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## SEPARATION OF SILVER-COPPER MIXTURES BY ION-EXCHANGE PARAMETRIC PUMPING

### I. TOTAL REFLUX SEPARATIONS

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#### SUMMARY

Silver-copper mixtures occur at various stages of metal recovery processes particularly in the refining of silver. Parametric pumping is proposed as a method of separating copper from silver. The process consists in making a periodic change in the temperature of a fixed bed of ion-exchange resin with a synchronized periodic relative flow of the liquid mixture.

Experimental results at total reflux (batch) are presented that show that a good separation can be made by this method using Duolite C265 resin. The results are interpreted by a graphical approach using standard ion-exchange breakthrough curves obtained experimentally. Changes in total concentration are observed and interpreted as being the effect of temperature on Donnan electrolyte uptake.

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#### INTRODUCTION

In the 1960s Wilhelm *et al.*<sup>1</sup> presented a new cyclic separation method that they called parametric pumping. Since then the method has been the subject of much research<sup>2</sup> and experiments have shown that parametric pumping is capable of giving good separations.

The principle of direct-mode thermal parametric pumping used here is as follows. A fixed bed of adsorbent surrounded by a water jacket is connected to two reservoirs. The operation consists in flowing the mixture to be separated through the bed alternately from the bottom reservoir to the top and then from the top reservoir to the bottom. At the same time the temperature of the adsorbent is changed in synchronization with the flow direction such that up-flow occurs in a hot bed and down-flow in a cold bed. If a binary mixture is to be separated then one of the components is concentrated preferentially in the top reservoir and the other in the bottom reservoir. The process is based on the temperature dependence of the affinity of the adsorbent for the different solutes. Wilhelm and Sweed<sup>3</sup> separated toluene from *n*-heptane using a bed of silical gel such that the ratio of the toluene concentration in the two reservoirs exceeded 10<sup>5</sup>.

Research on parametric pumping has been carried out in various directions: different types of adsorbent have been tried for separating a variety of mixtures (hydrocarbons, ionic solutions, sugars, etc.) and several continuous systems have been proposed. Theory has been developed for both batch and open parametric pumps for linear isotherms<sup>4,5</sup> and for non-linear isotherms<sup>6</sup>. Recent investigations into staged open parametric pumps have demonstrated the analogy with distillation<sup>7</sup>.

The possibility of using ion-exchange resins in parametric pumping was demonstrated by Butts *et al.*<sup>8</sup>, who separated alkali metal ions. Mixed bed<sup>9</sup> and composite resins<sup>10</sup> have also been proposed for desalting water. Little other work has been reported on the thermal separation of metals by ion-exchange resins<sup>11</sup>.

In this paper we present experimental results to demonstrate the feasibility of separating copper and silver nitrates by parametric pumping using a standard commercial cationic resin.

### SILVER-COPPER SEPARATIONS

Mixtures of copper and silver are encountered in various hydrometallurgical processes. Other metals are also found in these mixtures, notably other precious metals such as palladium. The standard method of separating these mixtures consists in many stages of electrolysis, cementation, precipitation, filtration, dissolution, etc.

This sequence of operations is due to the necessity of recovering the precious metals, as well as the reagents used, as completely as possible and also to the need for purifying the effluents prior to their being emitted into the environment.

The first useful characteristic of parametric pumping is that it gives a direct separation of a mixture without the need for additional regenerants and chemicals. A second interesting feature is that parametric pumping is capable of giving close to complete separation. Finally, in terms of the energetics of the process the long-term fundamental advantage is that it achieves separation using only hot and cold water such as could be obtained from warm waste process effluents and a cold source such as a river<sup>12,13</sup>.

For thermal parametric pumping to be possible it is necessary that the exchange isotherm for copper and silver on the resin varies with temperature. We have determined these isotherms by simple batch equilibrations at the two temperatures used in the work, namely 20 and 60°C, and at a concentration of 0.5 *N*. Ion-exchange isotherms at 4°C have also been measured and have been published elsewhere<sup>14</sup>. The resin used is Duolite C265, a commercial strongly acidic macroporous cation-exchange resin with 20% divinylbenzene made by Diaprosim (Chauny, France). A particle size range of 200–400  $\mu\text{m}$  was used.

Fig. 1 shows the results: it is clear that silver is preferred by the resin over copper and that this preference is greater at 20°C than at 60°C. Thus we may expect an accumulation of silver in the top reservoir filled at 60°C and an accumulation of copper in the bottom reservoir filled at 20°C.

### EXPERIMENTAL

The apparatus (Fig. 2) consists of a glass column of 1.5 cm I.D. filled with Duolite C265 resin (bed depth 54 cm, bed volume  $v_1 = 95$  ml). A peristaltic pump

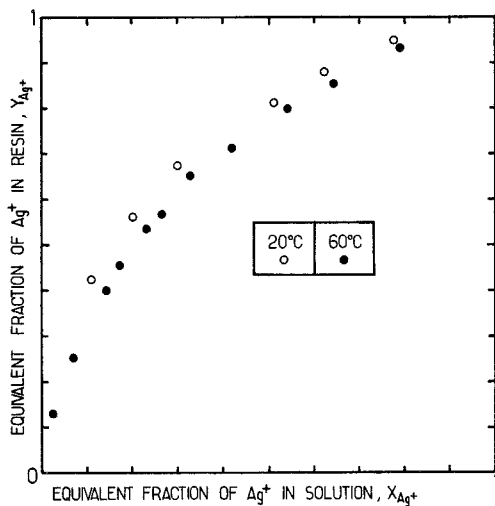


Fig. 1. Isotherms for  $\text{Ag}^+ - \text{Cu}^{2+}$  ion exchange on Duolite C265.

