TREATMENT OF COPPER LEACH SOLUTIONS BY ION EXCHANGE RESINS

K. Hussain

PCSIR Laboratories, Lahore 16

M. Rumeau

Laboratoire de Genie Chimique C.U.S.B.P. 143, 73011 Chambery, France

The paper deals with the treatment of copper leach solutions with ion exchange resins. Four Duolite resins have been used to study the concentration of these solutions and an attempt has been made to study the separation of copper from the iron present in leach solutions as an impurity. It has been observed that only strong sulphonic acid type resin may be used for concentration and separation purposes.

INTRODUCTION

Ion exchange resins for the recovery of uranium from sulphuric acid leach solutions, separation of rare earths from one another, separation and production of fission products in nuclear industry have long been used on an industrial scale. However, in the field of base metal recovery, resins have not yet been used on large scale although many attempts have been made to adapt the process for the recovery of copper from its leach solutions [1–8].

Copper ores may be leached either by sulphuric acid or by ammonical ammonium carbonate solutions. The resulting solutions are either treated by cementation or liquid—liquid extraction to obtain copper powder or concentrated $CuSO_4$ solutions [9]. The copper powders from cementation are subjected to refining while pure copper sulphate solutions are electrolysed for cathode copper.

The concentration of acid copper leach solutions varies widely; for example the solutions resulting from *in situ* leaching, tailings dump leaching or bacterial leaching usually contain around 1 g/1 of copper whereas those resulting from vat leaching or agitation leaching contain much higher amounts of copper per litre. The pH of these solutions also varies from process to process. The treatment of these solutions by solvent extraction over wide ranges of concentration of copper and hydrogen ions is being practised on an industrial scale. However, the initial plant cost is very high and the space requirement is also great for the treatment of a given volume of solutions. Treatment of such solutions by ion exchange resins is another possibility. Because of the nonpolluting nature of the ion exchange process we have studied the behaviour of resins with synthetic acid leach solutions.

Resins, Chemicals and Apparatus Used. Resins: Four Duolite ion exchange resins, made by La Societe Diaprosim, France, were used during this study. (1) Duolite C20 —— strongly acidic resin containing SO_3 functional groups, (2) Duolite CC3 —— weakly acidic resin containing COO functional groups, (3) Duolite ES 466 —— a chelating resin, containing aminodiacetate groups, $CH_2N: (CH_2-COO)_2$; and (4) Duolite ES 467 —— a chelating resin, containing $NH-NH-CH_2-PO_3^2$ aminophosphonic groups.

These resins, when put in contact with water, behave differently: whereas the first and second are completely and partially dissociated respectively, the other two are dissociated only very slightly; thus the response of these resins towards the exchange process is markedly different. While C20 undergoes a simple exchange process with the ions present in the solution, the CC3 behaves sometimes as a complexing agent and sometimes as an ion exchanger. The other two resins, ES 466 and ES 467, form chelates with the metal ions which are then destroyed and eluted with mineral acids.

Chemicals. The following chemically pure reagents were used to make the solutions in distilled water. $CuSO_4 \cdot 5H_2O$, $Fe_2(SO_4)_3$ and H_2SO_4.

Apparatus

Columns. Glass columns were used throughout this study. The diameter of each column was precisely measured. Before putting the resin in the column, a glass-wool plug was introduced to support the resin. The resin was then introduced into the column and another glass wool plug was added to avoid the disturbance of the resin bed

due to the introduction of solution.

Pump. A Gilson Minipuls II peristaltic pump was used throughout the study. The solution feed rate could be adjusted with a potentiometer control.

Fraction Collector. A Gilson Microcol TDC 80 fraction collector was used to collect the fractions at the outlet of the column. The pump and the fraction collector could be connected in such a way as to collect fractions of a predetermined volume automatically.

Atomic Absorption Spectrophotometer. A Varian model 1100 atomic absorption spectrophotometer was used for all analytical purposes. The instrument has a nonlinearity correction system when the Beer–Lambert law is not followed.

EXPERIMENTAL

We have studied the fixation of Cu^{+2} and Fe^{+3} ions on different types of resin as a function of H_2SO_4 concentration in the solution. The concentration of Cu^{+2} ions used was 3.18 g/l whereas for Fe^{+3} it was 0.5 g/l (5.10^{-2} and 9.10^{-3} M).

