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Hydrometallurgy Wastewater Split-Up by Fluidized-Bed Ion-Exchange Continuous Equipment

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ABSTRACT

A proposed operation of a semicontinuous fluidized-bed ion-exchange system was studied. The system splits a liquid current into two currents, one being more concentrated and the other more depleted. This operating technique has been used to split up a mixture of alkaline ions (Na^+, K^+) using a strongly acidic resin. The equipment operates simultaneously in two multistage columns, one for loading and the other for elution of the resin. The experimetal testing system employs a hydrometallurgy wastewater containing cobalt and copper as heavy metallic ions, and the resin used was of the chelating iminodiacetic type, Lewatit TP-207. At cyclic steady state, the equipment can split up the wastewater, producing an effluent concentrated in cobalt in the outlet stream of the loading column, and a concentrated stream of copper in the effluent of the elution column. The hydrodynamics and approach to the stationary state of the system were analyzed, and the selective recovery of metals was subsequently tested experimentally. This behavior presents certain similarities with a parametric pumping operation of the system, with the two columns operating at different pH values or temperatures.

Key Words. Ion exchange; Fluidized bed; Hydrometallurgy wastewater; Split-up; Iminodiacetic resin

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INTRODUCTION

Ion-exchange operations have traditionally been carried out in fixed-bed equipment for softening water. Since this initial use, the field of application of ion exchange has grown considerably. Nowadays, fluidized-bed ion-exchange operations have been developed specially for the treatment of solutions with suspended solids (1) as is the case of hydrometallurgic industry wastewaters. In these cases, fixed-bed columns cannot be used because the columns may become clogged.

Initially, a number of designs of continuous or semicontinuous systems were developed to soften water using fixed beds (2–5). Later on, the utilization of a fluidized bed (6–9) as the phase contact mode meant that these systems could be used in the treatment of dirty solutions (1). Some fluidized-bed systems have been used for the recovery of uranium in the nuclear and hydrometallurgy industries (10–12). The principal advantage of fluidized-bed systems in relation to fixed-bed systems is a better mass transfer between the solid and liquid phases because of better contact between these phases.

One of the biggest problems in ion-exchange operations is the utilization of the regeneration solutions, since frequently these solutions cannot be reused, thus making this technique environmentally unfriendly. If a heavy metal is retained in the column, the regeneration is carried out using acids, hence contamination of the metal may be avoided, but the problem caused by the acid solution remains. The use of operations such as parametric pumping, which by means of a cyclic operation does not produce this wastewater stream, is an interesting proposal. In parametric pumping the retention of an ion in a resin, due to the effect of different temperatures or the ionic strength, is used to separate selectively two or more ions without using an elution current. Parametric pumping is more useful when the equilibrium lines at different temperatures or pH are more widely separated. However, operation with only one column means that too many cycles are necessary to obtain good separation. A system using the principles of parametric pumping presents some analogies to the process operation presented in this paper. This includes equipment with two columns, one for loading and the other one for elution. A resin presenting a different selectivity to two metallic ions, such as Co^{2+} and Cu^{2+}, of the chelating iminodiacetic type (Lewatit TP-207), can be adapted to separate eachion in the load and the regeneration solutions, respectively. A similar technique has been used in a full-scale operation in South Africa (13, 14), with columns up scale, with a column with four stages and a volume of 10 cm^3 in each stage, to separate sodium and potassium chlorides from a mixture using a strongly acidic sulfonated polyestyrene resin, Zeo-Kard 225.

In this work the split-up of a current composed of a mixture of cobalt and copper using a fluidized-bed system with two columns is carried out. In this way cobalt may be obtained in the load effluent and copper in the eluent effluent. This makes the two effluent streams useful for recycling to different processes of a hydrometallurgic industrial process. The proposed equipment can operate in two operation modes: elution and division. Only the elution operation mode has been tested experimentally to date, although hypothetical results are proposed for both operation modes.

