-Cu} > 1$) indicating a depletion of the head part of the eluate with copper in comparison with Cu^{2+} concentration in the feed solution. In other words, the shape of the first half-wave shows that the initial period of the thermostripping cycle is characterised by desorption of zinc accompanied by a simultaneous sorption of copper by the resin. The same conclusion follows from the results presented in Fig. 2, where the variation of relative Cu^{2+} and Zn^{2+} concentrations in the resulting eluate is shown for Cu:Zn = 1:8.5 feed solution. The first half-wave observed is followed by the second one, in which the concentration of Cu^{2+} first continues to increase (surpassing its initial concentration in the feed solution and, thus, resulting in a value of $R_{Zn-Cu} < 1$, see

Fig. 1) up to a certain maximum value. Then it gradually decreases approaching the concentration in the stock solution, when a sufficient volume of solution is passed through the resin bed. As follows from Fig. 1, the initial decrease and further increase of copper concentration (initial increase of R_{Zn-Cu}) is the higher, the higher the ratio of Zn to Cu in the feed solution, i.e. the amplitudes of both the first and the second half-waves increase with Zn:Cu ratio. At the same time, the decrease of Cu^{2+} concentration in the feed solution (corresponding to higher Zn/Cu ratios) results in increasing the tail of the second half-wave so that a considerably higher volume of solution is needed to achieve the equilibrium. For this reason, the composition of stock solution with Cu:Zn = 1:19 has been chosen as optimal to study the effect of pH on the efficiency of the thermostripping process.

3.2. Effect of pH

The R_{Zn-Cu}-volume histories obtained by using stock solutions with constant Zn:Cu ratio = 1:19 at different pH are shown in Fig. 3. As seen, the increase of pH (decrease of H^+ concentration) leads to more intensive sorption of copper by the resin phase from the first portions of the eluate resulting in an increase of R_{Zn-Cu} values corresponding to the first half-wave. At the same time, a more intensive desorption of copper from the resin (lower R values) is observed at lower pH values. For example, at pH = 3.5, R_{Zn-Cu} does not reach a value lower than one indicating the complete disappearance of the second half-wave corresponding to a higher concentration of copper over zinc in the eluate collected.

3.3. Effect of resin bed height

Thermostripping curves obtained in experiments carried out by varying the height of the resin bed are shown in Fig. 4. This series of experiments was performed by using a stock solution with Zn:Cu = 1:80 at a pH of 3.5. As seen in Fig. 4, a higher pH value of solution used (see above Fig. 3) results in formation of only the first half-wave in all experiments carried out. As also follows from Fig. 4, the sorption of copper increases with the height of the resin bed. At the same time, the maximum value of
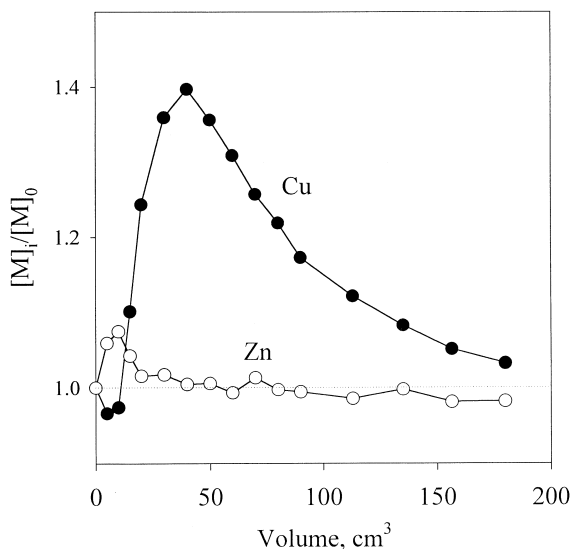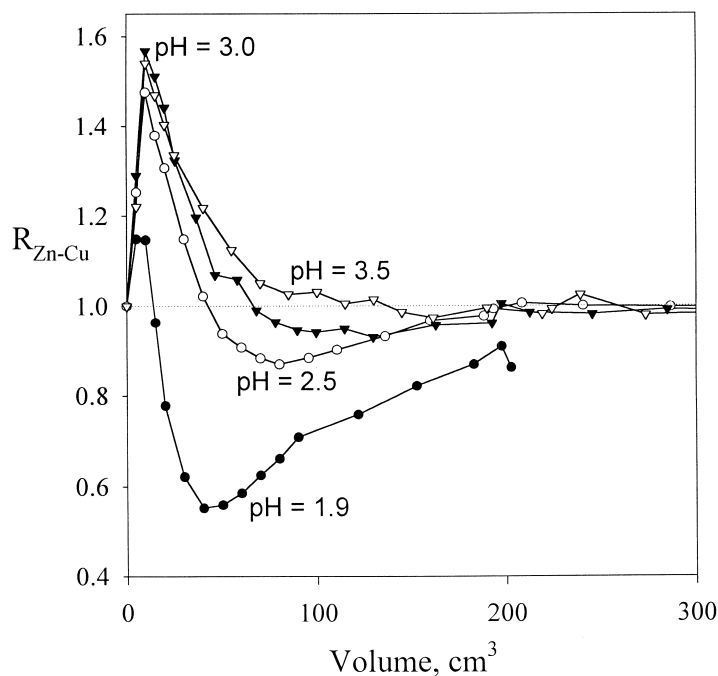

