INTRODUCTION

Since federal legislation has banned the disposal of metal sludges in landfills unless it is stabilized\textsuperscript{1}, electroplaters and metal finishers are seeking alternatives to conventional waste treatment techniques. Primary interest has focused upon waste treatment technologies which reduce the amount of hazardous waste generated and allow metal to be recovered in the elemental form (i.e., metallic sheets or granules) or as purified metal salts. These materials can be recycled into useful products and are therefore not classified as hazardous waste.

Ion exchange (IX) is one technology which provides an opportunity for such metal recovery and recycling. Several articles\textsuperscript{2-8} have been published describing the application of ion-exchange methods for the treatment of electroplating and metal finishing wastes. These reports provide general descriptions of ion-exchange treatment operations, but they do not typically address specific operating procedures and processes which are necessary components of an efficient ion-exchange metal recovery system. The purpose of any wastewater treatment system should be to achieve compliance in the most economical and efficient manner. Therefore, this paper describes, in detail, certain operational criteria and system components which should be part of an efficient and economical ion-exchange system.

SEGREGATION

The first issue to consider when planning the installation of an ion-exchange waste treatment system is waste stream segregation. In any operation there will be certain streams which can be mixed and treated together and other streams which should be isolated and treated individually. Segregation is primarily determined by two important factors:

1. The compatibilities in the chemistry of the various metal bearing waters to be treated.
2. The economic impact of the segregation on capital and operating costs for the ion-exchange and recovery equipment.

As an example, consider a printed circuit board operation where tin/lead and copper wet processes are utilized. One would not choose to commingle acid copper bearing rinses and lead bearing rinses since the precipitation of lead sulfate would foul filters and resin beds, causing resin channeling and poor flow distribution as well as producing a sludge which would require hazardous waste disposal. Figure 1 illustrates the effect of stripping a lead bound ion-exchange column with sulfuric acid. As seen, in the figure, the amount of wastewater which can be treated before the column is "exhausted", steadily decreases with each regeneration. This is a result of lead precipitate filling the column and reducing the amount of available metal binding sites. One alternative often employed is to use an acid in which lead is soluble, like fluoboric acid or methane sulfonic acid. However, these acids are 14-26 times as expensive as sulfuric acid. Therefore, it makes most sense to segregate the lead bearing stream away from the copper bearing stream and use the inexpensive acid (sulfuric)to strip the copper bound columns and only use the more expensive acid (fluoboric and methane sulfonic) to strip the isolated lead bearing resins. This will significantly reduce the operating costs for the system and provide for more efficient operation.
By the same token, one would not choose to mix chelated metal rinses with nonchelated metal rinses since different ion-exchange resins are required to accommodate the two different chemistries. The weak base anion resin and the chelating resin in figure 2 had no success in binding the EDTA based chelated copper solution.

While the chelating resin performs well in nonchelated copper applications, it is misapplied for chelated copper applications since its metal-ion binding structure is almost identical to that of EDTA (figure 3). Such streams should, therefore, be segregated and the most appropriate resin applied to each in order to optimize the metal removal efficiency of the overall system.

**Figure 1**

**Figure 2**

**Figure 3**
In order to take advantage of the benefits associated with segregation of noncompatible waste streams, a new ion-exchange design philosophy is required. In the past, ion-exchange waste treatment systems were simply single or dual train demineralizers which were sized to accommodate the entire commingled waste treatment flow of a given plating or metal finishing operation. Such systems are expensive to operate and produce a mixed metal regenerant concentrate which does not permit direct recovery or recycle of specific metals. A much more appropriate design would incorporate separate ion-exchange columns which are sized to accommodate a specific segregated component of the total waste stream. Each column in such a system can then be operated at maximum efficiency and can produce a directly reusable or recyclable product.

RESIN SELECTION

The central part of a typical ion-exchange metal-recovery system is a column or columns containing ion-exchange resin. The choice of resin is determined by the type of metal being recovered and the chemical composition of the solution to be treated.