EXPERIMENTAL METHODS

Equipment

A semicontinuous ion-exchange system was designed and constructed with the aim of splitting up an industrial wastewater. The system consists of two multistage fluidized-bed columns. Saturation is carried out in one column and elution is carried out in the other. Figure 1 shows a simplified scheme of the equipment. Each column (A and B) is divided into four stages. Each stage is separated by punched plates. C represents tubes for transferring the

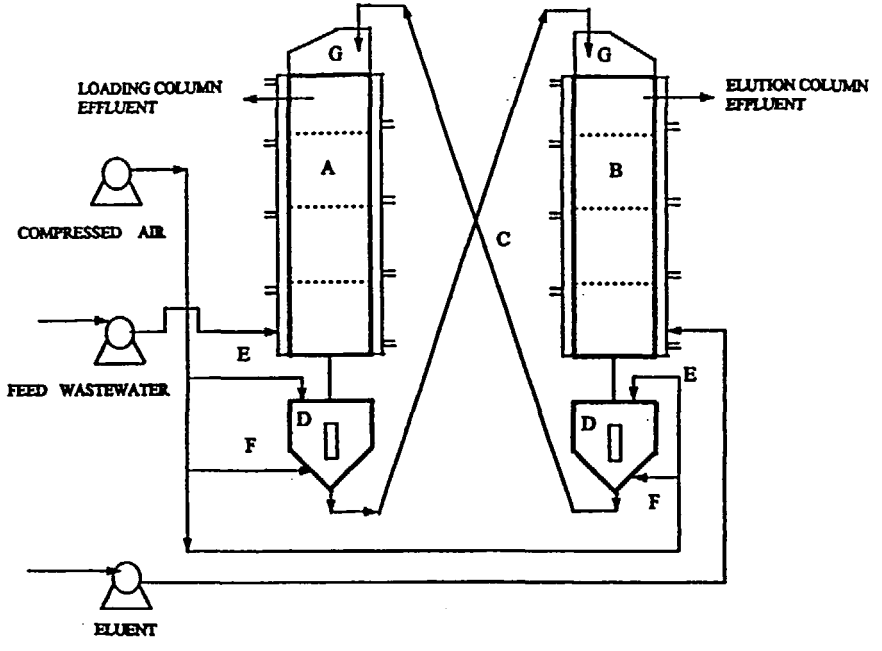

FIG. 1 Simplified scheme of the continuous countercurrent ion-exchange system.

resin from one column to the other, and D are two tanks for collecting the resin before it is transferred to the other column by compressed air introduced into the tanks at points E and F. At the top of the columns, there are two tanks (G) which separate the resin from the liquid dragged by the air. Two valves, placed between the bottom of the columns and tanks D, control the discharge of each stage; when the valves are opened, the resin and liquid in the first stage fall into the tanks, and the resin in the rest of the stages falls into the stage below it. The equipment has an automatic control system PLC (programmable logic controller), and the functioning of each step is controlled by a program.

The columns are constructed of a transparent methacrylate material. The parts subject to high stresses and high pressures are made of steel, as are the tanks. Each stage in the column is 1 m high and 0.1 m in diameter, with a capacity of 7.85 L. The capacity of the bottom tanks is 8 L each.

Solutions

The wastewater introduced in the loading column of the equipment was a mixture of cobalt and copper chlorides, in concentrations of 35 and 33 mg/L (6×10^{-4} M) of each metal, respectively, with 20 g/L of NaCl to adjust the salinity. The eluent solution was 3% HCl with 20 g/L of NaCl to maintain the same salinity as in the loading column. The flow rate was 110 L/h in all the experiments carried out in both columns.

The analyses for cobalt and copper ions was carried out by atomic absorption using a Philips PU-9100 spectrophotometer, with wavelengths of 240.7 nm for cobalt and 324.8 nm for copper.

Resin

The principal characteristics of the resin Lewatit TP-207 are summarized in Table 1. This resin presents good physical and chemical properties for its

TABLE 1
Characteristics of Lewatit TP-207

Ionic form supplied	Na
Matrix	Polystyrene
Ionogenic groups	Iminodiacetic
Size (mm)	0.3–1.25
Apparent density (kg/m^3)	700–800
Humidity (% weight)	45–50
Color	Beige clear
Total capacity (mol/L in H form)	2.7
Thermal stability (°C)	−20 to 80
pH stability	1–14

use in the equipment. The liquid flow rate was 110 L/h in all experiments. This flow rate is adequate for maintain the resin as a fluid without it being dragged into the columns. The "equivalent" resin flow rate was 40 L/h in the third step of the operation. The designed interstage separators mean the volume of resin in each stage will be no higher than 5 L. This volume of resin is exactly that needed to make the resin fall completely from an upper stage to the stage below. The height of the fluidized resin in the column is 0.75 m, which is $\frac{3}{4}$ of the total volume of the stage. The porosity of the fluidized bed is 0.6

EQUIPMENT OPERATION CHARACTERISTICS

The equipment and operation proposed here includes several interesting features.

