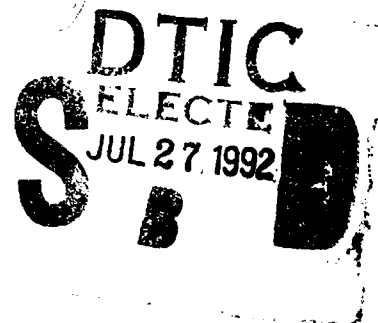AD-A253 404

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US Army Corps
of Engineers

Toxic and Hazardous
Materials Agency

Report No. CETHA-TS-CR-92027
FINAL REPORT

Waste Reduction for
Electroless Nickel Plating Solutions at
U.S. Army Depots

June 1992
Contract No. DACA31-91-D-0074
Task Order No. 0001

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Prepared by:

IT Corporation
11499 Chester Road
Cincinnati, OH 45246

Prepared for:

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, Maryland 21010-5423

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US Army Corps of Engineers

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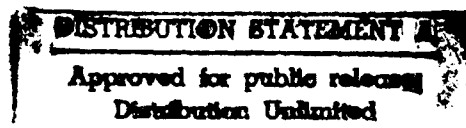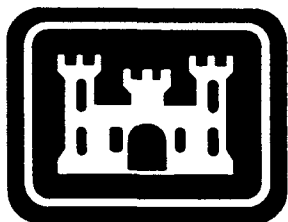Report No. CETHA-TS-CR-92027
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Waste minimization is one of the most pressing environmental issues currently facing U.S. Army depots. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) conducts research and development to support Army depots in implementing technologies to reduce waste generation. The Joint Depot Environmental Panel (JDEP) identified electroless nickel (EN) plating, which is currently used at Corpus Christi Army Depot (CCAD), Red River Army Depot (RRAD), and Sacramento Army Depot (SAAD) as a target for waste minimization research. This report presents the results of an evaluation conducted by USATHAMA regarding minimizing waste from EN-plating operations. The objective of this evaluation was to formulate recommendations for depots regarding implementation of waste minimization technologies. This evaluation was performed through site visits, a literature search, and discussions with vendors of EN processes and decontamination technologies.

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19. (continued)

EN plating is used at Army depots to apply a protective nickel coating to metal parts. It involves electrochemical mechanisms that result in the deposition of nickel without the use of electricity. Plating solutions contain numerous components--including nickel, reducing agent (such as sodium hypophosphite), complexing agents, stabilizers, and pH--that must be maintained in proper balance to obtain good coating quality and avoid decomposition of the solution. By-products, most importantly orthophosphite, are produced which interfere with plating and ultimately result in the need for disposal of the plating solution. Other contaminants, such as particulates and metallic ions, also result in premature disposal of solutions.

EN-plating solution volumes at the three depots (CCAD, RRAD, and SAAD) range from 50 to 225 gallons. These solutions are typically disposed of one to three times per year, resulting in the generation of a total of 500 gallons/yr and disposal costs of $5800/yr, with an additional $2900/yr spent for chemical makeup. Unit disposal costs range from $6 to $22/gal. EN waste solutions are not RCRA-characteristic or listed hazardous waste, but are regulated as hazardous wastes in California (SAAD) and as Class 1 industrial wastes in Texas (CCAD, RRAD). Each of the depots has implemented some waste minimization techniques, including filtration for particulate removal, cooling solutions, reducing orthophosphite accumulation, minimizing contamination from dust and other sources, controlling the purity of makeup water, and, at one depot, the use of automatic controls.

Waste minimization techniques discussed in this report include basic chemistry considerations, proper maintenance, contaminant prevention, and decontamination technologies. Orthophosphite-removal technologies are currently being developed by vendors to extend the plating bath life. One disadvantage of these technologies is that they are capital intensive and payback periods at depots would range from 5 to 17 years. These technologies also have other disadvantages, including the generation of side waste streams (such as sludges and ion exchange regeneration solutions), require additional chemical analysis, and may impart negative effects on bath chemistry. Most of these technologies are in early stages of development, and comprehensive operating and cost data are not available. Automatic monitoring and control is a less expensive technology and can maintain bath chemistry within a narrow range, providing more consistent coating quality and bath stability, and thus has the potential for reducing waste. In-tank plate-out of nickel and treatment of the resulting liquid in a wastewater treatment plant may be a cost-effective alternative to off-site disposal; however, this treatment technique may be impacted by State and local regulations. Technologies such as electrolysis and carbon treatment were found to have potential for removing metals and organics, respectively, from EN solutions, but they may also have deleterious effects on solution chemistry.

The data collected during this study indicate that EN operations within the Army are relatively insignificant waste generators. Pursuit of the major decontamination technologies discussed in this report does not appear to be cost-effective at this time. Recommendations are presented, however, for implementing relatively inexpensive techniques that should improve solution quality in addition to reducing waste. These recommendations include selection of proper bath chemistry, implementing simple waste-reduction methods, and installing an automatic monitoring system to provide increased bath stability and provide good recordkeeping. Finally, because the conclusions of this project are dependent on waste generation rates and disposal costs, the results should be transferred to the Air Force and Navy so that they can determine whether the technologies discussed are suitable for the EN operations at their facilities.

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List of Acronyms

BPA	Blanket Purchase Agreement
CCAD	Corpus Christi Army Depot
CFR	Code of Federal Regulations
CPVC	Chlorinated Polyvinyl Chloride
DMWR	Depot Maintenance Work Request
DOD	Department of Defense
DOE	Department of Energy
DRMO	Defense Reutilization and Marketing Office
EN	Electroless Nickel
IWTP	Industrial Wastewater Treatment Plant
JDEP	Joint Depot Environmental Panel
JPCG-DM	Joint Policy Coordinating Group on Depot Maintenance
M	Molar (moles per liter)
N	Normal (gram equivalent weight per liter)
NPDES	National Pollution Discharge Elimination System
PP	Polypropylene
ppm	Parts Per Million
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
RRAD	Red River Army Depot
SAAD	Sacramento Army Depot
SPC	Statistical Process Control
SS	Stainless Steel
TCLP	Toxicity Characteristic Leaching Procedure
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency

List of Chemicals and Abbreviations

Al^{+3}	Aluminum ion
As^{+3}	Arsenic ion
AsO_2^-	Arsenite ion
B	Boron
BH_4	Borohydride ions
Bi^{+3}	Bismuth ion
Ca^{+2}	Calcium ion
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$CaSO_4 \cdot 0.5H_2O$	Calcium sulfate hemihydrate
$(C_2H_5)_2NHBH_3$	Diethylamine borane (DEAB)
$C_3H_5O_3$	Lactate ion
$CH_2C(COOH)CH_2COOH$	Itaconic acid
$CH_3CH(OH)COOH$	Lactic acid
CH_3CH_2COOH	Propionic acid
$(CH_3)_2NHBH_3$	Dimethylamine borane (DMAB)
Cd^{+2}	Cadmium ion
Cl	Chloride ion
CO_3^{-2}	Carbonate ion
Cu^{+2}	Copper ion
Fe^{+3}	Ferric ion
$FeCl_3$	Ferric chloride
H^+	Hydrogen ion
H_{abs}	Hydrogen atomic, absorbed onto catalytic surface
H_2	Hydrogen (gas)
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
Hg^+	Mercury ion
H_2O	Water
$H(H_2PO_2)$	Hypophosphorous acid
H_2HPO_3	Phosphorous acid (orthophosphorous acid)
$HOOC(CH_2)_2COOH$	Succinic acid

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$HOOC(CH_2)_3COOH$	Glutaric acid
$HOOC(CH_2)COOH$	Maleic acid
$HOOCCH_2(OH)C(COOH)_2$	Citric acid
$HOCH_2COOH$	Glycolic acid
HPO_3^{-2}	Orthophosphite, mono-hydrogen[a] (or phosphite)
$H_2PO_3^-$	Orthophosphite, di-hydrogen[a]
$H_2PO_2^-$	Hypophosphite ion
IO_3^-	Iodate ion
K^+	Potassium ion
KOH	Potassium hydroxide
Mg^{+2}	Magnesium ion
$MgHPO_3 \cdot 3H_2O$	Magnesium phosphite trihydrate
MgO	Magnesium oxide
$Mg(OH)_2$	Magnesium hydroxide
$MgSO_4$	Magnesium sulfate
MoO_4^{-2}	Molybdate ion
Na^+	Sodium ion
$NaBH_4$	Sodium borohydride
NaH_2PO_2	Sodium hypophosphite
Na_2HPO_3	Sodium orthophosphite
$NaOH$	Sodium hydroxide
Na_2SO_4	Sodium sulfate
N_2H_4	Hydrazine
NH_4^+	Ammonium ion
NH_4OH	Ammonium hydroxide
$(NH_4)_2CO_3$	Ammonium carbonate
NH_2CH_2COOH	Aminoacetic acid
Ni^0	Nickel metal (coating)

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[a] Various literature sources use different forms for orthophosphite. In this report, these formulas are used essentially interchangeably.

Ni^{+2}	Nickel ion
NiB	Nickel boride
$Ni(C_2H_3O_2)_2$	Nickel acetate
$NiCl_2$	Nickel chloride
$Ni(H_2O)_6^{+2}$	Hexaquonickel ion
$Ni(H_2O)_4(OH)_2$	Hydrated basic nickel salt (example)
$Ni(H_2PO_2)_2$	Nickel hypophosphite
Ni_2P, Ni_3P_2, Ni_5P_2	Nickel phosphide
$NiSO_4$	Nickel sulfate
NO_3^-	Nitrate ion
OH^-	Hydroxyl ion
P	Phosphorus
Pb^{+2}	Lead ion
Pd^{+2}	Palladium ion
$PdCl_2$	Palladium chloride
S	Sulfur
Sb^{+3}	Antimony ion
Se	Selenium
$Si_2O_5^{-2}, SiO_3^{-2}, SiO_4^{-4}$	Silicate ions
Sn^{+2}	Tin ion
SO_4^{-2}	Sulfate ion
Te	Tellurium
Zn^{+2}	Zinc ion

1.0 Introduction

1.1 Background

The electroless nickel (EN) plating process is used at Army depots to apply a protective nickel coating to various metal parts. Compared with other metal coatings, its advantages include coating uniformity, corrosion and wear resistance, lubricity, ability to plate on nonconductive substrates, solderability, and desirable magnetic and electrical properties. The Joint Depot Environmental Panel (JDEP) [a Joint Policy Coordinating Group on Depot Maintenance (JPCG-DM) chartered panel] identified EN plating as a potential source of significant hazardous waste generation during Department of Defense (DOD) depot maintenance operations. Electroless nickel is currently used by the Army at Corpus Christi Army Depot (CCAD), Red River Army Depot (RRAD), and Sacramento Army Depot (SAAD).

1.2 Objective

The primary objective of this evaluation was to document and assess methods currently used at Army depots to remove contaminants from EN-plating baths, extend the useful lives of these baths, and reduce hazardous waste generated by disposal of spent EN solutions. Another objective was to identify and evaluate other potential methods in use or being developed by industry or other government facilities for the decontamination of EN solutions. The final objective of this evaluation was to formulate recommendations regarding implementation of the most promising technologies or, alternatively, to recommend additional research and development (R&D) projects to further develop potentially applicable technologies.

1.3 Technical Approach

The technical approach to this project consisted of performing four separate tasks, which are briefly described in the following paragraphs. Additional details regarding these tasks are presented in subsequent sections.

> Task 1. Data Acquisition. Initially, a literature search was conducted to collect information regarding the characteristics of EN-plating solutions and to identify technologies applicable for decontaminating these baths. In addition, contacts were made with trade associations, EN users, and vendors of both electroless nickel and decontamination processes.

Task 2. Depot Visits. Project teams including personnel from USATHAMA and IT Corporation visited CCAD, RRAD, and SAAD to observe the EN-plating operations and to collect information regarding waste generation and waste reduction for EN-plating solutions. These visits included discussions with plating operators, supervisors, and depot engineers responsible for identifying and implementing waste minimization technologies.

Task 3. Data Evaluation/Technology Assessment. Information collected during this project from the literature search, vendor contacts, and depot visits was evaluated to determine the advantages and disadvantages of each EN decontamination technology identified. The evaluation criteria included the potential for waste reduction and cost-effectiveness, current commercial state of development, and identification of data gaps and problem areas.

Task 4. Report Preparation. The results of the completion of Tasks 1 through 3 are summarized and presented in this project report. Included are descriptions of EN processes in general and those currently in use at Army depots. The results of the evaluation of solution decontamination technologies are discussed along with other waste minimization technologies for EN waste. The report includes recommendations on implementing the most promising technologies and on conducting R&D programs to provide data necessary for conducting further evaluations.

1.4 Report Organization

The remaining sections of this report present discussions regarding the tasks outlined above. Section 2 contains a description of EN technology. Included are its advantages and disadvantages over other metal-plating options, the variables of the bath chemistry that could affect waste generation, equipment needed for EN plating, and the parameters of bath contamination and their effects on bath quality. Section 3 contains a description of the EN processes used at the three Army depots visited. Section 4 contains a description of decontamination and other waste minimization technologies identified in the literature and during the site visits. Section 5 presents an evaluation of applicable technologies used for decontaminating EN solutions. Finally, Section 6 presents conclusions and recommendations.

2.0 Electroless-Nickel-Plating Process

EN plating involves a series of complex chemical reactions among several bath components. A thorough understanding of EN chemistry is a prerequisite to this evaluation because solution stability and purity have a direct impact on plating speed, product quality, and waste generation. Improper chemical balance and excess contaminants will hasten spontaneous decomposition of the bath or decrease the plating rate or quality below acceptable levels. Additionally, any waste minimization or decontamination methods may impact the solution chemistry, and this impact must be accounted for in the selection of any technologies considered for implementation at the depots.

2.1 Introduction to Electroless-Nickel Plating

The EN process deposits an engineering coating frequently used for its excellent wear and corrosion resistance. Also, EN is used to provide a solderable surface on aluminum and to improve lubricity and part release in molds and dies. Some of the advantages and disadvantages of the EN process, compared with alternative metal coatings, are listed below (Fields, 1982, pp. 219 and 223):

Advantages

- Good resistance to wear and corrosion
- Excellent uniformity
- Solderable and brazable
- Low labor costs

Disadvantages

- High chemical cost
- Brittleness
- Poor welding characteristics of nickel-phosphorus deposits
- Need to copper strike plate alloys containing lead, tin, cadmium, and zinc before EN can be applied
- Slower plating rate than electroplating

In electroplating, electric current density and rate of metal deposition vary with distance from the anode. Plating thickness can thus vary significantly depending on the shape of the part and the distance of different sections of the part from the anode. For example, the raised areas or projections of a part such as a screw will have greater thicknesses than the recesses.

On the other hand, the EN process deposits a uniform coating regardless of the shape or surface irregularities of the part being plated. Uniformity is achieved because the coating is applied without the use of electric current. Plating rate, and thus plated thickness, will be the same on any section of the part exposed to fresh EN-plating solution. The EN process is also characterized by a uniform plating rate with respect to time; therefore, the operator can precisely control the coating thickness by controlling the immersion time in the EN bath.

Instead of electricity, the EN process deposits nickel by using an autocatalytic electrochemical mechanism. The term "autocatalytic" means that the nickel deposit resulting from the electrochemical reaction catalyzes the reaction mechanism. The electrochemical mechanism is characterized by oxidation and reduction (redox) reactions in the solution.

Currently, hot (200°F) acid hypophosphite-reduced EN-plating baths are used to plate steel, aluminum, and other metals. Because the EN coating does not rely on an electric current for application, nonconducting substances such as plastics can also be plated. Plastics and non-metals are plated in warm (95°F) alkaline hypophosphite baths (Henry, 1991). In Europe, borohydride-reduced baths are used to plate iron and copper alloys (Fields, 1982, p. 219).

The sum of the redox mechanism for a hypophosphite-reduced reaction can be represented by the following equation (Fields, 1982):

$$Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni^0 + H_2PO_3^- + 2H^+ \qquad \text{Eq. 1}$$
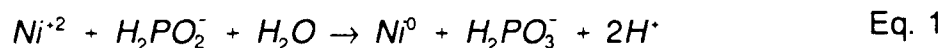
The overall reaction equation has been written in the literature as (Randin and Hintermann, 1970):

$$Ni^{+2} + 4H_2PO_2^- + H_2O \rightarrow Ni^0 + 3H_2PO_3^- + H^+ + P + \frac{3}{2}H_2 \qquad \text{Eq. 2}$$
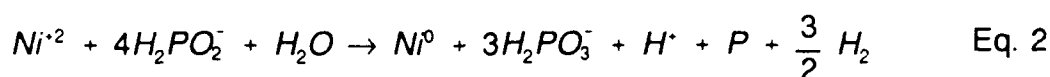
As shown in Equation 2, phosphorus is codeposited with nickel to form a nickel-phosphorus alloy. Typical phosphorus content in the coating ranges from 6 to 12 percent. Higher phosphorus content results in a continuous coating with increased corrosion resistance in acid environments, tensile strength, and ductility, but decreased hardness, wear resistance, and corrosion resistance in alkaline environments. High-phosphorus coatings also have neutral or compressive internal stress, which is preferable to the tensile internal stress of lower-phosphorus coatings. Codeposition of phosphorus provides the natural lubricity of EN coatings.

Three published specifications for EN-phosphorus used as an engineering coating are available:

1) AMS 2404C, Electroless Nickel Plating (Society of Automotive Engineers, 1984)

2) ASTM B656, Autocatalytic Nickel Deposition on Metals for Engineering Use (ASTM, 1984)

3) MIL-C-26074C, Military Specification Requirements for Electroless Nickel Coatings (1985)

These standards present guidelines for testing and quality control via visual examination and simple thickness and adhesion tests; however, none of the standards includes requirements for structural quality, wear resistance, or corrosion resistance.

2.2 EN-Plating Bath Components

EN-plating solutions contain a complex mixture of components. These components include:

- A source of nickel ions
- A reducing agent
- Complexing agents
- Stabilizers/inhibitors
- Energy

If all of the above components are not in the correct balance, the redox reactions may cease or the solution may decompose rapidly.

2.2.1 Nickel Ion Source

A nickel ion source is needed to supply the nickel ions (Ni^{+2}) that are chemically reduced to become the EN coating. The most common source of nickel cations is nickel sulfate ($NiSO_4$). Nickel chloride, nickel acetate, and other salts are also used but in very limited applications. The chloride anion can be harmful to aluminum substrates and can decrease the corrosion resistance of ferrous alloys. Nickel acetate cost versus the cost of nickel sulfate does not outweigh minor advantages in performance and deposit quality gained by nickel acetate (Mallory, 1990a). The ideal nickel salt is nickel hypophosphite, [$Ni(H_2PO_2)_2$], which eliminates the buildup of sulfate ions in the plating solution. Sulfate ions can impair solution quality by decreasing corrosion resistance and increasing the internal stress of the deposit.

EN plating can occur over a wide range of nickel concentrations: 3 to 100 g/L (0.05 to 1.7 M). Commercial acid hypophosphite-reduced baths have nickel concentrations within the range of 4.5 to 11 g/L (0.08 to 0.19 M), with most baths in the range of 5.5 to 7.5 g/L (0.09 to 0.13 M). When the nickel concentration is greater than 5 g/L (0.085 M), it has little or no effect on the plating rate. The nickel concentration in solution influences the phosphorus content of the deposit only when the nickel concentration in solution is less than 6 g/L (0.1 M). Above a 6 g/L concentration of nickel, the phosphorus content will remain constant as long as the hypophosphite concentration is constant (Mallory, 1990b, p. 62).

2.2.2 Reducing Agents

EN-plating baths contain a reducing agent to drive the reaction that reduces the nickel ions to their metallic state. Four reducing agents are used:

- Sodium hypophosphite
- Sodium borohydride
- Aminoboranes
- Hydrazine

Sodium Hypophosphite. Sodium hypophosphite (NaH_2PO_2) currently is the most common and most developed reducing agent. The advantages of sodium hypophosphite over the other reducing agents include lower cost, greater ease of control, and better corrosion resistance of the deposit.

