# METALS REMOVAL FROM ACID MINE DRAINAGE BY ION EXCHANGE

## MEND Report 3.21.1(b)

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# METALS REMOVAL FROM ACID MINE DRAINAGE BY ION EXCHANGE

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WORK PERFORMED FOR:

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# *EXECUTIVE SUMMARY*

The extraction of Sb, Cd, Cu, Ni and Zn from acid mine drainage solutions using various ion exchangers was studied with batch and column tests. The extraction was studied at low pH, at mildly acidic pH and at neutral pH. The interference caused by the presence of Al, Ca, Mg and Fe was monitored.

It was found that most commercial ion exchangers do not exhibit a marked selectivity for the metals of interest. Consequently, the co-extraction of iron is a major obstacle for the application of ion exchange to acid mine drainage solutions. The selectivity did not improve significantly when Fe(III) was reduced to Fe(II). The co-extraction of calcium becomes a problem at higher pH when lime is used to neutralize the solution. The most promising results were obtained with copper and antimony, which were amenable to extraction even at low pH.

While the selective extraction of Cd, Ni or Zn was not feasible under most conditions, the simultaneous extraction of all three metals can be done at neutral pH using either a chelating resin or a synthetic zeolite. This fact could be used to reduce the amount of lime that is normally added to ensure the complete precipitation of metals.

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# 1 BACKGROUND

Most Canadian mining operations contain sulphide minerals, either in the ore or the surrounding waste rock. When these sulphide minerals, particularly pyrite and pyrrhotite, are exposed to oxygen and water, they begin to oxidize almost immediately. In the absence of calcareous materials, the initial chemical reactions produce acid, which liberates the heavy metals associated with the waste deposit. Bacteria and ferric iron catalyze the chemical reactions. Rainfall and snow melt flush the toxic solutions from the waste sites into the downstream environment.

Acid drainage solutions usually contain significant concentrations of base metals, such as cadmium, iron, lead, copper, zinc and nickel. If left untreated, the acid drainage can contaminate ground water and local watercourses, damaging the health of plants, wildlife and fish (Filion et. al, 1990).

The conventional method to treat acid drainage is lime neutralization (Figure 1). Normally, Fe(II) is oxidized to Fe(III) in order to enhance the precipitation of iron. Upon the addition of lime, calcium sulphate and metal hydroxides precipitate into a bulky sludge, which is allowed to settle and subsequently stored in ponds. Questions have been raised about the long term stability of the neutralization sludge; for example, metals may be leached out if exposed to acid rain over a long period of time (Penn Environmental Consultants, 1973). Another concern about lime neutralization is that the treated effluent has a high pH due to the excess of lime added to ensure the complete precipitation of all metals. A subsequent pH adjustment with acid may become necessary in the future to meet stricter limitations of effluent pH (see for example MISA regulations for Ontario beginning 1997).

Ion exchange is a mature technology and numerous metallurgical applications have been reported (Bolto and Pawlowski, 1987; Dorfner, 1990). The most important ion exchangers are synthetic polymeric resins to which specific active groups have been attached. Ion exchange resins are usually classified as anionic, cationic or chelating depending on the structure of the active groups. Inorganic ion exchangers, or zeolites, are also available. These are either natural or synthetic aluminosilicate minerals, which are usually less selective and have lower capacity than polymeric resins. However, in recent years considerable interest has been raised on the use of zeolites for the treatment of effluents due to their low cost and high resistance to harsh conditions (Dorfner, 1990).

In the case of acidic drainage, the bulk extraction of all metals, although technically feasible (Penn Environmental Consultants, 1973), is not economically attractive because the most abundant metals, i.e. iron, aluminum and calcium, have little value. By contrast, the selective extraction of some metals which are valuable and/or toxic may significantly improve the economic and environmental aspects of lime neutralization. This project addresses the selective extraction of metals, but does not propose the use of ion exchange as a replacement for lime neutralization.

Figure 2 shows how the conventional lime neutralization process could be improved by ion exchange stages. Specifically, removing some metals prior to lime neutralization, would reduce the metal content and the toxicity of the neutralization sludge. Similarly, removing those metals that are still in solution after the free acid has been neutralized, may be a better alternative for cleaning the effluent than adding excess lime. Also, some revenue may be generated from the recovery of metals.

This report describes a series of batch and column experiments intended to evaluate the extracting capabilities of various ion exchangers. The feasibility of improving the economic and environmental aspects of lime neutralization, by means of ion exchange, are discussed.

# 2 EXPERIMENTAL

## 2.1 SOLUTIONS, REAGENTS AND MATERIALS

Samples of acid mine drainage solutions were obtained from Homestake Canada and Equity Silver Mines. A sample of mine water was provided by Falconbridge. The chemical analysis of these solutions showed that only the Equity Silver solution had most of the metals of interest. The Falconbridge solution contained mostly copper and nickel, but much less iron than is normally found in acid mine drainage solutions (Wilson, 1994). The Homestake solution contained few metals other than iron. In order to facilitate the experimental procedure, the concentration of selected metals was increased in some cases to desired levels by adding one or more of the following compounds: $CuSO_4$, $3CdSO_4C$ $8H_2O$, $NiSO_4$, $Fe_2(SO_4)_3$, $Sb_2O_3$, $PbSO_4$ and $ZnSO_4C$ $7H_2O$.

All the experimental work was done with the three solutions shown in Table 1. The Equity Silver solution was used to prepare Solution A, the Homestake solution was used to prepare Solutions B and C, and the Falconbridge solution was used as received. The metal concentration in these solutions changed slightly over the several months during which this project was developed (the numbers shown are the initial concentrations when the solutions were prepared and they may differ slightly from those quoted on specific tests).

A number of ion exchange resins was selected for the experiments on the basis of previous experiments, published information and theoretical considerations. Samples were then obtained from the manufacturers: Rohm and Haas, Bayer, Dow Chemical, Reilly Industries and Schering. A natural zeolite (clinoptilolite) was obtained from Rocky Mountain Zeolites (Colorado) and a synthetic zeolite (Zeolite 4A) was obtained from Union Carbide. Table 2 presents a complete list of the ion exchangers used.

## 2.2 EXPERIMENTAL TECHNIQUES

### 2.2.1 Batch tests

The equilibrium and kinetic experiments were carried out by contacting appropriate amounts of resin and solution with mechanical agitation. The resins were hydrated, washed with water several times and used as such. The "wet settled volume" was used to measure the amount of resin, as is the common practice in ion exchange applications. Therefore, the metal loadings are expressed as grams of metal per litre of wet settled resin.

### 2.2.2 Column tests

Columns tests were carried out by passing the solution, using a peristaltic pump, through a 1-cm-diameter column containing 5 to 15 mL of resin. The column effluent was sampled with an automatic fraction collector and analyzed. The flowrate of the solution through the column is expressed in bed volumes per hour (BV/h). The "bed volume" is, by definition, the total volume occupied by the packed resin bed in the column, including the space between the beads.

### 2.2.3 Chemical analysis

The concentration of metals in solution was analyzed by either atomic absorption or ICP spectrophotometry. The metal loading on the resin was either estimated by solution difference or determined by eluting the resins. In a few cases, the resins were completely digested in acids and the resulting solution was analyzed for metals.

# 3 RESULTS AND DISCUSSION

## *3.1 NEUTRALIZATION OF ACID MINE DRAINAGE*

The feed solutions were subjected to lime neutralization tests to study the behaviour of metals during the process, to determine the lime consumption, and also to generate a sample of neutralization sludge. All this information was needed for the analysis and discussion of the ion exchange tests.

### 3.1.1 Behaviour of metals during lime neutralization

It is well known that some metals hydrolyze and precipitate more readily than others when an acid solution is neutralized (Monhemius, 1977). Furthermore, when a mixture of metals is present, there may be a considerable amount of coprecipitation and other physicochemical effects, which make it impossible to predict the behaviour of each metal from thermodynamic constants obtained under ideal conditions. When lime is used, the formation of insoluble calcium sulphate introduces another complication. Thus, the response of metals to lime neutralization in a given solution was determined experimentally.

Solution B was subjected to a stepwise lime neutralization and the concentration of metals in the supernatant solution was determined as a function of the pH. The results presented in Table 3 and Figure 3 show that although most metals were precipitated readily on addition of lime, the complete precipitation of some specific metals from solution was not attained until the pH was strongly alkaline. While antimony, lead, copper, aluminum and iron were practically precipitated at pH 7, the concentration of the other three metals was: Ni, 2.3 ppm; Cd, 33 ppm; and Zn, 19 ppm. A considerable excess of lime was needed to eliminate these metals.

### 3.1.2 Lime consumption

Table 4 and Figure 4 present the consumption of lime needed to raise the pH of solution B from its initial pH of 1.8 up to 11. It can be seen that the lime consumption was 3.6 g/L to reach pH 7 and 4.5 g/L to reach pH 11. This means that 80 percent of the lime was used to neutralize the free acid and to precipitate the large majority of the metals, while 20 percent was used exclusively to precipitate the last traces of cadmium, nickel and zinc. It follows that a considerable amount of lime could be saved if Cd, Ni and Zn were removed from solution using another method. Furthermore, this option may open the possibility of using limestone to replace lime. Limestone (calcium carbonate) is a cheaper product than lime, but it is not widely used in this case partly because, being a weak base, it cannot yield a strongly alkaline pH (SENES Consultants, 1994). Table 5 presents the consumption of limestone as a function of the pH.

### 3.1.3 Toxicity of the neutralization sludge

Two large samples (2.5 litres each) of solution C were neutralized with lime to pH 10.5 and 4.5, respectively. Table 6 presents the physical characteristics of the sludges. These sludges were filtered, dried at 110°C for 24 hours and subjected to the toxicity test of the Regulation 347, Environmental Protection Act of Ontario (Leachate Extraction Procedure). This test determines whether metals are leached out from a solid in significant amounts when contacted with a mildly acidic aqueous solution (pH 5.2 adjusted with acetic acid).

The results of the toxicity tests for the two dry sludges are presented in Table 7. The composition of the dry sludges show that, as expected, calcium and iron are the main components. When the solution was neutralized to pH 10.5, the concentration of copper and zinc in the solids was very high, i.e. 0.8 and 2.89% respectively. The contents of toxic metals in the solids, especially Zn, decreases considerably when the solution is only partially neutralized (pH 4.5), although it is still significant. Table 7 shows also the amount of metals that were leached out, along with the leachate quality criteria that are used to evaluate the toxicity nature of a solid. The Ontario Environmental Protection Act states that if a waste produces a leachate containing any of the contaminants listed in Schedule 4 at a concentration in excess of 100 times that specified in the Schedule, it is classified as "leachate toxic waste" or "hazardous waste" and regulated accordingly. As can be seen, the concentrations of arsenic, cadmium, lead and mercury are below the specifications of Schedule 4. However, if these sludges can be considered not hazardous, it is mostly because many metals, such as Cu and Zn, are not listed in Schedule 4 at the present time. Since the neutralization sludges released high amounts of copper and zinc into the leachate, it can be anticipated that they may become an environmental liability, should other metals be included in future regulations.

## *3.2 SCREENING OF ION EXCHANGERS*

A large variety of ion exchangers are currently available. The two main groups are organic (resins) and inorganic (zeolites). Ion exchange resins are normally classified as anionic, cationic and chelating. The first two types are widely used for the purification of water. Anionic resins have amine groups and are used for extracting amphoteric elements or metals that form anionic complexes. Cationic resins have either sulphonic or carboxylic groups and are used to extract polyvalent cations. Chelating resins have organic groups, which can form coordinate bonds with specific transition metals. Therefore, chelating resins are more selective than cationic and anionic resins. Zeolites are exclusively cationic exchangers, which exhibit some selectivity as a result of the regular size of the molecular pores within their aluminosilicate structure. Thus, cations larger than the molecular pores are excluded from the zeolite.

The selection of ion exchangers for this work was based largely on CANMET's expertise in ion exchange (Koren, 1991) and the results of an extensive literature review on the application of ion exchange to the treatment of acid mine drainage (Dinardo et al., 1991). The difficulty of the task at hand is to identify ion exchangers that will exhibit a marked selectivity for the metal(s) of interest over the non-valuable metals, such as iron, calcium and aluminum. Thus, only two cationic resins (Amberlite IR-120 and Amberlite IRC-50s) were included in the screening (mostly for comparison purposes), as they are known to be non-selective (Holmes et al., 1972). Instead, most of the resins selected for this project belong to the chelating type, including two iminodiacetic resins (Amberlite IRC-718 and Lewatit TP-207), three picolylamine resins (Dowex XFS-4196, XFS-4195, and XFS-43084), and one hydroxyquinoline resin (TN-02328), all of which have exhibited good extracting properties for copper (Dorfner, 1991). A thiol resin (Duolite GT-73), which extracts several metals having a strong affinity for the sulphide ion, was also included. Amberlite IRA-743, Duolite C-467, Reillex 425 have polyol, aminophosphonic and pyridine functionality, respectively, and have been proposed for various metallurgical applications. Some anionic resins having primary, secondary and tertiary amine group (Duolite A-7 and Dowex WGR) exhibit chelating properties for transition metals at neutral pH (Hazen, 1960) and were also included in this work. Initially zeolites were not considered suitable for this project because these materials are not stable in acid media. However, two zeolites (clinoptilolite and Zeolite 4A) were tested for the treatment of neutralized effluent in the later stages of the project.

### 3.2.1 Metal extraction at natural (low) pH

A simple batch test was used to get an indication of the affinity of every ion exchanger for each metal. The test consisted of contacting 1 mL of each ion exchanger with 100 mL of solution using mechanical agitation during 24 hours. The resin loading was then estimated or determined as explained above. The equilibrium distribution between the resin and solution was then tabulated.

Table 8 presents the equilibrium distribution of copper, iron and zinc between Solution A (at its natural pH) and various resins. Copper and zinc were selected because these metals are usually present in AMD solutions in concentrations high enough to justify their recovery (Wilson, 1994). Iron is invariably present in AMD and it is likely to compete with the metals of interest for the ion exchangers. The resin loadings were determined by eluting the resins with 1 M sulphuric acid, except Dowex XFS-4195 whose metal loading was calculated by solution difference because this resin is known to be poorly eluted by acids (Grinstead, 1984). A significant result was that all resins, except for Duolite GT-73, extracted large quantities of iron. At the same time, several resins also extracted copper, but none of the resins was a good extractant for zinc.