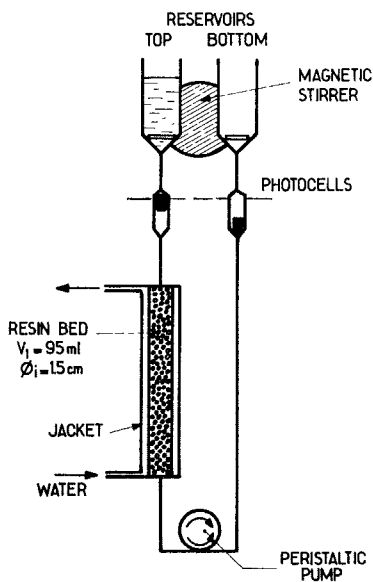


Fig. 2. Flow diagram of apparatus.

with a flow inverter is used to pump the solution at a flow-rate of 1.8 ml/min. This arrangement is used in place of the system of syringes and pistons used by other investigators. It has the advantages of being simpler, allowing a wider range of flow volumes to be used and allowing samples to be taken easily. The main disadvantage is that the column is not under pressure and slow degassing of the liquid phase can occur in the bed, causing problems in experiments of long duration. The end of each half-cycle, that is when a reservoir is empty and the other is full, is indicated by

a photo-cell system which detects the presence or absence of a float in a small glass cell. The dead volume in the system is 2 ml. The programming of the various phases of the operation is effected by a punched card programmer.

One cycle of a total reflux experiment includes the following steps:

(1) with solution flow stopped, hot water is circulated in the water jacket to bring the bed up to the required temperature (4 min);

(2) solution is allowed to flow through the bed from the bottom reservoir to the top reservoir (time depends on the volume to be passed);

(3) the water jacket is emptied of hot water and the reservoirs are agitated (1 min);

(4) the cold water is circulated in the water jacket to bring the bed to the cold temperature; no solution flows (4 min);

(5) solution is allowed to flow through the bed from the top reservoir to the bottom reservoir (time depends on the volume to be passed).

Samples of 10  $\mu$ l were taken periodically from the reservoirs and were analysed by atomic-absorption spectrophotometry.

The initial state of the column in all of these total reflux experiments was that at equilibrium at 60°C with the solution to be separated and with a volume,  $V_R$ , of the same solution in the bottom reservoir. Three experiments were performed with different volumes  $V_R$ , that is, with different relative penetration,  $\eta$ , defined by

$$\eta = \frac{V_R}{\varepsilon v_1} \quad (1)$$

where  $\eta$  is the number of column void volumes displaced per half-cycle. This is summarized in Table I. A fourth experiment with a very concentrated solution of copper and silver containing some palladium was also performed.

TABLE I

$\text{Cu}^{2+}$ - $\text{Ag}^+$  BATCH SEPARATIONS

Bed volume,  $v_1 = 95$  ml. Temperatures: up-flow, 60°C; down-flow, 20°C.

Parameter	Run No.		
	1	2	3
Reservoir volume, $V_R$ (ml)	40	80	200
$\eta$	1.05	2.1	5.3
Number of cycles	55	91	26
Cycle time (min)	55	100	230
Initial state:			
$C^0$ (equiv./l)	0.50	0.50	0.49
$x_{\text{Ag}^+}^0$	0.49	0.50	0.52
$y_{\text{Ag}^+}^0$	0.75	0.76	0.78
Final state:			
$C$ (equiv./l) $\left\{ \begin{array}{l} \text{TR} \\ \text{BR} \end{array} \right.$	0.83	0.56	0.50
$x_{\text{Ag}^+}^0$ $\left\{ \begin{array}{l} \text{TR} \\ \text{BR} \end{array} \right.$	0.20	0.45	0.48
	0.98	0.996	0.84
	0.014	0.002	0.19

## RESULTS AND DISCUSSION

Figs. 3-5 show the variations in the ionic fractions and in the total concentrations observed in each reservoir as a function of the number of cycles. As was expected on the basis of the exchange isotherms, where silver was found to be preferred by the resin more at 20°C than at 60°C, the  $\text{Ag}^+$  ions accumulate in the top reservoir and the  $\text{Cu}^{2+}$  ions in the bottom reservoir. The results shown in these figures may be discussed from three different aspects:

