

Metal Removal and Recovery from Process Solutions Using Short Bed Ion Exchange

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ABSTRACT: Ion exchange has historically proven, in certain applications, to be an effective method for the metal finishers to minimize waste, ensure effluent compliance, provide water recycle, and even produce a concentrate suitable for recycle back to the process bath. One of the more interesting innovations in ion exchange technology over the past few decades has been the Recoflo short bed ion exchange process. Typical applications using this process involve the recovery of nickel salts from rinse water, the removal of contaminants from chromic acid plating solutions, and the removal of Al from anodizing and etching baths.

INTRODUCTION

Metal removal by ion exchange is not one of the common topics of discussion at the International Water Conference, but does have a significant history of industrial application. IX resins have been used for purification and recovery in metal surface finishing operations such as the electroplating of nickel and chrome, steel galvanizing, the pickling of mild and stainless steels, the anodizing, brightening and etching of Al, and recovery of Cu from printed circuit board production.

They have also been used in hydrometallurgical processes in the primary metals industries. Here they have been used to remove Sb, Bi, and Fe from copper refinery electrolytes, Au from CN solutions, the recovery and separation of Ni and Co, and Cu and Zn removal from both sulphate and chloride solutions. Ion exchange resins have also been useful for the removal of toxic heavy metals, such as As, from groundwater.

The solution chemistries and the objectives of the processes in which these resins are used are significantly different from those associated with water demineralization. In many cases metals must be removed selectively from solutions containing the following: very high TDS, strong oxidizing chemicals like chromic or nitric acid, high acid concentrations, and a high temperature.

While SAC and SBA resins are widely used, the challenging environments and the need for selective metal removal often requires the use of more expensive specialty chelating resins. Beyond the functional groups, consideration must also be given to what resin matrix should be used and with what degree of cross-linkage.

Other significant differences relate to overall process considerations and objectives. For example, in some cases temperature reduction is necessary to avoid potentially explosive conditions or rapid resin oxidation. Routinely the metal must be recycled or recovered to other plant processes, thus making the spent regenerant stream the product. This can raise concerns related to concentration, pH and purity of the recovered metal.

This paper discusses the short bed (Recoflo) ion exchange process and its application to metal recovery and separation. Short bed technology addresses many of the limitations of conventional ion exchange technology and is particularly suited to use with expensive chelating resins.

SHORT BED ION EXCHANGE

FEATURES – Short bed ion exchange has been extensively used in the metal finishing industries since the early 1970's (1,2). This technology optimizes the ion exchange process and offers a number of significant advantages over conventional ion exchange. The principal features and benefits of this technology are presented below.

Fine Mesh Resin Resin bead size is typically 20-25% the size of conventional resin. Reducing the size greatly improves the kinetics of the ion exchange process. This allows the use of higher flowrates and reduces the length of the mass transfer zone. This is particularly important for chelating resins, which have very slow exchange kinetics. In fact, the analysis conducted by Price (3) indicates that a macroporous parallel diffusion model is most suited to describing chelating resin kinetics. This

model and the data collected by Price, shown in Figure 1, indicate that the rate of ion exchange, above very low flowrates, is inversely proportional to the square of the particle diameter. Thus, halving the particle size increases the exchange rate by 400%. The higher flowrates such an increase permits significantly reduces the volume of resin required. This is particularly important when using expensive chelating resins.

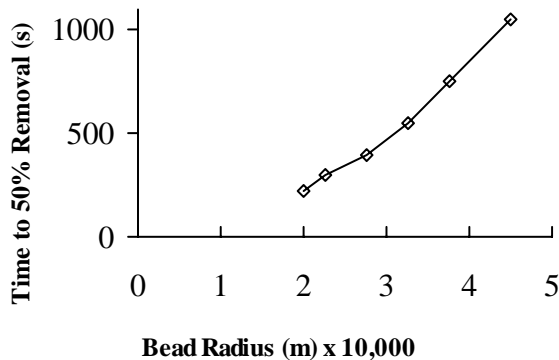


Figure 1 - Effect of Bead Size on Exchange Kinetics for Chelating Resin (3)

Finer particles also aid in fluid displacement. The rinsing process is improved by the higher diffusion rates and the smaller individual interstitial voids associated with finer bead. This helps to sharpen the rinse profile, which more closely approximates a plug flow pattern. Ultimately this results in a reduction in rinse volume requirements.

