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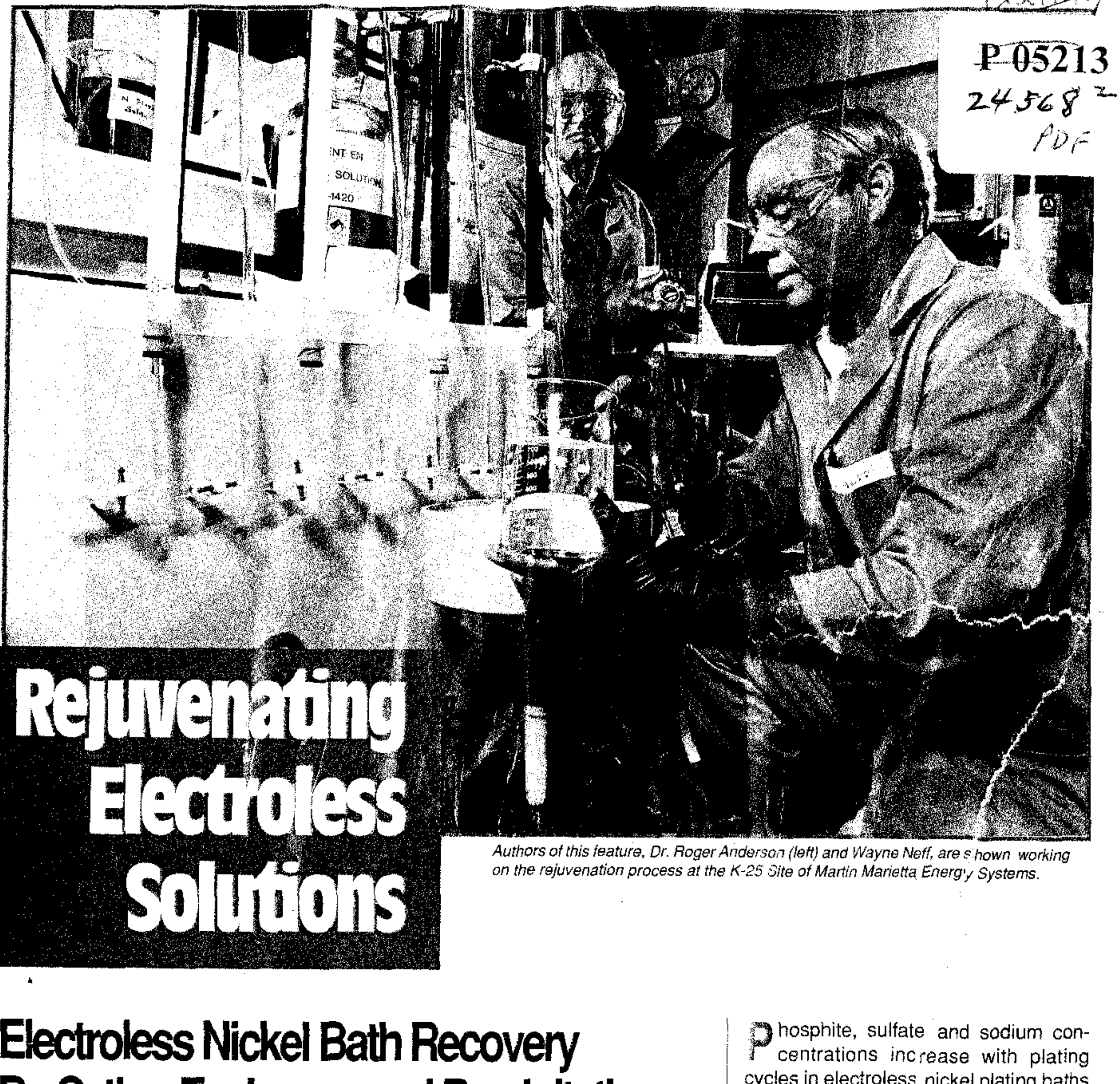

Rejuvenating Electroless Solutions

Authors of this feature, Dr. Roger Anderson (left) and Wayne Neff, are shown working on the rejuvenation process at the K-25 Site of Martin Marietta Energy Systems.