Continuous operating mode, so that load and elution are carried out simultaneously
A fluidized bed as the phase contact mode. This operation mode improves mass transfer between the liquid and solid phases
Countercurrent mode phase flow, which improves the efficiency and several steps in both the load and regeneration columns

We shall now discuss two operation modes, and subsequently the main operational problems.

Operation Modes

Elution Operation Mode

In the elution mode, presented in Fig. 2 saturation takes place in one column and elution with hydrochloric acid in the other. The resin is transferred from one column to the other; the operation is similar to two fixed-bed columns, one in saturation and the other in regeneration for a time, with the function of each column changing at the end of the operation cycle. The elution operation mode takes place in three steps. These three steps are consecutive; at the end of the third step when all the resin in the tanks has been transferred, the first step begins again.

1. In the first step, load and elution solutions are introduced into the columns from the bottom and cross the interstage separators, thus fluidizing the resin particles inside them. Load and regeneration are carried out at the same time. The flow rate must be sufficient to maintain the resin without dragging. When the resin inside the load and regeneration columns is saturated or regenerated, feed is cut off, and the two valves under the

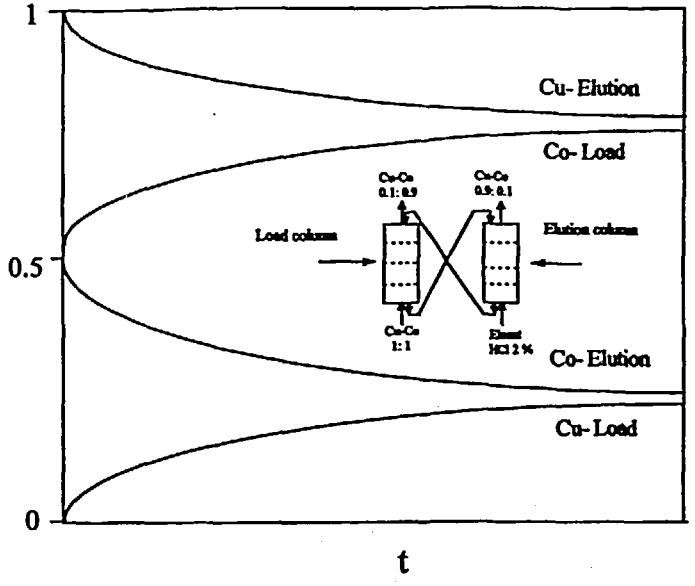

FIG. 2 Qualitative scheme of the elution operation mode of the equipment.

columns are opened. This step requires knowledge of the capacity of the resin so the time of the cycle can be adjusted.

2. In the second step, the resin of each stage falls to the stage below. That of the first stage is re-collected in the tanks under the columns. The time must be adjusted to allow for the fall of all the resin from one stage to the stage below or to the tanks.
3. Later, the resin in each tank is transferred to the opposite one by pneumatic transport in such a way that the regenerated resin begins to be saturated and the saturated one begins to be eluted.

It can be observed in Fig. 2 that in a hypothetical operation of the system under certain conditions, the effluent of the loading column is where cobalt is concentrated and the effluent of the elution column is where copper is concentrated. Thus, about 90% of the cobalt may be recovered with the loading effluent, the rest remains in the elution effluent. The opposite happens with copper, so 90% of the copper may be recovered with the elution effluent and 10% remains in the loading effluent.

Division Operation Mode

This consists of introducing the wastewater at different pH levels into each column in such a way that the effluent of the column at high pH is diluted

with respect to the initial wastewater and is more concentrated in the ion which is retained less by the resin, while the effluent of the other column (at low pH) is more concentrated with respect to the initial wastewater, and more concentrated in the ion which is retained more by the resin. The steps involving falling and transfer of the resin are similar to the elution operation mode.

A qualitative scheme of the hypothetical results that we hope will be obtained in the division operation mode of the equipment is shown in Fig. 3. With this operation mode the effluent of the elution column (in this case the column at low pH) is more concentrated than the initial solution, especially for copper. In the saturation column outer flow (at high pH), the cobalt concentration is nearly the same as in the initial solution because cobalt is retained less than copper. Copper is highly retained in the column, so good separation of cobalt and copper may be achieved.

