Mines Branch Information Circular IC 252

ION-EXCHANGE RECOVERY OF COPPER, ZINC AND NICKEL FROM ACID-SULPHATE AND ALKALINE-CYANIDE WASTE WATER

by

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ABSTRACT

The literature of the past twenty years describing the use of ion-exchange methods for the treatment of copper-, zinc- and nickel-bearing acid-sulphate or alkaline-cyanide wastes is reviewed. Applications of sulphonic, carboxylic, and weak-base ion-exchange resins to the treatment of a variety of base-metal-bearing waste solutions from industrial plants and mines are described. One investigation of the treatment of alkaline cyanide solution containing base-metal-cyanide complexes with a strong-base ion-exchange resin is reviewed. The literature suggests that an ion-exchange process based on a sulphonic-type resin could be useful for the treatment of acid-sulphate mine or metallurgical waste, but further work to develop design criteria is necessary. Further work of a more preliminary nature is needed to determine whether present ion-exchange media have a potential application to the treatment of alkaline-cyanide waste solutions.

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Direction des Mines

Circulaire d'information IC 252

LA RÉCUPÉRATION PAR ÉCHANGE IONIQUE DU CUIVRE, DU ZINC ET DU NICKEL CONTENUS DANS LES EAUX RÉSIDUAIRES À BASE DE SULFATE ACIDE OU DE CYANURE ALCALIN

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RÉSUMÉ

L'auteur passe en revue les travaux publiés au cours des vingt dernières années sur l'emploi des méthodes d'échange d'ions pour la récupération du cuivre, du zinc et du nickel des eaux résiduaires à base de sulfate acide ou de cyanure alcalin. Il décrit les applications des résines échangeuses d'ions sulfoniques, carboxyliques et faiblement basiques au traitement de divers effluents miniers et industriels contenant des métaux communs. Il relève en particulier une étude du traitement des solutions de cyanure alcalin contenant des complexes de cyanures de métaux communs à l'aide d'une résine échangeuse d'ions fortement basique. Les ouvrages étudiés laissent croire qu'un procédé à échanges d'ions fondé sur une résine de type sulfonique pourrait servir utilement au traitement des effluents miniers ou métallurgiques à base de sulfate acide, mais qu'il faut en approfondir l'étude avant de mettre au point des critères de conception. De même, il faudra d'autres travaux préliminaires pour déterminer si les échangeurs d'ions peuvent servir au traitement des solutions résiduaires à base de cyanure alcalin.

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INTRODUCTION

This report is a "state of the art" review relative to the treatment, by ion-exchange techniques, of dilute acid-sulphate or alkaline-cyanide waste solutions containing low concentrations of the common base metals such as copper, zinc and nickel. Solutions of this type are produced as a waste product in some mining operations, and where this situation exists these solutions might be a potential source of pollution. Solutions having a pH value as low as 2.0, and containing base metals, have occurred as mine water or surface drainage water in base-metal operations. Waste water from base-metal flotation operations, where an alkaline cyanide salt is used as a depressant, sometimes contains dilute concentrations of base metals, presumably as cyanide complexes. It was obvious that a review of this type would be of value to those mine operators who might be faced with the problem of acid-sulphate or alkaline-cyanide waste effluents.

Most of the recorded data on base-metal recovery from sulphate or cyanide systems by ion exchange have been derived from the study of processes used to recover metals from wastes from the plating and textile industries. In these applications, dilute concentrations of base metals are concentrated from the rinse wastes by sulphonic-type cation exchangers and then re-circulated for in-plant use. The base-metal concentrations of

these wastes are usually in the same order as those of the wastes from surface drainage and mine operations. Pilot-plant work on dilute mine waters has indicated that carboxylic-acid resins also have some potential for base-metal recovery from some mine waters, although it is not clear that the carboxylic resins are capable of producing a discardable waste.

The adsorption of dilute concentrations of base metals from alkaline cyanide solutions on anion exchangers has been briefly examined on a laboratory scale only.

COPPER RECOVERY FROM SULPHATE SOLUTIONS WITH SULPHONIC-TYPE RESINS

Copper recovery by ion exchange from dilute sulphate solutions has been examined more frequently than either zinc or nickel recovery.

