Nickel Salt Recovery Using Recoflo® Short Bed Ion Exchange

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Since its commercialization over thirty years ago, the Recoflo® short bed ion exchange process has been extensively utilized for recovery of a wide variety of acids and metal salts. The process has a number of unique features such as utilization of fine mesh resins in a compressed bed, typically 12 – 24 inches in height, which together make it ideal for these types of applications. With current prices in effect for nickel, considerable interest in recovering nickel salts from duplex nickel electroplating operations exists.

This paper outlines the specific aspects for effective nickel salt recovery from rinse water, outlines critical design features, and reviews a specific installation in place at Amory, Mississippi. Field performance data, operating experience, and an economic evaluation will be provided.

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INTRODUCTION

The recent dramatic and unprecedented surge in the price of nickel has prompted electroplaters to seek out methods to recover and recycle nickel dragged out into rinse waters following their plating baths. Particularly for duplex nickel electroplating operations, a number of items need consideration when endeavoring to recover this nickel.

NICKEL RECOVERY CONSIDERATIONS

Key objectives for most electroplaters include the need to get production out on time, to meet or exceed customer expectations, and to keep production costs within budget. The purpose of a recycling strategy is to reduce these production costs. Recycling can, however, lead to troubles with the plating solutions if care is not taken with the design and operation of the system. A number of factors must be considered as outlined below.

i) **Purity** - Contaminants that have accumulated in the rinse tanks should be removed before the nickel solution is recycled to the plating bath. If not, these recycled contaminants would build-up in the bath and cause an adverse effect on the plating quality and bath life.

ii) **Brighteners** - Brighteners are usually sodium-salts of organic compounds and they are consumed/degraded in the plating process or lost to drag out. This actually provides an important outlet for the degraded brighteners and sodium. While recycling brighteners might appear to be beneficial, four problems can be encountered:

- degraded brighteners are recovered, increasing the load on carbon filters,
- some decanting of the tank may be required to control sodium levels,
- brightener control is difficult when a portion of the brightener package is recycled,
- salts recycled to the semi-bright tanks cannot contain brighteners.

iii) **Composition** - The recovered solution should be sufficiently concentrated so that the volume can be returned to the plating tank without the need for additional evaporation equipment. A nickel concentration of 30-40 g/L is usually sufficient. As the nickel exists as both a chloride and sulfate salt in the plating tank, it is preferable to recover it in this mixed form.

iv) **pH** - The pH of the recycled nickel solution needs to be in the correct range to facilitate direct return to the plating bath. Chemically undertaking pH adjustment results in unwanted chemicals being added to the plating baths.

v) **Concentration** - In duplex nickel plating systems, it is common for plated parts to move from the semi-bright tank to the bright tank without an intermediate rinsing step. As the nickel salt contents of the two tanks are similar, the drag out from the semi-bright tank replenishes the salt content in the bright tank. Nickel salts recovered from the rinses after the bright tank must be recycled to the semi-bright tank.

SHORT BED ION EXCHANGE

The short bed ion exchange process has been extensively used in the metal finishing industries since the early 1970's [1,2]. It effectively addresses the above considerations to ensure a system of integrity for the recovery of nickel. This unique 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 Resins

Short bed systems use resin beads with much smaller diameters than conventional ion exchangers. Reducing the size greatly improves the exchange kinetics. This allows operation at higher flowrates and reduces the length of the mass transfer zone. Work by Price (3) indicates that the exchange rate is inversely proportional to the square of the particle diameter. Thus, halving the particle size can effectively increase the exchange rate by 400%. The higher flow rate such an increase permits significantly reduces the volume of resin required. Finer beads also aid in fluid displacement, which allows a reduction in rinse volume requirements.

Short Depth Resin Beds

During the operation of a fixed bed process, exchange takes place only in the fraction of the bed occupied by the mass transfer zone. Upstream, the resin has been exhausted, while downstream, the resin remains in the regenerated form. In a conventional column, the majority of the resin is inactive. The short bed process reduces the depths of these inactive regions and makes more effective use of the remaining resin. The result is that the increased kinetics reduces the depth of the mass transfer zone to 12 – 24 inches.

Counter-Current Regeneration

Counter-current regeneration introduces the regenerant into the resin bed 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 complete regeneration thereby minimizing leakage.

Fully Packed Bed

In the short bed design, the vessel is completely packed with resin leaving no freeboard. 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 packed bed eliminates this dilution and also helps to maintain the concentration profiles developed within the resin bed.

Acid Separation

Short bed technology has been adapted to acid separation and is provided as an acid purification unit, APU™. This process uses ion exchange resins that selectively absorb free acid but reject dissolved metal salts. The absorbed acid can be removed by passing water over resin. While the use of a specific type of ion exchange resin is required, the process is strictly speaking not ion exchange. The acid is not exchanged onto a specific site and the process capacity is not limited by the resins ion exchange capacity.