Fixation of Copper

On Sulphonic Acid Resin C20. This type of resin may be used over a pH range of 0–14. But as the leach solutions have a pH around 2 and less, we have studied the take up of Cu^{+2} ions from solutions containing sulphuric acid from 5.10^3 to $1M$ (2.0--0.3 pH). The results are shown in Fig. 1. It may be remarked that the fixation is important at concentrations less than 10^{-1} M in H_2SO_4. The resin used was initially in the H^+ form. The resin volume was 6.164 ml and column capacity 13.27 meq.

On Carboxylic Acid Resin CC3. The fixation of Cu^{2+} on this resin and the other two, i.e. ES 466 and ES 467, was attempted with the resin in the hydrogen form. But the take up was so small that it was decided to use the resin in the NH_4^+ form. This was affected by passing NH_3 solution over the resin bed and removing the interstitial NH_3 by passing distilled water equal in volume to the voidage of the column. The exchange of Cu^{2+} ions with NH_4^+ was quantitative. The results are shown in Fig. 2. This being a weak acid resin it has a large affinity for hydrogen ions, so it could not be used for higher concentrations of H_2SO_4 in solution. The acid concentration used was, therefore, $5.10^{-2} - 5.10^{-4}$ M (1–3 pH). It may be observed that at higher concentrations of H_2SO_4 there is an enrichment of Cu^{2+} ions at the head of the column. (Resin volume 7 9 ml, bed capacity 35.7 meq).

On resin ES 466. The results obtained for the fixation of Cu^{2+} ions on ES 466 in NH_4^+ form are presented in

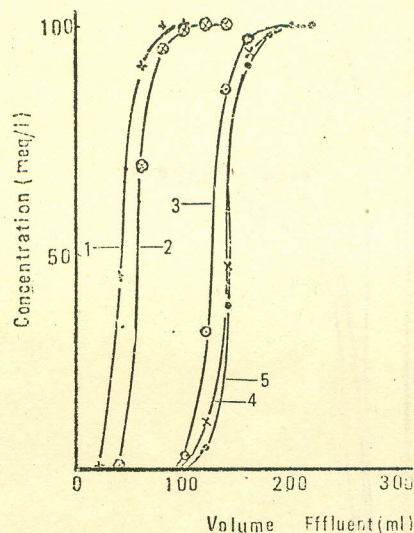Fig. 1. Fixation of Cu^{2+} on sulphonic acid resin Duolite C20 (H^+) at different concentrations of sulphuric acid : (1) 1, (2) 5.10^{-1}, (3) 5.10^{-1}, (4) $1.5.10^{-2}$, (5) 5.10^{-3} M; Column : section 0.92 cm², bed height 6.7 cm, flow rate 0.8 ml min⁻¹ cm⁻².

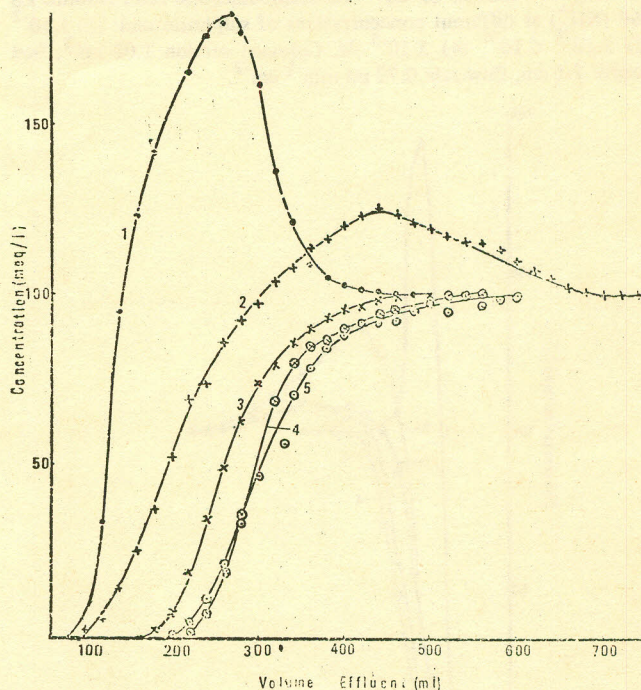

Fig. 2. Fixation of Cu^{2+} on carboxylic acid resin Duolite CC3 (NH_4^+) at different concentrations of sulphuric acid: (1) 5.10^{-2}, (2) $1.5.10^{-2}$, (3) 5.10^{-3}, (4) $2.5 10^{-3}$, (5) 5.10^{-4} M. Column : section 1.15 cm², bed height 6.9 cm flow rate 0.64 ml min⁻¹ cm⁻².