Fig. 2. Relative concentration–volume history obtained in the thermostripping cycle by using a stock solution with Cu:Zn = 1:8.5. Conditions: $[Zn^{2+}] + [Cu^{2+}] = 0.156$ h; pH = 1.9; $H_{RB} = 3.2$ cm; $T_1 = 293$ K; $T_2 = 333$ K.

Fig. 3. R_{Zn-Cu}-volume histories obtained in thermostripping cycles by using stock solutions with different pH. Conditions: $[Zn^{2+}]+$ $[Cu^{2+}]=0.156$ h; Cu:Zn$=1$:19; $H_{RB}=3.5$ cm; $T_1=293$ K; $T_2=333$ K.

R_{Zn-Cu} (R_{Zn-Cu}^{max}) is not as high as might be expected due to substantial widening of the peak.

3.4. Capacity and separation factor values

The partial capacities of the resin towards Cu^{2+} and Zn^{2+} and values of separation factors for the various compositions of stock solutions used in this study are shown in Table 2. As seen from Table 2, the variation of metal ion ratio in the stock solution dramatically affects both the resin capacities and, in particular, the value of the separation factor: a fourfold decrease of α is observed when the Cu:Zn ratio varies from 1:4 to 1:40. The resin capacities towards metal ions are also influenced by the changes of the Cu:Zn ratio: the capacity towards copper decreases while that towards zinc increases.

The solution pH less remarkably affects the value of the separation factor. Nevertheless, an increase of pH leads to a decrease of α values due to non-equal increase of the metal ion uptakes by the resin with pH. Indeed, the increase of solution pH from 1.9 to

3.5 results in ~50% rise of q_{Cu} value while q_{Zn} simultaneously increases by almost 80%.

The main conclusion, which can be derived from the above presented results can be formulated as follows: formation of temperature-induced concentration waves in the course of thermostripping of a Cu and Zn mixture from the resin results in depletion of the first portions of the eluate with copper (first half-wave) while succeeding eluate samples appear to be enriched with these metal ions (second half-wave). This gives a possibility to partially separate metal ions under study due to either tailored concentration or depletion of copper over zinc in the stripping solution. Adjustment of pH in the stripping (stock) solution can be used to regulate both the mode of separation and the separation efficiency. A higher efficiency of Zn purification from Cu admixture by using the temperature-induced concentration wave (TICW) technique must be achieved at low copper concentrations (high Zn:Cu ratios) and a relatively high pH in the solution under treatment. The repetitive treatment of partially purified solution in sequential thermosorption–thermostripping cycles
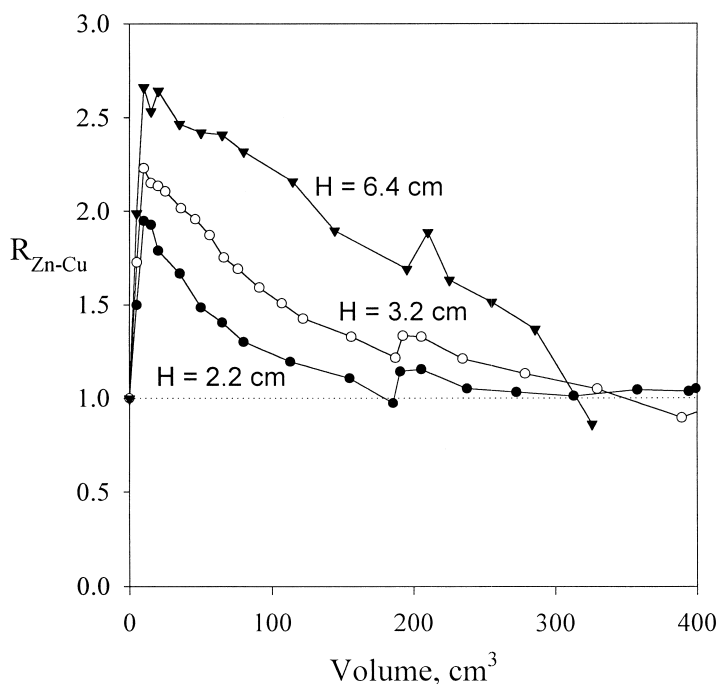
Fig. 4. R_{Zn-Cu}-volume histories obtained in thermostripping cycles by using resin beds of different height. Conditions: $[Zn^{2+}]+[Cu^{2+}]=$ 0.156 h; Cu:Zn=1:80; $H_{RB}=3.5$ cm; $T_1=293$ K; $T_2=333$ K (see Table 1).

must increase the purification efficiency due to multiplication of a single separation effect.