Operational Problems

The main problems found in the designed operation of these systems are related to the movements of solids. Initially, compressed air was introduced

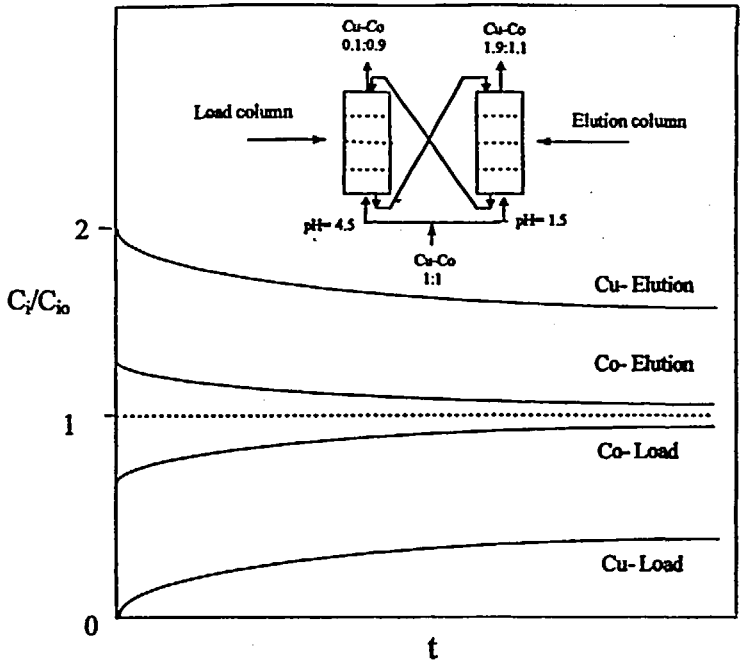

FIG. 3 Qualitative scheme of the division operation mode of the equipment.

only at point E, but this meant the resin remained compacted at the bottom of the tank. The problem was solved by introducing compressed air simultaneously at points F and E. Also, during the fall of the resin it is under different conditions at the top and at the bottom of the column. For Lewatit TP-207, the difference between the volume when it is loaded with a metal and regenerated with acid is 25%; this produces great differences between the volume of the resin at the top and at the bottom of the columns.

Another fact is that the pressure supported by the resin is higher in the first stage than in the fourth stage. If the free area for the resin to fall through in the plates is the same in all stages, there will be problems of retention of the resin in the higher stages, and the lower stages may be empty. One solution to this problem was to modify the number of holes in each interstage separator; after some preliminary experiments the number of holes used for each stage was 11 in the first stage, 16 in the second, 25 in the third, and 37 in the fourth.

Holes with different were used in each column to avoid the problem of the change of volume of the resin when it is charged or regenerated: the diameter used were 5 mm in the loading column and 3 mm in the regeneration column. With these modifications the equipment ran adequately, achieving steady state.

Another problem associated with the operation mode can be resin particle damage to valves due to attrition. To avoid this problem, the resin used in this equipment must have good physical and chemical resistance, and Lewatit TP-207 does.

SYSTEM OPERATION FOR SPLITTING-UP A Cu–Co MIXTURE

Once the mechanical functioning of the system was found to be satisfactory, the possibility of selective metal recovery in the previously designed semicontinuous ion-exchange equipment was analyzed. In this paper, experiments were carried out using the elution operation mode. The results are useful for verifying the theoretical analysis presented above.

The amount of time for each step depends on the experimental conditions, the saturation time depends on the solution concentrations, the falling time depends on the volume of resin in each stage, and the transfer time must be the minimum needed to achieve complete transport of the resin from the tanks to the opposite column. Under the experimental conditions used in this work, the operation time (loading and elution simultaneously) was 5 minutes, the falling step of the resin was 8 seconds, and the resin transfer step was 3 minutes. These times were the choices after several preliminary experimental tests: time for operation was calculated knowing the resin capacity (2.7 eq/L

resin), the concentration of copper and cobalt in the solutions, and the volume of resin in each stage in such a way that the resin capacity was reached. Time for falling step was that just necessary to allow all the resin in a stage to fall in to the stage below, and finally the time for resin transfer was the time needed for the equipment to transfer all the resin in the bottom tanks to the top of the other column. For another ionic system or resin, it would be necessary to carry out the previously mentioned tests to obtain an adequate time for each step.

