Water Recycling and Nickel Recovery Using Ion Exchange

Kenneth Price (Oldsmobile) & Charles Novotny (Industrial)*

In 1972 Oldsmobile installed two ion exchange systems supplied by Industrial Filter & Pump Mfg. Co. The exchange systems were designed to treat nickel rinse water from the bumper plating lines at Plants #1 and #3. The treatment systems were designed to accomplish three purposes: (1) Reduction of nickel metal in the plant effluent discharged to the City of Lansing, (2) Recovery of nickel metal, (3) Recovery of the rinse water itself.

General Process Description

The nickel rinse water from the spray rinse following the final nickel plating step is collected in a sump and pumped to a 10,000 gallon filter supply tank. The transfer pumps operate automatically and are controlled by level controls in the sump tank.

From the filter supply tank, the water is pumped through a filter to remove Dur-Ni solids present in the final plating step before rinsing. A coagulant is added to aid in the filtration.

The filtrate then passes through one of two, three-bed ion exchange trains. The first column is a cation exchanger using Dowex HCR-W strong acid resin. This column removes the nickel and other cations present in the water. The water continues on through a weak base exchanger containing Dow WGR resin and a strong base exchanger containing Dow SBR resin.

This combination of weak base exchange followed by strong base exchange takes advantage of the high capacity and efficiency of weak base resin regeneration to remove most of the anions and the ability of the strong base resin to remove silicates and borates for a final "polish."

The solution emerging from the strong base exchanger is high quality demineralized water. This is stored in a 5000 gallon D. I. water tank and recycled back into the plating process as the nickel spray rinse. Make-up water is added to the storage tank as required. This water is also deionized.

When one train becomes exhausted, the other train is put on stream and the exhausted train is regenerated. The cation column is regenerated with sulfuric acid. A quadruple column is employed to reduce the amount of excess acidity in the spent regenerant.

The anion exchangers are regenerated in series. Fresh sodium hydroxide solution is pumped into the strong base exchanger and then into the weak base exchanger. There is enough free sodium hydroxide left after passing through the strong base column to regenerate the weak base column.

The recovered nickel sulfate solution, at about 5.0 - 5.5 oz/gallon nickel metal, is further concentrated to 10.0 - 11.0 oz/gallon nickel metal using an atmospheric evaporator. The concentrated solution is sold for reprocessing.

During periods of downtime on the plating process - weekends, breakdown, etc. - a level control in the filter supply tank diverts the water from the strong base exchanger back to the filter supply tank. This permits a constant "head" on the filter and prevents potential "souring" of water that would stay in the exchange columns if flow were stopped.

Process Specifications

An ion exchange train is considered exhausted when the water emerging from the strong base exchanger has a resistance of 20,000 ohms @ 60° F. A freshly regenerated train is considered ready for service at the same point.

The resin volumes for the exchange columns are: Plant #3: Cation 100 ft.³, weak base 135 ft.³, and strong base 50 ft.³. At Plant #1: Cation 65 ft.³, weak base 85 ft.³, and strong base 30 ft.³. The size differences between plants are due to the fact that the plating capacity at Plant #1 is less than Plant #3. The rinse rate is also lower at Plant #1.

The cycle time for one three-bed system is approximately 60 hours at each plant. Since each cubic foot of cation resin has an estimated capacity of 2.0 - 2.4 pounds of nickel, each cycle removes 200 - 240 pounds of nickel at Plant #3 and 130 - 155 pounds of nickel at Plant #1.

The cation resin at Plant #3 is regenerated with 500 gallons of 20% sulfuric acid (950 pounds). The anion resins are regenerated with 510 gallons of 10% caustic, (950 pounds of 50% NaOH).

Correspondingly, for Plant #1, the cation resin requires 350 gallons of 20% sulfuric acid (665 pounds); the anion resins use 300 gallons of 10% caustic (550 pounds).