3.5. Thermostripping cycles

The results obtained in three sequential thermosorption-stripping purification cycles are shown in Fig. 5.

Table 2
Partial resin capacities and separation factor values determined in different systems at 293 K

Solution parameters	q_{Cu} mmol/g	q_{Zn} mmol/g	α_{Zn}^{Cu}
Cu:Zn (pH=1.9)			
1:4	1.79	0.19	39.1
1:8.5	1.73	0.27	56.2
1:19	1.40	0.28	97.6
1:39	1.14	0.28	159.2
pH (Cu:Zn=1:19)			
1.9	1.40	0.28	97.6
2.5	1.93	0.43	87.9
3.0	2.02	0.45	85.5
3.5	2.12	0.49	82.8

The concentrations and pH of the stock solutions used in each cycle are given in Table 3. As seen in Fig. 5, a sufficiently big volume of solution, in which the concentration of copper is equal to ~10% of its concentration in the initial stock solution (used in the first cycle) is obtained in the course of the third cycle using the reagentless TICW process.

4. Discussion

The main parameters of all TICW separation processes carried out are collected in Table 4. The R_{Zn-Cu}^{max} and R_{Zn-Cu}^{min} (minimal R_{Zn-Cu} value) characterise the efficiency of metal separation in the first and in the second half-wave, respectively. The quantitative characteristics of sorption of copper in the first half-wave and its subsequent desorption in the second half-wave are presented in Table 5. As seen, the degree of copper depletion in the first half-wave progressively increases along with enrichment of the solution with this ion in the second half-wave when the Cu:Zn ratio decreases. These results confirm the
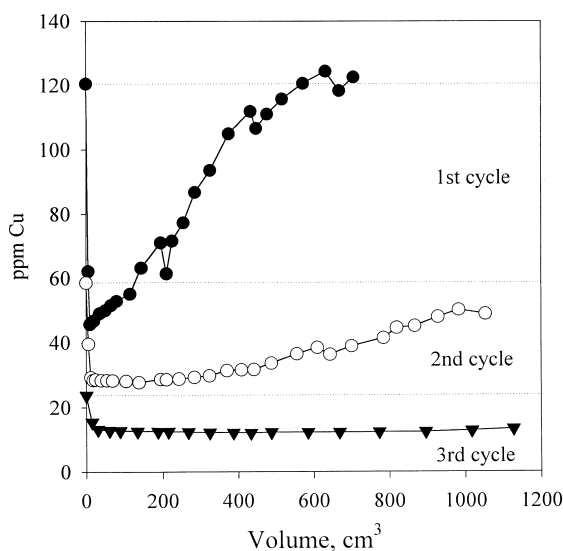
Fig. 5. Copper concentration–volume histories obtained in sequential thermostripping cycles. Conditions: $H_{RB} = 6.4$ cm; $T_1 = 293$ K; $T_2 = 333$ K (other conditions see Table 3).

possibility of applying the TICW process both to increase and/or to decrease the metal ratio in solution of their mixture. The efficiency of this process depends on the relative content of the slower diffusing ion in the mixture (Cu^{2+} in our case). The increase of pH of the stock solution enhances copper uptake by the resin (efficiency of copper removal from the solution corresponding to the first half-wave increases). At the same time, the enrichment of copper in the second half-wave decreases. This is clearly seen both from Tables 4 and 5: both R_{Zn-Cu}^{max} and R_{Zn-Cu}^{min} progressively increase with pH. The copper enrichment decreases and its subsequent depletion increases when the pH of the stock solution is varied from 1.9 to 3.5. At a relatively high pH it appears impossible to both decrease and increase the copper concentration in the stripping solution. Under these conditions only sorption of copper is observed

Table 3
Composition of stock solutions used in sequential thermostripping cycles

Cycle no.	[Cu], ppm	[Zn], ppm	pH
1	120.4	10 180	3.5
2	58.6	10 262	4.5
3	23.7	10 150	5.0