Short Depth Resin Beds During the operation of a fixed bed process, ion exchange takes place only in the fraction of the bed occupied by the mass transfer zone. Upstream of this zone the resin has been exhausted and is saturated with the exchanged counter ion. Downstream, the resin has not yet been exposed to the ion being removed from solution. Thus, in a conventional ion exchange column, the majority of the resin is effectively inactive. The Recoflo process reduces the depths of these inactive regions and makes more effective use of the remaining resin. It should also be noted that the increased kinetics associated with the smaller bead size reduces the depth of the mass transfer zone. These two changes result in a typical Recoflo column that is only 0.15 m - 0.61 m in depth. As with the higher kinetics this

feature allows a significant reduction in resin volume

Counter-Current Regeneration Counter-current regeneration introduces the regenerant acid in the direction opposite to the feed solution. This technique is a well known chemical engineering principle, which in this case, helps to reduce the amount of regenerant, required, maximizes the concentration of the recovered metal, and ensures high regeneration efficiency so that a minimal level of metal is left on the resin at discharge end of the column.

Fully Packed Bed A short bed column is operated without any freeboard and in fact the resin is slightly compressed. In a conventional column, mixing of the various solutions being processed occurs in the freeboard space. The resulting dilution is very undesirable when processing concentrated solutions. A fully packed bed of compressed resin eliminates this dilution; acts to maintain the concentration profiles developed within the resin bed, ensure uniform flow distribution, and facilitate counter-current regeneration.

While these features offer many benefits the following disadvantages should be noted. Unfiltered feed solutions will quickly foul fine mesh resin and a packed bed does not allow fluidized backwashing of the resin to remove any entrained solids. Thus it is necessary to properly prefilter all solutions fed to a short bed. Also, fine mesh resins are not standard materials and as a result are more expensive on a per unit basis and can be more difficult to obtain.

METAL REMOVAL/RECOVERY APPLICATIONS

CHELATING RESINS

Cu Removal and Recovery The production of printed circuit boards involves the dissolution and plating of copper. As a result numerous copper bearing waste streams are produced. Legislation prevents discharge of copper and given the scarcity of water in the regions where such plants operate water recycle is a common plant objective.

With these objectives in mind the waste streams were segregated into those suitable for water recycle and streams to be treated

and discharged. Often streams in the latter category have TDS levels in excess of 1,000 mg/L. Therefore, to ensure selective Cu removal and discharge to levels less than 1 ppm an iminodiacetate chelating resin is used. Ultimately, the Cu is regenerated from the resin and sent to an electrowinning cell and recovered as a grade A scrap material.

A typical system was installed at the Diceon Electronics plant in Southern California. One of the short bed Cu IX systems is shown in Figure 2. Figure 3 is a photo of the complete system including the electrowinning cell in the foreground.

A 15 – 25 gpm stream containing about 200 mg-Cu/L is passed to a 6 inch high - short bed column with a diameter of 1-foot. The vessel is filled with fine mesh iminodiacetate. The bed height in a conventional column would be 3 feet. Assuming operation at the same hydraulic flowrates this results in an 80% reduction of resin. No doubt flowrates through the conventional column would have to be lower as a result of the slower kinetics associated with the larger bead size. Typical short bed results are shown in Table I. It is important to note that iminodiacetate resins are sensitive to pH and it was necessary to adjust the feed pH to a value greater than 3 to ensure Cu uptake.

Table I

Cu Recovery Printed Circuit Board Plant

| Stream | Flowrate | Cu |
|--------------|---------------|----------------|
| Feed | 15 – 25 gpm | 200 mg/L |
| Effluent | 15 – 25 gpm | 0.1 – 0.3 mg/L |
| Recovered Cu | 0.2 – 0.3 gpm | 15 – 20 g/L |



Figure 2 – Copper removal Ion exchange unit.



Figure 3 – Copper removal overall system layout

Co and Ni Removal and Recovery Short bed systems have been supplied to a specialty metals producer for the recovery of nickel and cobalt from two ammonium sulphate byproduct streams. In order to utilize this ammonium sulphate as feedstock for a fertilizer plant, it was necessary to remove these metals from solution.

The process objectives were to reduce the cobalt and nickel to ammonium sulphate ratio in the barren streams to less than 0.011 mg-Co/g-(NH₄)₂SO₄ and 0.044 mg-Ni/g-(NH₄)₂SO₄. Additionally, the cobalt was to be recovered at a concentration of greater than 25 g/L, to facilitate its recycle to the production process.

In this case, a chelating resin must be used because of the high ammonium salt background and the low levels to which the nickel and cobalt must be reduced. A resin with an iminodiacetate functional group was selected and tests with a short bed pilot plant were conducted to develop the operating conditions.