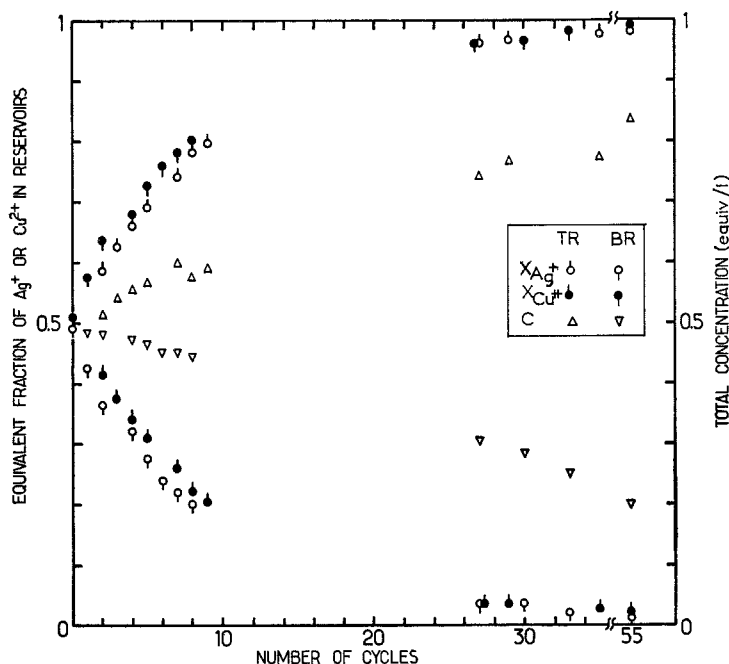


Fig. 3. Variation of concentration in top and bottom reservoirs for run 1.

(1) *The limiting separation.* At the end of experiments 1 and 2 an almost complete separation is achieved, with no copper in the top reservoir and no silver in the bottom reservoir. The separation is, however, only partial in experiment 3.

(2) *The total concentration.* It can be seen that there is an increase in total concentration in the top reservoir and a decrease in the bottom reservoir. This effect is large in experiment 1, small in experiment 2 and almost negligible in experiment 3. This variation in total concentration is unexpected in an ion-exchange operation. Ion exchange is characterized by a stoichiometric exchange of ions between the fluid and solid phases and the total number of ions in each phase is invariant.

(3) *The approach to the limiting separation.* The transition period to the limiting separation is shorter in experiment 3 than in experiment 2 and shorter in experiment 2 than in experiment 1. This is in agreement with previous theoretical work<sup>15</sup>, which indicated that the number of cycles required to reach the limiting separation is reduced when the penetration is increased.

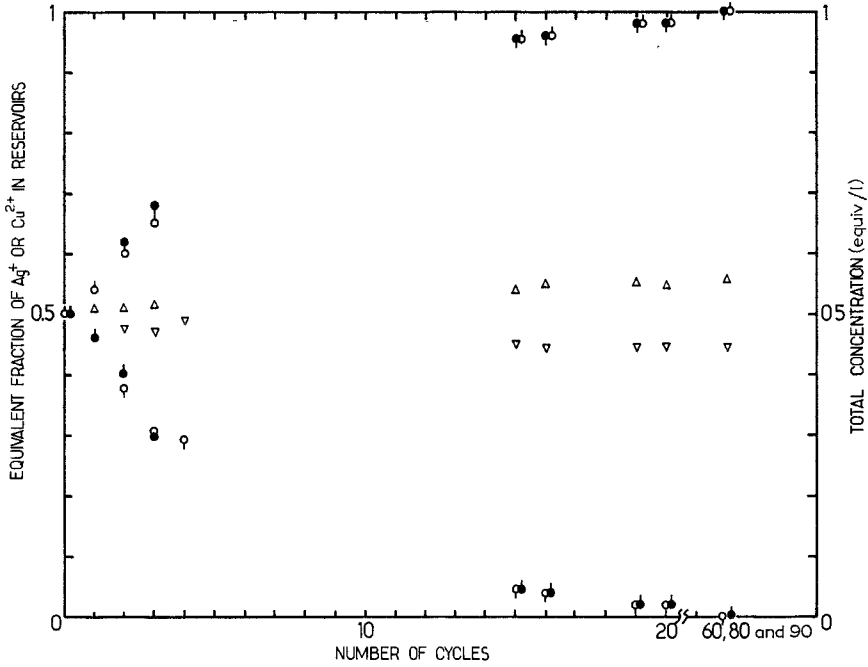


Fig. 4. Variation of concentration in top and bottom reservoirs for run 2 (for symbols, see Fig. 3).