Fig. 3. The concentration of H_2SO_4 in solution ranged between $5.10^{-2} - 5.10^{-5}$ M (1–4 pH). This fixation is found to be small as compared to C20 and CC3.

On resin ES 467. The results are shown in Fig. 4. The acid concentration used was of the order of $5.10^{-2} - 5.10^{-4}$ M (1–3 pH). An enrichment at the outlet of the column is observed as in the case of CC3 and ES 466. As explained earlier, these resins have higher affinity for the proton hence this enrichment. A comparative plot of the distribution coefficient P versus pH for the above four resins is
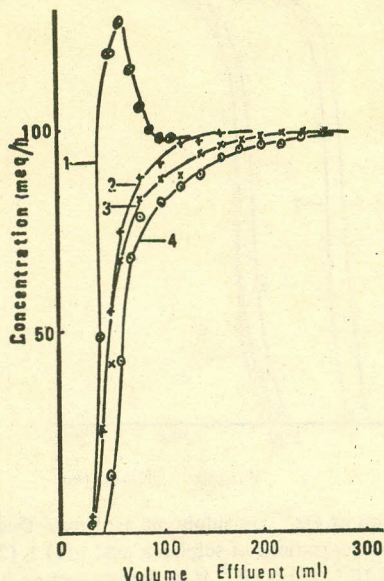
Fig. 3. Fixation of Cu^{2+} on aminodiacetate resin Duolite ES 466 (NH_4^+) at different concentrations of sulphuric acid: (1) 5.10^{-2} (2) 5.10^{-5} 5.10^{-4} (4) 5.10^{-5} M. Column: section 1.02 cm^2, bed height 7.1 cm, flow rate 0.72 ml min^{-1} cm^{-2}.
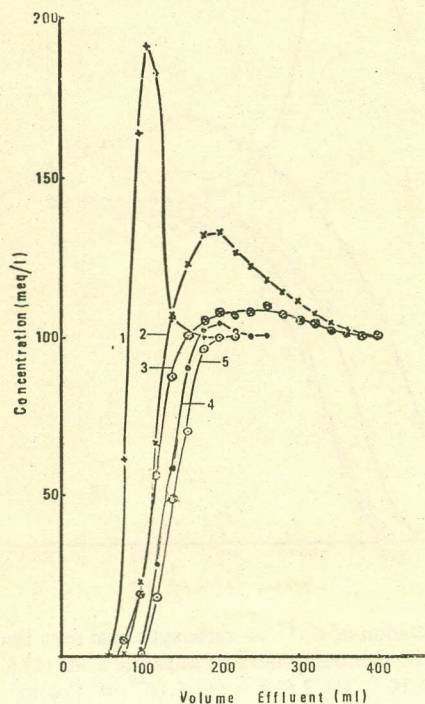

Fig. 4. Fixation of Cu^{2+} on aminophosphonic resor Duolite ES 467 at different concentrations of sulphuric acid (1) 5.10^{-2} (2) $1.5.10^{-2}$ (3) 5.10^{-3} (4) $2.5.10^{-3}$ (5) 5.10^{-4} M. Column : section 0.96 cm^2, bed height 7.5 cm, flow rate 0.76 ml min^{-1} cm^{-2}.

presented in Fig. 5. (P is calculated as shown in the Annexure).

Fixation of Iron Fe^{3+}

On Sulphonic Acid Resin C20. In this case the results obtained for the fixation of Fe^{3+} ions on the resin in H^+ form are presented in Fig. 6. The concentration of H_2SO_4
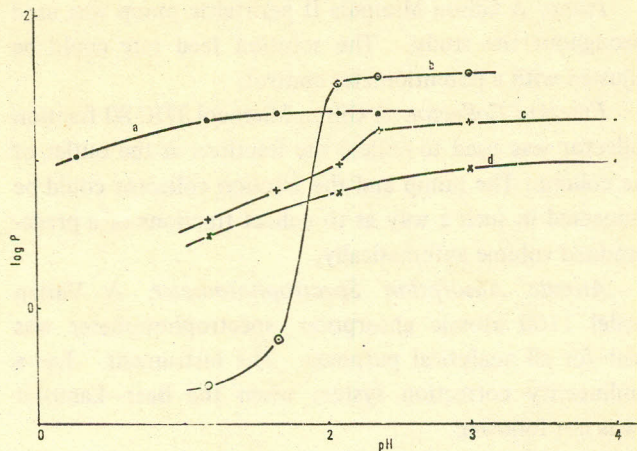

Fig. 5. Variation of log $P = f$ (pH) for the fixation of Cu^{2+} for different types of resin : (a) C 20, (b) CC 3, (c) ES 467, (d) ES 466.

