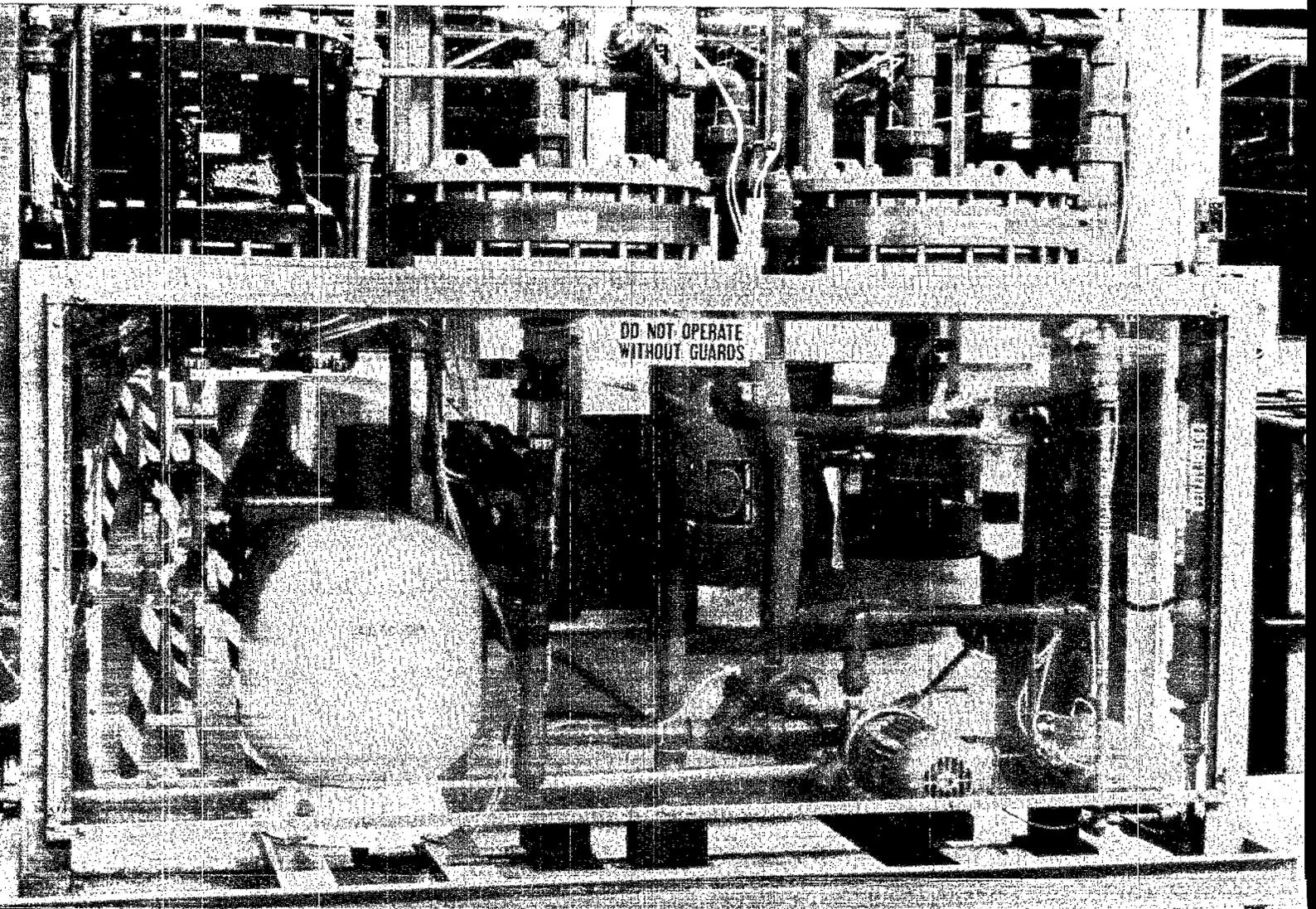


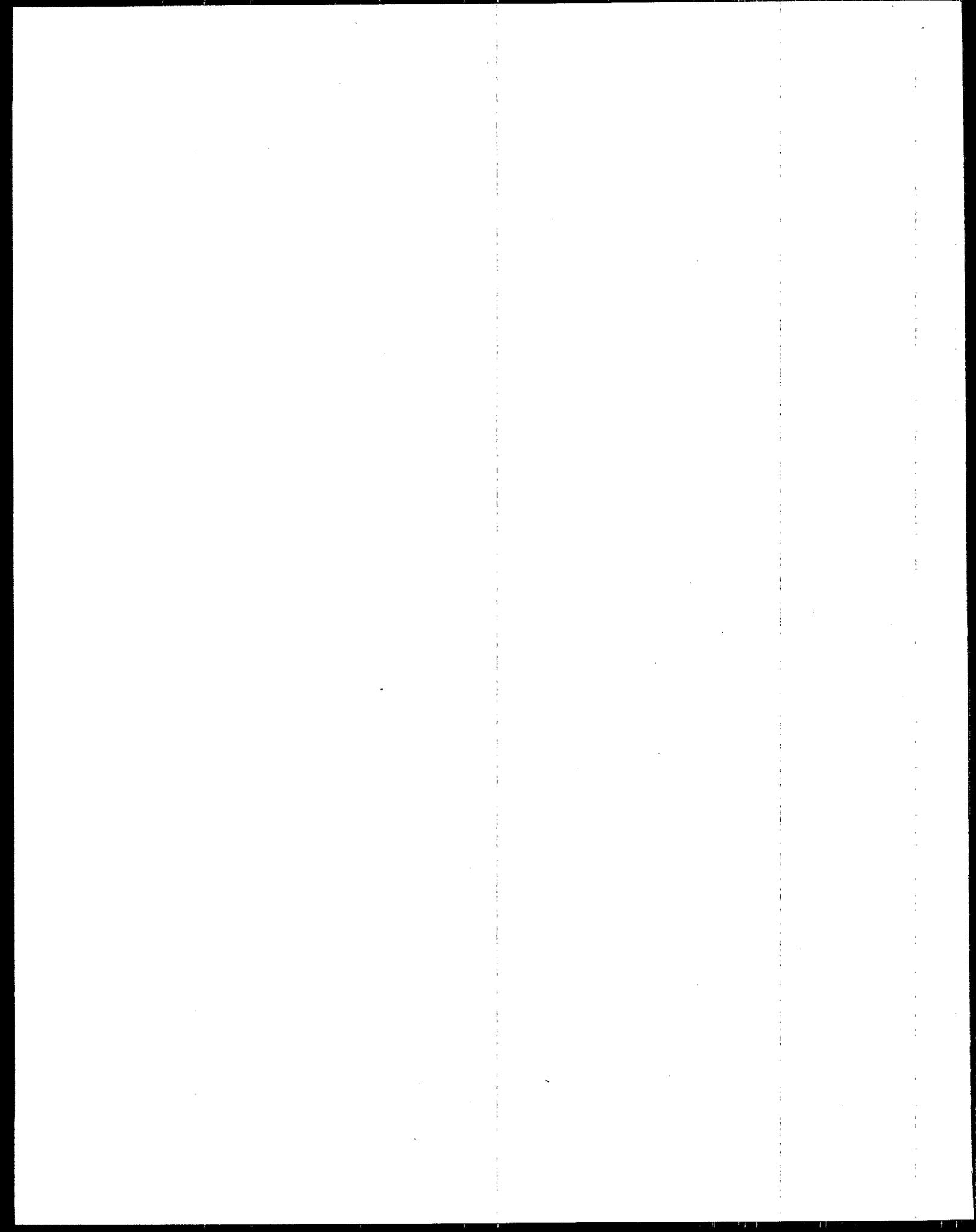


Summary Report

Control and Treatment Technology for the Metal Finishing Industry

Ion Exchange





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COVER PHOTOGRAPH: Reciprocating Flow Ion Exchanger used for chromic acid recovery.

Overview

Ion exchange is a versatile separation process with potential for broad application in the metal finishing industry, both for raw material recovery and reuse and for water pollution control. Three major areas of application have been demonstrated:

- Wastewater purification and recycle
- End-of-pipe pollution control
- Chemical recovery

Although the ion exchange process has been commercially available for many years, widespread interest in its use for metal finishing pollution control has developed only recently.

The main impetus for the interest in ion exchange technology is the broad range of resins manufactured today. With proper resin selection, ion exchange can provide an effective and economical solution to pollution control requirements. As a further stimulus to the use of the process, the metal-bearing sludge generated by hydroxide treatment systems is considered a hazardous material and must be disposed of in an environmentally safe manner. The ion exchange process can concentrate the heavy metals in a dilute wastewater into a concentrated metal solution that is more amenable to metal recovery than is a sludge, and this ability should lead to more widespread use of the technology.

This summary report is intended to promote an understanding of the use of ion exchange in the metal finishing industry. The sections that follow discuss ion exchange process theory in general and evaluate each of the three major areas of application in terms of performance, state of development, cost (in 1980 dollars), and operating reliability.

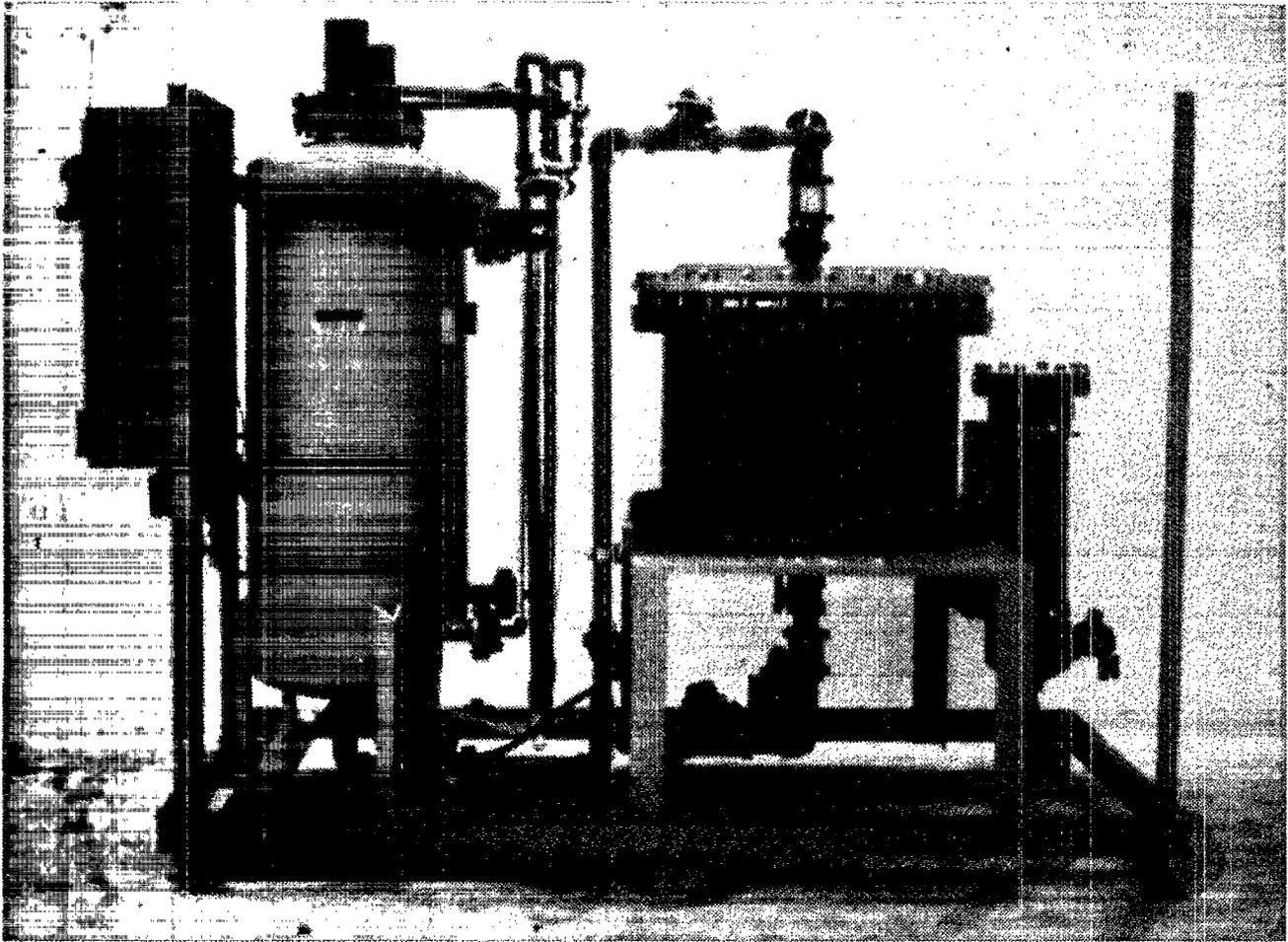
Water Purification and Recycle

In the first area of application, mixed rinse solutions are deionized to permit reuse of the treated water. The contaminants in the rinses are concentrated in the small volume purge streams, and are thereby made more economical to treat.

Because ion exchange is efficient in removing dissolved solids from normally dilute spent rinse waters, it is well suited for use in water purification and recycle. Most of the plating chemicals, acids, and bases used in metal finishing are ionized in water solutions and can be removed by ion exchange. Several factors make the ion exchange process effective for this application:

- Ion exchange can economically separate dilute concentrations of ionic compounds from water solutions.
- The process can consistently provide high purity water over a broad range of loading conditions.
- The resins used for separation are durable in severe chemical environments.

Application of the ion exchange process in a wastewater purification and recycle system will significantly reduce water consumption and the volume of wastewater discharged, thus reducing water use and sewer fees and the size and cost of the pollution control system. Also, for plants that discharge wastewater directly to waterways and that are regulated by mass-based pollutant discharge limits, the reduction of discharge volume will allow for higher concentrations of pollutants in the discharge and facilitate compliance with these limits.



Ion exchange acid purification unit used for sulfuric acid anodizing solutions

End-of-Pipe Pollution Control

In the second application, toxic heavy metals and metal cyanide complexes are removed selectively from combined waste streams before discharge. The key to this application is that the ion exchange resins remove only the toxic compounds and allow the nontoxic dissolved ionic solids to remain in solution.

The ion exchange process can be used in two different forms for end-of-pipe pollution control: it has been demonstrated as a means of polishing the effluent from

conventional hydroxide precipitation to lower the metal concentration in the discharge; it has also been applied as a means of directly treating wastewaters to remove heavy metal and metal cyanide pollutants.

Most plating shops can remove sufficient metal to comply with wastewater discharge regulations using the conventional hydroxide precipitation process. Where unusually strict limits are placed on the effluent metal concentration, however, or where the metals are complexed with chemical constituents that interfere with their precipitation as metal hydroxides, conventional treatment may not be reliable for compliance with

the discharge limits. Ion exchange can be used in such cases to polish the effluent from the conventional treatment and reduce the metal concentration further. In this application, the process can provide a relatively inexpensive means of upgrading system performance for compliance with the discharge regulations.

Ion exchange has been used to a limited extent to remove toxic pollutants selectively from an untreated wastewater while allowing most of the nontoxic ions to pass through. Approaches employed to facil-

itate this application include using:

- Weak acid cation resin in an application of the wastewater-softening type to remove heavy metals and other divalent cations from a wastewater solution with a high concentration of sodium ions
- Heavy-metal-selective weak acid or chelating cation resin to remove only the heavy metal ions while allowing sodium, calcium, and magnesium ions to pass through
- A stratified bed of resin containing strong and weak acid cation and strong base anion resins to remove heavy metal and metal cyanide complex ions from solution while allowing most of the wastewater ionic constituents to pass through

In each of these approaches, wastewater pretreatment entails pH adjustment, to ensure that pH is within the operating range of the resin, and filtration, to remove suspended solids that would foul the resin bed. The pollutants removed from the wastewater are concentrated in the ion exchange regenerant solutions. The regenerants can be treated in a small batch treatment system using conventional processes. Firms with access to a centralized treatment system to

dispose of the regenerant solutions resulting from treatment would not need to install chemical destruct systems. In neither case would it be necessary to invest in sophisticated pH control systems, flocculant feed systems, clarifiers, and other process equipment associated with conventional metal precipitation systems. And, as a further advantage, ion exchange units are compact and easy to automate compared with conventional precipitation systems.

Chemical Recovery

In the chemical recovery application, segregated plating rinse waters are treated to concentrate the plating chemicals for recycle to the plating bath. The purified rinse water is also recycled.

Ion exchange, evaporation, reverse osmosis, and electrodialysis have all been used in the plating industry to recover chemicals from rinse solutions. These processes have in common the ability to separate specific compounds from a water solution, yielding a concentrate of those compounds and relatively pure water. The concentrate is recycled to the plating

bath and the purified water is reused for rinsing. Determination of the separation process best suited for a particular chemical recovery application usually requires evaluating both general and site-specific factors:

- General factors include rinse water concentration, volume, and corrosivity, among others.
- Site-specific factors include, for example, availability of floor space and utilities (steam, chemical reagents, electricity, and so forth) and the degree of concentration needed to recycle the chemicals to the bath.

As a rule, ion exchange systems are suitable for chemical recovery applications where the rinse water feed has a relatively dilute concentration of plating chemicals and a relatively low degree of concentration is required for recycle of the concentrate. Ion exchange is well suited for processing corrosive solutions. Ion exchange has been demonstrated commercially for recovery of plating chemicals from acid-copper, acid-zinc, nickel, tin, cobalt, and chromium plating baths. The process has also been used to recover spent acid solutions and to purify plating solutions for longer service life.

Basic Concepts

Ion Exchange Reactions

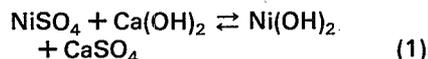
Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

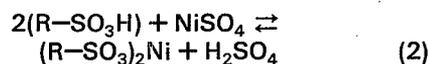
Most plating process water is used to cleanse the surface of the parts after each process bath. To maintain quality standards, the level of dissolved solids in the rinse water must be regulated. Fresh water added to the rinse tank accomplishes this purpose, and the overflow water is treated to remove pollutants and then discharged. As the metal salts, acids, and bases used in metal finishing are primarily inorganic compounds, they are ionized in water and could be removed by contact with ion exchange resins. In a water deionization process, the resins exchange hydrogen ions (H^+) for the positively charged ions (such as nickel, copper, and sodium), and hydroxyl ions (OH^-) for negatively charged sulfates, chromates, and chlorides. Because the quantity of H^+ and OH^- ions is balanced, the result of the ion exchange treatment is relatively pure, neutral water.

Ion exchange reactions are stoichiometric and reversible, and in that way they are similar to other

solution phase reactions. For example:

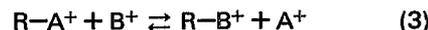


In this reaction, the nickel ions of the nickel sulfate ($NiSO_4$) are exchanged for the calcium ions of the calcium hydroxide [$Ca(OH)_2$] molecule. Similarly, a resin with hydrogen ions available for exchange will exchange those ions for nickel ions from solution. The reaction can be written as follows:



R indicates the organic portion of the resin and SO_3 is the immobile portion of the ion active group. Two resin sites are needed for nickel ions with a plus 2 valence (Ni^{+2}). Trivalent ferric ions would require three resin sites.

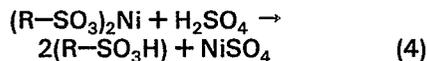
As shown, the ion exchange reaction is reversible. The degree the reaction proceeds to the right will depend on the resin's preference, or selectivity, for nickel ions compared with its preference for hydrogen ions. The selectivity of a resin for a given ion is measured by the selectivity coefficient, K, which in its simplest form for the reaction



is expressed as: $K = (\text{concentration of } B^+ \text{ in resin} / \text{concentration of } A^+ \text{ in resin}) \times (\text{concentration of } A^+ \text{ in solution} / \text{concentration of } B^+ \text{ in solution})$.

The selectivity coefficient expresses the relative distribution of the ions when a resin in the A^+ form is placed in a solution containing B^+ ions. Table 1 gives the selectivities of strong acid and strong base ion exchange resins for various ionic compounds. It should be pointed out that the selectivity coefficient is not constant but varies with changes in solution conditions. It does provide a means of determining what to expect when various ions

are involved. As indicated in Table 1, strong acid resins have a preference for nickel over hydrogen. Despite this preference, the resin can be converted back to the hydrogen form by contact with a concentrated solution of sulfuric acid (H₂SO₄):



This step is known as regeneration. In general terms, the higher the preference a resin exhibits for a particular ion, the greater the exchange efficiency in terms of resin capacity for removal of that ion from solution. Greater preference for a particular ion, however, will result in increased consumption of chemicals for regeneration.

Resins currently available exhibit a range of selectivities and thus have broad application. As an example, for a strong acid resin, the relative preference for divalent calcium ions (Ca⁺²) over divalent copper ions (Cu⁺²) is approximately 1.5 to 1. For a heavy-metal-selective resin, the preference is reversed and favors copper by a ratio of 2,300 to 1.

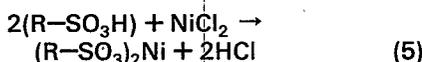
Table 1.
Selectivity of Ion Exchange Resins, in Order of Decreasing Preference

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia	
Sodium	
Hydrogen	

Resin Types

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

Strong Acid Cation Resins. Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO₃H) and salt (R-SO₃Na) form. They can convert a metal salt to the corresponding acid by the reaction:



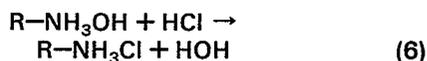
The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na⁺ and H⁺ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium chloride solution. For Equation 5, hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride (NiCl₂) solution.

Weak Acid Cation Resins. In a weak acid resin, the ionizable group is a carboxylic acid (COOH) as opposed

to the sulfonic acid group (SO₃H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated.

Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH. Figure 1 shows that a typical weak acid resin has limited capacity below a pH of 6.0, making it unsuitable for deionizing acidic metal finishing wastewater.

Strong Base Anion Resins. Like strong acid resins, strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH) form for water deionization. They will react with anions in solution and can convert an acid solution to pure water:



Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form.

Weak Base Anion Resins. Weak base resins are like weak acid resins, in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 (Figure 1). These resins merely sorb strong acids; they cannot split salts.