The affinity between a resin and a metal is commonly expressed by the distribution coefficient, D, which

$$D = \frac{\textit{Metal loading on the resin (mg / L)}}{\textit{Aqueous metal concentration (mg / L)}}$$

is defined as follows:

Distribution coefficients provide a good measure of the intrinsic affinity between a resin and a metal because, unlike loadings, the solution concentration is taken into account. However, loadings are important from a practical point of view because even if the affinity for a given metal is low, its resin loading may still be high if the aqueous concentration of that metal is high. Both loadings and distribution coefficients are useful to evaluate a resin/metal equilibrium.

Table 9 presents the distribution coefficients of copper, iron and zinc for each resin. It can be seen that Dowex XFS-43084 is the best extractant for copper, on account of having the largest DCu among all the resins and a relatively low DFe. Although Duolite GT-73 exhibits the highest selectivity for copper because its DFe is zero, the DCu of Duolite GT-73 is an order of magnitude lower than that of Dowex XFS-43084. Another important result is that none of the resins showed any selectivity for zinc.

A number of resins did not exhibit any promising capabilities and were eliminated from the screening process at this point: Amberlite IRC-50s, Amberlite IRA-743, Reillex 425 and TN-02328. Dowex XFS-4196 was also eliminated because its performance was inferior to both XFS-4195 and XFS-43084. The weak-base resins, Amberlite IRA-93 and Duolite A-7, are clearly not active at low pH, but they may show better performance at a higher pH.

Table 10 presents the results of another set of equilibrium tests, which were done by contacting 1 mL of every ion exchanger with 100 mL of Solution B. In this case, the following metals were monitored: Al, Sb, Cd, Ca, Cu, Fe, Mg, Ni and Zn. Every ion exchanger extracted large amounts of iron, which presents a significant problem for the extraction of the metals of interest. Interestingly, Duolite C-467 extracted much more antimony than any other resin. Significant copper loadings were observed with the picolylamine resins (Dowex XFS-4195 and XFS-43084). The copper loadings of the two iminodiacetic resins (Amberlite IRC-718 and Lewatit TP-207) was also significant, although slightly lower than those of the picolylamine resins. Amberlite IR-120 attained the highest loadings of cadmium, nickel and zinc. However, this cationic resin is clearly not selective as it extracts also the largest amounts of calcium, iron and magnesium. This resin would be useful for the bulk removal of metals, but it is not suitable for the objectives of this project.

A comparison of the distribution coefficients (Table 11) shows that Duolite C-467 has the highest affinity for antimony. Although this resin also extracts other metals, its preference for antimony is apparent. The distribution coefficients of the picolylamine resins (Dowex XFS-4195 and XFS-43084) for copper are much higher than those for other metals, which offers good prospects for the extraction of copper. Of the two resins, Dowex XFS-43084 can be considered the best choice for the extraction of copper because XFS-4195 is difficult to elute (Grinstead, 1984). None of the ion exchangers exhibited a strong affinity for either Cd, Ni or Zn at this low pH. Similarly, the extraction of Al, Ca and Mg is rather low with all the resins, except with Amberlite IR-120. The distribution coefficients for iron are in general intermediate, but because of its high concentration, iron is clearly the main interference for the extraction of copper and antimony. The chemical analysis showed that iron was 100% present as Fe(III) in all cases. However, it is known that fresh acid drainage solutions contain a considerable portion of iron as Fe(II) form. Therefore, it was undertaken to determine the effect of reducing Fe(III) to Fe(II) on the extraction of metals.

### 3.2.2 Metal extraction from solutions containing iron as Fe(II)

Fe(III) was reduced to Fe(II) by adding 7 g/L of solid sodium bisulphite, $NaHSO_3$, to the solution B and allowed to react for 2 hours. The excess of $SO_2$ produced was removed by sparging nitrogen gas through the solution until no $SO_2$ was detected with a Draeger tube. The chemical analysis showed that iron was now 87.2% Fe(II). This solution was contacted as before with a number of selected ion exchangers and the results are presented in Table 12 and Table 13. Surprisingly, it was found that reducing Fe(III) to Fe(II) had relatively little effect on the extraction of iron. The largest difference was observed with Dowex XFS-43084, which loaded 1,900 mg Fe/L instead of the 4,900 mg Fe/L when iron was present as Fe(III). However, the copper loading remained at the same level (>7,000 mg/L), which means that despite the increase in selectivity for copper over iron of Dowex XFS-43084, the latter is still extracted to a significant extent, even when it is present as Fe(II). Similarly the selectivity of Duolite C-467 for antimony over iron did not increase.

### 3.2.3 Metal extraction at low pH in the absence of iron

The solution supplied by Falconbridge was essentially iron-free (Table 1). Thus, it provided an opportunity to measure the effect of Fe(III) on the extraction of other metals. The equilibrium distribution between this solution (300 mL) and four selected resins (1 mL) is shown in Table 14 and the corresponding distribution coefficients are presented in Table 15. Significantly high extractions of copper and nickel were observed. The DNi of Dowex XFS-43084, Dowex XFS-43084, and Lewatit TP-207 are fairly large, although smaller than the corresponding DCu in each case. The extraction of zinc was somewhat better than in previous experiments, but still not promising. It can be concluded that the prospects for extracting nickel increase significantly when iron is not present in the solution. The extraction of copper and zinc also increase to some extent.

### 3.2.4 Metal extraction at mildly acidic pH

The extraction of most metals, except for Cu and Sb, was poor at low pH. In general, the ion exchange extraction of metals improves as the pH increases. The following experiment was conducted to evaluate the extraction of metals under mildly acidic conditions.

A sample of Solution C was neutralized with lime to pH 4.1. After filtration, the composition of the filtrate was: Al 0.4 ppm; Ca 671 ppm; Cu 38 ppm; Fe 0.9 ppm; Mg 202 ppm; Sb 1 ppm; Zn 284 ppm. Thus, raising the pH effectively removed iron, aluminum, and antimony from the solution. More than half of the copper precipitated, the concentration of zinc did not change and the calcium concentration increased as a result of the lime addition. This solution was contacted as before with a number of resins at the same ratio of 1:100. Table 16 and Table 17 present the equilibrium solution/resin distribution and the distribution coefficients, respectively. A few weak-base anionic resins (Amberlite IRA-93, Dowex WGR and Duolite A-7) were included in the experiment because these resins exhibit metal complexing capabilities through their free amine groups. This mechanism is only possible at neutral or mildly acidic pH. While carrying out the experiments, it was observed that the equilibrium pH shifted considerably from its initial value because of the hydrolytic reaction of some resins, in particular the weak-base resins. In these cases, it was decided to run two experiments for each resin: one with the resin in the free amine form and another with the resin in the hydrogen or protonated form (i.e. preconditioned with an acid solution). This fact accounts for the two pH levels found in the tables for the weak-base anionic resins.

The results show that the extractions of calcium, copper, magnesium and zinc increase substantially under mildly acidic conditions with respect to acid conditions. Most of the resins extract large amounts of calcium, which becomes the main interference once iron has been eliminated. The extraction of zinc increases in most cases, although none of the ion exchangers showed a strong selectivity for this metal. A number of chelating resins (Dowex XFS-43084, Amberlite IRC-718, Lewatit TP-207 and Duolite GT-73) attained a very high DCu. The weak-base resins (Amberlite IRA-93, Dowex WGR and Duolite A-7) exhibited some extraction capabilities, especially for copper. The performance of weak-base resins is clearly very sensitive to the pH, which indicates that the elution of these resins could be accomplished readily with a weak acid solution. Since the two iminodiacetic resins (Amberlite IRC-718 and Lewatit TP-207) showed practically identical characteristics, only one of them was used in future tests.

### 3.2.5 Metal extraction at near neutral pH

For this test, a sample of solution B was neutralized with lime to pH 6. After filtration, the solution had the following composition: Al 0 ppm; Ca 727 ppm; Cd 179 ppm; Ni 29 ppm; Cu 0.1 ppm; Fe 0 ppm; Sb 0 ppm; Zn 47 ppm. Table 18 presents the equilibrium distribution between the neutralized solution and some selected resins. The equilibrium pH, which is slightly different from the initial pH in some cases, is also tabulated. Table 19 presents the corresponding distribution coefficients. The data indicate that Amberlite IRC-718 is a good extractant for cadmium, nickel and zinc. Duolite GT-73 exhibits a relatively good affinity for cadmium over other metals. The two weak-base anionic resins (Dowex WGR and Amberlite IRA-93) showed fairly high DZn, but other metals are also extracted.

## *3.3 EXTRACTION OF COPPER*

Copper is eliminated quite effectively from solution by lime neutralization (see Table 3). However, as discussed in section 3.1.3., a high concentration of copper in the neutralization sludge may contribute significantly to its toxicity. While this fact provides an environmental incentive, the relatively good price of copper provides an economic reason for the recovery of copper from acid mine drainage.

The experimental results showed that the two picolylamine resins (Dowex XFS-4195 and XFS-43084) were able to extract copper effectively at low pH. While the elution of Dowex XFS-4195 is difficult, Dowex XFS-43084 is amenable to elution with sulphuric acid (Grinstead, 1984). Therefore, Dowex XFS-43084 was chosen for further evaluation. At mildly acidic conditions, the iminodiacetic resins (Amberlite IRC-718 and Lewatit TP-207) also extracted copper effectively and were also selected for further tests.

### 3.3.1 Loading capacity

Figure 5 presents equilibrium copper distribution isotherms for Dowex XFS-43084 and solutions A and B. In both cases the copper loading exceeds 30 g/L, which is a very promising result. The copper extraction is more efficient from Solution B than Solution A, probably because the former contains less iron.

### 3.3.2 Selectivity

The selectivity trends of Dowex XFS-43084 were studied by means of a saturation profile. This procedure involves subjecting a small amount of resin to a series of successive contacts with fresh aliquots of the feed solution. The cumulative loading of metals on the resin after each contact is calculated and plotted. The purpose is to determine the changes in metal loadings as the resin approaches saturation.

Table 20 presents the saturation profile of Dowex XFS-43084 obtained by means of 6 successive contacts with solution B, each at a 100:1 solution-to-resin ratio. It can be seen that the resin exhibits a preference for copper over iron, which is manifested by a slight displacement of the loaded iron by copper as the resin becomes saturated. The distribution coefficients of copper and iron at saturation can be estimated as 373 and 6.3, respectively. The separation factor (defined as the ratio between both distribution coefficients) is then: SCu/Fe = DCu/DFe = 59.2. This value is favourable for copper and indicates that it would be possible to "scrub" the iron off the loaded resin with a dilute copper solution. For example, a portion of the weak electrolyte if there was an electrowinning circuit.

### 3.3.3 Extraction kinetics

The extraction kinetics of copper were studied by contacting 1 mL of Dowex XFS-43084 with 100 mL of the Solution A using strong mechanical agitation. The solution was sampled and analyzed periodically for copper. The results are presented in Table 21, along with the fractional approach to equilibrium (calculated assuming that equilibrium is reached at 24 hours). From the graphical representation of these data (Figure 6), the equilibrium half time, t2 (the time at which the resin has attained 50% of the equilibrium loading), can be estimated to be about 1.5 hours. It should be pointed out that this value depends on the resin-to-solution ratio and it is useful for comparison purposes only. As such, this result indicates that the extraction kinetics of copper with Dowex XFS-43084 is relatively slow, which is a common finding with chelating extractions.

### 3.3.4 Column extraction

Two column experiments were carried out to determine a suitable flowrate for the extraction. Figure 7 presents breakthrough curves for the extraction of copper from Solution A at two flowrates: 6 and 3 BV/h. These experiments were done with columns containing 10 and 15 mL of Dowex XFS-43084, respectively. Better results were obtained with the slower flowrate, i.e. 3 BV/h, which is consistent with the slow kinetics observed during the batch tests. The residence time (or contact time) of the solution as it passes through the resin bed can be calculated as follows:

$$Residence\ time\ (h) = \frac{Voidage\ of\ the\ Resin\ Bed}{Flowrate\left(BV / h\right)}$$

Assuming a typical voidage of 40%, the residence time for a flowrate of 3 BV/h is 8 minutes. This is a relatively long residence time, which implies that a large resin inventory will be required for an application. It is possible, however, to increase the kinetics by using finer resin particles.

### 3.3.5 Elution

The elution of copper from Dowex XFS-43084 was done readily and efficiently with 1 M $H_2SO_4$, passed at 3 BV/h, as shown in Table 22. The copper elution attained a peak concentration of about 20 g Cu/L and the elution was completed with about 10 bed volumes. In this case, the eluate was contaminated with iron because no scrubbing was done. Since the affinity of this resin for copper is much higher than it is for iron, the prospects of scrubbing iron from the saturated resin appear to be good. Additional tests, preferably in a larger scale, would be required to determine the operation parameters of the scrubbing stage. This was considered to be outside the scope of this project.

### 3.3.6 Extraction at mildly acidic pH

As expected, the extraction of copper improves as the pH is raised and a larger number of resins can extract copper at mildly acidic pH. However, a significant fraction of copper may be eliminated from solution due to precipitation and co-precipitation.

A sample of solution C was neutralized with lime to pH 4.5 and filtered. The filtrate had the following composition: Ca 711 ppm; Cu 54 ppm; Fe 0.0 ppm; and Zn 274 ppm. This solution was passed through a column containing Dowex XFS-43084 at 3 BV/h. As shown in Table 23, the extraction of copper was excellent. No breakthrough for copper was observed even after passing 175 bed volumes of solution. Limited amounts of calcium and zinc were extracted, mostly at the beginning of the experiment.

A similar experiment was carried out with one of the iminodiacetic resins. In this case, the filtrate had the following composition: Ca 804 ppm, Cu 50 ppm, Fe 0.0 ppm and Zn 311 ppm. This solution was passed through a column containing Amberlite IRC-718 at 3 BV/h. As in the previous case, the copper extraction was excellent since no breakthrough for copper was observed despite treating more than 800 bed volumes of solution (see Table 24). The elution of Amberlite IRC-718 with 1 M sulphuric acid at 2 BV/h is presented in Table 25 and it can be seen that copper was efficiently eluted. A significant amount of zinc was found in the eluate along with smaller amounts of calcium.

### 3.3.7 Summary

The extraction of copper from acid mine drainage appears to be very promising. At low pH, the extraction is feasible with Dowex XFS-43084, a picolylamine resin. Although the kinetics are relatively slow and some iron co-extraction takes place, both drawbacks could be overcome by using finer particles and scrubbing the loaded resin, respectively. Under mildly acidic conditions, copper can be extracted very efficiently with either Dowex XFS-43084 or one of the iminodiacetic resins.