Given the high concentration of cobalt required in the product stream and the low level required in the barren, a dual bed and dual pass system were both considered. In the dual bed system two beds operate in series. The metals accumulate to a high level on the first bed and the second bed is used to remove the residual metal in order to meet the barren target.

In a dual pass system the feed solution is passed through the column twice. The incoming feed is processed through the column to build up the metal level on the resin. The effluent solution produced during this step is stored in a tank and is processed

through the same column again, immediately after the resin has been regenerated. The effluent from this second pass becomes the barren. A review of the capital costs associated with both approaches indicates that the single bed - dual pass system is preferable. After loading, the resin is counter-currently regenerated with 100 g/L sulphuric acid.

The feed solution was provided at a temperature of 60°C, which greatly improved the kinetics of the exchange process. To ensure adequate uptake the feed pH was adjusted to 7. Typical performance results are shown in Table II.

A short bed column 2.5 feet in diameter, 1 foot in depth with 140 L of resin was required to treat this stream. A photograph of the system is shown in Figure 4. As previously described the same advantage of at least an 80% reduction in resin volume for the short bed technology vs. a conventional system would apply.



Figure 4 – Short bed system.

AL REMOVAL FROM ETCHING SOLUTION –
The production of Al capacitor foil involves electrochemical etching in various acids, such as nitric, sulphuric, and phosphoric. To ensure proper morphology of the Al surface the bath chemistry must be carefully controlled to a uniform concentration. Therefore, the Al that enters the bath solution as a result of etching must be removed. Simply bleeding the solution would control the Al build-up, but would result in the loss of acid, would necessitate waste treatment, and would discharge of nitrate. The main process objectives of an Al removal system would therefore be to prevent Al build-up, to minimize acid lost, and to minimize nitrate discharge.

Meeting these objectives using an ion exchange system presents a number of challenges. For example, high free acid concentrations can limit the uptake of Al, minimizing acid loss requires efficient rinsing, the high selectivity of Al requires a very large excess of regenerant, and large changes in solution concentration and the presence of oxidizing chemicals can rapidly degrade the resin.

The DPU system incorporating short bed technology was developed for this type of Al separation. In this process a short bed of cation resin is coupled with a deacidification short bed. A simplified operating cycle is described below.

1. **Loading** – The etch solution passes through the cation bed removing Al. Approximately 90% of the Al is removed from the feed solution. See Figure 5

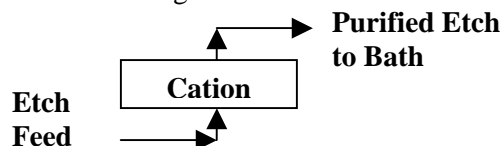


Figure 5 - Loading

Table II
Ni and Co Removal Specialty Metals Plant

| Stream | Relative Volume | Co (g/L) | Ni (g/L) | (NH ₄) ₂ SO ₄ (g/L) | pH |
|-----------------|-----------------|----------|----------|---|--|
| Feed | 34.2 | 1.01 | 0.014 | 208 | pH 7 |
| Recycle | 3.3 | 1.06 | 0.013 | 149.3 | pH <2.4 |
| Barren | 30.9 | 0.0021 | 0.0006 | 216.6 | pH 3.3 |
| Regenerant Void | 1.6 | 0.42 | 0.009 | 127.2 | |
| Product | 1 | 30.25 | 0.345 | 17.4 | 7 g- H ₂ SO ₄ /L |

- Regeneration** – A 14-18% w/w HCl solution is used to counter-currently regenerate the resin. The concentration and volume of the regenerant solution passing through the cation resin result in a 900% increase over the stoichiometric minimum. The majority of this excess acid is recovered by passing the spent regenerant through a de-acidification bed, DAU. This acid removal technology is well proven and has a long history of industrial use (2,4). The net result being a reduction of the stoichiometric excess to 50% or less. See Figure 6.

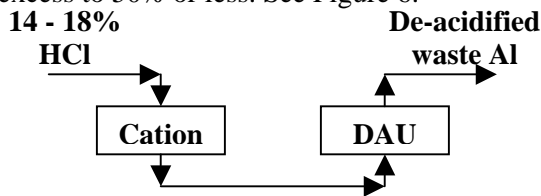


Figure 6 - Regeneration

- Wash** – The HCl recovered by the DAU is removed by washing the resin with water. Concentrated make-up acid is added to the recovered material, which is then used in the next regeneration. See Figure 7.

