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Simulation of Dual Temperature Ion-Exchange Separation Process Taking into Account Complex Formation in Solution

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ABSTRACT

A mathematical modeling of a dual temperature ion-exchange separation system is reported. The nonlinear nonequilibrium model created takes into account the following physicochemical processes: kinetics, ion-exchange reactions, complex formation accomplishing the chemical equilibria. The model was applied for a system containing Cu^{2+} and Zn^{2+} in acidic sulfate solutions and the iminodiacetic ion-exchange resin Amberlite IRC-718. Good agreement to the experimental data was found. The dependence of the separation efficiency on different factors was tested. The advantage of nonequilibrium operations for the effective separation was shown. The optimal separation cycle was calculated for a sulfate solution containing 2.5 mM Cu and 20 mM Zn at pH 2.05. An ion-exchange column can process 207 bed volumes of the treated solution during one cycle. The effluent is separated for three fractions. The first fraction (75 bed volumes) is the solution containing the 9 times reduced Cu concentration. The second one (36 bed volumes) is the concentrate of Cu. The third fraction is mixed and recycled for repeated treatment.

INTRODUCTION

Ion-exchange processes are widely used for the separation of ions from dilute solutions. However, the application of the traditional ion-exchange

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technique for the separation of more concentrated solutions is ecologically questionable because of the use of large acid and/or alkali volumes needed for the desorption/regeneration steps.

Another type of ion-exchange separation technique is based on applying ion-exchange resins with a distinct temperature dependence in their selectivity toward desired ions (1–7) (dual temperature technique). This technique allows ecologically clean ion-exchange processes using no or minimum reagents to be designed. In earlier publications we described the dual temperature separation of copper and zinc from acidic sulfuric solutions (8, 9) and experimental results on the separation cycle optimization to improve the separation efficiency (10). However, extending the work to a wide diversity of practical conditions and solutions treated cannot be performed by laboratory experimental work alone. A mathematical modeling approach can be helpful for obtaining quantitative characteristics of the process at a wide variety of conditions. It is particularly important if the conditions make the laboratory experiment especially difficult (long durability, very high ratio between the volumes of treated solution and resin bed, etc.).

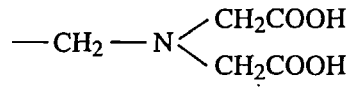
The earlier considered dual temperature separation process (9, 10) is accomplished by complex formation in solution. Most of the metal ions present in solution are bonded in complexes (Fig. 1) whose stability is temperature-dependent. There is no publication on quantitative modeling of the ion-exchange dynamics of this kind of nonlinear nonequilibrium process. Therefore, simulation of this process is interesting from the methodological point of view as well.

The present work reports the description and mathematical model for the dual temperature separation of copper and zinc from acidic sulfate solution using the chelating resin Amberlite IRC-718. All quantitative characteristics of the model are obtained. Examples of the created model applications are presented.

EXPERIMENTAL

Resin

Amberlite IRC-718 resin was received from Rohm & Haas (USA). It is a styrene-divinylbenzene resin containing iminodiacetic functional groups



The resin was preconditioned. The conditioning included three alternating treatments with the following HCl solutions: 0.5, 1, 2, 3, 2, 1, 0.5 M; and NaOH solutions: 0.1, 0.2, 0.5, 1, 0.5, 0.2, 0.1 M. The material was washed with water at each reagent change. The washing efficiency was controlled

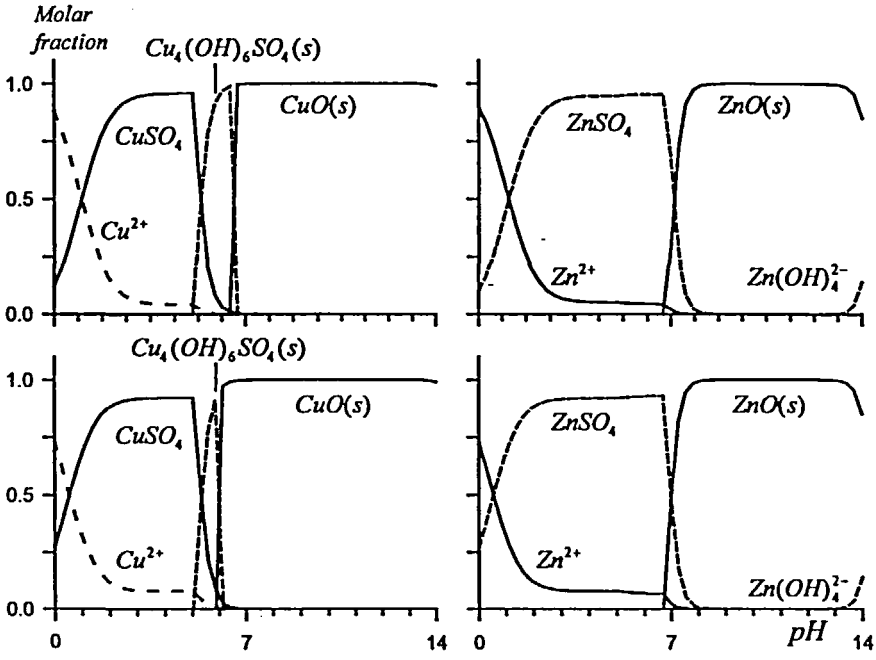


FIG. 1 Complex formation in solution containing 12 mM $CuSO_4$, 100 mM $ZnSO_4$, and 50 mM H_2SO_4. pH is adjusted using an indifferent background; (s) represents this solid phase.

by the methyl orange test (washing after the acidic treatment) and by the sodium flame test (washing after the alkali treatment). The thiocyanate test was done at the 3 M HCl treatment to test for the absence of iron. After the conditioning, the resin was completely transferred in hydrogen form by the 0.5 M HCl treatment (flame test), washed with water (methyl orange test), and stored.

