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SEPARATION OF COPPER AND ZINC FROM WASTE ACIDIC MINE EFFLUENTS OF RIO TINTO AREA

by

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ABSTRACT

A study of removal of Copper and Zinc from acidic mine effluents by means of chelating ion exchange resins has been carried out. The effluents having pH ranging from 1.7 to 1.9, contain mainly iron, copper and zinc and some other elements at much lower concentrations. The study includes chemical characterisation of effluents samples, the assessment of chelating resins and their selectivity for the separation of copper and zinc. Chelating resins containing either carboxylic, phosphoric or/and amine groups have been employed. The results obtained are correlated to the specific metal-complexing group attached to the polymer matrix. Resins containing carboxylate groups were found to provide most selective copper/zinc separations. A conceptual flowsheet of the separation process based on the data obtained for treating the effluents with different resins is presented.

INTRODUCTION

Mine effluents are one of the generic origins of metal-bearing wastes. Among these effluents, acidic mine water containing large amounts of iron, zinc and copper proceed typically from pyritic ores (Ritcey, 1989). On the other hand, the recovery of zinc and copper have been considered to have a relatively high priority based upon the environmental risk and reserve depletion rate (Patterson, 1987).

Convention technologies for metal separation are based on precipitation processes or a combination of oxidation or reduction/precipitation. Recognised and emerging technologies includes ion exchange, membrane separation, differential precipitation, solvent extraction and selective adsorption. Among them,ion exchange is a well established technology that is specially suitable for treatment effluents of low metal concentration or produced at high flowrate (Warshowsky, 1984). Its potential for metals pollution control is well recognised, however although its applications are quite limited.

The aim of the present work is to provide a basic knowledge of the chemical characteristics of some mine effluents of Rio Tinto area as well as the possibility of using some selective resins for the removal of toxic and valuable metals, specially copper and zinc.

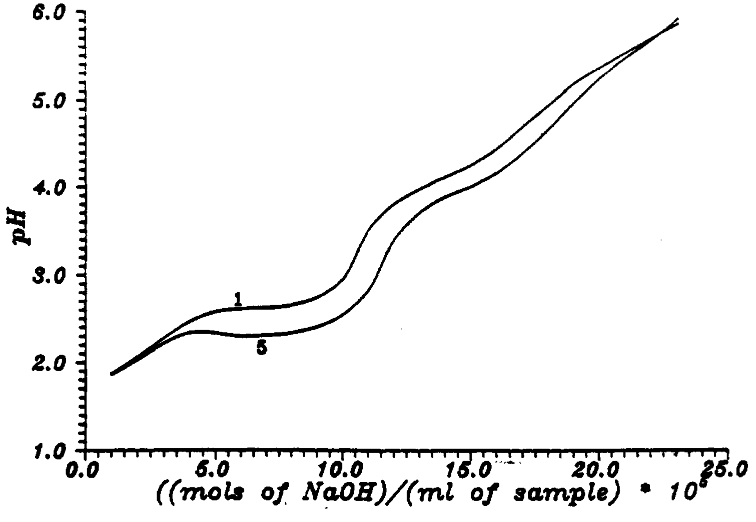

Figure 1 Acid Base Titrations of Sample 1 for Different Reaction Time Intervals (1 and 5 Minutes)

RESULTS AND DISCUSSION

Study of some chemical parameters

Mine effluents with different level of metal content were sampled to carry out the present study. Major metal components are Fe, Zn, Cu and Al, a typical composition is given in Table 1. Composition of these samples is not similar as they proceed from two different streams. The concentrations of different metal ions also vary seasonally. The stream is being produced at flowrate = 700,000m^3/year.

TABLE 1¯A TYPICAL METAL COMPOSITION OF THE SAMPLED EMPLOYED IN THE PRESENT WORK

	Sample 1 (ppm)	Sample 2 (ppm)
Fe(III)	3600	1300
Fe(II)	4700	1800
Cu	250	140
Zn	1800	520
Al	620	700
Mn	90	60
P	10	10
As	25	20

Experiments have been carried out to determine some chemical characteristics of effluents. In this sense the work includes:

(a) acid-base characteristics
(b) variation of metal content with pH
(c) effect of acidity on the redox potential