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pounds of 50% NaOH). The table below summarizes these data:

<table>
<thead>
<tr>
<th></th>
<th>Plant #3</th>
<th>Plant #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rinse Flow</td>
<td>100 gpm</td>
<td>60 gpm</td>
</tr>
<tr>
<td>Cation Regenerant</td>
<td>100 ft.</td>
<td>65 ft.</td>
</tr>
<tr>
<td>Weak Base Resin</td>
<td>135 ft.</td>
<td>DOW-WGR</td>
</tr>
<tr>
<td>Strong Base Resin</td>
<td>50 ft.</td>
<td>DOW-SBR</td>
</tr>
<tr>
<td>Cation Regenerant</td>
<td>950 lbs.</td>
<td>HSO4</td>
</tr>
<tr>
<td>Anion Regenerant</td>
<td>950 lbs.</td>
<td>NaOH</td>
</tr>
<tr>
<td>Cycle Time</td>
<td>60 hours</td>
<td>60 hours</td>
</tr>
<tr>
<td>Ni conc. in Feed</td>
<td>40 - 60 PPM</td>
<td>40 - 60 PPM</td>
</tr>
</tbody>
</table>

Regeneration

Regeneration of a train is initiated by the attendant simply by energizing the first step in an automatically sequenced series of regeneration steps. The indexing from one step to another is then controlled by a timer or level control. Each step may be controlled by a manual advance cycle button if an extended time on a given step is desired.

The quadruple use of acid is accomplished by using a series of five tanks. The last tank is the final used acid and the first is the fresh acid.

During regeneration, the thrice used acid is pumped into the exchanger and displaced by twice used acid; the twice used acid is displaced by once used acid; the once used acid by fresh acid; and the fresh acid by water. Thus the solution is displaced down the line of tanks until the final concentrated solution is obtained.

The caustic regenerant is pumped into the strong base exchanger and on into the weak base exchanger. The regenerant is then displaced from the strong base through the weak base with decactionized water and the columns reused in series.

Finally the entire three-bed train is rinsed - usually an hour to one and one half hours - until a water quality of 20,000 ohms is reached.

Problems

The original intent of the recovery system was to recycle the water and reuse the nickel sulfate solution back in the plating tanks.

In order to do this, a number of conditions needed to be met:

1. The pH of the solution to be 3.0 - 3.5. 2. Only minute quantities of contaminating metals could be present. 3. A low level of sodium ion - 2000 ppm or below - had to be achieved.

To adjust the final used acid to an acceptable level, the process was to employ a single weak base exchange column containing DOW-WGR resin.

The solution from the cation regeneration was to be pumped through this column where the excess acidity was to be removed. The weak anion resin was expected to be capable of removing this excess acid without splitting the neutral nickel sulfate salts.

This was never achieved. The metal precipitated in the column causing fouling. Partial regeneration to reduce column capacity was attempted but no improvement was noted. The problem appeared to be due to the fact that although the volume of resin available has the capability of removing the excess acidity from a batch of solution, only a small amount of solution contacts the resin at a given time. The pH of the environment precipitates the nickel that eventually plugs the column and prevents the continued flow of acid solution. The precipitated metal can not be redissolved by incoming low pH solution.

Efforts to utilize ion exchange to adjust the pH of the solution were abandoned and nickel carbonate was used to achieve the desired pH.

A low level of sodium ion was required because the solution was to be added to the semi-bright nickel plating tank. Dragout from one plating tank into the other meant that the first nickel plating step needed the vast majority of nickel salt additions. Sodium ion is known to have a limiting effect on current in semi-bright nickel.

Since the amount of sodium ion in Dur-Ni plating bath is higher in proportion to the nickel metal than is acceptable in semi-bright, immediate regeneration of a cation column after exhaustion would have resulted in excess sodium levels in the recovered solution.

To remove unwanted sodium ion from the cation column, a displacement step was used.

Displacement takes advantage of the fact that although a cation resin will remove all cations from a solution, it will hang on to some much more tightly than others.