Table 4
Parameters of TICW obtained in different thermostripping cycles

System parameters	TICW parameters			
	R_{Zn-Cu}^{max}	R_{Zn-Cu}^{min}	Cu sorbed, mequiv.	Enrichment of Cu, %
Cu:Zn[a]				
1:4	1.04	0.81	0	26.0
1:8.5	1.10	0.72	0.0098	39.7
1:19	1.15	0.55	0.0107	83.8
1:39	1.53	0.48	0.0258	119.3
1:80	1.69	0.46	0.0342	121.7
pH[b]				
1.9	1.15	0.55	0.0107	83.9
2.5	1.48	0.87	0.0871	19.0
3.0	1.57	0.94	0.148	6.7
3.5	1.54	0.97	0.164	3.2
H_{RB}[c]				
2.2 cm	1.95	1	0.140	–
3.2 cm	2.23	1	0.299	–
6.4 cm	2.66	1	0.598	–

[a] pH=1.9; H_{RB}=3.2 cm.
[b] Cu:Zn=1:19; H_{RB}=3.2 cm.
[c] pH=3.5; Cu:Zn=1:80.

resulting in purification of the head part of the eluate collected from the column with this metal ion.

The increase of the height of the resin bed, H, results in the enhancement of the efficiency of TICW separation (see Fig. 4) leading in fact to the 'amplification' of the amplitude of concentration wave in the column. Under conditions of this series of experiments, which correspond to the formation of only the first half-wave (Cu:Zn=1:80; pH=3.5) the increase of H resulted in both the lower concentration of Cu^{2+} in the head part of the eluate collected and a bigger volume of the solution partially purified from copper. Hence, the height of the resin bed appears to be another parameter, which can be used to increase the efficiency of the TICW separation process. The maximum efficiency in this case can be evidently achieved by using countercurrent IE columns, known to be characterised by an endless resin bed [20,44,45].

4.1. Physical and mathematical models of the TICW process

The formation of TICW in the course of the

Table 5
Sorption and desorption of copper in different thermostripping cycles

System	Cu sorbed, mequiv.	Cu depletion, %	Cu desorbed, mequiv.	Cu enrichment, %
Cu:Zn[a]				
1:4	0	0	0.812	26.0
1:8.5	0.00976	2.6	0.934	39.7
1:19	0.0107	8.2	1.090	83.8
1:39	0.0258	26.8	1.127	119.3
1:80	0.0342	36.7	–	121.7
pH[b]				
1.9	0.0107	8.2	1.093	83.8
2.5	0.0871	29.8	0.199	19.0
3.0	0.148	33.8	–	6.7
3.5	0.164	33.8	–	3.2
H_{RB}[c]				
2.2 cm	0.140	47.1	–	–
3.2 cm	0.299	54.6	–	–
6.4 cm	0.598	62.1	–	–

[a] pH=1.9; H_{RB}=3.2 cm.
[b] Cu:Zn=1:19; H_{RB}=3.2 cm.
[c] pH=3.5; Cu:Zn=1:80.

thermostripping cycle and the separation effect observed is primarily attributed by the different diffusivities of metal ions under study (Cu^{2+} and Zn^{2+}) and also by the presence of the third ion in the system (H^+). Explanation of the results obtained can be based on the physical model reported in the previous communication of this series [42]. The process of Zn^{2+} release from the resin phase must proceed rather rapidly due to a far higher value of the diffusion coefficient of this ion, $\overline{D}_{Zn}$, in comparison with $\overline{D}_{Cu}$ [42]. The flux of released Zn^{2+} ions must be compensated by an equivalent flux of H^+ ions entering the resin phase. However, the concentration of H^+ ions in the stripping solution (see Table 1) is not sufficiently high to balance completely the desorption of Zn^{2+}. This must result in an unbalance of charges in the system leading to the appearance of a local electric field in the resin phase, which equalizes the ion fluxes [42]. Hence, the field must 'draw' Cu^{2+} ions into the ion exchanger. This must lead, in turn, to a drop of Cu^{2+} concentration in the first portions of the stripping solution collected (in the first half-wave). At a

constant pH this effect must be clearer pronounced at low Cu^{2+} content in the stock (stripping) solution (high Zn:Cu ratios) when the concentration of copper becomes comparable with H^+ concentration in the solution phase. On the other hand, at a constant Cu^{2+} a stronger copper sorption due to unbalance of charges in the system must be observed at higher pH (lower H^+ concentration). The confirmation of the validity of the model proposed is clearly seen in Figs. 1 and 3. The main conclusion, which can be derived from the results of this series of experiments can be formulated as follows: variation of pH of a solution containing a mixture of metal ions with different diffusivities in the resin phase can be used as a tool to select the desired mode of separation by using the TICW technique (see above).