Several mechanisms have been proposed for the electrochemical reactions that occur in a hypophosphite-reduced EN bath. The most widely accepted mechanism is illustrated in the following equations (Fields, 1982):

$$(H_2PO_2) + H_2O \xrightarrow[cat]{\Delta} H^+ + (HPO_3)^{-2} + 2H_{abs} \qquad \text{Eq. 3}$$
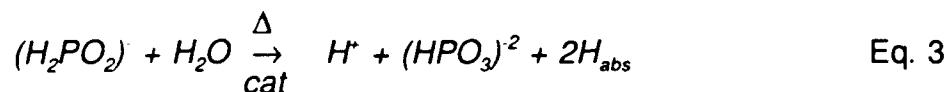
As shown in Eq. 3, the hypophosphite ion ($H_2PO_2^-$) is oxidized in water in the presence of heat and a catalyst to form hydrogen ions (H^+), orthophosphite ions (HPO_3^{-2}), and atomic hydrogen (H_{abs}), which is absorbed at the surface of the catalyst.

$$Ni^{+2} + 2H_{abs} \rightarrow Ni^0 + 2H^+ \qquad \text{Eq. 4}$$

Nickel at the surface of the catalyst is reduced by the absorbed active hydrogen to form the elemental nickel deposit and hydrogen ions (Eq. 4). Simultaneously, some of the hydrogen absorbed at the surface reduces some of the hypophosphite at the surface of the catalyst to water, hydroxyl ions, and phosphorus (Eq. 5).

$$(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P \qquad \text{Eq. 5}$$
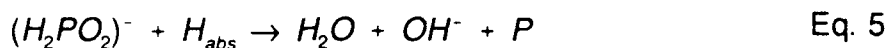
Phosphorus is deposited with the nickel to form a nickel-phosphorus alloy (Eq. 5). Most of the hypophosphite taking part in the reaction is oxidized at the catalyst surface to ortho-phosphite and hydrogen gas (Eq. 6).

$$(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{-2} + H_2 \; (g) \qquad \text{Eq. 6}$$
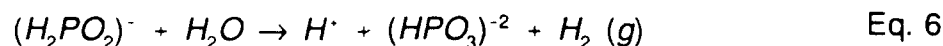
This results in a low efficiency in sodium hypophosphite usage (about 37 percent) (Fields, 1982, p. 220). About 5 kg of sodium hypophosphite is required to reduce 1 kg of nickel.

Even though EN plating can occur over the wide range of nickel concentrations given above, a more limited concentration range for the hypophosphite ion is required to achieve optimum plating conditions. The molar ratio of nickel ion to hypophosphite ion should be in the optimum range of 0.30 to 0.45 (Gutziet and Krieg, 1953). In general, an increase in the concentration of the hypophosphite ion will tend to increase the phosphorus content in the deposit (Mallory, 1990b, pp. 63 and 64).

Sodium Borohydride. Sodium borohydride ($NaBH_4$) and aminoboranes are used as reducing agents to produce nickel-boron coatings. Compared with nickel-phosphorus deposits, nickel-boron coatings have higher hardness and wear and abrasion resistance, but they are much more costly and have lower corrosion resistance. In acidic or neutral sodium borohydride solutions, the hydrolysis of borohydride ions is very rapid. With the addition of nickel ions to this solution, nickel boride may form spontaneously. Thus, the sodium borohydride-reduced bath must be maintained between a pH of 12 to 14 to suppress the formation of nickel boride and obtain elemental nickel as the principal reaction product. The solution pH decreases during the course of the reaction. Thus, alkali hydroxide must be constantly added to the bath.

Aminoboranes. Dimethylamine borane (DMAB) [$(CH_3)_2 NHBH_3$] and diethylamine borane (DEAB) [$(C_2H_5)_2NHBH_3$] are the two aminoboranes commercially used in EN plating. DMAB is used primarily in the United States, whereas DEAB is primarily used in Europe. Aminoborane-reduced EN baths are operated usually in the ranges 6 to 9 pH and 120° to 180°F (50° to 80°C). At these operating conditions, aminoborane baths are useful for plating plastics and nonmetals (Fields, 1982, p. 221).

Hydrazine. Solutions reduced by hydrazine (N_2H_4) have also been used to plate EN. Even though the deposit of nickel from a hydrazine-reduced EN bath is 97 to 99 percent nickel, it does not have a metallic appearance. Also, the deposit is brittle and highly stressed with poor corrosion resistance. The operating conditions are 195° to 205°F (90° to 95°C) and 10 to 11 pH. As a result of the instability of hydrazine at high temperatures, the baths are very unstable and difficult to control. Hydrazine is a suspected carcinogen. Currently, there is very little commercial use for hydrazine-reduced EN baths (Fields, 1982, p. 221).

2.2.3 Complexing Agents

Complexing agents are used in EN-plating baths to avoid spontaneous decomposition and to control the reaction so that it only occurs on the catalytic surface. To achieve the above tasks, the complexing agents control the amount of free nickel available for reaction, prevent the precipitation of basic nickel salts and orthophosphite, and buffer the plating solution to prevent the pH from decreasing or increasing too rapidly.

In aqueous solutions, nickel ions are typically bound to either four or six water molecules, e.g., [$Ni(H_2O)_6]^{+2}$. The hexaquonickel ion can hydrolyze to less-soluble hydrated basic nickel salts (e.g., [$Ni(H_2O)_4(OH)_2$]), which can precipitate out of solution. Chelation of the nickel by complexing agents replaces the water molecules by the complexing ligands and increases the nickel complex's resistance to hydrolysis. An equilibrium is established between the complexed nickel and free nickel ions (i.e., nickel loosely coordinated with water molecules). The plating reaction occurs at the free nickel coordination sites, and the plating rate is a function of the free nickel ion concentration. Complexing agents serve to maintain the free nickel ion concentration at a level low enough to stabilize the solution and prevent hydrolysis.

Complexing agents are typically polydentate organic acids or their salts. Commonly used complexing agents include succinic, glutaric, lactic, propionic, and aminoacetic acids.

Table 2-1 presents a list of complexing ligands used in the EN baths (Mallory, 1990a, p. 28; Fields, 1982, p. 220). The anions of propionic, succinic, and glutaric acids activate the hypophosphite anion and enhance the EN-plating rate.

Table 2-1
Complexing Ligands Commonly Used in EN-Plating Baths

Anion	Structure (Acid)
Monodentate	
Acetate	CH_3COOH
Propionate	CH_3CH_2COOH
Succinate	$HOOCCH_2CH_2COOH$
Lactate	$CH_3CH(OH)COOH$
Bidentate	
Hydroxyacetate	$HOCH_2COOH$
α-Hydroxypropionate	$CH_3CH(OH)COOH$
Aminoacetate	NH_2CH_2COOH
Ethylenediamine	$H_2NCH_2CH_2NH_2$
β-Aminopropionate	$NH_2CH_2CH_2COOH$
Malonate	$HOOCCH_2COOH$
Pyrophosphate	$H_2O_3POPO_3H_2$
Tridentate	
Malate	$HOOCCH_2CH(OH)$-$COOH$
Quadridentate	
Citrate	$HOOCCH_2(OH)C$-$(COOH)COOH$

The complexing agents also help stabilize the solution by retarding the precipitation of nickel orthophosphite (which is formed as a byproduct of the electrochemical reaction). Figure 2-1 illustrates the complexing ability of the agents commonly used by showing the solubility of orthophosphite in solutions complexed with citric and glycolic acids as a function of pH. By increasing bath stability, the bath life is ultimately increased, thereby reducing spontaneous decomposition and waste generation.

Complexing agents must be chosen carefully because they can affect the quality of the deposit by affecting the phosphorus content, internal stress, and porosity (Fields, 1982, p. 221). They
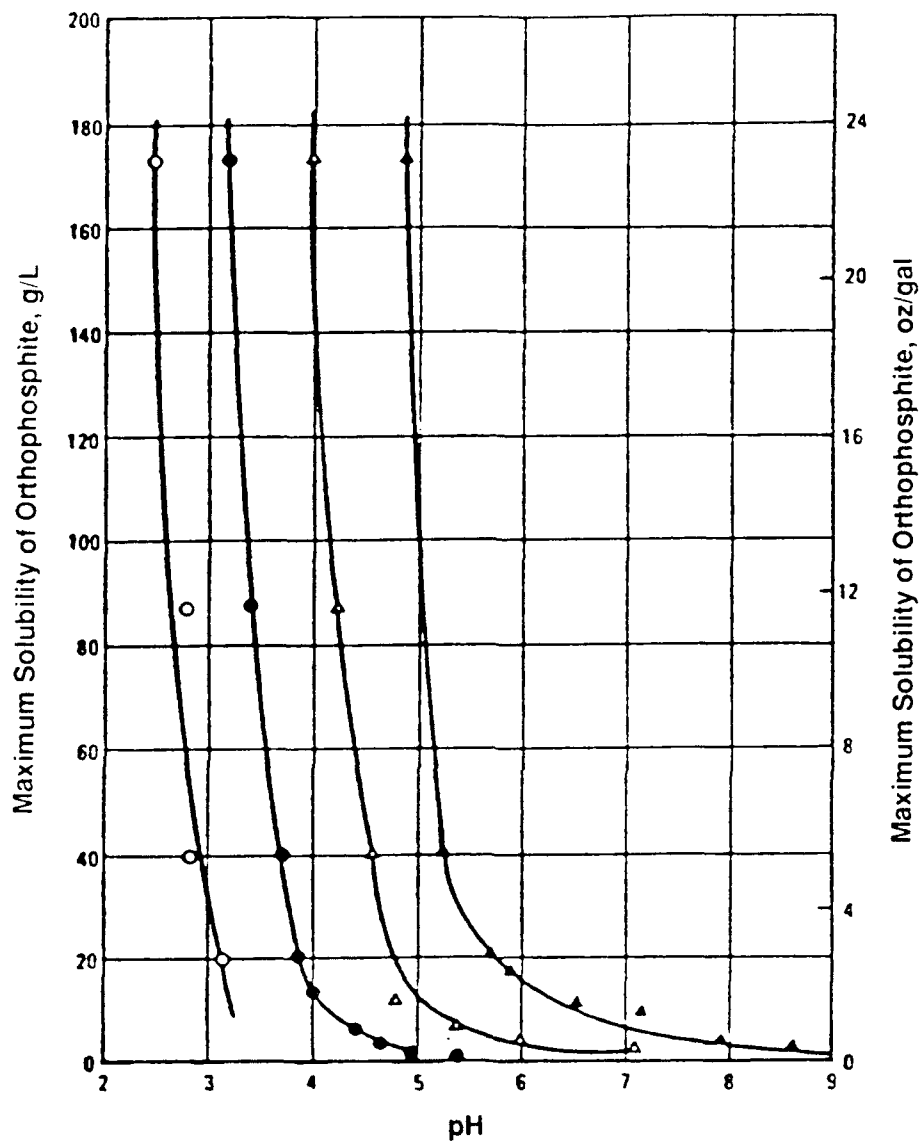
Solutions contain 30 g/L (4 oz/gal) nickel chloride (NiCl$_2$) and 10 g/L (1.3 oz/gal) sodium hypophosphite (NaH$_2$PO$_2$). ○: without a complexing agent; ●: with 15 g/L (2 oz/gal) citric acid; △: with 39 g/L (5.2 oz/gal) glycolic acid; ▲: with 78 g/L (10 oz/gal) glycolic acid

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Figure 2-1.
Limits of Solubility for
Orthophosphite in Electroless
Nickel Solutions

Source Fields, 1982

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also affect the plating rate. The initial addition of complexing agent increases the plating rate of the bath. As the concentration of the complexing agent is increased, the plating rate will pass through a maximum and then decrease. Deposition rates and phosphorus content are affected by the stability of the specific complexing agents used in an EN formulation. Complexing agents that produce more stable nickel complexes result in lower deposition rates and lower phosphorus content in the deposited coating (Mallory, 1990b, pp. 69 and 70).

2.2.4 Stabilizers/Inhibitors

Stabilizers are used in EN-plating baths to prevent spontaneous decomposition of the entire plating bath and to prevent plate-out of the nickel on the tank wall. Decomposition is usually initiated by the presence of colloidal, solid nuclei in the solution. These particles may be foreign matter (dust or blasting media) or buildup of orthophosphite ions past the solubility limit. Spontaneous bath decomposition is usually preceded by increased hydrogen evolution and the appearance of a fine-grained black precipitate. This precipitate consists of particles of nickel and nickel phosphide. Other particles that initiate bath decomposition could also be the hydroxides of metal contaminants. For example, iron and aluminum precipitate as gelatinous hydroxides above a pH of 5.0 (Mallory, 1990a, p. 35).

An EN-plating bath can be operated without stabilizers under normal operating conditions for extended periods of time; however, the bath may decompose spontaneously at any time. The stabilizer must be chosen to assure compatibility with the process chemicals to avoid any adverse effect resulting from interaction with any other bath additives. Only trace amounts of stabilizers are required to virtually eliminate spontaneous decomposition (Mallory, 1990a, p. 35).

Stabilizers are adsorbed on the surface of any colloidal particles present in the solution and prevent the reduction of nickel on their surface (Fields, 1982, p. 222). The specific reaction/inhibition mechanisms depend on the specific class of stabilizers used. The most effective stabilizers can be divided into four classes (Mallory, 1990a, p. 35):

1) Compounds of Group IV elements: S, Se, Te
2) Compounds containing oxygen: AsO_2^-, IO_3^-, MoO_4^{-2}
3) Heavy metal cations: Sn^{+2}, Pb^{+2}, Hg^+, Sb^{+3}
4) Unsaturated organic acids: Maleic, itaconic

Since only trace amounts of stabilizers are required, concentrations in the EN-plating bath are very critical. Substances that are classified in either Class 1 or Class 2 can function effectively at concentrations in the plating bath as low as 0.10 part per million (ppm). Usually, when the concentration of the stabilizers in either of these classes reaches about 2 ppm, the plating reaction can be completely inhibited (Mallory, 1990a, p. 36).

Stabilizers of Classes 3 and 4 are measured by molar concentrations. The concentration range for Class 3 stabilizers is 10^{-5} M to 10^{-3} M and 10^{-3} M to 10^{-1} M for Class 4 stabilizers (Mallory, 1990a, p.36). When unsaturated organic acids (Class 4) are used as stabilizers, they are consumed during the deposition reaction and must be replenished periodically to maintain stability (Mallory, 1990a, p. 45).

Some stabilizers also increase the plating rate of the bath and affect the phosphorus content and internal stress of the deposit. As the concentration of certain stabilizers increases, the reducing agent efficiency may increase and cause ' increase in the plating rate and nickel content of the deposit. However, most stabilizers decrease the rate of plating and some of these can completely inhibit plating at low concentrations. Excessive concentrations of stabilizers can result in edge pull-back at sharp edges on the plated substrate.

Air agitation can provide some stabilization to an EN-plating solution. Agitation with the inert gas argon, however, was found to be ineffective in increasing stability (Gabrielli and Raulin, 1971).

In summary, the use of stabilizers can increase the useful life of a bath by preventing spontaneous decomposition. Excessive concentrations of stabilizers, however, have a detrimental effect on plating rate and product quality. Bath chemistry and maintenance, therefore, should focus on a given range of stabilizer concentrations.

2.2.5 Energy

One of the most important variables in the EN-plating bath is the amount of energy (heat) contained in the EN solution. In the hypophosphite-reduced solutions, the rate of deposition is low at temperatures below 140°F (60°C), but increases rapidly with increased temperature (Figure 2-2). The reaction rate increases exponentially with temperature. The rate constant K is given by:
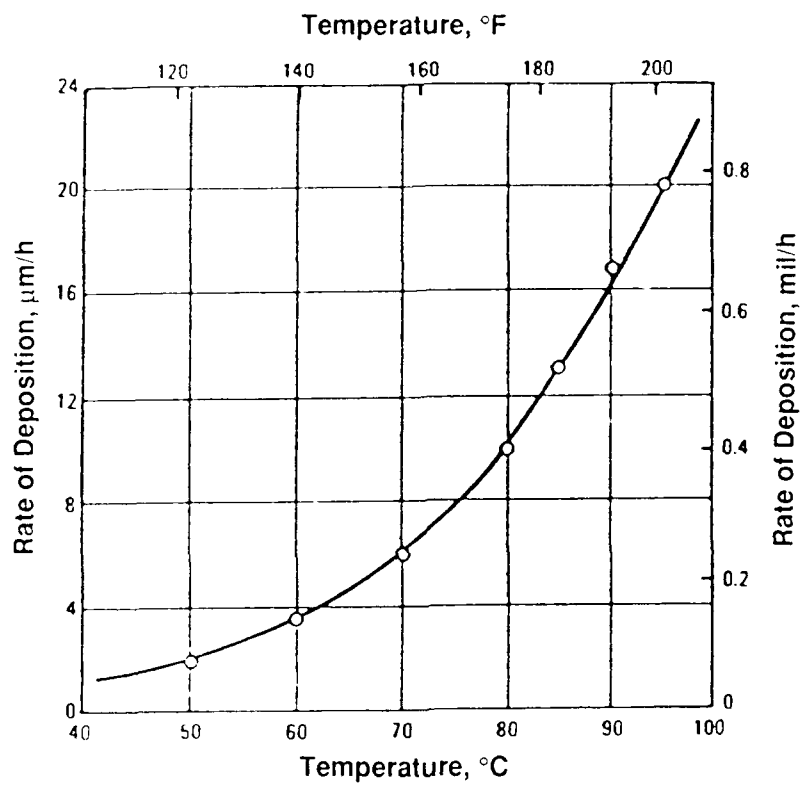
Figure 2-2.
Effect of Temperature on
Plating Rate.

Source Fields, 1982

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$$K = A \exp (-E_a/R \, T) \qquad \text{Eq. 7}$$

where A is a constant, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature (Mallory, 1990a, p. 54). The preferred operating range for hypophosphite-reduced baths is 185° to 205°F (85° to 95°C) (Fields, 1982, p. 221). Bath decomposition can occur at temperatures above 212°F (100°C).

Temperature also affects the solubility of chemical compounds in aqueous solution. The solubility of most chemicals in water increases with an increase in temperature. Orthophosphite, however, is less soluble at higher temperatures.

2.2.6 Vendor Formulations

As discussed in this section, at least four chemical reactants influence the electrochemical reaction in the hypophosphite-reduced EN bath. These reactants must be maintained in the appropriate concentration ranges to achieve plating at a suitable rate, give good product quality, and increase bath stability. Vendor formulations are typically sold in multiple-part sets to aid shop operators in maintaining proper reactant concentrations. Such a set may contain solutions for bath makeup, replenishing nickel and reducer, replenishing organic additi·es, and adjusting pH.

2.3 Reaction By-Products

As discussed in Subsection 2.1, the electrochemical EN reaction results in the production of chemical byproducts, primarily hydrogen ions (H^+) and orthophosphite (HPO_3^{2-} or $H_2PO_3^-$). This subsection discusses each of these constituents.

2.3.1 Hydrogen Ions

Hydrogen ions (H^+) are generated as a byproduct of the oxidation-reduction reactions. Three moles of H^+ are generated for every mole of Ni^{+2} deposited (Mallory, 1990b, p. 58). As the hydrogen ions increase in concentration and pH decreases, the deposition rate decreases, orthophosphite solubility increases, and phosphorus content of the deposited coating increases. Very low plating rates are observed below a pH of 4.0. A higher pH results in an increased deposition rate, decreased phosphorus content, and improved adhesion on steel. A high pH, however, will lower the solubility of orthophosphite and result in decreased solution stability,

leading to bath plateout. The effects of pH on solution and coating properties are summarized in Table 2-2.

Table 2-2
Effect of pH Change on EN Processes[a]

Change	Effect on Solution	Effect on Deposit
Raise pH	Increased deposition rate; lower phosphite solubility.	Decreased phosphorus content; shift in stress to tensile direction.
	Decreased stability with resultant plateout.	Poorer adhesion on steel.
Lower pH	Decreased deposition rate; improved phosphite solubility.	Increased phosphorus content; shift in stress to compressive direction.
		Improved adhesion on steel.

[a] Reprinted with permission from *Electroless Plating: Fundamentals and Applications,* Glenn O. Mallory and Juan B. Hajdu, editors. American Electroplaters and Surface Finishers Society, 12644 Research Parkway, Orlando, Florida 32826-3298. Reference Mallory, 1990b.