In an ion exchange wastewater deionization unit, the wastewater would pass first through a bed of

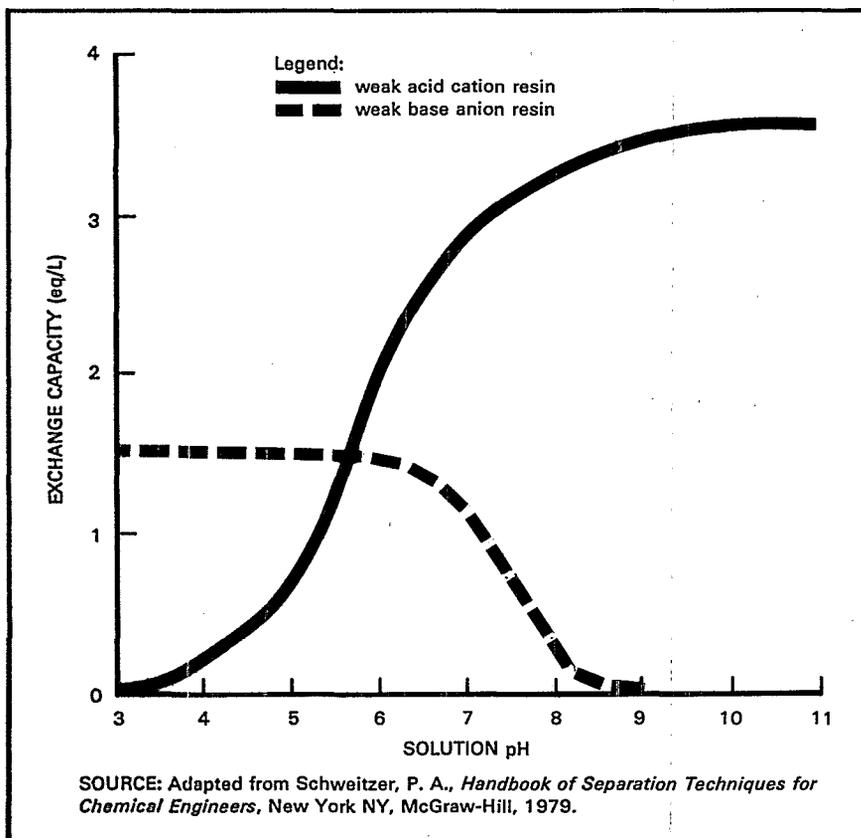


Figure 1.
 Exchange Capacity of Weak Acid Cation and Weak Base Anion Resins as a Function of Solution pH

strong acid resin. Replacement of the metal cations (Ni^{+2} , Cu^{+2}) with hydrogen ions would lower the solution pH. The anions (SO_4^{-2} , Cl^-) can then be removed with a weak base resin because the entering wastewater will normally be acidic and weak base resins sorb acids. Weak base resins are preferred over strong base resins because they require less regenerant chemical. A reaction between the resin in the free base form and HCl would proceed as follows:



The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, regeneration needs only to neutralize the absorbed acid; it need not

provide hydroxide ions. Less expensive weakly basic reagents such as ammonia (NH_3) or sodium carbonate can be employed.

Heavy-Metal-Selective Chelating Resins. Chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact, the functional group used in these resins is an EDTA^a compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

^aEthylenediaminetetraacetic acid.

The high degree of selectivity for heavy metals permits separation of these ionic compounds from solutions containing high background levels of calcium, magnesium, and sodium ions. A chelating resin exhibits greater selectivity for heavy metals in its sodium form than in its hydrogen form. Regeneration properties are similar to those of a weak acid resin; the chelating resin can be converted to the hydrogen form with slightly greater than stoichiometric doses of acid because of the fortunate tendency of the heavy metal complex to become less stable under low pH conditions. Potential applications of the chelating resin include polishing to lower the heavy metal concentration in the effluent from a hydroxide treatment process, or directly removing toxic heavy metal cations from wastewaters containing a high concentration of nontoxic, multivalent cations.

Table 2 shows the preference of a commercially available chelating resin for heavy metal cations over calcium ions. (The chelating resins exhibit a similar magnitude of selectivity for heavy metals over sodium or magnesium ions.) The selectivity coefficient defines the relative preference the resin exhibits for different ions. The preference for copper (shown in Table 2) is 2,300 times that

Table 2.
 Chelating Cation Resin Selectivities for Metal Ions

Metal ion	K^M/Ca^a
Hg^{+2}	2,800
Cu^{+2}	2,300
Pb^{+2}	1,200
Ni^{+2}	57
Zn^{+2}	17
Cd^{+2}	15
Co^{+2}	6.7
Fe^{+2}	4
Mn^{+2}	1.2
Ca^{+2}	1

^aSelectivity coefficient for the metal over calcium ions at a pH of 4.

for calcium. Therefore, when a solution is treated that contains equal molar concentrations of copper and calcium ions, at equilibrium, the molar concentration of copper ions on the resin will be 2,300 times the concentration of calcium ions. Or, when solution is treated that contains a calcium ion molar concentration 2,300 times that of the copper ion concentration, at equilibrium, the resin would hold an equal concentration of copper and calcium.

Their high cost is the disadvantage of using the heavy-metal-selective chelating resins. Table 3 compares the cost of these with the

Table 3.
Cost of Commercially Available Resins

Resin	Cost (\$/ft ³)
Strong acid cation.....	50-100
Weak acid cation.....	100-150
Strong base anion.....	150-200
Weak base anion.....	150-200
Chelating cation.....	200-300

Note.—1980 dollars.

costs of the other commercially available resins.

Batch and Column Exchange Systems

Ion exchange processing can be accomplished by either a batch method or a column method. In the first method, the resin and solution are mixed in a batch tank, the exchange is allowed to come to equilibrium, then the resin is separated from solution. The degree to which the exchange takes place is limited by the preference the resin exhibits for the ion in solution. Consequently, the use of the resin's exchange capacity will be limited unless the selectivity for the ion in solution is far greater than for the exchangeable ion attached to the resin. Because batch regeneration of the resin is chemically inefficient, batch processing by ion exchange has limited potential for application.

Passing a solution through a column containing a bed of exchange resin is analogous to treating the solution in an infinite series of batch tanks. Consider a series of

tanks each containing 1 equivalent (eq) of resin in the X ion form (see Figure 2). A volume of solution containing 1 eq of Y ions is charged into the first tank. Assuming the resin to have an equal preference for ions X and Y, when equilibrium is reached the solution phase will contain 0.5 eq of X and Y. Similarly, the resin phase will contain 0.5 eq of X and Y. This separation is the equivalent of that achieved in a batch process.

If the solution were removed from Tank 1 and added to Tank 2, which also contained 1 eq of resin in the X ion form, the solution and resin phase would both contain 0.25 eq of Y ion and 0.75 eq of X ion. Repeating the procedure in a third and fourth tank would reduce the solution content of Y ions to 0.125 and 0.0625 eq, respectively. Despite an unfavorable resin preference, using a sufficient number of stages could reduce the concentration of Y ions in solution to any level desired.

This analysis simplifies the column technique, but it does provide insights into the process dynamics. Separations are possible despite

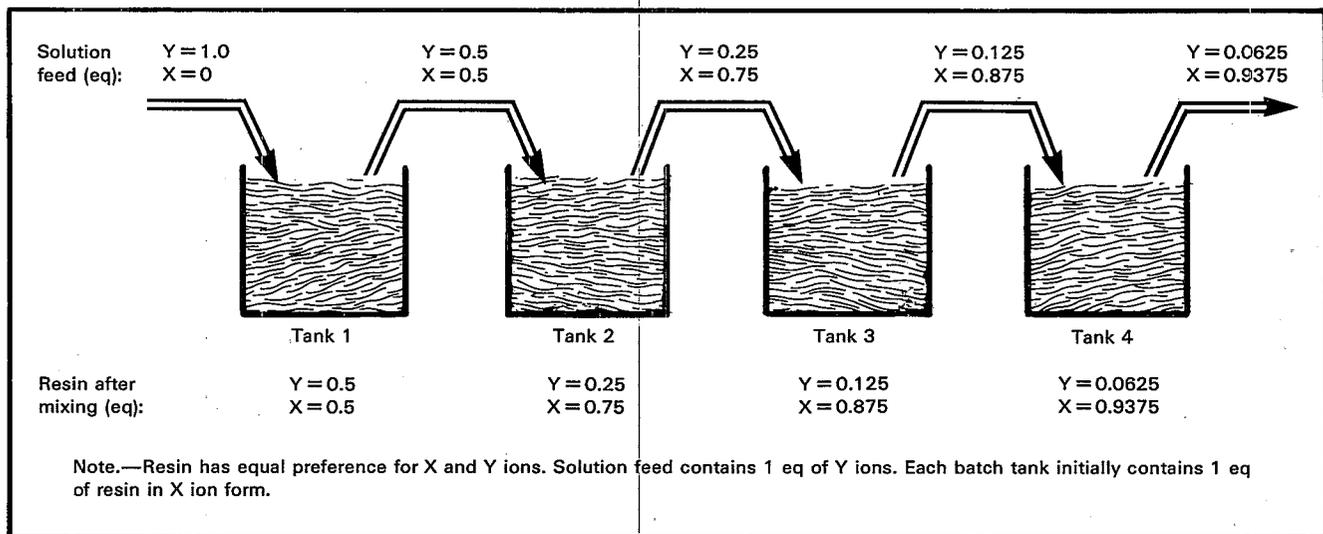


Figure 2.
Concentration Profile in a Series of Ion Exchange Batch Tanks

poor selectivity for the ion being removed.

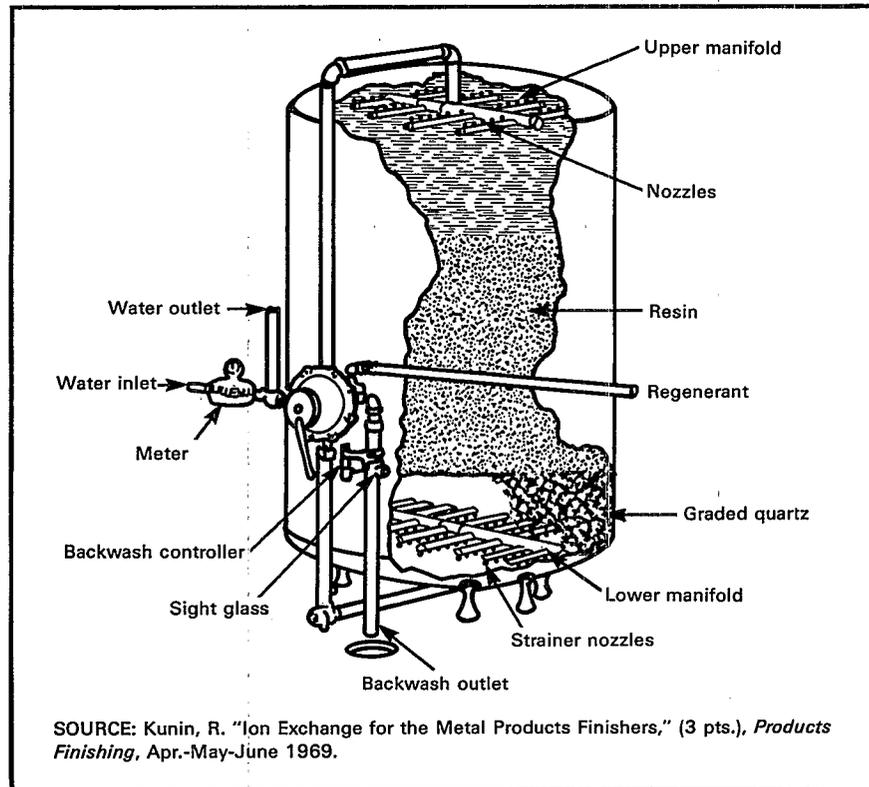
Ion Exchange Process Equipment and Operation

Most industrial applications of ion exchange use fixed-bed column systems, the basic component of which is the resin column (Figure 3). The column design must:

- Contain and support the ion exchange resin
- Uniformly distribute the service and regeneration flow through the resin bed
- Provide space to fluidize the resin during backwash
- Include the piping, valves, and instruments needed to regulate flow of feed, regenerant, and backwash solutions

Regeneration Procedure. After the feed solution is processed to the extent that the resin becomes exhausted and cannot accomplish any further ion exchange, the resin must be regenerated. In normal column operation, for a cation system being converted first to the hydrogen then to the sodium form, regeneration employs the following basic steps:

1. The column is backwashed to remove suspended solids collected by the bed during the service cycle and to eliminate channels that may have formed during this cycle. The backwash flow fluidizes the bed, releases trapped particles, and reorients the resin particles according to size. During backwash the larger, denser particles will accumulate at the base and the particle size will decrease moving up the column. This distribution yields a good hydraulic flow pattern and resistance to fouling by suspended solids.
2. The resin bed is brought in contact with the regenerant solution. In the case of the cation resin, acid elutes the collected ions and converts the bed to the hydro-



SOURCE: Kunin, R. "Ion Exchange for the Metal Products Finishers," (3 pts.), *Products Finishing*, Apr.-May-June 1969.

Figure 3.
Typical Ion Exchange Resin Column

3. The bed is brought in contact with a sodium hydroxide solution to convert the resin to the sodium form. Again, a slow water rinse is used to remove residual caustic. The slow rinse pushes the last of the regenerant through the column.
4. The resin bed is subjected to a fast rinse that removes the last traces of the regenerant solution and ensures good flow characteristics.
5. The column is returned to service.

For resins that experience significant swelling or shrinkage during regeneration, a second backwash should be performed after regeneration to eliminate channeling or resin compression.

Regeneration of a fixed-bed column usually requires between 1 and 2 h. Frequency depends on the volume of resin in the exchange columns and the quantity of heavy metals and other ionized compounds in the wastewater.

Resin capacity is usually expressed in terms of equivalents per liter (eq/L) of resin. An equivalent is the molecular weight in grams of the compound divided by its electrical charge, or valence. For example, a resin with an exchange capacity of 1 eq/L could remove 37.5 g of divalent zinc (Zn^{+2} , molecular weight of 65) from solution. Much of the experience with ion exchange has been in the field of water softening; therefore, capacities will frequently be expressed in terms of kilograins of calcium carbonate per cubic foot of resin. This unit can be converted to equivalents per

liter by multiplying by 0.0458. Typical capacities for commercially available cation and anion resins are shown in Figure 4. The capacities are strongly influenced by the quantity of acid or base used to regenerate the resin. Weak acid and weak base systems are more efficiently regenerated; their capacity increases almost linearly with regenerant dose.

Cocurrent and Countercurrent Regeneration. Columns are designed to use either cocurrent or countercurrent regeneration. In cocurrent units, both feed and regenerant solutions make contact with the resin in a downflow mode. These units are the less expensive of the two in terms of initial equipment cost. On the other hand, cocurrent flow uses regenerant chemicals less efficiently than countercurrent flow; it has higher leakage concentrations (the concentration of the feed solution ion being removed in the column effluent), and cannot achieve as high a product concentration in the regenerant.

Efficient use of regenerant chemicals is primarily a concern with strong acid or strong base resins. The weakly ionized resins require only slightly greater than stoichiometric chemical doses for complete regeneration regardless of whether cocurrent or countercurrent flow is used.

Regenerant Reuse. With strong acid or strong base resin systems, improved chemical efficiency can be achieved by reusing a part of the spent regenerants. In strongly ionized resin systems, the degree of column regeneration is the major factor in determining the chemical efficiency of the regeneration process. (See Figure 5.) To realize 42 percent of the resin's theoretical exchange capacity requires 1.4 times the stoichiometric amount of reagent [2 lb HCl/ft³ (32 g HCl/L)]. To increase the exchange capacity available to 60 percent of theoretical

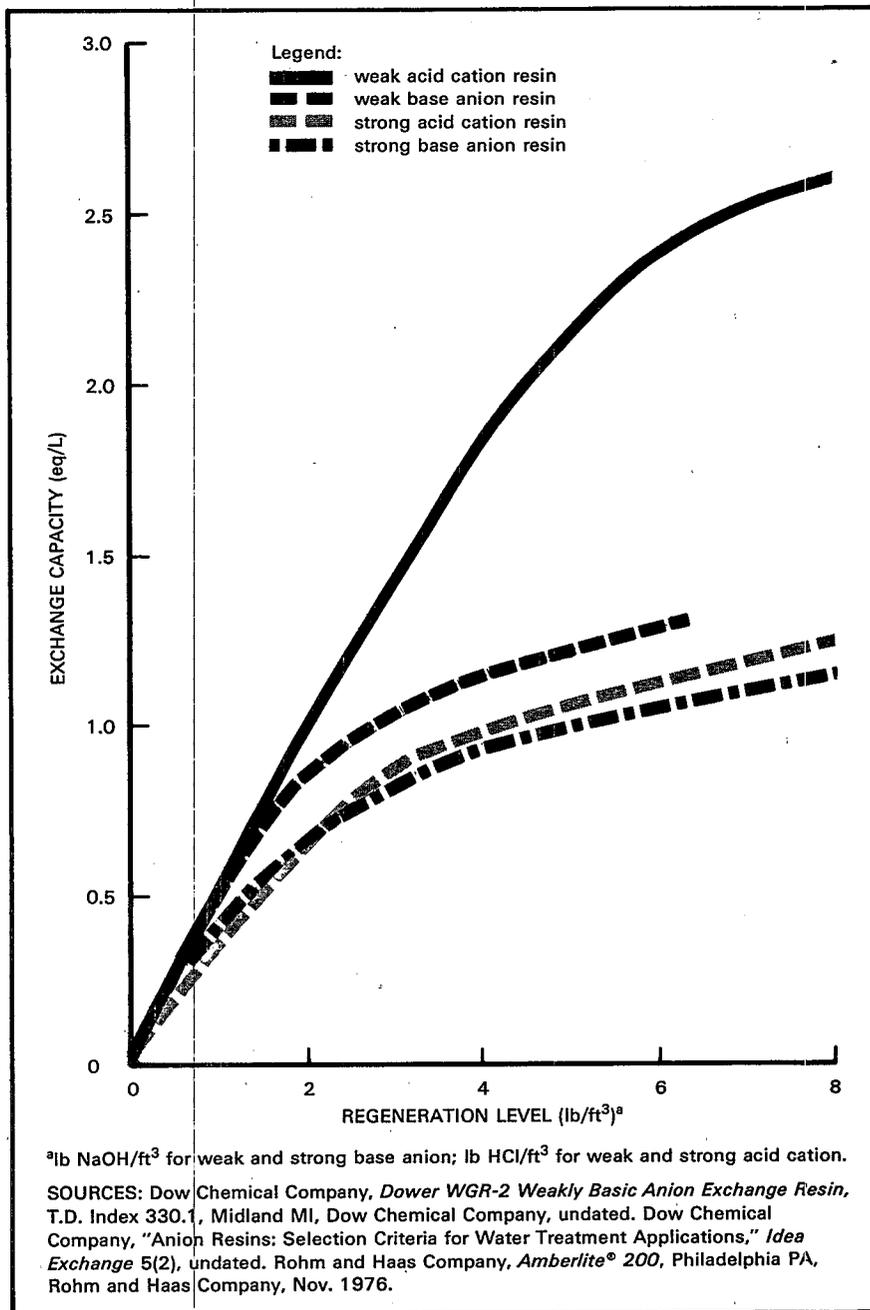


Figure 4.
Resin Exchange Capacities

increases consumption to 2.45 times the stoichiometric dose [5 lb HCl/ft³ (80 g HCl/L)].

The need for acid doses considerably higher than stoichiometric means that there is a significant concentra-

tion of acid in the spent regenerant. Further, as the acid dose is increased incrementally, the concentration of acid in the spent regenerant increases. By discarding only the first part of the spent

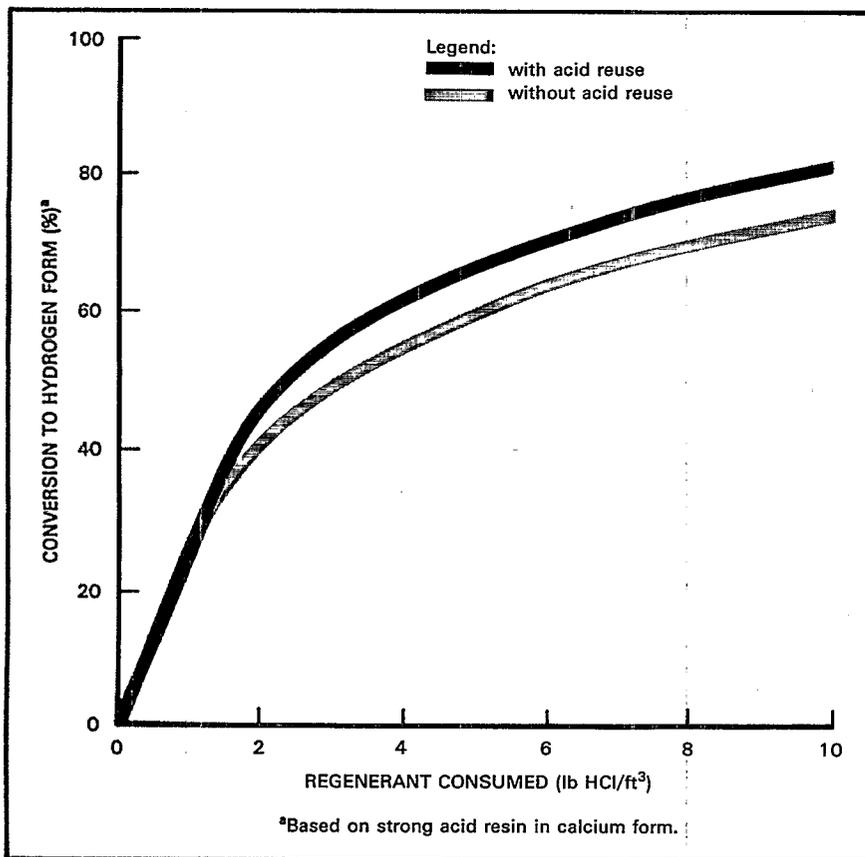


Figure 5.
Effect of Reusing Acid Regenerant on Chemical Efficiency

regenerant and saving and reusing the rest, greater exchange capacity can be realized with equal levels of regenerant consumption. For example, if a regenerant dose of 5 lb HCl/ft³ (80 g HCl/L) were used in the resin system in Figure 5, the first 50 percent of spent regenerant would contain only 29 percent of the original acid concentration. The rest of the acid regenerant would contain 78 percent of the original acid concentration. If this second part of the regenerant is reused in the next regeneration cycle before the resin bed makes contact with 5 lb/ft³ (80 g/L) of fresh HCl, the exchange capacity would increase to 67 percent of theoretical capacity. The available capacity would then increase from 60 to 67 percent at equal chemical doses. Figure 5 shows the improved reagent utilization achieved by this manner of reuse over a range of regenerant doses.

Regenerant reuse has disadvantages in that it is higher in initial cost for chemical storage and feed systems and regeneration procedure is more complicated. Still, where the chemical savings have provided justification, systems have been designed to reuse parts of the spent regenerant as many as five times before discarding them.

Wastewater Recycle Systems

In usual practice, metal finishing wastewater is treated and then discharged to a river or sewer system; as an alternative, the wastewater can be deionized by ion exchange and reused in the plating process. Wastewater deionization will significantly reduce water consumption and the volume of wastewater requiring treatment, with the following primary economic advantages:

- Water use and sewer fees are reduced.
- Although treatment of pollutants is not eliminated, the size and cost of the pollution control system is significantly reduced.

The volume reduction resulting from wastewater recycling can also make pollution discharge limits easier to achieve. For plants discharging wastewater to municipal treatment systems, the national pretreatment standards call for more lenient discharge limits if a plant discharges less than 10,000 gal/d (37,000 L/d). Plants discharging directly to surface waters are typically regulated by mass-based pollutant discharge limits. When translated to a concentration limit based on a volume of discharge, these limits may be difficult to achieve by conventional pollutant removal systems. The reduction of discharge volumes resulting from water recycle will allow for higher concentrations of pollutants in the discharge.

Inorganic plating chemicals such as acids, bases, and metal salts are ionized in water solutions and can be removed from process waters by ion exchange. Some dissolved organic compounds, oils, and free chlorine are typically present in mixed wastewaters and their presence constitutes a potential for fouling or deterioration of the ion exchange resin. Electroplating facilities using ion exchange on mixed wastewaters have found the resins to be operable and stable, however, when the recycle system

incorporates wastewater pretreatment to remove constituents that degrade the resins. When ion exchange is used to remove chromate and zinc from cooling tower blowdown there is similar potential for resin deterioration. Nevertheless, the effects have not been found severe enough to preclude the successful use of ion exchange for this application.

Hexavalent chromium (Cr^{+6}) can be removed if the mixed wastewater is passed through an anion column. Cyanide and metal cyanide complexes are ionized and could also be removed directly from the wastewater by anion exchange. Mixing cyanide wastes with the rest of the plant's wastewater is potentially hazardous, however; toxic hydrocyanic gas (HCN) would result from contact with acidic wastes. Therefore, cyanide wastewaters are normally pretreated before they are blended with the rest of the wastewater. In many cases, an integrated chemical waste system (Figure 6) can provide cyanide pretreatment that is low in cost and easy to operate.