Stationary State Running

An important fact, once the equipment starts to function, is to know how many cycles are needed to achieve a steady state. Experiments were carried out using a solution of cobalt and copper in the same concentrations as the industrial wastewater. The concentration of the solution was indicated in the Experimental Section: 6×10^{-4} M for each metallic ion and 0.34 M in NaCl. Several samples were analyzed in each cycle at each stage. The measurements were carried out at the mid-point of the cycle. Figure 4 shows the approach to the stationary state for the loading of cobalt and copper in the first stage of the loading column. The copper concentration remains nearly constant and the cobalt concentration grows until it reachs 90% of the initial concentration,

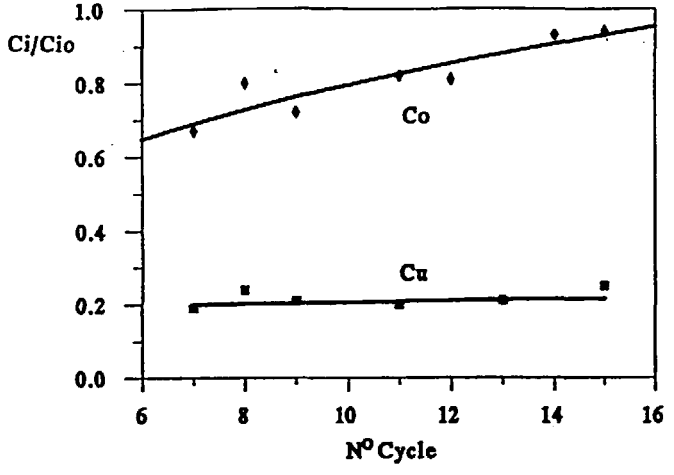

FIG. 4 Approaching the stationary state in the running of the load column in the continuous fluidized-bed equipment.

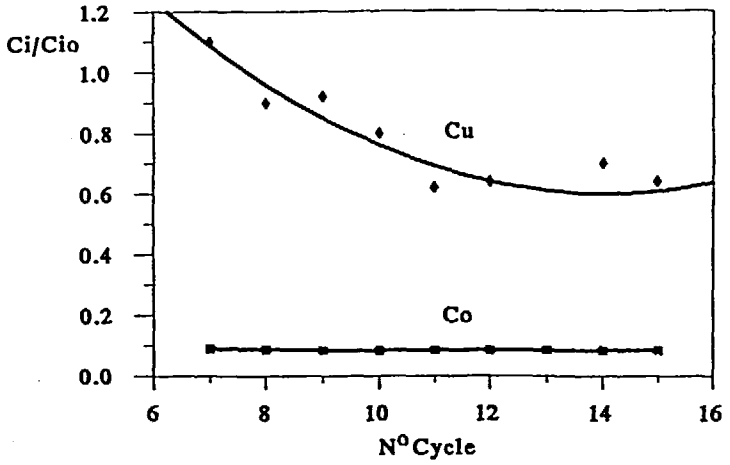

FIG. 5 Approaching the stationary state in the running of the elution column in the continuous fluidized-bed equipment.

i.e., 5.4×10^{-4} M. Figure 5 shows the approach to the stationary state for the second stage of the elution column. In this figure the copper concentration remains constant after Cycle 11 and the cobalt concentration is constant throughout the experiment, as in this stage the cobalt concentration in the resin is very low. It can be seen in these figures that 15 cycles are the minimum needed to achieve a stationary running state of the system. This high number of cycles is needed in order to reach the stationary state due to the complex operation of the system with the liquid and resin flowing continuously.

Experimental Results at Stationary State

Load/elution runs were carried out in the equipment with a mixture of cobalt and copper salts. To carry out the assays, the system ran for 15 cycles before reaching the stationary state; then samples were taken at minute intervals in order to analyze the outlet solution in each stage and to determine the breakthrough curves. Figure 6 shows the results obtained in Stages 1 to 3 for the loading column. It can be observed in this figure that the best separation between Co and Cu is reached in the third stage, while in the first stage the separation is lower. At the end of the cycle the concentration of cobalt in the outlet current is nearly the same as in the initial wastewater. Copper is retained by the resin in the column so the concentration of Cu in the outlet stream is only 10% of the total concentration in the initial wastewater. Figure 7 shows the results for the elution column at the same time. The effluent of the two

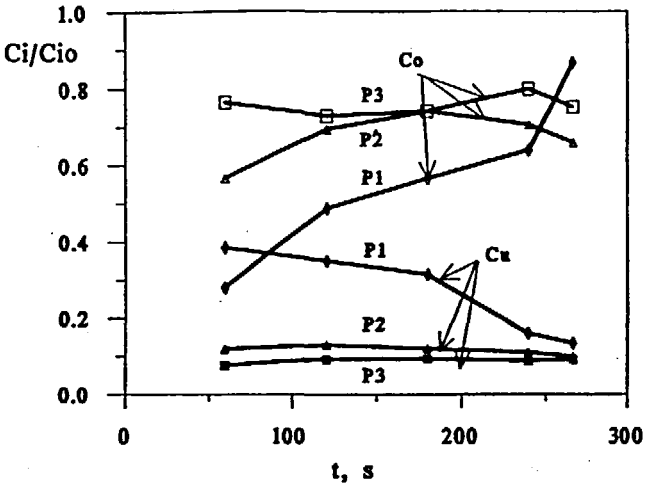

FIG. 6 Experimental results in the load column at stationary state running in the split-up of a 1:1 mixture of Co–Cu hydrometallurgy wastewater.