Electroless Nickel Bath Recovery By Cation Exchange and Precipitation

By R.W. Anderson and W.A. Neff

An energy-efficient process* for the rejuvenation and recycling of chemicals used in electroless nickel plating has been developed. The process eliminates the discharge of hazardous wastes normally associated with electroless plating, and it will improve plating quality and speed while significantly reducing costs. Undesirable by-products are removed from the plating process in forms that are environmentally safe so that they can be used as fertilizers or disposed of in sanitary landfills. In addition, the process recovers the nickel and other valuable chemicals from the plating solution and recycles them. It is estimated that hazardous wastes currently generated from the electroless nickel plating industry is more than 20,000 tons/year in the U.S. alone. This new process is claimed to have the capability of reducing the total amount of waste to less than 10 percent of the current tonnage.

Phosphite, sulfate and sodium concentrations increase with plating cycles in electroless nickel plating baths with feeds of sodium hypophosphite, nickel sulfate and sodium hydroxide† used to maintain target hypophosphite, nickel and pH conditions. As a consequence, plating rates decrease and plated parts rejection may increase to reduce the production capacity of the plating bath. Eventually baths must be replaced either by fresh solutions, or by phosphites, and eventually accumulated sodium and sulfate must be removed to restore plating capacity.

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* ENVIRO-CP, developed by Martin Marietta Energy Systems, Inc., Oak Ridge, TN

† Inhibitor and anti-pit wetting agent concentrations must also be maintained within target levels.

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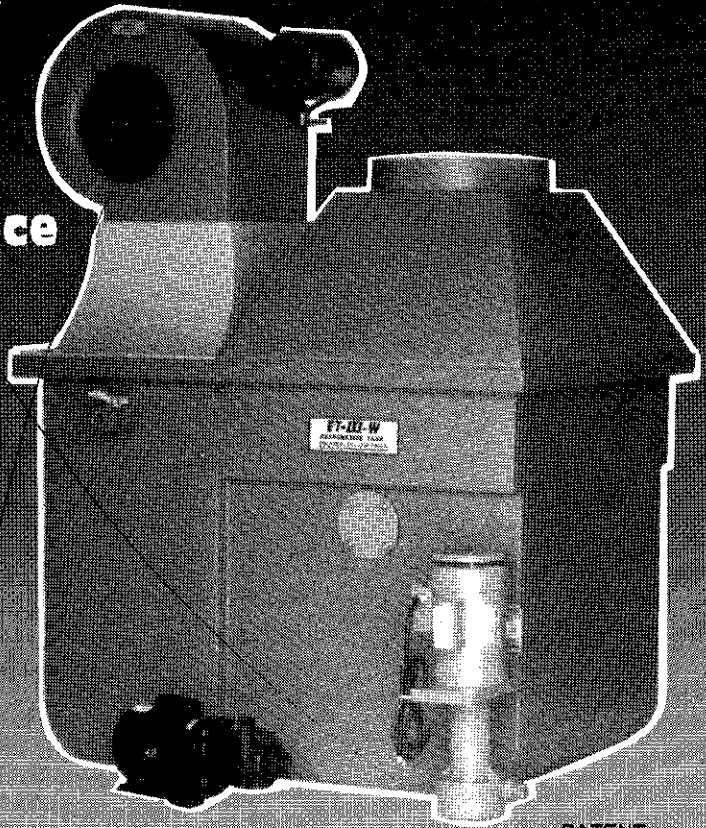

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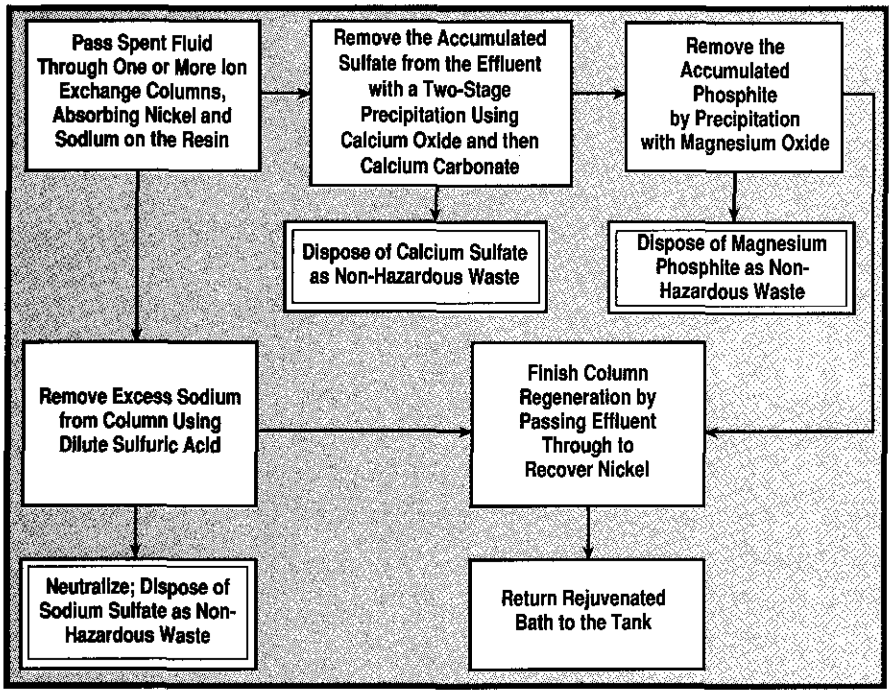