The mixed ionic form required for the second experiment was prepared in the ion-exchange column by pumping the desired solution (see initial conditions below) until there was an equivalent composition of influent and effluent. The temperature of the column was controlled by a thermostat.

The particles diameter (H-form imbibed in water) was 0.64 ± 0.11 mm. The change of the bed volume at total ionic form conversion was within 7%.

Reagents

$CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, HCl, NaOH (KEBO Lab, Sweden), and H_2SO_4 (Merck, Germany) of analytical grade were used as received. All solutions were prepared using deionized water.

Analyses

The concentrations of Cu and Zn were determined by AAS (Perkin Elmer 603) and ICP (ARL 3520B) techniques. The error of the spectrochemical analysis was less than 1% for Cu and 2% for Zn. The pH was measured by the standard procedure using a glass electrode (Orion 92-02).

Determination of the Total Exchange Capacity

Determination of the chelating resin ion-exchange capacity by the generally accepted methods (11) is not reliable. These methods use the exchange between hydrogen and sodium or potassium ions. However, the alkali metal forms of chelating resins are susceptible to hydrolysis (8, 12). The total exchange capacity was determined toward Cu^{2+} since the resin has the highest selectivity for this ion. The validity of this method was proved earlier (8). A precisely weighted sample of the resin (10 g of the air-dried H^+-form) was placed in a glass column. The amount of water in the resin was determined separately. The resin was totally loaded by Cu^{2+} using 0.1 M $CuSO_4$ and washed with deionized water until copper was absent in the effluent. Copper was eluted from the resin by 1 M H_2SO_4. The total exchange capacity (Q) was calculated from analysis of the eluate:

$$Q_r = \frac{C_{Cu} V_{el}}{m_{d.r.}} = 5.08 \text{ meq/g dry resin} \quad (1)$$

where C is the concentration of the eluate (meq/mL), V_{el} is the volume of the eluate (mL), and $m_{d.r.}$ is the weight of the dry resin (g). The result was confirmed by separate titration experiments. The value obtained did not differ significantly from that indicated by Eq. (1). However, the method proposed produces much less dispersion than the results of acid–base titration.

Determination of the Resin Water Content

Three 0.3000–0.5000 g samples of the air dry resin (H^+-form) were weighted simultaneously with the samples intended for each experiment. The samples were dried in vacuum over P_2O_5 until the weight was constant. The average water content was calculated. The dry resin weight was used for all calculations.

Selectivity Coefficients of the Ion-Exchange Equilibria

Dynamic experiments to determine the ion-exchange equilibria selectivity coefficients were described earlier (9). Thermostatic glass columns were used to provide heating/cooling of both the resin and solution phases. The diameter

of the columns was 1 cm. Each column was loaded with the air-dried resin (2 g of the H^+-form). The amount of water in the resin was determined separately. The feed solution was passed through each column at a constant velocity of 0.37 m/h. The achievement of ion-exchange equilibrium was monitored by a comparison of the concentration of each cationic species in the effluent with that of the feed solution. Then the feed solution residual was removed by applying vacuum suction. 1 M H_2SO_4 was used for elution of sorbed ions. The concentrations of Cu and Zn and the pH in the eluate obtained were determined. The amount of ions eluted was used to calculate the selectivity coefficients. It was assumed that the ion-exchanger phase includes both the resin network and the internal solution.

Separation Experiments

The separation experiments were carried out in a thermostatic glass column which provided the heating/cooling of both the resin and solution phases. The column was loaded with 4 g of the air-dried resin. The bed volume was 13.5 mL; the bed height was 17.2 cm. The feed solution containing $CuSO_4$, $ZnSO_4$, and H_2SO_4 was passed through the column at a constant flow rate of 0.5 mL/min, corresponding to a velocity of 0.37 m/h in the column. The temperature was alternated between 15 and 75°C. The effluent was collected in 25 mL samples which were analyzed for Cu, Zn, and the pH.

Figure 2 shows the automatic system used for the experiments. The system included an ion-exchange column, a computer, and three computer-operated parts: a thermostating system, a feed system, and a sample collecting system.

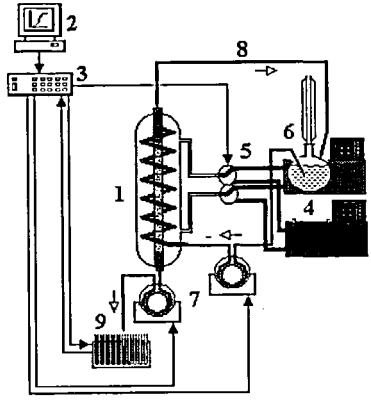


FIG. 2 The automatic system created for the nonstop separation experiments. 1: ion-exchange column, 2: computer, 3: interface, 4: thermostats, 5: valves, 6: refluxed flask, 7: peristaltic pumps, 8: recycling tube, 9: sampler.

An IBM-PC computer with an I/O card (FPC-046) and an especially developed relay interface were used.

The thermostating system contained two thermostats (Julabo F40-H provided the cooling system and Lauda B12) and two three-way solenoid valves. The solenoid valves were used to change the flow of the thermostatic liquid for column temperature switching at the desired times. The valves were coupled and operated by the computer.