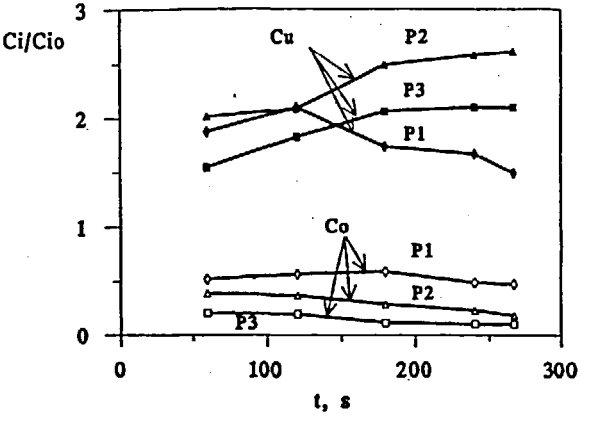

FIG. 7 Experimental results in the elution column at stationary state running in the split-up of a 1:1 mixture of Co–Cu hydrometallurgy wastewater.

columns is collected in tanks during all the operation time (first step) in order to determine the average concentration of copper and cobalt in the oulet of the two columns and verify the general mass balance in the system. The results of the fourth stage are not represented in Figs. 6 and 7 because in these stages there is a mixture of the solution and the resin transferred in the third step of the operation of the system, and therefore the results are nto representative. It is more accurate to determine the average concentration in the operation cycle. In the loading column the concentration of copper and cobalt introduced was 6×10^{-4} M for each ion; at the oulet the average concentration was 4.8×10^{-5} M for the copper and 4.75×10^{-4} M for the cobalt. In the elution column the initial concentrations are zero because only HCl is introduced in the bottom of this column; at the oulet the average copper concentration was 5.5×10^{-4} M and for cobalt 1.15×10^{-4} M. These results mean that 80% of the initial cobalt and 8% of the initial copper are obtained in the loading column effluent. The remaining 20% of cobalt and 92% of copper are obtained in the elution column effluent.

In the elution column the results are the opposite of those of the saturation column. During elution the resin is regenerated by the acid and the retained copper is exchanged. The concentration of the copper in the oulet regeneration current is twice that of the initial wastewater. For cobalt the concentration in the outlet current is very low compared to the initial concentration. At the end of the saturation cycle the resin is saturated with copper while the cobalt is not retained because it leaves the saturation column in the outlet stream. In the elution column the copper is eluted when the resin is regenerated with the acid and the copper is recovered in the outlet stream of this column. The two ions are thus separated.

The experimental results show greater selectivity of the resin for copper than for cobalt, and this allows good separation of the two metals. Previous published works (15–17) have shown the equilibrium parameters obtained in batch laboratory experiments for these ions using the Lewatit TP-207 resin. These results confirm the theoretical results presented above and have been used for modeling the column results.

MODELING OF THE SYSTEM

The operation of one stage in a cycle can be simulated by using a model that takes into account the hydrodynamics of the system. The hydrodynamic characteristics of the equipment were determined experimentally.

Hydrodynamics

Studies were carried out in the column based on RTD analysis (18, 19). A pulse of tracer ($LiNO_3$ of 63.6 g of Li/L) was injected into the first stage

of one of the columns, and the outlet stream tracer concentration was measured at the end of the first and second stages by monitoring the tracer concentration with time at the outlet of the two stages. In order to predict the column behavior, a nonideal flow model, such as the tanks-in-series model, was applied (18, 20). Statistical parameters such as variance and average time can be calculated with the experimental points. The number of tanks is obtained from

$$N = \bar{t}^2/\sigma^2 \tag{1}$$

where $\bar{t}^2$ is the average time of the response curve and σ^2 is the variance. Conversely, the response curve is calculated by using

$$E = \frac{1}{\bar{t}_i}\left|\frac{t}{\bar{t}_i}\right|^{N-1} \frac{1}{(N-1)!} e^{-t/\bar{t}_i} \tag{2}$$

The RTD is carried out at the determined flow rate which maintains the resin fluidized. The use of a tracer to measure the residence time distribution in this type of equipment was described by Bennet et al. (20), who showed the validity of the model for fluidized beds. The results obtained in the assays were $\bar{t}_i = 68.8$ seconds and $\sigma^2 = 1528.5$ for the first stage, giving an adequate fitting of the experimental results with three tanks in series. For the second state, $\bar{t}_i = 205$ seconds and $\sigma^2 = 7004.1$ were obtained, which fit correspondingly well to six tanks. Figure 8 shows the fitting of the model to the experimental results.