The usual ion exchange sequence is cationic exchange followed by anionic exchange. The reverse sequence is avoided because passing the solution first through an anion exchange column would increase pH and could precipitate heavy metal hydroxides.

System Description

An ion exchange wastewater recycle system is shown in Figure 7. The major process components include:

- Wastewater storage
- Prefilters
- Ion exchange columns
- Regeneration system
- Batch treatment for regenerant solutions
- Deionized water storage

Wastewater Storage. A collection sump or storage tank is needed to provide a surge volume in the

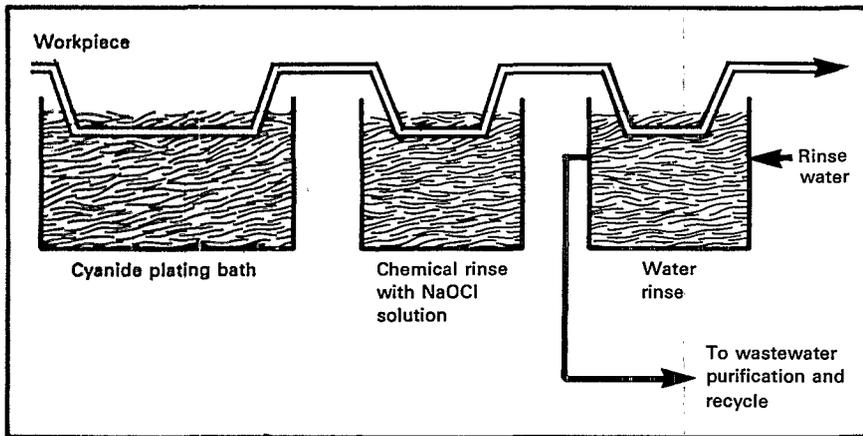


Figure 6.
Integrated Chemical Rinse to Oxidize Cyanide Compounds

Regular skimming can then purge the oil from the recycle system.

Prefilters. Activated carbon columns are commonly used as ion exchange prefilters. The carbon columns provide a versatile pretreatment system; they can:

- Filter out suspended solids that could hydraulically foul the columns.
- React with free chlorine or other strong oxidants that could physically degrade the resin.
- Adsorb organics that would otherwise build up in the recirculated wastewater.
- Adsorb oils that would gradually foul the resin.

system and allow the exchangers to be fed at a constant rate. The unagitated collection tank can also be used to settle coarse solids in the wastewater. The collected

solids can be pumped out at regular intervals and disposed of. Tank design should allow any free oil to separate and then collect on the surface of the wastewater.

The columns are typically back-washed daily to remove collected suspended solids. The backwash water goes either to the wastewater storage tank or to the batch treatment tank. Carbon replace-

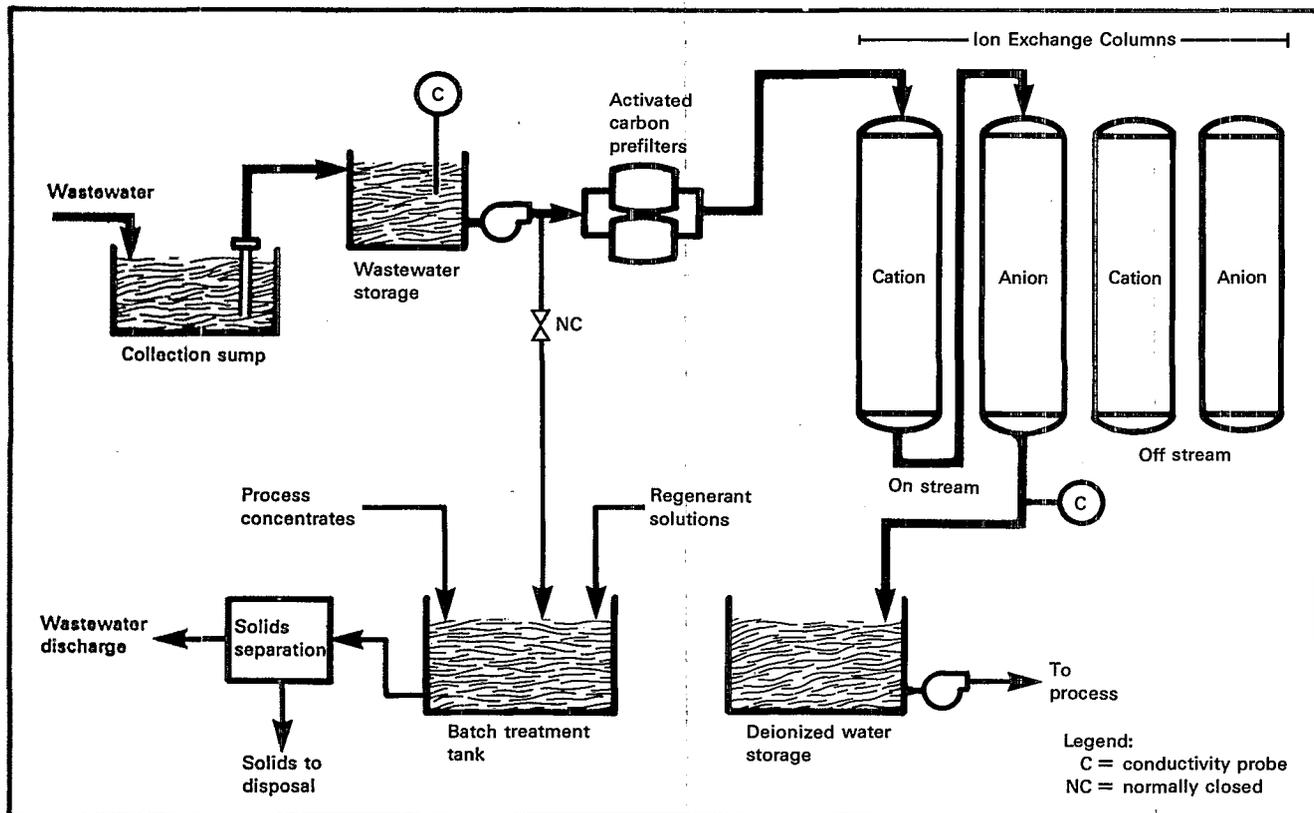


Figure 7.
Ion Exchange Wastewater Purification and Recycle System

ment frequency depends primarily on loading of oils or organics. If the carbon is not replaced, organic impurities can gradually build up in the recycle water. Some long chain organic molecules will foul strong base resins. Oil not removed by pretreatment collects on the resin and reduces its exchange capacity, resulting in more frequent regeneration and higher operating costs. Cleaning solutions are available from resin manufacturers to restore the performance of oil-fouled resin beds.

Ion Exchange Columns. In the most common column configuration, wastewater passes in series through a strong acid cation resin column and then through either a strong or weak base anion resin column. Weak base resins have higher exchange capacities and require less regenerant than do strong base resins. On the other hand, weak base resins are not effective in removing weakly ionized bicarbonates, borates, and silicates, nor can they operate effectively at high pH. These limitations may not be a concern for metal finishing wastewaters, and weak base resins are recommended. If these anions are present in significant amounts, an anion bed containing both strong and weak base resins can be used. A bed of this kind will approach the higher exchange capacity and regeneration efficiency of a weak base system but provide complete deionization.

To provide uninterrupted system operation when column regeneration is required, two sets of columns are frequently installed. When one set has been exhausted, flow is switched to the off-stream set and the spent columns are regenerated.

Regeneration System. The cation exchange column should be regenerated with hydrochloric acid after exhaustion. Despite its higher cost, HCl is favored over H₂SO₄ for regeneration if the wastewater contains a significant amount of calcium.

In such a case, regeneration with sulfuric acid can result in precipitation of calcium sulfate and hydraulic fouling of the resin bed. Calcium sulfate precipitation can be avoided by using dilute sulfuric acid solutions (2 percent by weight). Strong base anion columns are regenerated with sodium hydroxide. Weak base resins can be regenerated with sodium hydroxide or less expensive basic reagents such as sodium carbonate.

Batch Treatment for Regenerant Solutions. The pollutants removed by the ion exchange system will be concentrated in the regenerant and wash solutions. These solutions must undergo conventional treatment before being discharged. The type of pollutants present (Cr⁺⁶ and heavy metals would be most common) dictates the treatment sequence that would be required.

Deionized Water Storage. A storage tank is used to provide an inventory of water for process needs. The effluent from the ion exchange column should be monitored with a conductivity probe to provide a relative index of the level of dissolved solids in the treated water. When the water conductivity increases to a certain level, the columns are switched and the spent columns are regenerated. Because complete water deionization is not needed for most process applications, the columns are loaded until the maximum allowable level of impurity is reached before they are regenerated; regeneration frequency and system operating costs are thus reduced.

Ion Exchange Column Specification

Columns are usually sized as a function of the ratio of wastewater volume to resin volume. Recommended rates vary depending on the application but as a rule range from 2 to 4 gal/min/ft³ (0.26 to 0.52 L/min/L) of resin. Higher rates will usually result in higher leakage, but will not affect the

quantity of ionic compounds the resin bed can exchange.

For rinse water recovery, leakage of small concentrations of ionic compounds would not signal the end of the cycle. Therefore, rates should be selected from the higher end of the recommended range to minimize the initial cost of the system. Smaller columns will increase regeneration frequency and the associated labor cost. For columns with automated regeneration packages, increased regeneration frequency will not significantly increase operating costs.

Cost

Conventional end-of-pipe treatment requires removing pollutants from large volumes of dilute wastewater. When pollutants are concentrated into small volume regenerant solutions, treatment is usually more economical. Moreover, recycling the purified wastewater reduces operating costs associated with water consumption and sewer fees.

As a rule, treating the concentrated regenerant solutions will consume chemicals in quantities smaller than are needed to treat the same mass of pollutants in a dilute waste stream. Capital costs of wastewater treatment systems depend primarily on the unit operations required and the volumetric flowrate of the wastewater. Total investment for an ion exchange water recycle system and a simplified batch chemical destruct unit to treat concentrated solutions will often be less than that for a conventional chemical destruct system designed to treat the total volume of water consumed by a plant.

Operating Cost. Operating costs for an ion exchange purification system to treat wastewater containing a variety of heavy metals will include:

- Chemicals for column regeneration

- Destruct chemicals for treatment of concentrated regenerant solutions and purged wash water
- Disposal of the treatment residue
- Labor for column regeneration and operation of the batch treatment system (if not automated)
- Maintenance
- Resin and activated carbon replacement
- Utilities

How these costs compare with the costs of operating a conventional hydroxide treatment process can be determined by evaluating the costs associated with each system treating the same waste stream. To simplify the analysis, equal labor, maintenance, and utility charges are assumed for both systems.

A typical waste stream (Table 4) consisting of rinses after nickel, copper, and chromium plating baths and acid and alkali process baths will be used in the cost analysis. In a water recycle system, only natural alkalinity brought in with makeup water must be treated; recycled water has already had its initial alkalinity removed. The wastewater used in conventional treatment, however, contains all the natural alkalinity brought in with the fresh water; as a result more alkali reagent will be consumed and more solid waste generated.

In light of the foregoing analysis, the next step is to determine the required column configuration and size of the ion exchange unit. Either of two column configurations can be used: strong acid and strong base or strong acid and weak base. In either case, ion exchange column sizing is based on volumetric loading. At the normally recommended service flowrate of 2 gal/min/ft³ (0.26 L/min/L) of resin, columns containing 15 ft³ (425 L) of resin will be needed. The ion exchange capacity of these columns will depend on the quantity of regenerant (dosage rate).

Using the resin capacities given in Figure 4, the columns will be

Table 4.
Wastewater Characteristics and Ion Exchange Capacity Requirements

Item	Treatment	
	Ion exchange	Conventional
Wastewater characteristic:		
Flowrate (gal/min)	30	30
Constituent (ppm):		
Cu ⁺²	40	40
Ni ⁺²	40	40
CrO ₄ ⁻²	50	50
Na ⁺	20	20
SO ₄ ⁻²	150	220
Total dissolved solids	310	470
Alkalinity, as Ca(HCO ₃) ₂ (ppm)	10	70
Wastewater concentrations to be treated by ion exchange (eq/L):		
Cations ^a	0.0036	—
Anions	0.00423	—
Ion exchange resin capacity needed for 15-ft ³ bed (eq/L): ^b		
Cation resin ^a	0.92	—
Anion resin	1.08	—

^aDoes not include hydrogen ions.

^b16-h operating cycle.

regenerated with sufficient acid and base to provide 1 day's operating capacity. The plant is assumed to operate 16 h/d. Table 4 includes the resin capacity needed for columns with 15 ft³ (425 L) of resin.

For the strong acid/strong base unit, sufficient capacity would be obtained in the anion column with a regenerant level of 6.5 lb NaOH/ft³ (104 g NaOH/L) of resin. The anion column would require greater capacity than the cation column because the wastewater is acidic; the higher anionic loading

rate results from the anions associated with the hydrogen ion acidity. Adequate capacity would be obtained in the cation column with a regenerant level of 4 lb HCl/ft³ (64 g HCl/L) of resin. In this case, however, the combined anion and cation column regenerant must be acidified to reduce Cr⁺⁶. Therefore, excess acid regenerant [6.5 lb/ft³ (104 g/L)] can be used to balance the excess NaOH in the anion regenerant.

Table 5 shows the chemical content and volumes of the regenerant solutions after they are mixed with

Table 5.
Regenerant Solution Chemical Content

Item	Strong acid/ strong base	Strong acid/ weak base
Volume	850 gal	800 gal
Cation column		
	20.3 lb CuCl ₂	20.3 lb CuCl ₂
	21.1 lb NiCl ₂	21.1 lb NiCl ₂
	12.1 lb NaCl	12.1 lb NaCl
	1.6 lb CaCl ₂	1.6 lb CaCl ₂
	67.0 lb HCl	29.5 lb HCl
Anion column		
	16.8 lb Na ₂ CrO ₄	16.8 lb Na ₂ CrO ₄
	53.3 lb Na ₂ SO ₄	53.8 lb Na ₂ SO ₄
	3.0 lb Na ₂ CO ₃	3.0 lb Na ₂ CO ₃
	56.9 lb NaOH	7.4 lb NaOH

the volume of wash water [50 gal/ft³ (6.5 L/L) of resin] usually required for the backwash and rinse stages of regeneration. Chemical cost of each regeneration cycle is \$29.83 for the strong acid and strong base system (based on Table 6).

Regeneration cost can be reduced if a weak base resin is used in the anion column. A weak base resin downstream of the strong acid column is suited for this application because the entering wastewater would always be acidic. Based on the capacity shown in Figure 5, sufficient resin capacity could be achieved with a sodium hydroxide dose equal to 3.2 lb/ft³ (51 g/L) of resin. The amount of acid consumed

Table 6.
Chemical Prices

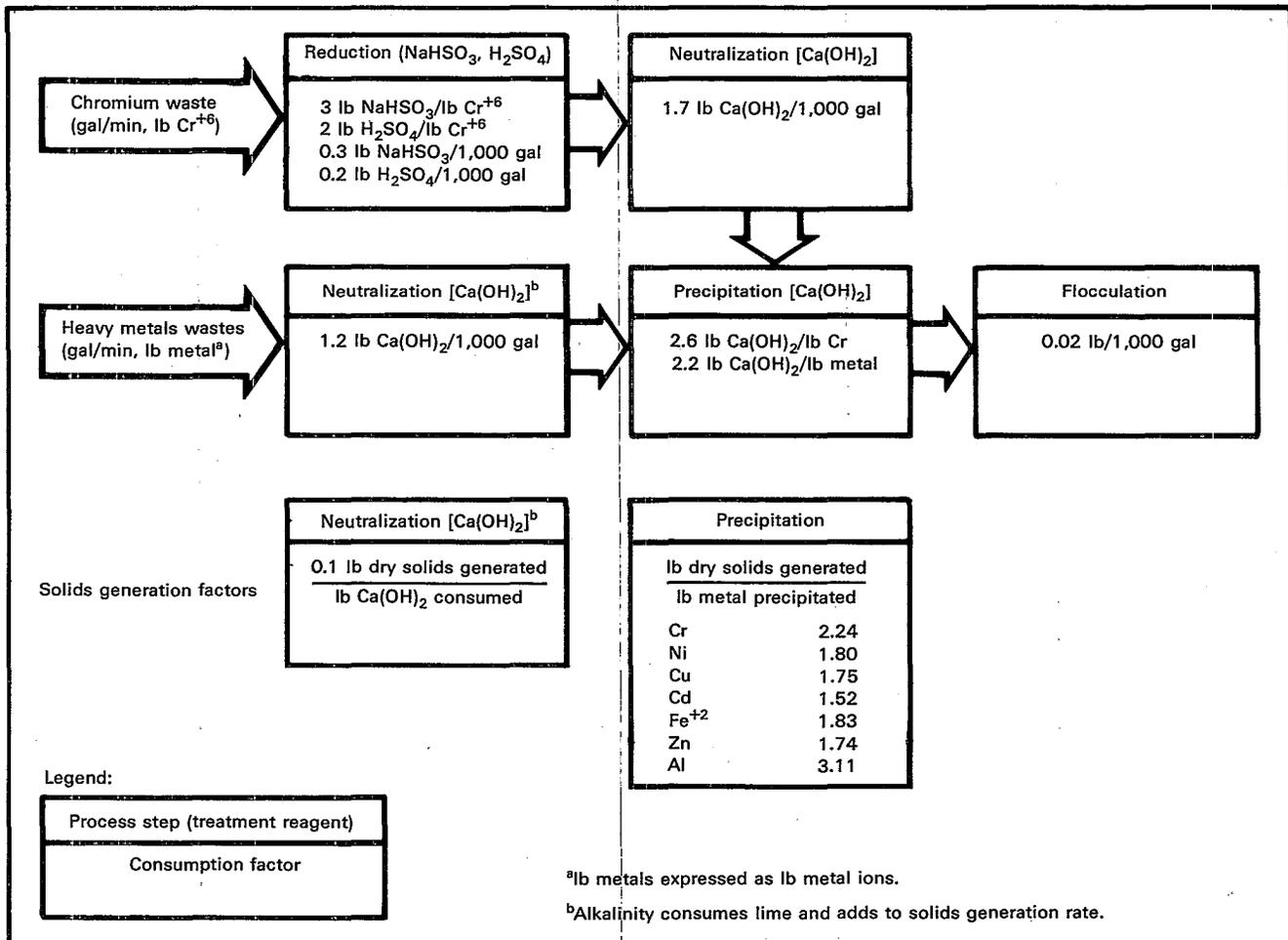
Reagent	Description	Cost (\$/lb) ^a
Hydrochloric acid	Carboys, 32% HCl	0.05
Sodium hydroxide	Carboys, 50% NaOH	0.075
Hydrated lime	100-lb bags	0.05
Sodium bisulfite	100-lb bags	0.20
Sulfuric acid	Carboys, 97% H ₂ SO ₄	0.05
Polyelectrolyte	Dry powder	2.50

^a1980 dollars.

for regeneration should be reduced to the minimum required for column capacity, 4 lb HCl/ft³ (64 g HCl/L) of resin. Table 5 includes the volume and chemical content of the regenerant solutions. Regen-

erant chemicals for this column configuration would cost \$16.56 for each cycle.

Based on treatment chemical consumption factors (Figure 8) and



^alb metals expressed as lb metal ions.

^bAlkalinity consumes lime and adds to solids generation rate.

Figure 8.
Conventional Treatment Chemical Consumption Factors

Table 7.

Daily Treatment Cost Comparison: Ion Exchange and Conventional Systems

Component	Treatment cost (\$/d)		
	Strong acid/ strong base	Strong acid/ weak base	Conventional
Chromium reduction:			
NaHSO ₃	3.34	3.34	3.82 ^a
H ₂ SO ₄	(^b)	(^b)	0.63
Neutralization: Ca(OH) ₂	3.76	4.08	5.16
Sludge disposal ^c	3.70 ^d	3.70 ^d	4.97 ^e
Ion exchange regeneration:			
HCl	15.21	9.36	(^b)
NaOH	14.62	7.20	(^b)
Total chemical cost	40.63	27.68	14.58
Water and sewer fee at \$1/1,000 gal	1.70	1.70	28.80
Total treatment cost	42.33	29.38	43.38

^aAssumes 10 gal/min of segregated Cr⁺⁶ wastewater.

^bNot required.

^c25% solids by weight at \$0.20/gal.

^dFor 46.3 lb dry solids.

^eFor 62.2 lb dry solids.

Note.—1980 dollars.

chemical costs (Table 6), Table 7 compares the daily cost to operate the two ion exchange systems with the cost for a conventional treatment system. Although the chemical costs are higher for the ion exchange systems, when the savings in water and sewer fees (assuming \$1/1,000 gal) are considered, the total cost is less than that of conventional treatment. The data also indicate that a strong acid/weak base column configuration is considerably less expensive to operate than the strong acid/strong base configuration. The economics of the ion exchange system could be improved further if the strong acid column regenerant were reused.

For deionization applications, commercially available resins cost between \$50/ft³ and \$200/ft³. Ion exchange resins usually need replac-

ing every 2 to 5 years, depending on the type of resin and the process application. Resins can be damaged by exposure to strong oxidants, long chain organic compounds, or oil. With proper selection of resins and effective pretreatment of the wastewater, the potential for resin deterioration and the cost for replacement will be reduced.

Granular activated carbon must be replaced when its adsorption capacity is spent. For small scale applications, regenerating the carbon is not economically feasible. Replacement frequency for activated carbon will depend on the level of organic compounds in the wastewater. Carbon adsorption is an economical means of removing trace amounts of organic compounds from solution. If high levels of organics are present, however, the cost becomes excessive and alternative removal techniques should be evaluated.

Effect of Pollutant Concentration.

The volume of wastewater that can be deionized by an ion exchange column is in direct proportion to the ionic concentration of the wastewater and is not influenced by the volume needing treatment. Consequently, when dilute solutions are processed, a large volume can be treated before column capacity is exhausted and regeneration is required. On the other hand, conventional treatment processes—such as chromium reduction, cyanide oxidation, and metal precipitation—must adjust the chemistry of the water solution to achieve the desired reaction. The chemical consumption associated with these processes therefore depends on both the mass of pollutant and the volume of solution to be treated. Because its cost is independent of solution volume, ion exchange processing is highly efficient in terms of chemical consumption when used to treat dilute concentrations of ionic contaminants.

Figure 9a shows the relative costs of deionization and conventional treatment techniques as a function of the concentration of wastewater contaminants for acid-alkali waste streams and for hexavalent chromium wastewater. Only chemical treatment costs are included, not water and sewer use fees. The treatment steps and assumptions used to derive the conventional treatment cost are presented in Table 6 and Figure 8. Also assumed is removal of natural alkalinity during treatment.