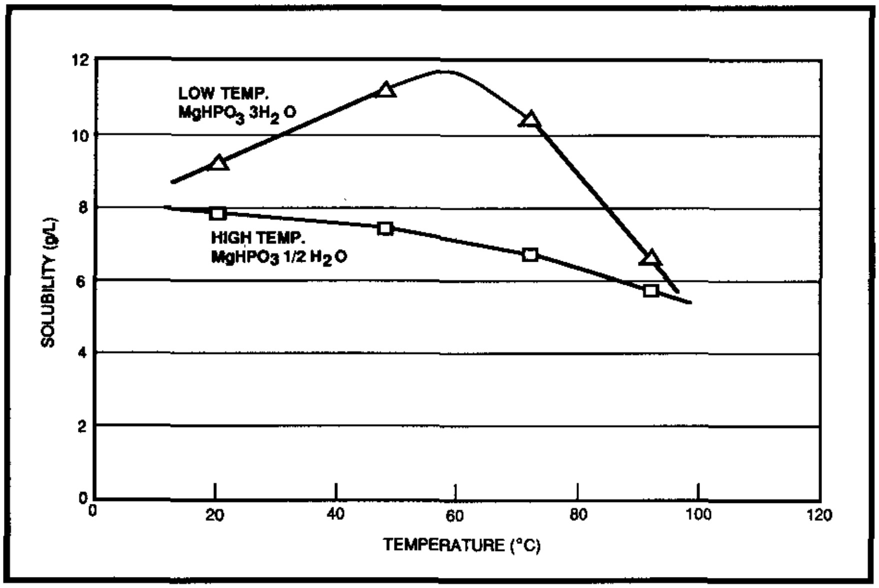
Summary of the electroless nickel recovery process.

Phosphite is generated during the plating process by the catalytic surface reactions:[1]

$$\mathrm{Ni^{+2}} + \underset{\text{(hypophosphite)}}{2\mathrm{PH_2O_2^-}} + 2\mathrm{H_2O} \rightarrow \mathrm{Ni^0}\downarrow + \underset{\text{(dihydrogen phosphite)}}{2\mathrm{H_2PO_3^-}} + 2\mathrm{H^+} + \mathrm{H_2}\uparrow. \tag{1}$$

$$2\mathrm{H^+} + 3\mathrm{PH_2O_2^-} \rightarrow 2\mathrm{P^0}\downarrow + \mathrm{H_2PO_3^-} + 3\mathrm{H_2O}. \tag{2}$$

When the P to Ni atom ratio in the plate is 0.18, reaction #1 predominates and the ratio of phosphite produced per hypophosphite consumed is about 0.92, and base addition is required to maintain pH. At K-25, plating rates fall to about half of the rates for fresh solutions by the time phosphite concentrations reach 1.2 mL.



Solubility of magnesium phosphite salts.

Studies to rejuvenate or extend the life of electroless nickel plating baths were initiated at K-25 because of costs associated with loss of expensive sodium hypophosphite and nickel sulfate reagents, and especially because of environmental, regulatory and health concerns. The proposed National Pollutant Discharge Elimination System (NPDES) limit for outfall from the present plating bath treatment facility is 0.1 mg Ni/L daily maximum. This level cannot be achieved by treatment of waste plating solutions using simple lime precipitation. Also, sludge produced by lime precipitation of electroless nickel bath solutions is hazardous and should probably be handled as carcinogenic if the nickel content exceeds 1000 ppm.