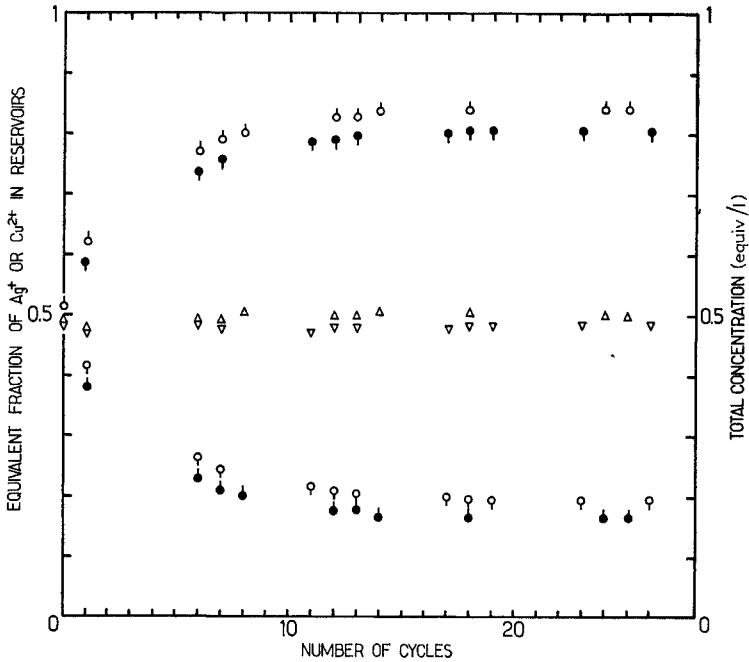


Fig. 5. Variation of concentration in top and bottom reservoirs for run 3 (for symbols, see Fig. 3).

The first two of these three points will be discussed at greater length in the following sections.

### *Analysis of the steady periodic state (SPS)*

As noted above, the limiting separation achieved in experiment 3, in which there was the largest volume passed per cycle (200 ml), is less than in the other two experiments. All of the theories of parametric pumping based on the hypothesis of local equilibrium between the resin and the solution indicate that the separation is reduced when the volume passed in each half-cycle is increased<sup>5,6</sup>. Camero and Sweed<sup>6</sup> have given a detailed analysis of the steady periodic state for non-linear isotherms such as those involved here. They showed that for a complete binary separation, that is, the ion preferred by the resin is found pure in the top reservoir and the ion less preferred by the resin pure in the bottom reservoir, there is only one transition zone in the bed. This transition zone is dispersive on up-flow, compressive on down-flow and at the end of the down-flow is a shock front. Here we give a graphical demonstration that this is a possible state of the column in experiments 1 and 2 but not in experiment 3. Thus the theory predicts a complete separation in experiments 1 and 2 but not in experiment 3. However, in contrast to the demonstration given by Camero and Sweed<sup>6</sup>, we use fronts obtained experimentally on an ion-exchange column independently of parametric pumping experiments.

These exchange fronts were obtained with a column of the same ion-exchange resin ( $v_2 = 166$  ml) as used for the parametric pumping experiments and with the same flow-rate. Fig. 6 shows the concentration of silver coming from the column

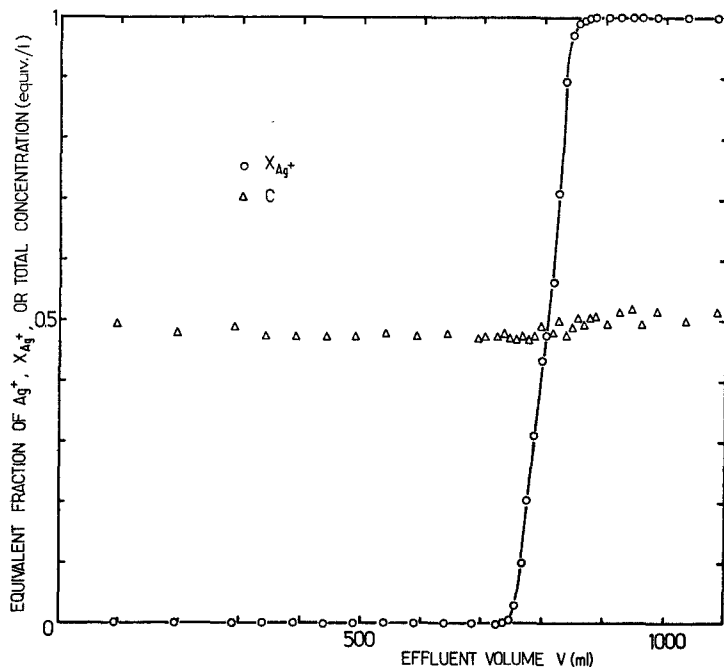


Fig. 6. Experimental stable front  $\text{Cu}^{2+}$ - $\text{Ag}^+$ . Column:  $v_2 = 166$  ml, I.D. = 1.5 cm, Duolite C265 ( $\text{Cu}^{2+}$ ); eluent: 0.5 N  $\text{AgNO}_3$ , flow-rate 2 ml/min; temperature: 20°C.

initially completely in  $\text{Cu}^{2+}$  form and through which a 0.5 N solution of silver nitrate is passed. Because the  $\text{Ag}^+$  ion is more preferred than the  $\text{Cu}^{2+}$ , the non-linear equilibrium theory predicts that this front should be a shock front. The spread seen in Fig. 6 is due to effects such as axial dispersion and the finite rate of mass transfer. Fig. 7 shows the concentration of silver coming from the same column initially completely in the  $\text{Ag}^+$  form and through which is passed a 0.5 N solution of copper nitrate. This exchange front is dispersive because the resin prefers  $\text{Ag}^+$  to  $\text{Cu}^{2+}$ .