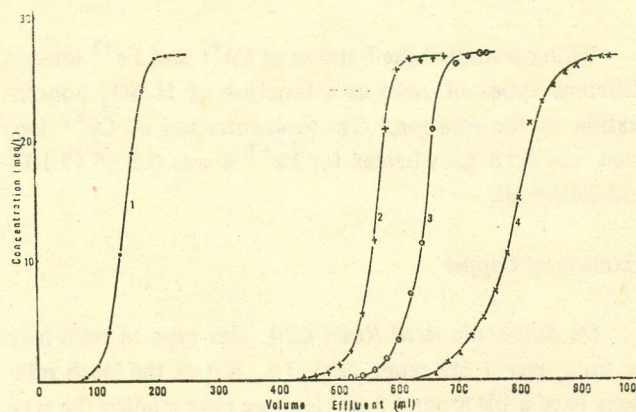Fig. 6. Fixation of Fe^{3+} on sulphonic acid resin Duolite C20 (H^+) at different concentrations of sulphuric acid (1) 5.10^{-1} (2) 5.10^{-2} (3) $1.5.10^{-2}$ (4) 5.10^{-3} M. Column : section 0.92 cm^2 bed height 6.7 cm, flow rate 0.8 ml min^{-1} cm^{-2}.

ranges between $0.5 - 5.10^3$ M (pH 0–2). From this figure it may be observed that the fixation of Fe^{3+} is better than that of Cu^{2+} ions. The column was the same as that used for fixation of Cu^{2+}. One may also note the change in the shape of the curves.

The Weak Resins (CC3, ES 466, ES 467). As in the case of Cu^{2+}, the fixation of Fe^{3+} on these resins in the H^+ form is very slight. When these resins are put in the NH_4^+ form, a precipitation of the hydroxy complexes of iron in the column is observed. Therefore, this study was not pursued.

Conclusion. From the above experimental evidence it may be concluded that only C20 resin may be usefully used for the fixation of Cu^{2+} at the pH encountered in industrial solutions. The other resins considered here may be used effectively for the treatment of dilute solutions at higher pH values.

Separation of Cu^{2+} and Fe^{3+}. This may be considered in two ways: (1) enrichment by frontal analysis, and (2) regeneration or elution separation.
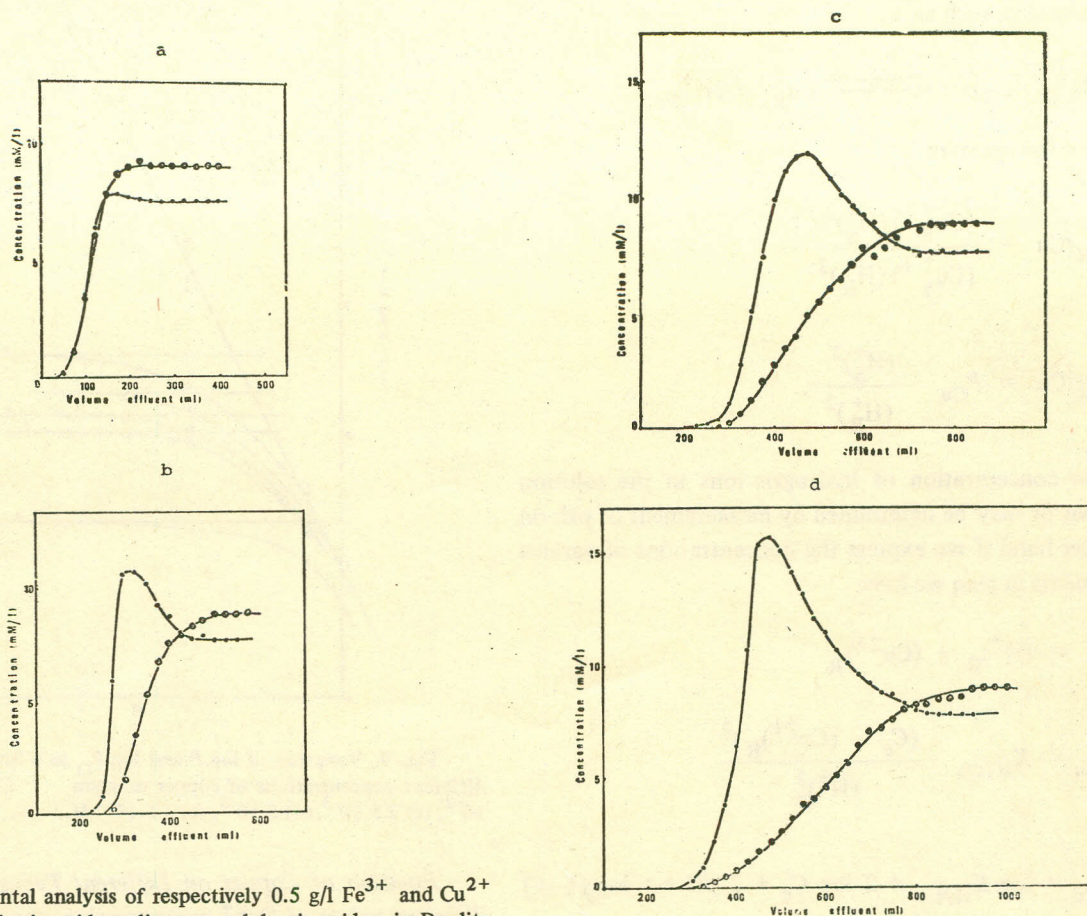
a