The mathematical model proposed in the present work is based on the same premises and similar basic equations as the model developed previously [42] but complements it through accounting for formation of $CuSO_4$ and $ZnSO_4$ complexes and the presence of HSO_4^- and SO_4^{2-} ionic species in the solution phase. The modified model includes the following equation:

Mass-balance equation

$$\epsilon \frac{\partial}{\partial t}(C_i + C_{i\mathrm{SO}_4}) + V \frac{\partial}{\partial x}(C_i + C_{i\mathrm{SO}_4}) + \frac{\partial q_i}{\partial t} = 0$$

(3)

Equation of IE kinetics

$$\frac{\partial q_i}{\partial t} = \beta_i \left(q^*_{\ i} - q_i + \frac{q^*_{\ i} + q_i}{2} E \right)$$

(4)

Mass-action law

$$K_{\mathrm{H}} \frac{C_{\mathrm{H}}}{q^*_{\ \mathrm{H}}} = K_{\mathrm{Cu}} \left(\frac{C_{\mathrm{Cu}}}{q^*_{\ \mathrm{Cu}}} \right)^{1/2} = K_{\mathrm{Zn}} \left(\frac{C_{\mathrm{Zn}}}{q^*_{\ \mathrm{Zn}}} \right)^{1/2};$$

$$k_i(T) = \frac{C_{i\mathrm{SO}_4}}{C_i\, C_{i\mathrm{SO}_4}}; K_i = K_i(q^*_{\ i}, T)$$

(5)

Electroneutrality equations

$$q_{\mathrm{H}} + 2(q_{\mathrm{Cu}} + q_{\mathrm{Zn}}) = Q_{\Sigma};$$
$$q^*_{\ \mathrm{H}} + 2(q^*_{\ \mathrm{Cu}} + q^*_{\ \mathrm{Zn}}) = Q_{\Sigma};$$
$$2(C_{\mathrm{Cu}} + C_{\mathrm{Zn}}) + C_{\mathrm{H}} = 2C_{\mathrm{SO}_4} + C_{\mathrm{HSO}_4}$$

(6)

Initial and boundary conditions

$$(C_{\mathrm{Cu}} + C_{\mathrm{CuSO}_4})_{x=0} = (C_{\mathrm{Cu}} + C_{\mathrm{CuSO}_4})_{t=0} = C^{\circ}_{\ \mathrm{Cu}};$$

$$(C_{\mathrm{Zn}} + C_{\mathrm{ZnSO}_4})_{x=0} = (C_{\mathrm{Zn}} + C_{\mathrm{ZnSO}_4})_{t=0} = C^{0}_{\ \mathrm{Zn}};$$

$$C_{\mathrm{H}_{x=0}} = C_{\mathrm{H}_{t=0}} = C^{0}_{\mathrm{H}}$$

(7)

The relative intensity of the local electric field, E, varies in the course of development of the thermostripping cycle. In the beginning of the cycle E has the maximum value around 1/10 that is particularly important as $q^*_{\ i} + q_i/2 |q^*_{\ i} - q_i|$ (see Eq. (4)).

4.2. Results of computer simulation

A computer simulation of the thermostripping breakthrough curves obtained in the separation of Cu^{2+} and Zn^{2+} by using the TICW technique was carried out by applying the proposed model. The values of model parameters (β, Q_{Σ}, K_i, etc.) were identical to those used in the previous work [42]. The boundary and initial conditions used in the computer simulation corresponded to those applied in experiments carried out.

A comparison of the experimental results with the results of the computer simulation is shown in Fig. 6. As seen, the results of the TICW process modelling (lines) are in good qualitative and quantitative agreement with the experimental data (points) that confirms the validity of the mathematical model proposed and testifies to the predicting ability of the physical model applied. The validity of the model was also confirmed by the coincidence of the ratio of the best fitting values of β_{Zn} and β_{Cu} with that of diffusion coefficients of respective metal ions found experimentally [42].

4.3. Sequential thermostripping cycles

The experiments on the separation of Zn^{2+} and Cu^{2+} in sequential thermostripping cycles were simulating a periodical mode of dual-temperature ion-exchange fractionation. One of the versions of this process is shown schematically in Fig. 7. The unit comprises several ion-exchange columns intermittently working in either thermosorption or thermostripping mode of operation depending on the temperature of solution entering the column. The first column produces the first either zinc or copper concentrate, depending on the pH value of the stripping solution and, hence, on either copper depletion (at higher pH) or copper concentration (at lower pH) mode of fractionation. The second column treats the first concentrate and produces the second concentrate, which is treated in the third column and so forth. Each concentrate is obtained by collecting the eluate fractions corresponding to either the first or the second half-wave (depending on the mode of operation). The concentration of copper in each concentrate corresponds to an average Cu^{2+} concentration across the respective half-wave.

