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RECOVERY OF COPPER AND ZINC FROM MINE WASTE EFFLUENTS WITH CARBOXYLIC-TYPE ION-EXCHANGE RESINS

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EXTRACTION METALLURGY DIVISION

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RECOVERY OF COPPER AND ZINC FROM MINE WASTE EFFLUENTS WITH CARBOXYLIC-TYPE ION-EXCHANGE RESINS

by

A. J. Gilmore*

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ABSTRACT

The recovery of copper and zinc from synthesized mine waste effluents containing up to 7.0 g/l of total metal with the Rohm and Haas Limited carboxylic-type resins Amerlite IRC 50 and IRC 84 has been investigated. The adsorption characteristics of the resins from the Na^+, NH_4^+ and H^+ forms at feed pH values of from 3.6 to 6.0 were determined. The results of the work showed that under all conditions investigated the metals broke through very early in the adsorption cycle. An ion exchange operation run under these conditions to produce an effluent containing <0.1 ppm of metal could be expensive, due to high capital cost in equipment and resin inventory.

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Direction des mines

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RÉCUPÉRATION DU CUIVRE ET DU ZINC CONTENUS DANS LES EFFLUENTS DE MINES À L'AIDE DE RÉSINES ÉCHANGEUSES D'IONS DU TYPE CARBOXYLÉ

par

A. J. Gilmore*

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RÉSUMÉ

L'auteur a étudié la récupération du cuivre et du zinc contenus dans des effluents de mines préparés artificiellement, avec des concentrations allant jusqu'à 7.0 g/l de métal total, à l'aide des résines de type carboxylé Amerlite IRC 50 et IRC 84, produites par la Rohm and Haas Limited. Il a déterminé les caractéristiques d'adsorption des résines de type Na^+, NH_4^+ et H^+, pour des valeurs de pH de la solution d'alimentation allant de 3.6 à 6.0. Les résultats de ce travail montrent que, dans les conditions d'expérience considérées, les métaux arrivent à filtrer presque dès le début du cycle d'adsorption. L'emploi industriel d'un procédé d'échange d'ions dans ces conditions en vue d'obtenir un effluent contenant moins de 0.1 ppm de métal pourrait être très onéreux, en raison du coût élevé des immobilisations requises en installations et en stocks de résines.

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INTRODUCTION

Recently, the Hydrometallurgy Section of the Extraction Metallurgy Division, Mines Branch, Ottawa, has been studying the feasibility of applying ion exchange methods to the removal of metals, such as copper, zinc and nickel, from acid sulphate waste solutions produced in mining and metallurgical operations. A literature review[1] done in connection with this study program indicated that the carboxylic-acid-type resins might be suitable for this application.

Several studies have been made in which Rohm and Haas Amberlite IRC 50 and Permutit H 70 resins were used to extract copper from dilute acid mine water[2,3], and copper from dilute concentrations of copper and zinc in weak acid media[3]. The reports of these investigations showed that about 90% of the copper present in a solution containing ≈0.3 g Cu/l at pH 4.0[3] could be adsorbed on these resins. It was also reported that similar copper extraction could be achieved from solutions of similar acidity containing up to 0.3 g Cu and Zn per litre with a carboxylic resin. The adsorbed copper was removed from the resin with 5 to 10% sulphuric acid solution. The resin had to be converted to the sodium or calcium form after elution and before adsorption. The resin was reported to be highly sensitive to pH, with practically no metal being adsorbed at pH 2.0 or lower[4].

In view of the information available in the literature, it was decided to conduct some bench scale work to develop typical adsorption curves for carboxylic-type resins in the pH range of 4.0 to 6.0. From these curves the feasibility of using these resins for producing essentially metal-free solution from copper-, nickel- or zinc-bearing mine water could be determined. This report is an account of this study.

PROCEDURE

Rohm and Haas Amberlite IRC 50 and IRC 84 carboxylic-type resins were tested with bench-scale, fixed-bed columns containing five or ten millilitres of wet settled resin. The cross sectional area of the columns was such that the resin depth in all tests was about 10 cm. The flow rates used were such that retention times of from two to eight minutes were investigated. At the beginning of adsorption the resin was in each of the Na^+, NH_4^+ or H^+ forms.