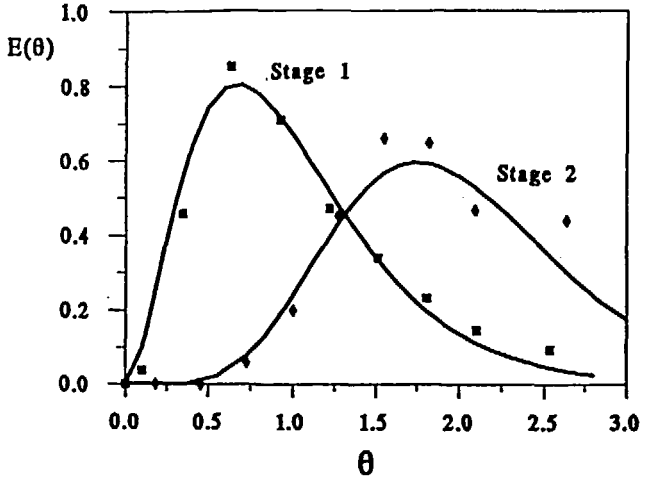

FIG. 8 Experimental and predicted hydrodynamic results for two stages of the saturation column.

Modeling and Experimental Testing

A simplified model was proposed based on the hydrodynamic behavior by considering each column stage as three CSTR (continuous stirred tank reactors). Ion exchange takes place only in the first one. In the other two, only mixing takes place. The volume determined for an equivalent CSTR is about the same as the fluidized resin in the stage.

Under these conditions, the equations for predicting the column behavior throughout one cycle may be written

$$V\frac{dc_{a,i}}{dt} = Q(c_{a,i-1} - c_{a,i}) - m\frac{dq_a}{dt} \qquad (i = 1) \tag{3}$$

$$V\frac{dc_{a,j}}{dt} = Q(c_{a,j-1} - c_{a,j}) \qquad (j = 2, 3) \tag{4}$$

and $q = f(c)$, which has previously been determined (16, 17), is determined by the isotherm of the exchanged ions. The model was developed in order to simulate experimental results for the first stage in the loading column and is shown in Fig. 9. A fairly good fit of the model to the experimental results is observed. It must be pointed out that some error in the experimental points may be due to problems in the collection of the samples due to the large volume of the equipment.

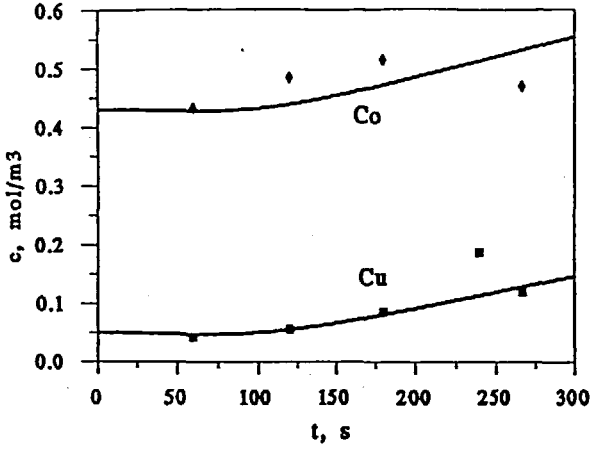

FIG. 9 Experimental and predicted results of metal depletion of the solution in the first stage of the load column at the fifteenth cycle.