## *3.4 EXTRACTION OF ANTIMONY*

As discussed above, the preliminary tests showed that an aminophosphonic resin, Duolite C-467, has a good affinity for antimony. Table 26 presents the results of a column experiment, in which Solution C (without pH adjustment) was passed at 10 BV/h through a column containing 10 mL of Duolite C-467. The results were very promising: there was a breakthrough at about 100 BV, but the resin continued to extract antimony even beyond 300 BV. A slower flowrate may be required to produce a sharper breakthrough curve and higher efficiency. The loaded resin was removed from the column and was dissolved in strong acids to determined its metal loadings. The analysis showed the following values: Ca 2,450 mg/L; Cu 750 mg/L; Fe 5,750 mg/L; Sb 2,750 mg/L; Zn 4,000 mg/L. Taking into account the relative concentration of each metal in the feed solution, it can be seen that the affinity of Duolite C-467 for antimony is remarkably good.

Although the extraction of antimony was not investigated any further, the preliminary results show that the extraction of antimony from acid mine drainage is promising.

## *3.5 EXTRACTION OF CADMIUM*

Cadmium is usually found in relatively low concentrations in acid mine drainage solutions (Wilson, 1994). However, it is extremely toxic to most living organisms and it is currently listed in Schedule 4 of the Ontario Environmental Act, as discussed above. As shown in Table 7, cadmium was readily released during the toxicity test and in one case (pH 10.5), it almost exceeded the specification set for hazardous wastes, even though the initial cadmium concentration in the AMD solution was only 4 ppm.

Cadmium does not precipitate readily on addition of lime. Table 3 shows that the concentration of soluble Cd was 7.8 ppm at pH 8 and 1.2 ppm at pH 9 in the lime neutralization experiment done with Solution B.

None of the resins showed any selectivity for Cd at low pH (Table 10 and Table 11). Under neutral conditions, Duolite GT-73 exhibited affinity for cadmium, whereas Amberlite IRC-718 showed high loadings of Cd, Ni and Zn (Table 18 and Table 19).

### 3.5.1 Column extraction

A sample of Solution A was neutralized with lime to pH 4 and filtered. The filtrate contained 157 ppm Zn and 151 ppm Cd. The filtrate was passed at 5 BV/h through a column containing 5 mL of Duolite GT-73 in the acid form (i.e. conditioned with 0.5 N $H_2SO_4$). As shown in Figure 8, a good separation of zinc and cadmium was obtained since only the latter was adsorbed. The performance of Duolite GT-73 is moderately good; the breakthrough for cadmium was observed at about 20 BV and the total cadmium loading was estimated at 7-8 g/L.

### 3.5.2 Extraction kinetics

Figure 9 presents the extraction kinetics of Cd with Duolite GT-73. As can be seen, the extraction proceeds fairly quickly to equilibrium. The t2 was estimated to be slightly less than 30 minutes. Again, this value is for comparison purposes only and it is not a direct measure of the contact time needed for the solution passing through the resin bed.

### 3.5.3 Elution

One elution test is shown in Table 27. A 0.5 M sulphuric acid solution was passed through the column at 3 BV/h. The elution under these conditions was not very efficient as the peak Cd concentration was only 625 ppm and after 23 BV the elution had not been completed. The efficiency of the elution would probably improve with a more concentrated acid solution. An important result is that the zinc loading was apparently very low, as there is practically none in the eluate. Thus, Duolite GT-73 may be useful to separate Cd from Zn.

### 3.5.4 Other tests

A synthetic zeolite, exhibited a high affinity for Cd at neutral pH. Since this zeolite also extracted Ni and Zn, it will be discussed in Section 3.8.

## *3.6 EXTRACTION OF ZINC*

Zinc is commonly found in acid mine drainage solutions, sometimes in relatively high concentrations (Wilson, 1994). Zinc is usually not completely precipitated at neutral pH; as shown in Table 3, the concentration of soluble Zn was 18.6 ppm at pH 7, 5 ppm at pH 8, and 0.5 ppm at pH 9.

None of the resins exhibited affinity for Zn at low pH. Under mildly acidic or neutral conditions, the extraction of zinc is feasible, but with low selectivity. The most promising resins for zinc are Dowex XFS-43084, iminodiacetic resins, and the cationic resin Amberlite IR-120.

The extraction of zinc and copper with chelating resins (Dowex XFS-43084 and Amberlite IRC-718 or Lewatit TP-207) under mildly acidic conditions was already discussed in Section 3.3. Moderate extractions of Zn were observed (Table 23, Table 24 and Table 25), but copper was extracted preferentially in all cases.

A method has been proposed in which Zn is extracted from a partially neutralized AMD solution with Amberlite IR-120, eluted with NaCl, precipitated as $Zn(OH)_2$ and calcined to produce ZnO (Gilmore, 1977). The process was considered to be economically viable. To evaluate this approach, a sample of solution C was neutralized to pH 4.5, filtered and passed through a column containing 10 mL of Amberlite IR-120 in the sodium form (i.e. conditioned with 0.05 M NaOH) at 5 BV/h. The filtrate had the following composition: Ca 650 ppm; Cu 24 ppm; Fe 0.5 ppm; Zn 269 ppm. Table 29 presents the analyses of Ca and Zn in the column effluent and the estimated metal loadings. The data clearly show that the resin became saturated very quickly and that it loaded three times more Ca than Zn. Although Amberlite IR-120 can extract Zn, its lack of selectivity is a serious drawback for the development of a large-scale application. This approach might be useful, however, in relatively clean solutions with a high concentration of zinc.

The bulk extraction of zinc, cadmium and nickel at neutral pH is discussed in Section 3.8.

## *3.7 EXTRACTION OF NICKEL*

Nickel is frequently a component of acid mine drainage (Wilson, 1994); it is present in AMD of all nickel mines and some gold, uranium and other mines. As shown in Table 3, nickel tends to stay in solution at neutral pH in low but environmentally significant concentrations. For example, the soluble Ni was 2.3 ppm at pH 7 and 0.4 ppm at pH 8.

The extraction of nickel from acidic drainage at low pH was poor (Table 10 and Table 11). However, a number of chelating resins extracted Ni (and Cu) effectively from an iron-free solution from Falconbridge (Table 14 and Table 15). At neutral pH, Amberlite IRC-718 extracted Ni very efficiently along with zinc and cadmium. This will be discussed in Section 3.8.

## *3.8 BULK EXTRACTION OF CADMIUM, NICKEL AND ZINC*

Cadmium, nickel and zinc are the metals which are most difficult to precipitate quantitatively with lime (Table 3). Consequently, attempts were made to find an effective extractant for these three metals. Such an extractant would provide an alternative way to clean and detoxify the effluent without raising the pH to objectionable levels, as is the case with lime neutralization.

Based on the results of batch contacts with mildly acidic and neutralized solutions (Table 16, Table 17, Table 18 and Table 19) a small number of ion exchangers was selected for the tests: 1) A weak-base resin (Amberlite IRA-93); 2) A chelating resin (Amberlite IR-718); 3) A natural zeolite (clinoptilolite); and 4) A synthetic zeolite (Zeolite 4A).

A sample of Solution B was neutralized with lime to pH 6 and filtered. The composition of the filtrate was: Cd 153 ppm, Ni 25 ppm and Zn 287 ppm. This solution was passed through a column containing 5 mL of Amberlite IRA-93 in the free base form at 5 BV/h. The results, presented in Table 30, show that the extraction of metals was very poor; only small amounts of Zn were extracted.

Another sample of Solution B was neutralized to pH 7.5 and filtered. In this case, the composition of the filtrate was: Cd 151 ppm; Ni 27 ppm; and Zn 45 ppm. This solution was then passed through a column containing 10 mL of clinoptilolite at 5 BV/h. Table 31 shows that the metal extraction with clinoptilolite was not efficient. Limited amounts of Cd, Ni and Zn were loaded on the zeolite, but the removal of metals from the solution was incomplete.

The experiment was repeated with Zeolite 4A. A sample of Solution B was neutralized to pH 7.5 with lime and filtered. The composition of the filtrate was as follows: Ca 636 ppm; Cd 33 ppm; Cu <0.04 ppm; Fe <0.07 ppm; Ni 6.4 ppm; Sb 0.73 ppm; and Zn 11.2 ppm. This solution was then passed through a column containing 5 cc of Zeolite 4A (ground to -20+65 Mesh) at 5 BV/h. The results are presented in Table 32. As can be seen, the extraction of cadmium and zinc was extremely good; the breakthrough for both metals was observed at about 300 bed volumes and even after that the extraction of both metals continued until the end of the experiment. By comparison, the extraction of nickel was considerably lower.

A sample of Solution B was neutralized to pH 7 with lime and filtered. The filtrate had the following composition: Ca 805 ppm; Cd 26 ppm; Cu <0.05 ppm; Ni 5.2 ppm; Fe <0.04 ppm; Sb 0.7 ppm; and Zn

8.7 ppm. This solution was passed at 10 BV/h through a column containing 5 mL of Amberlite IRC-718. Table 33 shows that the extraction of the three metals was very efficient. The breakthrough for Cd was observed at about 170 bed volumes and the one for Zn was observed at about 220 bed volumes. No breakthrough for nickel was observed even after 479 BV of solution had been treated.

In conclusion, both Zeolite 4A and Amberlite IRC-718 are effective extractants of metals at neutral pH. Zeolite 4A extracts Cd and Zn very strongly and Ni to a lesser extent. Amberlite IRC-718 can remove all three metals very efficiently.

# 4 ECONOMIC CONSIDERATIONS

A detailed economic analysis is beyond the scope of this project. Although some potential applications have been identified, a complete flowsheet was not developed. A proper economic evaluation would require experimental data for each stage of the flowsheet, including elution and regeneration of the ion exchanger, metal recovery from the eluate, resin recycling and reagent consumption. Furthermore, the economics of a specific application, such as the recovery of copper, would be necessarily site-specific because it would depend on the volume and composition of the solution. Therefore, only some preliminary estimates will be made in this section.

As discussed before, an excess of lime is normally added to AMD solutions in order to ensure the complete precipitation of metals. This report shows that the most difficult metals to precipitate are Cd, Ni and Zn and that these threee metals could be removed efficiently with an ion exchange resin or a zeolite. This raises the question whether the savings in lime consumption would offset the cost of an ion exchange process. Although practically no tests were done on the elution and regeneration of the ion exchanger, a preliminary comparison can be made on the basis of a hypothetical example. Normally, the ion exchange resin would be eluted with dilute sulphuric acid and regenerated with dilute sodium hydroxide. The zeolite would be eluted with a concentrated sodium chloride solution.

Table 34 presents an annual cost comparison of full neutralization to pH 11 followed by re-acidification to pH 7, and two proposed alternatives: A) Partial neutralization to pH 6 followed by metal extraction with an ion exchange resin and B) Partial neutralization to pH 6 followed by metal extraction with a zeolite. The flowrate has been chosen arbitrarily as 10,000 $m^3$/day.

In this example, the cost of the ion exchange resin alternative is only slightly cheaper than full neutralization; however, sulphuric acid is available in many locations at much lower cost. The cost of the zeolite alternative is considerably lower than the cost of full neutralization. An important consideration is that the two ion exchange alternatives offer the possibility of metal recovery if the concentration warrants it. Since a high pH is not required for the last two alternatives, limestone could also be used for the neutralization instead of lime. Limestone is often overlooked as a neutralization agent because of its poor reactivity at near neutral pH even though it can be highly cost effective. Where pH values must be raised to above 6.5, a second stage of alkaline addition is normally required (NaOH, CaO). For strong strength AMD solutions, limestone can meet typically 90 to 95% of the alkali demand at perhaps one third the cost of quicklime. Furthermore, sludges may be more granular and dense (SENES Consultants, 1994).

# 5 CONCLUSIONS AND RECOMMENDATIONS

It was found that most commercial ion exchangers do not exhibit a marked selectivity for the metals of interest, i.e. Sb, Cd, Cu, Ni and Zn. Consequently, the co-extraction of iron is a major obstacle for the application of ion exchange to acid mine drainage solutions. The selectivity did not improve significantly when Fe(III) was reduced to Fe(II). The co-extraction of calcium becomes a problem at higher pH when lime is used to neutralize the solution. The most promising results were obtained with copper and antimony, which were amenable to extraction even at low pH.

While the selective extraction of Cd, Ni or Zn was not feasible under most conditions, the simultaneous extraction of all three metals can be done at neutral pH using either a chelating resin or a synthetic zeolite. This fact could be used to reduce the amount of lime that is normally added to ensure the complete precipitation of metals. A preliminary cost comparison based on a hypothetical example indicates that the ion exchange alternatives are cheaper than full neutralization, especially if synthetic zeolites can be used.

It is recommended that additional work be undertaken to further develop the ideas generated in this work: A) Copper extraction and recovery, B) Antimony extraction and disposal, and C) Bulk extraction of Cd, Ni, and Zn from neutral effluent with resins and/or zeolites. These experiments should address the recovery of metals from solution (cementation, electrowinning), so that a proper economic evaluation can be done. Special emphasis should be given to assess the performance of zeolites with respect to recycling, kinetics, and fouling.