In the copper and brass industry, the cation exchanger Amberlite IRC 120, made by Rohm and Haas, was proposed for the recovery and concentration of copper from typical rinse waste solutions from metal-plating plants [1]. These solutions contained on the average 8.5 to 35 ppm Cu, 3.1 to 7.4 ppm Zn, 0.3 to 0.6 ppm Ni, 6.4 ppm Cr^{3+}, 190 to 503 ppm H_2SO_4, and total hardness equivalent to about 50 ppm $CaCO_3$. Solution pH ranged from 2.0 to 3.7. The optimum adsorption flow rate was 2 gal/cu ft resin/min, and a flow rate of 8 gal/cu ft resin/min was estimated to be the limit for good operation. It was reported that >95%

of the Cu and Zn was adsorbed. Adsorption was stopped when the copper analysis of the effluent was 5% of that of the influent, or 2 ppm, whichever was least.

A resin loading of about 1.5 lb Cu/cu ft of resin was obtained before copper reported in the effluent, when treating a solution containing 73 ppm Cu, 62.4 ppm H_2SO_4 and total hardness equivalent to 56 ppm of $CaCO_3$. When treating a solution containing 4.5 ppm Cu, 5.9 ppm Zn, 684 ppm H_2SO_4 and a total hardness equivalent to 56 ppm $CaCO_3$, the loading up to the point when metal reported in the effluent was about 0.3 lb (Cu + Zn)/cu ft of resin. The much lower metal loading obtained in this second test was thought to be due to the higher concentration ratio of total hardness to metal rather than to pH, since it is known that the sulphonic-type resins are relatively insensitive to pH change in the acid side [9]. This work also showed that when zinc was present with copper in the feed solution, the sulphonic type resin would not preferentially adsorb either of the two metals.

When copper only was loaded on the resin, 99 to 100% of the copper was recovered from the loaded resin with a 20% H_2SO_4 eluting solution. The first 25% fraction of the eluate, which contained up to 12 g Cu/litre, was returned to the plating plant as pickle liquor make-up. The balance of the eluate was retained as eluting solution for the next cycle.

The following data were provided by T. J. Fadgen of the General Motors Corporation and were based on an operation for the recovery of copper by ion exchange using Rohm and Haas IRC-120 resin from 6,000 gallons of acid rinse solution per day:

Adsorption

Resin capacity	0.31 lb Cu/cu ft
Resin volume per column	9 cu ft
Adsorption flow	45 gpm
Solution volume treated per adsorption	1,200 gal
Cu recovered per adsorption	2.81 lb

Elution with 10% H_2SO_4

10% acid consumed	20 lb/cu ft
Elution flow	4.5 gpm
Eluate volume per column	117 gal

Cycle Times

Adsorption	0.45 hr
Elution	0.43 hr
Water flush	0.10 hr
Total	0.98 hr

Since only one column was used, five cycles were required to treat the 6,000 gallons rinse water daily.

For about 25 years, copper has been recovered by ion-exchange methods from dilute waste solutions resulting from the manufacture of textiles in the cuprammonium cellulose industry [3]. The Zeo-Karb cation exchanger used is basically a sulphonic-acid resin with phenolic and/or carboxylic acid groups. These solutions contain 25 ppm copper, as an ammonium cationic complex $[Cu(NH_4)_2^{++}]$, with a few thousand ppm of Na_2SO_4 and $(NH_4)_2SO_4$. At the beginning of adsorption the resin is in an ammonium form, and the copper is exchanged for the ammonium ion on the resin as follows, where R represents the ion exchange resin:

$$(NH_4)_2R + Cu(NH_4)_2^{++} \longrightarrow Cu(NH_4)_2R + 2NH_4^+$$
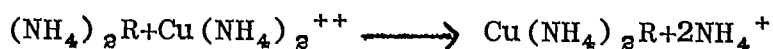
The copper is eluted with sulphuric acid to produce an eluate containing 32 g Cu/l. After elution, the resin is converted to the ammonium form with ammonium hydroxide:

$$Cu(NH_4)_2R + H_2SO_4 \longrightarrow Cu(NH_4)_2SO_4 + H_2R$$
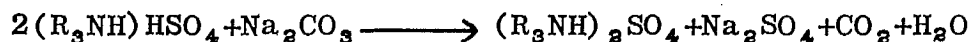
$$H_2R + 2NH_4OH \longrightarrow (NH_4)_2R + 2H_2O$$
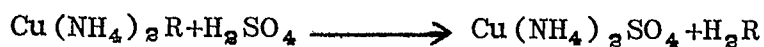
where R is a sulphonated cation resin.