Ion exchange does not compare favorably with hydroxide precipitation of acid-alkali waste streams except at very dilute concentrations. For treating typical metal finishing wastewater, hydroxide precipitation will usually have lower

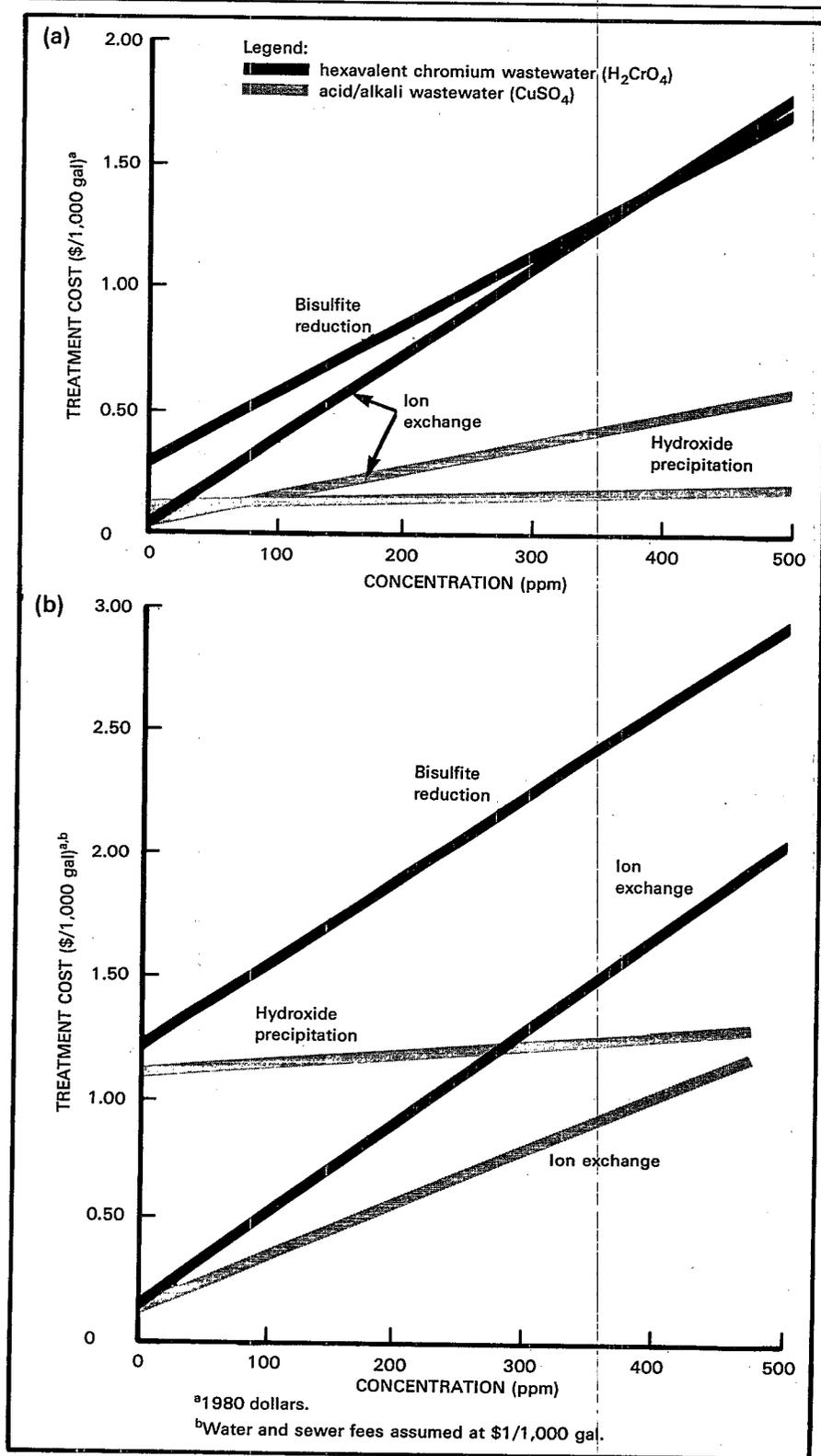


Figure 9.
 Cost Comparisons for Ion Exchange and Conventional Treatment Systems:
 (a) Chemical Cost Only and (b) Chemical Cost and Water Use Fees

chemical costs. For hexavalent chromium wastewater, however, ion exchange has a treatment cost advantage up to a concentration of 440 ppm of chromic acid (H₂CrO₄). Ion exchange treatment is efficient for this application partly because, except for contaminants, chromic acid wastewater has no cations other than hydrogen; consequently, treatment by ion exchange would not affect cation column operating costs.

In Figure 9a the cost for conventional treatment of acid-alkali wastes includes the volume-related cost for lime to adjust solution pH and to react with naturally occurring bicarbonate alkalinity, and for polyelectrolyte conditioners to aid in precipitant settling. The curve for chromium reduction using bisulfite includes these cost components plus costs for acid needed to bring the wastewater to required reaction pH and base for subsequent neutralization.

The ion exchange system costs are based on 90 percent water recycle; they include the cost for column regeneration and treatment of regenerant solutions by conventional techniques. The regenerant chemical consumption is based on a strong acid/weak base column configuration.

An ion exchange water recycle system becomes considerably more attractive than conventional treatment techniques if the credit for savings in water and sewer fees is included in the analysis. Figure 9b compares treatment costs of the same two waste streams but includes a cost equal to \$1/1,000 gal water consumed.

Waste Reduction. The waste stream volume reduction achieved by a wastewater deionization system relates directly to the con-

centration level of the dissolved ionic solids in the wastewater. The reduction in volume of the waste stream and its favorable effect on both the initial and operating cost of wastewater treatment are part of the justification for using ion exchange.

Each cubic foot of resin in a column system can remove a specific quantity of ions; regenerating and washing that volume of resin will result in a purge stream of limited concentration.

Consider an ion exchange system with a strong acid/weak base column configuration. Assume the resin in each column has a capacity of 1.5 eq/L, and that regenerating the columns produces purge (regeneration plus rinsing) in the amount of 50 gal/ft³ (6.5 L/L) of resin. The maximum concentration of the ionic solids in the combined purge streams from both columns, then, would be 0.11 eq/L. Expressed in terms of a typical metal salt, the maximum concentration of copper sulfate (CuSO₄) in the purge solution would be 1.75 percent. Using this relationship, Figure 10 presents the volume reduction for treating wastewater over a range of ionic concentrations.

The relationship developed in Figure 10 is based on normal operating procedures. Concentration can be improved by selective recycle of part of the purge stream; however, the poor chemical efficiency of the ion exchange process for treating concentrated solutions and the poor degree of concentration achieved make other methods of treatment more suitable.

Capital Cost. In the metal finishing industry, most of the wastewater requiring treatment results from rinsing operations. Selective treatment and reuse of rinse streams by ion exchange can result in

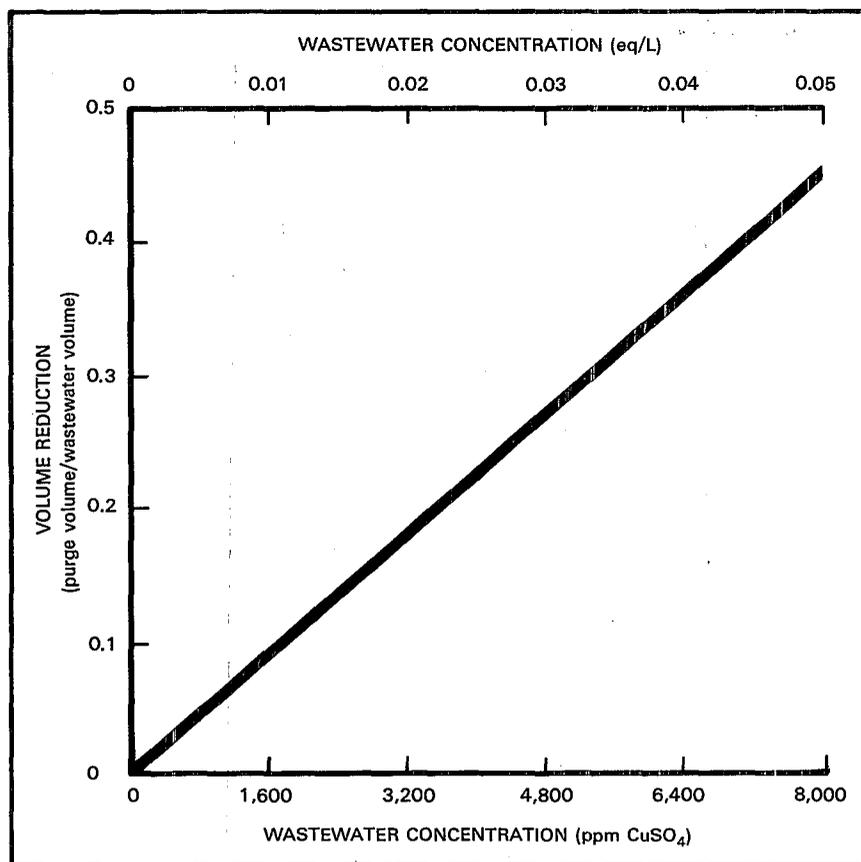


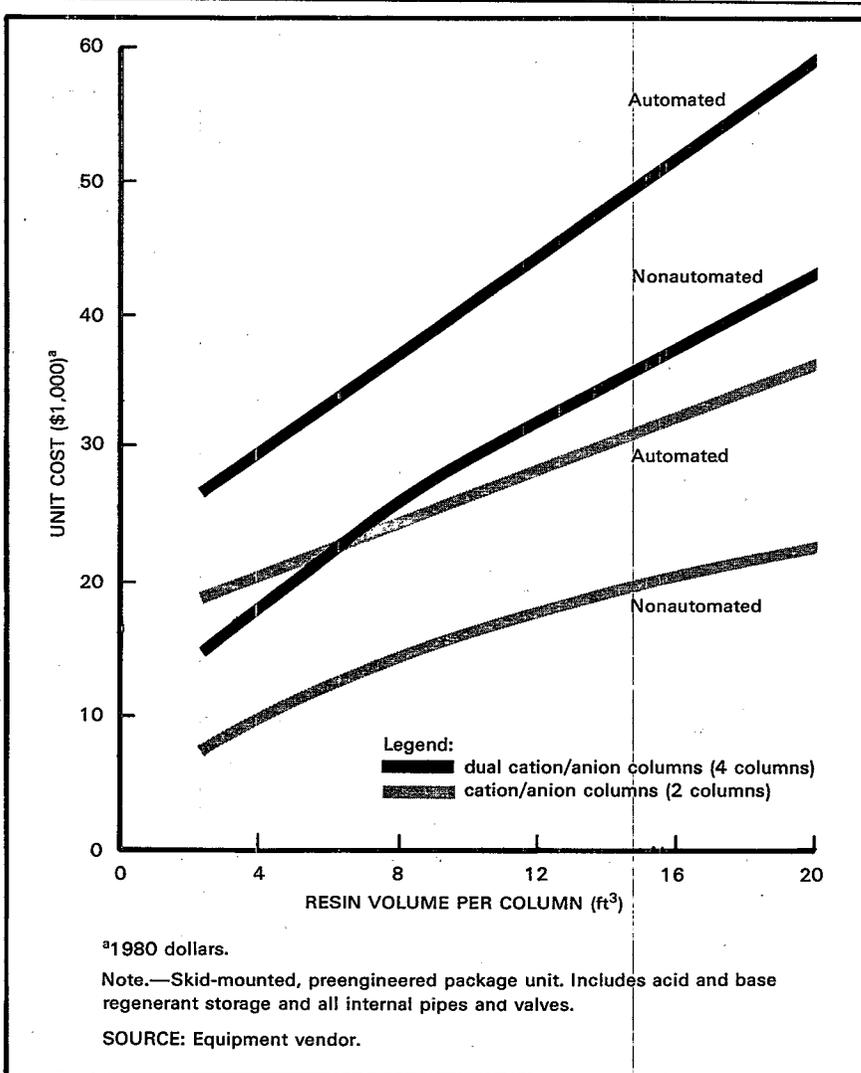
Figure 10.

Relationship of Waste Volume Reduction to Wastewater Ionic Concentration

considerable savings in the investment necessary for end-of-pipe treatment systems. This investment is usually a function of wastewater flowrate and the required unit operations. For flows above 15 to 20 gal/min (57 to 76 L/min), automated continuous treatment systems are usually recommended. A deionization water reuse system can result in flow reduction sufficient to make a single batch treatment tank feasible for treating regenerant solutions and any concentrated process dumps.

The cost for ion exchange column systems is increased significantly when dual cation-anion column configurations are needed for

continued operation during regeneration. Automation adds considerably to the initial cost of the unit but, in addition to savings in labor, can permit the use of smaller columns with more frequent regeneration. Figure 11 compares costs for two- and four-column ion exchange units, automated and nonautomated, as a function of resin volume in each column. The systems illustrated are skid mounted and preengineered; costs include the columns, an initial supply of resin, reagent storage, and internal piping and valves necessary for service and regeneration flow.



The cost of the auxiliary equipment described earlier for ion exchange water recycle will add considerably to the total capital cost associated with using the technology. The total cost, however, may still compare favorably with that for a conventional end-of-pipe treatment system.

Figure 11.
 Cost for Deionization Units With and Without Automation

End-of-Pipe Systems

Ion exchange can be used in two different ways for end-of-pipe pollution control. The process has been demonstrated as a means of polishing the effluent from conventional hydroxide precipitation to lower the heavy metal concentration further, and it has been used to process untreated wastewaters directly for removal of heavy metals and other regulated pollutants.

Most plating shops can achieve sufficient metal removal to comply with discharge regulations by employing the conventional hydroxide precipitation process. Conventional treatment may not be reliable, however, in achieving compliance with discharge limits in certain cases, including where:

- Unusually strict limits are placed on the effluent metal concentration.
- The metals are complexed with chemical constituents that interfere with their precipitation as metal hydroxides.

In such cases, the use of ion exchange to polish the effluent can provide relatively inexpensive upgrading of system performance for compliance with the regulations.

The development of special chelating resins made ion exchange feasible for selective removal of trace heavy metals from a water solution containing a high concentration of similarly charged, nontoxic ions. These resins exhibit a strong selectivity, or preference, for heavy metal ions over sodium, calcium, or magnesium ions. Weak acid cation resins also display a significant preference for heavy metal ions, and in some applications they are superior to the chelating resins in performance characteristics. In a polishing application, both resins can remove the heavy metal ions from the wastewater while leaving most of the nontoxic ions in solution. The preference for heavy metal ions allows a large volume of water to be

treated per unit of resin volume before the resin must be regenerated. The regenerant solution, which contains a high concentration of metal ions, is treated upstream in the conventional process (Figure 12a).

Ion exchange has received limited commercial application for selective removal of heavy metal and metal cyanide pollutants from an untreated wastewater while allowing most of the nontoxic ions to pass through. Various approaches have been employed to facilitate this application:

- A weak acid cation resin has been used in wastewater softening to remove heavy metals and other divalent cations from a wastewater solution with a high concentration of sodium cations.
- Heavy-metal-selective weak acid or chelating cation resin has been used to remove the heavy metal ions while allowing sodium, calcium, and magnesium ions to pass through.
- A stratified resin bed, containing strong and weak acid cation resins and strong base anion resins, has been employed to remove heavy metal cations and metal cyanide complex anions while allowing other ions to pass through.

In each of these approaches, wastewater pretreatment requirements consist of pH adjustment to ensure that pH is within the operating range of the resin, and filtration to remove suspended solids that would foul the resin bed (Figure 12b). The pollutants removed from the wastewater are concentrated in the ion exchange regenerant solutions. The regenerants can be treated in a small batch treatment system using conventional processes. Firms with access to a centralized treatment facility that accepts industrial wastes can use the

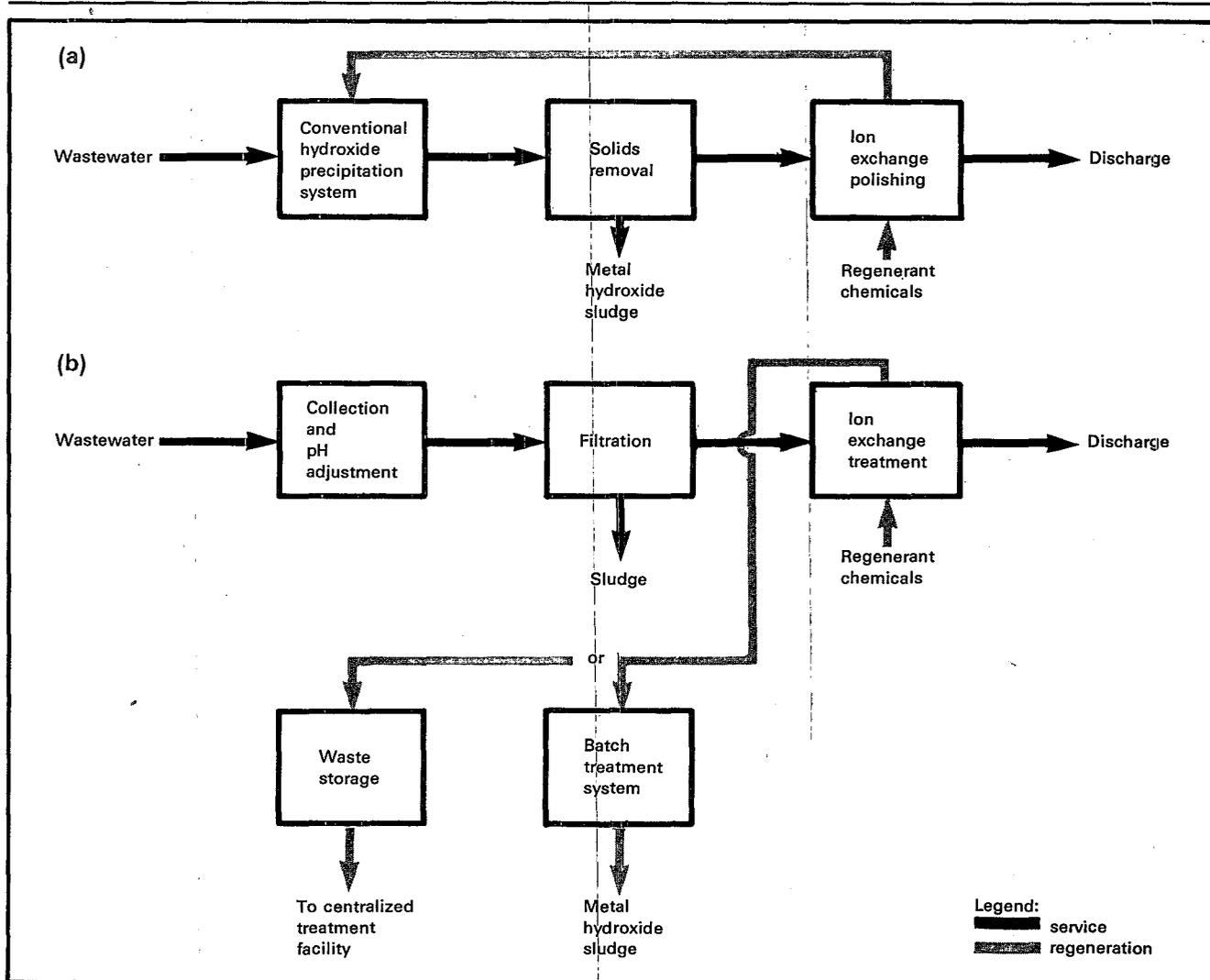


Figure 12.
 Ion Exchange Systems: (a) Polishing and (b) End-of-Pipe Treatment

facility to dispose of the regenerant solutions and need not install chemical destruct systems. In either case, no investment is needed for sophisticated pH control systems, flocculant feed systems, clarifiers, and other process equipment associated with conventional continuous treatment systems, and ion exchange becomes attractive in terms of cost. And, as a further advantage, ion exchange units are compact and easy to automate compared with conventional treatment systems.

Ion Exchange Polishing Systems

Process Description. Figure 13 shows a treatment system employing:

- Hydroxide neutralization to control pH and to precipitate heavy metals as metal hydroxides
- Flocculation to agglomerate the suspended solids
- Clarification and deep-bed filtration to remove the precipitated metals and suspended solids

- Ion exchange polishing to reduce residual metal solubility before the water is discharged

For effective metal removal by hydroxide precipitation, pH must be controlled within the narrow range where the metals are least soluble. Such narrow control usually requires sufficient retention time within the pH adjustment tank to ensure minimum variation in neutralizing reagent demand. Multistage neutralizers and sophisticated control loops are also used to minimize deviation from the pH

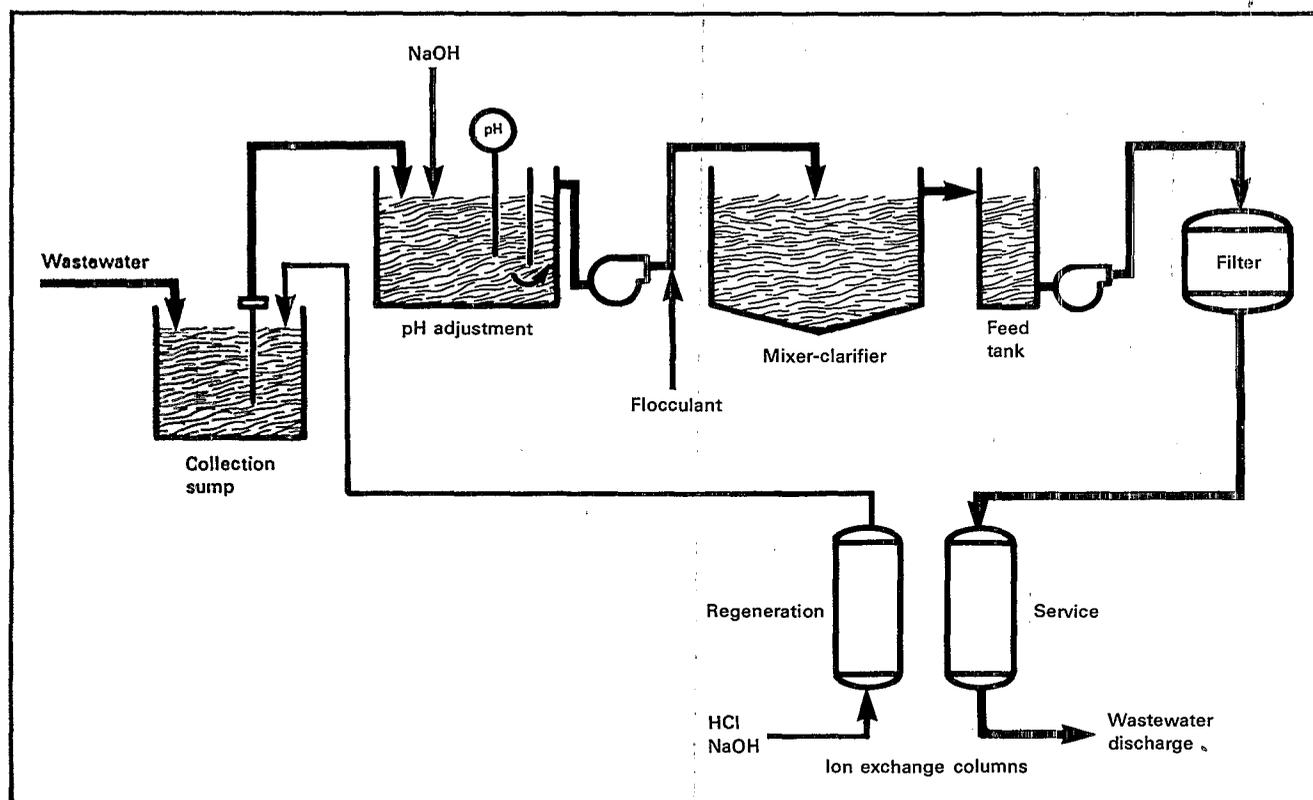


Figure 13.
Conventional Treatment System With Ion Exchange Polishing

control set-point. With effective pH control, most of the metals in the wastewater will precipitate as metal hydroxides.