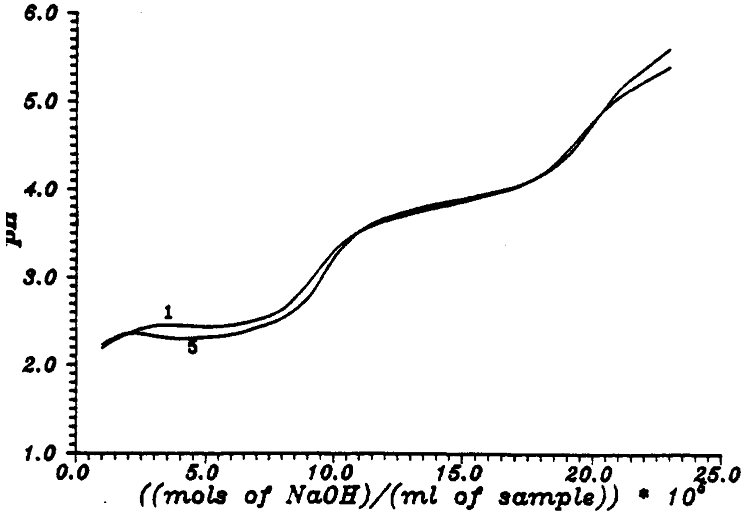

Figure 2 Acid Base Titrations of Sample 1 for Different Reaction Time Intervals (1 and 5 Minutes)

(a) Potentiometric acid-base titrations of the samples were carried out at different conditions by varying the reaction time interval between 1 and 5 minutes. Figures 1 and 2 show the results of these experiments where the response of the system is found to be quite fast, i.e. the pH variation is less

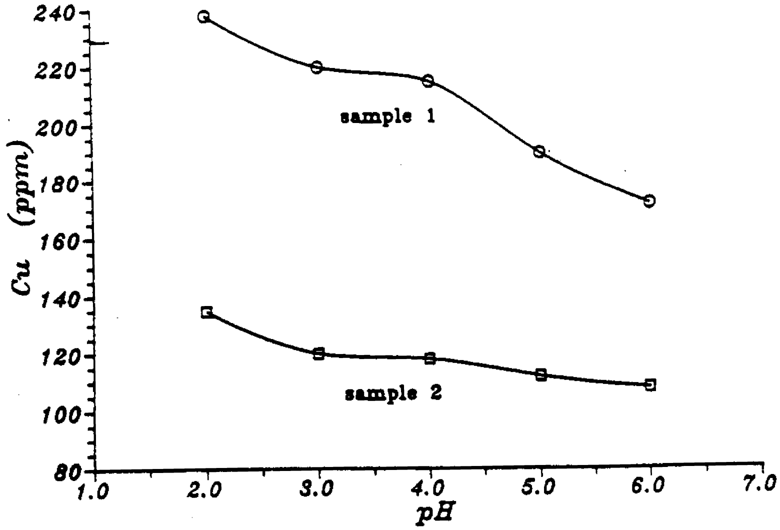

Figure 3 Effect of pH on Copper Concentration

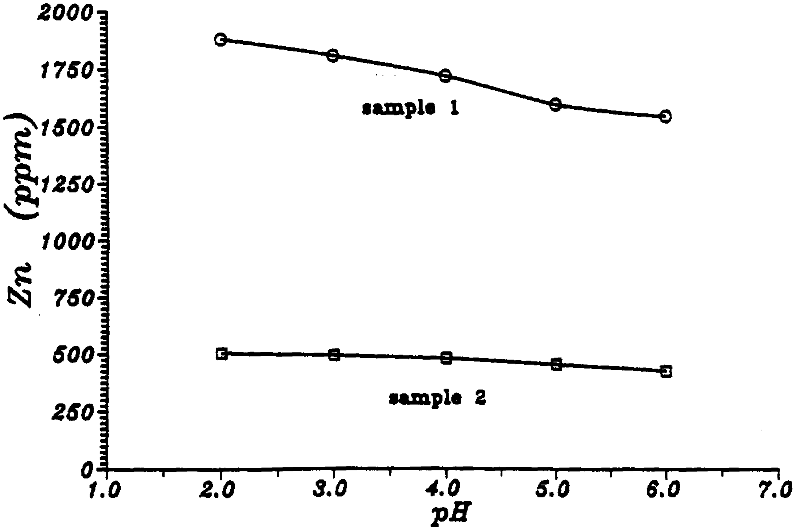

Figure 4 Effect of pH on Zinc Concentration

than 0.4 units for sample 1 and 0.1 for sample 2 during 5 minutes. From these data we can also determine directly the alkali needed to achieve a certain pH value directly.