b

c

d

Fig. 7. Frontal analysis of respectively 0.5 g/l Fe^{3+} and Cu^{2+} mixture in sulphuric acid medium on sulphonic acid resin Duolite C20 (H^+): (a) 5.10^{-1}, (b) 5.10^{-2}, (c) $1.5.10^{-2}$, (d) 5.10^{-3} M. Column: section 0.92 cm^2, bed height 6.7 cm, flow rate 0.8 ml min^{-1} cm^{-2}
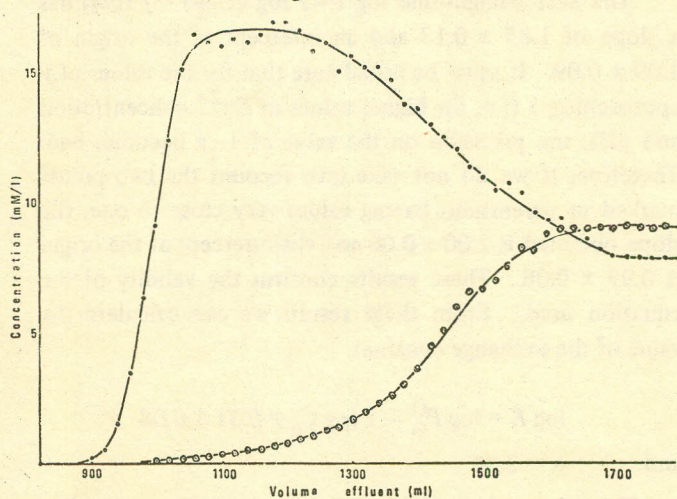

Fig. 8. Frontal analysis of 0.5 g/l Fe^{3+} – Cu^{2+} mixture in 5.10^{-3} M sulphuric acid on sulphonic acid resin Doulite G20 (H^+). Column: section 0.96 cm^2, bed height 17 cm, flow rate 0.83 ml min^{-1} cm^{-2}.

Frontal Analysis of a Mixture of Cu^{2+}: Fe^{3+} on Resin C20. We have studied the separation of Cu^{2+} and Fe^{3+} ions by frontal analysis. The feed solution contained 0.5 g/l each of Cu^{2+} and Fe^{3+} and 5.10^{-1} to 5.10^{-3} M H_2SO_4. The resin used was the sulphonic acid C20 in a column con-

taining 6.1 ml resin in the hydrogen form. The results obtained are shown in Figure 7 (a – d). A similar experiment was conducted on a longer column containing 16.2 ml resin and the results are shown in Fig. 8.

From these figures it is seen that the fronts of Cu^{2+} and iron leave the column practically at the same time but with increasing pH they become separated. It may also be seen that a complete separation is not possible but the quantity of Fe^{3+} in the concentrated copper solution may be diminished and controlled. This effect is more pronounced on the longer column.