This particular application is not relevant to the treatment of mine waters which contain metals in acid sulphate solution. However, where there are waste solutions from a hydro-metallurgical process that involves copper amine complexes, this process may be of interest.

COPPER RECOVERY FROM SULPHATE
SOLUTIONS WITH WEAK-BASE RESINS

In a preliminary investigation [4], copper was recovered from a dilute synthetic mine water with a loading of 0.93 lb Cu/cu ft resin on the weakly basic anion exchanger Duolite A-30. The synthetic mine water contained 295 ppm Cu, 3900 ppm Zn, 3140 ppm Fe, and 500 ppm H_2SO_4. This water was adjusted to pH 4 before continuous counter-current contact with the resin. The resin was pH-conditioned, before adsorption, to about pH 4 with sodium carbonate, and the adsorbed copper was eluted with 6-10% H_2SO_4 solution as follows:

$$2(R_3NH)HSO_4 + Na_2CO_3 \longrightarrow (R_3NH)_2SO_4 + Na_2SO_4 + CO_2 + H_2O$$

$$2(R_3NH)_2SO_4 + CuSO_4 \longrightarrow Cu(R_3N)_4SO_4 + 2H_2SO_4$$

$$Cu(R_3N)_4SO_4 + 4H_2SO_4 \longrightarrow 4(R_3NH)HSO_4 + CuSO_4.$$

When the resin was used in the acid form, copper selectivity and total metal-loading capacity were decreased. Ferric iron was adsorbed when the mine water pH was 2.0 and the resin was used in the acid form. At pH 4, the ferric iron was precipitated during pH adjustment of the water and could be eliminated by filtering out the precipitate prior to the ion exchange step.

Because the resin was used in mixer-settler equipment rather than in a column, the results of the work do not tell us what loadings might be expected when the copper content of the effluent is limited to 21 ppm. The effluent from the mixer-settlers contained about 5 ppm copper.

COPPER RECOVERY FROM DILUTE SOLUTIONS
WITH CARBOXYLIC-ACID-TYPE RESINS

Rohm and Haas Amberlite IRC-50 and Permutit H-70

carboxylic-acid-type resins were used by T.A.A. Quarm to

selectively adsorb >85% of the copper present in ion-exchange

feed solutions containing 0.15 to 0.3 g Cu/1, 0.2 to 0.4 g Zn/1,

1.5 to 3.0 g Fe/1, 0.01 to 0.03 g As/1, and up to 0.5 g H_2SO_4/1.

The pH values of these solutions were about 4.0 [5].

With a column containing 200 ml of H-form Amberlite

IRC-50 resin, subsequently converted to the sodium form with

sodium carbonate, over 87% of the copper was adsorbed by the

resin from pH 3.6 mine water. The adsorption flow rates varied

from 0.25 to 0.50 ml/min/ml of resin, giving retention times of

from 0.8 to 1.6 min. The resin loading on the resin was 0.96 lb

per cu ft of H-form resin.

The copper was eluted with saturated NaCl solution to

a concentration of 3 g Cu/1 in the eluate. The eluate flow

rate was 0.125 ml/min/ml of resin, giving a retention time of

3.2 min. A 10% H_2SO_4 wash was required, after elution, to dissolve

a precipitate that coated the resin and to elute another 5% of

the adsorbed copper. In Quarm's work there is no mention of the

recovery or separation of zinc.

Because the Na_2CO_3 used for resin conversion was considered

to be costly, another test was done on a larger column which

contained 1.95 litres of H-form Permutit H-70 resin subsequently

converted to the Ca form with calcium hydroxide. The pH of the mine water was adjusted to 4.0 and fed to the column at a rate to give a retention time of 2.7 minutes. Copper loaded to about 0.6 lb Cu/cu ft H-form resin, which is about two-thirds the loading obtained with the IRC-50 resin in the Na-form.

The copper was eluted and concentrated by a factor of 50 with 5% H_2SO_4. A refined copper powder of 99.98% Cu was obtained by electrolysis of the eluate. The reagent consumption per pound of copper recovered were reported to be 12.8 lb limestone for neutralization, 7.1 lb lime for resin conversion, and 5.4 lb H_2SO_4. Presumably the acid consumed could be reduced by recirculating acid recovered from electrolysis.