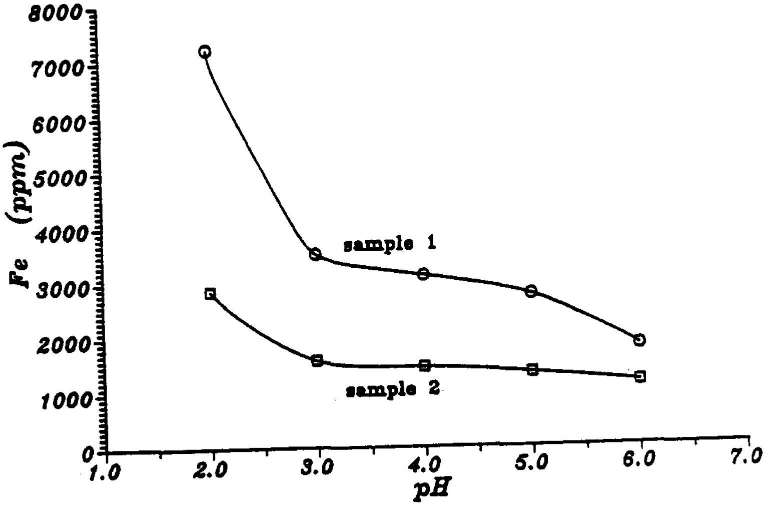

Figure 5 Effect of pH on Iron Concentration

(b) The metal content of the samples is observed to vary with pH. Figures 3 to 5 show the results obtained for the different samples in pH range between 2 and 6. As expected, the sharpest decrease corresponds to the decrease of Fe(III) concentration which, however, at pH = 6 still remains in solution due to the presence of Fe(II). On the other hand, the decrease for copper and zinc (less than 10%) may be due to a possible adsorption of these metal ions on the solid ferric hydroxide, a recovery of these adsorbed metals could be done by processing the solution resulting from thickening off the precipitate.

(c) Data collected in Figure 6 show the variation of the redox parameter pE with pH of the solutions. These data have been obtained by potentiometric titrations of the corresponding samples and measuring simultaneously the redox potential (using a Pt electrode) and the pH with a glass electrode. This information is of particular interest due to the important presence of the redox pair Fe(III)/Fe(II) besides the influence of this parameter on the interaction with some chelating systems.

A comparison of results obtained in b and c reveals that the precipitation of Fe(III) by increasing the pH of solution (Figure 5) provides a decrease of pE (Figure 6). In this sense, the differences observed between samples 1 and 2 are related to the different ratio Fe(III)/Fe(II) in the two samples, i.e. the decrease of pE observed between pH2 and 3 is of 0.3 units for sample 1 and 0.6 units for sample 2 which correspond to the logarithms of the respective decrease of iron concentration (mainly Fe(III)).

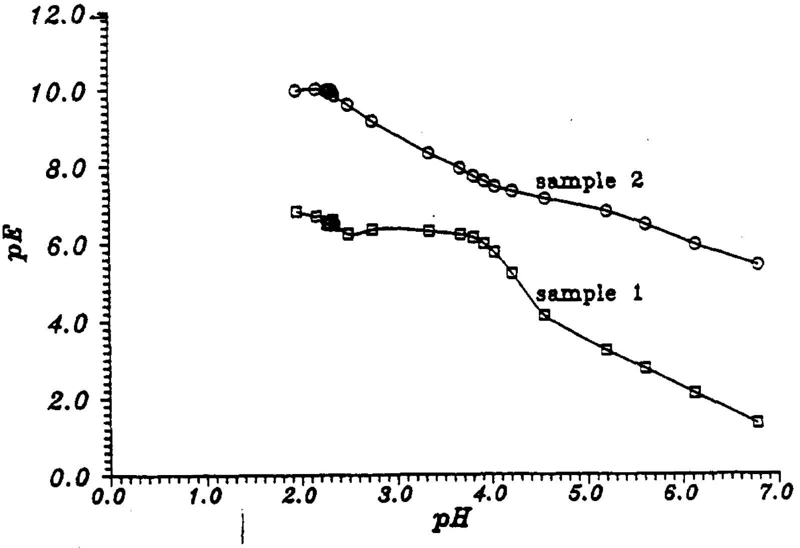

Figure 6 Variation of Radox Characteristics, pE with pH

Separation of Copper and Zinc by Chelating Resins

The separation of Cu(II) and Zn(II) from the acidic effluents has been studied by using two different chelating resins having functional groups of different chemical nature:

Resin A: $-CH_2 - NH - CH_2PO_3^{2} 2Na^+$
Resin B: $-CH_2 - N(- CH_2 - CH_2 - COO)_2^{2} 2Na^+$

The experimental procedure includes conditioning of the systems and separation of copper and zinc metal ions.