Separation by Elution or Regeneration. Elution by H_2SO_4 in cocurrent and countercurrent systems was tried but it was found that the separation was not possible. The use of complexing agents such as citric acid gave better results. Gradual elution with a mixture of H_2SO_4 and H_3PO_4 was much more successful but further work in this direction was discontinued as this introduced a new chemical reagent into the scheme.

INTERPRETATION OF RESULTS

If we consider the ion exchange equilibrium between a resin in hydrogen form and a concentrated acid solution

of copper ions, such as

$$2 H^+_R + Cu^{2+}_S \xrightarrow{\hspace{1.5cm}} Cu^{2+}_R + 2H^+_S$$
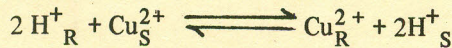
with the constant

$$K_{H/Cu} = \frac{(Cu^{2+}_R)(H^+_S)^2}{(Cu^{2+}_S)(H^+_R)^2}$$

or

$$K_{H/Cu} = P_{Cu}\frac{(H^+_S)^2}{(H^+_R)^2}$$

The concentration of hydrogen ions in the solution is known or may be determined by measurement of pH; on the other hand if we express the concentrations of various constituents in meq we have

$$C_e = (H^+)_R + (Cu^{2+})_R$$

or

$$P_{Cu} = K_{H/Cu}\frac{(C_e - (Cu^{2+})_R)^2}{(H^+)^2_S}$$

or

$$\log P_{Cu} = \log K_{H/Cu} + 2\log C_e + 2\,pH + 2\log(1-y)$$

The plot $\log P_{Cu} - 2\log(1-y) = f(pH)$ is a straight-line with a slope of 2 and an intercept at the origin of $\log K_{H/Cu} + 2\log C_e$.

If the concentration of H^+ in solution is not known, one may write

$$C_O = (H_S) + (Cu^{2+}_S)$$

or

$$(H^+_S) = C_O - (Cu^{2+}_S)$$

and

$$\log P_{Cu} = \log K_{H/Cu} + 2\log C_e + 2\log\frac{1-y}{1-x} - 2\log$$

In the limiting case, of P_O is called the limiting distribution coefficient

$$\log P_{Cu} = \log P_O + 2\log\frac{1-y}{1-x}$$

C_O, total concentration of an ion in solution,
C_e, total capacity of the resin in the column,
P, distribution coefficient,
P_O, distribution coefficient in the limiting case,
P_O, ordinat at the origin,
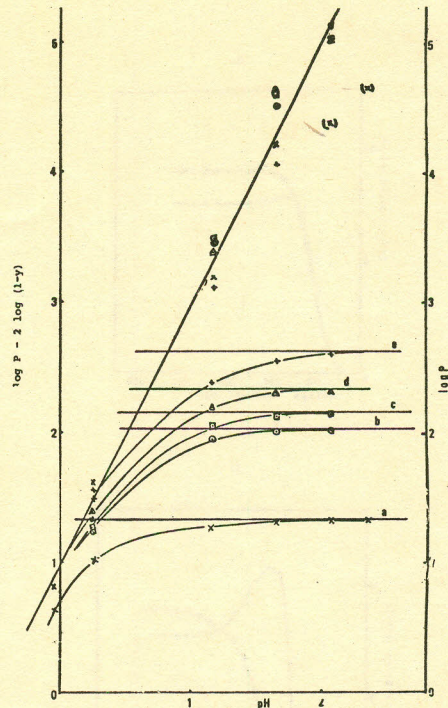$K_{H/Cu}$, $K_{H/Fe}$ equilibrium constants for H–Cu, H–Fe exchange when H is in the resin initially.

Fig. 9. Variation of $\log P$ and $\log P_O$ as a function of pH for different concentrations of copper on resin C20 (a) 10^{-2}, (b) 10^{-2}, (c) $2.5\cdot10^{-3}$, (d) $5\cdot10^{-3}$, (e) $1.5\cdot10^{-3}\,M$.

Fixation of Copper on Different Types of Resin. For different values of Cu^{2+} concentration, the values of P and P_O obtained as a function of pH are reported in Fig. 9.