As follows from the results obtained in the separation of Cu^{2+} from Zn^{2+} in three sequential thermostripping cycles (see Fig. 5), it is possible to pre-calculate the number of cycles (or columns, see Fig. 7) required to produce the final concentrate with the desired copper content. The medium Cu^{2+} concentration in a given volume of concentrate obtained after each cycle (from each column) is connected with the initial copper concentration (in the previous concentrate) as follows:
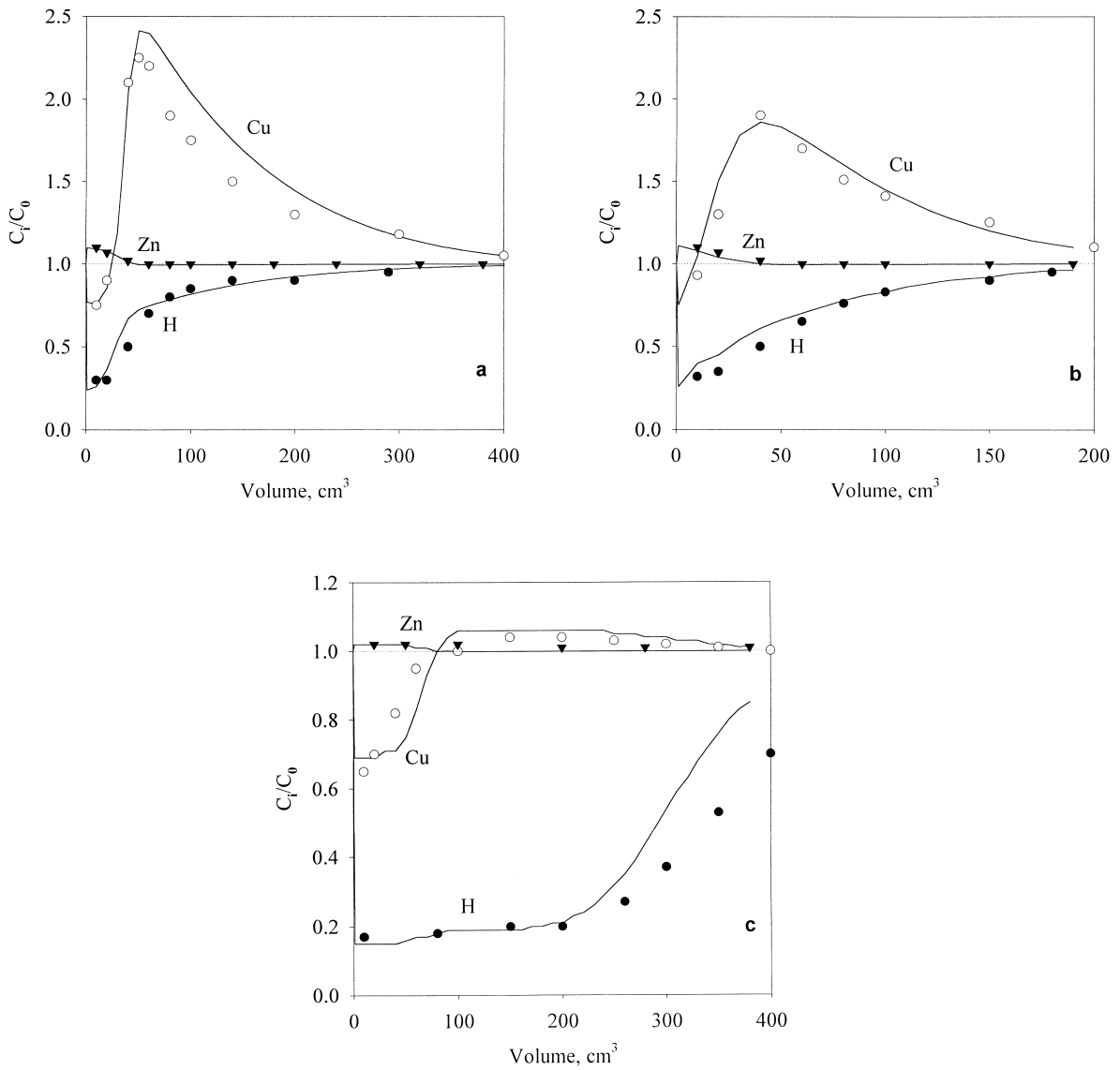
Fig. 6. Results of the computer simulation of thermostripping breakthrough curves by using the mathematical model of the TICW process (see text). Curves (computed), points (experiment). Conditions: (a) Cu:Zn = 1:39; pH = 1.9; (b) Cu:Zn = 1:19; pH = 1.9; (c) Cu:Zn:Cu = 1:19; pH = 3.5; H_{RB} = 3.2 cm.