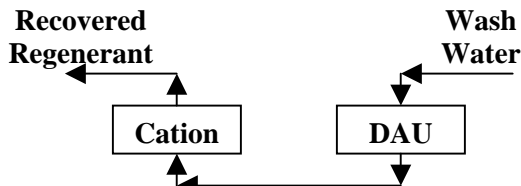


Figure 7 - Wash

Various washing steps have been omitted from this description. Some of the advantages offered by short bed technology include the following: a significant reduction in regenerant consumption through use of the DAU technology and improved rinsing and bead strength through the use of fine mesh resins. A typical unit for this application was installed at a Japanese capacitor foil plant. The total mass of Al removed is 78.5 kg/h with a feed flowrate of 60 gpm. The cation bed used in the DPU was 8 feet in diameter and 1 foot in depth. A photograph of the DPU is shown in Figure 8. Typical DPU performance is shown in Table III.

Table III
Al Removal from Capacitor Foil Etch Solution

| Stream | Relative Flow | Al (g/L) | NO ₃ g/L | H ⁺ (eq/L) |
|---------------|---------------|----------|---------------------|-----------------------|
| Etch Feed | 1.5 | 8.5 | 68.5 | .23 |
| Make-Up HCl | 0.18 | - | - | 10.2 |
| Purified Etch | 1.5 | 0.2 | 59 | - |
| Waste Al | 0.85 | 13.5 | 7 | .44 |



Figure 8 – DPU

NICKEL REMOVAL AND RECOVERY – The DPU system can also be applied within decorative plating operations in order to recover nickel salts from rinse water. With nickel metal prices approaching \$ 13 per pound, it makes good economic sense to recover this material for reuse. When considering nickel recovery, numerous items need to be addressed to ensure that the recycled product from the ion exchange system is of integrity. For a typical Watts semi-bright/bright plating operation, these items can be summarized as;

- Purity concerns - Contaminants that have accumulated in the rinse tanks should be removed before the nickel solution is recycled to the plating baths. If not, these recycled contaminants would buildup in the baths and cause an adverse effect on the plating quality and bath life.
- Brighteners - Brighteners are usually sodium salts of organic compounds and are consumed/degraded in the plating process or lost to dragout. Dragout actually provides an important outlet for these degraded brighteners and sodium. While recycling brighteners might appear to be beneficial, problems such as bath control and increased sodium contamination can occur. Of most importance, however, is the fact that nickel salts recycled to the semi-bright plating baths cannot contain brighteners.

- pH - The pH of the recycled nickel solution needs to be in the correct range to facilitate direct return to the plating bath.
- Composition - As the nickel exists as both a chloride and sulfate salt in the plating baths, it is preferable to recover it in this mixed form.

A typical recovery system consists of the skid mounted nickel recovery unit with both the cation and de-acidification resin beds and all the necessary valves, piping, associated tanks and pumps. The system is integrated into a typical plating process as shown in Figure 9.



Figure 9 - typical nickel recovery process

Rinse water is pumped through cartridge filters and then through the strong acid cation resin bed where the nickel is exchanged for the acid on the resin. The effluent from the onstream step is essentially free of nickel and is to be pH adjusted prior to discharge. Regeneration is accomplished using a mixture of sulfuric and hydrochloric which is pumped into the cation resin bed. Regeneration yields a concentrated nickels sulfate and nickel chloride product which then passes through the de-acidification bed to remove excess acids.

The resulting concentrated, purified (no brighteners), pH adjusted, nickel chloride/nickel sulfate product is stored and added to the bath as required. The excess acid is stripped from the de-acidification bed by water and saved for reuse. Recovering the excess acid this way not only increases the pH of the recovered nickel product but reduces the amount of concentrated makeup acid required.

By ensuring that all the salts recovered can be safely and fully recycled, the reciprocating flow ion exchange system for nickel recovery can reduce related operating costs by over 90% and recover 95% of the nickel that would other wise be lost to the plant waste treatment system. A typical economic evaluation based on a nickel dragout loss of 5 lb/hr is outlined in Table IV.

PURIFICATION OF HARD CHROME PLATING SOLUTION - A layer of chrome is typically electrochemically applied to the surface of a steel substrate in order to provide protection, reduce friction and abrasion effects. A consistent, predictable bath performance is essential to ensure the quality standards needed for the work piece to perform its function.

A major contributor that leads to plating problems in a chrome bath is the buildup of dissolved metallic contamination. Implementing bath purification alleviates this buildup and promotes chrome deposition quality in addition to addressing waste minimization issues.