Appropriate resin selection is crucial to the efficiency of the metal recovery. Properly matching the ion-exchange resin and the process chemistry will result in efficient operation, quality byproducts and lower operational costs. Inappropriate selection of resin for a particular process chemistry will make it impossible to achieve the required compliance standards and/or significantly raise the cost of operation.

There are now over 100 different types of metal-binding resins available on the market. Some resins are much more efficient than others for particular applications. For example, some resins are more efficient for metal cation removal at low pH, and some resins can selectively adsorb one metal ion in preference to other metal ions. Yet other resins are much more amenable to stripping metal ions from the resin with a chemical medium that allows more efficient recovery of the metallic element or reuse of the metal ion in the plating process.

A good example of proper resin selection being the key to cost effective operation is where a 60/40 tin/lead process rinse requires treatment for metal removal. If the tin is not regulated, it makes most sense to select a resin and treatment protocol which can remove the lead from the water and pass the tin (figure 4). This will allow the resin bed’s capacity to be used for the regulated metal (lead) only. This means that operating dollars are not needlessly spent to bind and strip the unregulated tin. Figure 4 shows the lead being bound to the resin with great efficiency while the tin is not binding, but passing through the resin.

![Tin/Lead Rinse Treatment](image)

**Tin/Lead Rinse Treatment**

Binding the Lead - Passing the Tin  
(9.5% w/w Pb Binding)

**Influent Concentration**  
- 200 ppm Sn  
- 90 ppm Pb

**Bed Volume**

Figure 4
If however, tin was regulated or the reclamation of tin was desirable, one would chose a resin and treatment protocol to remove both the tin and lead from the rinsewater. In figure 5, both the tin and lead are being effectively removed from the tin/lead rinsewater using the same ion-exchange column.

Figure 5

Figure 6 further illustrates that the right resin and treatment protocol can save capital and operating dollars. First, the lead is selectively stripped from the resin, then the column is restriped to remove the tin ions. The individual regenerants can be recycled efficiently without further separation. This approach achieves compliance with tin and lead standards without requiring dual treatment equipment.

Figure 6

Also, some resins have a much higher capacity for metal-ion adsorption than others. Under a given set of conditions, use of the resin with the highest metal-ion capacity will result in lower chemical operating costs since the resin will not require regeneration as often. In addition, concentrations of metal ion recovered from high capacity resins will be higher, thereby allowing more efficient metal recovery.

pH ADJUSTMENT

The operating pH dependence of a specialty ion-exchange resin used to recover acid copper from electroplating rinses is illustrated in figure 7. Quite clearly, proper pH adjustment is critical for most efficient operation. In this instance the treatment protocol which pH adjusts the rinse stream to 4.5 is able to treat 28% more water than that stream which was pH adjusted to 3 and 80% more efficient than the stream which was adjusted to 2. Optimum loading pH's will depend upon the metal to
be recovered, the chemistry of the stream being treated and the nature of the ion-exchange resin. All three issues must be carefully considered when contemplating the application of ion-exchange technology. If operating pH, solution chemistry and ion-exchange resin type are not properly matched, poor efficiency will result.

![Acid Copper Loading at Various pH Levels](image)

**Figure 7**

When an ion-exchange resin reaches metal-ion saturation, the concentration of metal in the column effluent will increase rapidly. This event is called breakthrough. If one is to obtain maximum operating efficiency from an ion-exchange system, regeneration should be started just at the point of column saturation. This, of course, requires some means of determining when the breakthrough point has been reached. Ion-exchange demineralizers have typically used conductivity meters to determine the onset of breakthrough and trigger the regeneration sequence. Conductivity is not, however, an effective means of detecting column breakthrough for metal recovery applications since the metal ion of interest makes such a small contribution to the overall conductivity of the treatment stream. Many waste treatment ion-exchange systems do not, therefore, regenerate at the breakthrough point.

Most systems regenerate based upon 1) elapsed time since the previous regeneration, or 2) the number of gallons treated since the previous regeneration. Since metal loading rates vary from day to day due to changes in production, regeneration is rarely done at the appropriate time, and operating efficiency suffers. What is needed is an on-line metal-ion detector which continuously monitors the concentration of critical metal ions in the column effluent. When metal-ion concentration reaches a specified level, the detector signals an automatic controller, or alerts an operator, and regeneration is begun. A state-of-the-art ion-exchange metal recovery system should incorporate such a detector to initiate the regeneration sequence.