Typically only a small volume of solution, less than the volume of the ion exchange resin bed can be processed during each cycle. This restriction coupled with the standard engineering design for most ion exchange processes delayed the successful commercialization of the acid retardation process until the late 1970's [4]. Since short bed technology uses a packed column and counter-current regeneration the problems associated with dilution and control faced by conventional designs are overcome.

The combination of ion exchange resin and acid separation resin ensure the effective recovery of nickel in electroplating operations.

NICKEL RECOVERY BY ION EXCHANGE

Nickel can be recovered by cation exchange according to the following equation:

$$Ni^{++} + 2RH \rightarrow 2H^{+} + R_2Ni \qquad (1)$$

'R' represents the cation exchange resin. 'RH' represents freshly regenerated resin in the hydrogen form.

By passing nickel wastewater through a bed of cation resin, it is possible to reduce the metal concentration from several grams per liter to the milligrams per liter range. The dilute acid in the effluent resulting from the exchange can be easily neutralized with alkali in the usual manner.

Upon exhaustion, the resin can be regenerated with acid to produce a concentrated nickel salt solution according to equation [2].

$$R_2Ni + 2H^{+} \rightarrow Ni^{++} + 2RH \qquad (2)$$

Ion exchange resins take up ions with varying preference. Cation resins do not recover anions and organics, but cation resins also show preference for some cations over others. Generally speaking, strong acid cation resins prefer ions with higher valence states. Unlike many other processes such as evaporation, ion exchange therefore has the ability to separate or purify as well as concentrate. For example, one can recover divalent nickel in preference to monovalent sodium and potassium contamination.

It is possible to treat and produce much more concentrated solutions using this technique than with conventional ion exchange systems. However, even with the improvements achieved with the short bed ion exchange technique, the pH of recovered metal salt product is still below plating bath level. Cation exchange by itself, then, is not a viable nickel salt recovery/recycle system.

As mentioned, certain ion exchange resins have the ability to sorb strong acids, while excluding salts of those acids. The acid can then be desorbed from the resin with merely water. This phenomenon has been extensively utilized for purification of acid pickling, etching and anodizing baths[4]. The same principle can be employed to de-acidify recovered metal salt solutions from cation exchange regenerants. The cation exchange and acid sorption beds are coupled in a manner that produces a concentrated de-acidified nickel salt product while recovering some of the residual acid for subsequent regenerations. The acidic nickel sulfate solution produced from regeneration of the cation bed is passed through a bed of acid sorption resin, to remove the excess acid and raise the pH. The acid is desorbed from the exhausted resin bed by washing the resin bed with water. No chemicals are required in the process. A typical nickel recovery system is depicted in Figure 1.

Figure 1 – Nickel Recovery System

The 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.

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 is essentially free of nickel and is to be pH adjusted prior to discharge. Regeneration is accomplished using a mixture of sulfuric and hydrochloric acids, which are pumped into the cation, resin bed. Regeneration yields a concentrated nickel sulfate and nickel chloride product, which then passes through the de-acidification bed to remove excess acids.

The resulting concentrated, purified, 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 also reduces the amount of concentrated makeup acid required.

By ensuring that all the salts recovered can be safely and fully recycled, the 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 drag out loss of 5 lb/hr is as follows.

Table 1 – Nickel Recovery System Economic Summary
Design Basis: 5 lb/hr nickel recovery requirement 6,000 hour per year operation

	Annual Cost ($US)	
Item Recovery System	**No Recovery**	**Recovery***
Nickel Metal	$ 600,000	$ 30,000
($ 20/lb)	(30,000 lb)	(1,500 lb)
93% H_2SO_4	-	$ 2,600
($ 100/ton)		(26 tons)
32% HCl	-	$ 5,760
($ 160/ton)		(36 tons)
DI Water	-	$ 5,500
($ 2/1000 gal)		(2.75 mil gal)
50% NaOH	$ 7,350	$ 8,400
($ 175/ton 50%)	(42 tons)	(48 tons)
25% Sludge	-	$ 1,750
($ 250/ton 25%)		(7 tons)
Maintenance, spare parts, operator time	-	$ 8,500
Annual Costs	**$ 607,350**	**$ 54,010**
Annual Savings	**$ 553,340**	

*Based on Eco-Tec's Recoflo® System

RECOVERED NICKEL PRODUCT INTEGRITY

To demonstrate integrity of system operation, samples of recovered nickel product and semi-bright bath were obtained for evaluation from a long time user of a Recoflo® System. No problems or issues associated with the product quality have ever been reported by this user.

A "sulfur in foil" test was undertaken by the users chemical supplier to determine the impact of the mixture of semi-bright bath and Eco-Tec recovered product. The following results were obtained.