Table IV
Ni Recovery System – Typical Economic Summary
Basis: 9.5 lb/hr nickel recovery requirement,
7,200 hr/year operation

| Item Recovery | Annual Cost (\$US) | |
|---|--------------------------|--------------------------|
| | No Recovery | Short Bed System |
| Nickel Metal (\$10/lb) | \$684,000 (68,400 lb) | \$36,000 (3,600 lb) |
| 93% H ₂ SO ₄ (\$80/ton 93%) | - | \$5,600 (70 tons) |
| 32% HCl (\$140/ton 32%) | - | \$4,620 (33 tons) |
| RO Water (\$2/1000 gal) | - | \$9,200 (4.6 mil gal) |
| 50% NaOH (\$175/ton 50%) | \$16,625 (95 tons) | \$24,500 (140 tons) |
| 25% Sludge (\$150/ton 25%) | - | \$1,500 (10 tons) |
| Annual Costs | \$700,625 | \$81,420 |
| Annual Savings | | \$619,205 |

As evidenced in examples provided above, the concept of ion exchange must be carefully applied in order to process hard chrome plating solutions. Since resin is a plastic material, it can degrade if left in contact with such an oxidative solution for extended periods of time. Chrome losses must be minimized as much as possible. Also, the concentrated nature of the chromic acid limits the exchange capacity that resin has for metals. The reciprocating flow ion exchange method is uniquely capable to overcome the natural limitations of conventional ion exchange techniques to undertake effective chrome plating bath purification. In particular, the short cycle times associated with this method enables the preservation of the ion exchange resin due to short contact time periods with the

actual chrome bath plating solution. The system incorporating the reciprocating flow ion exchange technique is known as ChromaPur.

One company that undertakes hard chrome plating as part of its operation is the R.R. Donnelley Printing Company performing gravure printing to produce, for example, newspaper inserts. The gravure process consists of printing on a fast moving paper web, up to 3,000 feet/minute, with large engraved cylinders. These printing cylinders are steel rollers of 8 feet in length with a layer of copper plated on it. The desired image must be engraved into the copper so that print areas are below the surface of the cylinder.

A chrome layer is added to the copper layer because copper alone is not able to withstand the friction for the run lengths required (greater than 1,000,000 copies). Chrome plating takes place in a special machine for gravure cylinders. There is no outlet for the metallic contaminants that build up in this plating bath. It is important that these metallic contaminants be controlled to ensure a chrome plate of integrity.

Operation of the ChromaPur unit is such that a portion of the plating solution is transferred to a feed tank to allow cooling to minimize oxidative effects. The solution is then pumped through the short column of fine mesh strong acid cation resin at 60% of its normal bath strength. The resulting purified solution, with up to 90% of the metallic impurities removed in a single pass is collected in a product tank for return back to the plating bath. Extra volume created by the dilution effect is not a problem as natural evaporation losses from the chrome bath itself creates a hydraulic balance. Regeneration is undertaken by using diluted sulfuric acid

Since startup, the unit has operated with little more than routine maintenance involving cartridge filter replacement and normal valve servicing. The resin bed was changed out once in close to three years of operation due, not to the degradative effect of the chromic acid as one might expect, but to an accidental spill of hydraulic oil in the chrome plating solution that found its way to the unit. Savings in bath haulage costs, chrome purchases, and energy costs have been realized in addition to product quality enhancements by ensuring a consistent chrome deposit. See Table V for the typical specifications and Figure 10 for a picture of the ChromaPur.

Table V
Typical Process Specification for ChromaPur

| ChromaPur Stream | Composition (g/L) | | | | |
|------------------|-------------------|-----|--------------------------------|------------------|------|
| | Chromic Acid | | H ₂ SO ₄ | Dissolved Metals | |
| | typical range | | | Low | High |
| Feed | 220 | 270 | - | 5 | 15 |
| Recovered Acid | 130 | 160 | - | 0.6 | 1.8 |
| Waste | <1 | <1 | 20-24 | 2.0 | 2.0 |



Figure 10 – ChromaPur

SUMMARY

Short bed ion exchange is a proven method to recover and separate metals. Through the use of fine mesh resins, short depth fully packed ion exchange columns, and counter-current regeneration, this unique technology allows significant improvements over conventional ion exchange equipment. The ability to process more concentrated feed solutions, the recovery of concentrated metal product streams and the much smaller volume of ion exchange resin are of particular advantage in metal separation applications.

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