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**Table 1 Composition of feed solutions.**

| | CONCENTRATION, mg/L | | | |
|---|---|---|---|---|
| | SOLUTION A | SOLUTION B | SOLUTION C | FALCONBRIDGE |
| ALUMINUM | 1,150 | 14 | 14 | --- |
| ANTIMONY | 2 | 7* | 7* | --- |
| ARSENIC | 39 | 0 | 0 | --- |
| CADMIUM | 191* | 140* | 4* | 0 |
| CALCIUM | 455 | 271 | 271 | 247 |
| COBALT | 13 | 0 | 0 | 4 |
| COPPER | 192 | 99* | 99* | 57 |
| IRON** | 1,950 | 1,155* | 1,155* | 2 |
| LEAD | 1 | 2* | 2* | --- |
| MAGNESIUM | 947 | 185 | 185 | --- |
| MANGANESE | 16 | 0 | 0 | --- |
| NICKEL | 12 | 26* | 1* | 123 |
| ZINC | 150 | 313* | 313* | 4 |
| pH | 2.5 | 1.8 | 1.8 | 2.8 |

* Concentration increased to this level by spiking; ** Iron was 100% Fe(III)

**Table 2 List of ion exchangers.**

| ION EXCHANGER | SUPPLIER | CLASSIFICATION, FUNCTIONALITY |
|---|---|---|
| Amberlite IR-120 | Rohm and Haas | Cationic, Sulphonic |
| Amberlite IRA-93 | Rohm and Haas | Weak-base anionic |
| Amberlite IRA-743 | Rohm and Haas | Chelating, Polyol |
| Amberlite IRC-50s | Rohm and Haas | Cationic, Carboxylic |
| Amberlite IRC-718 | Rohm and Haas | Chelating, Iminodiacetic |
| Dowex XFS-4195 | Dow Chemical | Chelating, Picolylamine |
| Dowex XFS-4196 | Dow Chemical | Chelating, Picolylamine |
| Dowex XFS-43084 | Dow Chemical | Chelating, Picolylamine |
| Dowex WGR | Dow Chemical | Weak-base anionic |
| Duolite A-7 | Rohm and Haas | Weak-base anionic |
| Duolite C-467 | Rohm and Haas | Chelating, Aminophosphonic |
| Duolite GT-73* | Rohm and Haas | Chelating, Thiol |
| Lewatit TP-207 | Bayer | Chelating, Iminodiacetic |
| Reillex 425 | Reilly Industries | Weak-base anionic |
| TN-02328 | Schering | Chelating, hydroxyquinoline |
| Clinoptilolite | Rocky Mountain | Natural zeolite |
| Zeolite 4A | Union Carbide | Synthetic zeolite |

* Formerly marketed as IMAC TMR

**Table 3 Behaviour of metals during lime neutralization.**

| EQUILIBRIUM pH | CONCENTRATION OF METALS IN SOLUTION (mg/L) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Ca | Cd | Cu | Fe(III) | Mg | Ni | Pb | Sb | Zn |
| 1.8 | 14 | 280 | 135 | 99 | 1,166 | 182 | 25 | 1.9 | 7.2 | 314 |
| 3.0 | 15 | 884 | 135 | 96 | 50 | 186 | 26 | 1.0 | 1.2 | 320 |
| 4.0 | 5 | 894 | 135 | 78 | 2.2 | 196 | 26 | 0.1 | 0.3 | 330 |
| 5.0 | 0.5 | 760 | 131 | 16 | 0.9 | 194 | 24 | <0.1 | 0.1 | 284 |
| 6.0 | 0.2 | 792 | 108 | 0.1 | 0.2 | 192 | 16 | <0.1 | <0.1 | 137 |
| 7.0 | <0.1 | 768 | 33 | <0.1 | <0.1 | 188 | 2.3 | <0.1 | <0.1 | 19 |
| 8.0 | <0.1 | 782 | 7.8 | <0.1 | <0.1 | 179 | 0.4 | <0.1 | <0.1 | 5 |
| 9.0 | <0.1 | 768 | 1.2 | <0.1 | <0.1 | 152 | 0.1 | <0.1 | <0.1 | 0.5 |
| 10.0 | <0.1 | 842 | 0.2 | <0.1 | <0.1 | 77 | <0.1 | <0.1 | <0.1 | 0.1 |
| 11.0 | <0.1 | 944 | <0.1 | <0.1 | <0.1 | 3 | <0.1 | <0.1 | <0.1 | 0.4 |

**Table 4 Consumption of lime versus equilibrium pH. Solution B.**

| CaO added g/L | Equilibrium pH |
|---|---|
| 0.0 | 1.8 |
| 0.7 | 2.0 |
| 1.5 | 2.4 |
| 2.1 | 2.8 |
| 2.8 | 3.0 |
| 3.1 | 4.1 |
| 3.2 | 5.0 |
| 3.4 | 6.0 |
| 3.6 | 7.0 |
| 3.7 | 8.1 |
| 3.9 | 9.0 |
| 4.4 | 10.0 |
| 4.5 | 11.0 |

**Table 5 Consumption of limestone (Continental, technical grade) versus equilibrium pH. Solution B.**

| Limestone added g/L | Equilibrium pH |
|---|---|
| 0.0 | 1.8 |
| 2.8 | 2.7 |
| 4.2 | 2.8 |
| 7.6 | 4.0 |
| 7.8 | 4.2 |
| 8.2 | 4.6 |
| 8.3 | 5.0 |
| 9.7 | 6.0 |
| 10.7 | 6.9 |
| 10.9 | 7.1 |
| 13.2 | 7.1 |

**Table 6 Some physical characteristics of the neutralization sludge. Solution C.**

| Test No. | Initial Solution Volume L | Final pH | Lime Consumption g/L | Volume of Settled Sludge mL | Weight of Settled Sludge g | S.G. of Settled Sludge g/L | Weight of dry solids[1] g |
|---|---|---|---|---|---|---|---|
| 1 | 2.5 | 10.5 | 4.00 | 162 | 198.3 | 1.22 | 25.4 |
| 2 | 2.5 | 4.5 | 3.15 | 115 | 131.1 | 1.14 | 20.2 |

[1] Dried at 110°C for 24 hours

**Table 7 Leachate extraction procedure (Toxicity test) for two neutralization sludges.**

| | LIME NEUTRALIZATION TO pH 10.5 | | LIME NEUTRALIZATION TO pH 4.5 | | Leachate Quality Criteria[3] (ppb) |
|---|---|---|---|---|---|
| | Composition of Dry Solids[1] (%) | Leachate Composition[2] (ppb) | Composition of Dry Solids[1] (%) | Leachate Composition[2] (ppb) | |
| ALUMINUM | 0.14 | 28 | 0.18 | 10 | NL |
| ARSENIC | --- | <2.0 | --- | <2.0 | 50 |
| CALCIUM | 18.45 | --- | 20.46 | --- | NL |
| CADMIUM | --- | 413 | --- | 36 | 5 |
| COPPER | 0.80 | 63,000 | 0.64 | 14,200 | NL |
| IRON | 7.29 | --- | 10.28 | --- | NL |
| MERCURY | --- | <2.0 | --- | <2 | 1 |
| MAGNESIUM | 0.85 | --- | 0.07 | --- | NL |
| LEAD | 0.01 | <1 | 0.02 | 4 | 50 |
| ANTIMONY | 0.06 | 24 | 0.08 | 3 | NL |
| ZINC | 2.89 | 906,000 | 0.41 | 122,000 | NL |

1 Solids were dried at 110°C for 24 hours

2 Determined by CANMET according to Regulation 347 of the Ontario Environmental Protection Act

3 From Schedule no. 4, Regulation 347 of the Ontario Environmental Protection Act

NL = Not listed

**Table 8 Extraction of metals from solution A. Equilibrium distribution between 1 mL resin and 100 mL solution.**

| ION EXCHANGER | COPPER | | IRON | | ZINC | |
|---|---|---|---|---|---|---|
| | Solution mg/L | Resin* mg/L | Solution mg/L | Resin* mg/L | Solution mg/L | Resin* mg/L |
| BLANK | 198 | 0 | 1,890 | 0 | 154 | 0 |
| Amberlite IRA-93 | 196 | 10 | 1,866 | 2,050 | 147 | 0 |
| Amberlite IRA-743 | 198 | 13 | 1,835 | 4,950 | 154 | 50 |
| Amberlite IRC-50s | 197 | 15 | 1,703 | 18,300 | 151 | 50 |
| Amberlite IRC-718 | 149 | 4,245 | 1,700 | 17,150 | 151 | 100 |
| Dowex XFS-4195 | 103 | 9,500 | 1,727 | 13,550 | 148 | 350 |
| Dowex XFS-4196 | 114 | 7,815 | 1,753 | 12,250 | 150 | 100 |
| Dowex XFS-43084 | 43 | 14,350 | 1,819 | 6,750 | 152 | 100 |
| Duolite A-7 | 191 | 605 | 1,846 | 2,090 | 152 | 150 |
| Duolite GT-73 | 177 | 1,480 | 1,883 | 750 | 151 | 50 |
| Lewatit TP-207 | 161 | 3,115 | 1,713 | 19,750 | 148 | 200 |
| Reillex 425 | 175 | 1,570 | 1,733 | 12,750 | 153 | 100 |
| TN-02328 | 95 | 8,395 | 1,669 | 17,950 | 154 | 50 |

* Determined by elution with 1 M $H_2SO_4$, except XFS-4195 which was calculated by solution difference.

**Table 9 Distribution coefficients. Solution A.**

| ION EXCHANGERS | DISTRIBUTION COEFFICIENTS | | |
|---|---|---|---|
| | Copper | Iron | Zinc |
| Amberlite IRA-93 | 0 | 1 | 0 |
| Amberlite IRA-743 | 0 | 3 | 0 |
| Amberlite IRC-50s | 0 | 11 | 0 |
| Amberlite IRC-718 | 28 | 10 | 1 |
| Dowex XFS-4195 | 18 | 8 | 2 |
| Dowex XFS-4196 | 69 | 7 | 1 |
| Dowex XFS-43084 | 334 | 4 | 1 |
| Duolite A-7 | 3 | 1 | 1 |
| Duolite GT-73 | 8 | 0 | 0 |
| Lewatit TP-207 | 19 | 12 | 1 |
| Reillex 425 | 9 | 7 | 1 |
| TN-02328 | 88 | 11 | 0 |

**Table 10 Metal extraction from Solution B. Equilibrium distribution between 1 mL of resin and 100 mL of solution.**

| ION EXCHANGER | Aluminum mg/L | | Antimony mg/L | | Cadmium mg/L | | Calcium mg/L | | Copper mg/L | | Iron mg/L | | Magnesium mg/L | | Nickel mg/L | | Zinc mg/L | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* |
| BLANK | 15 | 0 | 5.9 | 0 | 151 | 0 | 262 | 0 | 100 | 0 | 1,145 | 0 | 188 | 0 | 27 | 0 | 312 | 0 |
| Amberlite IR-120 | 8 | 700 | 5.9 | 0 | 106 | 4,530 | 195 | 6,700 | 85 | 1,500 | 863 | 28,200 | 162 | 2,600 | 19 | 770 | 269 | 4,300 |
| Amberlite IRC-718 | 13 | 200 | 4.9 | 100 | 146 | 500 | 258 | 400 | 55 | 4,500 | 957 | 18,800 | 187 | 100 | 25 | 160 | 309 | 300 |
| Dowex XFS-4195 | 14 | 100 | 5.5 | 40 | 135 | 1,600 | 261 | 100 | 11 | 8,900 | 1,079 | 6,600 | 186 | 200 | 21 | 560 | 303 | 900 |
| Dowex XFS-43084 | 14 | 100 | 5.9 | 0 | 147 | 400 | 260 | 200 | 25 | 7,500 | 1,096 | 4,900 | 185 | 300 | 22 | 460 | 309 | 300 |
| Duolite C-467 | 15 | 0 | 1.2 | 470 | 143 | 800 | 253 | 900 | 90 | 1,000 | 1,087 | 5,800 | 183 | 500 | 26 | 68 | 301 | 1,100 |
| Duolite GT-73 | 14 | 100 | 4.3 | 160 | 137 | 1,400 | 248 | 1,400 | 89 | 1,100 | 1,104 | 4,100 | 182 | 600 | 23 | 323 | 300 | 1,200 |
| Lewatit TP-207 | 14 | 100 | 4.9 | 100 | 144 | 700 | 259 | 300 | 56 | 4,400 | 960 | 18,500 | 186 | 200 | 24 | 260 | 308 | 400 |

S Solution

R Resin

* Estimated from concentration difference

**Table 11 Distribution coefficients. Solution B.**

| ION EXCHANGER | DISTRIBUTION COEFFICIENTS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Al | Sb | Ca | Cd | Cu | Fe* | Mg | Ni | Zn |
| Amberlite IR-120 | 88 | 0 | 34 | 43 | 18 | 33 | 16 | 41 | 16 |
| Amberlite IRC-718 | 15 | 20 | 2 | 3 | 82 | 20 | 1 | 6 | 1 |
| Dowex XFS-4195 | 7 | 7 | 0 | 12 | 809 | 6 | 1 | 27 | 3 |
| Dowex XFS-43084 | 7 | 0 | 1 | 3 | 300 | 4 | 2 | 21 | 1 |
| Duolite C-467 | 0 | 392 | 4 | 6 | 11 | 5 | 3 | 3 | 4 |
| Duolite GT-73 | 7 | 37 | 6 | 10 | 12 | 4 | 3 | 14 | 4 |
| Lewatit TP-207 | 7 | 20 | 1 | 5 | 79 | 19 | 1 | 11 | 1 |

* 100% as Fe(III)

**Table 12 Adsorption of metals from solution B after reduction treatment. Distribution between 1 mL of resin and 100 mL of solution.**

| ION EXCHANGER | Aluminum mg/L | | Antimony mg/L | | Calcium mg/L | | Copper mg/L | | Iron** mg/L | | Magnesium mg/L | | Zinc mg/L | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* | S | R* |
| BLANK | 14 | 0 | 5.8 | 0 | 249 | 0 | 94 | 0 | 1,128 | 0 | 174 | 0 | 303 | 0 |
| Amberlite IRC-120 | 8 | 600 | 5.6 | 20 | 176 | 7,300 | 78 | 1,600 | 918 | 21,000 | 147 | 2,700 | 256 | 4,700 |
| Dowex XFS-4195 | 13 | 100 | 5.5 | 30 | 243 | 600 | 11 | 8,300 | 1,099 | 2,900 | 172 | 200 | 291 | 1,200 |
| Dowex XFS-43084 | 14 | 0 | 5.0 | 80 | 246 | 300 | 22 | 7,200 | 1,109 | 1,900 | 171 | 300 | 301 | 200 |
| Duolite C-467 | 10 | 400 | 1.3 | 450 | 245 | 400 | 92 | 200 | 1,012 | 11,600 | 172 | 200 | 296 | 700 |
| Duolite GT-73 | 13 | 100 | 5.2 | 60 | 239 | 1,000 | 72 | 2,200 | 1,099 | 2,900 | 169 | 500 | 296 | 700 |
| Lewatit TP-207 | 13 | 100 | 5.2 | 60 | 245 | 400 | 20 | 7,400 | 968 | 16,000 | 173 | 100 | 299 | 400 |

S Solution

R Resin

* Estimated from concentration difference

** 87.2% as Fe(II)

**Table 13 Distribution coefficients. Solution B after reduction treatment.**

| ION EXCHANGER | DISTRIBUTION COEFFICIENTS | | | | | | |
|---|---|---|---|---|---|---|---|
| | Al | Sb | Ca | Cu | Fe* | Mg | Zn |
| Amberlite IR-120 | 75 | 4 | 41 | 21 | 23 | 18 | 18 |
| Dowex XFS-4195 | 8 | 5 | 2 | 755 | 3 | 1 | 4 |
| Dowex XFS-43084 | 8 | 16 | 1 | 327 | 2 | 2 | 1 |
| Duolite C-467 | 40 | 346 | 2 | 2 | 11 | 1 | 2 |
| Duolite GT-73 | 8 | 12 | 4 | 31 | 3 | 3 | 2 |
| Lewatit TP-207 | 8 | 12 | 2 | 135 | 17 | 1 | 1 |