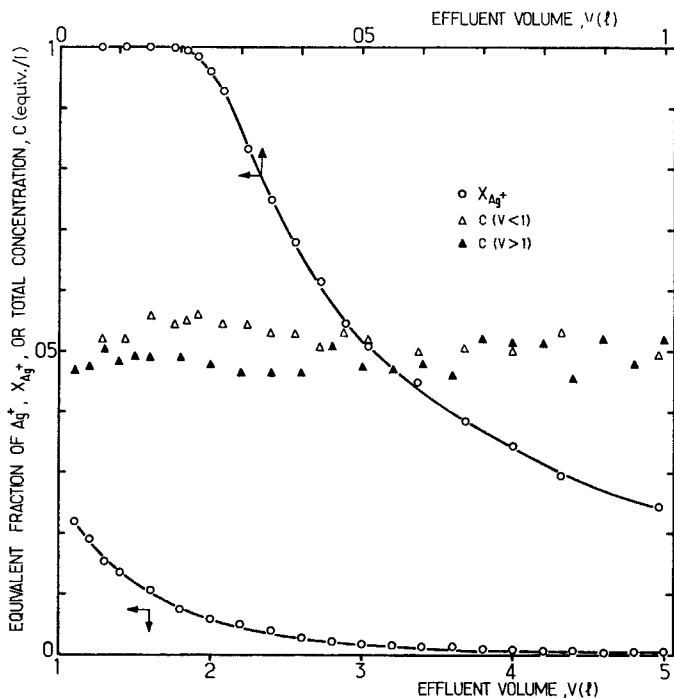


Fig. 7. Experimental dispersive front  $\text{Ag}^+$ - $\text{Cu}^{2+}$ . Column:  $v_2 = 166$  ml, I.D. = 1.5 cm, Duolite C265 ( $\text{Ag}^+$ ); eluent: 0.5 N  $\text{Cu}(\text{NO}_3)_2$ , flow-rate 2.3 ml/min; temperature: 60°C.

With these two fronts, considered as indications of what occurs in up-flow and down-flow, it is possible to reconstitute the concentration profiles in the bed in the SPS in parametric pumping. The compressive front in Fig. 6 is sharp compared with the dispersive front in Fig. 7 and as a first approach we shall take it to be a pure shock front, that is, a discontinuity. This hypothesis will be reconsidered later.

Fig. 8 represents the state of the column in parametric pumping with the equivalent fraction of  $\text{Ag}^+$  in the interstitial fluid phase as ordinate. The abscissa is the length along the column. According to the theory of Camero and Sweed<sup>6</sup>, if there is a complete separation, there is a shock front at the end of the down-flow period. The upper part of the bed is then in  $\text{Ag}^+$  form and the lower part in  $\text{Cu}^{2+}$  form. The bottom reservoir is filled with pure copper nitrate. This shock front is positioned by a mass balance between the initial state of the column and the above-mentioned con-



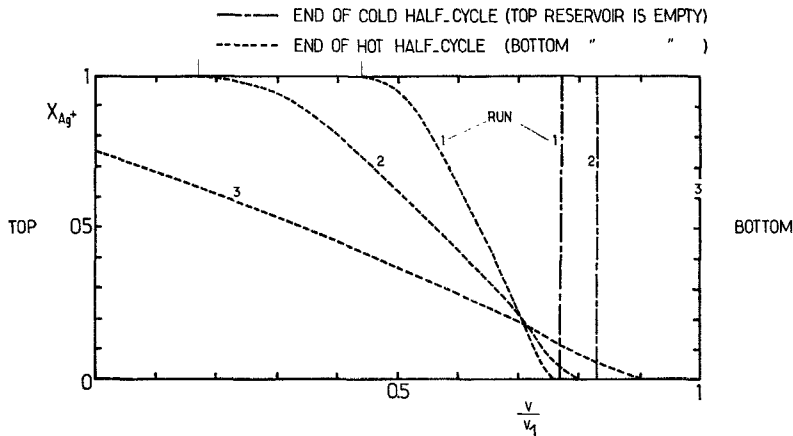


Fig. 8. Graphical construction of profiles in terms of  $\text{Ag}^+$  ions in the bed by stable fronts idealized as discontinuities. The figure shows that complete separation is not possible for run 3.

figuration at the end of down-flow at SPS. The values of  $v/v_1$  of 0.77, 0.83 and 1 are obtained for the experiments 1, 2 and 3, respectively (we assume that the total concentration remains constant and equal to  $C^0$ . If we take into account the concentrations actually observed, then these values are slightly different for experiments 1 and 2).

At this point in the discussion it can be seen that as the shock fronts do not leave the column to enter the bottom reservoir in experiments 1 and 2, then only pure copper nitrate is collected in the bottom reservoir. In experiment 3 we are at the limit and, as the compressive front is not really a perfect discontinuity, there is something less than pure copper nitrate collected in the bottom reservoir.