The targeted pH range and the allowable pH variance depend on the desired solution characteristics and deposition properties. The control of pH is accomplished through the components of the bath formulations as well as the addition of other chemicals. Complexing agents and other buffers help neutralize the hydrogen ion formation. Organic acids used as buffers include acetic, propionic, and succinic acids, which also act as complexing agents as discussed in Subsection 2.2.3. Chemicals such as ammonium or alkali metal hydroxides or carbonates are typically added periodically to neutralize excess hydrogen ions. An optimum pH range of 4.5 to 5.2 has been provided in the literature (Mallory, 1990b, p. 61).

2.3.2 Orthophosphite

As the EN-plating reactions proceed, hypophosphite ions ($H_2PO_2^-$) are oxidized to orthophosphite ions (HPO_3^{2-} or $H_2PO_3^-$). (The term phosphite is sometimes used in the literature as a synonym for orthophosphite.) Approximately 4 grams of orthophosphite are produced for each gram of nickel deposited. As the solution ages and the orthophosphite concentration increases, the plating rate decreases, phosphorus content of the coating increases, the intrinsic stress of the deposit increases, and corrosion resistance may be reduced. (Increased stress and decreased corrosion resistance, however, may result from the buildup of sodium and sulfate ions, as discussed later in this section.) At a concentration of about 30 g/L, orthophosphite

2-13

begins to compete with the complexing agent for nickel ions. The relatively insoluble compound nickel orthophosphite is formed and precipitates, causing rough deposits and perhaps spontaneous decomposition of the bath (Mallory, 1990b, p. 65).

As discussed in Subsections 2.2.3 and 2.3.1, orthophosphite solubility is dependent on the concentrations of complexing agents and hydrogen ions in the EN solution. The correlation between orthophosphite solubility, pH, and concentrations of complexing agents is shown in Figure 2-1. The addition of excess complexing agent when nickel orthophosphite formation is first observed may solubilize the compound and prevent its precipitation. Operating the EN bath at the lower end of its allowable pH range may also increase the orthophosphite tolerance of the solution.

Different formulations of EN solutions have different tolerances for orthophosphite concentrations. Depending on the complexing agent used, an orthophosphite concentration of 60 g/L may cause a minor or major decrease in plating rate. Since 4 grams of orthophosphite are generated for every gram of nickel deposited, about 24 g/L of orthophosphite will accumulate after one metal turnover of a bath containing 6 g/L nickel. A metal turnover is achieved when an amount of nickel equal to the amount in the initial solution has been plated out. Orthophosphite accumulation will also depend on the percent dragout, however, as shown in Figure 2-3 (Bayes, 1990).

2.4   Bath Contamination

The EN-plating reaction is also affected by contaminants that accumulate in the solution. The contaminants may be introduced to the EN bath by the following mechanisms:

- Contamination from substrate metals
- "Drag-in" from water, cleaners, other tanks, etc.
- Reaction by-products (Subsection 2.3)
- Accumulation of replenishment chemicals
- Airborne contamination

These mechanisms yield four categories of contaminants into the bath solution:

- Particulates
- Metallic ions
- Other inorganic ions
- Organic contaminants

Bath Turnovers/Cycles

Legend:
- No dragout
- 5% dragout
- 10% dragout
- 12% dragout
- 15% dragout

Y-axis: Orthophosphite, g/L
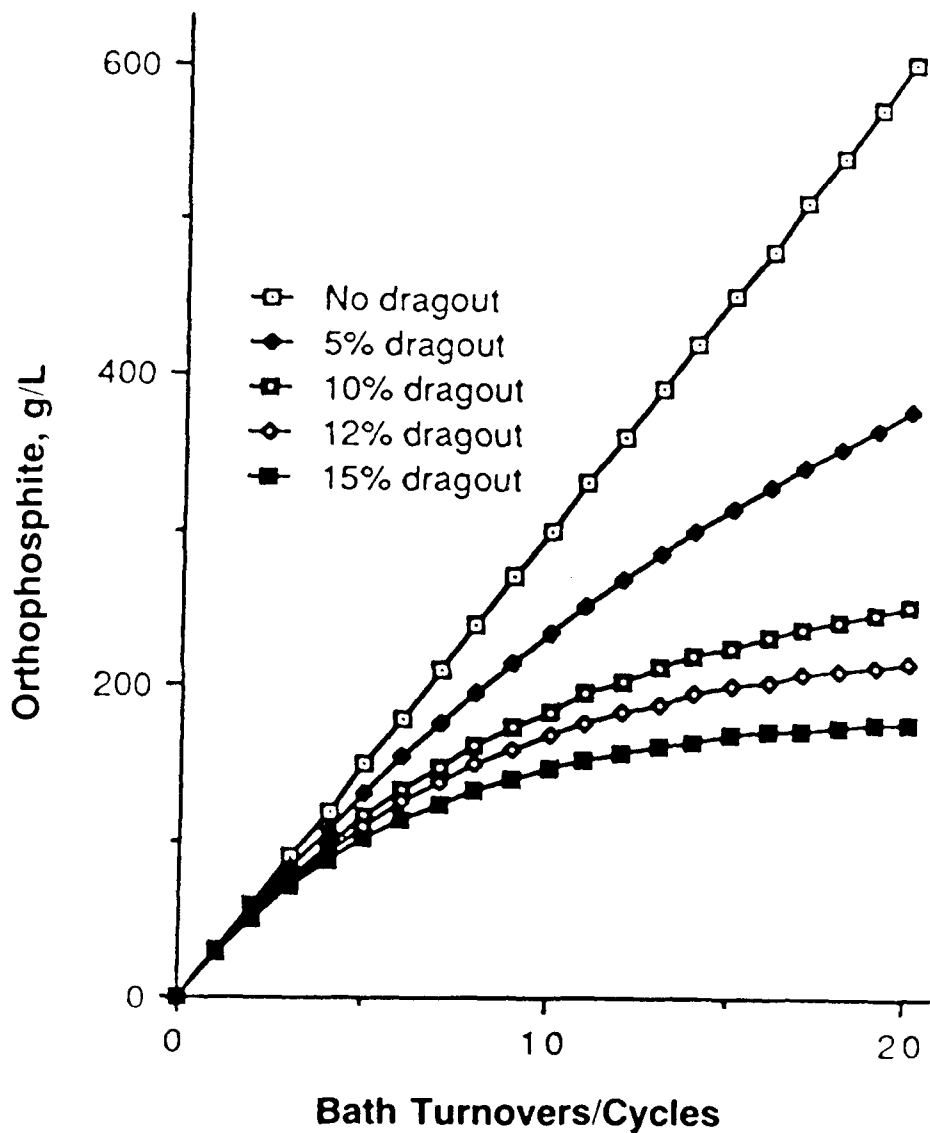
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1990. Elsevier Science Publishing Co., Inc., New York, NY

Figure 2-3.
Orthophosphite Buildup as a
Function of Metal Turnovers and
Percent Dragout Per Cycle.

Source Bayes, 1990

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2.4.1 Particulates

Particulates may be introduced into the EN bath by contamination from outside sources or as a result of chemical reactions. External contamination results from "drag-in" of other solutions or from the plating shop air--containing dust and other contaminants--coming into contact with the surface of the solution. Particles that form within the solution include insoluble nickel phosphite (as discussed in Subsection 2.3). Also, iron and aluminum ions entering the bath from the processing of aluminum and steel parts will precipitate as hydroxides at a pH greater than 5.0.

Particles cause severe problems in EN baths because they create a large surface area that serves as a catalyst for the electrochemical reaction. Thus, the nickel reduction reaction occurs throughout the solution rather than only on the part to be coated, and leads to spontaneous decomposition of the entire bath.

2.4.2 Metallic Ions

Metal ion contaminants are introduced into the plating bath by the dissolution of the substrate, by "drag-in" from other tanks, and by the water used for makeup and rinsing. Most metallic ions will plate out with the nickel, with little effect on the solution or coating if they are present in small amounts. Deposited coatings may contain as much as 0.25 percent of elements other than nickel and phosphorus with no harmful effects (Fields, 1982, p. 223). Excessive concentrations of metallic contaminants, however, can have a profound effect on EN plating. Metals of special concern include lead, cadmium, copper, bismuth, arsenic, palladium, calcium, and magnesium (Aleksinas, 1990, p. 104).

Lead may build up in the EN-plating solution by improper use of lead masking material and stabilizers and by the dissolution of lead alloy substrates. Lead affects the deposit quality, plating rate, and bath life. Dark deposits, skip plating, pitting, short bath life, and cessation of plating occur at a lead concentration as low as 5 ppm.

Cadmium may build up in the EN-plating solution through contact with improperly cleaned racks previously used in cadmium plating, as well as by drag-in from contaminated cleaners and brighteners. Dark deposits, feathering around holes, and skip plating occur at cadmium concentrations as low as 3 ppm.

Copper can be introduced into the EN-plating solution as a result of improper pretreatment of copper substrates, which leads to the substrates dissolving in the EN solution. Another source of copper ions is improper preplate, where an acid pickle leaves a copper immersion deposit on ferrous substrates. Copper concentrations of 100 ppm or more cause adhesion problems of the EN plate.

Palladium is introduced into the EN-plating solution from pretreatment of noncatalytic substrates (e.g., copper). Palladium chloride is sometimes used to activate such noncatalytic substrates, although one reference does not recommend this procedure (Hajdu, 1990). Palladium ions will be introduced to the EN bath if a pretreated substrate is not rinsed properly. Palladium ions or particles form nuclei and cause spontaneous decomposition of the EN-plating bath.

Magnesium and calcium are introduced into the EN-plating solution from the water supply (i.e., hard water) used for rinsing, replenishing, etc. These ions eventually build up in the solution as a result of evaporation, which necessitates replenishment of water to the EN solution. Magnesium and calcium cause insoluble compounds to precipitate, which leads to spontaneous decomposition of the plating solution. These ions also cause rough, hazy, and pitted deposits.

2.4.3 Other Inorganic Ions

Other cations and anions accumulate in the EN bath by the replenishment of used reactants and from the neutralization of the hydrogen ions generated during the EN-plating reaction. Replenishment additions of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium or potassium hydroxide ($NaOH$, KOH), ammonium hydroxide (NH_4OH), or ammonium or potassium carbonate [$(NH_4)_2CO_3$, K_2CO_3] introduce the cations Na^+, K^+, and NH_4^+. Nickel ion replenishment from nickel sulfate or nickel chloride ($NiSO_4 \cdot 7H_2O$ or $NiCl_2 \cdot 6H_2O$) introduces the anions SO_4^{-2} and Cl^-.

The effect of these ions has not been thoroughly established. One author theorizes that sodium and potassium may react with the nickel complex, affecting the equilibrium reaction, decreasing the plating rate, and increasing phosphorus content (Mallory, 1990b, pp. 72 and 73). Some researchers discovered that the sulfate anion in sufficient quantities will increase the tolerance of the solution to the orthophosphite ions (Hajdu and Yarkosky, 1981). In one

experiment, the addition of 152 g/L of sodium sulfate to a new EN-plating bath with a pH of 5.0 increased the amount of orthophosphite required to precipitate metal ions from 28 to 70 g/L. Thus, additions of sodium sulfate may enhance the solubility of the orthophosphite ions.

Some researchers have found that adding orthophosphite alone to new solutions did not affect plating rate or phosphorus content. Sodium sulfate and sodium orthophosphite together, however, did decrease the deposition rate and affect the phosphorus content. One reference theorizes that the effects typically attributed to orthophosphite in an aged bath may be due to the alkali metal content of the bath, including sodium (Mallory 1990b, pp. 72 and 73). Another reference reported that the decrease in plating rate is attributable to the buildup in orthophosphite ions, while the increase in internal stress and decrease in corrosion resistance results from the buildup of sodium and sulfate ions (Linka and Riedel, 1991).

Other inorganic ions that contaminate the EN-plating bath include nitrates and silicates. Nitrates are introduced to the solution from improperly rinsing the plating tanks after passivation with nitric acid. Nitrates at high concentrations can reduce the plating rate significantly or even stop plating altogether. Silicates are introduced to the solution by drag-in of preplate cleaners. Silicates cause a cloudy and pitted deposit.

2.4.4 Organic Contaminants

Organic chemicals can also contaminate an EN-plating bath. These organic contaminants include: degreasing solvents, oil residues, mold releases, drag-in of cleaners, and acid inhibitors. Organic contamination can cause a cloudy, streaked deposit with poor adhesion.

2.5 EN-Plating Equipment Requirements

The major pieces of equipment required for EN plating are:

- Plating tanks
- Passivation solution tank
- Heat exchanger
- Filter
- Automatic control system (optional)

An EN-plating system typically consists of two plating tanks used alternately. One tank is used for plating while the other is cleaned. As necessary, the plating solution is pumped from one tank to the clean tank and the first tank is then cleaned.

The plating tanks for EN are usually lined with polypropylene (PP) or chlorinated polyvinyl chloride (CPVC), or constructed of stainless steel (SS). PP is the most widely used in industry because of its relative low cost and versatility of design. Some disadvantages of the PP tanks are that it is oxidizable by nitric acid used to clean the tank, has a finite life span, and is flammable. On the other hand, CPVC is less flammable and is not oxidizable by nitric acid, but is more costly than PP. SS is usually used as the tank in which the PP or CPVC liners are placed. However, SS tanks are also used without liners in EN plating. When used without the liners, the SS tank experiences plate out of EN on the walls of the tank, which causes increased cleaning and necessitates down-time of the process (Kuczma, 1990).

A passivation solution tank is needed as part of the EN process to hold the nitric acid solution. The passivation solution is used to dissolve any plated metal on the process tank and other process parts in contact with the EN-plating solution. This tank is usually constructed with PP (Kuczma, 1990).

Typical heat exchangers used in EN-plating baths are electric immersion heaters or steam-coil heaters. These heat exchangers are contained within the bath. Electric immersion heaters are usually constructed of stainless steel 304. The advantages of using immersion heaters are their low initial capital cost and easy installation. On the other hand, electric immersion heaters are prone to plate out on the heater as well as posing a possible fire and electrical hazard if improperly maintained (Kuczma, 1990).

Steam heat exchangers have greater initial capital costs, but lower long-term operation costs. Two types of coil configurations are commonly used. These configurations are panel coils made of stainless steel and "spaghetti coils" made of Teflon®. Panel coils have lower cost over the Teflon coils but have the potential for plate out onto the coils. Panel coils can also cause hot spots between the coils and the tank wall, causing solution decomposition in these areas. Teflon coils are inert to all plating solutions and cleaners. Teflon, however, is very expensive and fragile. Once the Teflon coils are installed in the plating tank, they cannot be moved without creating the potential for leaks. This fragility increases with age.

Filtration systems are typically specified with all EN-plating operations. The literature and vendors typically recommend that the EN-plating bath be filtered continuously with a 1-μm filtering medium at a rate of 6 to 10 tank turnovers per hour. Bag filters and cartridge filters can be used. Bag filters use a polypropylene felt bag that solution is pumped into and allowed to filter through by gravity flow. Cartridge filtration is a closed-chamber unit utilizing pressure from a pump to force the solution through the polypropylene felt media. Bag filters are usually the more cost-effective.

Automatic analyzers and control systems are sometimes used in EN operations to reduce analytical labor and increase the frequency and accuracy of chemical additions. The typical automatic control system consists of four parts: sampling and analytical equipment, micro-computer controller, display and recording units, and chemical dosing equipment. Figure 2-4 illustrates a schematic diagram of such equipment.

To begin an analysis/control cycle, a sample of the EN-plating solution is taken and the bath temperature is recorded. The sample is then cooled, filtered, and degassed to prevent degradation and failure of the sensors (some automatic controllers do not require solution cooling). The pH and nickel concentration of the sample are then measured. The temperature of the cooled solution is recorded to correct the pH value. The pH is typically measured by a standard calomel electrode, and the nickel concentration is measured by a double-beam photometer. A microcomputer controller compares measured data with programmed data and turns the chemical replenishing pumps on and off as required. The reducer concentration is typically not monitored, but is replenished in a set ratio to the nickel replenishment.

Automatic control systems on EN-plating baths result in a constant plating rate and a deposit having constant chemical and physical characteristics (Verhaeven, 1986, p. 20). These results stem from the tight controllability of the nickel and pH. The nickel concentration can be controlled within ±2 percent, while the pH is controlled to ±0.05 unit. Automatic controllers have several advantages: ability to keep accurate records of the life of the bath, removal of costly human errors during analysis and replenishment, consistent quality of nickel deposit, increase in bath stability, and increase in operating life of the bath (Kuczma, 1990).
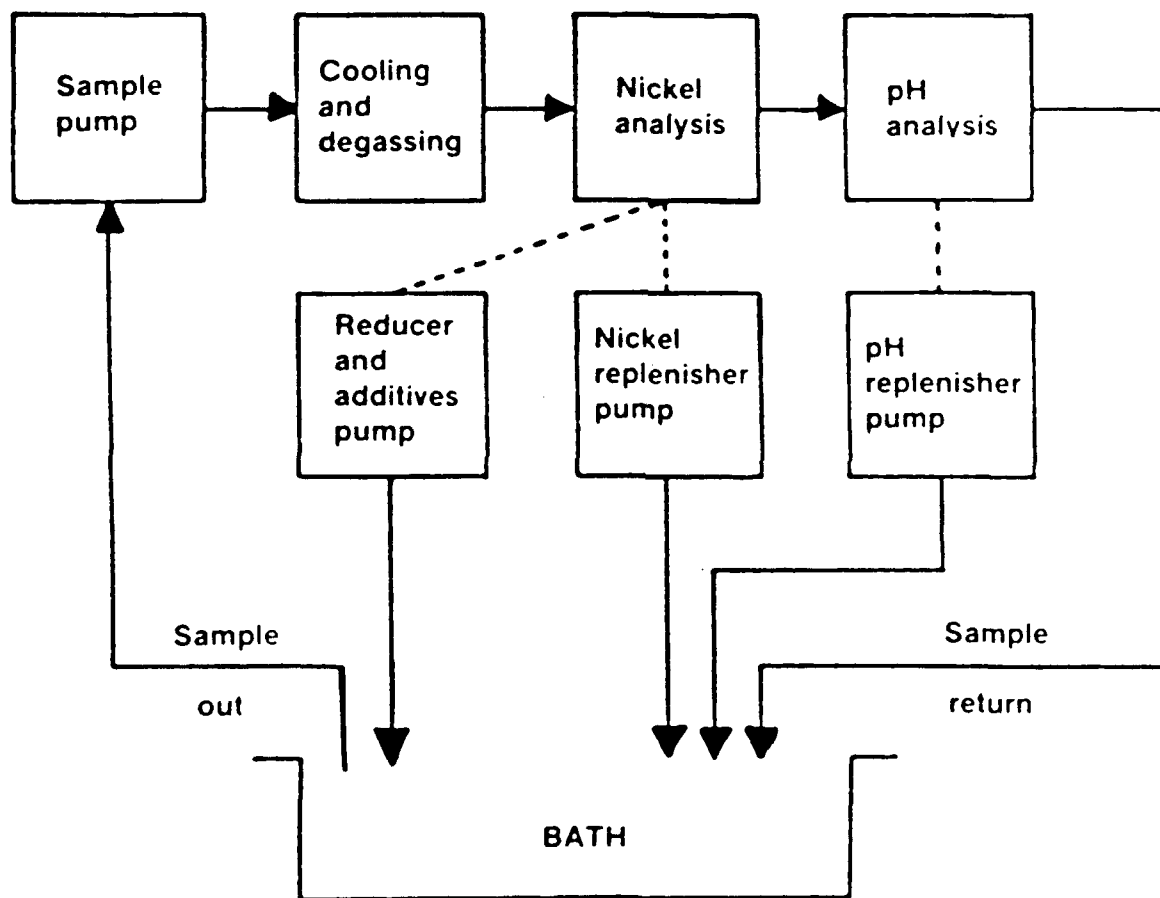
Sample pump

Cooling and degassing

Nickel analysis

pH analysis

Reducer and additives pump

Nickel replenisher pump

pH replenisher pump

Sample

out

Sample

return

BATH

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Figure 2-4.
Flow Diagram for Automatic Control of Electroless Nickel Solutions.

Source: Kuczma, 1990.

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3.0 Electroless-Nickel Operations at U.S. Army Depots

Site visits were conducted at the three Army depots that use EN plating: CCAD, RRAD, and SAAD (IT Corporation, 1991, 1992a, 1992b). The objective of these visits was to observe the EN processes and discuss current and potential waste minimization methods with depot engineers and plating operators. This section presents details of the EN process at each depot. Information regarding waste minimization processes is discussed in Section 4.