Phosphite Precipitation

Initial efforts to decrease phosphite levels without precipitating nickel by magnesium oxide additions achieved only minimal reductions of phosphite. Analyses of phosphites precipitated by addition of magnesium oxide revealed that at temperatures less than about 60°C, a crystalline magnesium phosphite trihydrate formed ($\mathrm{MgHPO_3 \bullet 3H_2O}$), for which solubility decreased with a reduction in temperature, whereas an easily filtered, less bulky, magnesium phosphite with about 0.5 waters of hydration ($\mathrm{MgHPO_3 \bullet 0.5\ H_2O}$) was produced at plating bath temperatures.

The chart (below, left) shows the variation with temperature of the amounts of these low- and high-temperature solids that dissolved in water. Additional studies showed that effective removal of phosphite requires replacement of sodium ions by hydrogen ions, followed by lime treatment to remove sulfate and hydrogen ions, so that higher concentrations of uncomplexed magnesium can be achieved.

Treatment of Spent Baths

A typical K-25 spent electroless nickel plating bath has a pH of 4.4 to 4.7 and contains:

- 0.210 to 0.300 m/L hypophosphite
- 0.1 to 1.0 m/L total phosphite (mostly $\mathrm{H_2PO_3^-}$)
- 0.065 to 0.095 m/L $\mathrm{Ni^{++}}$
- 0.25 to 0.65 m/L total lactate ($\mathrm{CH_3CHOHCO_2^-}$)
- 0.1 to 1.0 ppm $\mathrm{Pb^{++}}$ as lead nitrate
- alkyl sulfate anti-pit, wetting agent to achieve an air-solution interfacial tension at 25°C of 45 to 58 dynes/cm
- 0.4 to 1.5 m/L sulfate
- 2.0 to 4.6 m/L sodium ion.

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INMETCO serves platers and surface finishers by recycling nickel and chrome bearing wastes.

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INMETCO operates the only secondary submerged arc smelting furnace in North America dedicated to the high temperature metal recovery of nickel, chromium and iron. The first step of the INMETCO process involves feed preparation. In this step, nickel, chromium and iron bearing solid wastes are fed via a screw conveyor to a pelletizing disk using either water or liquid wastes such as spent chromic acid or nickel stripper solution. Pellets are transferred to a rotary hearth furnace operating at 2300° F for the reduction of oxidized metal species to the metallic form. Reduced pellets are fed to a submerged arc furnace where they are smelted for the extraction of their metal components. The molten metal is cast into "pigs" weighing aproximately 30 pounds which are used in the production of stainless steel.

Steps in the INMETCO Process

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- Reduction
- Smelting
- Casting

Recycling liquid wastes through the INMETCO process eliminates landfill liability.

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Recycling liquid wastes through the INMETCO process eliminates landfill liability and, at the same time, it allows platers and surface finishers to achieve their goals aimed at waste minimization and pollution prevention.