* 87.2% as Fe(II)

**Table 14 Metal extraction from the Falconbridge solution. Equilibrium distribution between 1 mL of resin and 300 mL of solution.**

| ION EXCHANGER | Calcium | | Cobalt | | Copper | | Nickel | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Solution mg/L | Resin[*] mg/L | Solution mg/L | Resin[*] mg/L | Solution mg/L | Resin[*] mg/L | Solution mg/L | Resin[*] mg/L | Solution mg/L | Resin[*] mg/L |
| BLANK | 247 | 0 | 4.2 | 0 | 57 | 0 | 123 | 0 | 4.4 | 0 |
| Dowex XFS-4195 | 247 | 75 | 4.1 | 0 | 12 | 13,500 | 82 | 11,750 | 3.8 | 250 |
| Dowex XFS-43084 | 246 | 75 | 4.2 | 0 | 16 | 14,000 | 88 | 11,750 | 4.4 | 200 |
| Duolite C-467 | 245 | 800 | 4.2 | 0 | 31 | 8,500 | 122 | 0 | 4.0 | 525 |
| Lewatit TP-207 | 243 | 1,150 | 4.2 | 0 | 9 | 15,000 | 96 | 8,500 | 4.1 | 250 |

* Determined by elution with 1 M sulphuric acid, except Dowex XFS-4195 which was eluted with 6 M HCl

**Table 15 Distribution coefficients. Falconbridge solution.**

| ION EXCHANGER | DISTRIBUTION COEFFICIENTS | | | | |
|---|---|---|---|---|---|
| | Ca | Co | Cu | Ni | Zn |
| Dowex XFS-4195 | 0 | 0 | 1,125 | 143 | 66 |
| Dowex XFS-43084 | 0 | 0 | 875 | 134 | 45 |
| Duolite C-467 | 3 | 0 | 274 | 0 | 131 |
| Lewatit TP-207 | 5 | 0 | 1,630 | 89 | 61 |

**Table 16 Metal extraction under mildly acidic conditions. Solution C. Equilibrium distribution between 1 mL of resin and 100 mL of solution.**

| | pH | Calcium | | Copper | | Magnesium | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|
| | | Solution | Resin* | Solution | Resin* | Solution | Resin* | Solution | Resin* |
| BLANK | 4.1 | 671 | 0 | 38 | 0 | 202 | 0 | 284 | 0 |
| Amberlite IRA-93 | 6.6 | 623 | 4,800 | 3 | 3,500 | 186 | 1,600 | 234 | 5,000 |
| " | 4.4 | 643 | 2,800 | 6 | 3,200 | 188 | 1,400 | 280 | 400 |
| Amberlite IR-120 | 2.9 | 382 | 28,950 | 30 | 800 | 149 | 5,300 | 228 | 5,600 |
| Amberlite IRC-718 | 2.5 | 643 | 2,800 | 3 | 3,500 | 198 | 400 | 192 | 9,200 |
| Dowex XFS-43084 | 3.3 | 663 | 800 | 1 | 3,700 | 198 | 400 | 264 | 2,000 |
| Dowex WGR | 6.3 | 627 | 4,400 | 4 | 3,400 | 187 | 1,500 | 242 | 4,200 |
| " | 4.7 | 644 | 2,700 | 19 | 1,900 | 197 | 500 | 280 | 400 |
| Duolite A-7 | 6.2 | 607 | 6,400 | 4 | 3,400 | 189 | 1,300 | 260 | 2,400 |
| " | 4.6 | 643 | 2,800 | 20 | 1,800 | 185 | 1,700 | 275 | 900 |
| Duolite GT-73 | 2.9 | 647 | 2,400 | 6 | 3,200 | 166 | 3,600 | 257 | 2,750 |
| Lewatit TP-207 | 3.6 | 640 | 3,100 | 4 | 3,400 | 199 | 300 | 204 | 8,000 |
| Clinoptilolite | 5.0 | 539 | 13,200 | 33 | 500 | 183 | 1,900 | 260 | 2,400 |

* Calculated from solution difference

**Table 17 Distribution coefficients. Solution C partially neutralized.**

| | pH | DISTRIBUTION COEFFICIENTS | | | |
|---|---|---|---|---|---|
| | | Calcium | Copper | Magnesium | Zinc |
| Amberlite IRA-93 | 6.6 | 8 | 1,167 | 9 | 21 |
| " | 4.4 | 4 | 533 | 7 | 1 |
| Amberlite IR-120 | 2.9 | 76 | 27 | 36 | 25 |
| Amberlite IRC-718 | 2.5 | 4 | 1,167 | 2 | 48 |
| Dowex XFS-43084 | 3.3 | 1 | 3,700 | 2 | 8 |
| Dowex WGR | 6.3 | 7 | 850 | 8 | 17 |
| " | 4.7 | 4 | 100 | 3 | 1 |
| Duolite A-7 | 6.2 | 11 | 850 | 7 | 9 |
| " | 4.6 | 4 | 90 | 9 | 3 |
| Duolite GT-73 | 2.9 | 4 | 533 | 22 | 11 |
| Lewatit TP-207 | 3.6 | 5 | 850 | 2 | 39 |
| Clinoptilolite | 5.0 | 24 | 15 | 10 | 9 |

**Table 18 Metal extraction at near neutral pH. Distribution between 1 mL of resin and 30 mL of Solution B.**

| ION EXCHANGER | Equilibrium pH | Calcium | | Cadmium | | Nickel | | Zinc | |
|---|---|---|---|---|---|---|---|---|---|
| | | Solution mg/L | Resin* mg/L | Solution mg/L | Resin* mg/L | Solution mg/L | Resin* mg/L | Solution mg/L | Resin* mg/L |
| BLANK | 6.0 | 727 | 0 | 89 | 0 | 29 | 0 | 47 | 0 |
| Amberlite IRA-93 | 5.1 | 672 | 1,650 | 81 | 240 | 16 | 390 | 11 | 1,080 |
| Amberlite IRC-718 | 6.5 | 341 | 11,580 | 0.8 | 2,646 | 0.6 | 852 | 0.8 | 1,386 |
| Dowex WGR | 6.2 | 663 | 1,920 | 40 | 1,470 | 18 | 330 | 7 | 1,200 |
| Duolite GT-73 | 4.3 | 622 | 3,150 | 5 | 2,520 | 25 | 120 | 38 | 270 |

* Estimated by solution difference

**Table 19 Distribution coefficients for a lime-neutralized solution.**

| ION EXCHANGER | DISTRIBUTION COEFFICIENTS | | | |
|---|---|---|---|---|
| | Calcium | Cadmium | Nickel | Zinc |
| Amberlite IRA-93 | 2 | 3 | 24 | 98 |
| Amberlite IRC-718 | 34 | 3,530 | 1,420 | 1,733 |
| Dowex WGR | 3 | 37 | 18 | 161 |
| Duolite GT-73 | 5 | 504 | 5 | 7 |

**Table 20 Saturation profile of XFS-43084. Solution B.**

| CONTACT No. | AQUEOUS CONCENTRATION, mg/L | | | | CUMULATIVE RESIN LOADING, mg/L | | | |
|---|---|---|---|---|---|---|---|---|
| | Calcium | Copper | Iron | Zinc | Calcium | Copper | Iron | Zinc |
| 1 | 259 | 26.4 | 1,096 | 310 | 0 | 7,170 | 5,000 | 200 |
| 2 | 259 | 31.3 | 1,127 | 311 | 0 | 13,850 | 6,900 | 300 |
| 3 | 258 | 41.1 | 1,132 | 312 | 100 | 19,550 | 8,300 | 300 |
| 4 | 258 | 58.6 | 1,145 | 313 | 200 | 23,500 | 8,400 | 200 |
| 5 | 259 | 66.5 | 1,149 | 312 | 200 | 26,660 | 8,100 | 200 |
| 6 | 258 | 77.0 | 1,154 | 312 | 300 | 28,770 | 7,300 | 200 |

1 mL of Dowex XFS-43084 contacted six consecutive times with 100 mL of Solution B.

**Table 21 Extraction kinetics for Dowex XFS-43084 (1 mL) and Solution A (100 mL).**

| TIME hours | AQUEOUS COPPER CONCENTRATION mg/L | RESIN LOADING[1] mg/L | FRACTIONAL APPROACH TO EQUILIBRIUM |
|---|---|---|---|
| 0.00 | 194 | 0 | 0.00 |
| 0.17 | 163 | 3,100 | 0.20 |
| 0.33 | 154 | 4,000 | 0.26 |
| 0.67 | 137 | 5,700 | 0.37 |
| 1.00 | 126 | 6,800 | 0.44 |
| 1.50 | 105 | 8,900 | 0.58 |
| 2.00 | 103 | 9,100 | 0.59 |
| 3.00 | 87 | 10,700 | 0.70 |
| 4.00 | 80 | 11,400 | 0.75 |
| 5.00 | 73 | 12,100 | 0.79 |
| 6.00 | 68 | 12,600 | 0.82 |
| 8.00 | 63 | 13,100 | 0.86 |
| 24.00 | 41 | 15,300 | 1.00 |

[1] Estimated from the solution analysis.

**Table 22 Column elution of XFS-43084 with 1 M sulfuric acid.**

| SOLUTION PASSED Bed Volumes | ELUATE CONCENTRATION, mg/L | |
|---|---|---|
| | COPPER | IRON |
| 0.0 | 0 | 0 |
| 1.1 | 1,195 | 1,603 |
| 2.1 | 19,507 | 7,210 |
| 3.1 | 7,480 | 810 |
| 4.1 | 1,247 | 43 |
| 5.1 | 269 | 13 |
| 6.6 | 87 | 7 |
| 8.9 | 37 | 0 |
| 16.0 | 5 | 0 |

**Table 23 Column extraction from a partially neutralized solution. Dowex XFS-43084 in the Na form.**

| SOLUTION TREATED BV | COLUMN EFFLUENT mg/L | | |
|---|---|---|---|
| | Calcium | Copper | Zinc |
| 10 | 488 | 0.3 | 3 |
| 20 | 707 | 0.0 | 52 |
| 30 | 711 | 0.0 | 138 |
| 40 | 749 | 0.0 | 202 |
| 51 | 715 | 0.0 | 235 |
| 61 | 717 | 0.0 | 259 |
| 71 | 719 | 0.0 | 274 |
| 82 | 713 | 0.0 | 284 |
| 92 | 719 | 0.1 | 292 |
| 103 | 717 | 0.1 | 288 |
| 114 | 712 | 0.0 | 289 |
| 125 | 716 | 0.1 | 301 |
| 136 | 707 | 0.0 | 285 |
| 147 | 717 | 0.0 | 280 |
| 157 | 712 | 0.2 | 274 |
| 175 | 703 | 0.1 | 273 |

Flowrate = 3 BV/h. Feed: Ca 711 ppm; Cu 54 ppm; Zn 274 ppm. pH = 4.5.

**Table 24 Column extraction from a partially neutralized solution. Amberlite IRC-718.**

| SOLUTION TREATED BV | COLUMN EFFLUENT mg/L | | |
|---|---|---|---|
| | Calcium | Copper | Zinc |
| 10 | 657 | 0.1 | 58 |
| 20 | 764 | 0 | 162 |
| 30 | 731 | 0 | 203 |
| 40 | 847 | 0 | 240 |
| 50 | 829 | 0 | 260 |
| 60 | 764 | 0 | 272 |
| 70 | 852 | 0 | 283 |
| 80 | 835 | 0 | 298 |
| 90 | 745 | 0 | 305 |
| 100 | 757 | 0 | 321 |
| 110 | 841 | 0 | 322 |
| 120 | 832 | 0 | 317 |
| 130 | 796 | 0.1 | 314 |
| 140 | 833 | 0 | 313 |
| 150 | 844 | 0 | 322 |
| 160 | 817 | 0 | 330 |
| 170 | 829 | 0 | 338 |
| 180 | 781 | 0 | 323 |
| 190 | 840 | 0 | 329 |
| 200 | 843 | 0 | 327 |
| 210 | 809 | 0 | 323 |
| 220 | 801 | 0 | 331 |
| 230 | 781 | 0 | 328 |
| 240 | 767 | 0 | 326 |
| 250 | 728 | 0 | 320 |
| 260 | 804 | 0 | 311 |

Flowrate: 3 BV/h. Feed: Ca 804 ppm, Cu 50 ppm, Zn 311, and Fe 0.05 ppm.

pH = 4.5.