The best straight-line $\log P - 2\log(1-y) = f(pH)$ has a slope of 1.85 ± 0.13 and an intercept at the origin of 1.09 ± 0.09. It must be noted here that for the values of y approaching 1 (i.e. for higher values of Cu^{2+} concentration and pH), the precision on the value of $1-y$ becomes bad. Therefore, if we do not take into account the two points marked in parenthesis having values very close to one, the slope obtained is 2.00 ± 0.06 and the intercept at the origin is 0.99 ± 0.08. These results confirm the validity of the equation used. From these results we can calculate the value of the exchange constant.

$$\log K = \log P^O_O - 2\log C_e = 0.31 \pm 0.08$$

and $K = 2.04$

The values of the slope and intercept at the origin for the other three resins are as follows:

CC 3 slope 2.43 ± 0.68; -3.32 ± 1.46 intercept
ES 466 slope 1.27 ± 0.11; -0.83 ± 0.31 intercept
ES 467 slope 0.32 ± 0.13; -0.39 ± 0.27 intercept

Fixation of Iron on C20. We have tried to explain the fixation of Fe^{3+} by the equation:

$$\log P = \log K + 3\log C_e + 3\,pH + 3\log(1-y)$$

but it was found that it did not correspond with the experimental results obtained. Therefore, we postulated the fixation of hydroxy complexes of iron such as $Fe(OH)^{2+}$ $Fe(OH)^+$ or $Fe_2(OH)_2^{2}$. Having tried the different equations, it appeared that the iron enters into the exchange reaction most probably in the form $Fe(OH)^{2+}$. The results obtained according to the equation.

$$\log P = \log K + 2 \log C_e + 2 \text{ pH} + 2 \log (1-y)$$

are presented in Fig. 10. From this figure it appears that the equation is generally well followed but for higher concentrations of iron and at higher pH values it is the complex $Fe(OH)_2^+$ (less charged complex) which is fixed, while at lower concentrations of iron and lower pH the hydroxy complexes are mostly destroyed and it is Fe^{3+} ions which are fixed. It appears, therefore, that the iron fixes with an average charge of about 2.

Under these circumstances the straight-line $\log P - 2 \log (1-y)$ has a slope of 1.97 ± 0.17 and an intercept at the
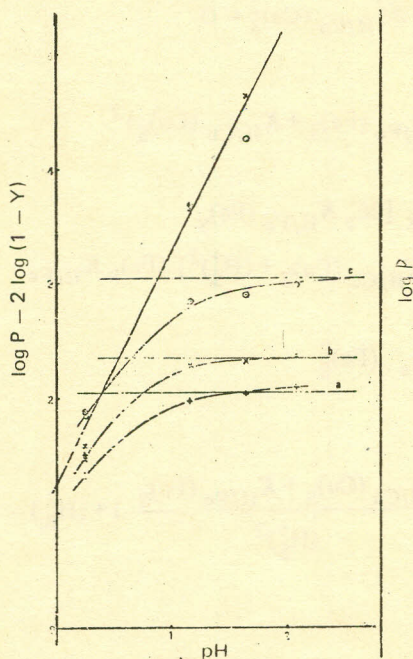

Fig. 10. Variation of $\log P$ and $\log P_O$ as a function of pH for different concentrations of iron on resin C20: (a) 10^{-2}, (b) 5.10^{-2}, (c) 10^{-3} M.

origin of 1.268 ± 0.22. The value of K obtained is 3.72.

Separation of Cu^{2+} and Fe^{3+}. As we have seen earlier the iron is fixed by the resin as a hydroxy complex of the form $Fe(OH)^{2+}$. Therefore, the resin can fix three ions out of which two have a charge of two, i.e. Cu^{2+} and $Fe(OH)^{2+}$ and one has a charge of one, i.e. H^+.

The fixation of each of these ions is dependent on the presence of the other two. The quantities of each of the ions fixed may be calculated from a second degree equation

developed for this purpose.

These equations may not be very precise, the cause being the different forms of iron being fixed at different values of pH. However, they may be utilized at least semi-quantitatively to calculate the quantities of the different ions fixed.

CONCLUSION

It may be observed that only the sulphonic acid type resin may be used for the concentration and purification of copper solutions because it is the only resin which may be used profitably at the pH of the leach solutions. The concentration of these solutions may be effected either in a fixed column or by a countercurrent system.

With all the resins tested the iron is better fixed than copper, therefore, the purification and separation of copper and irron may not be possible in a single operation. However, copper specific resins or resins with copper specific reagents (as used in liquid—liquid extraction of copper) fixed on them, may be helpful in obtaining the two objectives in one step.

In the case of dilute solutions containing less than 1 g/l of copper, the concentration may be done on ion exchange resins followed by a separation step by liquid extraction.