The feed system contained a flask for the feed solution, two peristaltic pumps (Masterflex), and a recycling tube. The flask was placed in the thermostat which had a higher temperature to prevent solvated gas from being fed to the column. A refluxing condenser was used to prevent evaporation. The first pump helped move the feed solution through the resin bed. It kept a constant flow rate. The second pump delivered the feed solution into the column. Its pumping speed was 10% higher than the speed of the first pump. The excess solution was returned to the flask by a recycling tube. The double-pumps system was made to maintain a constant solution level inside the column. Both pumps were operated by the computer.

The sample collecting system was an automatic sampler (7000 Ultrorac Fraction Collector) which was controlled by the computer. The back connection was used to protect against solution leakage during the sampler operations.

The software was written in both DOS (Borland Pascal 7.0) and WINDOWS (Visual Basic 3.0) versions. The computer controlled the experiment according to conditions specified in the input.

PHYSICOCHEMICAL DESCRIPTION OF THE SEPARATION SYSTEM

The physicochemical system considered includes a water solution and the chelating ion-exchange resin Amberlite IRC-718. The following ions are present: Cu^{2+}, Zn^{2+}, H^+, SO_4^{2-}. The following ion exchange reactions take place:

$$2RH + Cu^{2+} = R_2Cu + 2H^+ \quad (2)$$

$$2RH + Zn^{2+} = R_2Zn + 2H^+ \quad (3)$$

$$R_2Zn + Cu^{2+} = R_2Cu + Zn^{2+} \quad (4)$$

where R is the resin matrix. However, the ion-exchange system is completely described by any pair of the three presented Eqs. (2)–(4). We have chosen Eqs. (2) and (3) for the following consideration.

The processes in the system are accomplished by complex formation in the solution phase. The formation of the following 1–1 complexes should be

taken into consideration for the given case of the acidic conditions studied (see Fig. 1):

$$Cu^{2+} + SO_4^{2-} = CuSO_4 \tag{5}$$

$$Zn^{2+} + SO_4^{2-} = ZnSO_4 \tag{6}$$

$$H^+ + SO_4^{2-} = HSO_4^- \tag{7}$$

Equilibria (5)–(7) have fast kinetics which may be neglected in our considerations.

In summarizing what is given above, we conclude that the model must take into account ion exchange (Eqs. 2 and 3) and equilibria in the solution (Eqs. 5–7) as well as the kinetics of the process.

MODELING

Mathematical Model

The model for the process considered includes a set of equations according to the above physicochemical description. The transport of components is described by (8)

$$e\frac{\partial}{\partial t}(C_{Ion} + C_{IonSO_4}) + F\frac{\partial}{\partial l}(C_{Ion} + C_{IonSO_4}) + \frac{\partial}{\partial t}q_{Ion} = 0$$
$$(0 \le l \le L, \quad t \ge 0, \quad Ion = Cu^{2+}, Zn^{2+}, H^+) \tag{8}$$

where e is the porosity of the sorbent bed; C is the concentration in solution; the index "Ion" represents the metal (Cu^{2+} or Zn^{2+}) or hydrogen (H^+) ion; t is the time; F is the solution flow rate; l is the longitudinal coordinate along the ion-exchange column; L is the length of the column; q_{Ion} is the ion content in the resin bed; $t = 0$ at the initial moment of the calculation (i.e., the beginning of the experiment); $l = 0$ at the top (inlet) of the column. Equation (8) must be rewritten for every ion (Cu^{2+}, Zn^{2+}, and H^+). The analytical concentrations of ions, which can be described as the sum of the free ion concentration (Cu^{2+}, Zn^{2+}, or H^+) and the concentration of the ion contained in the complex ($CuSO_4$, $ZnSO_4$, and HSO_4^-, respectively), are considered. C and q are the functions of the time and the coordinate: $C = C(l, t)$ and $q = q(l, t)$. The equivalent concentration scale was chosen to simplify the calculations.

Equation (9) describes the kinetics of the ion-exchange process:

$$\partial q_{Ion}/\partial t = k_{Ion}(q^*_{Ion} - q_{Ion}) \tag{9}$$

This is the well-known kinetics equation which describes particle diffusion; k_{Ion} is the kinetic coefficient for the ion; q^*_{Ion} is the equilibrium content of

the ion in the sorbent; $q^* = q^*(l, t)$. When equilibrium is not achieved, q^*_{Ion} is the ion concentration under the bead surface at moment t. Equation (9) must be rewritten for every ion.

Equation (10) presents the principle of constant exchange capacity:

$$\sum_{i=Cu,Zn,H} q_i = Q \tag{10}$$

where Q is the total volume ion-exchange capacity of the resin bed.

Equation (11) describes the mass action law:

$$\frac{C_H}{q^*_H} = K^{Cu}_H \left(\frac{C_{Cu}}{q^*_{Cu}}\right)^{1/2} = K^{Zn}_H \left(\frac{C_{Zn}}{q^*_{Zn}}\right)^{1/2} \tag{11}$$

where K^{Me}_H is the ion-exchange selectivity coefficient for Reactions (2) and (3). It should be noted that the selectivity coefficients depend on the temperature $K = K(T)$. It was assumed that the selectivity coefficients are constant in the range of the conditions used. This assumption is correct because a constant ionic strength of the external solution was used.

Equation (12) describes complex formation in solution:

$$\frac{1}{2}\beta_{IonSO_4} = \frac{C_{IonSO_4}}{C_{Ion}C_{SO_4}} \tag{12}$$

where β_{IonSO_4} is the complex formation constant. The complex formation constants depend on the temperature as well [$\beta = \beta(T)$]. The coefficient $\frac{1}{2}$ is introduced in Eq. (12) because the equivalent concentration scale is used. Equation (12) must be rewritten three times based on the three complex formation reactions present (see Eqs. 5–7).