Now let us reconstitute the state of the column at the end of the up-flow half-cycle. For this we use the experimentally determined dispersive front shown in Fig. 7. For each ionic fraction,  $x$ , on the front we can calculate the corresponding dimensionless throughput parameter,  $T$ , defined by<sup>16</sup>

$$T \equiv \frac{C(V - \epsilon v_2)}{q v_2} = \frac{V - \epsilon v_2}{v \epsilon v_2} \quad (2)$$

where  $V$  is the volume of effluent at which the ionic fraction  $x$  leaves a bed of volume  $v_2$ , and  $v$  is the capacity ratio, defined by

$$v = \frac{q}{C \epsilon} \quad (3)$$

$T$  can be seen to be the number of void volumes that have passed through the column divided by the capacity ratio,  $v$ . This equation can now be applied to the column used in the parametric pumping experiments where the volume of the bed  $v_1 = 95$  ml. At the end of the up-flow half-cycle the volume of liquid passed through the column is  $V_R$  and the position of a given composition  $x$  in the column measured by the volume  $v$  of the bed is associated with a corresponding value of  $T$ :

$$T = \frac{C[V_R - \epsilon(v_A - v)]}{q(v_A - v)} \quad (4)$$

where  $v_A$  is the position of the discontinuity at the start of up-flow. Rearranging and normalizing by  $v_1$  we obtain

$$\frac{v}{v_1} = \frac{v_A}{v} - \frac{\eta}{1 + vT} \quad (5)$$

where  $\eta$  is the penetration. Thus, for a given experiment ( $\eta, v_A$ ) we can construct the dispersive front at the end of the up-flow period point by point.

From Fig. 8 it can be seen that the dispersive front does not leave the column in experiments 1 and 2 and therefore only silver nitrate is collected in the top reservoir. On the other hand, in experiment 3 the front does leave the column and a certain amount of copper nitrate is introduced into the top reservoir with the silver nitrate. Summing up, a complete separation is expected in experiments 1 and 2 but not in experiment 3, and this is as found in the experimental results.

Now we examine the effects of dispersion on the shock front to see if a complete separation is still expected in experiments 1 and 2. When a shock front moves through a column the spreading effects due to axial dispersion and mass transfer resistance are compensated for by the compressive effects due to the favourable exchange isotherm. After a short transition period these two opposing effects are in equilibrium and lead to the accepted idea<sup>16</sup> that such a shock front moves through the bed in a constant form, retaining its shape. All of the concentrations in the front move with the same velocity, which is the same as that of the stoichiometric point. Therefore, each concentration moves through a bed volume  $\Delta v$  when the effluent volume is increased by  $\Delta V$  such that

$$\Delta v = \frac{C}{C\varepsilon + q} \cdot \Delta V \quad (6)$$

Thus, for each composition  $x$  on Fig. 6 we measure the  $\Delta V$  to the stoichiometric point and we calculate  $\Delta v$ . This then indicates the position of the composition  $x$  with respect to the stoichiometric point, which is itself given by a mass balance. This is valid for the column of volume  $v_2$  and also for the column of the parametric pump which has the same cross-sectional area and flow-rate<sup>16</sup>. We thus obtain the normalized stable front in Fig. 9 (the volumes  $\Delta v$  are normalized by  $v_1$ ). It can be seen that even

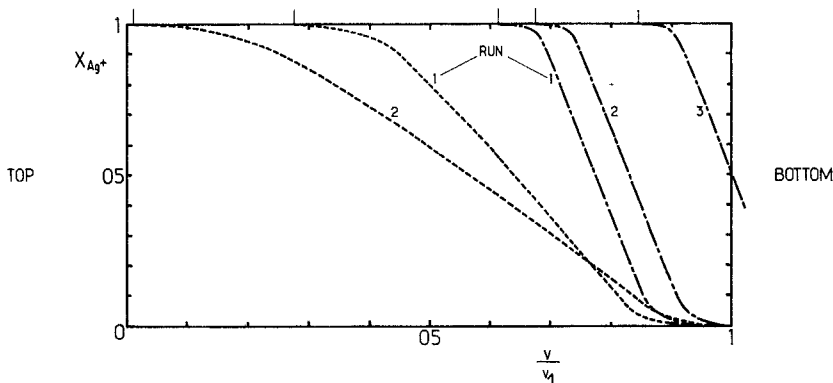


Fig. 9. Graphical construction of profiles in terms of  $\text{Ag}^+$ , including spreading effects on the stable front. The figure shows that complete separation is still possible.

with the dispersion about the stoichiometric point these stable fronts do not leave the column at the end of the down-flow half-cycle in experiments 1 and 2 and that the bottom reservoir contains only copper nitrate. However, in experiment 3 the front does leave the column and introduces silver ions into the bottom reservoir.

The dispersive fronts in Fig. 9 were obtained by adding the spread, noted on the stable fronts, to the dispersive fronts taken from Fig. 8. It should be noted that in doing this we neglect the change in shape of the stable front induced by the re-equilibration when the temperature is changed between the two half-cycles. This seems to be justified, however, as these effects do not change the position of the extremities of the stable front but only the form of the front between its extremities. This means that one end of the dispersive front  $x_{\text{Ag}^+} = 1$  is the same both before and after the change in temperature and the resulting equilibration. It can be seen from Fig. 9 that, as with the stable fronts, the dispersive fronts do not leave the column and therefore that even by including spreading effects no silver nitrate should enter the top reservoir in experiments 1 and 2. Inclusion of the spreading effects in the analysis of the results of experiments 3 does not add any information because, as is shown in Fig. 8, the dispersive front already leaves the column even without including the spreading effects.