From his studies, Quarm concluded that ion-exchange recovery of copper from mine water was economic despite the low capacity loading. According to Breton and Schlechten [9], increasing the pH of the feed solution would increase the metal loading on the carboxylic-type resin. However, adjusting the pH to values greater than 4.0 would result in precipitation of copper from the feed solution. Quarm pointed out that what is needed is a resin with the selective characteristics of the carboxylic type of resin and the pH characteristics of the sulphonic type. Such a resin would be not only selective but also applicable in both acid and alkali solutions.

Subsequent to Quarm's study, J.S. Jacobi [6] reported
a summary of a 3-column pilot-plant study using the Ca form of
Rohm and Haas Amberlite IRC-50 carboxylic acid resin. In this
investigation, 91% of the copper was recovered from a mine water
containing 0.26 g Cu/litre and neutralized to pH 3.5 with
limestone. Prior to ion-exchange treatment the mine waters were
clarified on a sand filter. While two columns were used in
series on adsorption, the third column was eluted with H_2SO_4
and then reconverted to the Ca form with calcium hydroxide.
Gypsum formed during conversion to the Ca form was flushed out
with water. Metallic copper was electrolytically recovered
from the eluate, which contained 109 g Cu/litre. The acid produced
during electrolysis was recycled to the elution step. Resin
volumes, loadings, and optimum conditions of operation were not
reported.

After nearly two years of pilot plant investigations,
Jacobi concluded that about 90% of the copper present in mine
waters containing about 0.3 g Cu/l could be recovered by an ion-
exchange process utilizing a carboxylic-acid resin in the calcium
form. Although the method was technically feasible, loadings
were low and overall costs were relatively high. In addition,
a study by Gilmore [7] on the copper-loading characteristics of
carboxylic acid resins showed that, in the pH range of 3.5 to 5.0,
copper values as high as 20 ppm were present in the barrens after

only 15 to 20 bed volumes had been passed through the column. All of this suggested that the carboxylic type of resin would not be particularly attractive for the treatment of waste effluent for the purpose of reducing copper concentration to 1 ppm or less.

THE SEPARATION OF COPPER AND ZINC
WITH CARBOXYLIC-TYPE RESINS

In 1951, Breton and Schlechten [9] conducted a study to determine the possibility of using carboxylic-type resins for the selective recovery of copper and zinc. They found that when treating a solution containing 160 ppm of copper and a similar concentration of zinc, both metals were adsorbed initially and then the adsorbed zinc cation was displaced by copper.

In addition, these investigators showed the very strong effect of pH on the capacity of the carboxylic resin to adsorb metal. Their data showed that essentially no metal was adsorbed at pH 4.0 but that over 2.0 lb metal/cu ft of resin was adsorbed at pH 7.0. No mention was made of the problem of metal precipitation at the higher pH values.

In this study the loaded resin was stripped with 40% H_2SO_4 solution. Since the resin must be in the sodium form for metal adsorption, the resin must be pH-equilibrated with sodium hydroxide after stripping.

The low loading characteristics of the carboxylic-type resin in the pH range common to mine waters containing base

metals, and the extra problems involved in converting the resin
to the sodium form, suggest that this type of resin would not be
attractive for the selective recovery of copper from zinc in
an acid-sulphate system.

ZINC RECOVERY FROM SULPHATE
SOLUTIONS WITH SULPHONIC-ACID-TYPE RESINS

In the method used for making rayon tire cord by the
viscose process, the cellulose filament at one stage is passed
through a solution containing about 12% Na_2SO_4, 15% H_2SO_4, and
1 g Zn/l. This solution is subsequently washed off the filament,
and the rinse water, which contains 4 g Na_2SO_4/l, 5 g H_2SO_4/l
and about from 0.1 to 3.0 g Zn/l, must be treated for metal
recovery.