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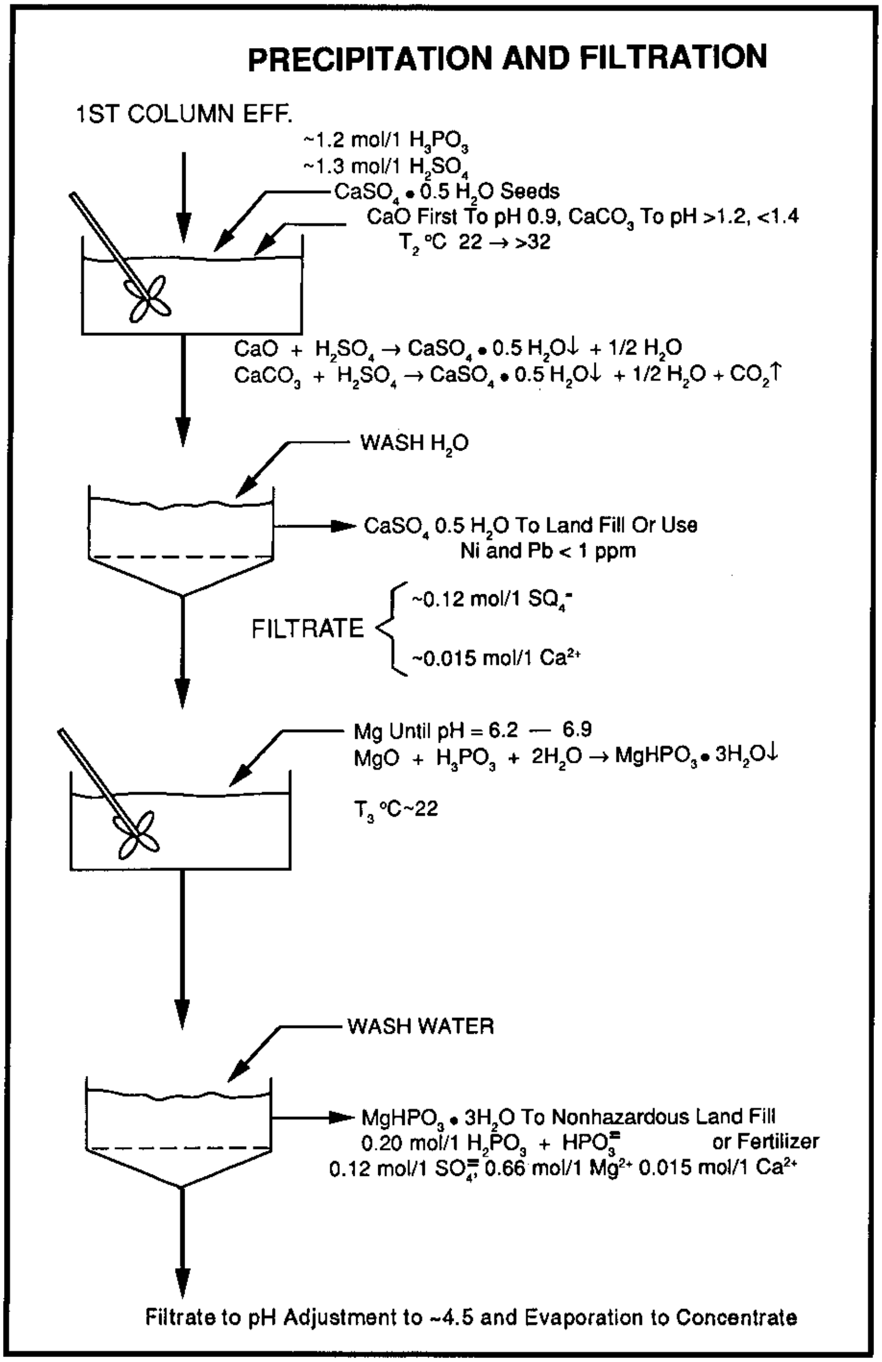


Schematic of the precipitation and filtration process.

Steps for Obtaining Rejuvenated Plating Solution

1. Spent solution at room temperature is passed down through a bed of strong acid cation exchanger in hydrogen form. A 4-in. inside diameter glass pipe containing 9L of 8 percent divinylbenzene cross-linked polystyrene resin with sulfonic acid exchange groups having a sodium ion exchange capacity of 2.068 gram equivalents (geq)/L of resin in H^+ form was used. The volume of solution used contains an amount of sodium plus nickel ion geq corresponding to about 70 percent of the resin exchange capacity. Sodium and nickel ions are sorbed by exchange with hydrogen ions, which are released to the solution.

2. Hypophosphorus, phosphorus, lactic and sulfuric acids, wetting agent, and complexed lead are eluted from the column with slightly more than one bed volume of distilled water.

3. The acid effluent is then treated with calcium oxide until the pH begins to increase (pH ~0.9). As calcium oxide is added, the temperature rises and calcium sulfate hemihydrate is precipitated. Addition of some previously precipitated $CaSO_4 \bullet 0.5\ H_2O$ as seed crystals results in a readily filtered precipitate. The final stage of calcium sulfate precipitation is accomplished with calcium carbonate as reagent to avoid a pH overshoot. When the pH is between 1.2 to 1.4, the calcium sulfate hemihydrate is removed by filtration and the cake is washed with enough water to displace mother liquor.