The electroneutrality equation is included in the model:

$$C_{Cu^{2+}} + C_{Zn^{2+}} + C_{H^+} = C_{SO_4^{2-}} + C_{HSO_4^-} \tag{13}$$

The model uses the following initial conditions ($t = 0$):

$$C_{Ion}\big|_{t=0} = C^{init}_{Ion}; \qquad q_{Ion}\big|_{t=0} = q^*_{Ion}\big|_{t=0} \tag{14}$$

and boundary conditions ($l = 0$):

$$(C_{Me} + C_{MeSO_4})\big|_{l=0} = C^{bound}_{Me}; \qquad C_H\big|_{l=0} = C^{bound}_H \tag{15}$$

(the boundary conditions are the conditions at the inlet of the column). A different way to write the boundary conditions for metals and hydrogen ions was used because the compounds were analyzed by different techniques in the experiments.

The system of Eqs. (8)–(15) forms the nonlinear, nonequilibrium mathematical model. The model takes into account the main factors of the process considered. The influence of other factors (longitudinal diffusion in the solution, influence of local electrical fields, dependence of coefficients upon the concentration of the components) has been checked by appropriate models. The influence of longitudinal diffusion was tested by including the term $D_{\text{Ion}} \cdot \partial^2 C_{\text{Ion}}/\partial l^2$ in Eq. (8), where D_{Ion} is the longitudinal diffusion coefficient (cm^2/s). The extra boundary condition $\partial/\partial l\ C_{\text{Ion}}|_{l=1} = 0$ was included to give the free output of the solution from the end of the column. The test calculations were done by varying the D values. The improvement of the experimental data fit does not exceed the experimental error. The influence of the local electrical fields was tested by including the terms described earlier (13, 17). The influence of such terms on the experimental data fits was within $\pm 2\%$ (estimated by the mean square metric). Therefore, the influence of these factors is small in the conditions considered. The corresponding terms were not included in equations of the model. However, the excluded factors may be important under other sets of process regimes, even for similar physicochemical systems. For example, longitudinal diffusion must be taken into account for the case of a large rate of solution flow. If the diffusion coefficients for components in resin beads are essentially different, and variations in the concentration of the components are comparatively small, the effects caused by local electrical fields may be much stronger than the dynamics of complexes in solution (13). Hence, other cases can be reasonable described by a model including some equations different from the model described by Eqs. (8)–(15).

The numerical calculations were done by using an approximation of the Eqs. (8)–(15) by the implicit difference scheme with a first order of accuracy (14, 15). The system of equations obtained was solved by the Newtonian method.

Parameters of the Model

The driving force of the dual temperature separation process is the temperature dependence of the ion-exchange selectivity coefficients [$K = K(T)$] and complex formation constants [$\beta = \beta(T)$]. The separation was investigated at two temperatures: $T_1 = 75°\text{C}$ and $T_2 = 15°\text{C}$. The values of $\beta_{\text{IonSO}_4}|_{T=T_1,T_2}$ at the temperatures used were calculated by the standard way using reference data (16). The value of the volume exchange capacity Q was calculated as

$$Q = \frac{m_{\text{d.r.}} Q_{\text{r}}}{v} = 1.5\ \text{eq/L} \tag{16}$$

where v is the volume of the resin bed. The values of the ion-exchange

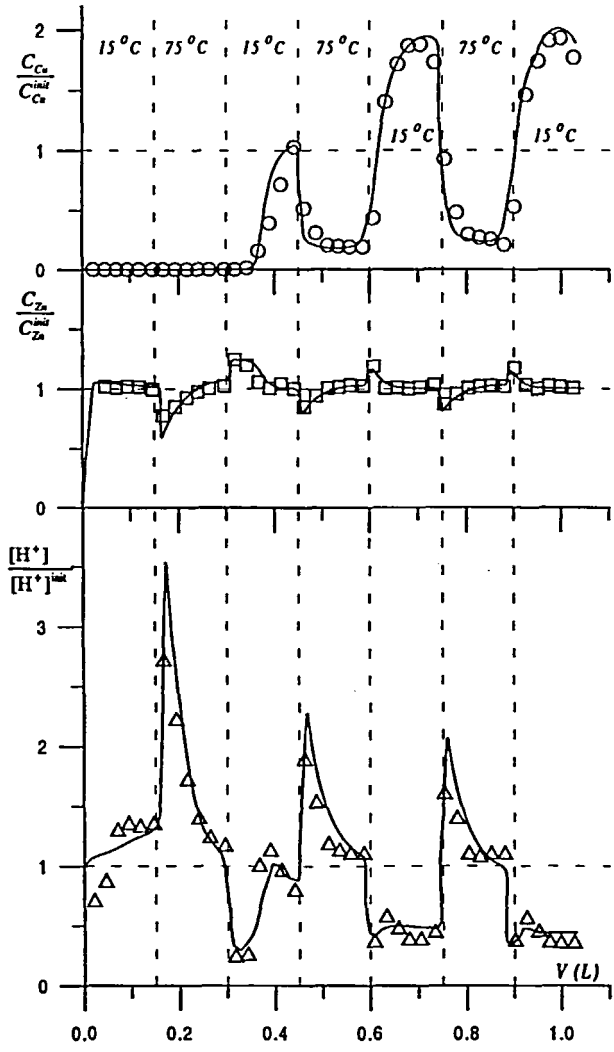


FIG. 3 Dependence of the ion concentrations in the effluent on the passed volume of the feed solution. The experimental and calculated curves for the separation process started from the H^+-form of the resin ($C_{Cu}^{init} = C_{Zn}^{init} = 0$). 150 mL of the feed solution is passed at each temperature ($C_{Cu}^{bound} = 0.024$ eq/L; $C_{Zn}^{bound} = 0.2$ eq/L; $C_{H}^{bound} = 0.022$ eq/L). The dashed lines accord to the moments of temperature change.