To summarize this discussion, it may be said that the model presented here, which is based on experimental exchange fronts and including spreading effects, predicts a complete separation between the two reservoirs in experiments 1 and 2, but not in experiment 3. In addition, the theory indicates that the volume passed in experiment 2 is the maximum consistent with complete separation. It can be seen that there is good agreement with the model by comparing these predictions with the experimental results shown in Figs. 3-5 and Table I. The less than complete separation observed in experiment 1 can be explained by the fact that the parametric pump had not reached its SPS at the end of the experiment (55th cycle) as may be seen in Fig. 3.

#### *Concentration and dilution effects*

The following gives only a brief interpretation of these phenomena and more detail is given in another paper<sup>14</sup>. At present, work is continuing on the dilution-concentration of electrolytes by parametric pumping and will be published later.

The variation in total concentration observed in the experiments reported here may be explained by the well known Donnan effect. In addition to their ability to fix ions on exchange sites, ion-exchange resins also retain electrolyte (cation + anion) in their pores. It seems that the amount of electrolyte retained diminishes with the strength of fixation of the cation on the exchange sites<sup>17</sup>. Thus, for weakly fixed cations, such as alkali metals, there is practically no electrolyte present in the pores of the exchange resins (Donnan exclusion). In contrast, for strongly fixed cations, such as  $\text{Ag}^+$ , the amount of electrolyte retained in the pores of the resin can become appreciable, of the order of 10% of the exchange capacity<sup>18</sup>. This sorption of electrolyte can be seen in Fig. 6: before the exchange front, whilst the bed is fixing  $\text{Ag}^+$  ions, there is also sorption of  $\text{AgNO}_3$  and consequently a reduction in the total concentration of the solution. After the passage of the exchange front the total concentration of the solution returns to the same value as that of the incoming solution. The opposite effect is seen in Fig. 7. It has also been shown<sup>14</sup> that the amount of electrolyte retained depends on the temperature and therefore the concentration-

dilution of electrolyte by the Donnan effect can be performed by parametric pumping.

Other experiments performed in our laboratory, but not described here, have shown that a parametric pump containing Duolite C265 in the  $\text{Ag}^+$  form and a solution containing only  $\text{AgNO}_3$  gives considerable concentration-dilution effects. The concentration in the top reservoir is greatly increased and that in the bottom reservoir is reduced (heating on up-flow half-cycle). If the same experiment is repeated with only  $\text{Cu}(\text{NO}_3)_2$  and the resin in the  $\text{Cu}^{2+}$  form then the effects are reversed: concentration in the bottom reservoir, dilution in the top reservoir. However, the effects are much less with  $\text{Cu}^{2+}$  than with  $\text{Ag}^+$ .

In experiments 1, 2 and 3 the amount of  $\text{Ag}^+$  in the pump is greater than that of the  $\text{Cu}^{2+}$  and we can conclude that the predominant effect follows that observed in the only silver-containing parametric pump, and that there is therefore an increase in total concentration in the top reservoir and a decrease in the bottom reservoir. This situation could be reversed if the amount of  $\text{Cu}^{2+}$  in the pump was greater than that of  $\text{Ag}^+$  and the effects would be seen to be as found in the exclusively  $\text{Cu}^{2+}$  parametric pump mentioned above. In this instance the total concentration would be increased in the bottom reservoir. This state of affairs is shown in experiment 4 (Fig. 10), other aspects of which will be discussed later. Returning to experiments 1, 2 and 3 we can see that the concentration-dilution effect decreases from experiment 1 through 2 to 3 in order of increasing reservoir volume, which is as expected.

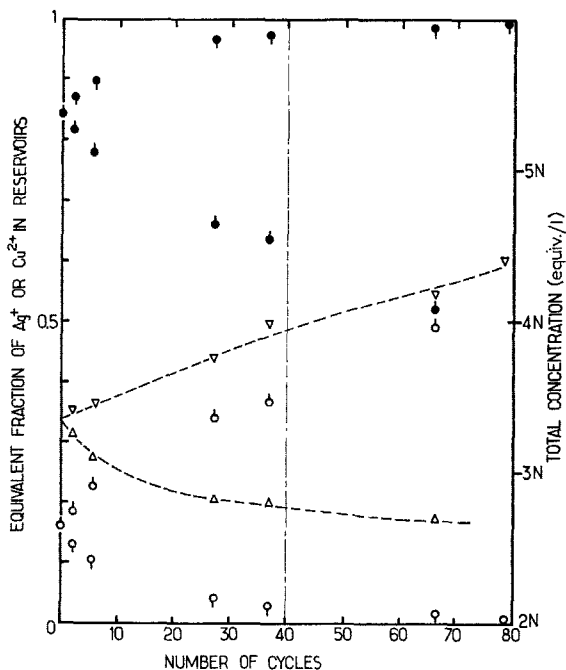


Fig. 10. Experimental separation of a concentrated mixture of  $\text{Ag}^+$ - $\text{Cu}^{2+}$ - $\text{Pd}^{2+}$  (run 4). Palladium concentration: initial, 2.73 g/l; final, 0.04 g/l (TR), 5.95 g/l (BR). For symbols, see Fig. 3.