Table 3-1 presents a summary of the EN processes at the Army depots. This information is discussed in greater detail in the following paragraphs.

CCAD, RRAD, and SAAD use EN solutions supplied by McGean-Rohco, Allied-Kelite, and Enthone, Inc., respectively, as shown in Table 3-1. These solutions typically consist of three parts containing nickel, reducing agent, and additives (complexing agents and stabilizers) used for either makeup or replenishment. For example, at SAAD, Part A contains the nickel sulfate and complexing agents used for makeup, Part B contains the sodium hypophosphite for makeup and replenishment, and Part C contains the nickel sulfate for replenishment only. At CCAD, one part contains the nickel metal for makeup and replenishment, another part contains the chemicals other than nickel needed for solution makeup, and the third part contains the sodium hypophosphite needed for replenishment. Ammonium hydroxide is added separately to adjust the pH. The solutions at RRAD consist of parts for nickel, reducer/stabilizer/complexing agent/buffer, and pH control.

CCAD had previously used an Enthone solution (Enplate 419). The plating shop experienced problems with adhesion and switched to the current McGean-Rohco solution in 1988. Depot personnel noted that the chemistry of the Enthone solution was somewhat easier to maintain than the current system. The Enthone equipment was installed in 1985 and is still used with the McGean-Rohco solution.

As shown in Table 3-1, total volumes of solution are 50 gallons at CCAD, 90 gallons at SAAD, and 225 gallons at RRAD. The EN process at RRAD has not been operational for over a year and will not be reactivated until the concrete floor under the process equipment is replaced. If necessary, RRAD will operate a small-scale EN-plating process during the interim. The EN process is used primarily to coat steel parts at CCAD and RRAD, and aluminum

	CCAD	RRAD	SAAD
Vendor	McGean-Rohco	Allied-Kelite	Enthone, Inc.
Name of solution	Rohco Armor HB	NIKLAD 794	Enplate NI-415
Total nominal volume of EN solution	50 gallons	225 gallons[a]	90 gallons
Type of parts processed	Steel	Steel	Aluminum and steel
Tank composition	Polypropylene	Stainless steel with polypropylene lining	Stainless steel, with polyurethane lining
Temperature	185-190 F[b,c]	195°F[b] 180°F[c]	185-190°F[b] 180°F[c]
Target nickel concentration[d]	5.2 to 6.6 g/L	6 g/L	8.25 to 9.75 g/L
Target pH	4.7 to 4.9	4.5 to 5.2	4.5 to 4.8
Reducing agent	Sodium hypophosphite 30 g/L	Sodium hypophosphite 30 g/L	Sodium hypophosphite 27 to 30 g/L
Complexing agent	Proprietary	Proprietary	Acetic acid Propionic acid
Thicknesses plated	up to 10 mils	NA[e]	up to 100 mils
Agitation	Air	Air	Filter system
Plating rate	0.2 to 0.5 mil/hr	0.7 to 0.8 mil/hr	0.5 to 0.7 mil/hr
Type of filtration	5 µm bag	5 µm bag, 30 gpm	Cartridge type by Flo King® in bath
Control system	None	WalChem Control System Model WC-30	None
Frequency of analysis	1 to 2 times daily	Once per week	1 to 2 months[f]
Lab analytes	Ni, hypophosphite, pH	Ni, pH	Ni, P, pH
Frequency of passivation	2-3 days to 1 week[g]	Once per week[h]	Once per week[h]
Typical metal turnovers - aluminum[h] steel[h]	NA	5 to 6 7	4 to 6 7 to 8
Waste generation	160 gal/yr	225 gal/yr[i]	110 gal/yr
Unit disposal cost	$2.20/lb	$0.73/lb	$2.50/lb $0.60/lb[j]
Disposal costs	$3,517/year	$1,636/year	$2750/year $660/yr[j]
Chemical costs - Makeup/year	$507	$1,329	$1,064
Chemical costs - Replenishment/year	$535[k]	NA	NA

Table 3-1
(Page 2 of 2)

	CCAD	RRAD	SAAD
Plans for expansion	Larger plating tanks; expect work load to increase	Considering a new plating shop with separate room for EN plating	None
Waste minimization methods in use	- EN operations in separate room	- Transfers solution to cool tank at the end of each shift	- Cooling of bath at end of shift
	- Dust covers	- Filtration	- Cartridge filtration
	- Circulating solution to cool faster	- Dust covers	- Dust covers
	- Bag filtration	- Automatic controller	- Reduced inventory by using a blanket purchase agreement
	- Rinse filter bags		- Keep stock of chemicals low
	- Tests conductivity of DI water		- Evaporate solution down to 55 gallons
Location of operation	Separate room for EN	- Located in general plating shop	- Plating shop is next to painting and blasting operations

[a] RRAD EN process has not been operational for over a year.

[b] Vendor specifications.

[c] Estimated by depot personnel.

[d] 1 oz/gal ~ 7.5 g/L.

[e] NA = Not available.

[f] pH is checked daily. Additions may be made daily based on past experience.

[g] Depends on age of bath.

[h] Depends on workload.

[i] Information for 1988, the only year identified in waste tracking reports.

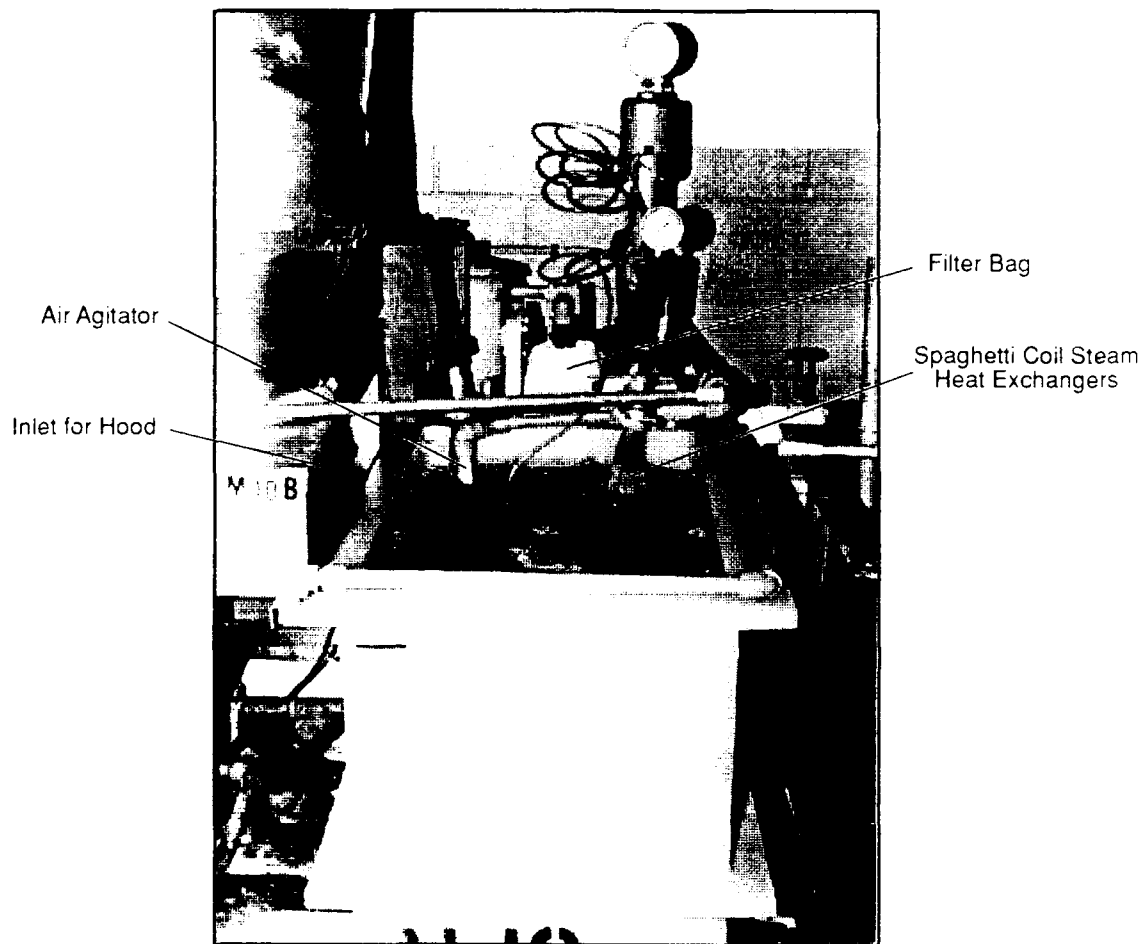[j] Lower contract price became effective in early 1992.

[k] Does not include costs for approximately 4.5 gal of ammonium hydroxide per year.

parts (with some steel) at SAAD. CCAD plates nickel coatings up to 10 mils thick, whereas SAAD sometimes plates up to 100 mils. At SAAD, the solution used can plate nickel smoothly up to a thickness of about 30 mils (1 mil = 0.001 inch = 25.4 μm). Application of thicknesses greater than 30 mils can result in roughness or spurs on the coating. If a thickness over 30 mils is required, the part is first plated up to 30 mils, machined down to a smooth surface, then plated with an additional 30 mils. This process is then repeated. SAAD has achieved coatings up to 100 mil thick by using this method. SAAD personnel indicated that they occasionally use other formulations for special applications such as heavy buildup or increased coating hardness. The specialty coatings, however, are more expensive and SAAD engineers indicated that they are satisfied with the performance of the general-purpose formulation currently in use.

All depots use a dual-tank arrangement for EN plating. CCAD uses a polypropylene tank, whereas RRAD and SAAD use stainless steel tanks with synthetic liners. The tanks at SAAD rest in two larger tanks that are partially filled with water; these tanks serve as secondary containment and as insulation for the solutions. Figures 3-1 and 3-2 are photographs of the EN tanks at CCAD and SAAD, respectively.

After a period of time, EN tanks become sensitized and amenable to nickel plate-out. To avoid this problem, the solution is typically transferred to a second tank, and the first tank is passivated with nitric acid. Each depot reported that the frequency of passivation is approximately once per week, depending on the workload. CCAD passivates its tanks every 2 to ?, days when a fresh solution is made up because the higher concentration of sodium hypophosphite used causes more rapid tank plate-out.

The SAAD EN operation takes place in the general plating shop, which is located near sandblasting and painting operations. Sand frequently enters the plating shop because of the negative pressure maintained in the building. During the depot visit, a layer of dust was observed on the floor and ventilation ducts. (Methods used to reduce and remove particulate contamination are discussed in Section 4.) The RRAD EN-plating process is also located in the general plating shop. Dust and dirt particulates frequently invade the plating area as a result of the negative pressure maintained in the building. By contrast, the EN-plating operations at CCAD are contained in a separate, negative-pressure room of the plating shop. This isolation

Air Agitator

Inlet for Hood

Filter Bag

Spaghetti Coil Steam
Heat Exchangers

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Figure 3-1.
EN Operation at CCAD.

Ventilation Hood

Cartridge Filters (Not in Use)

Hooks for Submerged Parts

Steam Lines for Submerged Heating Coil

Pump for Submerged Cartridge Filters

Figure 3-2.
EN Operation at SAAD.

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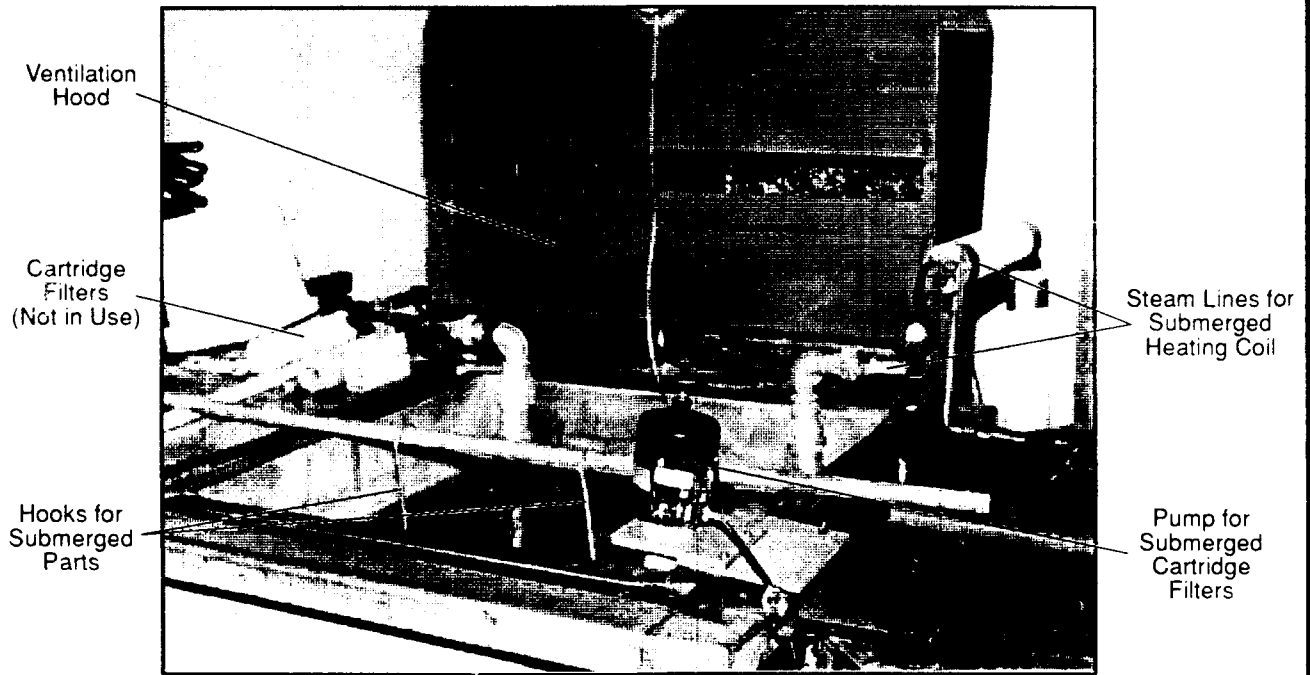
of the EN operations reduces contamination of the EN bath by airborne particulates and fumes.

Each depot uses sodium hypophosphite as the reducing agent at concentrations around 30 g/L. Target nickel concentrations are from 5.2 to 6.6 g/L at CCAD and 8.25 to 9.75 g/L at SAAD, and target pH values range from 4.5 to 5.2. Steam coils supply heat to the baths, which are typically operated at 180° to 195°F. CCAD and RRAD use air agitation and filtration with 5-µm filter bags. SAAD, however, uses a cartridge-type filtration system supplied by Flo King®; the agitation supplied by this filter system is sufficient to preclude the use of air agitation.

The frequency of laboratory analysis ranges from 1 to 2 times daily at CCAD to once every 1 to 2 months at SAAD. Additions are made after each analysis to keep the solution within specifications. SAAD personnel noted that additions are often made daily without the benefit of analysis based on experience regarding the average nickel-depletion rate. The analytes are typically nickel and pH; CCAD analyzes for hypophosphite and SAAD analyzes for phosphorus. Sodium hypophosphite and complexing agents are generally added in set ratios to nickel additions and are not analyzed for specifically. Ammonium hydroxide is used to adjust pH.

RRAD is the only depot currently using an automatic monitoring and control system. This system analyzes for nickel and pH, then adds nickel, hypophosphite (in a set ratio to the nickel addition), and ammonium hydroxide. The system has not been in use long enough, however, to have comprehensive data on the benefits achieved by the system.

All depots indicated a low rate of rejection for parts plated with the EN process. Parts at CCAD are rejected primarily because of problems in the pre-plating operations; for example, residual oil on parts sometimes contaminates the bath and causes problems in EN plating. Causes of defects at SAAD were cited as: inadequate zincate pretreatment, residual paint or smut on the part, or the fact that different grades of aluminum may react differently to the EN-coating process. SAAD personnel noted that most parts with defective coatings are caught by the operators; the part may then be ground down to remove the deformity, and the appropriate amount of nickel replated.

Vendor literature indicates that EN solutions used at Army depots typically last for four to six metal turnovers for aluminum processing, and seven to eight turnovers for steel processing. The depots dispose of the EN solutions when they cease plating (CCAD), or when they have reached the specified life span based on vendor recommendations and past experience (SAAD). The baths are typically disposed of about 1 (RRAD) to 3 (CCAD) times a year. Waste generation rates are 110 to 225 gallons per year per facility. The combined total for the three Army depots evaluated is approximately 495 gallons (4950 lb) per year.

Spent EN solutions are neither RCRA listed nor RCRA characteristic hazardous wastes. The RCRA criterion for a corrosive waste (D002) is pH less than 2 or above 12.5; EN solutions typically have a pH of 4 to 5. The State of California, however, regulates any substance containing more than 2000 ppm nickel as hazardous waste under Title 22, California Code of Regulations, Section 66261.24 (Characteristic of Toxicity). The Texas Water Commission regulates spent EN solutions as Class 1 industrial nonhazardous wastes because they contain more than 500 ppm total metals. This classification requires wastes to be manifested to Class 1 permitted treatment/disposal facilities. EN solutions at CCAD have been given the Texas Waste Code 142480, "nickel plating sludge."

Spent EN solutions generated at SAAD are usually combined with RCRA listed plating wastes and disposed of as F007 (spent cyanide plating bath solutions from electroplating operations). The EN waste is then disposed of as part of a bulk shipment rather than as a single 55-gallon drum. RRAD indicated that spent EN solutions are disposed of by the Defense Reutilization and Marketing Office (DRMO). As an option to off-site disposal, CCAD personnel are evaluating the feasibility of treating spent EN solutions in the IWTP. They have not yet completed their treatability evaluation or an assessment of regulatory considerations.

Disposal costs currently are $0.60/lb at SAAD, $0.73/lb at RRAD, and $2.20/lb at CCAD (the density of an EN solution is approximately 10 lb/gal). Disposal costs at SAAD were recently reduced from $2.50/lb to $0.60/lb, a 76 percent reduction, as a result of a change in disposal contractors. As shown in Table 3-1, these unit costs result in total waste disposal costs of $660/yr (SAAD at the new contract rate) to $3,517/yr (CCAD).

Data were also collected, where available from the vendors and depots, on chemical makeup and replenishment costs. Makeup costs ranged from $507/yr (CCAD) to $1,329/yr (RRAD). The only costs for replenishment chemicals were obtained from CCAD at $535/yr.

The depots have experienced increases in the use of EN over the past few years. CCAD expects its work load to increase because of recent Depot Maintenance Work Requests (DMWRs) that allow the depot to use EN rather than the chromium required in older DMWRs. This depot is also beginning to process Black Hawk helicopters, which contain some EN-plated parts. A cadmium finish on one type of part was recently replaced with an EN coating since the EN process coats recesses more effectively. Because of the expected increase in EN use, long-term plans include installation of larger EN tanks in the plating shop. Electroless nickel has been used as a replacement for some chromium plating at RRAD, and depot personnel are considering constructing a new plating shop with a separate room for EN plating. SAAD has also experienced increased EN use, but currently does not have plans for expansion.

Waste minimization methods in use at the depots are listed in Table 3-1. These methods are discussed in greater detail in Section 4. To reduce the disposal volume, SAAD evaporates the EN solution from 90 gallons down to 55 gallons. Also at SAAD, EN solutions are purchased under a blanket purchase agreement (BPA). Under this system, certain electroplating personnel can place orders as needed, rather than ordering in bulk. Because of the one-year shelf life of the solutions, ordering in bulk may lead to quantities of chemicals that are no longer useful when a fresh solution is first made up. By using the BPA, SAAD minimizes waste from the disposal of excess and expired stock.

4.0 Waste Minimization and Decontamination Methods

This section presents a description of waste minimization methods in use at Army depots and currently being developed by industry for EN-plating solutions. The scope of this report focuses primarily on decontamination methods; however, other waste minimization methods are discussed briefly for completeness.

Waste minimization methods pertaining to EN plating can be divided into three distinct areas:

- Chemistry considerations/proper maintenance
- Prevention of contamination
- Decontamination technologies

Each of these areas will be discussed separately in this section.

Many components of EN solutions sold today are proprietary. A facility considering implementing the methods in this report, therefore, should always consult with the vendor of the solution to determine if a particular technique is suitable for the bath chemistry.