TABLE 1
Experimental Parameters Used for the Calculations

Ion	C^{bound} (eq/L)	C^{init} (eq/L)	K_H^{Me} 15°C	K_H^{Me} 75°C	β_{IonSO_4} 15°C	β_{IonSO_4} 75°C	k (min^{-1})
Cu^{2+}	0.024	0	0.16	0.73	203	415	0.02
Zn^{2+}	0.20	0	0.017	0.060	201	335	0.08
H^+	0.022	0.022	1	1	72	451	0.04

selectivity coefficients $K_H^{Me}|_{T=T_1,T_2}$ were recalculated from data published earlier (9).

The model calculations were compared with experimental data set to adjust the K_H^{Me} values (within ±15%) and to determine the k_{Ion} values. The experiment was run using a feed solution of the following composition: analytical concentration of copper = 774 mg/L; analytical concentration of zinc = 6600 mg/L; pH 1.72. One hundred fifty milliliters of the effluent was collected at each half-cycle. It is equivalent to 5 hours per half-cycle at a flow rate of 0.5 mL/min. The initial H^+-form of the resin was chosen. Figure 3 shows good agreement between the calculations and the experiment. The parameters used for these calculations are collected in Table 1. The parameters K, β, and k shown in Table 1 were unchanged in all the following calculations. Note that any stable double temperature cycle is totally independent on the initial ionic form used. Therefore the initial conditions influence only the first 2–7 half-cycles which precede stabilization of the cyclic process. However, agreement between the experimental data and the model for the initial cycles is essential to prove the validity of the model.

Examination of the Model

We made calculations for another separation experiment to examine the model. In contrast to the previous experiment, the resin was equilibrated with the feed solution at 75°C before the experiment was started, i.e. $C_{Cu}^{init} = 0.024$ eq/L; $C_{Zn}^{init} = 0.2$ eq/L. Two hundred twenty-five milliliters of the effluent was collected at each half-cycle. A similar feed solution as in the previous experiment was used except for a slightly different pH. The analytical concentration of copper = 750 mg/L; the analytical concentration of zinc = 6600 mg/L; pH 1.78. The good fit of the experimental results with the calculation (Fig. 4) testifies to the agreement of the model with the physicochemical process.

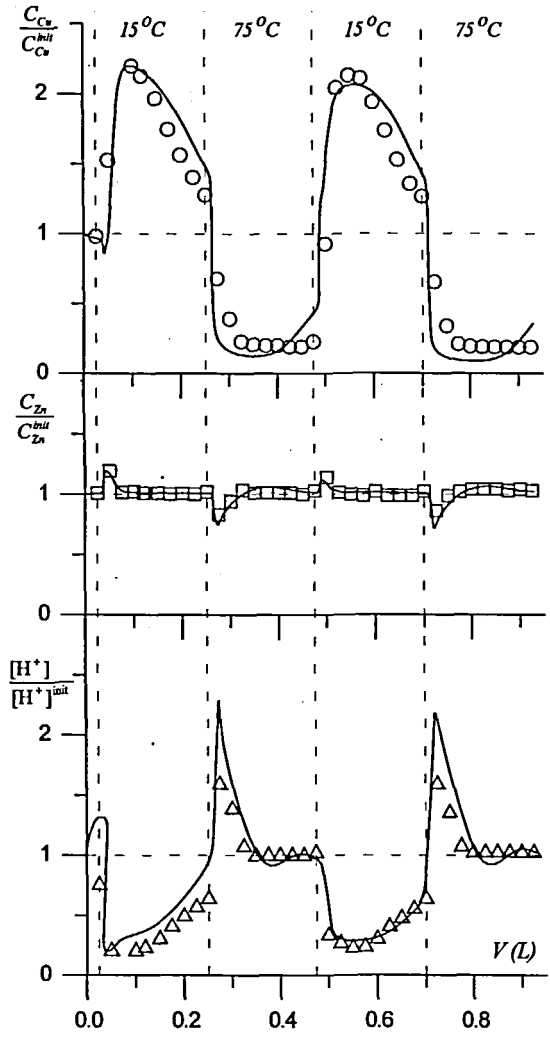


FIG. 4 Dependence of the ion concentrations in the effluent on the passed volume of the feed solution. The experimental and calculated curves for the separation process started from the resin equilibrated with the feed solution at 75°C ($C_{Ion}^{init} = C_{Ion}^{bound}$). 225 mL of the feed solution is passed at each temperature ($C_{Cu}^{bound} = 0.024$ eq/L; $C_{Zn}^{bound} = 0.2$ eq/L $C_{H}^{bound} = 0.022$ eq/L).

USING THE MODEL TO PREDICT THE SEPARATION RESULTS

Modeling of the Mine Effluent Treatment

The treatment of mine effluents is an example of a practical probler which can be solved by the dual temperature method. Copper and zinc are the main hazardous contaminants contained in such wastes. The separation of these two metals is important in their recycling procedure. Typical concentrations of Cu and Zn in these solutions are approximately 5 times as diluted compared with the examples calculated above. The analytical concentrations of the metals chosen for the calculations were 155 mg/L Cu and 1320 mg/L Zn; pH 2.05 (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.04 eq/L; C_{H}^{bound} = 0.011 eq/L). Experimental testing of the separation process is inconvenient because of the high volumes of the solution treated and the long duration of the process. The aim of this model calculation was to find the optimal separation cycle parameters. The dependence of the separation efficiency on the fraction volumes was tested. The characteristics of the separation efficiency were introduced earlier (10). We use four of them in the present calculation. The maximal concentrating factor (Φ_{max}) was calculated according to

