Treating Spent Electroless Nickel Baths

Filtration system treats waste EN solutions as well as other plating solutions . . .

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Disposing of effluents containing heavy metals is becoming increasingly difficult. Advances in techniques for measuring contaminant levels have led to wastewater quality standards that are either impossible or too expensive to meet with traditional treatment processes.

The usual industry practice has been to combine waters from all unit processes within a manufacturing facility into one wastewater stream for treatment and discharge to sewer. Though contributing fairly small flows to the final stream, the highly polluted wastes contaminate the relatively clean flows from other process steps and create a high volume of wastewater. Industries that continue this practice will price their products out of the market. Those who exercise water and wastewater management "in-house" will succeed.

Forward thinking industries are looking to cellular manufacturing, where each manufacturing step will be a separate entity with its own water and wastewater treatment. In this way, recovery of both the metals and water can be achieved within the context of one process step.

Current Treatment Practice. Traditional continuous or batch treatment processes rely on a series of steps to convert dissolved heavy metals into solids that can then be separated from the liquor using some type of settling. The liquors are then discharged, and the solids dewatered and hauled off as toxic solid wastes.

These treatment techniques suffer from three problems. First, the size of particles created by chemical additions are too small to separate effectively, even if traditional multimedia filtration is employed downstream. Second, additives in the plating solutions complex the metal ions, making them difficult to precipitate without special treatment. Finally, if the effluent streams containing complexing agents join with other streams, the combined effluent will be difficult to treat.

Principles of Treatment. The principles employed in treating heavy-metal bearing effluents are very simple:

- Segregate each effluent,
- Apply optimum treatment to each effluent,
- Separate solids from liquid,
- Discharge or reuse the liquids,
- Dispose of the solids.

Technologies traditionally used to treat these effluents include batch chemical treaters, continuous chemical treaters (clarifiers), ion-exchange, and concentrators. Regardless of the treatment technology used, dissolved metals will at some stage be converted to sludges.

FILTER ELEMENT shows the module element and cast-end assembly

The metal removal stage of each of the aforementioned technologies relies on gravity settling. Providing the chemistry is correctly performed, the hydraulic loading rate is constant. Most particles can be grown to a size where they can be settled, possibly with the help of polyelectrolytes. However, there will always be smaller particles that will escape, which, if collected in an effluent sample for analysis, will yield a comparatively high metal result.

Furthermore, upsets in particle growth and chemistry may occur because of things such as chemistry errors, surfactants or other materials that interfere with the settling characteristics, or accidental overloads due to unexpected dumps.

Traditional settling systems may need to be replaced by a physical barrier that removes even the finest precipitated particles, without the need to grow them, if stringent effluent discharge standards are to be met consistently. A tubular membrane barrier used to separate particles and effluent has certain advantages over gravity separator systems. Those advantages are:

- It tolerates variations in flow because higher flows create greater back pressures causing compaction of membranes with consequent better quality filtrate.

• It is unaffected by variation in effluent strength, even gross accidental dumps, because the concentration of the recirculating slurry present in a membrane system swamps the effects of shock loadings.

• Rapid chemical mixing provides highly efficient reactions.

Chemical Principles. Chemical treatment of metal plating wastes converts soluble metal ions to insolube metal salts. At the correct pH, each metal has a known minimum solubility, most of which are below those required for acceptable discharge standards.

With hydroxide treatments, the solubility of the metal reduces as the pH is raised, but increases again after the optimum pH for minimum solubility is exceeded, thereby returning metals into solution.

However, where mixed metals occur in solution, different pH values may be needed to effectively remove each. Clearly this is impossible unless multiple-stage treatment is used.

This problem can be overcome using sulfide to precipitate metals. The solubility of the metal sulfide continues to fall through the range of increasing pH, and a single pH can be found where the solubility of all metals is in the desired range.

A combination of hydroxide and sulfide treatments is recommended for all metal waste treatment if the residual concentration of metals in the effluent to be discharged is low (0.10 ppm or below).

Effects of Complexing Agents. Association between metal ions and coordinating ligands is a well know phenomenon. The complexes formed by these substances are often highly soluble, and the ligands inhibit maximum precipitation of metal hydrous oxides in pollution treatment.

The most commonly encountered ligands are shown in Table I together with their relative complexing powers. Table I provides a qualitative idea of the relative strength of the complexing agents. The values given are actually as log K_1, where K_1 is the 1:1 association constant.

Taking EDTA as an example, because it has the highest strength, Table II illustrates the difficulty of removing a heavy metal complexed with this agent.

Table II shows the best values of residual metal concentration after treatment using caustic or lime treatment. It shows that lime is a better

TABLE I—Commonly Encountered Ligands and Complexing Powers

Complexing Agent	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
Ammonia	2.55	4.04	2.72	2.21
EDTA	16.36	18.7	18.52	16.44
Pyrophosphate	-	7.6	5.94	8.7

ELECTROLESS NICKEL treatment systems with reaction and dosing tanks

alkali than caustic soda, and that with EDTA present it is not possible to produce treated effluent having low residual metals concentration using hydroxide precipitation alone.

Furthermore, the presence of these complexing agents also affects the ability of technologies such as ion exchange to remove the desired metal ion. Therefore, treatment to remove or circumvent complexing is needed if the metal ions are to be released sufficiently to permit them to be precipitated to low residual soluble concentrations.