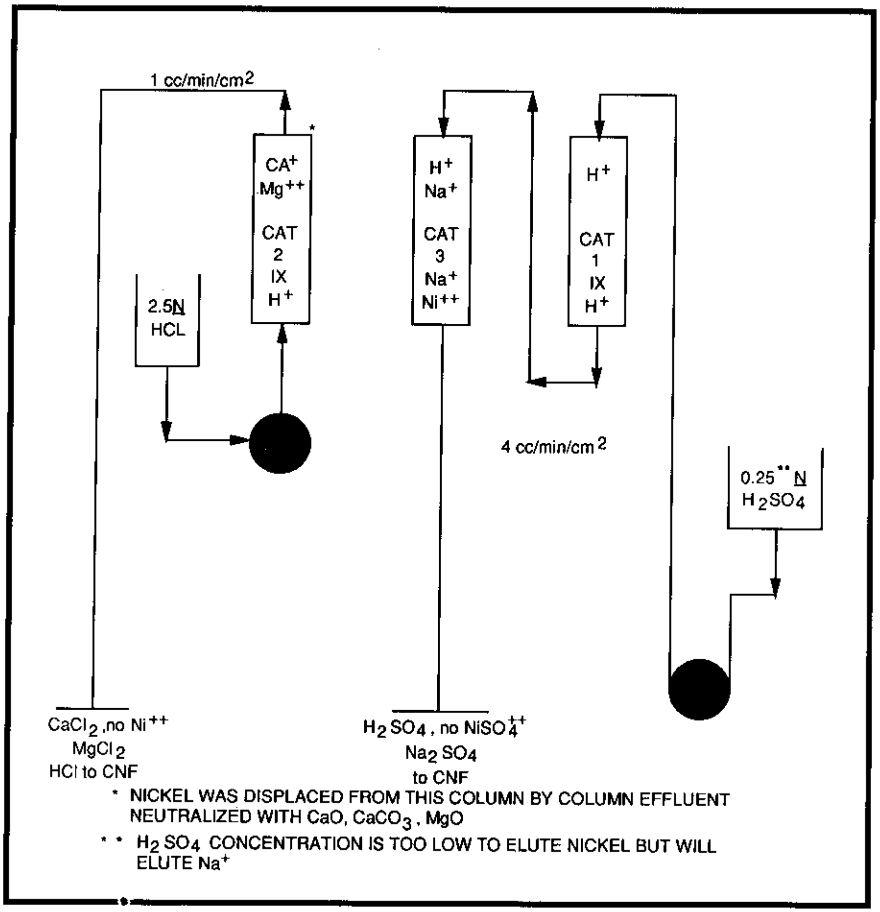
4. The filtrate is then treated with magnesium oxide to precipitate phosphite as $Mg\ HPO_3 \bullet 3H_2O$. Precipitation typically begins at a pH of about 3.8. After cooling to room temperature at pH values of 5.68 and 6.14, phosphite remaining in solution is about 0.49 and 0.19 to 0.25 m/L, respectively.

5. Various alternate cation exchange column treatments are possible at this stage, depending upon whether a rejuvenated bath containing magnesium and calcium ions or a bath with only sodium cations is desired. Various alternatives are still being investigated at K-25 to optimize the process. To obtain a rejuvenated bath containing magnesium with a small amount of calcium, the cation exchange column is treated with ~0.25 N sulfuric acid to elute sodium as sodium sulfate, but retain essentially all nickel within the cation exchange column.

6. The cation exchange column is then treated with ~1.3 m/L magnesium sulfate to displace nickel from the column as nickel sulfate in a sulfuric acid solution. Feed of magnesium sulfate is stopped when enough magnesium sulfate has been added to elute the sorbed nickel, but not obtain a significant magnesium concentration in the effluent.

7. The nickel sulfate-sulfuric acid effluent is then evaporated to concentrate the nickel to about 0.4 m/L.

8. Sulfuric acid is then removed from the nickel sulfate solution by treatment with CaO and $CaCO_3$ as done with the first column effluent. The calcium sulfate hemihydrate filter cake is then washed free of nickel sulfate solution with distilled water.



* NICKEL WAS DISPLACED FROM THIS COLUMN BY COLUMN EFFLUENT NEUTRALIZED WITH CaO, $CaCO_3$, MgO

** H_2SO_4 CONCENTRATION IS TOO LOW TO ELUTE NICKEL BUT WILL ELUTE Na^+

Regeneration of cation strong acid ion exchangers.

9. The MgO-treated first column effluent is then evaporated to decrease its volume by about 35 percent.
10. The concentrated magnesium phosphite, magnesium lactate and sulfate solution is then mixed with the concentrated nickel sulfate solution from step 8.
11. The mixed solution is then treated with activated carbon and filtered to remove any organics from the resin or initial bath that might poison the solution.
12. Finally, after analysis for ingredients, any make-up chemicals are added and the bath is diluted with distilled water to target concentrations.
13. The cation exchange resin column is regenerated for future treatment cycles with ~2 m/L hydrochloric acid or sulfuric acid to convert it back to the H^+ form. Acidic column effluents are neutralized in the central neutralization facility to give nontoxic aqueous effluents and solids.