$$\left[\overline{Cu}\right]_{V,\,n} = a_n\left[\overline{Cu}\right]_{V,\,n-1} \tag{8}$$

where n is the number of cycle, $\left[\overline{Cu}\right]_{V,n}$ is the medium concentration of copper in the concentrate of volume V obtained in cycle number 'n', and a_n is the copper depletion degree, which is determined from the results of the first thermostripping cycle as follows:

$$a_n = 1 - \frac{\Delta[Cu]_1}{[Cu]_0} \tag{9}$$

where $\Delta[Cu]_1$ is the absolute decrease of copper concentration in the thermostripping solution of volume V after the first cycle, and $[Cu]_0$ is the concentration of copper in the initial stock solution. The a_n values appear to be constant for all cycles
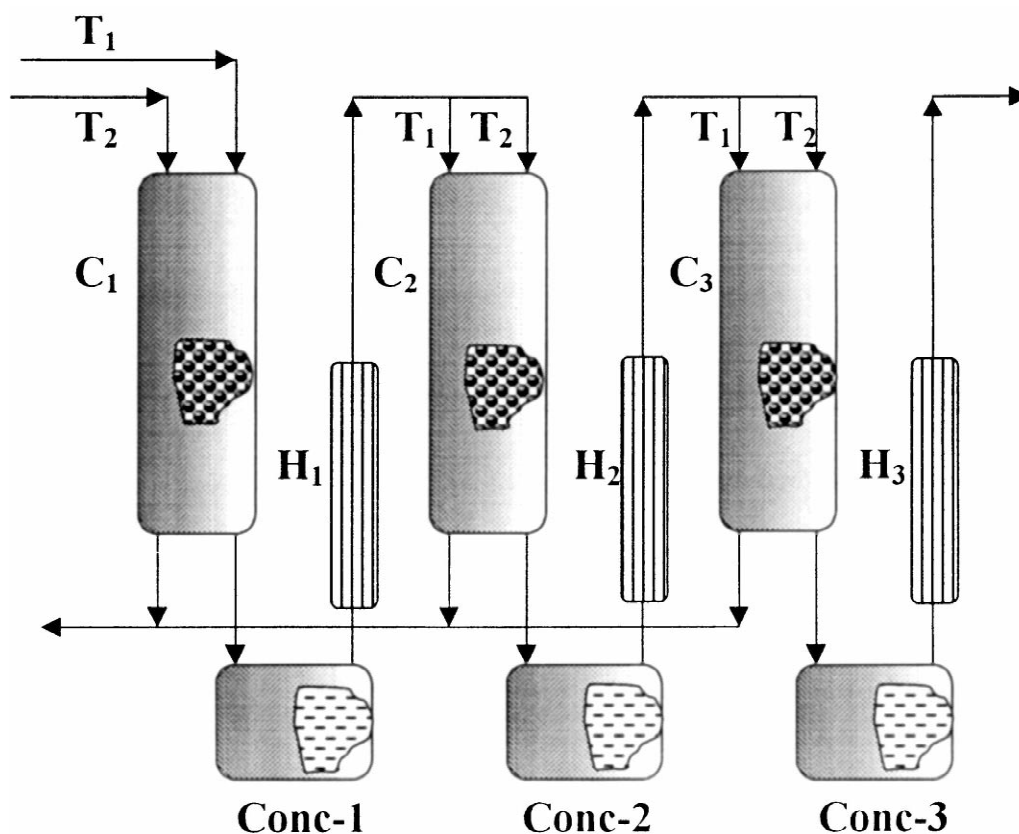
Fig. 7. Schematic diagram of unit for reagentless separation of metal ions by using the TICW technique. C_1–C_3 – ion-exchange columns; H_1–H_2 – heaters; Conc-1–Conc-3 – tanks for purified solutions; $T_{1,2}$ – working temperatures (see text).