$$\Phi_{max} = C_{Cu}^{max}/C_{Cu}^{bound} \tag{17}$$

The gross concentrating factor of copper ($\overline{\Phi}$) was calculated as follows:

$$\overline{\Phi} = \overline{C}_{Cu}C_{Cu}^{bound} \tag{18}$$

The average concentration of metal ($\overline{C}_{Me}$) in Eq. (18) was calculated by

$$\overline{C}_{me} = \frac{1}{V_T}\int_{V_T} C_{Me}dV \tag{19}$$

where V_T is the volume of solution passed at one temperature (half-cycle). T = 15°C for calculating $\overline{\Phi}$. The gross purification factor ($\overline{P}$) and the maximal purification factor (P_{max}) of zinc were calculated as follows:

$$\overline{P} = \frac{(\overline{C}_{Cu} + \overline{C}_{Zn})}{\overline{C}_{Cu}} \frac{C_{Cu}^{bound}}{C_{Cu}^{bound} + C_{Zn}^{bound}} \tag{20}$$

$$P_{max} = \left\{\frac{(C_{Cu} + C_{Zn})}{C_{Cu}}\right\}_{max} \frac{C_{Cu}^{bound}}{C_{Cu}^{bound} + C_{Zn}^{bound}} \tag{21}$$

The separation cycle including equivalent half-cycle volumes was tested first. Results of the modeling are shown in Fig. 5.

Comparison of the data obtained and results of the experimental study of the separation of more concentrated solutions (10) shows that the ion exchan-

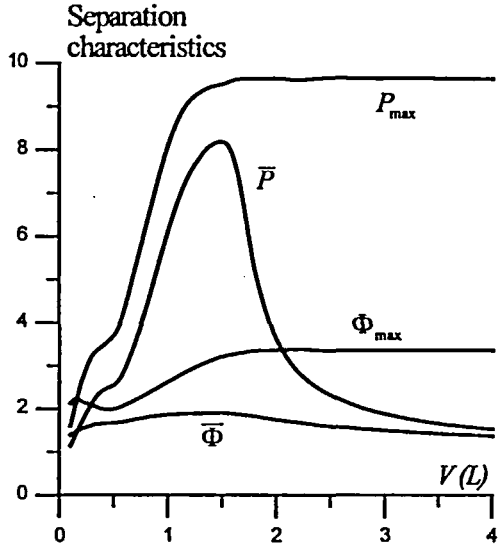


FIG. 5 Dependence of the separation efficiency parameters on the half-cycles volume in the case of equivalent volumes of both half-cycles (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.04 eq/L; C_{H}^{bound} = 0.02 eq/L).

ger works more efficiently in solutions of lower concentration. The separation characteristics are improved with decreasing treated solution concentration. Also, better use of the ion exchanger can be illustrated by the higher total amount of ions passed through the same column in the optimal separation cycle. The existence of two following processes explains this.

The proportional decrease of the concentrations of all compounds in the treated solution leads to an increased quota of bivalent ions sorbed at equilibrium (T = 75°C) and, therefore, to an increase of the amount of copper desorbed at 15°C.

The system with a low concentration of components is characterised by a lower speed of ion exchange. Hence, a higher volume of the solution passed is required to attain equilibrium.

The sum of these two factors is the reason why a reduction of the feed solution concentration leads to an increase in the separation efficiency. It also leads to a shift of the $\overline{\Phi}$ and $\overline{P}$ optimum positions (see Fig. 5) toward the highest V.

The optimal separation cycle selected (see Fig. 5) is shown in Fig. 6. Volumes of 1500 mL are passed at each half-cycle. It seems quite clear that Cu

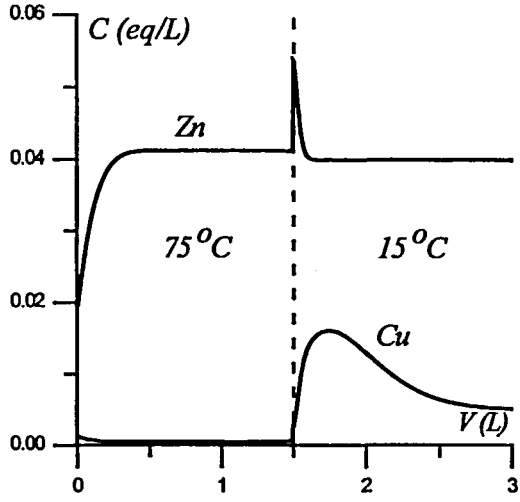


FIG. 6 Calculated dependence of the ion concentrations in the effluent on the passed volume of the feed solution. The separation cycle contains two 1500 mL half-cycles (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.04 eq/L; C_{H}^{bound} = 0.02 eq/L).

is sorbed by the resin during the all 75°C half-cycle. However, the efficient part of the 15°C half-cycle is shorter, so an appropriate reduction of the 15°C half-cycle length is reasonable. Hence, volumes of 1500 mL at 75°C and 1300 mL at 15°C should be passed during one separation cycle.

Three effluent fractions should be collected in the real technological process. One of them contains the solution decontaminated of copper. The second one contains the concentrated Cu solution. The third is obtained by mixing of the effluent produced at the beginning and at the end of each half-cycle. This fraction is recycled into the same column. The concentrations of all ions in the mixed fraction must be equivalent to the ions concentration in the feed solution to prevent destabilizing the separation cycle. Figure 7 illustrates the fractions collecting in the separation cycle described above. Therefore, the ion-exchange column containing 4 g of the ion-exchange resin Amberlite IRC-718 can process 2800 mL of the treated solution during one separation cycle. The following solutions are produced: 1017 mL of the decontaminated solution containing a 9 times reduced concentration of copper; 481 mL of the concentrate containing 456 mg/L of Cu ($\overline{\Phi}$ = 2.9).