To provide effective removal of precipitated metals and other suspended solids, coagulating-flocculating compounds are added to the neutralized wastewater to agglomerate the solids and facilitate their removal. Most of the suspended solids can be removed by clarification; however, removal of fine particles (including precipitated metals) requires filtration. Deep-bed filters, which remove solids by passing the wastewater through a bed of sand and gravel, are used most frequently.

For most waste streams, the unit operation sequence of hydroxide precipitation, flocculation, clarification, and filtration will produce an effluent with a minimum heavy metal content and achieve compliance with discharge permit regulations. In cases where the metal content exceeds the permit limit, and the excess is in the form of dissolved metals (as opposed to metal hydroxide particles not removed during solids separation), a polishing treatment using ion exchange resins will reduce the effluent metal concentrations.

The failure of hydroxide precipitation to reduce metal solubility to the required level can be caused by one of the following:

- Failure to control pH within the narrow range necessary for minimal metal solubility

- The presence of chelating compounds that combine with metals to form complexes not effectively removed by hydroxide precipitation
- Discharge limits requiring those metal concentrations below those which a hydroxide treatment system can achieve consistently and reliably

Resin Selection. Ion exchange heavy-metal polishing systems will usually use a chelating heavy-metal-selective cation resin. A resin of this kind forms an essentially non-ionized complex with divalent metal ions. Consequently, once an exchanger group is converted to the heavy metal form, it is relatively unreactive with other similarly charged ions in solution. Despite high concentrations of non-heavy-

metal cations competing for the exchange sites, the resin has sufficient preference for the heavy metal ions to exhibit a high metal-holding capacity per unit of resin volume. The chelating resins will effectively remove heavy metal cations from solutions with a pH above 4.0.

Weak acid cation resins also have potential for use in ion exchange polishing systems. These resins have the advantage of being less expensive than chelating cation resins, and they require less chemicals for regeneration. On the other hand, weak acid resins are not effective in acidic solutions; moreover, they are less selective for heavy metal cations over other divalent calcium and magnesium ions than are chelating resins.

Polishing System Equipment and Auxiliaries. The ion exchange polishing system consists of:

- Column or columns containing the resin
- Acid regenerant storage
- Sodium hydroxide regenerant storage
- Piping and valving to facilitate on-stream wastewater treatment, and regeneration and backwashing of the resin bed

Three ion exchange column configurations for a polishing system are:

- Single column
- Series column
- Parallel column

Unlike deionization systems, which require both a cation and an anion resin column, the polishing system usually requires only one kind of resin. Consequently, a single column design is feasible for small flows where the wastewater discharge can be interrupted to allow for column regeneration. Discharge permits are usually based on a daily composite sample, and this factor should be considered in evaluating use of a single column. Often the composite effluent quality of a treatment system that is

off stream 10 percent of the time for regeneration in any given day will achieve the discharge permit limits. Mechanical failures and system maintenance are inevitable consequences of using the process, however, and the reliability of a single column design is probably inadequate in most applications.

In none of the polishing system column configurations is there a simple means of detecting the breakthrough of metal ions that would indicate a need for column regeneration. Metal breakthrough is avoided by loading the column only to some fraction of its exchange capacity. A series column configuration, where the total flow of wastewater passes through each column, is particularly reliable in ensuring contact of the wastewater with a large volume of unreacted resin. After the up-stream column is exhausted, it is taken off stream, regenerated, and returned to service as the down-stream column. This configuration minimizes the possibility that the resin will be exhausted and that metal breakthrough will occur. On the other hand, pressure drop over the system will be high and each column must be sized to process the total flow.

A parallel column configuration employing three or more columns has advantages, particularly for larger flows. Both equipment cost and reliability are intermediate between the single and series column configurations. In a parallel configuration, each column is sized based on the assumption that one column is always off stream for regeneration. This design reduces the total resin volume requirements compared with those of a series column design. Using a bank of small columns does increase regeneration frequency; many of the units are designed with automated regeneration capabilities, however, and more frequent regeneration does not increase the need for operating labor.

Operating Procedure. Operation of an ion exchange polishing system is complicated by the lack of practical means for determining when the column is exhausted and metal breakthrough occurs. Unlike deionization systems, where a conductivity probe will signal the end of a column cycle, polishing systems have no simple, direct technique for continuously monitoring the levels of heavy metals in the effluent. To compensate for this lack, the columns are operated on either a time or flow cycle. This approach requires determining the column exchange capacity and the loading per unit volume of wastewater. Then, based on the resin volume in the column, the volume of wastewater that can be processed before exhausting the exchange sites can be estimated. As a rule, to provide a factor of safety, a capacity equal to three-quarters of the actual exchange capacity is used to determine the volume that can be processed per cycle.

For a constant flow system, the volume capacity can be converted to a cycle time. A flow totalizer can be used for variable flow systems to monitor the cumulative volume and indicate when the column should be regenerated. Many manufacturers provide automatic regeneration capabilities with their column systems. For such systems, the control mechanism can be directed to begin regeneration by either a timing device or a flow totalizer.

The regeneration sequence for a chelating and a weak acid cation resin is:

1. Water backwash to remove suspended solids from resin bed
2. Acid regeneration
3. Water wash to remove residual acid
4. Sodium hydroxide regeneration
5. Water backwash to remove residual caustic and reclassify the resin particles
6. Cocurrent fast rinse to ensure that the resin bed's flow charac-

teristics are adequate and to remove any unused reagents
 7. Return to service

The resin is used in the sodium form even though it adds extra steps to the regeneration process and increases the chemical consumption. Treating an alkaline waste stream with a resin in the hydrogen form would gradually result in conversion of the resin to either the sodium or calcium form; however, the exchange for hydrogen ions would depress the effluent pH below the control limitations and result in a period of noncompliance. Also, the resin exhibits a greater selectivity for heavy metals in the sodium form.

Hydrochloric acid is normally used for acid regeneration although it is more expensive than sulfuric acid. Sulfuric acid regeneration could result in the precipitation of magnesium or calcium sulfate during regeneration, and the resin bed could thus be hydraulically fouled. This effect can be avoided, however, if a dilute (2-percent) sulfuric acid regenerant solution is used.

The final backwash to reclassify the resin bed is critical. "Classification" refers to positioning the resin particles so that the largest particles are at the base of the column and the particle size gradually decreases as distance from the base increases. This arrangement results in maximum flowrate per unit of pressure drop and makes the bed more resistant to fouling from suspended solids in the column feed.

With strong acid and base resins, an initial backwash before regeneration is usually sufficient to ensure good flow characteristics during the service cycle. In the case of weak acid or chelating resins, however, the resin beads swell considerably when converted to the hydrogen form and subse-

Table 8.

Ion Exchange Polishing System Performance Characteristics

Item	Characteristic	Value
Ion exchange column	Chelating resin	10 ft ³
	Wastewater volume	120,000 gal/cycle
	Resin capacity	0.87 lb Ni/ft ³ 0.03 lb Cu/ft ³
Service:		
Wastewater to column	pH	8.4
	Ni ⁺²	8.9 ppm
	Cu ⁺²	0.3 ppm
Discharge	pH	8.4
	Ni ⁺²	0.16 ppm
	Cu ⁺²	0.02 ppm
Regeneration:		
Flow to column	Wash water	500 gal/cycle
	5% NaOH	68 gal/cycle
	5% HCl	65 gal/cycle
Purge streams	Volume	633 gal/cycle
	Nickel	0.16%
	Copper	0.006%

quently shrink when converted to the sodium form, which necessitates a final backwash before the column is returned to service.

All regenerant and wash solutions are sent to the hydroxide treatment system for processing. Table 8 presents a typical polishing system performance with volume of wastewater processed and the relative volumes of the regenerant streams.

System Performance. The number of ion exchange polishing systems installed to date is limited; however, abundant pilot test data verify system effectiveness in reducing the soluble metal content of a neutralized waste stream. The data from these controlled experiments can lead to a better understanding of how process variables and design factors influence performance.

Volumetric loading for ion exchange systems is usually expressed in bed volumes (bv) of solution treated per hour or in gallons per minute per cubic foot (liters per minute per liter) of resin. Both measures describe loading in terms of the volume of solution treated per volume of resin in a unit

of time. In essence, they define the length of time the solution is in contact with the resin.

Figure 14 shows the concentration profile of the effluent from a pilot test column containing a chelating resin. The feed solution has an initial cadmium concentration of 50 ppm, a calcium chloride (CaCl₂) concentration of 1,000 ppm, and a pH of 4.0. Tests were run at two different volumetric loadings: 8 bv/h [1 gal/min/ft³ (0.13 L/min/L)] and 16 bv/h [2 gal/min/ft³ (0.26 L/min/L)]. The higher loading resulted in earlier breakthrough. Assuming the column cycle is terminated at a cadmium concentration of 2.0 ppm in the effluent, the 8-bv/h system could treat 400 bv before regeneration, compared with 325 bv for a system operating at 16 bv/h.

The influence of volumetric loading on capacity results in a trade-off between investment and operating cost. Specifying a larger, more expensive column will result in greater capacity per unit volume of resin and less frequent and more efficient regeneration.

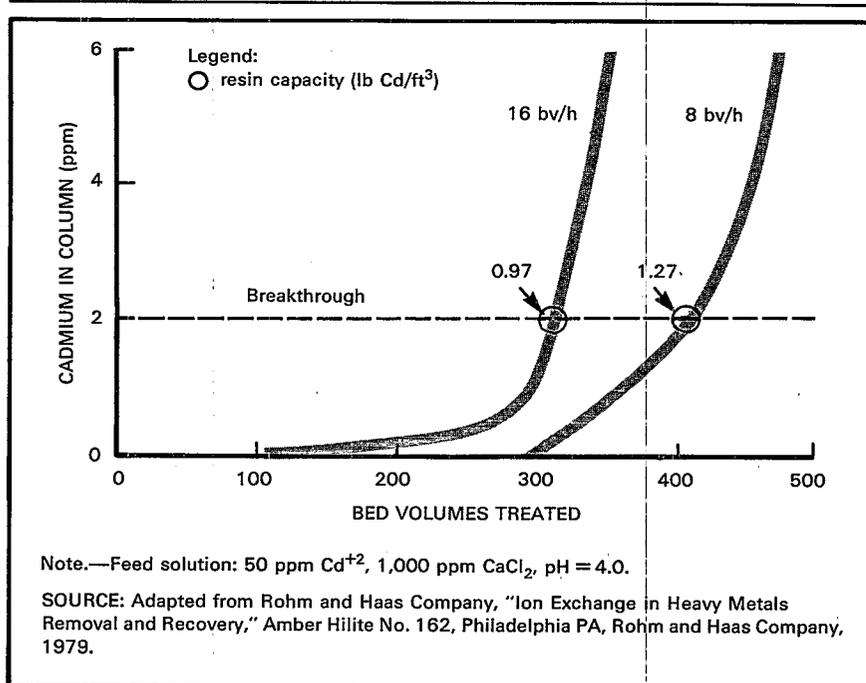


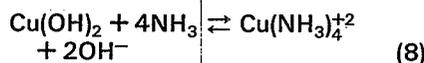
Figure 14.

Influence of Flowrate on Chelating Resin Capacity

Figure 15 shows concentration profiles of the effluent from two pilot test columns. One column contained a chelating resin, the other a weak acid resin. Each column treated a solution with 50 ppm cadmium and 1,000 ppm calcium chloride at pH 2.07, 4.0, and 8.0. Neither resin is effective at a pH of 2.07. The chelating resin shows approximately equal capacity at pH 4.0 and 8.0. The weak acid resin shows a capacity increase when pH is increased from 4.0 to 8.0. It is significant that the weak acid resin showed greater capacity than the chelating resin at pH 4.0 and 8.0. Where they are suitable, the less expensive weak acid resins are the resins of choice in metal removal applications.

Ion exchange polishing is often considered because hydroxide precipitation cannot effectively reduce metal solubility in the presence of compounds that form

stable complexes with the heavy metals. Ammonia, a common constituent of many plating wastewaters, tends to increase metal hydroxide solubility. For example, in a copper solution containing dissolved ammonia, the ammonia would compete for copper ions as follows:



In the presence of many chelating compounds, a chelating resin is more effective in removing heavy metals than a weak acid resin because it forms a less-ionized complex with the heavy metal ion. This effect is demonstrated in Figure 16, which shows the superiority of the chelating resin in removing copper from solutions containing ammonia. A similar situation would be expected for other complexed metal ions.

Pilot evaluations have also been performed with actual plating wastewater. Figure 17 shows the feed and effluent concentrations of copper and nickel when the effluent from a hydroxide precipitation system was treated by ion exchange polishing. After adjustment to a pH of 8.4, the wastewater still contained a high level of nickel, although copper was removed to less than 1 ppm. Dissolved ammonia content was approximately 80 ppm. The weak acid cation resin in sodium form was ineffective in removing the nickel and the test was terminated after 700 bv of solution had been treated. The chelating resin in sodium form consistently removed the nickel to levels below 0.5 ppm and the copper to below 0.1 ppm until 1,600 bv of solution had been treated. The equivalent would be processing 12,000 gal/ft³ (1,600 L/L) of resin before regeneration would be needed.

When the resin is selected for a polishing application both weak acid and chelating cation resins should be tested. The lower initial cost, greater capacity, and more efficient use of regeneration chemicals make weak acid resins the choice for those applications where they are effective in metal removal. Many wastewater applications, however, will require the chelating resins' greater affinity for heavy metals to achieve the necessary effluent quality.

Ion Exchange Wastewater Treatment Systems

The conventional practice of converting the heavy metal pollutants in metal finishing wastewater to a hydroxide sludge was thought to be a means of eliminating any environmental hazard the metals might pose. In fact, a solid waste stream is generated that, although its volume is much smaller than that of the wastewater, requires further controls to ensure that disposal of

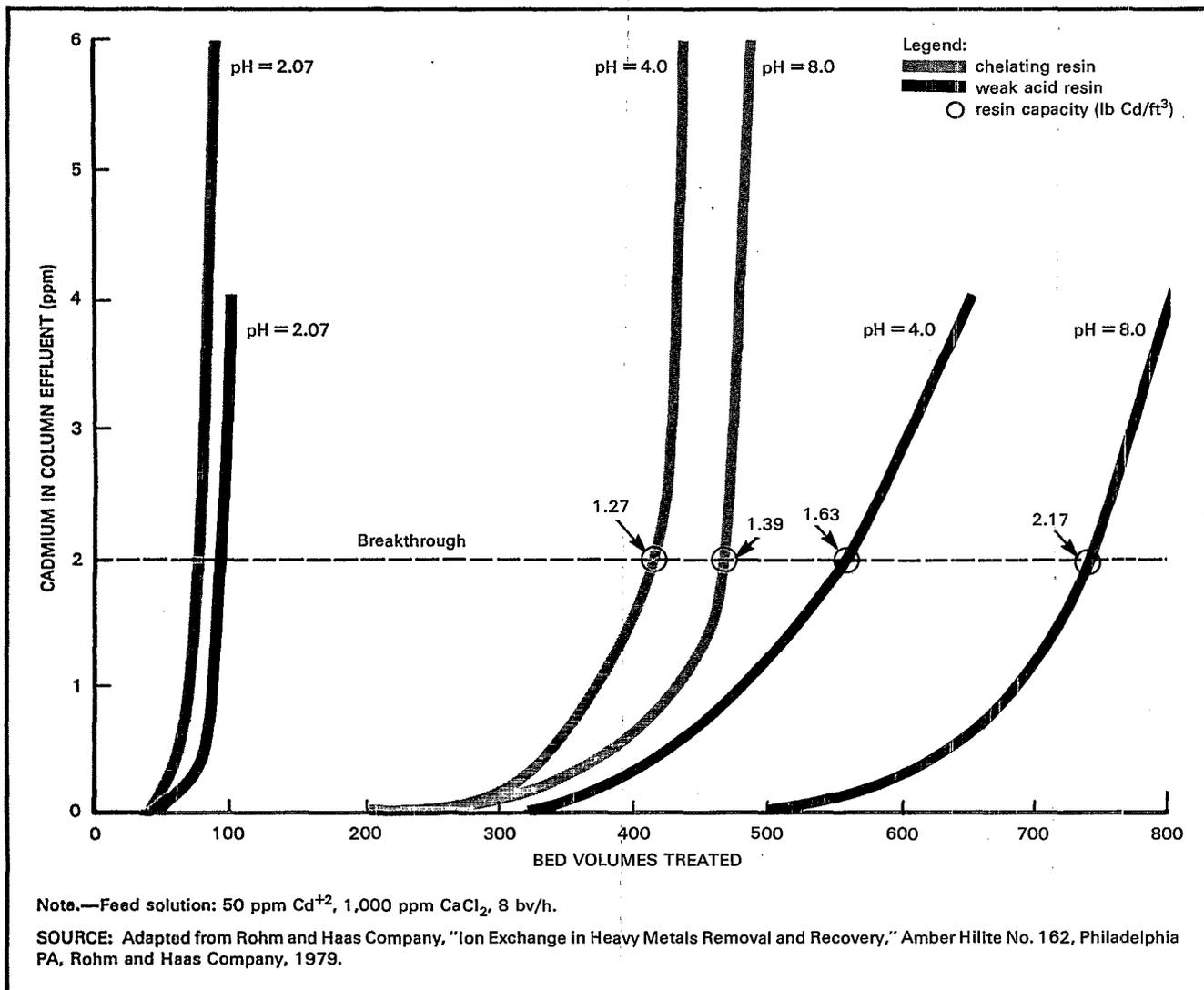


Figure 15.
 Influence of Solution pH on Chelating and Weak Acid Cation Resin Capacity

the metal residue is environmentally acceptable.

Ion exchange represents an alternative means of concentrating the pollutants. The metals are concentrated in the regenerant solutions and are then in a form more easily handled and more amenable to further processing. With the increasing cost of virgin metals and the significant cost of heavy

metal waste disposal, the development of processes that recover metals from mixed metal wastes is inevitable. When metal recovery is commercialized on a wide scale, the ion exchange regenerant solutions will represent a byproduct of metal finishing operations, not a waste product.

Currently, firms using ion exchange for end-of-pipe pollution control must also install small batch treatment systems to treat the regenerant and wash solutions. These systems,

which use conventional destruct processes, result in a residue with the same disposal criteria as the sludge from a conventional treatment process. The ion exchange system may still present a less costly means of complying with pollution control regulations. The key to using ion exchange for waste treatment is to remove only the toxic pollutants while allowing most of the nontoxic ions in solution to pass through the column. Normally, the toxic compounds represent

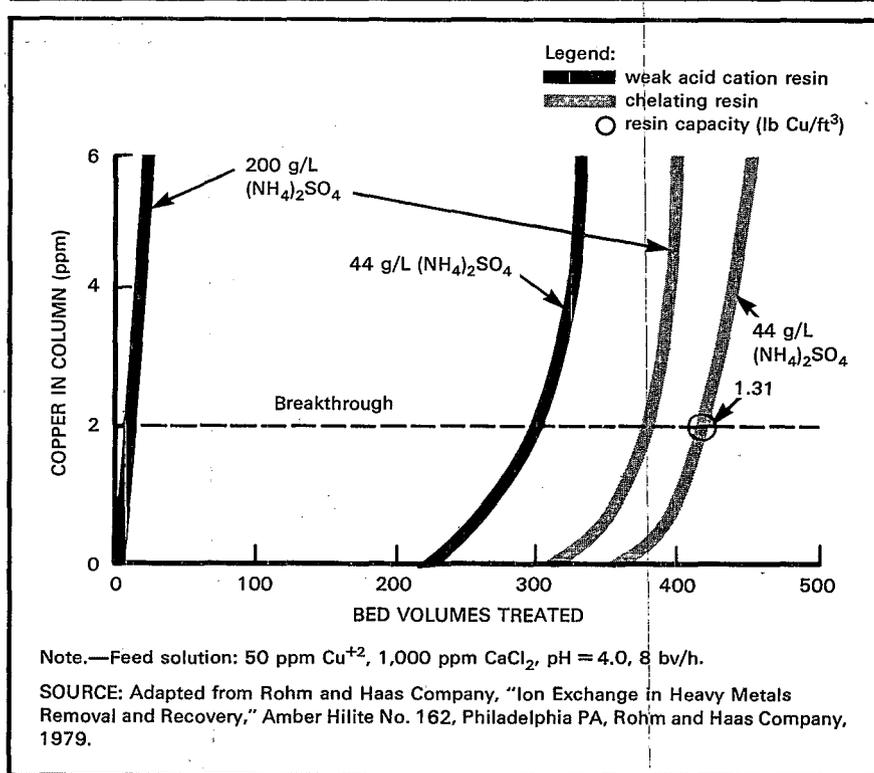


Figure 16.

Influence of Ammonia on Chelating and Weak Acid Cation Resin Capacity

only a small percentage of the ionic solids in the wastewater. If the ion exchange system is not selective in the species it removes from the wastewater, the column capacity required and the regenerant chemicals consumed will result in prohibitive costs.

Ion exchange has proved successful in selectively removing many of the pollutants encountered in metal finishing wastes. Proper application of the process requires selecting the appropriate resin and regeneration sequence and, usually, some pretreatment of the wastewater before ion exchange.

Process Description. Wastewater treatment systems employing ion exchange include the following components:

- Wastewater collection
- Wastewater pretreatment
- Ion exchange columns

- Ion exchange column regeneration system
- Batch treatment for regenerants (or waste storage if regenerants are shipped off site for treatment or recovery)

Wastewater collection most frequently consists of gravity drainage of rinses to a collection sump below ground. The sump provides a storage volume to allow the flow to the treatment system to be controlled at a constant rate. If the ion exchange columns employ either weak acid or weak base resins, the capacity and performance of the resins will be influenced by pH. Consequently, the collection sump should include coarse pH adjustment capabilities. The pH adjustment system must only ensure that the solution pH does not deviate from the broad operating range of the resin. This pH control

requirement is substantially different from those of hydroxide precipitation systems, which need minimum deviation from the control set-point.

As a rule, filtration to remove suspended solids is the only other pretreatment required. Suspended solids in the feed would hydraulically foul the resin bed. Different filters have been employed, including deep bed, diatomaceous earth precoat, and activated carbon filters. In one approach, a filter with fine resin particles is used to trap suspended solids. Regardless of the filter type, the resulting purge stream containing the suspended solids must be processed and disposed of.

The specifications of the column system containing the ion exchange resin depend on the flowrate and the pollutants in the wastewater. Two potential cases emerge with respect to pollutants:

- Heavy metal cations alone
- Heavy metal cations along with cyanides, and complex metal anions

In the case of wastewater containing only heavy metal cations, a column with the sodium form of a weak acid or heavy-metal-selective chelating cation resin would be employed. For a weak acid resin, a pH close to neutral is recommended. If a chelating resin is used, the pH can be slightly acidic (>4.0). In both cases, strongly basic conditions should be avoided because such conditions favor formation of anionic metal complexes.