Ion Exchange

Please refer to the schematic flow diagram for cation exchange column operation. These three column operations represent sodium and nickel ion sorption, sodium stripping with dilute H_2SO_4, while retaining nickel on the column and displacement of nickel from the column.

Precipitation and Filtration

A schematic flow diagram for calcium sulfate and magnesium phosphite precipitation and filtration is shown on page 22. The precipitation treatments yield nontoxic solids and decrease phosphite from about 1.2 to 0.20 m/L, and sulfate from about 1.3 to 0.12 m/L. With appropriate addition of calcium oxide and carbonate, the calcium ion concentration in solution will be only about 0.015 m/L. Magnesium sulfate is very soluble, and the magnesium ion complexes sulfate so that subsequent operations do not precipitate additional calcium sulfate.

Prior to evaporating the filtrate after magnesium oxide treatment, the pH is adjusted downwards to the target bath value of about 4.5 to 4.6.

If the volume of spent bath solution, which is fed to the H^+ form cation resin

Itemized Chemical Cost Breakdown When Baths Are Wasted—5.587 Cycles

Chemical	\$/mil-ft^2
(Nickel) $NiSO_4 \cdot 7H_2$)	0.0796
(Hypo) $NaPH_2O_2 \cdot H_2O$	0.1919
(Lactic Acid) 85%/$CH_3CH(OH)COOH$	0.2328
(Laurel Sulfate) Anti Pit #7	0.0181
(Lead) $Pb(NO_3)_2$	9.6 x 10^{-6}
(Caustic Soda) NaOH	0.0589
Total Chemicals	0.5815

Chemical Costs Associated with the Rejuvenation Process

Item	Cost (\$/mil-ft^2)
CaO at \$0.192/lb, 0.201 g-moles CaO/Mil-ft^2	0.004988
$CaCO_3$ at \$0.1397/lb, 0.07004 g-moles/mil-ft^2	0.002157
MgO at \$0.456/lb, 0.691 g-moles/mil-ft^2	0.02509
HCl column regeneration, \$39.00/55 gal 12 N	0.05574
H_2SO_4 Na^+ displacement at \$67.20/55 gal	0.01890
CNF neutralization of HCl and H_2SO_4 excess for column regeneration with lime at \$0.00752/g-mole	0.01382
$CaSO_4 \cdot 0.5\ H_2O$, 0.280 g-moles/mil-ft^2, ~34 cc/mil-ft^2, disposal cost ~\$0.0095/mil-ft^2	0.0095
$MgHPO_3 \cdot 3H_2O$ 0.6191 g-moles/mil-ft^2, ~98 cc/mil-ft^2, disposal cost	0.0274
Total Chemical Costs	0.1576

Comparison of Total Costs for Dumping/Disposal Of Spent EN Baths vs. Recycling

Bath cycle	Spent Bath Disposal (\$/mil-ft^2)	Recycling (\$/mil-ft^2)
3	3.38	0.34
4	2.53	0.34
5	2.03	0.34
5.6	1.81	0.34

column, contains more equivalents of sodium and nickel than about 70 percent of the column capacity, some nickel ions will be present in the column effluent. A small portion of these will coprecipitate with magnesium phosphite, so it is important to restrict the cation equivalents of bath feed to 70 percent or less of the column exchange capacity. No nickel coprecipitates with calcium sulfate hemihydrate, so calcium sulfate precipitation from a nickel sulfate solution is acceptable. Mother liquor containing nickel, however, must be washed out of the $CaSO_4 \cdot 0.5\ H_2O$ filter cake void spaces in order to obtain nonhazardous $CaSO_4 \cdot 0.5\ H_2O$ solids.

Electroless Plating

Excellent electroless nickel plates were obtained on steel coupons and titanium foil with treated baths containing magnesium salts. Large magnesium concentrations in solution did not significantly increase magnesium concentrations of nickel plates. For example, a treated bath solution containing 8600 mg Mg/L gave a plate containing 120 ppm Mg,whereas a laboratory bath containing 96 mg Mg/L gave nickel plate containing 100 ppm Mg.

Nickel-to-phosphorous ratios of plates may be decreased by high magnesium concentration in baths because inductively coupled plasma emission analyses of a treated bath with Mg^{++} and a standard laboratory bath gave plates having nickel-to-phosphorous atom ratios of 8.8 and 10.3, respectively.