Modeling of the Double-Step Separation

The double-step dual temperature separation process aimed at the purification of zinc was modeled. The solution under treatment was the same as that

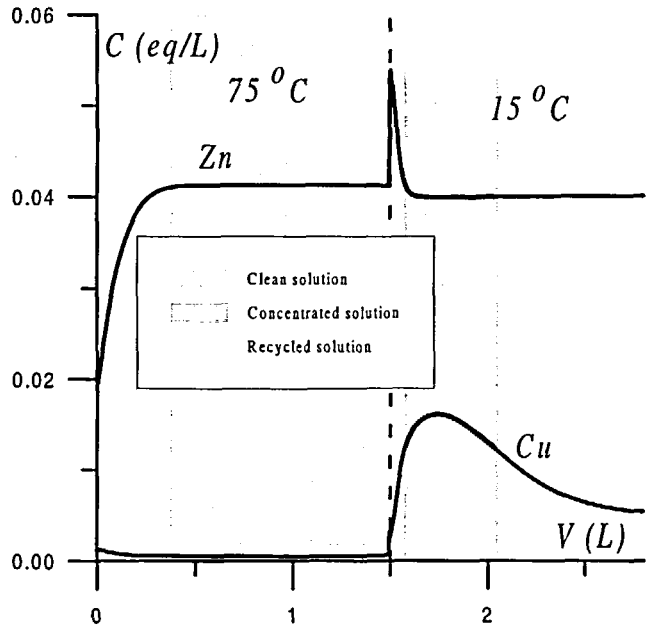


FIG. 7 Calculated dependence of the ion concentrations in the effluent on the passed volume of the feed solution. The separation cycle contains the following half-cycles: 1500 mL of the feed solution is passed at 75°C; 1300 mL of the solution is passed at 15°C (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.04 eq/L; C_{H}^{bound} = 0.02 eq/L).

used earlier (Table 1). The first step of the separation is identical to that described above for the chosen solution. This step produces a solution containing about a 5 times less concentration of copper compared to the treated solution (see Fig. 4). The analytical concentration of copper after the first step is 157 mg/L; the analytical concentration of zinc is 6330 mg/L; pH 1.66. The modeling was applied for the second step of the separation. The following boundary conditions were used: C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.19 eq/L; C_{H}^{bound} = 0.026 eq/L.

The dependence of the separation efficiency characteristics (see Eqs. 17–21) on the volume of solution passed during each half-cycle is shown in Fig. 8. The copper content in the sorbent bed at equilibrium is comparatively less than in the previous example. However, the higher concentration of H^+-ion forces regeneration to intensity. This phenomenon results in a higher maximal concentrating of copper in the regeneration half-cycle. The $\Phi_{max} = \Phi_{max}(V_T)$ curve achieves saturation at a higher V_T value compared to the

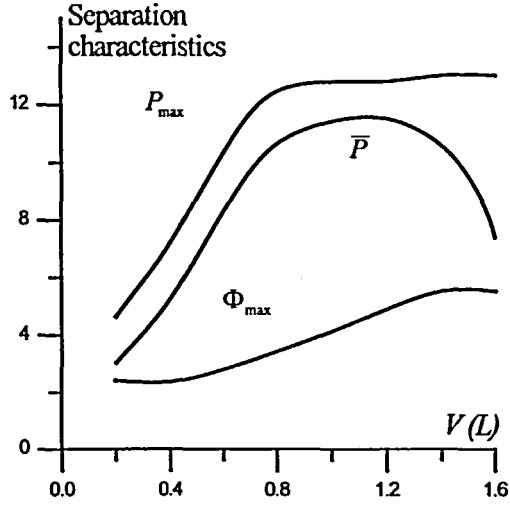


FIG. 8 Dependence of the separation efficiency parameters on the half-cycles volume in the second step of the double-step separation process. The half-cycles have equivalent volumes (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.19 eq/L; C_{H}^{bound} = 0.026 eq/L).

case shown in Fig. 5 because the desorption of copper does not start at the moment when the temperature changes from 75 to 15°C. Cu desorption takes place only after the greater part of zinc has been desorbed (Fig. 9). The total efficiency of the double-step purification process can be estimated by replacing the boundary ion concentrations in Eqs. (20) and (21) by the ion concentrations in the treated solution. The values obtained are $\overline{P}^{total}$ = 48 and P_{max}^{total} = 54.

Dependence of the Separation Efficiency on the Solution Flow Rate

The dependence of separation efficiency on the treated solution flow rate (F) can be examined by the proposed model. The Φ_{max} characteristic was chosen to illustrate the flow rate influence. Figure 10 shows the dependence of Φ_{max} on $\Phi_{max}(F)$ for different volumes of solution passed at each temperature (V_T). The feed solution composition was the same as that used earlier (Table 1). The maximal copper concentrating factor increases as the flow rate decreases because a flow reduction leads to sharpening of the desorption peak. The growth of Φ_{max} with increasing V_T was explained earlier when Fig. 5 was considered.