When a column becomes exhausted, nearly all the sites on the column are occupied by a cation. If a mixture of cations in solution is allowed to pass through this exhausted column the resin will continue to exchange. The resin will exchange a weakly held cation for a more strongly held cation.

In this case, when nickel rinse water is passed through an exhausted column, the column will exchange a nickel ion in the solution for a sodium ion on the resin. Thus the sodium ion is displaced from the resin into the solution. The sodium laden rinse water is permitted to pass from the cation column into the plant effluent.

The displacement is allowed to continue until enough sodium has been displaced that the regenerant solution is low enough to be used in the plating bath.

The time required to displace sodium was expected to be 30 min. During this period, the nickel rinse water flowed into the cation column and into the plant effluent. Thus, no water was recycled while sodium was being displaced.

It was found that 30 min. did not allow sufficient time to displace sodium. In order to achieve acceptable levels of sodium ion a four to six hour displacement period was required.

This long period of displacement depleted the supply of D.I. water. The original process used soft water at Plant #3 and city water at Plant #1 as make-up. The addition of large amounts of city water at Plant #1 elevated calcium levels in the recovered solution. Calcium salts precipitated in the plating tank on the air
agitation system and eventually forced us to discontinue the reuse of the solution in the plating tanks.

At Plant #3 the soft water make-up added enough sodium ion that the displacement step did not reduce sodium levels enough to allow use of the solution. The long displacement time was due to two factors:

One was that changes in the configuration of the bumpers reduced the nickel concentration in the incoming rinse water by 50 - 60 percent. This meant less metal was available to displace the sodium and displacement time was increased.

The second reason was that the use of city and soft water as make-up introduced additional sodium into the system which also lengthened displacement time. Oldsmobile felt that D. I. water make-up was not necessary even though it was recommended by the equipment manufacturer.

It is now felt that if deionized (or at least decationized) water were used for make-up, the recovered nickel would be reusable directly into the plating tanks. First, there would be few cations present other than nickel and the displacement of sodium step would be much shorter.

Next, the recovery ion exchange system cycles would be lengthened by the reduced load. Overall operating expenses would not be increased by addition of make-up water demineralizers since the mineral content of the make-up is now being removed by the recovery system. In fact, overall economics would be improved.

Summary

Although the ion exchange processes at Oldsmobile did not fully achieve all the objectives hoped for, it still recycles a combined 50 million gallons of water and recovers about 30,000 lbs. of nickel metal annually.

In addition, significant reductions of nickel metal in plant effluent has been observed.

Oldsmobile is also able to rinse following a Dur-Ni plating step with only one rinse tank. In many cases, several rinse steps are used - reclaim, cold water, hot water - to conserve water and reduce nickel dragout.

Using one tank instead of two or three is accomplished because a high volume of water may be employed without wasting water. The metal, in very small concentration, can also be recovered.

This can be an advantage if space requirements are a consideration when a new installation or modification of old equipment is contemplated.

Resin attrition rates indicate that a constant replacement of resin at high expense is not a factor for consideration in this type of ion exchange application.

Periodic checks of the resins show the following losses in total resin capacity per year:

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Loss (%)</th>
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<tbody>
<tr>
<td>Cation Resin</td>
<td>2% - 3%</td>
</tr>
<tr>
<td>Weak Base Resin</td>
<td>Under 1%</td>
</tr>
<tr>
<td>Strong Base Resin</td>
<td>3% - 4%</td>
</tr>
</tbody>
</table>

Normal cleaning of resins is limited to an occasional (once or twice per year) soaking of the resins with warm (140° F.) inhibited hydrochloric acid.

Most waste treatment processes will not be self-supporting. The ion exchange process described is not self supporting since not all of the operating costs are recovered. However, recycling does eliminate much of the cost associated with methods that generate a solid waste that must be disposed.

Recovery and recycling using ion exchange has wide application in the electroplating industry. Its use should be given careful consideration when waste treatment systems are being designed.