carried out and equal to $0.47 \pm 10\%$. Hence, it is easy to demonstrate that:

$$[\overline{Cu}]_{V,n} = (a_n)^n [Cu]_0 \tag{10}$$

By taking the logarithms of Eq. (10) one obtains:

$$\log[\overline{Cu}]_{V,n} = n \log a_n + \log[Cu]_0 \tag{11}$$

Taking into account that for the system under study $\log(0.47) = -0.33$, Eq. (11) in our case takes the form:

$$\log[\overline{Cu}]_{V,n} = \log[Cu]_0 - 0.33n \tag{11a}$$

Fig. 8 shows $\log[\overline{Cu}]_{V,n}$ versus n dependence (for $V = 200$ cm^3) obtained in three thermostripping cycles carried out. As obviously follows from Fig. 8 (and can also be easily calculated from Eq. (11a) six thermostripping cycles are required to decrease the

copper content in the Zn^{2+}–Cu^{2+} mixture from 120 to 1 ppm. The concentration of zinc in the solution under treatment remains essentially constant (see Fig. 6b and c) in the course of all thermostripping cycles carried out. The purification process based on the TICW technique appears to be reagentless and wasteless, as a result.

5. Conclusions

The following main conclusions can be derived from the results of the presented studies:

(a) formation of TICW (oscillation of ion concentrations in the course of thermostripping cycle) associated with both the difference in Cu^{2+} and Zn^{2+} ion diffusivities in the resin phase and the presence
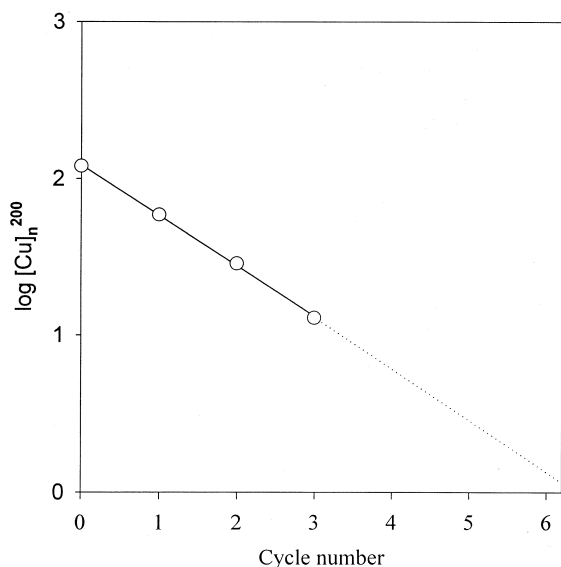
Fig. 8. Logarithm of medium copper concentration in the first 200 ml of collected eluate obtained in different thermostripping cycles (see text).

of the third (H^+) ion in the solution phase strongly depends on the ratio of metal ions and pH in the stock solution;

(b) the shape and the amplitude of TICW can be varied by the modulation of pH in the stock solution so that only formation of the first or the second half-wave is observed. This effect makes it possible to carry out a reagentless separation of metal ions by using either metal depletion or metal concentration mode of operation;

(c) the efficiency of the TICW-based separation process by using metal depletion mode appears to the higher the lower relative concentration of metal ion under removal (slower diffusing ionic species);

(d) the mathematical model proposed allows for qualitative and quantitative description of thermostripping processes in a wide range of pH and solution compositions;

(e) the results of the separation of Zn and Cu obtained in sequential TICW cycles testifies to the possibility to use the TICW technique in ultra-purification processes;

(f) the physical model of the TICW process proposed makes it possible to account for the influence of different process parameters and generalise the applicability of the TICW separation

technique to the binary mixtures of any metal ions with different diffusivities.

6. Abbreviations

a_n	Depletion factor
C_i	Concentration of ion 'i' in an eluate portion solution (equiv./dm^3)
C_{iSO_4}	Concentration of sulphate complex of ion 'i' in solution phase (equiv./dm^3)
C_i^0	Initial concentration of ion 'i' in solution (equiv./dm^3)
$\overline{D}_i$	Effective diffusion coefficient of ion 'i' in resin phase (cm^2/s)
E	Intensity of electric field in dimensionless units
H_{RB}	Height of resin bed, cm
k_i	Stability constant of the sulfate complex of 'i' ion in solution
K_i	Reduced equilibrium coefficient in mass-action low (relative equilibrium constant)
n	Number of thermostripping cycles
q_i	Amount of ion 'i' in resin beads per volume unit of resin bed (equiv./dm^3)
q_i^*	Equilibrium amount of ion 'i' in resin beads per volume unit of resin bed (equiv./dm^3)
Q_Σ	Total resin capacity (equiv./kg)
R_{Zn-Cu}	Ratio of Zn^{2+} and Cu^{2+} concentrations in eluate samples
t	Time
T	Temperature, K
V	Volume of eluate collected (cm^3)
x	Longitudinal coordinate along ion-exchange column (cm)
β_i	Kinetic parameter of ion 'i' (min^{-1})
ε	Resin bed porosity

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