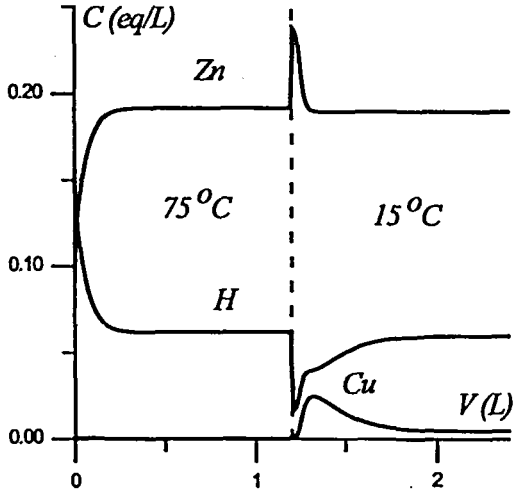


FIG. 9 Calculated dependence of the ion concentrations in the effluent on the passed volume of the treated solution in the second step of the double-step separation. The cycle contains two 1200 mL half-cycles (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.19 eq/L; C_{H}^{bound} = 0.026 eq/L).

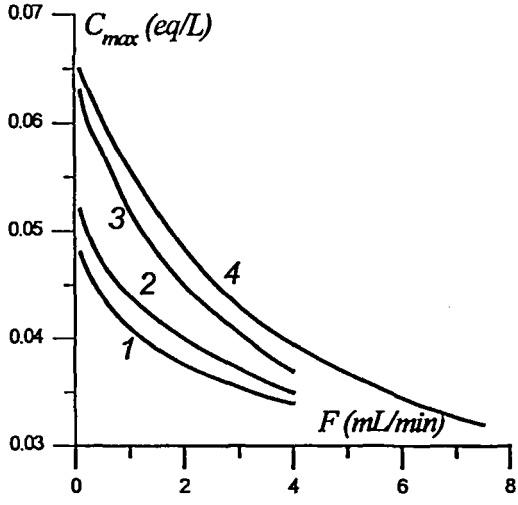


FIG. 10 Calculated dependence of the copper concentration on the flow rate for different volumes of the treated solution passed at each half-cycle: 1: V_T = 100 mL, 2: V_T = 200 mL, 3: V_T = 400 mL, 4: V_T = 600 mL (C_{Cu}^{bound} = 0.005 eq/L; C_{Zn}^{bound} = 0.04 eq/L; C_{H}^{bound} = 0.004 eq/L).

TABLE 2
Experimental Parameters Used for the Calculations at the Narrow Temperature Difference

Ion	C^{bound} (eq/L)	K_H^{Me} 30°C	K_H^{Me} 60°C	β_{IonSO_4} 30°C	β_{IonSO_4} 60°C
Cu^{2+}	0.024	0.23	0.53	243	347
Zn^{2+}	0.2	0.024	0.046	228	294
H^+	0.022	1	1	114	285

Affecting the Separation by Reduction of the Temperature Difference

Separation under a relatively narrow temperature difference was modeled. According to data published earlier (9), an assumption of the linear temperature dependence $\ln K_H^{Me} = f(1/T)$ may be considered. The following temperatures were chosen: $T_1 = 60°C$, $T_2 = 30°C$. The parameters of this process are shown in Table 2.

The model calculation for $V_T = 225$ mL shows that twice the reduction of the temperature difference forces a 1.7 times reduction of Φ_{max}($\Phi_{max} = 1.3$, in contrast to 2.2 obtained for a wider temperature interval). This agrees to the approximately linear dependence of the separation efficiency on the temperature difference.

CONCLUSIONS

The dynamics of ion exchange in the system Cu^{2+}–Zn^{2+}–H^+ (SO_4^{2-})–Amberlite IRC-718 can be successfully described by the model considered (see Eqs. 8–15). The model must take into account the following physicochemical processes: kinetics, ion-exchange reactions, formation of complexes in solution. Other factors (for the physicochemical system considered) do not affect the process sufficiently to be included in the model.

The model allows quantitative evaluations of the separation process to be made and the dependence of the separation efficiency on the working conditions to be predicted. It is also helpful for a qualitative explanation of the experimental results.

The evaluations performed show the efficiency of the process under changing conditions from laboratory testing to real separation needs (diluted solutions).

SYMBOLS

C	concentration in solution (eq/L)
D_{Ion}	longitudinal diffusion coefficient (cm^2/s)
e	porosity of the sorbent bed
F	solution flow rate (cm/min)
K_{H}^{Me}	the ion-exchange selectivity coefficient for replacing hydrogen by the metal Me
k	kinetic coefficient (min^{-1})
L	the length of the ion-exchange column (cm)
l	longitudinal coordinate along the ion-exchange column (cm)
Me	metal (Cu or Zn)
$m_{\text{d.r.}}$	weight of dry resin (g)
$\overline{P}$	gross purification factor of zinc
$P_{\max}$	maximal purification factor of zinc
Q	total volume ion-exchange capacity of the resin bed (eq/L of resin bed)
Q_{r}	ion-exchange capacity of the resin (meq/g of dry resin)
q_{Ion}	ion content in the resin bed (eq/L of resin bed)
q^*_{Ion}	equilibrium content of ion in the resin bed (eq/L of resin bed)
R	the resin matrix
T	temperature (°C)
T_1	temperature of the first (sorption) half-cycle (°C)
T_2	temperature of the second (regeneration) half-cycle (°C)
t	time (min)
V	volume of solution (mL)
V_{T}	volume of solution passed at temperature T (in one half-cycle) (mL)
v	volume of the resin bed (mL)

Greek

β_{IonSO_4}	constant of the complex formation in solution
$\overline{\Phi}$	gross concentrating factor of copper
$\Phi_{\max}$	maximal concentrating factor of copper

Superscript and Subscripts

bound	notation showing the point of entry of the ion-exchange column ($l = 0$)
init	notation showing the initial moment of the process ($t = 0$)
Ion	any cation: metal (Cu^{2+} or Zn^{2+}) or hydrogen (H^+) ion

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