### Table 25 Column elution of Amberlite IRC-718 with 1 M sulfuric acid.

| SOLUTION PASSED Bed Volumes | ELUATE CONCENTRATION, mg/L | | |
|---|---|---|---|
| | CALCIUM | COPPER | ZINC |
| 3.0 | 409 | 910 | 756 |
| 5.4 | 335 | 5,139 | 1,060 |
| 8.0 | 139 | 374 | 153 |
| 10.9 | 80 | 38 | 42 |
| 13.7 | 38 | 18 | 25 |
| 16.6 | 18 | 13 | 20 |
| 19.6 | 11 | 11 | 19 |
| 22.6 | 11 | 11 | 20 |
| 25.3 | 12 | 10 | 20 |

Flowrate: 2 BV/h

### Table 26 Column extraction of antimony with Amberlite C-467.

| SOLUTION TREATED BV | CONCENTRATION OF ANTIMONY IN THE COLUMN EFFLUENT mg/L |
|---|---|
| 20 | <0.1 |
| 40 | <0.1 |
| 60 | <0.1 |
| 80 | <0.1 |
| 100 | 1.0 |
| 120 | 1.0 |
| 140 | 1.1 |
| 160 | 1.2 |
| 180 | 1.2 |
| 200 | 1.3 |
| 220 | 1.3 |
| 240 | 1.3 |
| 260 | 1.4 |
| 280 | 1.4 |
| 300 | 1.5 |

Flowrate 10 BV/h.  Feed:  Sb 8.8 ppm, pH 1.8

**Table 27 Elution of Duolite GT-73 with 0.5M sulfuric acid.**

| SOLUTION TREATED BV | ELUATE COMPOSITION, mg/L | |
|---|---|---|
| | Cadmium | Zinc |
| 0.0 | 0 | 0 |
| 2.6 | 607 | 17 |
| 5.8 | 625 | 17 |
| 8.6 | 195 | 8 |
| 12.4 | 77 | 4 |
| 14.5 | 47 | 3 |
| 17.7 | 36 | 2 |
| 19.9 | 31 | 3 |
| 23.5 | 26 | 2 |

Flowrate: 3 BV/h

**Table 28 Extraction kinetics for Duolite GT-73 (2 mL) and Solution A (100 mL).**

| TIME hours | AQUEOUS CADMIUM CONCENTRATION mg/L | RESIN LOADING mg/L | FRACTIONAL APPROACH TO EQUILIBRIUM |
|---|---|---|---|
| 0.00 | 159 | 0 | 0.00 |
| 0.17 | 105 | 2,700 | 0.40 |
| 0.33 | 92 | 3,350 | 0.49 |
| 0.67 | 74 | 4,250 | 0.63 |
| 1.00 | 65 | 4,700 | 0.69 |
| 1.50 | 55 | 5,200 | 0.76 |
| 2.00 | 49 | 5,500 | 0.81 |
| 3.00 | 40 | 5,950 | 0.88 |
| 4.00 | 35 | 6,200 | 0.91 |
| 5.00 | 31 | 6,400 | 0.94 |
| 6.00 | 29 | 6,500 | 0.96 |
| 24.00 | 23 | 6,800 | 1.00 |

**Table 29 Column extraction of zinc and calcium with Amberlite IR-120.**

| SOLUTION TREATED BV | EFFLUENT COMPOSITION mg/L | | RESIN LOADING[1] mg/L | |
|---|---|---|---|---|
| | Zinc | Calcium | Zinc | Calcium |
| 8 | <0.2 | 0.6 | 2,374 | 5,754 |
| 25 | <0.2 | 0.4 | 7,146 | 17,320 |
| 42 | 85 | 18 | 10,452 | 28,499 |
| 59 | 225 | 303 | 11,401 | 34,847 |
| 72 | 286 | 632 | 11,346 | 35,560 |
| 83 | 274 | 653 | 11,431 | 35,888 |
| 93 | 274 | 662 | 11,513 | 36,114 |
| 103 | 274 | 655 | 11,594 | 36,406 |
| 113 | 276 | 651 | 11,653 | 36,732 |
| 123 | 269 | 672 | 11,782 | 36,851 |
| 133 | 275 | 673 | 11,852 | 36,961 |
| 143 | 276 | 676 | 11,911 | 37,040 |
| 153 | 272 | 658 | 12,009 | 37,294 |

[1] Estimated from the solution analyses. Flowrate = 5 BV/h

**Table 30 Column extraction of Cd, Ni and Zn with Amberlite IRA-93.**

| SOLUTION TREATED BV | EFFLUENT COMPOSITION, mg/L | | |
|---|---|---|---|
| | Cadmium | Nickel | Zinc |
| 22 | 105 | 8 | 4 |
| 44 | 163 | 22 | 39 |
| 66 | 156 | 25 | 57 |
| 87 | 158 | 26 | 68 |
| 108 | 151 | 26 | 78 |
| 129 | 153 | 25 | 77 |
| 149 | 146 | 26 | 78 |
| 170 | 150 | 25 | 78 |
| 192 | 153 | 25 | 73 |
| 213 | 151 | 24 | 78 |

Flowrate: 5 BV/h. Feed: Cd 153 ppm, Ni 25 ppm and Zn 287 ppm. pH = 6.0

**Table 31 Column extraction of Cd, Ni and Zn with Clinoptilolite.**

| SOLUTION TREATED BV | EFFLUENT COMPOSITION, mg/L | | |
|---|---|---|---|
| | Cadmium | Nickel | Zinc |
| 2.5 | 1 | 1 | 2 |
| 5.0 | 3 | 2 | 1 |
| 7.6 | 13 | 14 | 3 |
| 10.1 | 30 | 25 | 9 |
| 12.7 | 48 | 30 | 14 |
| 15.2 | 69 | 31 | 20 |
| 17.7 | 88 | 32 | 24 |
| 20.2 | 104 | 31 | 28 |
| 22.7 | 119 | 31 | 33 |
| 25.8 | 132 | 30 | 34 |
| 28.4 | 149 | 29 | 31 |
| 30.9 | 150 | 29 | 37 |
| 33.5 | 152 | 27 | 38 |
| 36.1 | 152 | 28 | 41 |
| 38.7 | 152 | 28 | 42 |

Flowrate: 5 BV/h. Feed: Cd 151 ppm; Ni 27 ppm and Zn 45 ppm. pH = 7.5

**Table 32 Column extraction of Cd, Ni and Zn from a neutralized solution with Zeolite 4A.**

| SOLUTION TREATED BV | COLUMN EFFLUENT COMPOSITION, mg/L | | |
|---|---|---|---|
| | CADMIUM | NICKEL | ZINC |
| 36 | <0.03 | <0.2 | <0.03 |
| 74 | <0.03 | 0.1 | <0.03 |
| 113 | <0.03 | 2.8 | <0.03 |
| 150 | <0.03 | 3.5 | <0.03 |
| 188 | <0.03 | 4.0 | <0.03 |
| 225 | <0.03 | 4.1 | <0.03 |
| 263 | <0.03 | 4.9 | <0.03 |
| 299 | 0.03 | 4.5 | 0.1 |
| 336 | 0.05 | 4.5 | 0.2 |
| 370 | 0.05 | 4.6 | 0.1 |
| 404 | 0.13 | 4.3 | 0.2 |
| 438 | 0.21 | 4.5 | 0.3 |
| 472 | 0.3 | 4.8 | 0.5 |
| 506 | 0.4 | 5.1 | 0.5 |
| 541 | 0.7 | 4.8 | 0.6 |
| 575 | 1.0 | 5.2 | 0.7 |

Flowrate: 5 BV/h. Feed solution: Ca 636 ppm; Cd 33 ppm; Cu <0.04 ppm; Fe <0.07 ppm; Ni 6.4 ppm; Pb <0.4 ppm; Sb 0.7 ppm; Zn 11.2 ppm. pH = 7.5

**Table 33 Column extraction of Cd, Ni and Zn from a neutralized solution with Amberlite IRC-718**

| SOLUTION TREATED BV | COLUMN EFFLUENT COMPOSITION, mg/L | | |
|---|---|---|---|
| | CADMIUM | NICKEL | ZINC |
| 25 | 0.02 | <0.2 | 0.1 |
| 50 | <0.01 | <0.2 | <0.1 |
| 75 | <0.01 | <0.2 | <0.1 |
| 99 | <0.01 | <0.2 | <0.1 |
| 124 | <0.01 | <0.2 | <0.1 |
| 149 | 0.04 | <0.2 | <0.1 |
| 174 | 0.18 | <0.2 | <0.1 |
| 199 | 0.4 | <0.2 | <0.1 |
| 224 | 0.8 | <0.2 | 0.1 |
| 249 | 2 | <0.2 | 0.2 |
| 274 | 3 | <0.2 | 0.5 |
| 299 | 4 | <0.2 | 0.6 |
| 323 | 7 | <0.2 | 1.2 |
| 345 | 9 | <0.2 | 1.2 |
| 365 | 10 | <0.2 | 1.5 |
| 391 | 15 | <0.2 | 2.4 |
| 419 | 14 | <0.2 | 2.8 |
| 444 | 19 | <0.2 | 2.6 |
| 479 | 23 | <0.2 | 2.6 |

Flowrate: 10 BV/h. Feed solution: Ca 805 ppm; Cd 26 ppm; Cu <0.06 ppm; Fe <0.04 ppm; Ni 5.2 ppm; Pb <0.4 ppm; Sb 0.7 ppm; Zn 8.7 ppm. pH = 7.0

**Table 34 Comparison of Annual reagent costs of three alternatives for the treatment of acid mine drainage.**

| CONDITIONS | FULL LIME NEUTRALIZATION TO pH 11 | LIME NEUTRALIZATION TO pH 6 AND ADSORPTION ON A RESIN | LIME NEUTRALIZATION TO pH 6 AND ADSORPTION ON A ZEOLITE |
|---|---|---|---|
| Flow, $m^3$/day | 10,000 | 10,000 | 10,000 |
| Initial pH | 2.1 | 2.1 | 2.1 |
| Reagent cost, $/year | | | |
| Lime[1] | 1,560,375 | 1,178,950 | 1,178,950 |
| Sulphuric acid[2] | 3,756 | 102,200 | N/A |
| Sodium hydroxide[3] | N/A | 69,987 | N/A |
| Sodium chloride[4] | N/A | N/A | 29,638 |
| Resin[5] | N/A | 83,333 | N/A |
| Zeolite[6] | N/A | N/A | 41,666 |
| **TOTAL** | **1,564,131** | **1,434,470** | **1,250,254** |

Note: The above estimates are based on a process running 24 h/day for 365 days/yr. This estimate includes reagent cost only. Capital and labour costs would be similar for the three options. Credits for the recovery of metal for the last two options are not included.

[1] The lime consumption was determined experimentally as 4.5 kg/$m^3$ for pH 11 and 3.4 kg/$m^3$ for pH 6. The quoted price of lime was $95 per ton.

[2] The sulphuric acid consumption to adjust the pH from 11 to 7 was determined experimentally as 14.7 g/$m^3$. The quoted price for sulphuric acid was $70 per ton.

[3] The amount needed to regenerate Amberlite IRC-718 was determined experimentally as 8.5 BV of 0.1 M NaOH. The quoted price for NaOH was $140 per ton.

[4] This assumes that the elution of zeolite can be done with 10 BV of 1 M sodium chloride and that 90% of the NaCl can be recycled. The quoted price of NaCl was $35 per ton.

[5] The cost of the resin was estimated assuming a life span of 10 years and a price of $15,000 per $m^3$. The resin inventory was calculated assuming a flowrate of 15 BV/h and two columns. The total resin inventory was estimated as 55.56 $m^3$.

[6] The cost of zeolite was estimated assuming a life span of 10 years, a price of $7.5 per $m^3$ (Cripps, 1994), a flowrate of 15 BV/h and two columns.

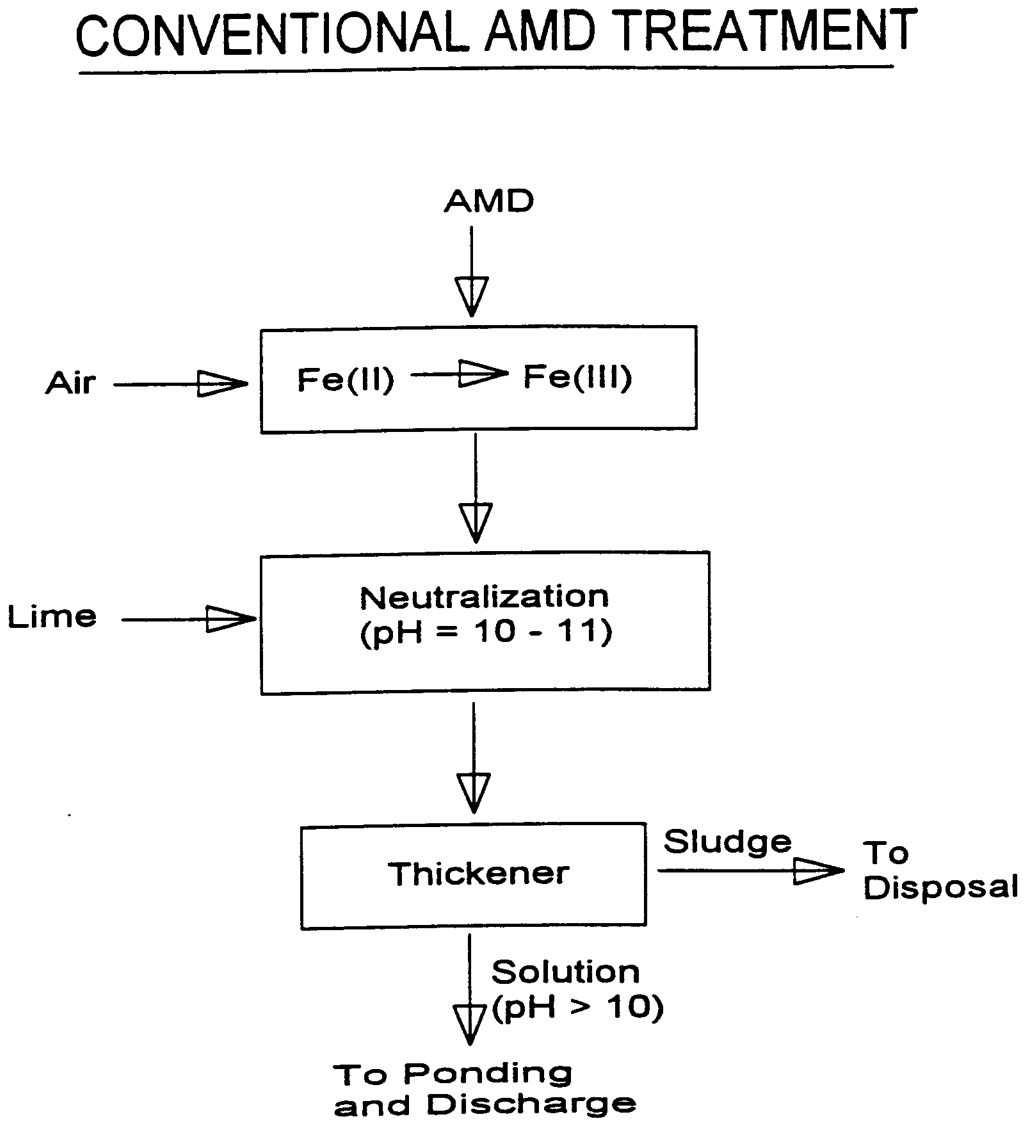

Figure 1 Simplified flowsheet of a conventional lime neutralization process.