With a spent production bath that was treated to decrease phosphite to 0.13 m/L and 0.40 m/L, plating rates increased from 0.29 mils/hr for this spent bath to 0.76 mils/hr and 0.57 mils/hr, respectively. These treated bath plating rates correspond to 19.4 and 14.6 um/hr.

Effect of Lime Contamination On Electroless Plating

Excellent plates were obtained for all treated baths except one, which was contaminated with 140 mg Zn/L as a consequence of a sulfuric acid leak that drained over galvanized flanges and into the treated bath solution. Plates obtained from the zinc-contaminated solution contained porosity. Solids filtered from the zinc-contaminated solution had atom ratios of ~1 Mg:1 Zn:2P. Therefore, a slightly soluble, $MgZn(HPO_3)_2$ phase may exist. Filtering the zinc-contaminated solution through activated carbon increased the plating rate from 0.17 to 0.46 mils/hr.Subsequently, all treated bath solutions were treated with activated carbon and filtered prior to final adjustments of ingredients to target conditions.

Analyses

Calcium and magnesium interfere with standard EDTA titrations for nickel and colorimetric dithizone analyses for lead. Consequently, a modified cyanide method for volumetric titration of nickel in the presence of calcium and large concentrations of magnesium was developed for nickel bath analyses. Trace concentrations of nickel were determined spectrophotometrically.

Prior to colorimetric dithizone analyses for lead, magnesium fluoride and calcium fluoride were precipitated from the solution in the presence of glacial acetic acid, and an ammonium fluoride-ammonium hydroxide buffer solution. The acetic acid complexed the lead and prevented its precipitation. The solids precipitated by the fluoride were much less viscous than magnesium hydroxide, which was precipitated in the absence of fluoride. Consequently, lead extraction into the dithizone-chloroform layer was efficient and excellent lead analyses were obtained.

Alternative Treatment Procedures

Alternative treatment procedures are being investigated to improve efficiency. By passage of initial column effluent that has been treated to remove phosphite, sulfate and sodium back through parts of the cation exchange resin, for example, magnesium and calcium salts can be converted back to sodium salts, and both reagent requirements for nickel recovery and discharges of acidic effluents can be decreased.

An alternative version of the process would be to periodically or continuously remove a small side stream from an electroless nickel plating bath for treatment. The rate would be such that phosphite and other ions that accumulate with time would be maintained constant in order to yield more consistent plates with consistent phosphorous concentrations.

Another possibility is to use a weak acid chelating resin from selective removal of nickel without sorbing sodium upstream from the strong acid resin. This would decrease cost and improve operation.

References

1. A. Gemmler, T. Bolch, H. Gut and W. Keller, *AESF SUR/FIN Proc.*, Vol. 1 (1990).
2. Wei Chi Ying, Robert R. Bank and James J. Duffy, *Metal Finishing*, 85, 418 (Dec. 1987).
3. Konrad Parker, *Plat. and Surf. Fin.*, 67, 48 (March 1980).

About the Authors

Dr. Roger W. Anderson is a chemical engineering consultant at Martin Marietta Energy Systems, Inc. in Oak Ridge, TN. He received his BS in chemical engineering from the University of Minnesota and doctorate degrees in physical chemistry and chemical engineering from the University of Tennessee.

Dr. Anderson recently retired from the Oak Ridge K-25 Site after more than 40 years of service, and currently is consulting in the areas of incineration, environmental chemistry and plating development. He holds 14 patents and belongs to several professional and honorary organizations.

Wayne A. Neff is principal technologist, Technical Division, Martin Marietta Energy Systems, Inc., the Oak Ridge K-25 Site, P.O. Box 2003, Oak Ridge, TN 37831-7274. He has worked at the K-25 Site for 30 years, with approximately 25 years' experience in plating and metal finishing technologies, specializing in electroless nickel plating. His other areas of expertise include radiological decontamination, nondestructive testing and evaluation and chemical analysis.

Anderson and Neff are recipients of a 1991 R&D-100 award for innovative technology development (for the ENVIRO-CP Process).

The Oak Ridge K-25 Site is managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under Contract DE-AC05-84OR21400.

Editor's note: This is an edited version of a paper presented at the 13th AESF/EPA Conference on Environmental Control, January 27-29, 1992, Orlando, FL.

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September (To be announced)
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Seattle, WA, area
Contact: Mike Kelly
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October (To be announced)
28th Mid-Atlantic Regional
Pocono area
Contact: Herb Tilton, CEF
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October (To be announced)
Piedmont Regional
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Mideast
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