Mindler [3] reports that this rinse solution has been
successfully treated in a number of plants by an ion-exchange
step in which H-form sulphonic-acid resins were used as the exchanger.
The Rohm and Haas Amberlite IRC-120 and Permutit Q resins are of
this type. After adsorption of the zinc, the metal is eluted
with 25-30% H_2SO_4 solution to produce five separate fractions of
eluate. The product fraction contains about 12% $ZnSO_4$, 8% H_2SO_4,
and 8% Na_2SO_4. This fraction is recycled to the filament bath.
In some cases the elution may be done with filament-bath
solution [10].

Specific applications of this ion-exchange method for zinc recovery from viscose plant wastes have been reported by the Cornwall, Ontario, plant of Courtaulds (Canada) Limited [11], and by Mindler, Gilwood and Saunders [12], and McGarvey [13]. In all of these applications, zinc loadings on the resin of up to 3 lb Zn/cu ft resin were obtained, while eluates were produced which contained zinc concentrations of up to 100 g Zn/l. It was observed that the zinc loading dropped off as the H^+ and Na^+ combined concentration rose above 15 g/l [11]. It was also observed that as the acid concentration increased above 1% H_2SO_4, zinc slippage from the resin tended to increase [12]. McGarvey [13] used 20% NaCl or Na_2SO_4 solution for elution.

NICKEL RECOVERY FROM SULPHATE SOLUTIONS WITH SULPHONIC-ACID-TYPE RESINS

C.F. Paulson [14] proposed a method for the recovery of 22 ppm Ni from sulphate rinse-water wastes from nickel electroplating operations. The resin used in this work was the sulphonic-acid cation exchanger, Permutit Q. Elution with 1 N H_2SO_4 solution produced an eluate containing 20 g Ni/litre and 20 g H_2SO_4/litre which was recycled to the plating bath. If required, the acidity of the recycled solution was adjusted to pH 5.0 with $NiCO_3$. Resin loading was not given.

T.J. Fadgen [15] treated 13,000 gal per day of sulphate rinse-water waste from an electrolytic plant. This waste contained

150 ppm Ni. The solution was fed to a column containing 7.5 cu ft of Rohm and Haas Amberlite IRC-120 at a flow rate of 37.5 gal/min. The resin loading attained was 1.09 lb Ni/cu ft resin and the column was loaded twice a day. The total cycle time was 3.4 hours. Elution was done with 10% H_2SO_4 at a flow rate of 3.75 gal/min. Acid consumption in the elution step was 2.4 lb H_2SO_4/lb Ni. The concentrated $NiSO_4$ solution was returned to the electroplating bath.

In a process similar to the preceding two [16], a loading of 1.9 lb Ni/cu ft of a cation exchanger was reported. A concentrated solution of 60 g Ni and 24 g H_2SO_4/litre, obtained by a split-elution procedure with H_2SO_4, was recirculated to the plating baths. Excess acidity was adjusted with $NiCO_3$.

In another paper [17], it was reported that 100% of the nickel present in an electroplating-plant waste solution at a concentration of 870 ppm Ni was adsorbed by a cation exchanger. The flow rate was 1300 gal/hour. A concentrated solution, produced on elution with HCl or H_2SO_4, was returned to the plating tank after pH adjustment with either acid or $NiCO_3$.

COPPER, ZINC AND NICKEL RECOVERY FROM
ALKALINE CYANIDE SOLUTIONS WITH STRONG-BASE RESINS

In laboratory-column studies, the capacity loading of Rohm and Haas Amberlite IRA-400 [18] resin for each of the complex cyanides was determined to be:

82.1 mg Cu/g dry resin, or 1.95 lb Cu/cu ft

81.6 mg Zn/g dry resin, or 1.93 lb Zn/cu ft

106.9 mg Ni/g dry resin, or 2.53 lb Ni/cu ft

The zinc was eluted with 0.1 N HCl. Nickel was rapidly eluted with 1 N HCl. Copper was eluted with 1 N and 2 N NaCN, 2 N and 4 N HCl, and 2 N NaCl. Caustic solutions [14] may also elute the copper.

DISCUSSION

The most commonly used method in the past for removing metal and other pollutants from mining and metallurgical waste products has been simple neutralization of the wastes. The neutralized waste is usually discharged to the mine tailings pond, where the precipitated solids have time to settle out. Although this method is simple, direct and relatively cheap, it has disadvantages. Metal values contained in the waste are lost because the cost of recovery from the very dilute slurries is high. Occasionally, pH changes, occurring after the neutralization step, result in re-dissolution of the metals.