REFERENCES

1. J. S. Jacobi, International Symposium on Unit Processes in Hydrometallurgy, Texas (1963), p. 617.
2. A. Sopkova, K. Vetejska and J. Buhanec, J. Chrom., **102**, 403 (1974).
3. M. J. Slater, Canad. J. Chem. Engg., **52**, 43 (1974).
4. I. M. Abrams, R.C. Knuff and C.J. Lewis, French Patent 433,760 (1966).
5. B. M. Laskorin *et al.* Tsvet Metal, **42**, 30 (1969).
6. M. J. Slater, J. Appl. Chem. Biotechnol., **25**, 367 (1975).
7. V.J. Pimenov and Startsev, Cvtn. Metal., **8**, 9 (1972).
8. J. O. Dasher and S. Nasher, Canad. Patent 584,315 (1959).
9. K. Hussain and M. Rumeau Informations Chimie, **171**, 247 (1977).

ANNEXURE

The distribution coefficient P is defined as the ratio between the concentration of an ion in the resin and solution:

$$P_M = \frac{(M)_R}{(M)_S}$$

The difficulty which is generally encountered in the calculation of P_M is that one does not know the value of $(M)_R$. For this purpose the following relations may be employed:

In case of Cu – H exchange, the material balance in the resin

$$C_e = Cu_R + H_R \quad (1) \text{ where } C_e \text{ is the total}$$
capacity of the resin

or $H_R = C_e - Cu_R$

on the other hand, we have

$$K_{H/Cu} = \frac{Cu_R}{Cu_S} \cdot \frac{H_S^2}{H_R^2} \quad (2)$$

or $\dfrac{Cu_R}{Cu_S} = \dfrac{1}{K_{H/Cu}} = \dfrac{H_R^2}{H_S^2} = \dfrac{(C_e - Cu_R)^2}{H_S^2}$

or $Cu_R = \dfrac{Cu_S \cdot K_{H/Cu} (C_e - Cu_R)^2}{H_S^2}$

$$Cu_R \cdot H_S^2 = Cu_S K_{H/Cu} (C_e^2 + Cu_R^2 - C_e Cu_R)$$

or $Cu_R^2 Cu_S K_{H/Cu} - Cu_R (H_S^2 + 2 C_e Cu_S K_{H/Cu}) +$

$Cu_S K_{H/Cu} C_e^2 = 0.$

which is a second degree equation in Cu_R. P_M may be obtained by inserting the value of Cu_R. The value of the equilibrium constant $K_{H/Cu}$ may be determined experimentally.

When there are three ions present in the solution, i.e. copper, iron and hydrogen, the fixation of each of these ions is dependent on the presence of the two. However, the quantities of each of them present in the resin at equilibrium may be calculated from the relations below:

$$K_{H/Fe} = \frac{(Fe)_R}{(Fe)_S} \cdot \frac{(H_S^+)^2}{(H_R^+)^2} \quad \text{(considering the fixation of iron as a doubly charged hydroxy complex as explained earlier)}$$

$$K_{H/Cu} = \frac{(Cu)_R}{(Cu)_S} \cdot \frac{(H_S^+)^2}{(H_R^+)^2}$$

and the material balance in the resin

$$C_e = (Cu)_R + (Fe)_R + (H^+)_R$$

The equations obtained for the three ions in the resin are found to be: for Cu_R

$$(Cu_R)^2 [K_{H/Cu}(Cu)_S + K_{H/Fe}(Fe)_S]^2$$

$$- (Cu)_R [2C_e K_{H/Cu}(Cu)_S$$

$$+ 2C_e K_{H/Fe}(Fe)_S + (H_S^+)^2] K_{H/Cu}(Cu)_S$$

$$+ C_e^2 \cdot K_{H/Cu}^2 (Cu)_S^2 = 0$$

for $(Fe)_R$

$$(Fe)_R^2 [(K_{H/Fe}(Fe)_S + K_{H/Cu}(Cu)_S]^2$$

$$- (Fe)_R [2C_e K_{H/Fe}(Fe)_S$$

$$+ 2C_e K_{H/Cu}(Cu)_S + (H_S^+)^2] (Fe)_S K_{H/Fe}$$

$$+ C_e^2 \cdot K_{H/Fe}^2 \cdot (Fe)_S^2$$

and for H^+

$$(H_R^+)^2 \left(\frac{K_{H/Cu}(Cu)_S + K_{H/Fe}(Fe)_S}{(H_S^+)^2} \right) + (H_R^+) - C_e = 0$$