For waste streams containing both heavy metals and cyanides, a stratified bed of resin has proven effective. This patented approach uses a bed of resin with successive layers of strong base anion, weak acid cation, and strong acid cation resins. The wastewater first comes in contact with the strong base resin, which selectively adsorbs the complex metal cyanide ions but

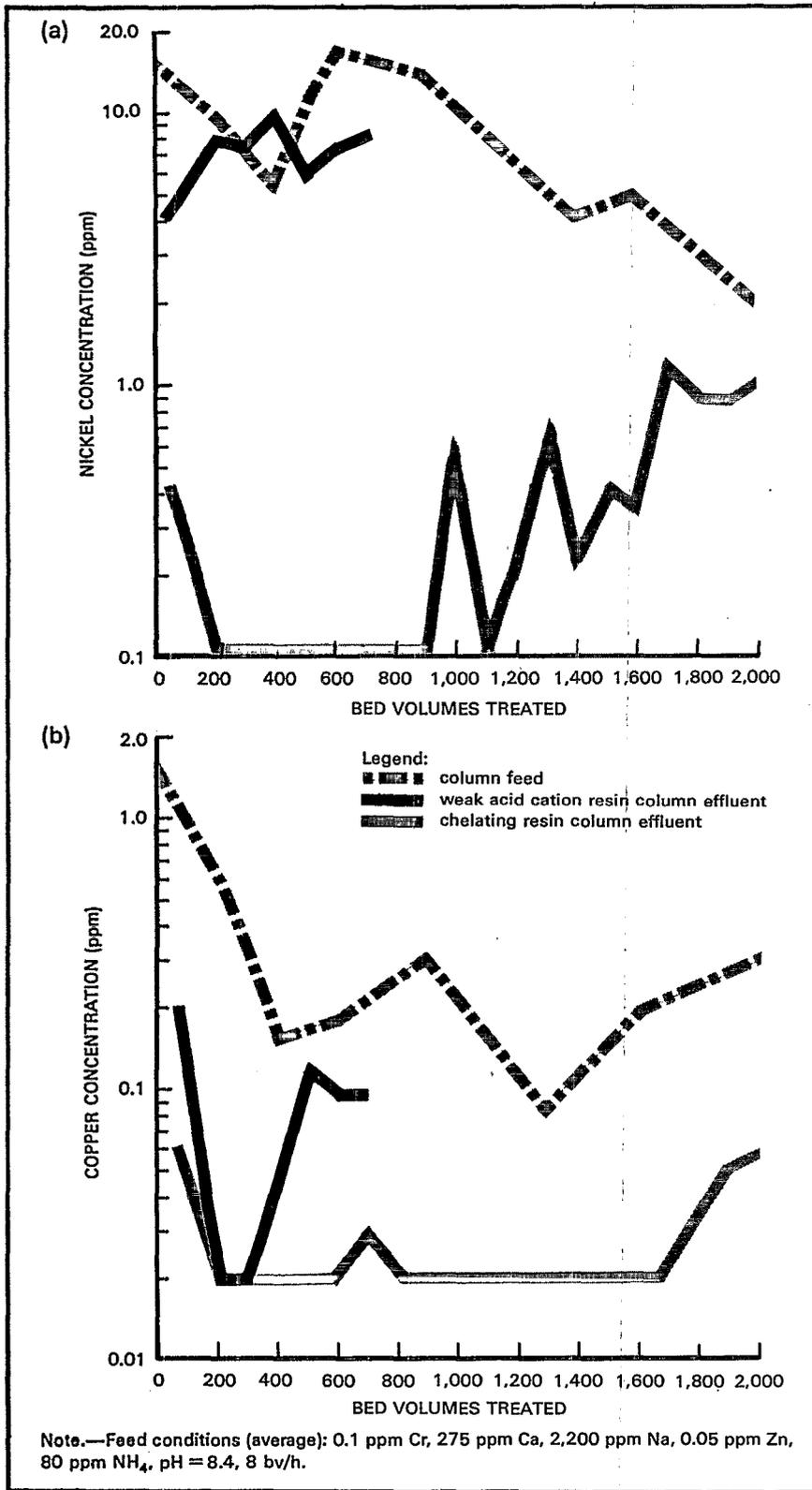


Figure 17.
Metals Removal Data: (a) Nickel and (b) Copper

allows the rest of the negatively charged ions to pass through. It should be noted that, although the resin will remove complexed metal cyanides selectively, the presence of free cyanide will result in early cyanide breakthrough. The strong base resin does not show significant selectivity for hexavalent chromium or free cyanide over the sulfate, chloride, and other non-toxic anions in a wastewater. For effective use of this type of resin system, hexavalent chromium wastes should be treated to reduce the chromium to the trivalent form before they are mixed with the rest of the wastewater. The trivalent chromium will be removed selectively by the weak acid resin.

The wastewater then comes in contact with the weak acid cation resin in the sodium form. The resin employed exhibits a strong preference for multivalent cations. Consequently, cation resin capacity is a function of the concentration of calcium, magnesium, and heavy metal cations. Finally, the resin makes contact with a layer of strong acid cation resin that is predominantly in the hydrogen form. The exchange of the hydrogen ions tends to balance the pH rise that normally would occur at the beginning of the cycle.

The system also employs a novel regeneration sequence for the stratified resin bed. In a conventional mixed bed system, cationic and anionic resins are separated by being backwashed into discrete layers. Each layer is then regenerated independently; acid is brought in contact with the cation resin and sodium hydroxide regenerates the anion bed. The bed is then mixed with air and the resin types are distributed equally throughout the bed.

With the stratified bed used for heavy metals and metal cyanide, the resin bed is first backwashed gently to remove suspended solids and the resin bed is fluidized. Because the three types of resins have

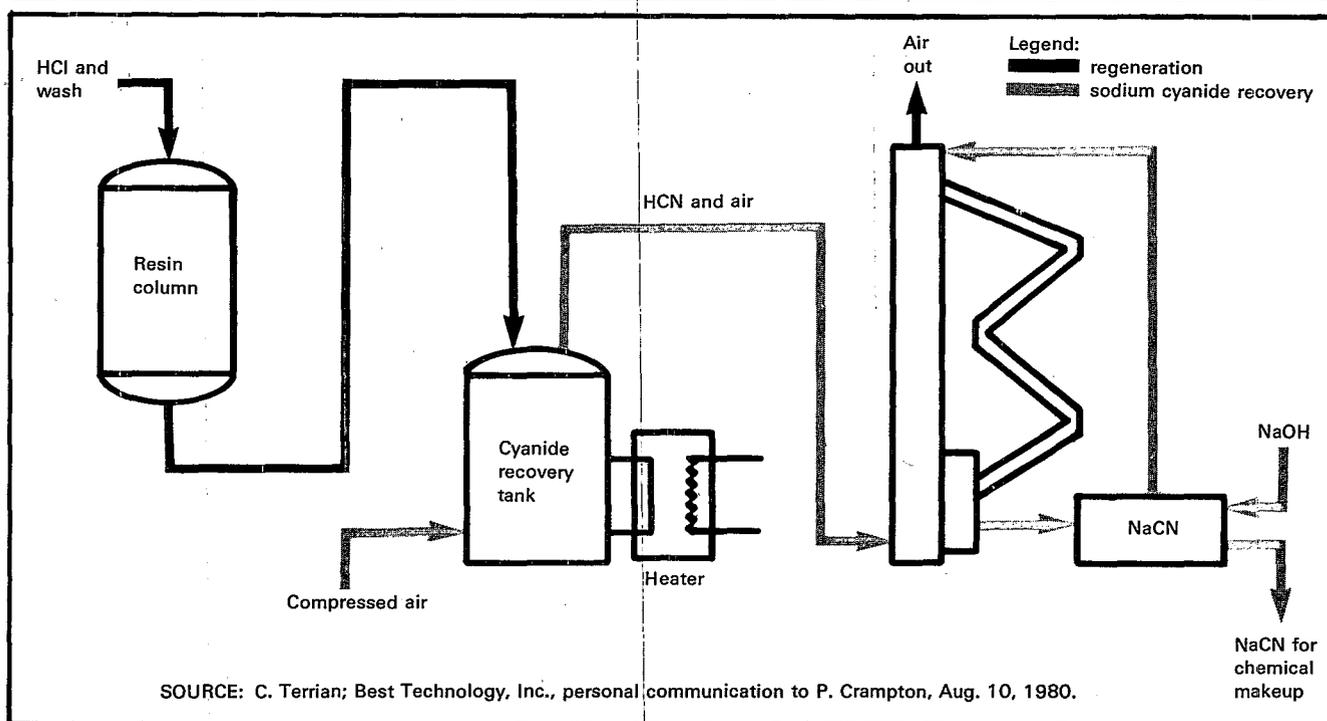


Figure 18.
Sodium Cyanide Recovery

different densities, the resin stratification can be maintained with proper backwashing. The strong base resin is least dense, the weak acid resin is intermediate, and the strong acid resin most dense. After backwash, the bed makes cocurrent contact with a 20-percent HCl solution. The acid elutes the metal cyanide complexes from the anion resin and replaces them with chloride ions. The heavy metals and divalent cations are removed from the weak acid cation resin and replaced with hydrogen ions. The strong acid resin is also converted to the hydrogen form.

After a water wash, the bed is washed with a 20-percent sodium hydroxide solution. The sodium hydroxide converts the anion resin to the hydroxide form and elutes any metal chloride complexes formed during the acid wash. The weak acid cation resin is converted to the sodium form. The sodium hydroxide is essentially depleted

by the time it reaches the strong acid resin. After another water wash, the column is returned to service.

The stratified bed system also features cyanide recovery to avoid the significant cost of treating the cyanide contained in the acid regenerant. The acid regenerant and the subsequent water wash are routed to a closed-top vessel (Figure 18) where heat is supplied to raise the solution temperature to 140° F (60° C) and air is bubbled into the solution. The result is a rapid release of HCN gas. The liberated gas is brought in contact with a caustic soda solution; the caustic soda absorbs the cyanide, yielding a sodium cyanide (NaCN) solution that can be used for chemical makeup in the cyanide plating baths.

Regenerant solutions from the ion exchange column are usually

treated in a small batch treatment system. Depending on the pollutants present, the system may need capability for cyanide oxidation, chromium reduction, and metal precipitation. The sludge resulting from batch treatment can be either settled and disposed of or mechanically dewatered before disposal.

A system treating a combined wastewater containing both ferrous ions and cyanides will have a significant concentration of ferrocyanides in the regenerant solution. These difficult-to-treat cyanide complexes result from mixing of the cyanide wastewater with acidic streams containing dissolved iron. An additional treatment step is needed to oxidize the ferrocyanides. In this step hydrogen peroxide is added to the wastewater, which is subjected to irradiation by ultraviolet light. The strong oxidizing power of this system is effective in treating the ferrocyanides.

When ion exchange column size is determined, hydraulic and contaminant loadings must be considered. Resin manufacturers recommend volumetric loading rates in the range of 1 to 2 gal/min/ft³ (0.13 to 0.26 L/min/L) of resin. Unless the contaminant loading results in unmanageable regeneration frequency, the hydraulic loading should be selected from the high end of the range.

System Performance. Operating data from ion exchange wastewater treatment systems is scarce because of the small number of facilities employing the technology; however, the available performance data indicate the potential for application in metal finishing wastewater treatment.

In one case, treatment was of a slightly acidic heavy metal wastewater containing a moderate concentration of calcium, magnesium, and sodium cations. A weak acid cation resin in the sodium form was evaluated for removing the heavy metals. The resin was able to remove both the zinc and cadmium selectively while allowing most of the calcium ions to pass through (Table 9). Initially, the resin exchanged its sodium ions for calcium ions in solution; however, the resin then exchanged these calcium ions for heavy metals. After 70 bv had been processed, the effluent contained essentially the same calcium concentration as the column feed. The column was regenerated with 3.6 percent HCl followed by conversion to the sodium form with NaOH. Table 10 shows the composition of the acid regenerant solution. In this case, ion exchange treatment reduced the waste volume associated with the pollutants to less than 5 percent of the original volume.

In a second application, an ion exchange waste treatment unit was installed to treat the combined waste flow from a plating shop performing copper, nickel, and assorted cyanide plating processes.

Table 9.

Removal of Zinc and Cadmium from Wastewater by Weak Acid Cation Resin^a

Bed volume sampled	Total loading (gal/ft ³ resin)	pH	Leakage (ppm)		
			Zinc	Cadmium	Calcium
10.....	75	10.1	0.01	0.01	1
25.....	190	10.1	0.01	0.01	3
35.....	260	8.3	0.01	0.01	53
55.....	410	7.2	0.01	0.01	303
70.....	520	6.0	0.16	0.01	338
100.....	750	7.0	0.1	0.01	385
150.....	1,120	6.9	0.13	0.01	404
160.....	1,200	6.8	0.25	0.01	405
165.....	1,230	6.8	0.37	0.01	407
175.....	1,300	6.7	0.56	0.01	404
190.....	1,420	6.8	0.64	0.01	395
200.....	1,500	6.8	1.3	0.01	394
225.....	1,680	6.8	6	0.01	395

^aNa form.

Note.—Feed characteristics: 391 ppm Ca, 91 ppm Zn, 0.12 ppm Cd, 350 ppm Mg, 57 ppm Na, 3.5 ppm Mn, 0.12 ppm Ni; pH = 4.7; 8-bv/h (1-gal/min/ft³) flowrate.

SOURCE: Rohm and Haas Company, "Ion Exchange in Heavy Metals Removal and Recovery," Amber Hilite No. 162, Philadelphia PA, Rohm and Haas Company, 1979.

Table 10.

Acid Regenerant Composition

Bed volume ^a	pH	Constituent (ppm)		
		Zinc	Cadmium	Calcium
1.....	6.0	600	3.2	3,380
2.....	2.4	13,000	14	6,944
3.....	0.4	3,000	1.8	1,003
4.....	0.3	2,600	1.3	677
5.....	0.5	290	0.12	67
6.....	2.2	3.3	0.01	1.7
7.....	3.0	0.2	0.01	0
8.....	3.1	0.06	0.01	0.6
Average.....		2,440	2.6	1,500

^a3.6% HCl in bv 1 through 4; distilled water in bv 5 through 8.

SOURCE: Rohm and Haas Company, "Ion Exchange in Heavy Metals Removal and Recovery," Amber Hilite No. 162, Philadelphia PA, Rohm and Haas Company, 1979.

The entire wastewater flow was collected in a single sump equipped with a pH control system to ensure that cyanide wastes were not subjected to acidic conditions. The ion exchange columns were stratified bed units containing strong base, weak acid, and strong acid resins. Table 11 gives the waste-

water composition at various points in the treatment system and the concentration of the purge streams. Sample points are raw feed, filtered feed, filter backwash, regenerant purge, and treated effluent (see Figure 12b).

The design of the ion exchange wastewater treatment system is es-

Table 11.

Treatment of Metal Cyanide Wastewater by Ion Exchange: Pollutant Analysis

Constituent	Content (ppm) at sample point				
	Raw feed	Filtered feed	Filter backwash	Regenerant purge	Treated effluent
Total cyanide	—	31.4	—	—	3
Cadmium	0.8	0.4	0.13	0.295	0.0001
Calcium	61.4	28.8	74.8	600	1.637
Chromium	1.37	0.52	3.47	13.4	0.356
Copper	2.11	0.28	3.8	4.57	0.41
Iron	14.2	3.3	65	11.5	0.195
Nickel	3.14	2.92	31.1	36.4	0.425
Zinc	42	23	95	251	2.62

SOURCE: C. Terrian, Best Technology, Inc., personal communication to P. Crampton, Aug. 10, 1980.

Table 12.

Commercially Demonstrated Resin Systems for Wastewater Treatment

Resin system	Application
Weak acid	Selective removal of heavy metals from untreated wastes
Chelating cation	Selective removal of heavy metals from untreated wastes Removal of trace concentrations of heavy metals from solutions with high background cation concentrations Selective removal of heavy metals from solutions containing metal complexing compounds
Stratified bed (strong base, weak acid, strong acid)	Selective removal of metal cyanide, anionic metal complexes, and multivalent cations from solution

essentially uniform over the range of pollutant removal capabilities it exhibits. Proper resin selection, however, is the key to effective and efficient pollutant removal. Testing to verify performance of a resin system is essential before system selection. Table 12 presents varieties of resin systems in commercial use for pollution control and the pollutant removal capabilities of each.

Equipment Cost

Whether ion exchange is used to polish the effluent of an existing treatment system or whether it

is applied to treat the waste directly, the ion exchange unit is basically the same. The major equipment cost differences between the two systems is in the auxiliaries. For a polishing application after conventional treatment, the auxiliary requirements are provided by the upstream process. In a direct treatment application, however, these items add significantly to the total system cost. Determinants of the total system cost include:

- Feed pretreatment requirements
- Volumetric and contaminant loadings (resin volume needed)
- Regeneration mode
- Equipment needed to process or store regeneration solutions and purge streams

To pretreat the wastewater before it passes through the ion exchange column, suspended solids removal and coarse pH adjustment are needed; removal of organic compounds may also be required. (Fouling by organics is primarily a problem with strong base anion resins.) Organics can be removed using activated carbon or synthetic adsorbent materials. The synthetic materials have the advantage of being regenerable; spent carbon must be disposed of and replaced. As a rule, filters that remove organics are also effective for removing suspended solids.

Similarly in a polishing application the upstream process can treat the regeneration purge streams. For direct treatment, a batch destruct system is needed. Table 13 presents typical costs for the auxiliaries commonly associated with ion exchange systems.

Exchange column size and the associated resin volume specifications depend on the wastewater flowrate and the contaminant loadings. Resin manufacturers usually recommend loadings for resin systems at about 2 gal/min/ft³ (0.26 L/min/L) of resin. Flowrate indicates the flow of solution related to the average period of time it is in contact with the entire resin bed. However, the active zone of an ion exchange system can be represented as an exchange front proceeding down the column (Figure 19). The depth of the active front is a function of the volumetric loading and the speed of the ion exchange reaction kinetics. For ion exchange applications where the columns are run to exhaustion, the benefits of low loadings include greater capacity per unit of resin and more efficient use of regenerant chemicals. In wastewater treatment, however, the lack of direct measurement techniques to signal column breakthrough precludes loading the column to exhaustion, and higher loading rates are recom-

Table 13.

Typical Costs for Ion Exchange Equipment Auxiliaries

Auxiliary	Installed cost (\$)
pH adjustment tank, by flowrate in gal/min: ^a	
25.....	25,000
50.....	32,000
75.....	45,000
100.....	51,000
Deep bed sand filters, by flowrate in gal/min: ^b	
25.....	25,000
50.....	38,000
75.....	45,000
100.....	49,000
Batch treatment system, by volume in gal: ^c	
250.....	7,000
500.....	8,500
1,000.....	10,750
1,500.....	12,250
2,000.....	13,500

^a20-min retention, pH-controlled addition of NaOH, skid-mounted unit.

^bDual filters with backwash system and backwash storage, skid-mounted unit.

^cAgitated reaction tank, pH-controlled addition of H₂SO₄ and NaOH, ORP-controlled addition of NaHSO₃, manual operation.

Note.—1980 dollars.

mended. Regeneration is based either on time or on cumulative volume interval. As the interval will be based on assumed wastewater concentration established by earlier testing, a safety factor must be used in determining the duration of the cycle.

The columns would typically be loaded to 75 percent of their actual capacity before regeneration. That is to say, there should usually be a band of unreacted resin left over at the end of the column on-stream cycle. For both wastewater treatment and polishing, higher volumetric loading rates, if they still result in a manageable regeneration frequency, offer the advantage of reduced equipment size and cost. Loading rates as high as 20 gal/min/ft³ (2.6 L/min/L) of cross sectional area [equal to 5 gal/min/ft³ (0.65 L/min/L) of resin volume, assuming a bed 4 ft (1.2 m) deep] have been used in some applications. High loading rates for polishing systems are particularly advantageous considering that the contaminant loading is usually low.

The regeneration sequence is labor intensive and automation is cost effective except where regeneration is needed infrequently. Regeneration of a column normally takes 1 to 2 h. As a rule, columns in multicolumn parallel flow arrangements are designed to operate at least 4 h before regeneration.

The costs for various column configurations are shown in Figure 20 for skid-mounted units that require only piping and utility connections for installation. The regenerants are metered into the units by eductors. Regeneration is manual for the single- and dual-bed units. The three-bed parallel flow unit is sized based on two columns in service while the third is being regenerated; costs are with and without automated regeneration.

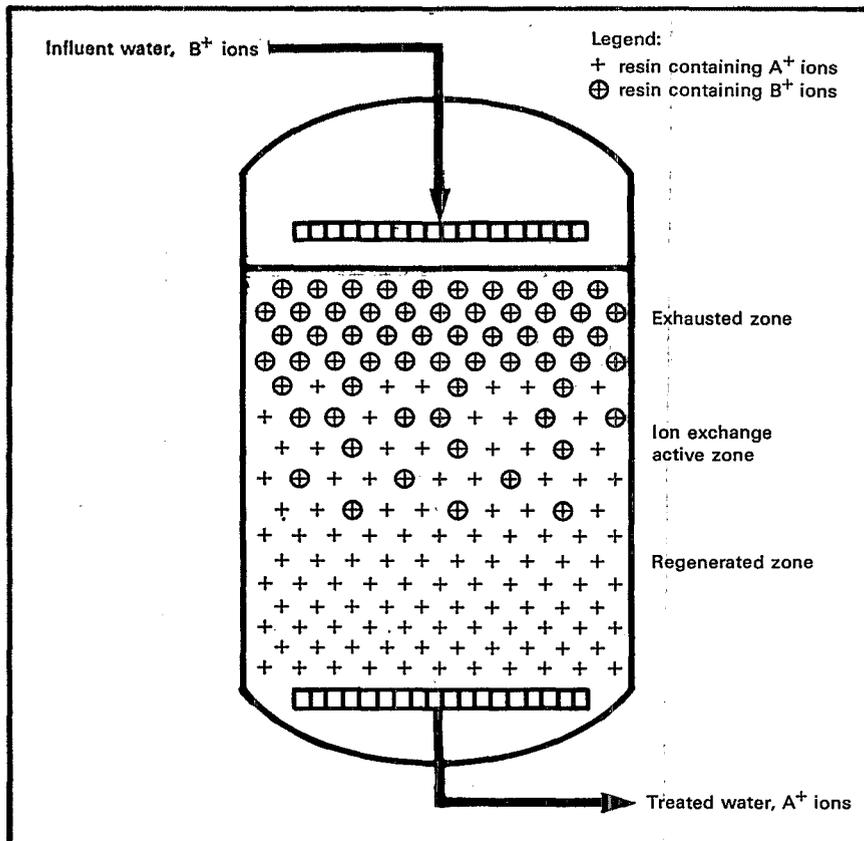


Figure 19.
Ion Exchange Column in Service

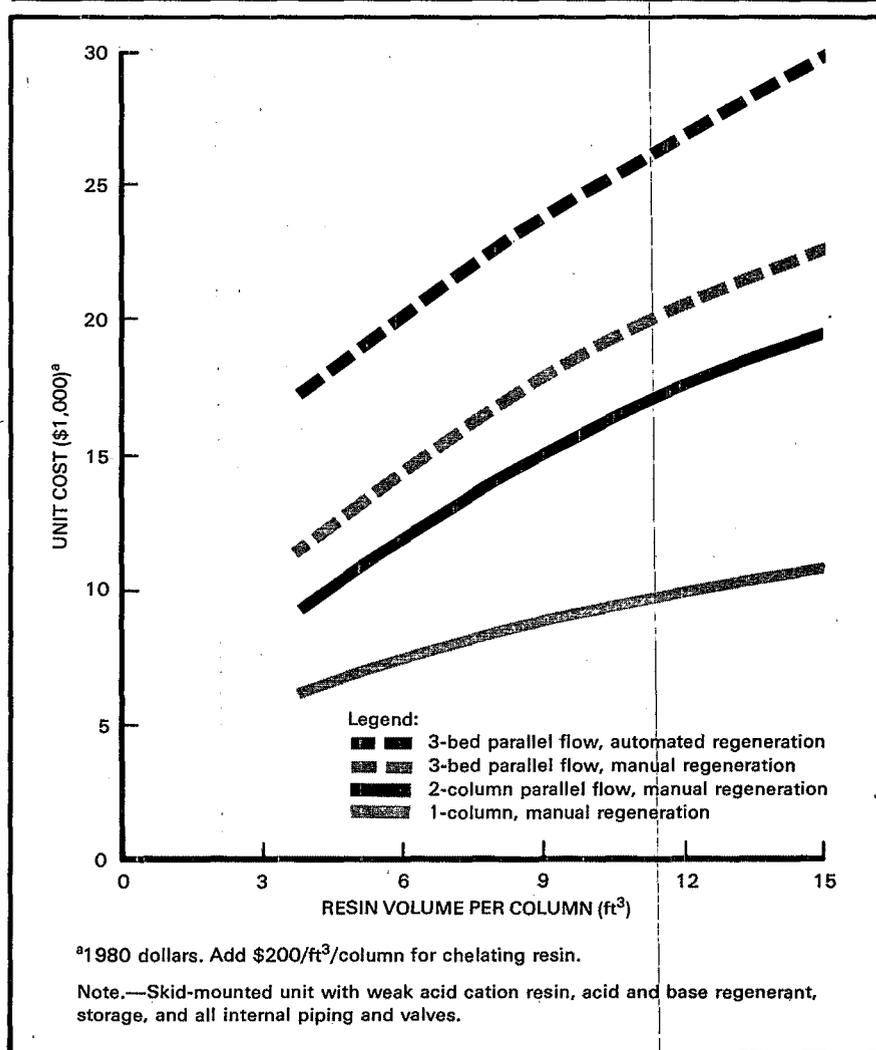


Figure 20.
Ion Exchange Unit Costs

Operating Cost

The chemical cost of operating an ion exchange system relates directly to the quantity of toxic contaminants removed from the wastewater by the resin bed. The chemical efficiency of the ion exchange reaction is a function of the resin selected and of the percentage of the resin's exchange capacity used. This relationship is

shown in Figure 21 for typical strong and weak acid cation resins over a range of acid regenerant doses. The weak acid resin requires significantly less regenerant per unit of exchange capacity.