The incorporation of an on-line metal detector into the ion-exchange treatment system also provides the opportunity to install a fail safe device on the system effluent. The detector would monitor the treatment effluent and automatically shut down the system should metal levels exceed allowable limits.

**PRIMARY-SECONDARY COLUMN OPERATION**

Since ion-exchange columns must be regenerated periodically, most ion-exchange systems incorporate a dual column arrangement in which one column is on line while a second column is on standby or undergoing regeneration. The treatment stream passes through either one column or the other, but never through both. This column configuration is illustrated in figure 8. Column 1 removes metal ions from the treatment stream while column 2 is regenerated then placed on standby. When column 1 becomes loaded with metal, the treatment stream is diverted to column 2, and column 1 is regenerated. Under this scenario column switching must take place before breakthrough or metal ions
will escape in the column effluent. Switching before breakthrough is, however, somewhat difficult to accomplish since metal must obviously be present in the column effluent in order to be detected. The net result is either a loss of operating efficiency due to early regeneration or frequent losses of metal ions in the system effluent.

An alternative column arrangement is shown in figure 9. This configuration overcomes the disadvantages associated with traditional dual column systems. During the majority of the operation, the treatment stream passes through first the primary column then the secondary column. Metal-ion concentration between the primary and secondary columns is monitored continuously. When breakthrough occurs, the primary column is taken off-line for regeneration and the treatment stream passes directly into the secondary column. The freshly regenerated former primary column is then returned for service in the secondary position and the former secondary column becomes the new primary column in the series.
This method of operation provides three important advantages over the traditional dual column approach:

1. The waste stream is given double treatment so the final system effluent is extremely low in metal-ion content.
2. The primary column is regenerated only when fully saturated with metal so maximum operating efficiency is obtained.
3. No metal ions escape from the system during primary column breakthrough since the secondary column is processing primary column effluent.

COUNTERFLOW VERSUS COFLOW REGENERATION

The regeneration protocol most frequently used in today's ion-exchange waste treatment systems is called coflow regeneration. Under the coflow scenario, the regenerant stream (usually acid or caustic) is passed through the column in the same direction as the treatment stream. A backwashing step which is usually included in the coflow scheme removes particulates from the resin.

A much more effective regeneration scheme called counterflow regeneration requires passing the regenerant stream through the column in a direction opposite to that of the treatment flow. A designated backwashing step may or may not be included in the counterflow regeneration sequence.

Two important treatment advantages are realized by applying the counterflow technique. The concentration of metal in the treatment effluent (leakage) will be minimized and the volume of water treated before reaching column saturation (breakthrough volume) will be maximized. A comparison of treatment performance between columns regenerated by coflow and counterflow methods is shown in figure 10. Larger amounts of water can be treated and lower effluent metal concentrations are achieved using counterflow regeneration.

Breakthrough Curves for Counterflow and Coflow Ion-exchange Systems

Figure 10

Lower metal leakage from the counterflow column can be explained as a function of the ion-exchange resin - metal-ion binding equilibrium. When the treatment stream containing metal ions comes in contact with the resin, metal ions in solution will bind to the resin according to the reaction shown in equation 1.

\[ R^- + M^+ = RM \]

where \( R^- \) is regenerated ion-exchange resin
\( M^+ \) is metal ion in solution
\( RM \) is metal ion bound to ion-exchange resin
The more highly regenerated the ion-exchange resin (larger R⁻), the further the equilibrium in equation 1 will be shifted toward metal binding and the lower the resulting effluent metal concentration. Lowest metal leakage will therefore be observed when the most highly regenerated resin lies at the exit end of the ion-exchange column. Resin regeneration (assuming acidic regenerant) proceeds according to equation 2.

\[ RM + H^+ = RM + M^+ \]

Resin exposed to more highly concentrated acid (larger H⁺) will be more completely regenerated. The most highly regenerated resin will therefore lie near the point where regenerant acid flows into the column. Under the counterflow regeneration protocol, the most highly regenerated resin will lie at the treatment flow exit so leakage will be minimized. Under the coflow scheme, the most highly regenerated resin lies at the treatment flow entrance and as a result, metal leakage will be higher. It is possible to achieve low leakage values using coflow regeneration. This is done by applying excess acid during the metal stripping steps so that equation 2 is forced further toward completion. Operating costs would, however, be substantially higher since chemical consumption would increase significantly.