4.1 Chemistry Considerations

The selection of a proprietary solution that is suitable for a particular application is the first step in ultimately preventing waste generation. Vendors contacted during this project often indicated that they sell solutions that achieve from three to fifteen metal turnovers. A metal turnover is achieved when an amount of nickel equal to the amount in the initial solution has been plated. Some companies specifically target longer bath life as a marketing concept. Longer bath lives and better stability are achieved by selecting complexing agents that have higher tolerances for orthophosphite and metal contaminants.

As orthophosphite increases, it begins to negatively affect the coating properties by increasing stress and decreasing corrosion resistance. (One reference, however, suggested that the negative effect on these properties resulted from the buildup of sodium and sulfate ions rather than orthophosphite ions.) Increasing bath life by merely extending orthophosphite solubility (as opposed to removing the orthophosphite) may not produce the desired coating for a critical application where low internal stress and high corrosion resistance are desired. A balance thus exists between bath life and certain desirable coating properties. Therefore, EN solutions

designed for critical applications (such as electronics) are often advertised as short-life solutions because they must be disposed of after only a few turnovers to achieve consistently good plating quality. EN solutions designed for applications where the impact of orthophosphite on coating quality is not as important are advertised as long-lived solutions.

As an example of bath selection, a contact with Enthone indicated that the solution currently used at SAAD was developed about 15 years ago (Vignati, 1992). Since then, Enthone reports that they have developed solutions that provide longer bath lives and are more suitable for the application at SAAD. According to this contact, the depot could achieve significantly longer bath lives simply by purchasing a solution that is better suited to meet current EN-plating needs. SAAD engineers, however, noted that the EN solution performs well as a general-purpose formulation, the EN operators have extensive experience with the solution, and the solution is less expensive than specialty formulations that SAAD occasionally purchases for applications such as heavy buildup or increased hardness.

Once bath selection is made, maintenance of the proper chemical balance is important to maintain bath stability and prevent the bath from becoming prematurely inoperative. As discussed in Section 2, concentrations of nickel, reducing agent, hydrogen ions, complexing agents, and stabilizers must be maintained in the proper balance to give good coating quality, bath stability, and deposition rate. Effective bath maintenance requires frequent bath analyses and replenishments to keep bath parameters within the acceptable narrow range. Small, frequent additions are more desirable than large, infrequent additions as they avoid shocking the bath and result in more consistent solution and deposit qualities. Section 2 also discussed the effect of orthophosphite on solution chemistry. For example, increasing the concentrations of hydrogen ions and complexing agents will increase orthophosphite solubility, thereby increasing the length of time before the bath becomes unstable and requires disposal.

Automatic monitoring and chemical replacement equipment has the ability to control the chemistry within a narrow range, depending on the frequency of analysis and replenishment, thereby providing more consistent solution and coating quality. The use of properly calibrated automatic control equipment also has the advantage of reducing human error. An additional advantage of automatic controllers is that records of analyses and additions can be kept to provide statistical process control data and to develop a better understanding of bath chemistry and life (e.g., how many metal turnovers are typically achieved).

One reference claims that operating experience has shown that automatic control may increase bath life as much as 50 percent (Verhaeven, 1986). An industry contact said that a large electronics company increased bath life from 2 months to 1 year by implementing automatic control equipment (Croly, 1991). Additions were made to the bath every 2 hours, compared with once a week when analyses were performed manually. The payback period for the equipment was less than a year.

RRAD is the only depot whose EN process is currently equipped with automatic control. The system analyzes nickel and pH and makes adjustments for these parameters. A solution containing the reducer replenishment is added at a set ratio to the nickel replenishment. The control unit has not been in operation long enough, however, for RRAD to obtain any data on the benefits achieved by the use of this equipment.

Troubleshooting charts have been published in the literature to allow identification of a problem, its possible source, and its remediation. In this manner, it may be possible to "save" an EN-plating bath by various techniques rather than disposing of it as a waste. At the very least, application of these troubleshooting charts may allow a problem to be identified so that its cause can be prevented in the future. Table 4-1 presents a troubleshooting chart from one literature source (Aleksinas, 1990).

4.2 Contaminant Prevention

The philosophy of waste minimization suggests that prevention of contamination is generally preferable to removal of contamination after it has occurred. This is analogous to the prevention of waste generation being preferable to the treatment of waste once it has been generated. Depots have taken a number of steps to prevent EN solutions from becoming contaminated.

EN-plating operations at Army depots are typically located in the general plating shop, where they can be exposed to airborne contamination, including organic compounds and dust. The SAAD EN operation is located in a negative-pressure building, which is located next to sandblasting and painting operations. During site visits, both SAAD and RRAD had noticeable accumulations of dust on pipes and the ventilation ductwork near the EN operations. On the other hand, the CCAD EN operation is located in a negative-pressure room separate from the plating shop.

Table 4-1
Troubleshooting Guide for Electroless Nickel[a]
(Page 1 of 3)

Problem	Probable Causes	Suggested Remedy
Poor adhesion and/or blistering	1) Improper surface conditioning 2) Poor rinsing 3) On aluminum, poor zincating 4) Metallic contamination 5) Organic contamination 6) Reoxidation 7) Improper heat treatment	1) Improve cleaning and pickling time 2) Improve rinse and transfer time 3) Analyze and correct zincating solution 4) Dilute or dummy plate solution 5) Carbon treat solution 6) Reduce transfer times 7) Correct time and/or temperature of heat treatment
Roughness	1) Suspended solids 2) Improper cleaning 3) Too high pH 4) Drag-in of solids 5) Contaminated liner or filter cartridges 6) Inadequate nickel chelation 7) Contaminated water supply	1) Filter solution and locate source of solids 2) Improve cleaning and rinsing 3) Lower pH 4) Improve rinsing, clean rinse tanks 5) Leach tanks and filters prior to use 6) Reduce drag-out, check replenishment cycles 7) Use deionized or distilled water
Pitting	1) Suspended solids 2) Excess loading 3) Organic contamination 4) Metallic contamination 5) Poor agitation	1) Improve filtration 2) Reduce workload, lower pH 3) Carbon treat solution 4) Dummy plate 5) Improve agitation, work rod preferred
Dullness	1) Too low temperature 2) Too low pH 3) Low nickel or hypo concentration 4) Metallic contamination 5) Organic contamination 6) Aged bath	1) Raise temperature 2) Raise pH 3) Check and correct 4) Dummy plate 5) Carbon treat 6) Replace with new bath

TABLE 4-1 (Page 2 of 3)

Problem	Probable Causes	Suggested Remedy
Patterns/streaking	1) Poor agitation	1) Improve agitation
	2) Poor surface preparation	2) Improve and correct cleaning cycle
	3) Metallic contamination	3) Dummy plate
	4) Surface residue	4) Improve rinsing, minimize silicate drag-in
	5) Gas patterns	5) Reposition work, increase agitation
Step/skip plating	1) Metallic contamination	1) Dummy plate
	2) Substrate effect (i.e., leaded alloy)	2) Copper or nickel strike prior to plating
	3) Bath overstabilized	3) Dummy plate or dilute bath
Low deposition rate	1) Low temperature	1) Increase operating bath temperature
	2) Low pH	2) Raise pH
	3) Low nickel or hypo content	3) Analyze and correct
	4) High orthophosphite content	4) Discard all or part of bath
	5) Too small a workload	5) Increase workload or reduce agitation
	6) Overstabilization	6) Dilute or dummy bath
Instability	1) Bath temperature too high	1) Lower temperature
	2) Too high pH	2) Lower pH
	3) Localized overheating	3) Locate and correct
	4) Improper passivation of tank	4) Improve passivation solutions and times
	5) Airborne contamination	5) Clean area of dust and loose dirt
	6) Drag-in of catalytic metals	6) Improve rinsing
	7) Large additions made of replenishers	7) Use more frequent additions to maintain consistent stabilizer concentration
No deposition	1) Overstablization	1) Dilute bath, avoid large additions of replenishers
	2) Improper substrate surface	2) Substrate may not be auto-catalytic and require a nickel or copper strike, i.e., stainless steel, copper
	3) Too low temperature or pH	3) Analyze and correct
	4) Metallic contamination	4) Electrolytically dummy solution

TABLE 4-1 (Page 3 of 3)

Problem	Probable Causes	Suggested Remedy
Dark deposits	1) Contaminated rinse after EN 2) Improper surface preparation 3) Too low pH and/or temperature 4) Low bath activity 5) Organic contamination	1) Improve rinsing 2) Improve pretreatment 3) Check and correct 4) Analyze bath constituents and correct 5) Carbon treat
Rapid pH changes	1) Drag-in of pretreatment 2) Excessive workload 3) Bath not at proper pH range	1) Improve rinsing 2) Reduce workload and check plate-out on tank and heaters 3) Check pH and adjust to optimum buffered range
High nickel usage	1) High drag-out 2) Bath decomposition 3) Plating on tank and equipment 4) High surface area	1) Reduce drag-out with replacement of stagnant rinse after plating tank 2) Cool and filter solution 3) Filter solution and strip tank and heaters 4) Reduce workload size
Cloudy plating solution	1) pH too high 2) Drag-out losses excessive 3) Under-complexed solution	1) Lower pH with dilute sulfuric acid or hydroxyacetic acid 2) Reduce sources of drag-out losses. Add more make-up additive 3) Add more make-up additive

[a] Reprinted with permission from *Electroless Plating: Fundamentals and Applications*, Glenn O. Mallory and Juan B. Hajdu, editors. American Electroplaters and Surface Finishers Society, 12644 Research Parkway, Orlando, Florida 32826-3298. Reference Aleksinas, 1990.

All three depots use dust covers on the EN tanks when not in operation to help prevent airborne contamination. Ideally, an EN tank should be isolated from other operations by locating the EN tank in a separate, positive-pressure room. SAAD personnel are considering an air lock to the plating shop to reduce airborne contamination entering from outside. Another method of preventing contamination is prevention of drag-in from other solutions and rinse waters. In one case at CCAD, the EN solution became contaminated by drag-in of copper from the nickel strike pretreatment operation. Personnel estimated that this particular solution achieved only 1.5 metal turnovers before requiring disposal (compared with a typical five to six turnovers). Improved rinsing and more attention to this source of contamination could prevent waste generated as a result of contamination by drag-in.

Other sources of contamination can include the water supply, air used for agitation, improper cleaning, or even filter bags. Water should be deionized or distilled and should be checked periodically. At CCAD, the deionized water is tested for conductivity before being added to the bath to ensure that it is free of contamination. Air used for agitation must be filtered. New filter bags used at CCAD were previously not rinsed before use. Personnel noted residue on the filter bags that could potentially contaminate the tank, and bags are now rinsed before use.

As discussed in Section 2, the electrochemical plating reaction rate is an exponential function of the absolute temperature, with a very low plating rate below 140°F. When parts are being plated, the plating rate is an important process parameter, and EN solutions are typically operated in the range of 185° to 205°F. When parts are not being plated, however, operational temperatures can catalyze continuing electrochemical reactions, causing solution degradation and plate-out on tank walls, filters, and other equipment or particulates in solution. This in turn leads to depletion of nickel and hypophosphite and a buildup of orthophosphite ions (and ultimately premature bath disposal and waste generation).

Because of the relationship of plating rate to temperature even when no parts are being processed, minimizing the amount of time the bath is maintained at elevated temperatures should decrease the extraneous depletion of nickel and reducer and the buildup of orthophosphite. Figures 4-1 through 4-3 demonstrate this phenomenon.
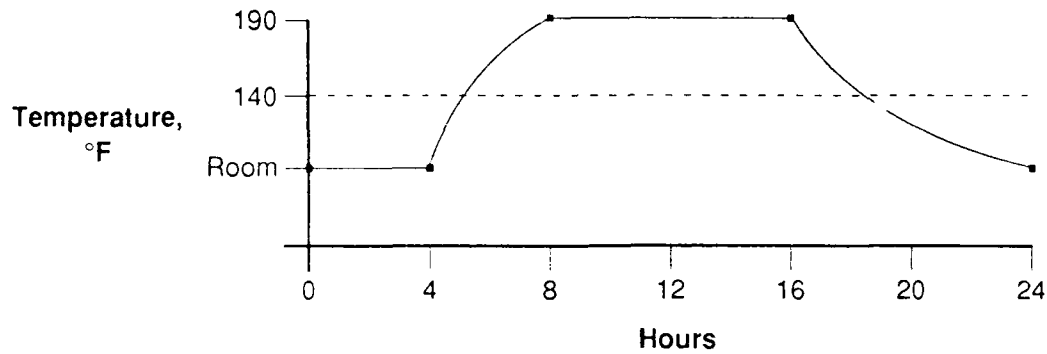
Figure 4-1.
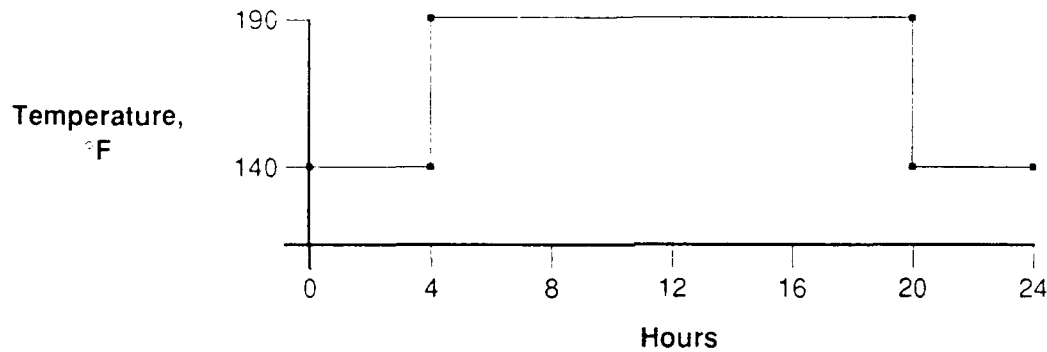Temperature Profile for a
Hypothetical EN Solution.

Figure 4-2.
Temperature Profile for an EN
Solution with Maximum Time at
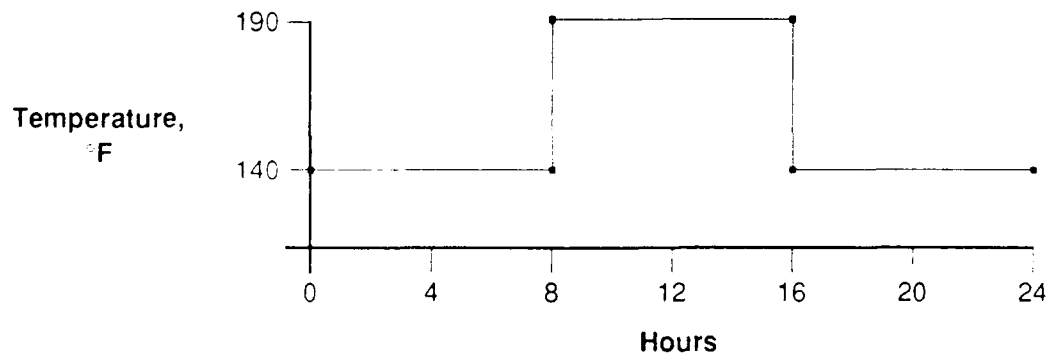Operating Temperature.

Figure 4-3.
Temperature Profile for an EN
Solution with Minimum Time at
Operating Temperature.

Figure 4-1 presents a theoretical temperature profile of a tank that is operated at a temperature of 190°F for an 8-hour shift. The graph shows the solution being heated from room temperature to operating temperature for the 4 hours prior to the beginning of the shift. After the shift is over, the temperature of the solution decreases to ambient temperature. The bath can potentially plate whenever the temperature is above 140°F. Figure 4-2 shows an ideal situation in which heating and cooling are instantaneous operations at the extreme points on the graph (i.e., at 4 hours when the steam is first turned on and at 20 hours when the bath has cooled to below 140°F). The area under this curve is proportional to the maximum amount of plating and represents the maximum rate of orthophosphite buildup. This method assumes that the nickel concentration remains above 5 g/L throughout the time period; at greater concentrations, the reaction rate is generally independent of nickel concentration. The effect of available surface area on the reaction rate has also been neglected. Because in reality parts are not being plated during heating and cooling, heating and cooling are not instantaneous processes, and heating and cooling do not occur over 4 hours, this scenario tends to overstate the rate of solution depletion. Because the purpose of this figure is to present the maximum possible depletion rates, these assumptions are justified.

Figure 4-3 shows the ideal temperature profile assuming heating and cooling are instantaneous exactly at the beginning and ending of the shift (i.e., at 8 and 16 hours). The area under this curve is again proportional to the plating rate and orthophosphite buildup. The curve represents the minimum amount of plating and orthophosphite increase.

By comparing Figures 4-2 and 4-3 in this example, it can be seen that the maximum depletion rate (Figure 4-2) is twice the minimum depletion rate (Figure 4-3). The difference between the two represents the maximum opportunity for reducing nickel and hypophosphite depletion, orthophosphite buildup, and ultimately, waste generation. Specifically, using the assumptions in this example, bath life could be extended by a factor of up to two by minimizing the time that the bath temperature exceeds 140°F.

All three depots visited during this project have implemented simple procedures to cool their EN baths quickly. At CCAD, the steam is turned off at the end of the shift, but the pump is kept on to circulate the solution until the temperature reaches 150°F. The circulation increases heat transfer and the rate of cooling. Depot personnel indicated that the solution cools from operating temperature to 150°F in about 2 hours.

At RRAD, the EN-plating solution is transferred from the hot tank in use to an empty tank at the end of each shift, thereby using the heat absorption by the cooler tank to cool the solution more quickly. This method also avoids heat transfer from steam remaining in the heat exchanger.

At SAAD, a cooling coil was added to lower the temperature of the bath at the end of the work day in 20 to 40 minutes rather than the 3 hours required previously. Figure 4-4 presents a photograph of the cooling coil (shown in a rinse tank). By this technique, SAAD staff indicated that bath life increased from an average of 2 to 4 weeks to 6 to 8 months, even though bath usage has increased. This increase in bath life is significantly longer than the theoretical maximum presented in the above example; the cause for this discrepancy is unknown. (Depot engineers indicated that no other operating changes have occurred that might contribute to the observed increase in bath life.) Currently, SAAD personnel are evaluating the use of a portable chiller to cool the EN solution even more quickly.

Although SAAD had tried using a Freon cooling system for the EN solution, this method resulted in leaks and lengthening of the time required to heat the EN solution to the operating temperature.

Another potential method for reducing the amount of time the bath spends at elevated temperatures is to increase the heating rate between 140°F and operating temperature. A higher heating rate would require additional heat exchanger surface area. According to SAAD personnel, the amount of time the EN bath spends between these temperatures, however, is relatively short compared with the overall processing time; the opportunity for bath life extension may be small.

4.3 Orthophosphite Decontamination Techniques

This section describes decontamination techniques that target removal of orthophosphite from EN solutions. Orthophosphite buildup is generally considered to be the limiting factor in the life of EN solutions. These techniques were identified during the literature search and through contacts with EN vendors.
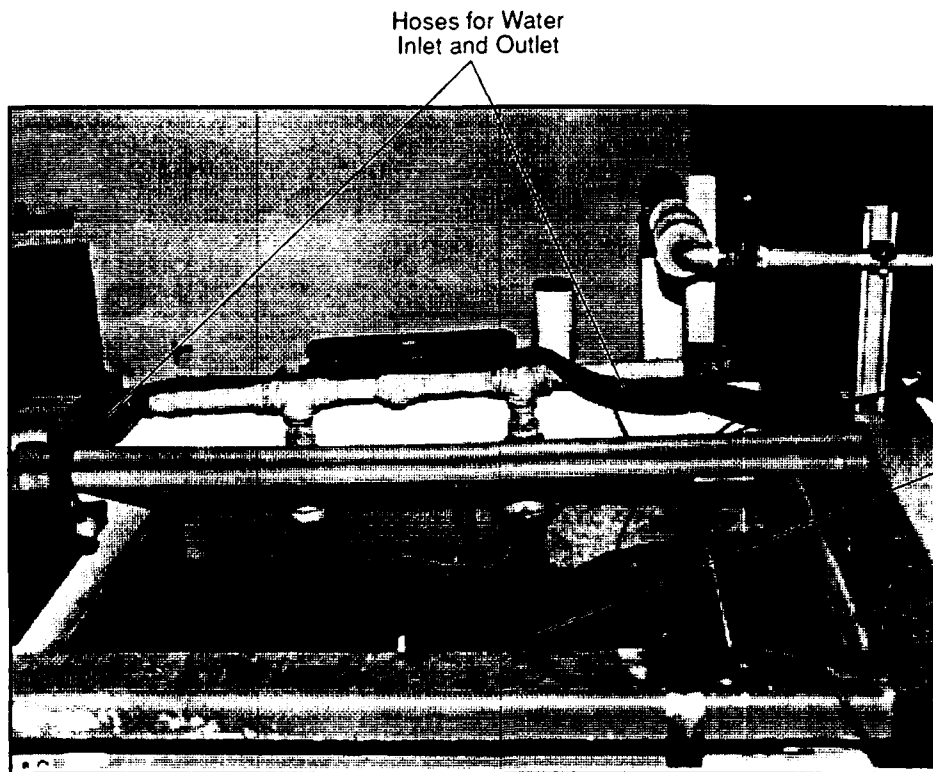
Hoses for Water
Inlet and Outlet

Cooling Coil
(Partially
Submerged)

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Figure 4-4.
CoolingCoil at SAAD.