The feed solutions for this work were synthetic and contained copper, zinc and magnesium sulphates. The pH value of the solution was adjusted by adding sulphuric acid. Two solutions were used during the test work: one containing 0.5 g/l Cu, 6.25 g/l Zn and 6.75 g/l Mg, and the other containing 0.02 g/l Cu, 0.25 g/l Zn and 0.35 g/l Mg.

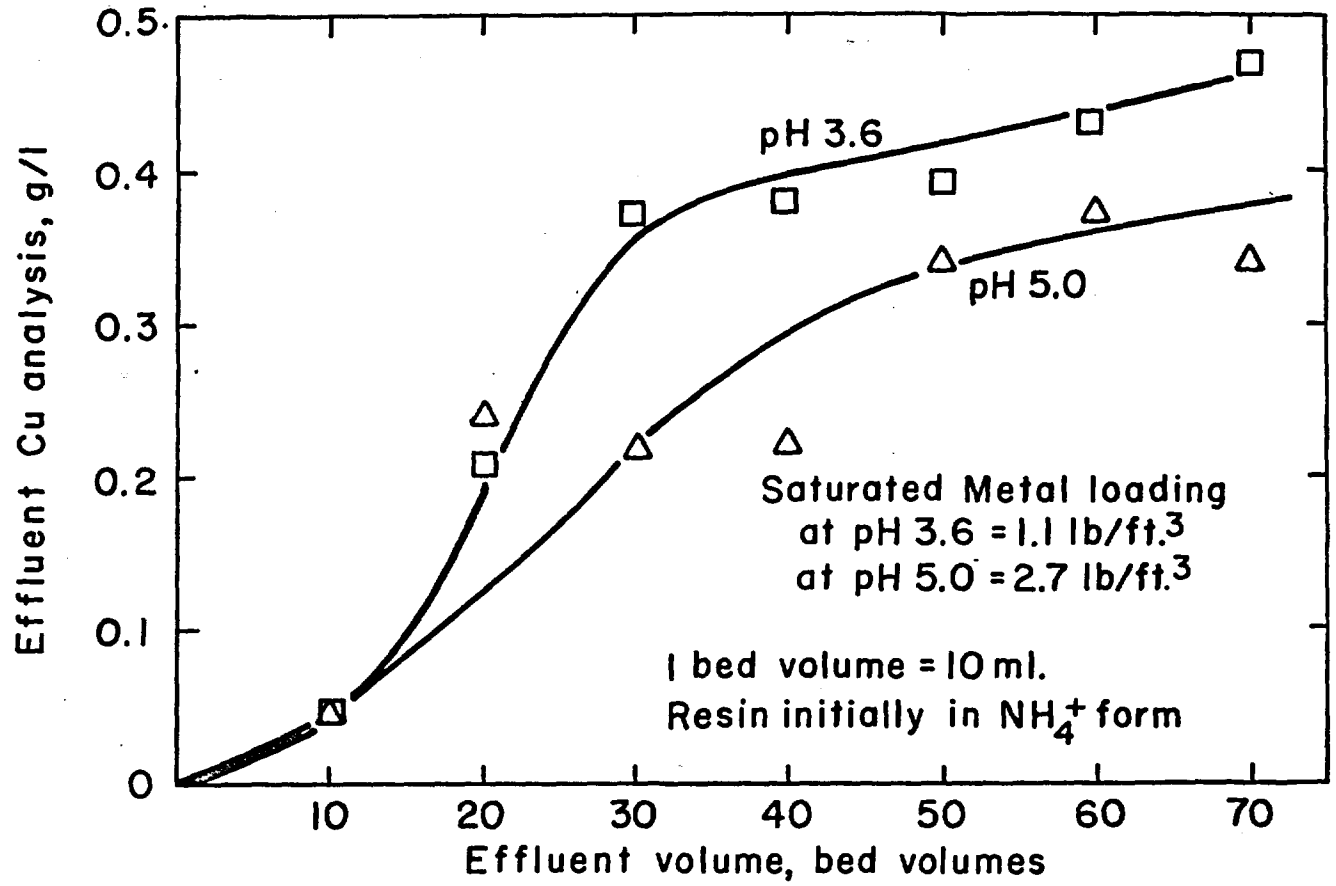
RESULTS

In the first series of tests, the two resins IRC 50 and IRC 84 were converted to either the Na^+ or NH_4^+ form and loaded