Figure 21 also shows that the capacity of weak acid resin increases almost linearly with the amount of regenerant. That is to say, increasing the regenerant dose 50 percent increases the exchange capacity by an almost equal ratio. The strong acid resin, on the other

hand, achieves much greater chemical efficiency per unit of regenerant at lower regenerant doses. Consequently, weak acid resin systems can be designed to use the total resin exchange capacity; this capability reduces either required resin volume or regeneration frequency. Strong acid systems will realize greater efficiency if they are designed to use approximately 40 to 60 percent of the total resin exchange capacity.

Determining exchange capacity requirements requires analysis of the wastewater feed and column effluent chemical concentrations. Consider the weak acid resin system whose performance for removal of zinc and cadmium was described in Table 9. Assuming that a concentration of 1 ppm zinc in the effluent signaled the end of the cycle, 175 bv of solution could be treated before regeneration. Table 14 gives the composite feed and effluent concentrations in milligrams per liter and equivalents per liter of solution. The change in the equivalents per liter represents the number of resin exchange sites that would be exhausted if 1 L of solution were passed through the exchange column. The test indicated that each liter of solution treated would exhaust 0.0145 eq of resin exchange capacity. Breakthrough occurred after 175 bv had been treated, indicating that the resin had a total capacity of 2.5 eq/L, which is the same as the resin manufacturer's data indicated.

Assuming a three-column parallel flow unit is selected to treat the 50-gal/min (190-L/min) waste stream and that the columns are operated on a 4-h cycle, the necessary column size can be determined. It is assumed that the resin capacity is actually 80 percent of the theoretical capacity. This adjustment is similar to applying a fouling coefficient to a heat transfer surface and accounts for gradual

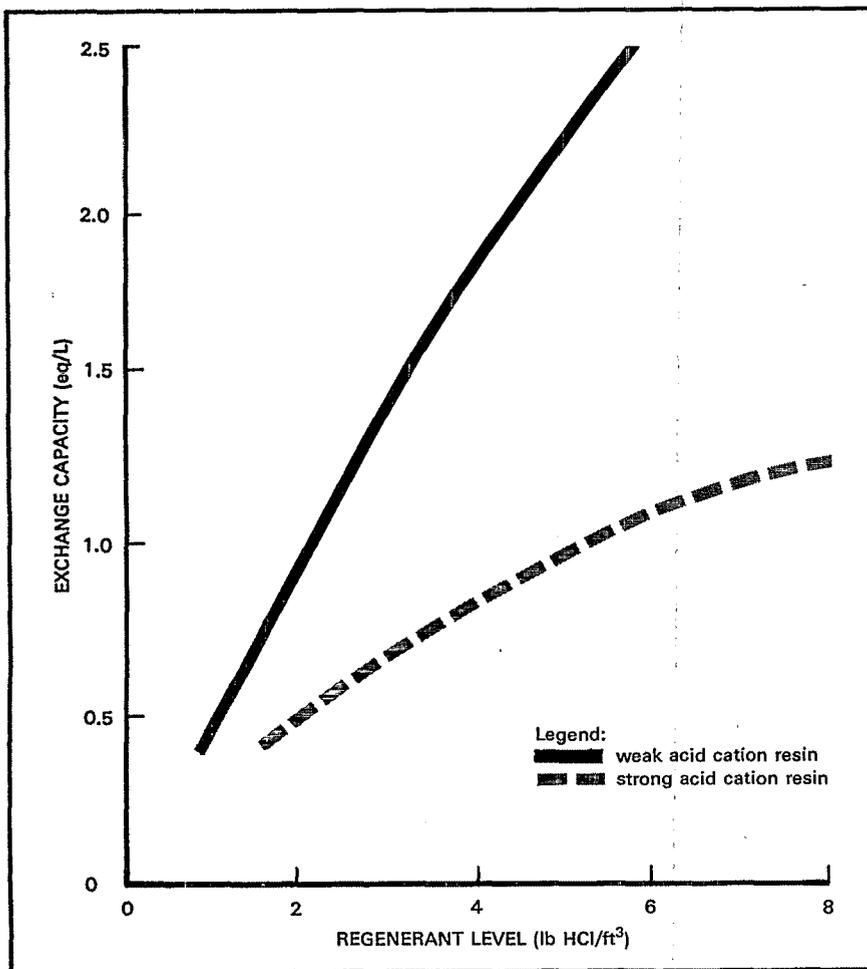


Figure 21.
Exchange Capacity versus Acid Regenerant Load for Cation Resins

Table 14.
Resin Capacity Based on Test Results

Constituent	Feed		Product		Change (eq/L)
	g/L	eq/L	g/L	eq/L	
Calcium	0.39	0.0195	0.3	0.015	0.0045
Magnesium	0.35	0.0292	0.27	0.0225	0.0067
Zinc	0.09	0.0028	(^a)	(^a)	0.0028
Sodium	0.06	0.0026	0.32	0.0139	-0.0113
Manganese	0.03	0.001	0.02	0.0006	0.0004
Cadmium	0.001	(^a)	(^a)	(^a)	0.0001

^aNegligible.

Note.—Exchange requirements: per liter of feed, 0.0145 eq/L; per 175 bv of feed, 2.53 eq/L of resin.

deterioration in resin performance. The adjustment yields a resin capacity of 2 eq/L.

The resin volume requirement calculation per column is shown in Table 15. The unit is designed to have two of the three columns on stream at any time. Assuming that the column is run to exhaustion, 5.8 ft³ (164 L) of resin would be needed per column.

No direct indication of column breakthrough is available for end-of-pipe process applications. To prevent discharging high concentrations of regulated pollutants, the columns can only be operated to some fraction of their actual capacity; 75 percent is a reasonable safety factor. Required resin volume would then increase to 7.8 ft³ (220 L) per column.

Two safety factors, then, have been used in sizing the ion exchange system; one to compensate for a gradual deterioration of resin exchange capacity and one to compensate for lack of direct means of determining column breakthrough.

Table 15 shows regeneration chemical consumption and cost, the purge streams from the unit, and the waste concentration factor. The purge stream containing the pollutants is approximately 7 percent of the original volume of wastewater. Consumption of HCl and NaOH for the system was assumed at 120 percent of the stoichiometric reagent requirement, based on the theoretical resin exchange capacity of 2.5 eq/L. Sodium hydroxide needs are only slightly above stoichiometric amounts, despite the resin's preference for being in the hydrogen form, because the product of the caustic regeneration reaction is not ionized. The caustic regeneration reaction is:



Once the resin's hydrogen ion is exchanged, it combines with a

Table 15.

Column Size Determination for Three-Column Parallel Flow Unit

Item	Factor
Flowrate:	
Per column	25 gal/min
Total	50 gal/min
Column cycle	4 h
Exchange capacity per liter of feed	0.0145 eq
Capacity needed per column	$4 \times 60 \times 25 \times 3.79 \times 0.0145 = 330 \text{ eq}$
Resin volume needed:	
Per column	$[330/(2 \text{ eq/L})] \times [1/(3.79)(7.48)] = 5.8 \text{ ft}^3$
With safety factor	$5.8/0.75 = 7.8 \text{ ft}^3$
Regenerant consumption per column per cycle:	
HCl (based on 100%)	45 lb
NaOH (based on 100%)	50 lb
Wash water	390 gal
Cost per cycle ^a	\$15.09
Waste concentration factor	$(6,000 \text{ gal wastewater per cycle})/(400 \text{ gal purge per cycle}) = 15$

^a1980 dollars.

Table 16.

Annual Cost of Ion Exchange Treatment System

Item	Cost
Investment (\$)	23,000
Operating cost (\$/yr):	
Labor, 1/2 h/shift at \$8/h	2,000
Maintenance, 6% of investment	1,400
Regenerant chemicals, 4,000 h at 2 h/cycle	30,180
Total operating cost	33,580
Fixed cost (\$/yr):	
Depreciation	2,300
Taxes and insurance	230
Total fixed cost	2,530
Total annual cost	36,110

Note.—1980 dollars. Operation 4,000 h/yr. Does not include water pretreatment or batch treatment system.

hydroxide ion to form a non-ionized water molecule and no longer competes for exchange sites.

The installed cost of a three-column parallel flow ion exchange system with 7.8 ft³ (220 L) of resin per column, skid-mounted with automated regeneration, is \$23,000 (Figure 20). Table 16 shows the total annual cost for a system operating 4,000 h/yr. Capital and operating costs of wastewater pre-

treatment and batch treatment are not included.

A similar analysis can be performed for a polishing system using performance data from Figure 17 and a flowrate of 50 gal/min (190 L/min). The major difference is in the large volume of solution that can be treated per unit volume of resin. In the direct treatment case, 175 bv could be treated before

resin exhaustion; for the polishing system (Figure 17) breakthrough does not occur until 1,600 bv of wastewater have been treated.

The longer column cycle associated with polishing often eliminates the justification for automated regeneration. If regeneration is manual, a two-column unit, operated in either parallel or series flow with each column sized to process the total flow, would probably be most effective in terms of regeneration frequency and reliability. For automated units, a three-column parallel flow unit, designed to have one column off stream for regeneration, would probably be most effective.

Safety features similar to those used in the direct treatment analysis will be applied to the polishing system. The theoretical capacity will be reduced to 80 percent of the capacity indicated in the test data to compensate for fouling, and the column will be exhausted to only 75 percent of its actual capacity to avoid breakthrough before regeneration. These features will yield a volume-processing capability of 960 bv of wastewater before regeneration.

Regeneration frequency is a function of column size. Table 17 gives regeneration frequencies, costs per regeneration cycle, and annual costs for units in three sizes, each operating 4,000 h/yr. Operating time for each regeneration cycle was assumed at 1 h. Operating costs are approximately the same for all three units, and would therefore favor the smaller unit, which requires the least capital outlay. The chemical cost for a polishing system is significantly lower than that for the direct treatment system (Table 16) because most of the metals are removed during conventional treatment.

Evaluating resin capacity by running a test column to exhaustion (Figure 17), is time consuming, particularly for a polishing application

Table 17.

Annual Cost for Ion Exchange Polishing Systems

Item	Regeneration frequency		
	16 h	24 h	36 h
Column resin volume (ft ³) ^a	6.7	10.0	15.0
Ion exchange unit cost (\$) ^b	15,700	19,000	24,000
Operating costs (\$/yr):			
Labor, at \$8/h ^b	2,000	1,330	890
Maintenance, at 6% of unit cost.....	780	900	1,140
Regeneration chemicals ^c	1,660	1,660	1,660
Total operating cost.....	4,440	3,890	3,690
Fixed costs (\$/yr):			
Depreciation.....	1,570	1,900	2,400
Taxes and insurance.....	160	190	240
Total fixed cost.....	1,730	2,090	2,640
Total annual cost.....	6,170	5,980	6,330

^aFor chelating resin column. 50-gal/min flowrate.

^b1 h labor per regeneration.

^cBased on 120% theoretical resin capacity = 1 eq/L.

Note.—1980 dollars. Systems operating 4,000 h/yr.

where the resin can process a large volume of solution before exhaustion. It is more expedient to pass only sufficient volume through the column until the column effluent reaches equilibrium, then analyze the feed and product for ionic constituents. The exchange per unit of feed solution will thus be determined and, when compared to the resin's theoretical exchange capacity (from manufacturer's literature), can be used to predict the solution volume the resin can process before exhaustion. The safety factors described earlier should be used with this approach.

The foregoing, then, are some of the alternatives and process variables to be considered in evaluating ion exchange systems. Actual testing, decisions regarding system specification, and type of resin should be left to experts in use of the technology. An awareness of the flexibility and power of the ion exchange process for waste treatment applications, however, can aid the metal finisher in obtaining the most effective system for the least total cost.

Chemical Recovery and Recycle Systems

Pollution control legislation has affected industry by increasing the economic penalty associated with inefficient use of raw materials. In the plating industry, for example, loss of raw material in the wastewater can result in costs in three distinct areas:

- Replacement of the material
- Removal of the material from the wastewater before discharge
- Disposal of the solid waste residue

In response to the increased cost of raw materials, plating shops are modifying their processes to reduce their losses. Recent years also have seen the cost-effective application of various separation processes that reclaim plating chemicals from rinse waters, permitting reuse of both the raw material and the water.

Ion exchange, evaporation, reverse osmosis, and electrodialysis have all been used in the plating industry to recover chemicals from rinse solutions. These processes have in common the ability to separate specific compounds from a water solution, yielding a concentrate of those compounds and relatively pure water. The concentrate is recycled to the plating bath and the purified water is reused for rinsing. To determine which separation process is best suited for a particular chemical recovery application, it is usually necessary to evaluate both general and site-specific factors, for example:

- General factors would include rinse water concentration, volume, and corrosivity.
- Among site-specific factors are floor space available, utilities (such as steam, chemical reagents, electricity) available, and degree of concentration needed to recycle the chemicals to the bath.

As a rule, ion exchange systems are suitable for chemical recovery when the rinse water feed has a relatively dilute concentration of

plating chemicals and the degree of concentration needed for recycle is not great. Ion exchange is well suited for processing corrosive solutions. The process has been demonstrated commercially for chemical recovery from acid copper, acid zinc, nickel, cobalt, tin, and chromium plating baths. It has also been used to recover spent acid solutions and for purifying plating solutions to prolong their service life.

Economic Analysis of Recovery Systems

To evaluate the economic benefit of installing ion exchange or other recovery processes, the following determination must be made:

- Quantity and replacement cost of the chemicals and water to be recovered
- Savings in wastewater treatment cost expected to result from recovery unit installation
- Reduction in solid waste and cost of sludge disposal expected to result from recovery unit installation

In evaluating a plating chemical drag-out recovery system, the rinse water volume and chemical concentration must first be measured. This step will establish the quantity of chemicals available for recovery. When the relationships of wastewater volume and metal content to the associated wastewater treatment and sludge disposal cost have been determined, the potential savings can be determined. Table 18 shows the economic penalties for losses of typical plating chemicals.

The high investment cost for installing an automated recovery process limits application of this process to plating operations with high drag-out rates, as illustrated for chromic acid recovery in Figure 22. The analysis assumed an

Table 18.

Economic Penalty for Losses of Plating Chemicals

Chemical	Cost (\$/lb)			
	Replacement	Treatment ^a	Disposal ^b	Total
Nickel:				
As NiSO ₄	0.84	0.31	0.38	1.53
As NiCl ₂	1.14	0.34	0.52	2.00
Zinc cyanide, as Zn(CN)₂:				
Using Cl ₂ for cyanide oxidation.....	1.55	0.80	0.50	2.85
Using NaOCl for cyanide oxidation...	1.55	1.68	0.50	3.73
Chromic acid, as H₂CrO₄:				
Using SO ₂ for chromium reduction...	0.98	0.53	0.64	2.15
Using NaHSO ₃ for chromium reduction.....	0.98	0.76	0.64	2.38
Copper cyanide, as Cu(CN)₂:				
Using Cl ₂ for cyanide oxidation.....	2.05	0.80	0.50	3.35
Using NaOCl for cyanide oxidation...	2.05	1.68	0.50	4.23
Copper sulfate, as CuSO₄.....	0.62	0.31	0.34	1.27

^aAt concentration of 100 mg/L in wastewater.

^b4% solids by weight at \$0.20/gal.

Note.—1980 dollars.

investment cost for the recovery system of \$30,000, with the unit depreciated over 10 years. Typical operating, labor, and maintenance costs for an ion exchange system were used to determine operating costs. Chemical savings were derived from Table 18, which indicated a total saving of \$2.15/lb of H₂CrO₄ recovered (equal to \$2.50/lb of CrO₃). From the foregoing, a reasonable rate of return is achieved for a CrO₃ drag-out rate above 3 lb/h (1.4 kg/h), for which payback equals 2.8 years. Plating operations with rates significantly lower than 3 lb/h (1.4 kg/h) would not be economically justified in installing this recovery system.

Tax credits associated with investments in pollution control hardware were not included in the foregoing analysis. The credits would improve the economy of otherwise marginal investments, but not enough to justify installing an automated recovery system in an operation with low drag-out rates.

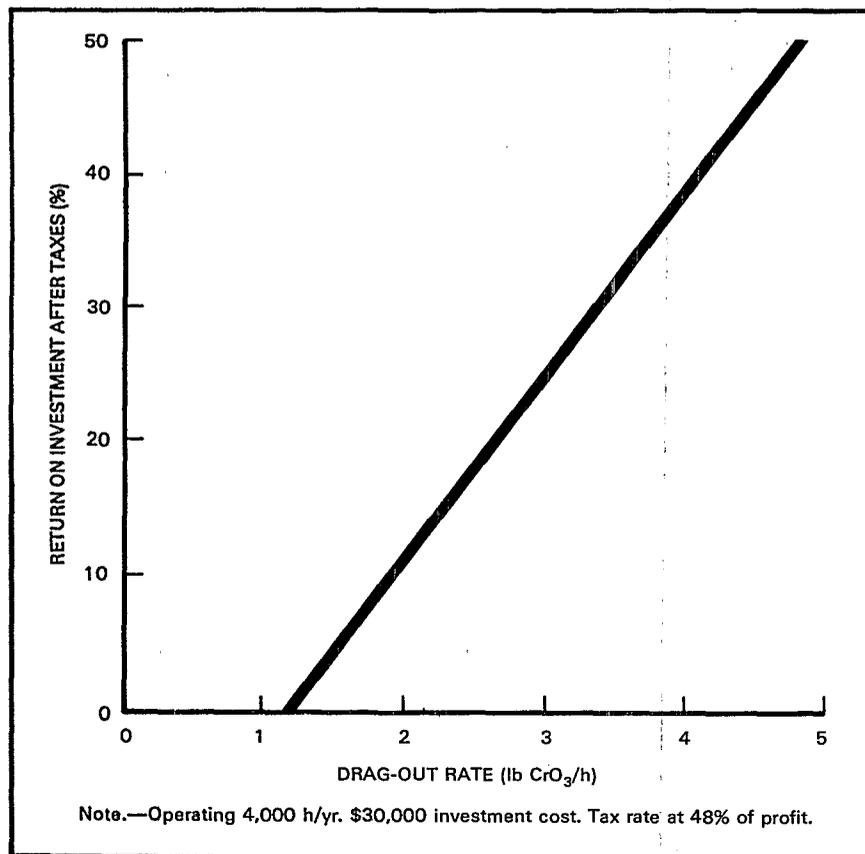


Figure 22.
Return on Investment in Chromic Acid Recovery Unit

Drag-Out Recovery by Ion Exchange

The Reciprocating Flow Ion Exchanger (RFIE) is the kind of ion exchange system most widely used for chemical recovery from plating rinses. This proprietary unit was especially developed for purifying the bleed stream of a large volume solution such as the overflow from a plating rinse tank. It operates on the principle that, for the short period of time the unit goes off stream for regeneration, the buildup of contaminants in the rinse system is negligible.

The RFIE units are more attractive than fixed bed systems for plating chemical recovery because the columns use smaller resin volumes and, therefore, capital costs and space requirements are usually lower. The units incorporate regenerant chemical reuse techniques to reduce operating costs and

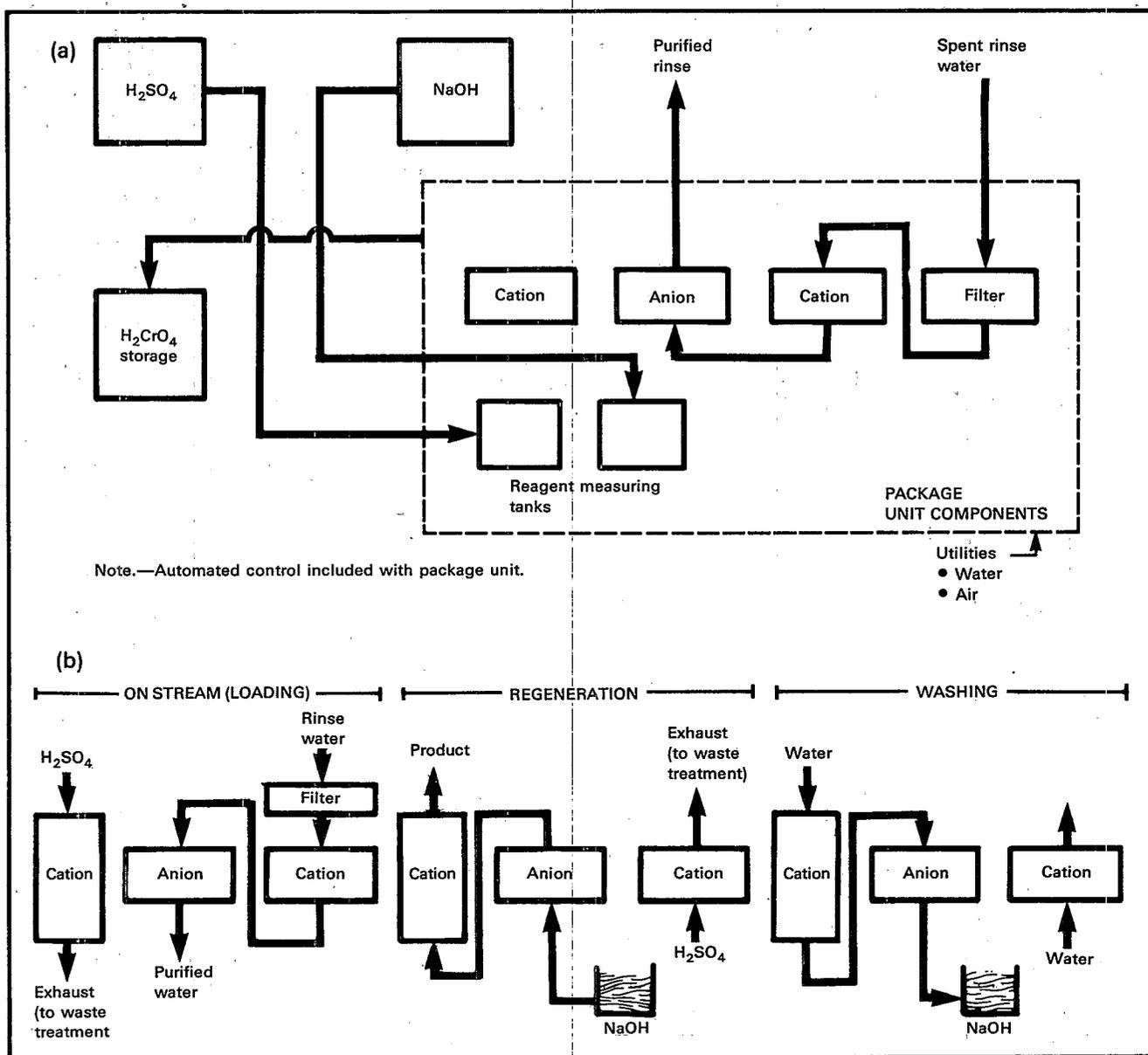


Figure 23.