Taking into account the properties of the chelating resins as well as the observed characteristics of the mine effluents, condition of the systems was carried out by neutralising the basicity of the resins to acidic pH and the acidity of the effluent samples to pH range 3 to 4. The objective of this treatment was to increase the efficiency of the resins for the selective separation of copper and zinc. On the other hand, the increase of pH of the samples contributes to the removal of Fe(III) by precipitation of corresponding hydroxide.

After conditioning the system,, the samples were treated by the chosen resins. These experiments were carried out in columns containing adequate resins beds. The samples were introduced in the column by a peristaltic pump at a determined flow rate. Periodical analysis of the end-of-pipe solution were carried out to determine the separation efficiency. The results of these experiments are

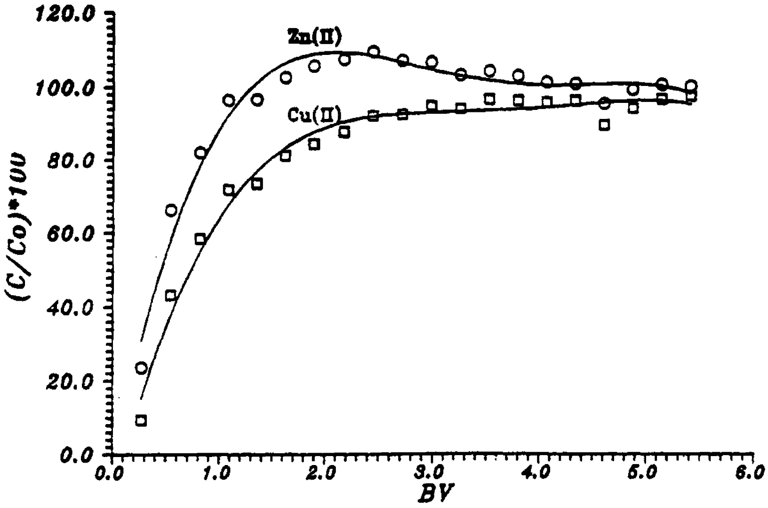

Figure 7 Results Obtained by Using Resin A. Treatment of Sample 1

collected in Figures 7 to 10 and have been expressed in terms of per cent of metal absorbed vs. bed volume (BV).