with a solution containing 0.5 g/l Cu, 6.25 g/l Zn and 6.75 g/l Mg. The pH values of the feed solutions were either 3.6 or 5.0. The retention time used in all of the tests in this series was 2 min. The adsorption curves for IRC 50 obtained in this work are shown in Figure 1. The results obtained with IRC 84 were inferior to those of IRC 50 and are not reported.

Figure 1 shows that when the IRC 50 is in either the Na^+ or the NH_4^+ form, copper breakthrough is early in the loading cycle. This characteristic obviously makes the resin in these forms unsuitable for reducing efficiently the metal content of waste solution to a level acceptable for disposal to the environment. Further tests with increased retention time did not provide significantly better results.

Another objection to the use of the IRC 50 in the Na^+ or NH_4^+ form was that the metal adsorbed by the resin could only be desorbed efficiently by sulphuric acid. Consequently, if the resin was to be loaded in the Na^+ or NH_4^+ form, it would be necessary to convert the resin from the H^+ form it is in after desorption to the required alkaline form. Test work showed that not only was this an expensive procedure, but also it proved to be very difficult to remove excess alkalinity from the converted resin, and precipitation of metals during adsorption was the result. This difficulty was observed by Jacobi[2].



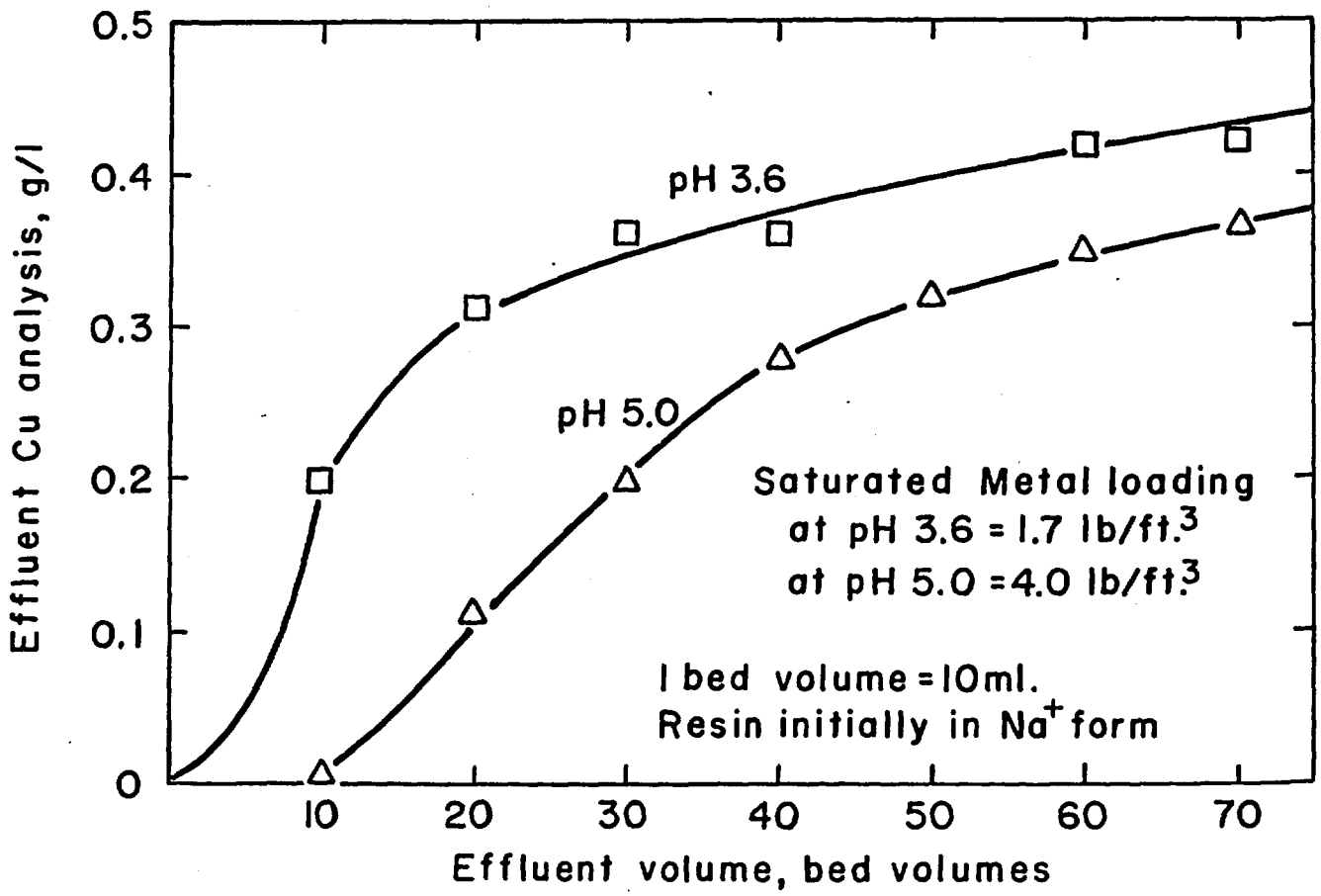


Figure 1. Copper adsorption on Amberlite IRC 50 resin in the Na^+ or NH_4^+ form.