Removing of Complexing Agents

Ammonia is commonly found in plating solutions or effluents from mixed plating operations. This can be handled using either alkaline chlorination to eliminate it or DTC (diethyldithiocarbamate).

DTC removes mixed metals complexed with ammonia. Good results have been achieved from electroless copper and nickel and also in the presence of other complexers.

Pyrophosphate complexers are best handled by lowering the pH to at least 2.0, where hydrolysis will occur. Add ferrous or ferric salts, slowly raise the pH to 4 - 5, where iron pyrophosphate will precipitate, releasing the metal for further precipitation by raising the pH with lime.

Gluconates. Success in releasing metal ions from gluconates and

TABLE II—Difficulty of Removing Heavy Metal Complexed with EDTA (all values are in ppm)

	pH	Ni	Zn	Ni+NaOH		Ni+Ca(OH)$_2$		Zn+NaOH			
				pH 8.5	pH 10.5	pH 8.5	pH 10.5	pH 8.5	pH 10.5	pH 8.2	pH 10.5
Test Solution	3.5	7.4	93.7								
No additive				2.0	3.7	0.8	0.1	0.1	9.8	0.1	0.2
EDTA				2.3	7.2	2.0	0.7	10.8	92.4	5.4	4.8

TABLE III—Results Using Microfiltration Systems on Mixed Metal Solution

Parameter	Sulphide		Hydroxide		DTC*	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Cadmium (Cd)	1.62	0.02	1.58	0.54	1.78	0.02
Chromium (Cr)	1.44	0.08	0.82	0.08	2.46	0.08
Cobalt (Co)	0.18	0.10	0.16	0.10	0.24	0.10
Copper (Cu)	3.9	0.22	3.26	1.98	5.06	0.18
Iron (Fe)	8.58	0.44	4.48	0.46	16	0.66
Lead (Pb)	1.24	0.3	0.68	0.36	1.92	0.24
Manganese (Mn)	1.66	0.53	1.26	0.10	2.4	0.6
Nickel (Ni)	3.56	1.86	2.66	1.54	4.88	1.46
Zinc (Zn)	14.18	0.57	7.36	0.47	23.2	0.78
pH	8.8	9.1	8.8	11.5	8.2	8.9

**DTC = diethyldithiocarbamate*

TABLE IV—Removal of Heavy Metals Complexed with EDTA Using Microfiltration

	Hydroxide			Sulfide		
	Ni	Zn	TDS	Ni	Zn	TDS
Feed (ppm)	5,800	25	250,000	5,800	25	250,000
Treated effluent (ppm)	0.45	ND	15,500	0.09	0.02	15,500
Sludge Yield (g/1)			180			180

ND= *non-detectable*

heptonates is possible by taking advantage of the fact that sequestering ability reduces as pH falls. Lowering the pH to about 2, adding iron salts and stirring for 20 min prior to rapidly raising the pH to 9 - 10 causes metal hydroxides to precipitate faster than the complexation can be reestablished.

EDTA is the most difficult of all complexing agents to remove. Success has been achieved in electroless nickel solutions by lowering the pH to less than 2, precipitating the EDTA and filtering it off, prior to raising the pH and precipitating the metals.

Other approaches are available using reagents such as sodium borohydride, but these are expensive and still do not produce an effluent with very low residual metal concentrations.

Once the metals are precipitated, particle size may be so small that their removal using clarifiers is either uneconomical or impossible.

Treatment of Mixed Metal Solutions Employing Microfiltration. When the solutions for treatment contain mixed metals, it is very hard to obtain good results. A membrane separation process can be used for the separation. One microfiltration system features non-destructible membranes made of flexible fabric that is readily cleanable. These membranes not damaged by any chemical encountered in the plating industry and systems are fully automated.

Table III shows the results on a mixed metal solution at a commercial waste disposal facility with the pH set for optimizing the discharge of all metals to a municipal sewer. The table shows that, with the exception of nickel, all metals have been reduced to values below 1.0 ppm. The nickel would have been reduced to these limits if the pH had been 9.4. However, all metals were well below discharge standards with the sulfide and DTC treatments.

Treatment of Waste Electroless Nickel. Waste electroless nickel solution uses EDTA as the complexing agent. Many tests were made before deciding on the correct procedure.

The pH of the raw solution was 4.8 and it was lowered to 1.5 using spent acid. This allowed the EDTA to free the metal ion. The EDTA was then precipitated and filtered off using the Exxflow microfilter. The pH of the resulting EDTA-free solution was steadily raised and the solids of precipitation were removed at each pH step to avoid redissolving.

Although a large amount of sludge is generated during the treatment, the metals are removed to low residuals, and the TDS (total dissolved solids) of the solution was reduced from 250,000 to about 15,500 ppm.

The high generation of sludge is due to the removal of the TDS. Reduction in the TDS is of great advantage where the effluents will mix for discharge to the sewer.

Electrowinning was also tested in conjuction with microfiltration. This is attractive for small batches, about 200 gpd, but the cells become costly for larger batches. The big advantage of the cell is that a proportion of the sludge is returned as nickel metal and not as a sulfide or hydroxide.

One cell reduced the waste nickel from 5,300 to 200 ppm in 24 hrs at a current density of 10.2 asf.

The use of a microfilter to separate the products of chemical precipitation of metals from plating solutions is an effective way to ensure that the quality of effluents discharged always meets the standards. **PF**

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