4.3.1 DOE Oak Ridge Laboratory - Martin Marietta Energy Systems, Inc.

Martin Marietta Energy Systems, Inc., in Oak Ridge, Tennessee, is currently developing a process, called ENVIRO-CP, for the Department of Energy (DOE) to rejuvenate EN-plating baths (Anderson, 1991; Palmer, 1992; Neff, 1992). The DOE researchers have applied for a patent on this process; the U.S. Government will hold the rights to this invention. The DOE has authorized Martin Marietta to enter into Cooperative Research and Development Agreements with private industry and government agencies to further develop this process. A company contact indicated that one cooperative agreement has been reached with a major EN supplier.

The goals of this process are to recover the valuable bath constituents (e.g., nickel and reducing and complexing agents) and to remove reaction by-products and other contaminants (e.g., orthophosphite ions, sodium ions, sulfate ions, and other metal ions) that have harmful effects on the EN-plating process. The useable bath components are recovered relatively free of the contaminant materials and are recycled back to the EN-plating bath.

The process consists of cation exchange columns and precipitation and evaporation processes. Figure 4-5 is a general block diagram of the basic steps of the process. The process is isolated from the EN plating bath by reservoirs so that the process may be operated continuously or periodically, as needed.

The developers used a nonproprietary, traditional EN solution feed to the process in laboratory testing. This EN solution composition was first described in U.S. Patent 2,822,294 (Gutzeit, 1958). It contained a lead concentration of 0.2 ppm, a hypophosphite concentration of 0.22 mol/L (14.3 g/L), a phosphite concentration of 1.2 mol/L (96.0 g/L), a nickel concentration of 0.082 mol/L (4.8 g/L), a lactate concentration of 0.48 mol/L, a sulfate concentration of 1.3 mol/L, and a sodium concentration of 4.2 mol/L. The pH of the solution was 4.5 and its temperature was 95°C. Laboratory testing was performed in a 4-inch-i.d. glass column filled with 9 liters of 8 percent divinylbenzene, cross-linked polystryene resins having sulfonic acid exchange groups.

4.3.1.1 Process Description

A portion of the EN-plating solution passes through a heat exchanger to reduce its temperature to ambient conditions (20°C) prior to being placed in a holding tank. This cooled
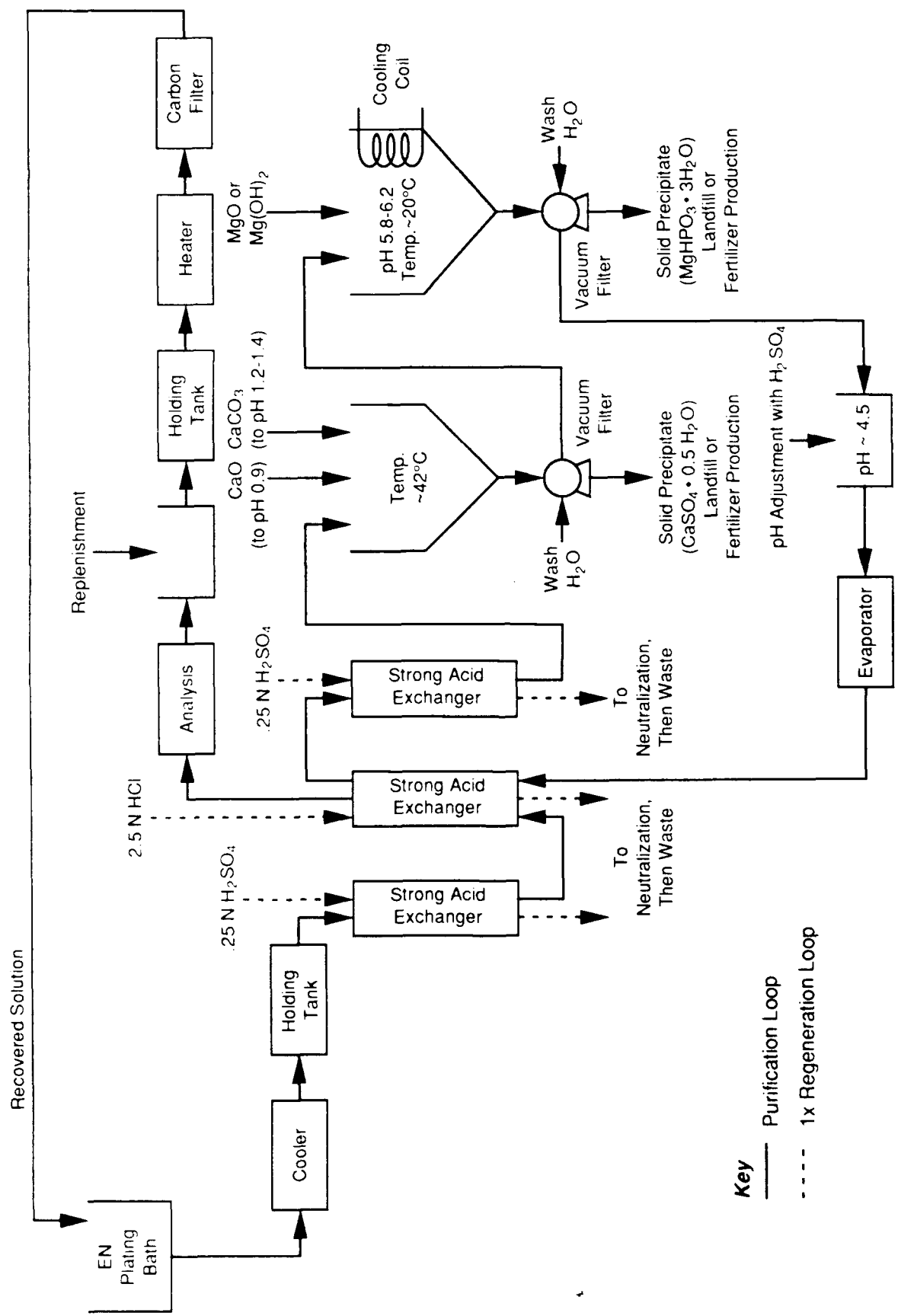
4-12

Figure 4-5.
DOE/Martin Marietta EN
Purification Process.

Key
— Purification Loop
- - - - 1x Regeneration Loop

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solution is fed to the acid cation exchangers to remove sodium and nickel cations. Strong or intermediate acid exchangers can be used. Currently, the strong acid exchanger alone is being researched at Oak Ridge and will be the focus of this subsection. The nickel and sodium cations displace the hydrogen ions and are thus sorbed on the resin. The strong resin used in the process can be Rohm and Haas' Amberlite IR120 in hydrogen form with sulfonic acid functional groups, or similar.

Three strong acid exchangers are used in series, as shown in Figure 4-5. Multiple exchange units are used to aid in the distribution of the nickel and sodium ions. The first of the exchangers substantially strips the solution of the sodium cations. As the bath continues through the second exchanger, the nickel is sorbed. Typically, the nickel will be sorbed in a small band within the second exchanger. The solution then passes through the third exchanger to remove residual cations. This distribution of cations within the series of exchangers occurs because the sodium cations are essentially uncomplexed by sulfate and lactate in the bath solution and the hydrogen ion concentration is not strong enough to prevent sodium sorption. As the pH decreases, the nickel cations become uncomplexed and are sorbed within the exchangers. After almost complete removal of the nickel and sodium cations in the ion exchanger, the concentration of all of the other constituents remains essentially the same and the pH decreases to about 0.35. A distilled water wash of the columns is required to assure complete removal of hypophosphorous, phosphorous, lactic and sulfuric acids, as well as wetting agent and complexed lead.

Once the majority of the cations have been removed by the cation exchangers, the solution is fed to a precipitator. The solution is treated with calcium oxide (CaO) to adjust the pH of the solution to 0.9. The temperature rises to about 42°C because of the heat of reaction from the addition of the calcium oxide. This treatment is followed by the addition of calcium carbonate ($CaCO_3$) to adjust the pH to the range of 1.2 to 1.4. The calcium carbonate addition enhances precipitation and prevents pH overshoot. The addition of these calcium salts results in the precipitation of calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$). This precipitate is washed with distilled water to remove the mother liquor, and the wash water is added to the filtrate solution. After washing, the researchers claim that this precipitate can be landfilled as non-hazardous waste or used in fertilizer production.

The effluent filtrate from the calcium sulfate precipitation process is fed to a second precipitation process, where the solution is treated with magnesium oxide (MgO) or magnesium hydroxide [Mg(OH)$_2$]. The magnesium salt is added until a stable pH of 5.8 to 6.2 is achieved. A cooling coil is used to keep the bath temperature at approximately 20°C to assure the precipitation of magnesium phosphite trihydrate (MgHPO$_3$•3H$_2$O). At higher temperatures, magnesium phosphite monohydrate (MgHPO$_3$•H$_2$O) can be precipitated and cause the undesirable occlusion of nickel ions in the precipitate. Also at higher temperatures, nickel metal can spontaneously form, thus causing a loss in nickel and hypophosphite from the solution. Seed crystals of the magnesium phosphite trihydrate are added to decrease the occlusion of the mother liquor and to improve filtration and washing characteristics of the solid. This precipitate is also washed with distilled water, and the resulting wash water is added to the filtrate solution. Once the precipitate is washed, the researchers claim it can also be used in fertilizer production or landfilled.

The researchers noted that their process would not reduce concentrations of organic acids used as complexing agents (e.g., lactic, citric, and malic acids). They also note that some loss is allowable because excess complexing agents may have been added to the bath to increase orthophosphite solubility.

Approximately 34 cm^3 of CaSO$_4$•0.5 H$_2$O sludge and 98 cm^3 of MgHPO$_3$•3H$_2$O sludge per mil•ft^2 of nickel coating were generated during testing. These generation rates were based on batch treating a bath that had been used for 5.6 metal turnovers. The researchers indicate that these sludges do not exhibit the RCRA characteristic of TCLP toxicity and therefore are non-hazardous. Table 4-2 presents TCLP toxicity data supplied by Martin Marietta.

The effluent filtrate from the magnesium salt precipitator is adjusted to the EN-plating bath pH of approximately 4.5 with sulfuric acid to prevent the possibility of reduction of nickel ions to metallic nickel during the elevated temperatures of evaporation. This solution is then subjected to evaporation to decrease the volume by about 35 percent. Evaporation is required since the solution has been diluted from the wash water of the two precipitates. The researchers believe that the extra water added during the precipitate wash steps could be balanced by the evaporation that will occur from the EN bath at the operating temperature. After evaporation, the concentrations of the constituents in the solution are approximately

0.1 M magnesium hypophosphite, 0.25 M magnesium lactate, 0.14 M magnesium orthophosphite, and 0.08 M calcium sulfate.

Table 4-2
TCLP Extract Data for Sludges Generated by the
DOE/Martin Marietta Process
(mg/L in extract)

Constituent	Regulatory Limit[a]	Sludges	
		$CaSO_4 \cdot 0.5\ H_2O$	$MgHPO_3 \cdot 3H_2O$
Arsenic (As)	5.0	<0.50	<0.50
Barium (Ba)	100	<1.0	<1.0
Cadmium (Cd)	1.0	<0.03	<0.03
Chromium (Cr)	5.0	<0.10	0.11
Lead (Pb)	5.0	<0.50	<0.50
Mercury (Hg)	0.2	<0.002	<0.10
Nickel (Ni)	-	<0.50	1.1
Selenium (Se)	1.0	<0.50	<0.50
Silver (Ag)	5.0	<0.10	<0.10

[a] 40 CFR 261.24, effective September 25, 1990.

Once concentrated, the solution can be used to displace the nickel cations from the cation exchanger containing the narrow band of nickel cations with magnesium and calcium cations. This results in the concentrations of the constituents in the solution to be approximately 0.082 M nickel sulfate, 0.2 M sodium hypophosphite, 0.5 M sodium lactate, 0.2 M sodium orthophosphite, and 0.2 M sodium sulfate. Using the concentrated solution, however, loads the exchanger with calcium and magnesium cations that must be displaced with hydrochloric acid solution. The concentration of hydrochloric acid solution used is 2.5 N at a rate of 1 cm³/min/cm². This effluent must also be neutralized before discharge or collected as waste.

Alternatively, a 2-M sulfuric acid solution or 1.3 M magnesium sulfate solution can be used to displace the nickel ions with hydrogen or magnesium cations, respectively. The resulting solution contains nickel ions as nickel sulfate and is concentrated by evaporation to a nickel concentration of about 0.4 M. It is then added to the original process solution.

After reclaiming the nickel ions from the cation exchanger, the solution contains nickel, hypo-phosphite, complexing agents, stabilizer, and anti-pit surfactant. This solution is analyzed for these constituents and replenished to the original bath composition. The solution is then reheated to the bath temperature, carbon filtered to remove any organic contaminants, and returned to the plating tank.

The other two cation exchangers that contain the sodium ions are regenerated separately from the nickel-ion-containing exchanger. Sodium is removed from these exchangers by feeding dilute sulfuric acid at a concentration of 0.25 N and at a rate of 4 cm³ per minute per cm² of resin area. This acidic effluent contains the exchanged sodium ions and must be neutralized before discharge or collected as waste.

4.3.1.2 Experimental Data

Table 4-3 presents a summary of experimental data collected at various points in the treat-ment process. These data are from treatment of 4.4 liters of an EN solution containing an amount of sodium plus nickel ion gram-equivalents corresponding to about 70 percent of the resin exchange capacity. Approximate amounts of chemicals needed for the 4.4 liters of solution were 100 g of calcium oxide, 90 g of calcium carbonate, and 199 g of magnesium oxide. As shown in this table, the phosphite concentration was reduced from 1.2 to 0.20 M, sulfate was reduced from 1.3 to 0.20 M, and sodium was reduced from 4.2 to 1.3 M. The researchers report that sodium is reduced to negligible amounts by treatment with ion ex-change. The final sodium in solution results from passage of the solution through a final ion exchange column to remove calcium and magnesium ions.

Table 4-3
Experimental Data for DOE/Martin Marietta EN Purification Process

	Feed	After Ion Exchange	After Precipitation and Filtration	Reju-venated
pH	4.5	0.35	5.8-6.2	4.5
Lead	0.2 ppm	0.28 ppm	-	-
Hypophosphite	0.22 M = 14.3 g/L	-	0.2	0.2
Phosphite	1.2 M = 96.0 g/L	-	0.28	0.20
Nickel	0.082 M = 4.8 g/L	<0.0008 M	-	0.082
Lactate	0.48 M	-	0.50	0.50
Sulfate	1.3 M	-	0.08	0.20
Sodium	4.2 M	-	-	>1.3

Experimentation during the development of this process by Martin Marietta revealed an increase in the plating rate of the EN bath from 0.29 to 0.76 mil per hour. The quality of the EN plate was found to be good without significant inclusion of either calcium or magnesium in the deposit. The researchers did not expect to obtain such good plating rates and plating quality because of the presence of calcium and magnesium ions in the EN solution. These metal ions are usually considered to interfere with the EN plating mechanism, causing the formation and precipitation of insoluble compounds, and causing rough, hazy, and pitted deposits (Aleksinas, 1990).

Since these results were obtained using the traditional EN bath, laboratory tests have been performed on other proprietary solutions. The DOE researchers indicate that the results have been favorable in terms of removing orthophosphite and increasing plating speed.

4.3.1.3 Cost Data

Cost information provided by Martin Marietta is summarized in Table 4-4. The estimated capital cost for a fully automated system on a 100-gallon EN tank is $25,000, but this figure is only preliminary. The researchers indicated that many unknowns will affect the final system cost, including the costs of automation.

4.3.2 Stapleton Company - INFINITY EN Process

The Stapleton Company, located in Long Beach, California, is currently marketing a purification system (under the name INFINITY) that continually removes chemical by-products from EN-plating solutions (Stapleton 1991, Stapleton 1992). This system includes a special set of purified chemicals to be used with the purification unit so that contaminants such as sodium and sulfates are not introduced into the bath.

The purification process equipment is available in two models: PU1 and PU2. The PU1 model is a fully automatic unit for plating tank volumes from 100 to 2000 gallons, while the PU2 model requires some manual additions and is for smaller volumes (50 to 500 gallons).

4.3.2.1 Bath Chemistry

The chemistry of the INFINITY EN bath is an integral part of the Stapleton Process. The key concept to the chemistry is that nickel hypophosphite $[Ni(H_2PO_2)_2]$ is used as the source of both nickel and hypophosphite ions. This method bypasses the use of nickel sulfate and

Table 4-4
Preliminary Cost Information for the
DOE/Martin Marietta EN Purification Process[a]

Current Disposal Methods	$/mil-sq.ft	DOE/Martin Marietta ENVIRO-CP Process	$/mil-sq.ft.
Chemicals for makeup solution	0.58[1]	Recycling chemicals	0.16[2]
Labor for replacing bath	0.51	Labor for recycling bath	0.15
Disposal of bath	0.58	Capital equipment	0.15[3]
TOTAL	1.81		0.46

[1] Estimated Value of Chemicals Discarded Under Current Disposal Methods (based on five to six cycles of use prior to discard):

Chemical	$/mil-sq.ft.
Nickel ($NiSO_4 \cdot 7H_2O$)	0.080
Hypo($NaPH_2O_2 \cdot H_2O$)	0.192
Chelating Agents	0.233
Antipitting Agents	0.018
Lead ($Pb(NO_3)_2$)	0.000
Caustic Soda (NaOH)	0.059
TOTAL	0.582

[2] Estimated Cost of Chemicals Required for Recycling a Bath:

Chemical	$/mil-sq.ft.
Calcium Oxide (CaO)	0.0050
Calcium Carbonate ($CaCO_3$)	0.0022
Magnesium Oxide (MgO)	0.0251
Hydrochloric Acid (HCl)	0.0557
Sulfuric Acid (H_2SO_4)	0.0189
Lime Neutralization	0.0138
Calcium Sulfate ($CaSO_4 \cdot 0.5\ H_2O$) Disposal	0.0095
Magnesium Hypophosphite ($MgHPO_3 \cdot 3H_2O$) Disposal	0.0274
TOTAL	0.1576

[3] Capital equipment costs are estimated at $25,000 (retail price) for a 100 gallon tank and a "fully automated" system. The cost could be reduced with less automation, but then the labor costs for recycling would increase. A 100 gallon tank plating about 33 sq. ft. of parts at 0.5 mil/hr., 8 hours a day, 5 days a week, 50 weeks a year would plate 165,000 mil-sq.ft. of nickel in five years, which works out to be about 15¢ per mil-sq.ft. attributable to capital cost, amortized over the five years.

[a] Source: Palmer. 1992.

sodium hypophosphite, which would otherwise contribute to the buildup of sodium and sulfate ions. The INFINITY process chemicals consist of the following set of solutions:

- Makeup solution: Four formulations are available:
  - INFINITY MX - 9 to 10.5 percent phosphorus and semibright coating
  - INFINITY MB - 7 to 10.5 percent phosphorus and semibright coating
  - INFINITY HX - 10.5 to 14 percent phosphorus and semibright coating
  - INFINITY HB - 10.5 to 14 percent phosphorus and bright coating

  The INFINITY MX is recommended by Stapleton Company to meet the Mil-C-26074C specification.