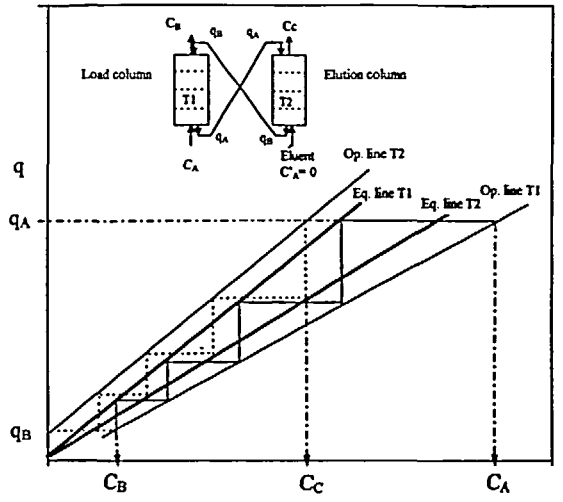

FIG. 10 Scheme of the operation of the proposed system in a McCabe–Thiele representation to be compared to a parametric pumping operation.

Analogies with Parametric Pumping

The results obtained in the elution operation mode of the equipment presented here show some analogies with a parametric pumping operation when the operation and equilibrium lines are plotted in a q versus c graph. In parametric pumping the two columns run at different temperatures so that the behavior of each column is determined by a different isotherm. The more the isotherms differ, the less cycles the system needs to obtain good separation. The advantage of parametric pumping is that no eluents are necessary because the differing capacity of the resin for the ions at different temperatures or pHs alone is capable of loading and regenerating the resin. In our equipment the results are analogous to parametric pumping since, in both cases, two useful currents (one concentrated in cobalt and the other concentrated in copper) are finally obtained. A qualitative scheme of the operation of the system is shown in Fig. 10.

This figure shows the operational scheme of our experimental system running in elution mode in order to present the analogies with a parametric pumping operation, It is assumed that the two columns have different conditions (temperature, for example), T1 for the loading column and T2 for the elution column. The equilibrium and operation lines for T1 and T2 are assumed to be linear. Initially, in the loading column, the concentration of ion A in the loading stream is C_A, the concentration of A in the resin that leaves

column T1 is q_A. Point (C_A, q_A) is on the operation line of T1. In the first stage, ion exchange (saturation of the resin by A) takes place until equilibrium line T1 is reached, then it passes to the second stage in the operation line, and so on. This McCabe–Thiele representation has been used in several works (21–23) dealing with the analogies between parametric pumping and distillation. After four stages the stream leaves the loading column with a concentration C_B, which is on the operation line at q_B. The concentration of ion A at the top of saturation column T1 is lower than in the initial solution because resin has retained the ion.

In the elution column, the regenerated solution is introduced at the bottom of T2, and the concentration of ion A in this solution is $C'_A = 0$; the resin that leaves from the bottom of column T2 has a concentration q_B, because it is regenerated. The point (0, q_B) is on operation line T2. In the first stage, the ion-exchange process (to be exact elution of the resin) takes place until equilibrium line T2 is reached. The evolution of the operation in the column is similar to that in the loading column, but at the end of four stages the outlet flow has a concentration C_C, and the resin at this point has a concentration q_A. The point (C_C, q_A) is on operation line T2. This is a simplified scheme, because we have arrumed the isotherms are linear in our approach, which is not the case for the Co–Cu exchange. The interesting fact is that the behavior found in the elution operation of the system can be formulated as analogous to parametric pumping.

CONCLUSIONS

A continuous fluidized-bed ion-exchange system has been designed and operated to split-up a current into two parts. Two operation modes are proposed for use in the equipment: the elution mode, where saturation is carried out in one column and elution is carried out in another column; and the division mode, where the effluent is introduced at different pHs in each column in such a way that selective retention is achieved in each column, allowing the separation of the two ions.

In this work the elution operation mode is proposed to split-up a hydrometallurgy wastewater composed of cobalt and copper as metallic cations. The cobalt goes with the effluent of the loading column and the copper with the effluent of the elution column, making both currents useful for recycling back into the process. An efficiency of 90% of initial cobalt and copper in the mixture that may be obtained in the two different streams was achieved.

The proposed system can be used for separations, concentrating a component that presents different equilibrium isotherms depending on the pH or temperature. Hydrodynamic results are used to propose a simplified model of a CSTR series. This model simulates the experimental results in one stage

of the equipment fairly well. The operation mode proposed presents some analogies with a parametric pumping operation running with, for example, different temperatures in each column.

SYMBOLS

a	counterions in solution
$c_{a,i}$, $c_{a,j}$	equivalent CSTR concentrations of model (mol/m^3)
E	curve response in the RTD experiments
m	mass of resin in a stage (m^3)
N	number of CSTR
Q	feed flow (m^3/s)
q	metal concentration in resin (mol/m^3 wet resin)
t	time (s)
$\bar{t}$	average time (s)
V	equivalent CSTR volume (m^3)

Greek Symbol

σ	variance

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