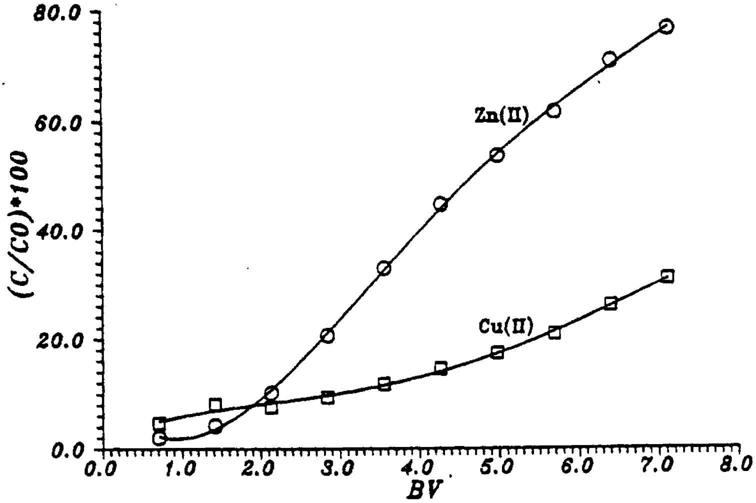

Figure 8 Results Obtained by Using Resin A. Treatment of Sample 2

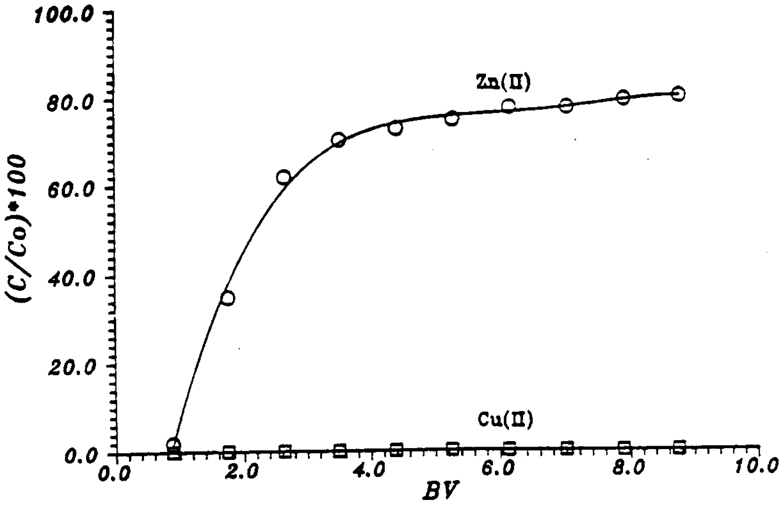

Figure 9 Results Obtained by Using Resin B, Treatment of Sample 1

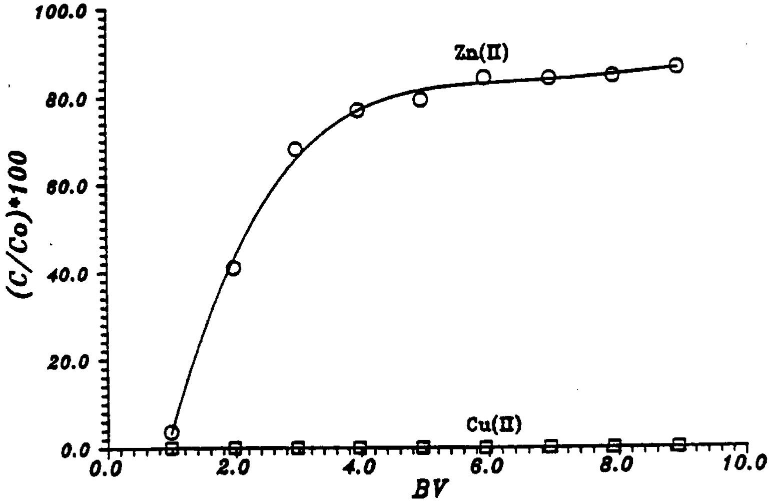

Figure 10 Results Obtained by Using Resin A. Treatment of Sample 2

Data obtained by using resin A are in Figures 7 and 8 corresponding to samples 1 and 2 respectively. As observed, the metal uptaken is very poor and differences observed between samples is related to the amount of metal contained.

Figures 9 and 10 show the results obtained by using resin B. In this case separation of copper is very effective (>99% in both samples) and selective with respect to zinc. No remarkable differences are observed between the two samples.

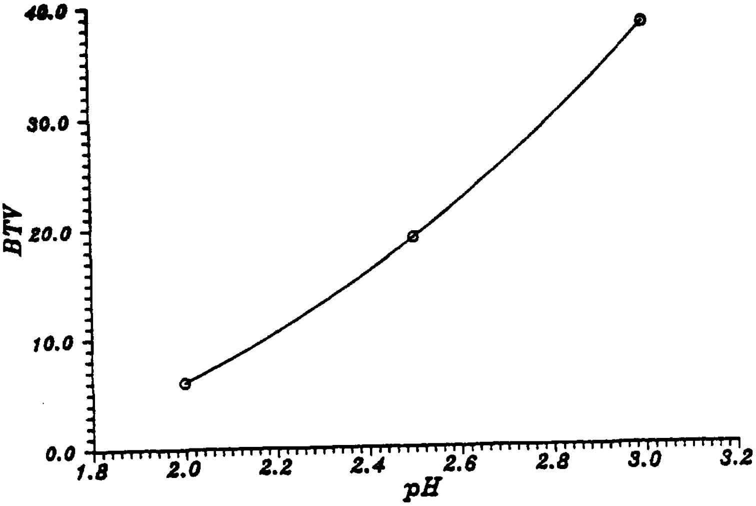

Figure 11 Effect of pH on the Breakthrough Volume, BTV Treatment of sample 1 by Using Resin B

The efficiency of resin B has been studied with respect to two important parameters: the working pH and the linear flow rate. The results obtained are shown in Figures 11 and 12. These results have been expressed in terms of the break-through volume (BTV) which is the BV value where the metal begins to pass through the column. As observed in Figure 11 the efficiency of the resin is very sensitive with respect to pH, so, the control of this parameter will be extremely important for the recovery of copper. On the other hand, the effect of the linear flow rate is shown in Figure 12. As seen the linear velocity has a strong effect on the BTV which increases four times by reducing a 35% the linear velocity.