- Maintenance solution: contains the nickel and reducer needed for replenishment.

- "Personality" solution - a highly concentrated solution of stabilizers used to adjust bath stability and replace drag-out. Available in four formulations.

- Purifier solution - a proprietary ingredient used as an additive to precipitate orthophosphite.

A small concentration of sodium is used in the HX and HB formulations for its effect on phosphorus content. Because nickel hypophosphite is still used as the source of the reducing agent, sodium is not added to the bath on a continual basis.

4.3.2.2 Process Description

In addition to these chemical formulations, the Stapleton process consists of a purification unit to remove orthophosphite and heavy metal contaminants from the EN solution. Figure 4-6 is a diagram of the INFINITY process. The purification unit consists of:

- Heat Exchangers
- Reactor (Precipitator)
- Vacuum Filter
- Pumps
- Bag Filter
- Programmable Controller

The purification unit is connected to the EN plating tank via piping to and from the purification unit. The smaller unit (PU2) weighs 800 lb and measures 44 in. by 86 in. by 60 in. high. The larger unit (PU1) weighs 1500 lb and measures 114 in. by 68 in. by 84 in. high.

4-20

Replenisher
Solution
$Ni(H_2PO_2)_2$

pH Control
NH_4OH

Control
Solution
(Stabilizers)

EN
Solution

Recovered
Solution

5%
Removal

Cool to 100°F

Purifier
Solution

Reactor

Vacuum Filter

Filtrate

Filter Cake
(Contains Orthophosphite and
Heavy Metal Contaminants)
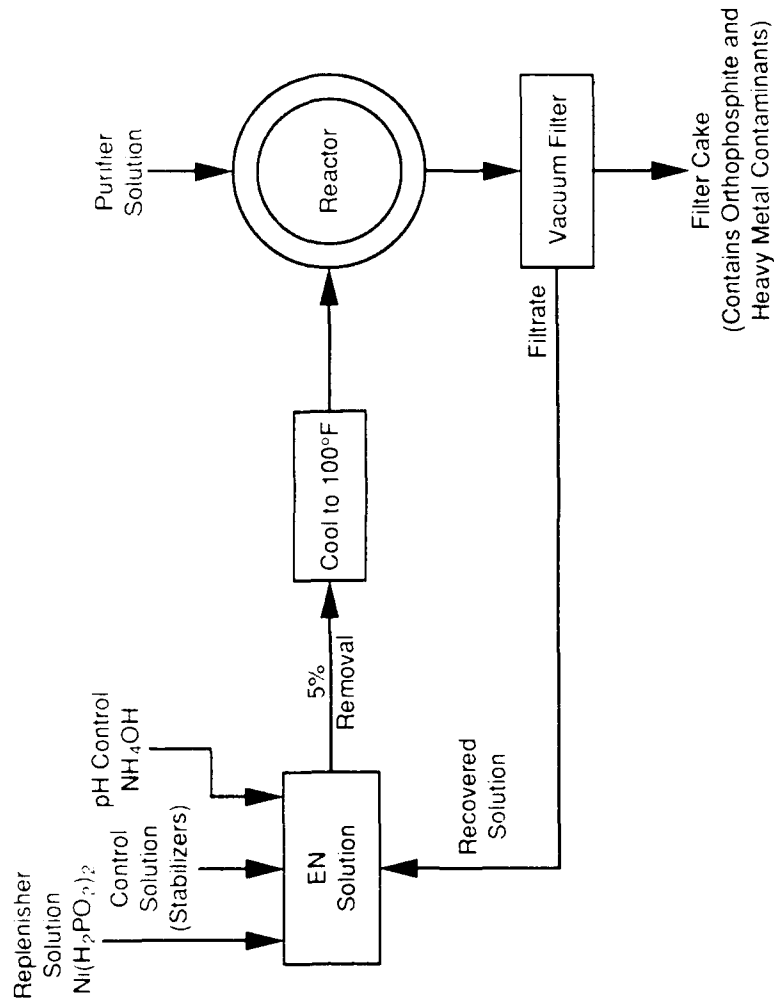
Figure 4-6.
Stapleton Technologies
INFINITY EN Process.

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The purification unit is activated by the operator depressing a key on the unit when the EN plating bath requires a 5 percent addition. The operator must perform the nickel and pH analyses manually in order to calculate when a 5 percent addition is required. The analyses involve a titration for nickel ions and electrode measurement of pH. Stapleton recommends that analyses be performed hourly.

Once the unit is in operation, 5 percent of the EN-plating solution is pumped from the plating tank to a cooling tank in the purification unit. After the solution is cooled to 100°F and the pH recorded, it is fed to the reactor compartment. The PU1 unit automatically adds a proprietary chemical called Purifier to increase the pH to 9.0 and precipitate orthophosphite. The PU2 unit requires that the operator manually add one unit of the Purifier chemical to the reactor. Heavy metals such as iron and zinc also precipitate in the reactor. Most of the nickel does not precipitate because it is complexed by the complexing agents. The vendor indicates that the nickel would precipitate at a pH of about 11. If present, ammonia and sulfate ions will combine in the reactor compartment and precipitate as ammonium sulfate.

After a reaction period of approximately 6 minutes in the reactor, the solution is pumped to a vacuum filter to remove the liquor from the precipitate. The PU1 unit uses a 500-yard roll of filter paper, while the PU2 unit uses a 2-ft x 2-ft sheet. The filter cake is rinsed and the residual liquid is also fed to the storage tank with the filtrate. The resulting solids are discharged to a drum for collection and disposal. The PU1 unit automatically rinses and discharges the filter cake, while the PU2 unit requires manual control to accomplish each task. The vendor claims that the precipitated filter cake contains over 60 percent solids and will be nearly free of nickel metal, thus allowing for recycling as a nonhazardous waste "under proper conditions." The filter cake will contain less than 100 ppm total nickel (using nitric acid digestion) and less than 20 ppm nickel in the extract of a Wet Extraction Test (WET, which involves extraction by citric acid for 48 hours).

Stapleton would like to offer a service whereby they accept the filter cake for recovery of phosphorous acid. However, the company would need to receive a large volume to make this service economically feasible. Stapleton will also need to resolve California regulatory requirements regarding the necessity for a RCRA Part B permit. This recycling service is not currently offered, and Stapleton recommends disposing of the filter cake as a RCRA F007 waste.

The filtrate from the vacuum filter is fed to a storage tank and heated to the bath temperature until the next 5 percent addition is required. When the operator pushes a button to begin processing the next batch, the recovered solution is pumped from the storage tank to the EN-plating bath. A replenisher solution, control solution ("Personality" solution containing stabilizers), and ammonium hydroxide are metered into the EN-plating bath to complete the volume.

The treatment time is approximately 13 minutes total; however, the PU1 unit can overlap tasks and provide a batch every 8 minutes. If the PU1 purification unit is inactive for 30 minutes, a rinse sequence is started. This rinse sequence flushes all piping and equipment with water and places the unit into a shutdown state to keep solids from building up inside the process. The PU2 unit does not have this feature.

The PU1 unit can be connected by a computer interface to the main computer at Stapleton to provide direct, real-time communications with vendor process engineers. Analytical results can also be logged into the controller of the PU1 unit to provide data for statistical process control (SPC). Alternatively, data can be transmitted to the computer at Stapleton for record keeping and evaluation.

Table 4-5 presents the concentrations of the important bath parameters before and after a 5 percent addition is made. As this table indicates, the processing of 5 percent of the solution at a time is designed to maintain the primary bath parameters within a narrow range.

Table 4-5
Concentrations Before and After 5 Percent Addition

Parameter	Starting Concentration	Concentration When 5% is Required	Concentration After Addition is Made
Nickel, g/L	6.65	6.32	6.65
Hypophosphite, g/L	19	18	19
Orthophosphite, g/L	28.5	30	28.5
pH, S.U.	4.80	4.72	4.80

4.3.2.3 Vendor Claims

According to the literature provided by the Stapleton Company, the purification unit maintains the EN-plating solution in the range of one to three equivalent metal turnovers (an EN-plating bath is typically discarded at a bath age of five to six metal turnovers). An equivalent metal

turnover is defined as the state of the bath when the concentration of orthophosphite is equal to the concentration in a bath that has been used for one nickel turnover. The purification unit controls the orthophosphite ion concentration in the range of 28 to 30 g/L.

The vendor claims that an INFINITY EN bath can be operated for several hundred metal turnovers and eventually obtain up to 8000 metal turnovers "under the proper conditions." Stapleton has achieved over 100 metal turnovers on a laboratory scale and 75 turnovers on a 20-gallon production EN bath. The solution was still functional after this time. The claim of 8000 metal turnovers is a calculation based on accumulation of sodium ions from sources such as the deionized water used for makeup.

Stapleton indicates that the purification unit will increase the efficiency of nickel usage from 75 to 85 percent without the unit to 99.99 percent with the unit installed. These calculations are based primarily on the amount of nickel that is discarded with a spent solution compared with the amount plated on parts.

Stapleton indicates that they have operated one of the large units (PU1) for over a year, but that its cost may be prohibitive for some plating shops. One of the smaller units was scheduled for installation in late March 1992 and Stapleton expects that up to 10 units will be installed by the summer of 1992.

The costs of the chemical supplies used with the process are:

- Infinity Maintenance, Replenisher - $14.90/gal
- Infinity HX Makeup - $ 9.60/gal
- Infinity HX Personality - $ 17.90 /gal
- Infinity Purifier - $ 1.30/lb

Table 4-6 presents an economic analysis provided by the Stapleton Company. The vendor claims that the INFINITY Process is cost competitive with conventional EN processes. The capital cost for the purification unit is $85,000 for the PU1 unit and $20,000 to $27,000 for the PU2 unit. The costs shown in Table 4-6 are based on plating at a rate of one makeup per week (one metal turnover per day). This plating and waste disposal rate is significantly greater than that experienced by any of the Army depots.

Table 4-6
Economic Analysis Provided by the Stapleton Company
for the INFINITY EN Purification Process

	$/mil•ft^2
Infinity Operating Costs	2.63
Equipment Costs	0.02
Cost Savings	
Waste Treatment and Disposal	-0.29
Premature Solution Contamination (Fe, Zn, Pb, Cd)	-0.15
Loss of Adhesion in Aluminum	-0.15
Rinsing and Staining Rejects	-0.08
TOTAL COST	1.97

4.3.3 Electrodialysis - Okuno Chemical Industries Co., Ltd.

Okuno Chemical Industries Co., Ltd., Japan, has been developing a method using electrodialysis to remove orthophosphite from EN plating solutions (Kuboi, 1989). The orthophosphite ions are selectively removed by electrodialysis using an ion exchange diaphragm to block out sodium orthophosphite.

4.3.3.1 Process Description

Figure 4-7 illustrates the experimental system used in laboratory testing. The electrodialysis system consists of:

- Electrodialyzer with ion exchange diaphragm
- Plating solution circulation system
- Condensed solution circulation system
- Electrolyte solution circulation system

During laboratory experiments, alternating plating and treatment cycles were performed. A fresh EN bath containing a nickel concentration of 6.7 g/L and a pH of 4.4 was used to plate parts for a total of three metal turnovers. A plating area of 70 dm^2 was processed in 70 liters of solution. During the plating cycle, the solution was analyzed and replenished every 10 minutes to maintain the nickel concentration and pH at constant values. Once the three metal turnovers were reached, the solution was cooled to 40°C to prevent destruction of the
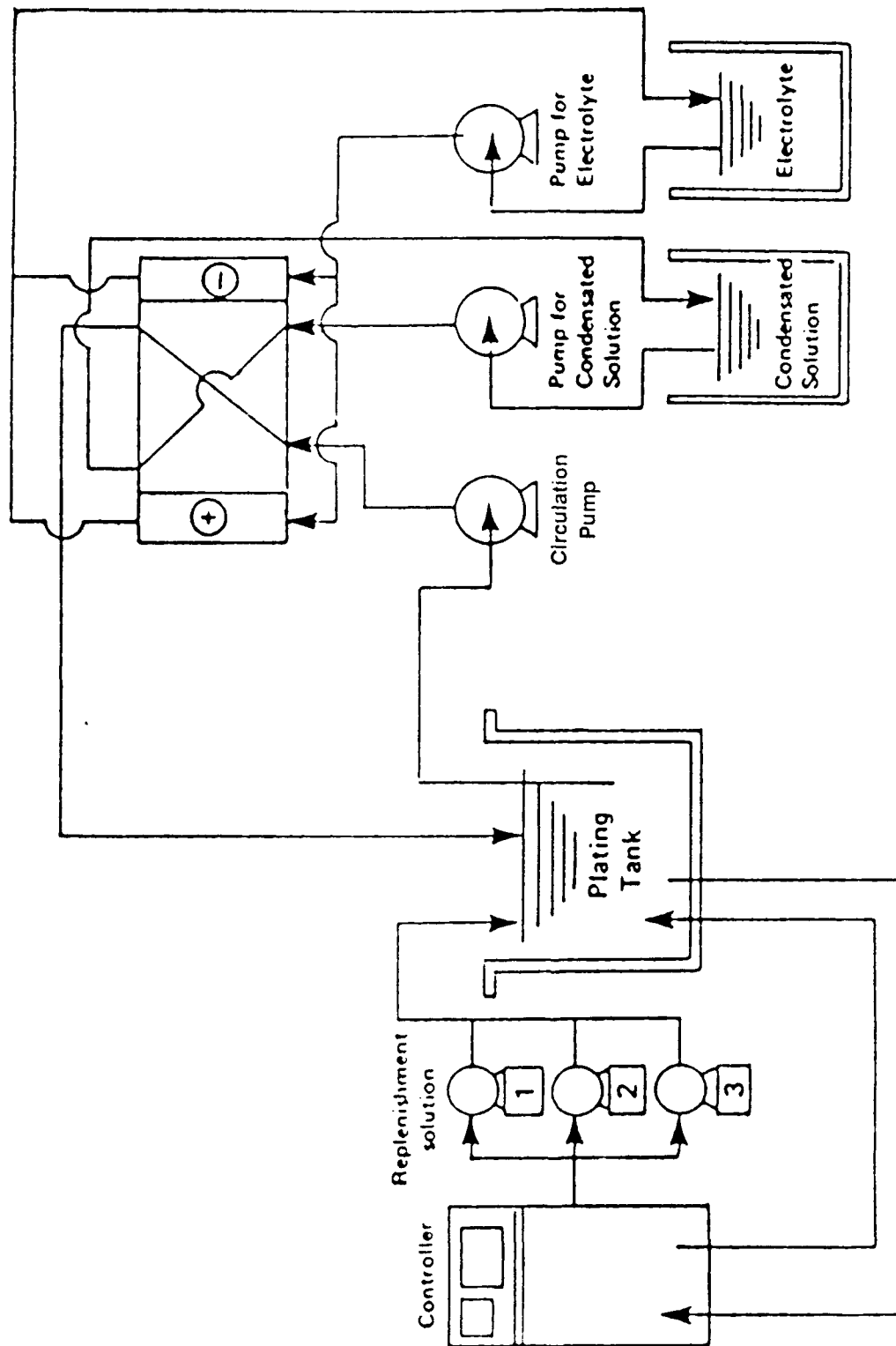
Figure 4-7.
Okuno Electrodialysis System
for Purifying EN Solutions.

Source: Kuboi, 1989.

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ion exchange membrane. The circulation pumps for the plating solution, condensed solution, and electrolyte solution were then activated to transfer the solutions to the electrodialysis unit at a rate of 8 liters per minute each.

Ion transport occurs in the electrodialysis unit as a result of electromotive forces, and is controlled by alternating cation and anion-permeable membranes. Figure 4-8 is a diagram demonstrating the electrodialysis mechanism. Direct current is applied to the electrodialyzer to cause the ion transport. The current density used in laboratory experimentation was 3 amperes per square decimeter of ion exchange diaphragm. In general, the electrical efficiency of electrodialysis decreases with decreasing ion concentrations.

Cations will tend to migrate toward the cathode end of the electrodialyzer, while the anions will tend to migrate toward the anodic end. The ion exchange diaphragms are placed between the anode and cathode as illustrated in Figure 4-8. Cationic and anionic diaphragms are placed alternately. Sodium ions and other cations pass through the cation exchange diaphragm (K) into the condensed solution, but not through the anion exchange diaphragm (A). Figure 4-8 also shows that orthophosphite and other anions will pass through the anion exchange diaphragm into the condensed solution, but not through the cation exchange diaphragm. The condensed solution consisted of 30 g/L sodium sulfate to create the electrical conductivity needed for ion transport. The ions that remain in the solution and are not passed through either cation or anionic diaphragm are returned to the EN-plating bath. During laboratory testing, electrodialysis was terminated when 40 ampere-hours were registered on an ampere-hour meter.

After treatment of the initial solution, it was then replenished, reheated, and reused for EN plating. When an additional metal turnover was reached, the EN solution was again subjected to cooling and electrodialysis. In actual operations, plating and electrodialysis would be repeated alternately for the life of the EN-plating solution.

4.3.3.2 Vendor Claims

The researchers noted that one metal turnover produced 50 to 60 g/L of sodium orthophosphite. Other researchers, however, have estimated that one gram of nickel plated will produce 4 grams of sodium orthophosphite (Mallory, 1990a). One metal turnover for a solution containing 6.7 g/L of nickel would create only 26.8 g/L sodium orthophosphite. According to an
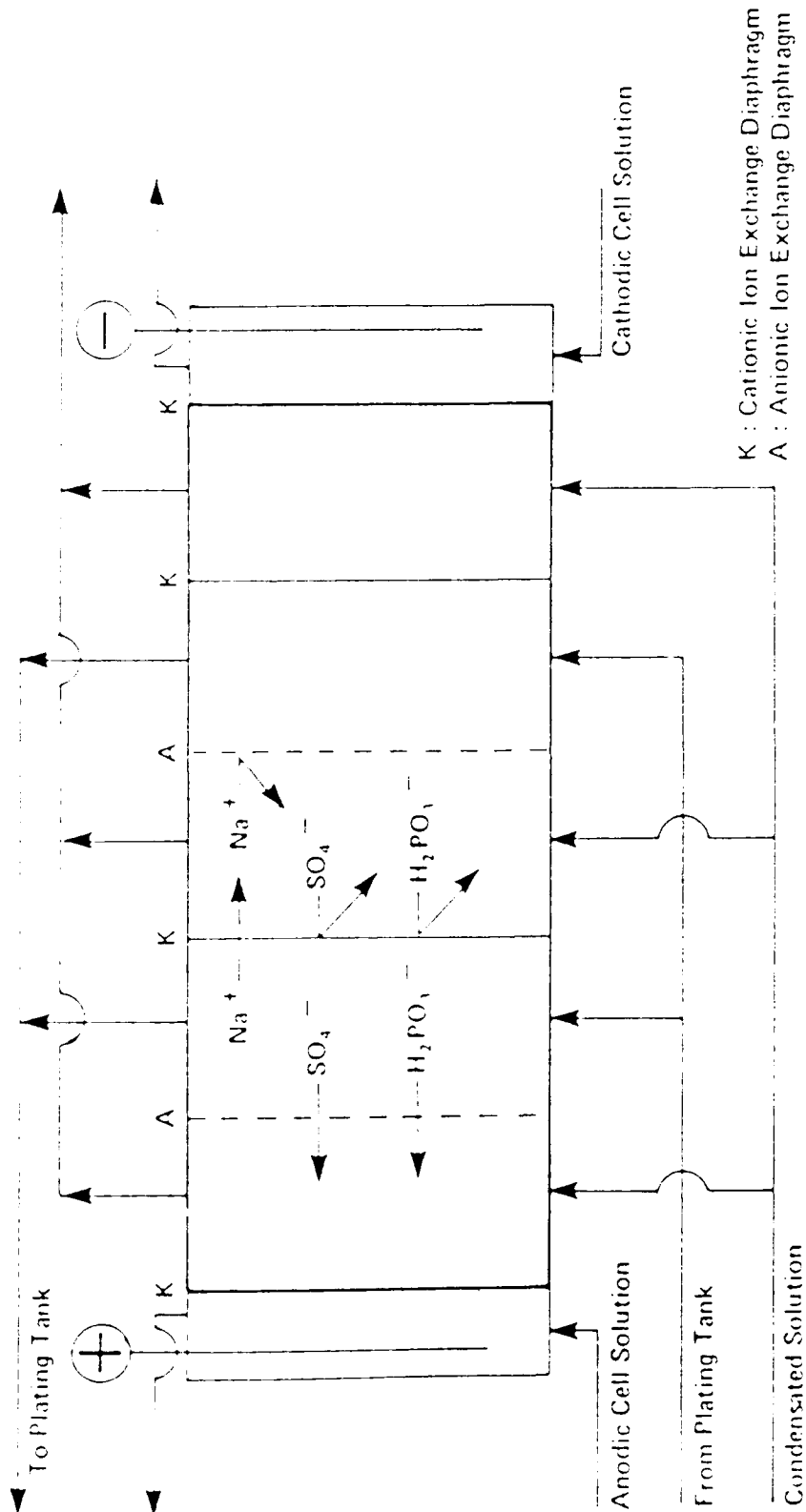
Figure 4-8.
Ion Transport Across Membranes,
Okuno Electrodialysis Process.