An alternate method for treating these wastes is by an ion exchange process. This method has been used to treat relatively small volumes of metal-bearing water wastes from the plating industries. However, there is no record of ion exchange being used to treat the relatively large volumes of waste that must be

handled in some mining or smelting operations. On the other hand, the concentrations of metals in the plating waste solutions which have been purified by ion-exchange techniques were in the same order as some mine waste waters.

Although the direct costs of an ion-exchange step would probably be higher than for a neutralization method involving the discharge of the neutralized solution to a tailings pond, the ion-exchange step would allow for the recovery of a saleable metal product which would offset all or part of the increased cost. Also, if a mine had to remove the precipitated base metals from the neutralized solution before discharge, ion-exchange methods would probably be cheaper, since the solution volume to be filtered to recover the precipitated metal would be greatly reduced. In discussing the differences between an ion-exchange operation and one in which the wastes are neutralized directly and then treated for solids recovery, McGarvey [1] states that the ion-exchange plant would involve lower initial investment, lower area requirements, and possibly lower reagent costs.

The literature indicates that the sulphonic-acid-type resins have a potential application in the removal of copper, zinc and nickel from acid-sulphate waste solutions by ion-exchange methods. It is also indicated that the chemical properties of these three metals, as related to ion-exchange methods,

are similar. This is in agreement with the conclusions of
McGarvey [13] and Mindler [19]. Although the literature shows
that resin loadings of two to three pounds of metal per cu ft
of resin have been achieved, and that metal concentrations in the
high-grade eluates of several hundred times the concentration of
the feed solution have been obtained, it contains only
limited information on the effect of other ions on the life or
loading capacity of the resin. The clarification of this point
would require additional test work.

The similarity in the ion-exchange characteristics of
copper, zinc and nickel means that the sulphonic-acid resins, such
as Rohm and Haas IRC-120 or Permutit Q, cannot be used to separate these
metals when they occur together in a solution. In order, then, to make
saleable products of the individual metals, preferential-precipitation,
or possibly solvent-extraction, methods would have to be applied to
the high-grade eluate. Preferential separation of the metals by
electrolytic means may also be possible.

Any iron in the waste solution, along with copper, zinc
or nickel, would also be adsorbed by the resin. Although this would
lower the resin capacity for the base metals, the over-all metal capacity
would likely be unchanged. After elution the iron could be separated
from the other metals by pH adjustment and filtration.

The carboxylic-type resins are of little interest in
the ion-exchange treatment of acid-sulphate waste solutions for the
recovery of copper, zinc, or nickel. The metal loadings possible with

these resins at low pH are very low. On the other hand, to operate

at a higher pH requires that the resin, which is eluted with

acid, must be converted to either the sodium or calcium form

after stripping. Not only is this expensive but also it is not very

effective in improving the loading characteristics.

Very little work has been done on the recovery of

copper, nickel and zinc from alkaline cyanide solutions by ion-

exchange methods. Strong-base anion exchange resin has been

shown to load about two pounds of either of these metals per

cu ft of resin [18]. However, apparently the nickel and zinc

can only be stripped with acid and this presents the problem of

handling HCN gas produced during elution.

CONCLUSIONS

On the basis of reported investigations and applications,

the sulphonic-type cation exchange resins, such as Rohm and Haas

Amberlite IRC-120, or Permutit Q, appear to be applicable in the Na^+ or H^+

form for the recovery of the common base metals and iron from acid

mine or metallurgical waste solutions. Further work on these

resins is necessary to determine the following:

(a) the design criteria for an ion-exchange plant

using a sulphonic-type cation exchange resin to

produce an effluent containing <1 ppm of metal;

(b)   suitable methods for recovering the metal values

from the high-grade eluate, preferably as saleable

products;

(c)   the determination, on the basis of the above data,

of the cost of an ion-exchange waste treatment

process and a comparison of this cost with other

methods.

The possibility of recovering metal values by ion-exchange methods from alkaline waste streams which contain the metals as cyanide complexes is uncertain on the basis of the literature. The reported work involves the evolution of HCN gas, which would make the process unattractive. However, no process operating as an alkaline system has been described. Further work on the ion-exchange treatment of cyanide wastes containing base metals will be necessary to determine, at least, whether any of the commercially available ion-exchange media is suitable for the treatment of these solutions.

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