In view of the results obtained with the resin in an alkaline form, a series of tests was done in which the resin was initially in the H^+ form and the retention time used was 8 minutes. Both IRC 50 and IRC 84 were investigated. The feed solution analyzed 0.02 g/l Cu, 0.25 g/l Zn, and 0.35 g/l Mg. These concentrations were chosen because it had been determined that the metals would not precipitate from this solution at the highest pH value investigated in this work. The pH values of the feed solutions were 4.0, 5.0, and 6.0. The results of this work, which are shown in Figure 2, show that with the resins in the H^+ form, copper breakthrough occurs early in the loading cycle. This is the same undesirable characteristic that was observed when the resins were loaded from either the Na^+ or the NH_4^+ form.

Only at pH 4.0 were the tests continued to full copper loading of the resin as indicated by the barren having the same copper analysis as the feed. With these conditions the loadings were 0.15 lb total metal/cu ft of IRC 50 and 1.0 lb total metal/cu ft of IRC 84. These are much lower loadings than were obtained with the resin in the Na^+ or NH_4^+ forms (Figure 1).

CONCLUSIONS

The carboxylic-type ion-exchange resins, Rohm and Haas Amberlite IRC 50 and Amberlite IRC 84, are unsuitable for reducing efficiently the copper and zinc concentrations of acid sulphate waste streams to levels of <1 ppm, for the following reasons:

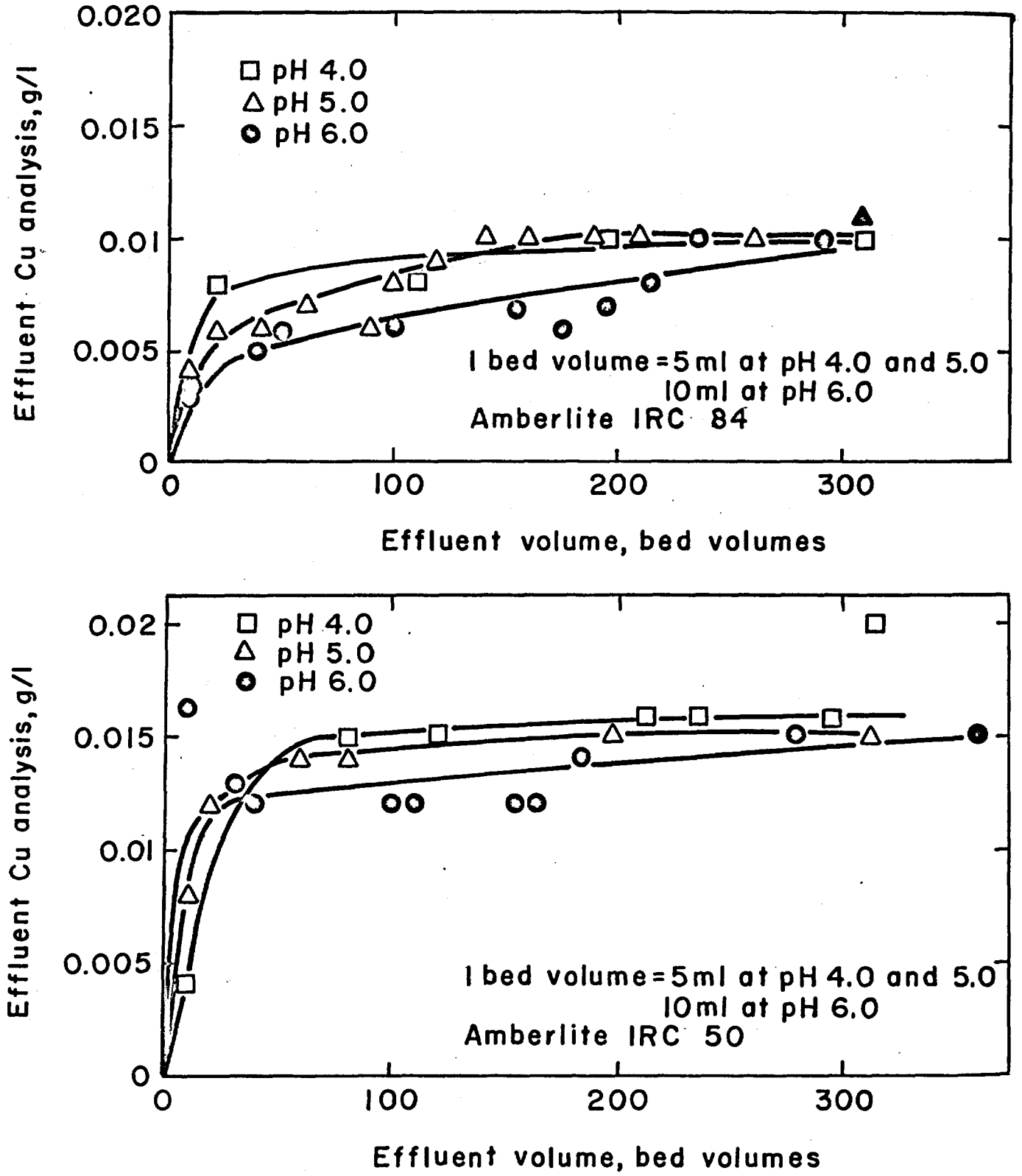


Figure 2. Copper adsorption on Amberlite IRC 50 and Amberlite IRC 84 in H^+ form.

(1) On adsorption, excessive metal values report in the effluent too early for an ion exchange system based on these resins to be efficient. The early breakthrough occurs regardless of whether the resin is in the Na^+, NH_4^+ or H^+ forms.

(2) Although loadings of up to about 4.0 lb metal/cu ft of resin were obtained on IRC 84, initially in the Na^+ form, the metal had to be desorbed with sulphuric acid and then reconverted to the Na^+ form. This is cumbersome and expensive.

(3) Loadings on these resins from the H^+ form are too low ($\leq$ 1.0 lb/cu ft) for an efficient operation.

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REFERENCES

1. A.J. Gilmore (1970), "Ion-Exchange Recovery of Copper, Zinc and Nickel from Acid-Sulphate and Alkaline-Cyanide Waste Water", Mines Branch Information Circular IC 252, Canada Dept. of Energy, Mines and Resources, Ottawa, Canada. 21 pp.

2. J.S. Jacobi (1963), "The Recovery of Copper from Dilute Process Streams", in Unit Processes in Hydrometallurgy, Vol. 24 of Metallurgical Society Conferences, A.I.M.E. (Gordon and Breach Science Publishers, Inc., New York), pp. 617-642.

3. T.A.A. Quarm (1954-1955), "Recovery of Copper from Mine Drainage Water by Ion Exchange", Transactions, Institution of Mining and Metallurgy (London), 64, pp. 109-117.

4. E.J. Breton and A.W. Schlechten (1951), "Separation of Copper and Zinc by Ion Exchange", Transactions A.I.M.E., Journal of Metals, 191, pp. 517-521.

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