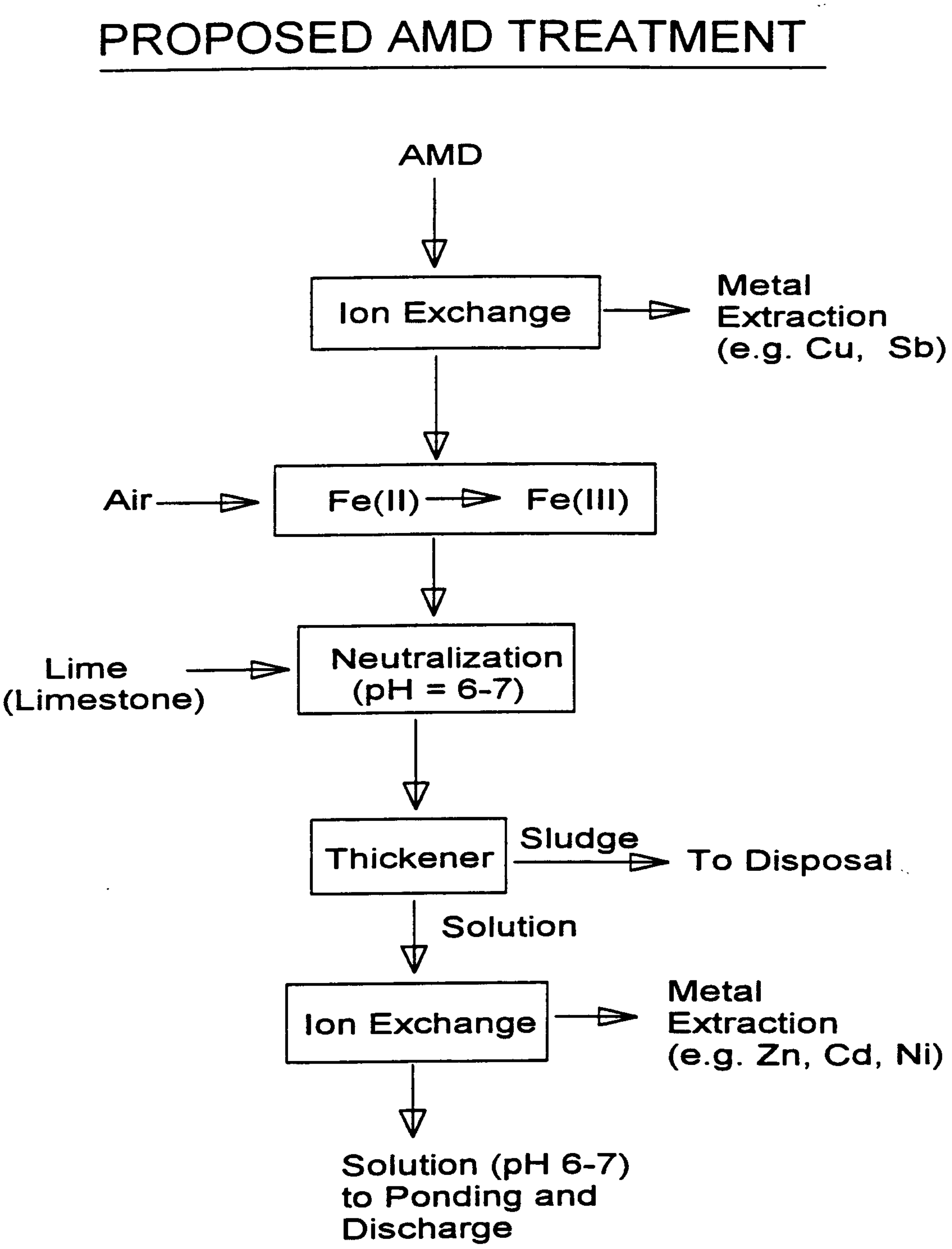

**Figure 2** Simplified flowsheet of a proposed process comprising lime neutralization and ion exchange.

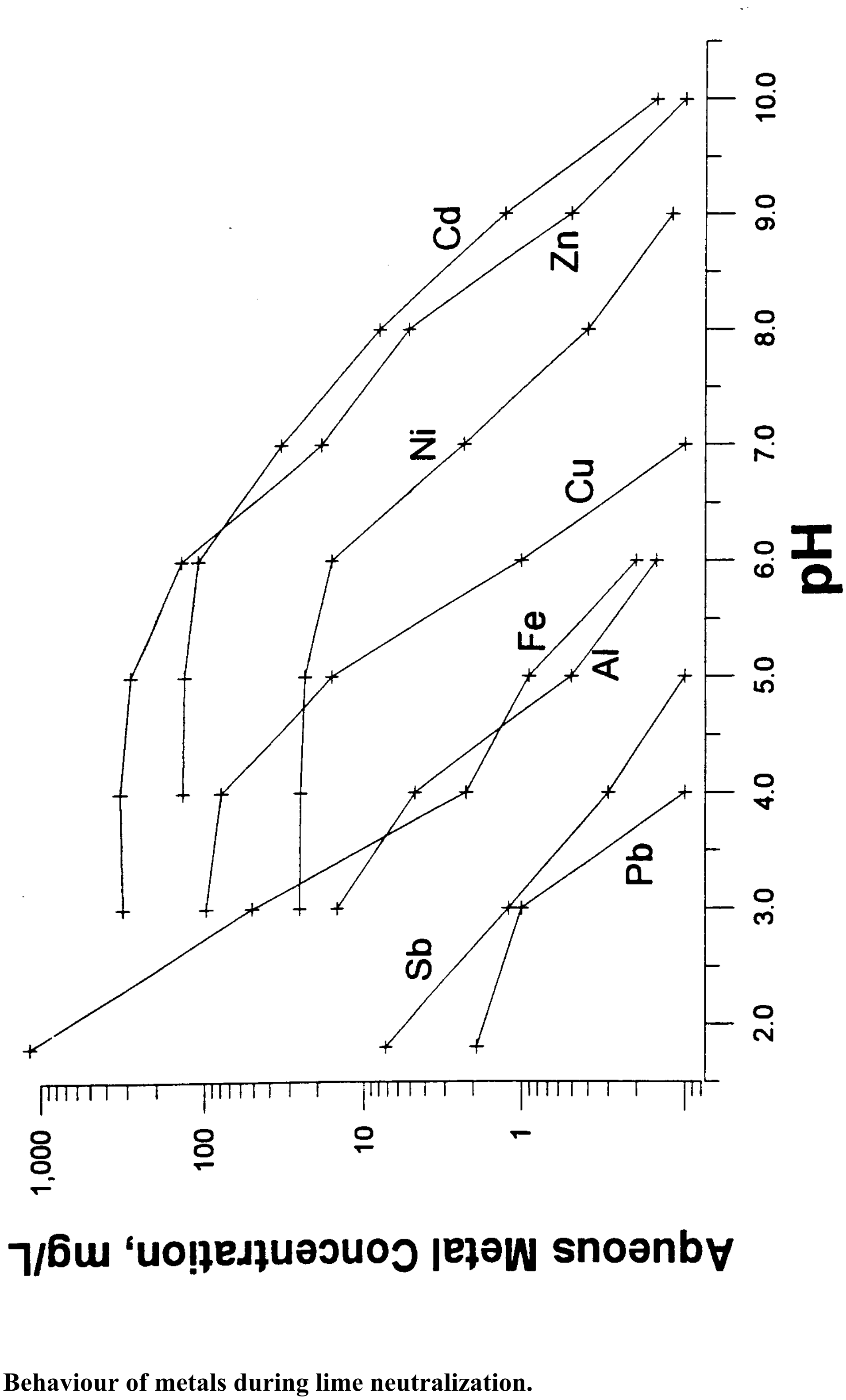

Figure 3 Behaviour of metals during lime neutralization.

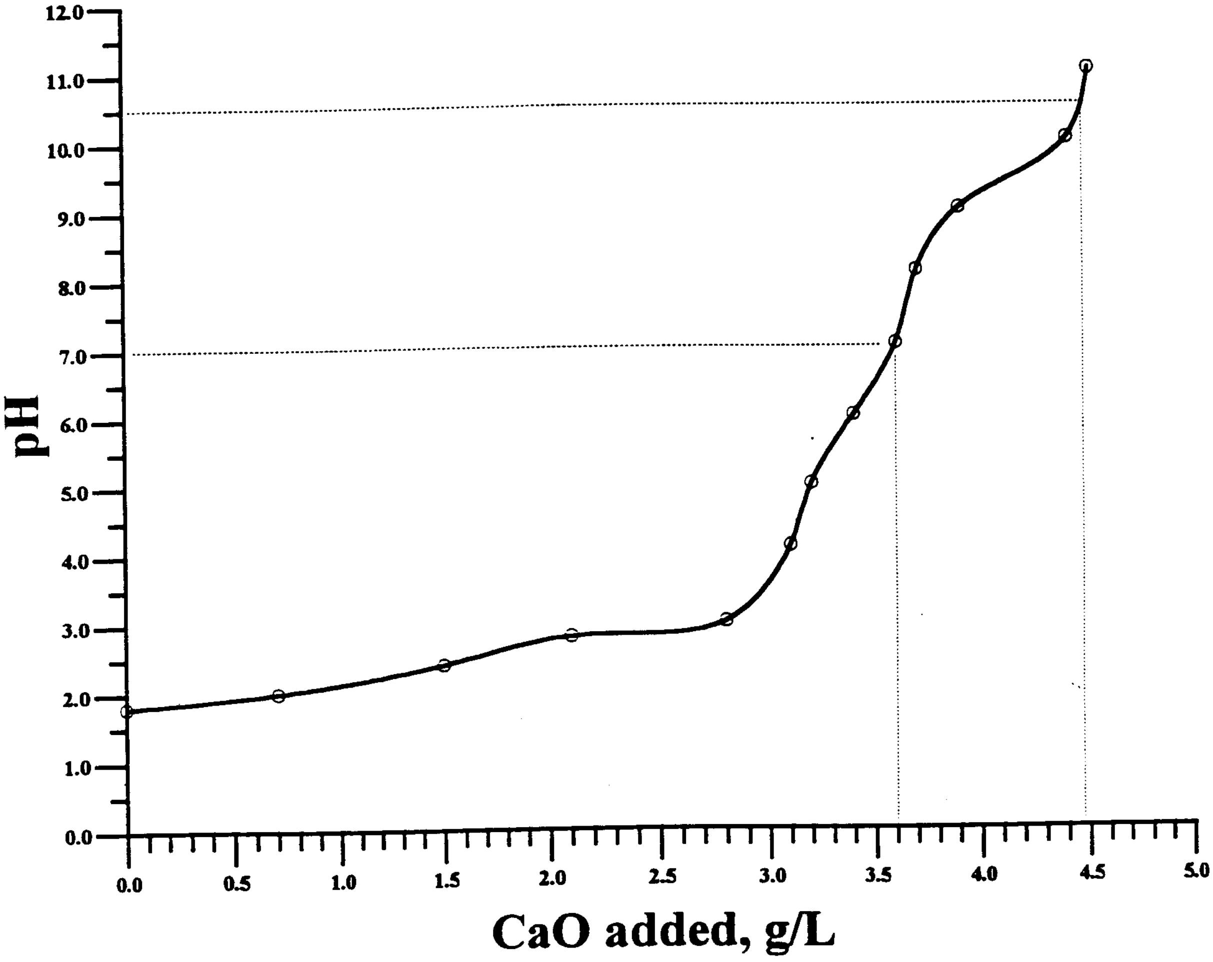

Figure 4 Consumption of lime as a function of pH.

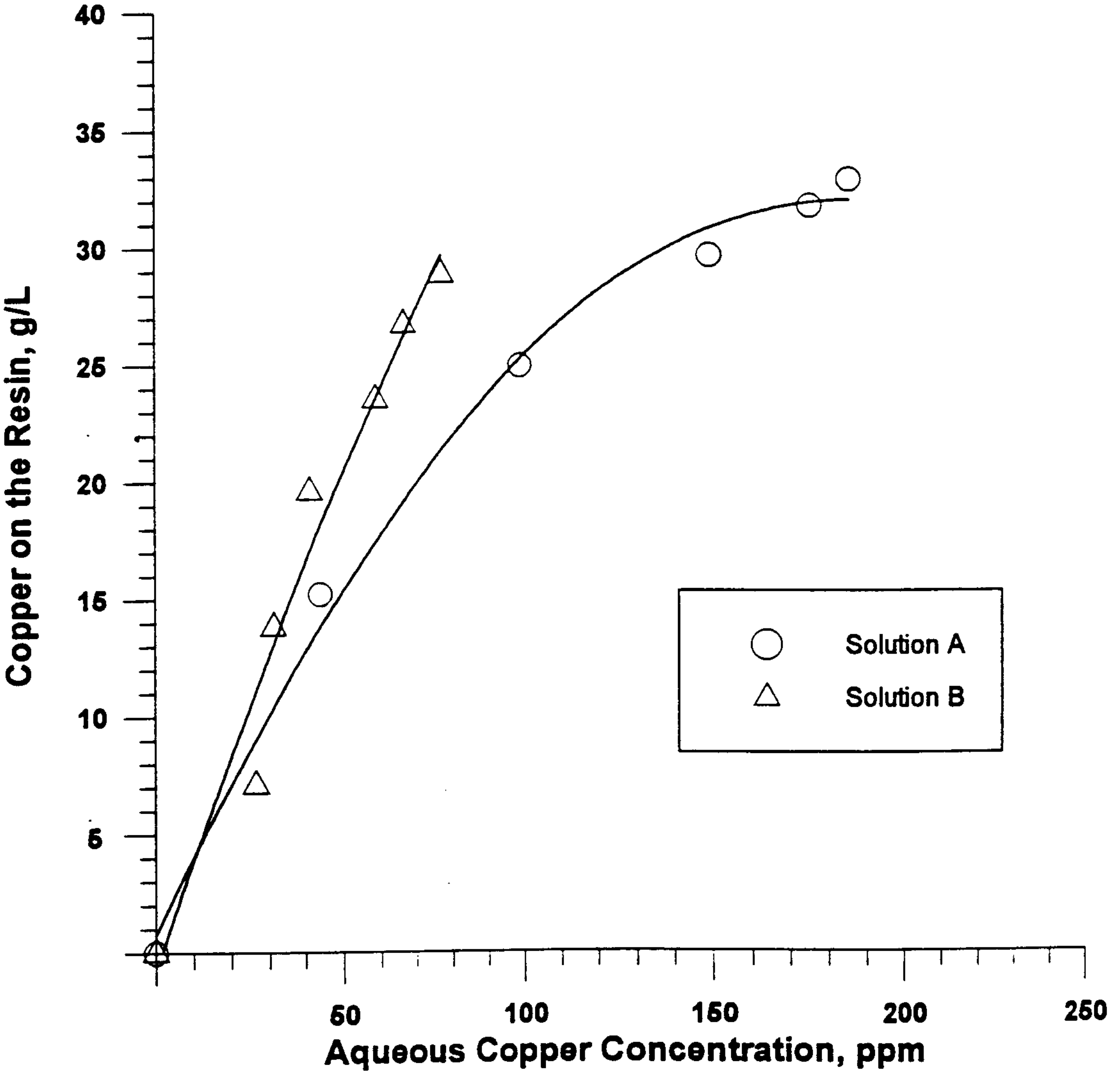

Figure 5 Copper equilibrium distribution isotherms.