The results described above show that resin B, bearing carboxylate chelating groups, is capable of selectively separating the copper contained in the studied acidic mine effluents of Rio Tinto area by a small variation of their acidic pH. The efficiency of this process strongly depends on the working pH as well as on the linear flow rate. On the contrary, resin A containing organophosphate chelating groups has shown to be inacting to pick up copper or zinc metal ions from the acidic effluents.

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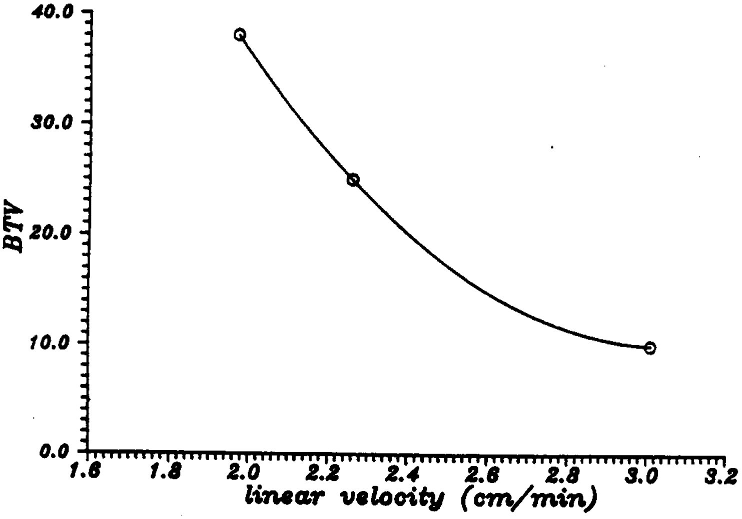

Figure 12 Influence of the Linear Flow Rate on the Breakthrough Volume, BTV, Treatment of Sample 1 by resin B

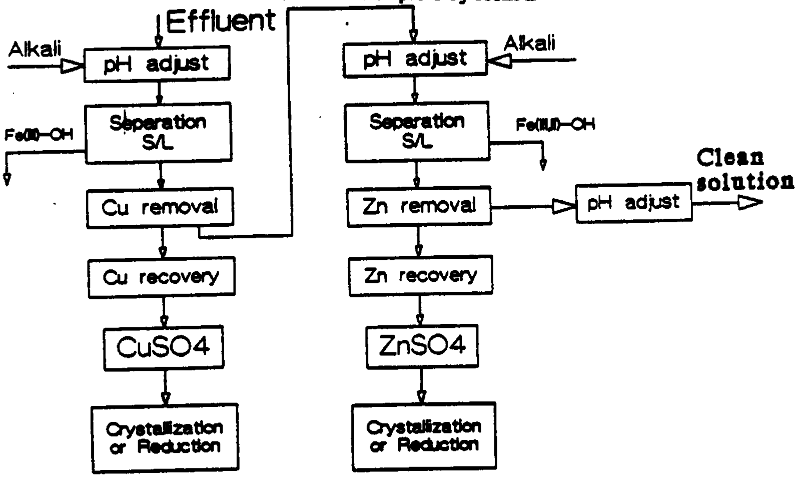

Figure 13 Conceptual Flowsheet for the Removal and Recovery of Copper and Zinc from Acidic Mine Effluents of Rio Tinto Area

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Taking into account the results obtained above this work, a conceptual flowsheet (see Figure 13) is suggested for the removal and recovery of copper and zinc.. The flowsheet appears as two main boxes columns which follow a similar step for the separation and recovery of copper and zinc respectively. Beginning with the adjust of pH using $Ca(OH)_2$, it follows a solid/liquid separation of the iron hydroxide precipitated, then removal of copper and zinc is achieved by using the resins described in this work. Recovery of the metals will be accomplished by elution with strong acid and them crystallization of the corresponding sulphate or electrolytic reduction of the metal.

This process is technically feasible. However we have not made any assessment for the process economy. Study of the process improvement and economic evaluation is under way.

ACKNOWLEDGEMENTS

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