An additional advantage realized from counterflow regeneration is increased metal concentration in the spent regenerant solution. Regenerant peaks from the coflow and counterflow regenerations are shown in figure 11. An explanation for this improved regeneration performance is derived from equations 1 and 2. During coflow regeneration, metal ions must be chemically pushed (equation 2) from the most highly metal loaded end of the column through the least loaded portion of the resin bed. As metal ions move into the lesser loaded regions of the column (larger R⁻ in equation 1), there is a tendency for metal to reattach itself to the more lightly loaded resin beads. Some of the stripped metal is in effect rebound before it can leave the bed.

![Regeneration Curves for Counterflow and Coflow Ion-exchange Systems](image)

Figure 11

During counterflow regeneration, the opposite is true. Metal is pushed from the least loaded regions of the column toward the most highly loaded (smaller R⁻ in equation 1) resin beads. Metal ions will then have less of a tendency to reattach and will exit the column at a higher concentration thus providing a more usable and consequently more valuable byproduct.
HYDRAULIC LOADING

Proper hydraulic loading includes three important components: (1) pre-entry solution filter, (2) inlet and backwash outlet and (3) header lateral distributor or collector. To begin, the pre-entry solution filter ensures that precipitates or other particles often present in process solutions are collected before entering the ion-exchange unit. Without a filter the solid particles enter the ion-exchange unit and often create an uneven film on top of the resin bed that acts as a plug. The uneven layer, when not impeding flow completely, creates channeling throughout the resin bed by allowing the process solution to penetrate at different rates through the resin bed. The pre-entry solution filter removes this problem of particle buildup on the resin bed and increases overall resin performance.

The inlet and backwash outlet evenly distributes the filtered process solution into the ion-exchange unit and consequently the resin surface and bed remain undisturbed for maximum efficiency without channeling.

Finally, the header lateral collector or distributor further maintains the stability of the resin bed by evenly collecting the process solution at the bottom of the ion-exchange unit through a lateral system of holes. During counterflow regeneration the outlet serves as an inlet and the header lateral collector becomes a distributor of fluid through the resin bed. Proper hydraulic loading with a pre-entry solution filter, inlet and backwash outlet, and header lateral distributor or collector ensures a stable resin bed and maximizes the efficiency of the ion-exchange unit.

CONCLUSION

Since land ban has been enacted, metal recovery and recycle techniques have become increasingly more attractive as alternatives to conventional waste treatment. Ion exchange is one recovery method which has stimulated considerable interest in recent years.

Ion-exchange treatment systems can provide an efficient, economical, and convenient means of reclaiming metals and other chemicals from plating and metal finishing waste streams. It is important, however, that certain critical design and operational issues be addressed when considering the installation of ion-exchange equipment. These issues include:

1) The segregation of component waste streams to ensure chemical compatibility, correct ion-exchange resin application and maximum recyclability.
2) Appropriate resin selection provides maximum efficiency of metal recovery and quality byproducts.
3) Proper pH adjustment to provide maximum resin loading capacity.
4) The use of an on-line metal detection system to initiate column regeneration and ensure compliance.
5) The incorporation of a primary-secondary column arrangement to ensure clean effluent and allow maximum use of available resin.
6) The application of counterflow regeneration techniques to obtain optimum operating efficiency.
7) Proper hydraulic loading results in a stable resin bed necessary for maximum loading.

Having addressed these issues, one can rest assured that the proper steps have been taken in the process of selecting an ion-exchange metal recovery system which will meet compliance requirements at the lowest possible cost.

References