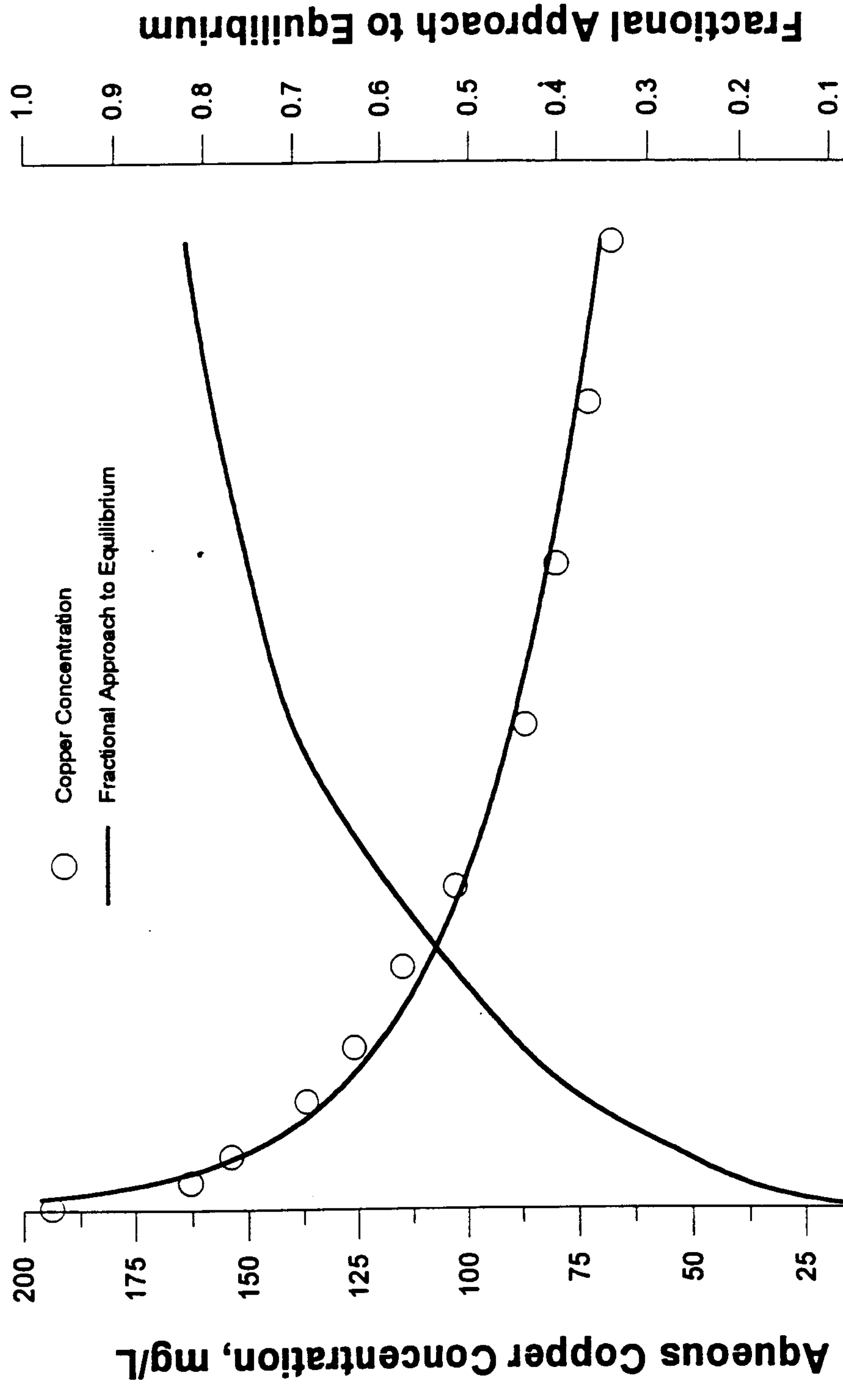

Figure 6 Adsorption kinetics of copper by Dowex XFS-43084.

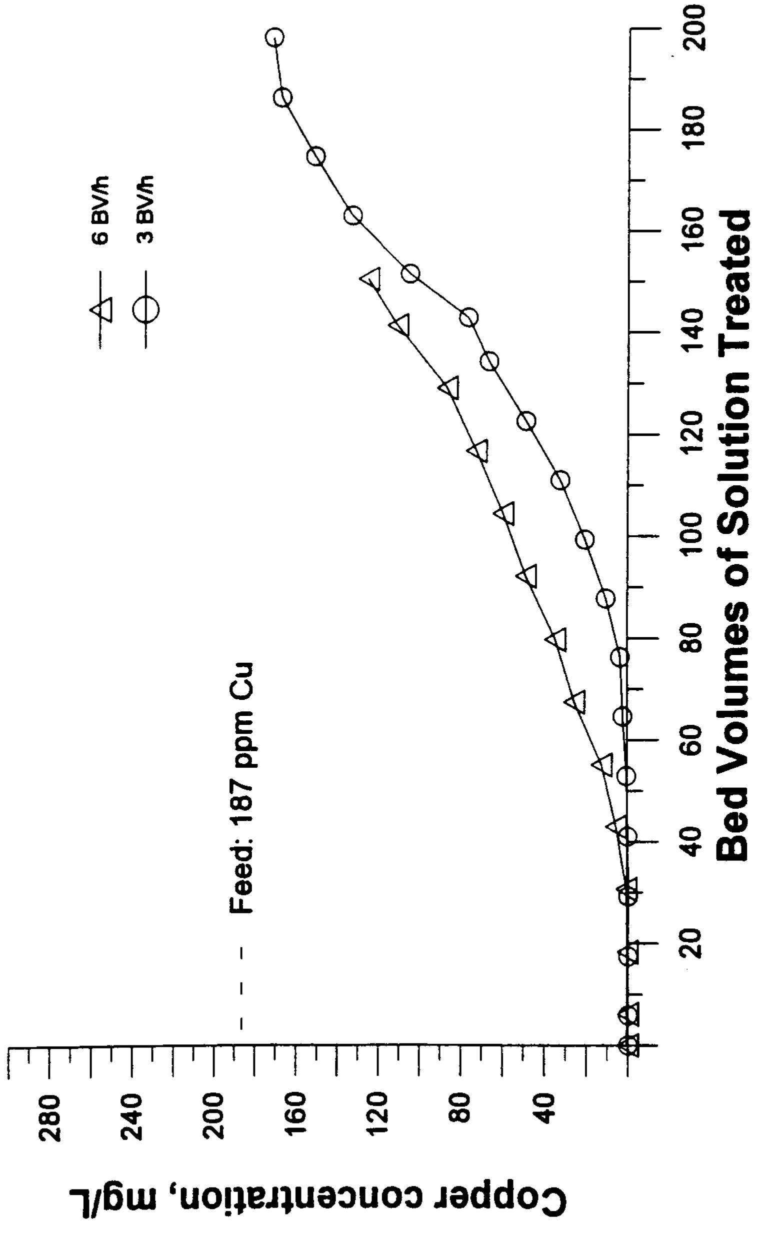

Figure 7 Column extraction of copper with Dowex XFS-43084.

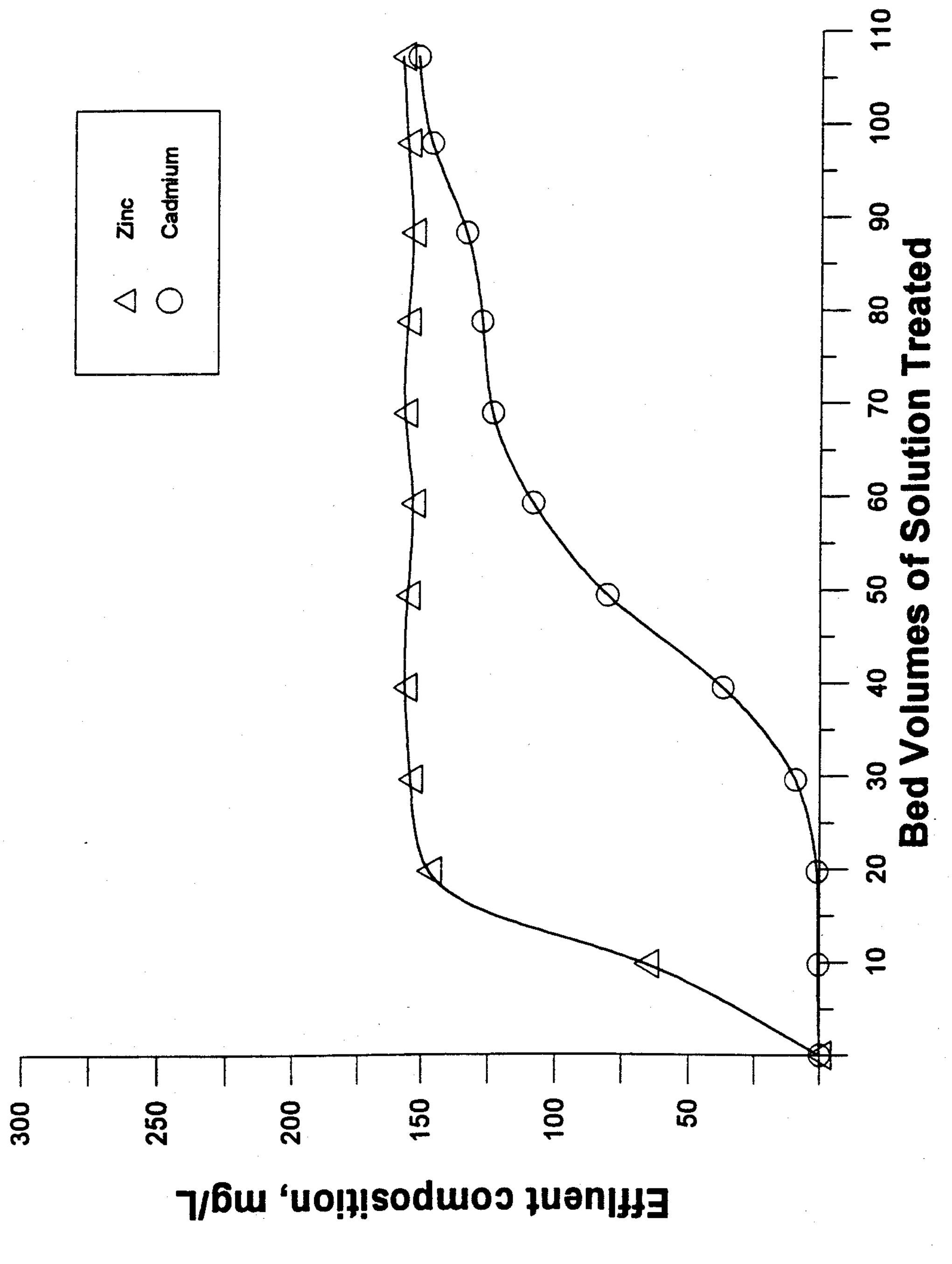

Figure 8 Column extraction of Cd and Zn with Duolite GT-73.

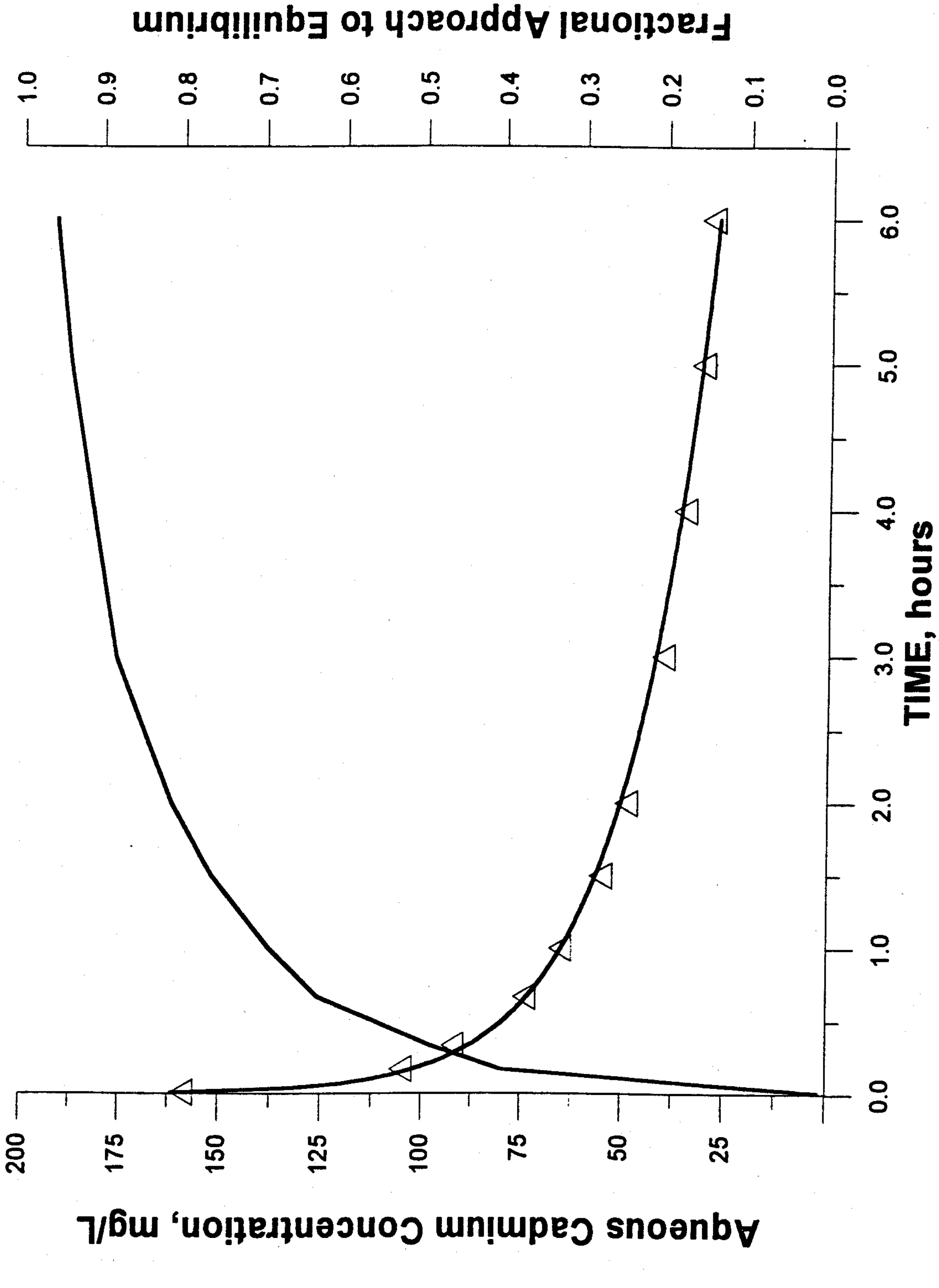

Figure 9 Adsorption kinetics of cadmium by Duolite GT-73.