*Batch separation of  $Ag^+ - Cu^{2+} - Pd^{2+}$* 

As mentioned previously, many silver and copper solutions found in hydrometallurgical processes are very concentrated and also contain a small amount of palladium. To investigate the behaviour of such mixtures in parametric pumping we performed an experiment with the ions  $Ag^+$ ,  $Cu^{2+}$  and  $Pd^{2+}$  and using the same column and temperatures as described above. The initial mixture had a total concentration of 3.35 *N* and contained 84% Cu. The palladium content was 2.73 g/l. The volume passed at each half-cycle was 40 ml up to the 40th cycle and was reduced to 20 ml afterwards in order to try to increase the separation. This was done by removing 10 ml from each reservoir at the 40th cycle.

It can be seen, in Fig. 10, that as in experiments 1, 2 and 3, the silver concentrates in the top reservoir and the copper in the bottom reservoir. However, in contrast to the previous experiments, the total concentration is increased in the bottom reservoir, as was explained in the previous section. Palladium is also separated from the mixture and is concentrated at the same side as the silver. This experiment shows that parametric pumping can separate silver and palladium from a mixture containing a large amount of copper.

## SYMBOLS

- $C$  Total concentration in liquid phase (mequiv./ml).  
 $C^\circ$  Total concentration at the start of an experiment (mequiv./ml).  
 $q$  Resin capacity (mequiv./ml of bed).  
 $T$  Throughput parameter (dimensionless).  
 $T_C$  Cold temperature.  
 $T_H$  Hot temperature.  
 $V$  Effluent volume (ml).  
 $V_R$  Reservoir volume (ml).  
 $v$  Bed volume as a measure of distance along the column (ml).  
 $v_1$  Bed volume in parametric pumping runs ( $v_1 = 95$  ml).  
 $v_2$  Bed volume in Figs. 6 and 7 ( $v_2 = 166$  ml).  
 $x$  Equivalent fraction in liquid phase (in  $Ag^+$ , if not otherwise mentioned).  
 $x^\circ$  Equivalent fraction of  $Ag^+$  in liquid phase and BR at the start of an experiment.  
 $y^\circ$  Equivalent fraction of  $Ag^+$  in resin phase in equilibrium with  $x_0$  at  $T_H$ .  
 $\varepsilon$  Porosity ( $\varepsilon = 0.4$ ).  
 $\eta$  Relative penetration (defined by eqn. 1).  
 $\nu$  Capacity ratio (defined by eqn. 3).  
 SPS Steady periodic state.  
 TR Top reservoir.  
 BR Bottom reservoir.

## REFERENCES

- 1 R. H. Wilhelm, A. W. Rice and A. R. Bendelius, *Ind. Eng. Chem. Fundam.*, 5 (1966) 141.
- 2 P. C. Wankat, in *Percolation Processes*, NATO Advanced Study Institute, Sijthoff en Noordhoff, Alphen aan de Rijn, 1980.
- 3 R. H. Wilhelm and N. H. Sweed, *Science*, 159 (1968) 522.
- 4 R. L. Pigford, B. Baker, III and D. E. Blum, *Ind. Eng. Chem. Fundam.*, 8 (1969) 144.

- 5 H. T. Chen and F. B. Hill, *Separ. Sci.*, 6 (1971) 411.
- 6 A. A. Camero and N. H. Sweed, *AIChE J.*, 22 (1976) 369.
- 7 G. Grevillot, *AIChE J.*, 26 (1980) 120.
- 8 T. J. Butts, N. H. Sweed and A. A. Camero, *Ind. Eng. Chem. Fundam.*, 12 (1973) 467.
- 9 R. W. Rolke and R. H. Wilhelm, *Ind. Eng. Chem. Fundam.*, 8 (1969) 235.
- 10 B. A. Bolto, *Chem. Tech.* (Easton), 5 (1975) 303.
- 11 M. Bailly and D. Tondeur, *J. Chromatogr.*, 201 (1980) 343.
- 12 P. Le Goff and D. Tondeur, *Entropie*, 88 (1978) 5.
- 13 P. Le Goff, *Energétique Industrielle*, Technique et Documentation, Paris, 1979.
- 14 G. Grevillot, *Thèse de Doctorat d'État*, Nancy, 1978.
- 15 G. Grevillot and D. Tondeur, *AIChE J.*, 22 (1976) 1055.
- 16 J. H. Perry, *Chemical Engineers' Handbook*, McGraw-Hill, New York, 4th ed., 1963.
- 17 B. Tremillon, *Les Séparations par les Résines Échangeuses d'Ions*, Gauthier-Villars, Paris, 1965.
- 18 O. D. Bonner, W. T. Argersinger and A. W. Davidson, *J. Amer. Chem. Soc.*, 74 (1952) 1044.