Chromic Acid Recovery RFIE System: (a) Hardware Components and (b) Operating Cycle

yield higher product concentration for recycle. They are sold as skid-mounted package units, which are automated to minimize operating labor requirements. Two basic units are available for drag-out recovery: one for chromic acid recovery and one for metal salt recovery. Another unit is designed to deionize mixed-metal rinse solutions to

recover only the water and concentrate the metals before treatment.

Chromic Acid. Figure 23 shows the hardware components of an RFIE chromic acid recovery system and necessary auxiliaries and describes the operating cycle. The segregated rinse water after a

chromium plating bath (or baths) is pumped to the ion exchange unit and passes in series through a cartridge filter, a strong acid cation resin bed, and a strong base anion bed. The demineralized water is returned to the rinse system. The RFIE unit regenerates itself automatically based either on a cycle timer or on the conductivity of the treated water. With the conduc-

tivity controller, the conductivity of the treated water is compared with that of the unit feed. When the unit is no longer achieving sufficient conductivity reduction, regeneration is initiated. Regeneration frequency is based on the quantity of chromic acid in the rinse and the unit's resin volume. The unit is off stream for regeneration for approximately 20 min. The chromate ions removed from the rinse are concentrated in the anion resin bed. They are eluted in the form of a sodium chromate solution when this bed is regenerated with sodium hydroxide. The sodium chromate solution is passed through a second strong acid cation resin bed to convert the sodium chromate to chromic acid. The recovered chromic acid solution is stored and used for chemical makeup in the chromium plating bath. The product concentration is approximately 10 percent chromic acid. After the resin beds are washed with water, the unit goes back on stream.

The RFIE units come in several sizes; higher chromic acid loading rates require larger resin bed volume. Ideally, the unit performs two cycles per hour. Each cycle reclaims a certain amount of chromic acid and consumes a set amount of regenerant chemicals. Table 19 shows the chemical savings, reagent cost, and amount of chromium recovered per cycle.

Figure 24a presents the purchase cost of RFIE units for chromic acid recovery as a function of the amount of chromic acid the unit can recover. Including reagent and product storage, piping and utility connections, startup, and shipping expenses, the total installed cost for a system should be approximately 120 percent of the unit cost.

Metal Salts. RFIE units are recovering plating drag-out from nickel, copper, zinc, tin, and cobalt plating rinses. The major area of application is for nickel plating baths. Two basic units are used for metal

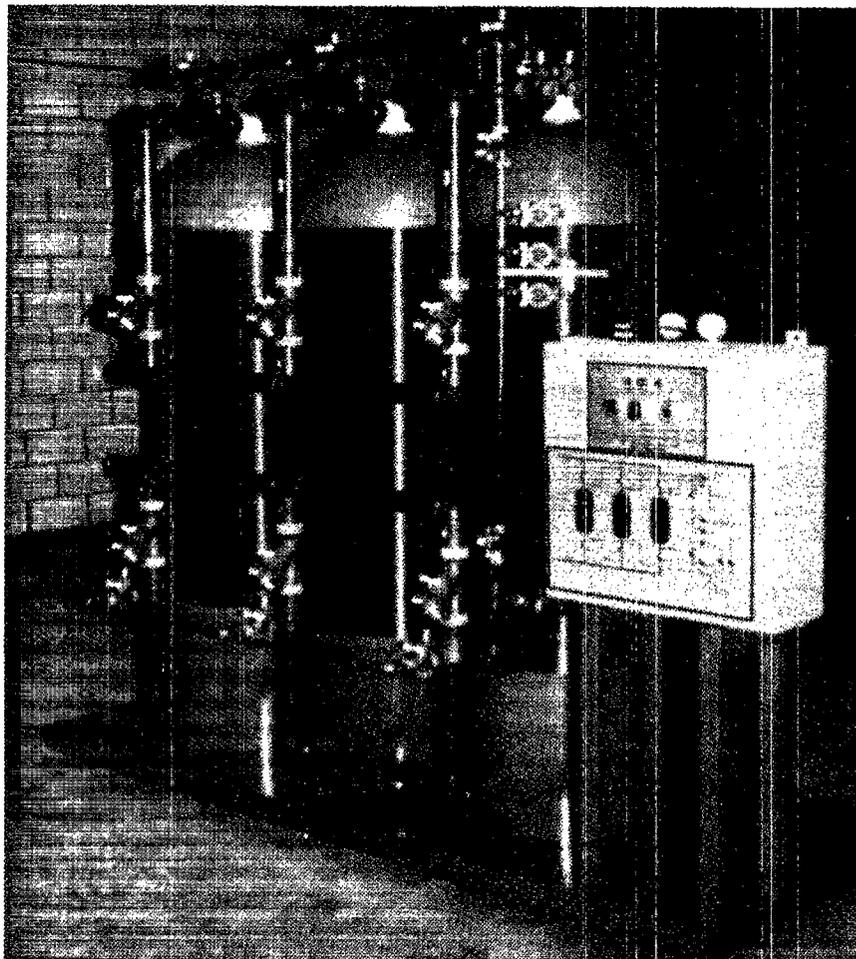
Table 19.

Performance of RFIE Chromic Acid Recovery Unit^a

Item	Value (per cycle)
Regenerant solutions:	
NaOH	3.7 lb
H ₂ SO ₄	12.2 lb
Water	80 gal
Spent rinse	1,200 gal/cycle; 200 ppm CrO ₃
Purified rinse	1,200 gal/cycle
Product, CrO ₃	2 lb each at 10% CrO ₃
Purge to waste treatment	80 gal
Chemical savings (\$):^b	
CrO ₃ , 2 lb at \$2.50/lb	5.00
NaOH at \$0.15/lb	-0.56
H ₂ SO ₄ at \$0.05/lb	-0.61
Total saving per cycle	3.83

^a0.35 ft³ anion resin.

^b1980 dollars.



Three-column parallel-flow ion exchange package unit ready for installation

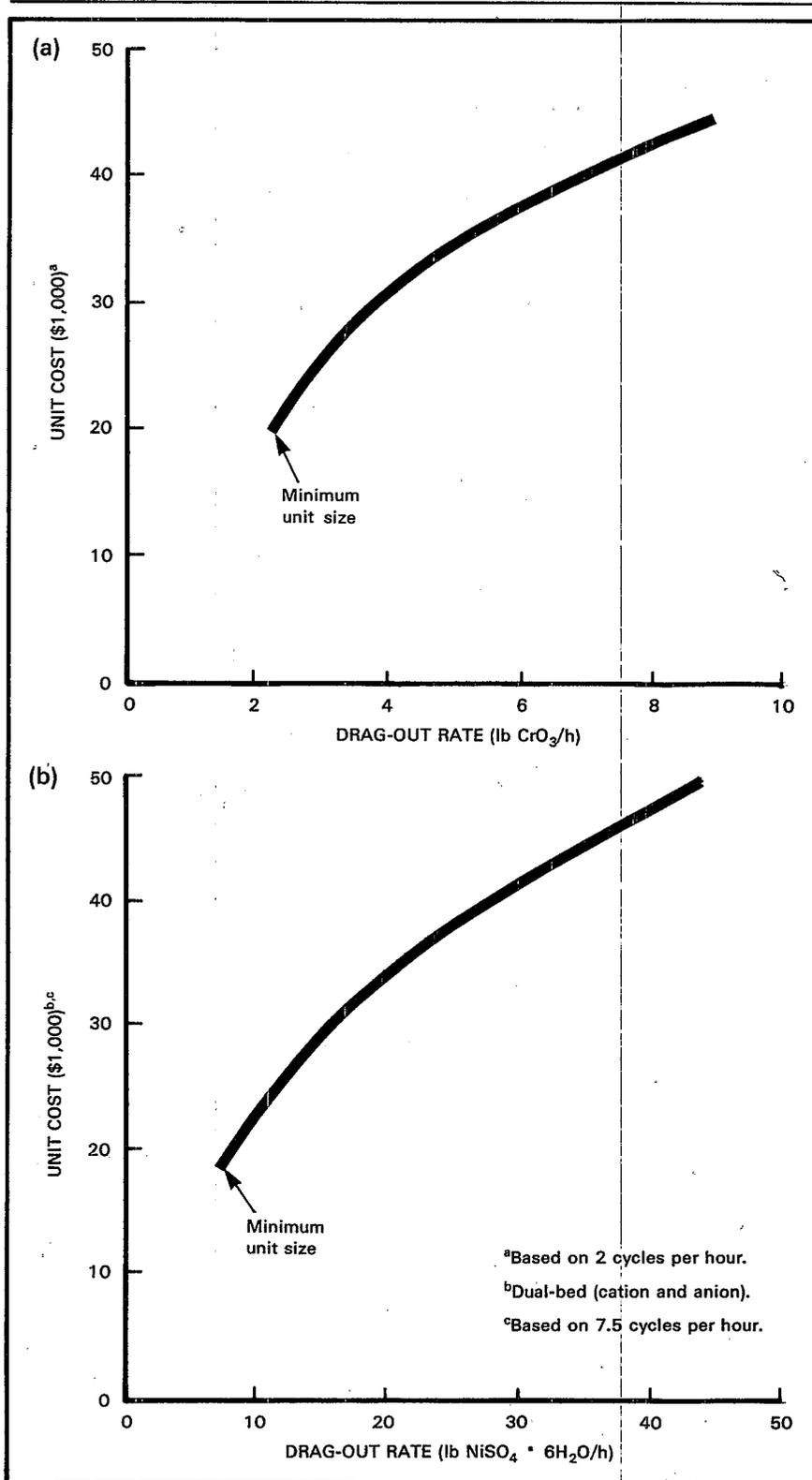


Figure 24.
Equipment Cost of RFIE Units: (a) Chromic Acid Recovery and
(b) Metal Salt Recovery

recovery. One employs a cation bed to reclaim the metal ions and an anion bed to remove the counterions; the deionized water is recycled to the rinse station. For applications where only recovery of the metal is desired, the anion bed is eliminated and the metal-free water is discharged.

Figure 25 presents RFIE system hardware and the necessary auxiliaries for metal salt and rinse water recovery and describes the operating cycle. The segregated rinse water after the plating bath (or baths) is pumped to the ion exchange unit and passed, in series, through a prefilter, a strong acid cation resin bed, and a strong base anion bed. The demineralized water is returned to the rinse system. The metal ions concentrate on the cation resin and are eluted with either sulfuric or hydrochloric acid. The concentrated salt solution (either the metal sulfate or chloride) is stored and used for chemical makeup in the plating bath. The regenerant from the anion bed is sent to waste treatment.

Metal salt recovery units also come in various sizes, with unit size determined by the amount of metal salts in the rinse water. Each cycle will reclaim a set amount of metal salts and consume a set amount of regenerant chemical. Table 20 shows chemical savings, reagent consumption, and the amount of metal recovered per cycle for nickel plating recovery.

The purchase cost for an RFIE metal salt recovery unit is presented in Figure 24b as a function of the amount of metal salts the unit can recover. The price is for a unit with both a cation and an anion bed; the price is approximately one-third less for a unit with a single cation bed. Including the basic RFIE unit, reagent and product storage, piping and utility connections, start-up, and shipping, the total installed

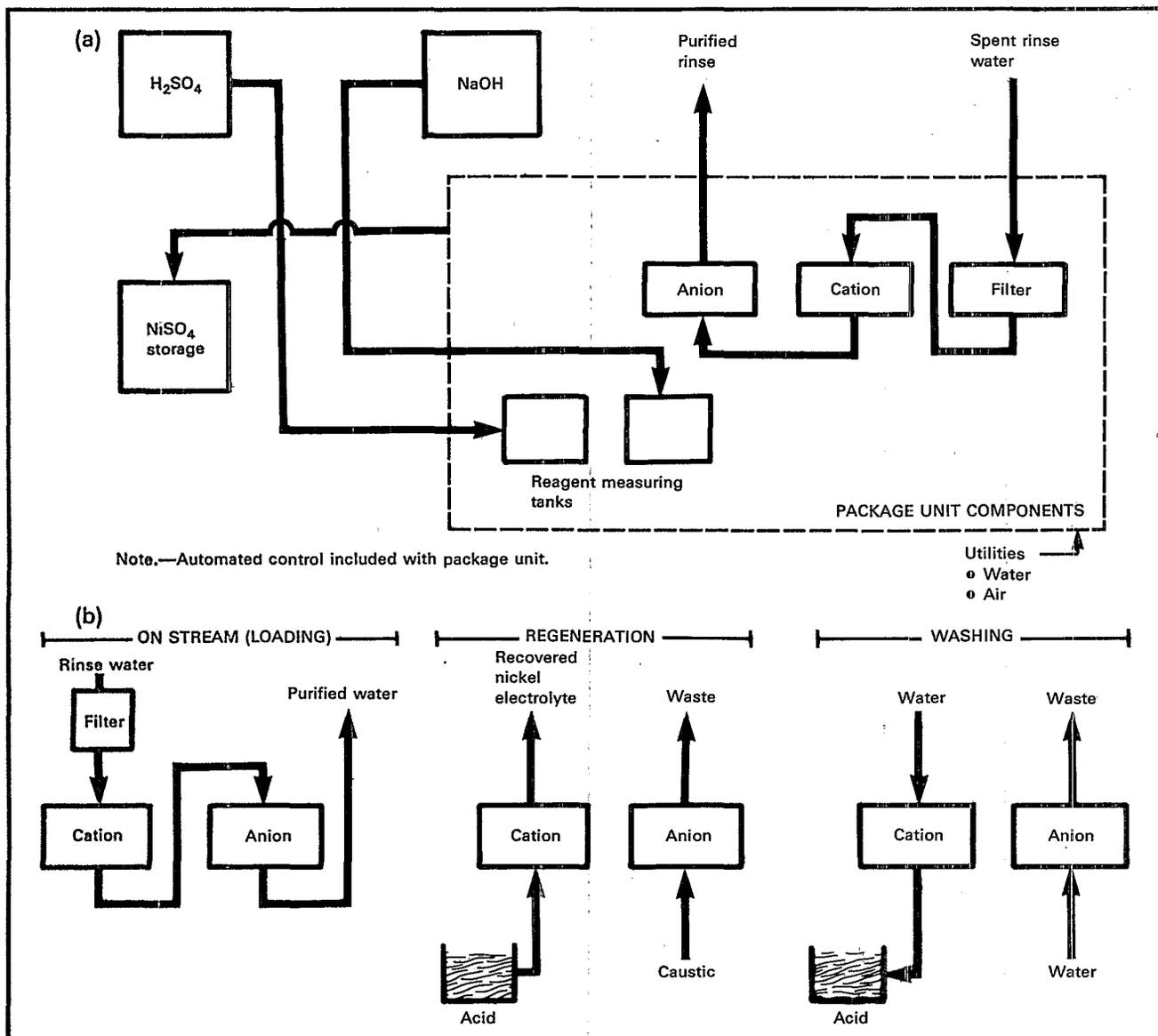


Figure 25. Metal Salt Recovery RFIE System: (a) Hardware Components and (b) Operating Cycle

cost for a recovery system should be 120 percent of the unit cost.

Acid Recovery Systems

Ion exchange is used to purify concentrated acids (such as sulfuric, hydrochloric, and nitric) that have

been contaminated by metal salts. The process, called acid retardation, brings an acid solution in contact with a strong base anion resin. The resin will sorb the strong acid but not the metal salts. The acid can

be desorbed with water. This technique has been commercialized using reciprocating flow methods similar to those described for chemical recovery.

The two process steps are shown in Figure 26. In the on-stream step (upstroke), the metal-

Table 20.

Performance of RFIE Metal Salt Recovery Unit^a

Item	Value (per cycle)
Regenerant solutions:	
NaOH.....	0.63 lb
H ₂ SO ₄	1.2 lb
Water.....	58 gal
Spent rinse.....	250 gal/cycle; 600 ppm NiSO ₄ • 6H ₂ O, 150 ppm NiCl • 6H ₂ O
Purified rinse.....	250 gal/cycle
Product, NiSO ₄ • 6H ₂ O.....	1.7 lb each at 17% NiSO ₄ • 6H ₂ O
Purge to waste treatment.....	58 gal
Chemical savings (\$):^b	
Anhydrous NiSO ₄ , 1 lb at \$1.53/lb.....	1.53
NaOH at \$0.15/lb.....	-0.09
H ₂ SO ₄ at \$0.05/lb.....	-0.06
Total savings per cycle.....	1.38

^a0.35 ft³ cation resin.

^b1980 dollars.

salt-contaminated acid is metered into the bottom of the resin bed. The free acid is sorbed by the resin and the metal salt byproduct solution flows out the top of the bed. In the regeneration step (down-stroke), water elutes the acid from the resin, yielding an acid concentration equal to that of the feed solution and a lower concentration of metal contaminants.

Two applications are seen for this system:

- Purification of strongly acidic process baths
- Recovery of excess acid from cation exchange regenerant solutions

Demonstrated uses of ion exchange acid purification include removing aluminum salts from sulfuric acid anodizing solutions, removing metals from nitric acid rack-stripping solutions, and removing metals from sulfuric and hydrochloric acid pickling solutions. The major area of application is for aluminum anodizing solutions.

Investment in an acid purification system is justified by the savings in purchases of replacement acid and of neutralizing reagents for treating the spent acid. The amount saved depends on the type of acid to be recovered, the volume and concentration of the spent acid discarded yearly, and the cost of treating the spent acid.

Acid purification systems are available in a range of sizes. Size is a function of the volume of acid that can be purified per unit of time; size requirement is determined by the rate at which metal salt accumulates in the acid bath. Table 21 shows the feed, product, and waste stream concentration of a purification system for sulfuric acid

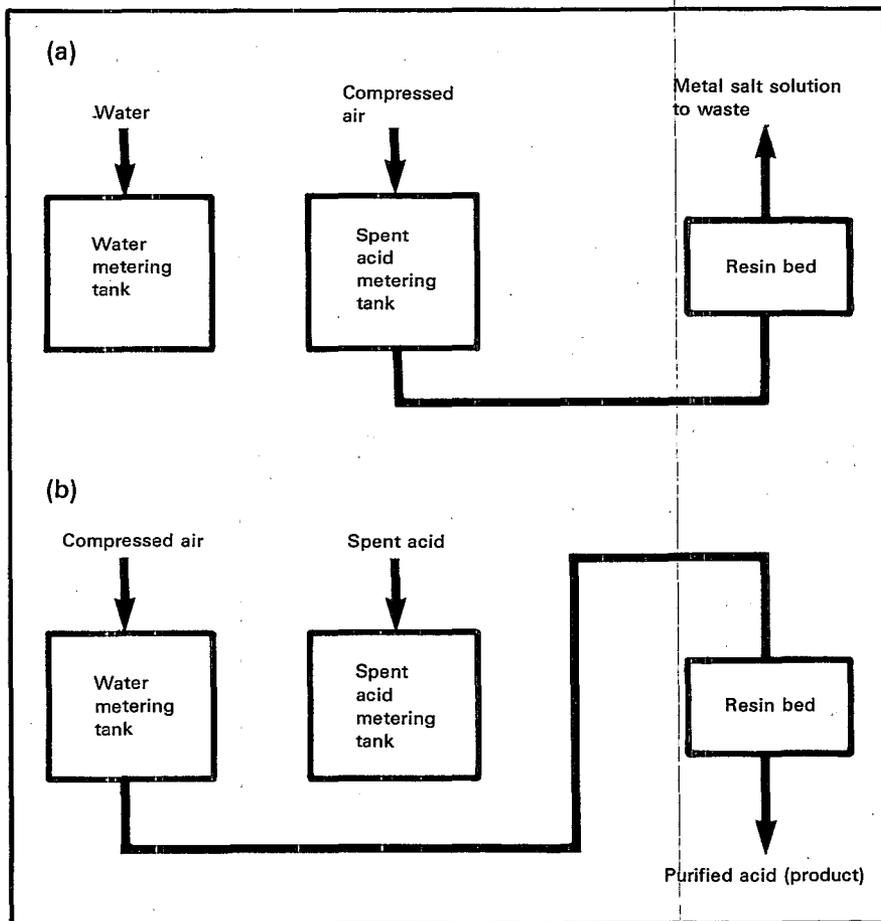


Figure 26.

Acid Recovery System Operation: (a) Upstroke and (b) Downstroke

Table 21.

Performance of Acid Recovery Unit for Purifying Sulfuric Acid Pickling Solution

Item	Performance
Water	7.0 gal/h
Feed, at 11 gal/h:	
H ₂ SO ₄	0.94 lb/gal
Iron.....	1.15 lb/gal
Product, at 10.4 gal/h:	
H ₂ SO ₄	0.94 lb/gal
Iron.....	0.74 lb/gal
Purge, at 7.6 gal/h:	
H ₂ SO ₄	0.07 lb/gal
Iron.....	0.65 lb/gal
Iron removed.....	4.9 lb/h
Acid recovered.....	94%

pickling solution. Based on the quantity of iron in the purge stream, the iron salt removal capacity can be determined from volume processing capacity. Once the rate of iron accumulation in the acid solution has been determined, a purification unit with equal salt removal capacity can be selected to control the buildup.

Table 22.

Cost^a and Iron Removal Capacity of Sulfuric Acid Purification Unit

Item	Unit size (ft ³ anion resin)		
	0.40	2.79	14.12
Unit cost (\$) ^b	10,000	20,000	56,000
Acid feed rate (gal/h).....	11	80	400
Iron removal rate (lb/h) ^c	4.9	35.8	179
Savings (\$/h): ^c			
H ₂ SO ₄ , at \$0.05/lb.....	0.31	2.26	11.32
NaOH, at \$0.08/lb ^d	0.41	3.02	15.09

^a1980 dollars.

^bSkid-mounted package unit, including filter and automated control systems.

^cBased on Table 21.

^dFor neutralization.

Acid purification systems are inexpensive and simple to install. Air supply and water are the only utilities needed. Piping requires only feed, product, and waste stream connections. Table 22 gives approximate costs for units of different sizes, the volume of sulfuric pickling acid they can process, and the value of the recovered acid.

In another, well-established application of ion exchange, metal buildup in dilute acid solutions is controlled by passing the solution through a cation exchanger in the hydrogen form. This approach has been used for hydrochloric and sulfuric acid etching solutions and to remove trivalent chromium and ferrous ions from chromic acid solutions.

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