Table 2 –Sulfur in Foil Test Summary

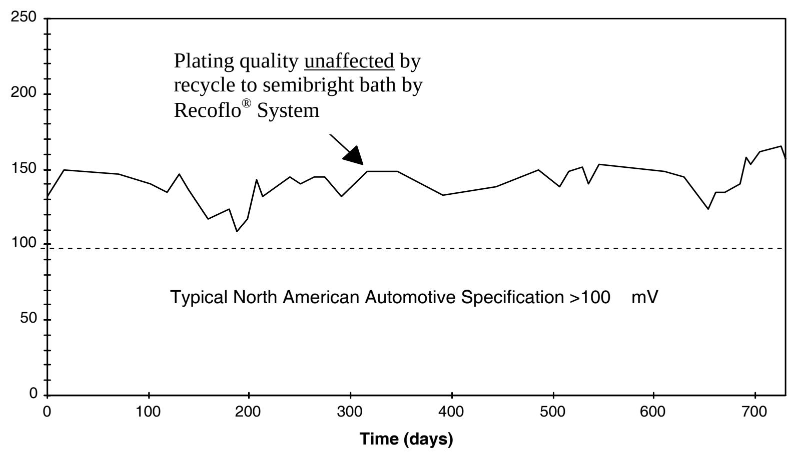
	Semi-Bright Nickel Bath	Recovered Nickel Product
Nickel	60.6 g/L	20.1 g/L
TOC	5170 mg/L	26.8 mg/L
Sulfur in Foil Test		**0.003 % B/W***

* - recovered product solution was concentrated to contain 50 g/L Ni
- 4 parts semi-bright bath solution: 1 part recovered product was prepared

The S.T.E.P. (Simultaneous Thickness and Electrochemical Potential) test, developed by Enthone-EMI, is a widely accepted quality assurance rating for duplex nickel coatings in the automotive industry. Automotive OEMs are mandated to have S.T.E.P. readings of 100 mV or greater on their final plated product.

S.T.E.P. test results were collected on a duplex nickel plating tank from a long time user of this System. As can be seen from the data in Figure 2, the S.T.E.P. results clearly indicate that recycling nickel salts recovered from this System had no adverse effects on the quality of the plated parts.

Figure 2 –S.T.E.P. Test Results



TRUE TEMPER - AMORY, MISSISSIPPI CASE STUDY

True Temper Sports is the leader in golf shaft technology and has been the number one shaft on the PGA Tour for over 70 years. Their mission statement is to be the worldwide innovator and provider of golf club components through the development and marketing of new designs, processes, and materials. All steel shafts bearing the True Temper name are produced at the Amory, Mississippi facility.

Background

An evaluation process was undertaken by plant personnel to incorporate technology new to the plant. A number of components were considered that comprised this process including environmental impact, cost saving measures, and production quality impact. This evaluation process took place in late 2003/early 2004. The project was originally conceived as a supplementary environmental project at that time but cost savings issues rapidly gained precedence as the price of nickel began its rapid ascent.

System Benefits

The system was commissioned in the fall of 2004 so there has now been close to three years of operating experience taken place to assess the initial perceived benefits of the system.

Operating Experience

The system is tied into two plating lines for treatment of the nickel bearing rinse waters. It has been performing at a 95% nickel recovery efficiency on a consistent basis. Close to 61,000 gallons of recovered product volume was returned back to the nickel plating baths in 2006. The nickel product concentration is typically in the 30 – 40 g/L range and pH of 3 – 4. Most of this product is returned to the semi-bright plating baths. A chemical supplier undertakes analyses such as S.T.E.P. and sulfur testing periodically.

One phenomena of note has been some precipitation of iron in the rinse waters feeding the system. There is some iron contamination being generated from the inside of the shaft as plating is undertaken. RO water is used as a feed source to the rinses in order to prevent the system from capturing any tap water contamination. It is believed that the iron precipitates once in contact with this RO water. Some additional bag filtration was put in place to remove these solids.

Environmental

Dramatic reduction in nickel losses to waste treatment has occurred since system installation. Even with this reduction in nickel sludge production, the plant continues to be able to sell off the remaining sludge that is generated.

Production Quality Impact

An important benefit attributed to the system involves the flexibility with which nickel product can be generated. As dictated by the production group, operators of the system will be asked to generate either straight nickel sulfate, straight nickel chloride, or a blend of nickel sulfate/nickel chloride product solution.

Cost Savings

The entire project resulted in a less than one year payback. Virtually no virgin salt additions have to be made to the plating baths. The success of this project is prompting the company to move towards future plans to implement water recycle strategies within their operations.

SUMMARY

Recoflo® short bed ion exchange systems are a proven method to recover and recycle nickel from duplex nickel plating rinse waters. In addition to ensuring consistent, acceptable rinsing, these systems also ensure the recovery of a nickel salt concentrate that is brightener-free, pH balanced, and in the proper sulfate/chloride balance. Implementation of the system has deemed to be a success based not only on cost savings but also environmental improvements and productivity enhancements.

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