Source: Kuboi, 1989.

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K : Cationic Ion Exchange Diaphragm
A : Anionic Ion Exchange Diaphragm

Okuno representative, this discrepancy between estimates by Okuno and others results from additional orthophosphite generated by air oxidation or thermal decomposition of excess sodium hypophosphite (Marutani, 1992).

The electrodialysis system limited the concentration of the orthophosphite to approximately 200 grams per liter for more than 20 turnovers. This concentration of orthophosphite corresponds to the concentration found in baths at 2.5 to 3.5 turnovers according to the vendors or 7 to 8 metal turnovers according to the reference cited above. Many plating shops dispose of their EN solutions before reaching this number of turnovers and concentration of orthophosphite, depending on the specific EN solution used and the desired plating speed and coating properties. A plating shop would need to evaluate whether the solution quality was adequate after treatment with the electrodialysis system.

Table 4-7 shows the changes in chemical composition of the EN-plating solution before and after electrodialysis at various metal turnovers. The concentration of sodium orthophosphite decreased the most by an average of 61 g/L each time the solution was treated by electrodialysis. Sodium sulfate also decreased significantly.

Table 4-7
Treatment Data for the Okuno Electrodialysis Process

	At turnovers		At turnovers		At turnovers	
	Before Dialysis	After Dialysis	Before Dialysis	After Dialysis	Before Dialysis	After Dialysis
			24.9	25.2	31.4	28.6
			4.1	14.2	40.1	35.3
			144.7	137.1	14.4	131.7
			56.2	36.1	71.1	44.2
			1.4	17.5	17.2	14.3
			4.6	5.4	4.1	5.1

By conducting electrodialysis for every turnover, an almost constant deposition rate and phosphorus content in the deposit was achieved. Figures 4-9 through 4-11 show the effect of electrodialysis on the sodium orthophosphite concentration, deposition rate, and phosphorus content of the applied coating. The overall effect of electrodialysis was to maintain these three parameters within relatively narrow ranges compared with a bath that is allowed to
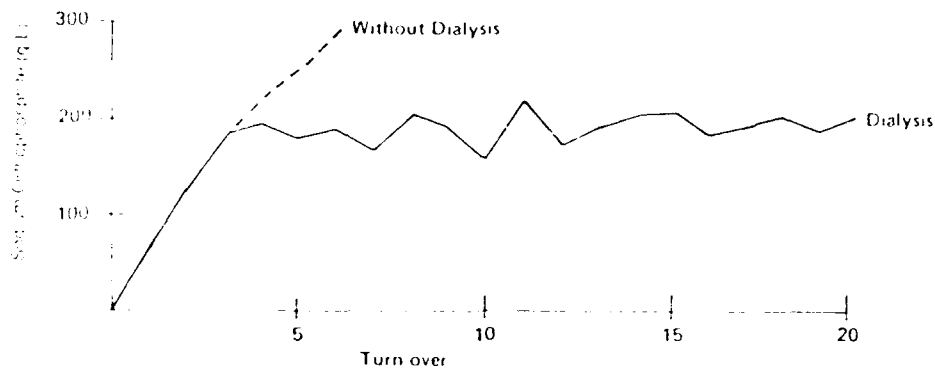
Figure 4-9.
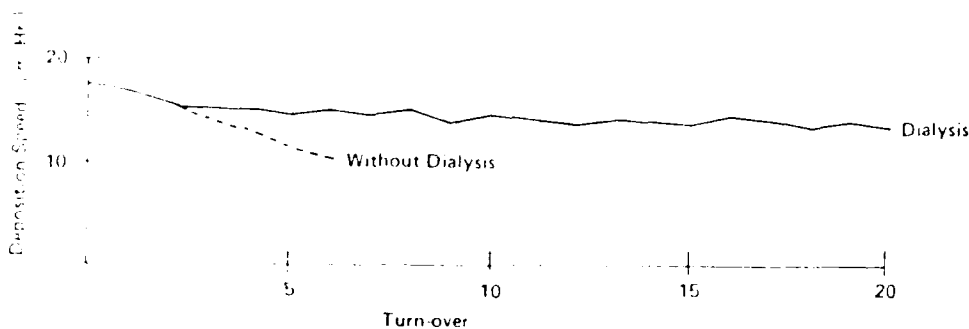Changes in Sodium Orthophosphite
Concentration of Plating Solution.

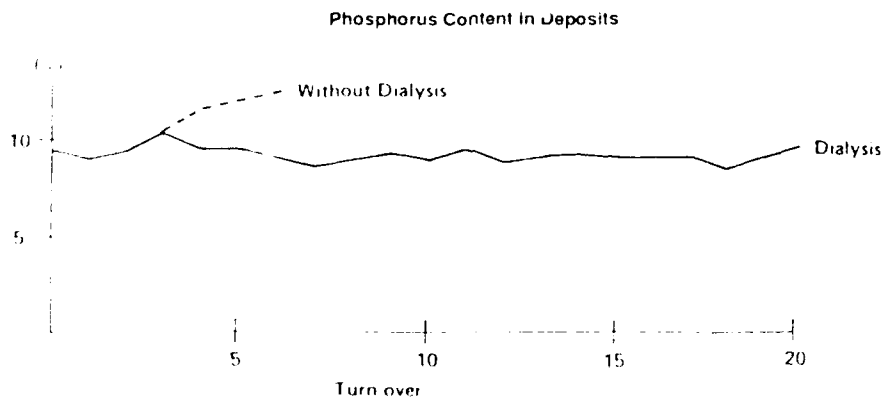Figure 4-10.
Changes in Deposition Speed
During Plating.

Phosphorus Content in Deposits

Figure 4-11.
Changes in Plating Coat
Phosphorus Content.

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continue the accumulation of orthophosphite. Data are not available, however, on other important coating properties such as corrosion resistance and internal stress.

Other important constituents of the EN-plating bath were also affected as shown in Table 4-7. Nickel sulfate and sodium hypophosphite were decreased slightly by the electrodialysis. Also, a chelating agent, hydroxy carboxylic acid, was decreased slightly. These constituents would require analysis and replenishment in actual operations.

4.3.3.3 Recent Developments

A full-scale Okuno electrodialysis system was installed on a 2,000-liter EN-plating tank in May 1990 at a plating facility in Japan (Marutani, 1992). The EN was plated at a rate of 1.1 to 1.3 metal turnovers per day. Because high temperatures can damage the membranes, the bath temperature was reduced to 40°C after plating and the electrodialysis system was operated on a batchwise basis.

The plating facility reported the formation of about 400 to 450 mL/min of condensated solution requiring treatment. For one metal turnover in an 8-hour shift, this resulted in about 200 liters of solution. Table 4-8 presents the concentrations of some constituents in the condensated solution.

Table 4-8
Concentration Data in Condensated Solution, Okuno Electrodialysis Process

Constituent	Concentration Range (g/L)
Nickel	0.4-0.6
Sodium hypophosphite	10-15
Sodium orthophosphite	400-450
Sodium sulfate	60-80
Chelating agent	10-20

The Okuno system is not designed for removal of heavy metals, although some may be transported through the cation membrane. An Okuno representative indicated that specific metals such as zinc could be removed by selecting the appropriate cation and anion membranes.

4.3.4 Ion Exchange - IBM Corporation

In 1987, researchers at IBM Corporation published a paper discussing the use of strongly alkaline ion exchange resins to remove excess phosphite from the EN-plating bath (Levy, 1987). The goal of the study was to exchange the phosphite ions in the EN-plating bath for the hypophosphite ions bound to the ion exchange resin, thereby simultaneously removing the harmful phosphite while replenishing the solution with the beneficial hypophosphite. This study was a bench-scale test and not applied to an operating EN-plating bath.

4.3.4.1 Study Description

The strong base ion exchange resin was regenerated with an aqueous sodium hypophosphite solution with a concentration of 11.1 grams of sodium hypophosphite per 275 milliliters of water. This procedure resulted in the resin containing bound hypophosphite. The resin was contained in a 20-by-1.75-centimeter column.

Table 4-9 lists the constituents and corresponding concentrations of the spent EN-plating solution to be regenerated and the results of the study. Twenty milliliters of the spent solution were fed through the ion exchange column followed by a water wash to reduce the loss of the nickel ions to the resin. Varying amounts of water (10 or 20 mL) were used to remove valuable constituents such as nickel from the resin. Eluent samples were collected to determine concentrations of bath constituents and contaminants.

Table 4-9
Results of Ion Exchange Laboratory Tests

Chemical Constituent	Spent EN Solution		20-mL Solution, 10-mL Wash[a]		20-mL Solution, 20-mL Wash[b]	
	Concentration (g/L)	Total Amount, (g)	Concentration in Eluent (g/L)	Amount in Eluent (g)	Concentration in Eluent (g/L)	Amount in Eluent (g)
Nickel (Ni^{2+})	6.0	0.120	1.937	0.0581	1.70	0.068
Sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$)	30.4	0.608	43.0	1.29	25.7	1.029
Sodium phosphite (Na_3PO_3)	25.7	0.514	1.03	0.0309	0.75	0.030
Sodium sulfate (Na_2SO_4)	19.7	0.394	2.40	0.0720	1.37	0.0549

[a] Results in eluent after passing 20 mL of spent EN solution through the ion exchange column followed by a 10-mL water wash.

[b] Results in eluent after passing 20 mL of spent EN solution through the ion exchange column followed by a 20-mL water wash.

4.3.4.2 Study Claims

Table 4-9 lists the concentrations of constituents before and after passing the EN solution through the ion exchange column and washing the column with water. Ion exchange removed about 94 percent of the sodium phosphite. In the test run with the 10-mL water wash, sodium sulfate decreased by 82 percent, while nickel decreased by 52 percent (i.e., 48 percent recovery). Sodium hypophosphite was increased by 112 percent.

Because of the low nickel recovery, the researchers also performed tests using 20 mL of water wash to recover additional nickel from the column. These results are also shown in Table 4-9. The nickel recovery was improved from 48 percent to 57 percent. The concentration of nickel decreased from 1.94 g/L to 1.70 g/L in the eluent, however, because of the additional 10 mL of water. Sodium sulfate was also reduced significantly in both runs. The maximum regeneration of the spent EN-plating solution of hypophosphite was obtained when 20 mL of spent EN solution and 10 ml of the water wash were passed through the ion exchange column. The researchers indicate that a significant amount of hypophosphite (25 to 50 percent) was lost in the overall process (including resin regeneration), although this is not shown by the data in Table 4-9.

The authors suggested changes to the ion exchange system to reduce the loss of the nickel ions. These changes include identifying other resins, changing the aspect ratio of the column, manipulating other ion exchange parameters, or changing the hypophosphite concentration used to treat the column.

Because of the water wash of the column, the total eluent liquid volume was twice the volume of the EN solution treated. Therefore, this procedure would only be useful where evaporation was sufficient to allow the addition of an amount of water equal to the amount of treated EN solution. No additional work has been conducted by these researchers since the results of this laboratory-scale study were published in 1987 (Doss, 1992). The researchers indicate that the process would not be economical on a large scale because of the loss of nickel (and hypophosphite) to the resins. Different resins could, however, produce different results.

4.3.5 Treatment with Ferric Chloride (FeCl₃)

A process to precipitate accumulated orthophosphite out of the solution by using ferric chloride was proposed in 1960 (Gorbunova and Nikiforova, 1960). The addition of the ferric

chloride forms an insoluble complex in the solution according to the following reaction equation:

$$H_2O$$
$$2\ NaH_2PO_3 + FeCl_3 \rightarrow Na_2[Fe(OH)(HPO_3)_2]\cdot20H_2O + 3\ HCl \qquad\qquad Eq.\ 8$$
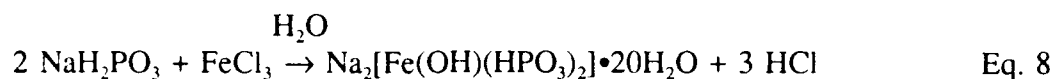
Less than the stoichiometric quantity of the ferric chloride is added to the plating solution in order to avoid contamination of the bath with ferric chloride.

One problem with this procedure is that a considerable amount of the hypophosphite is separated from the EN-plating bath along with the precipitated orthophosphite complex. A second problem, as illustrated in the chemical equation in Eq. 8, is the formation of hydrochloric acid. Enough hydrochloric acid is formed that the pH of the bath is lowered to a level where the bath ceases plating. Thus, after removal of the precipitated orthophosphite complex by filtration, the pH of the bath must be raised to its optimal range in order to continue plating. The literature recommends that the neutralizing agent be added simultaneously with the ferric chloride (Mallory, 1990b).

The two cited articles were the only references identified during this project that discuss this technique. No other information has been identified to indicate that the technique has been used in industry.

4.3.6 Proprietary Orthophosphite-Removal Technologies

Several EN suppliers contacted during this project indicated that they were developing systems to remove orthophosphite and extend EN bath lives. In one case, the company contact indicated that the basic purification chemistry had been developed but that the automatic controls for a full-scale system would be expensive and time-consuming to develop. Ongoing development has been slowed because of higher priorities and the economic recession.

Details of these EN purifications processes were not available for this report because, once developed, they would become part of the overall EN process marketed by the company. Another company, Ionsep Corporation, Inc., of Rockland, Delaware, is currently developing an EN purification process based on the use of electrodialysis to remove contaminant anions and control the solution pH (Vaughan, 1992). At this time, however, details of the process cannot be divulged, pending completion of European patent findings.

Information on these proprietary processes may be available in the future from vendors as the systems are granted patents and are marketed to EN users.

4.4 Other Decontamination Techniques

This section presents a discussion of decontamination techniques that are designed to remove contaminants other than orthophosphite from EN-plating baths. The technologies presented are filtration for particulates, electrolysis for metals, and carbon treatment for organics.

4.4.1 Filtration

Filtration is generally specified as basic equipment with all EN-plating operations. Filtration is discussed here as a separate decontamination method because of its ability to remove particulate contaminants from the EN-plating solution. These contaminants include dust, dirt, sand, and masking material, which can cause premature disposal of the EN bath.

The literature recommends that filtration be conducted continuously at a minimum rate of 10 bath turnovers per hour with a 1-μm filter medium. A sub-micron filter medium should be used for critical applications or for thick plating deposits (Kuczma, 1990). Daily filter changes are recommended.

With proper filtration of the EN-plating bath, the deposit and solution quality can be maintained. The filter medium removes the particulates, which can cause plate-out. Plate-out is the plating of the nickel on particulates in the solution, which can occur because the EN process is autocatalytic. This plate-out leads to roughness and pitting problems of the deposit and also affects the bath quality by causing decomposition of the bath.

Filtration of EN-plating baths can be in the form of either bag filtration or cartridge filtration. Both of these forms require an external circulation pump to feed the EN-plating solution through the filter medium. In bag filtration, the entrance to the filter is mounted above the EN-plating tank. The solution is pumped to the open top portion of the bag and allowed to gravity flow-through the filter medium. The filter medium is usually polypropylene felt constructed into a bag form.

Three factors should be considered when using bag filtration (Kuczma, 1990):

- The metal ring in the mouth of the bag should be made of stainless steel and not zinc- or cadmium-coated steel because zinc or cadmium may dissolve in the solution and act as an inhibitor to the plating reactions.

- The filter should be mounted such that at least half of the filter bag is in the solution. If the filter bag were allowed to hang above the solution, the pressure of the solution weight and pump pressure would stretch the filter bag, thus decreasing the effectiveness of the filter. Also, visible dirt and oil lines at the submersion line on the bag will alert the operator of evidence of contamination to the bath.

- Bag filters with filter chambers located outside the tank are available. Exterior filter chambers allow for better use of the EN-plating tank space, but inspection and observation of the filter medium and signs of possible contamination are not possible.

Cartridge filters are wound-type filters supported in CPVC or polypropylene chambers. The filter chamber is usually located outside the plating tank, but some are mounted inside the plating tank. These filters rely on pressure from the circulation pump to move the EN-plating solution through the filter medium. As the filter medium collects particulates in its pores, the back pressure builds up and causes the flow and the pump life to be reduced.

Bag filters are the more cost effective-filters (Kuczma, 1990). Installation and maintenance costs are relatively high for the cartridge filters.

Each of the three Army depots uses filtration as a regular part of the EN operations. At CCAD. 5-μm filter bags are used to continuously filter particulates from the solution. Previously, the filter bags were not rinsed before use and personnel noted residue on the filter bags that could potentially contaminate the bath. Therefore, the bags are now rinsed before being used. Personnel reported that the filter bags work well for the EN application.

RRAD also uses 5-μm filter bags to continuously filter particulates from the solution. The plating foreman indicated that the filter bags are also used when transferring the solution from one tank to another at the end of each shift. This allows for filtration of the entire solution. Otherwise, circulating a tank solution through the filter does not guarantee that the entire solution will be filtered.

At SAAD, continuous cartridge filtration is used. The filters can be checked easily by the operator and changed if necessary. A contained filter system had been attempted previously to remove particulates, but it became clogged. Continuous out-of-tank bag filters were also attempted, but these led to excessive evaporation of the solution. The solution is pumped through a bag filter when it is transferred to the second EN tank prior to passivation of the first tank. This operation is usually performed once a week.

4.4.2 Electrolysis (Dummying)

Electrolysis is a potential technique for removing heavy metal contaminants from EN solutions. This process is known as "dummying" in the industry. Metal contamination can cause poor adhesion, blistering, pitting, dullness, streaking, and skip plating of the nickel deposit and low or no deposition rate.

Electrolysis is performed in the EN-plating tank by placing two electrodes in the solution. A voltage is applied across the electrodes and the metals plate out onto the cathode. One vendor's literature indicated that electrolysis could be performed with insoluble carbon anodes at 2 to 5 amp/ft^2 with good agitation for an hour. Lower bath temperatures should be used to avoid corrosion of the anode. Electrolysis is not a selective process; thus, nickel may also plate out onto the cathode with the other metals, although one contact indicated that low concentrations of metals such as cadmium, chromium, and lead should plate out before significant amounts of nickel are deposited. After electrolysis, the nickel that is plated out must be replenished in the solution before EN plating is continued. Excessive dummying may also reduce the concentrations of hypophosphite and stabilizers (Aleksinas, 1990). Electrolysis could also destroy the lead-based stabilizers used in some solutions.

Vendors contacted during this project indicated that industry does not generally use electrolysis for removing contaminant metals. Most said that orthophosphite was the primary contaminant limiting bath life. Alternatives to electrolysis for metal contaminants may be more desirable; for example, complexing agents may be available to increase the bath tolerance for low concentrations of copper (<5 ppm).

SAAD was the only depot visited which has tried to use electrolysis to decontaminate the EN-plating bath. The SAAD EN-plating bath occasionally becomes contaminated with metals from drag-out from precleaning operations; contaminates may include zinc, cadmium, and

chromium. An overly contaminated bath is typically disposed of. SAAD personnel noted that the metals can sometimes be plated out using the electrolysis technique, but it removes a significant amount of nickel from their bath. They also reported that electrolysis is not always successful in removing the contaminant metals.

4.4.3 Carbon Treatment

Carbon treatment may be used in some cases when the EN-plating bath becomes contaminated with organic contaminants. Organic contaminants include degreasing solvents, oil residues, and mold release agents. They can also be contributed by drag-in of cleaners or acid inhibitors, and by unleached equipment or filter media. The organic contaminants are removed from the solution by adsorption onto the carbon surface.

Most EN chemical formulations for sale by chemical manufacturers contain constituents that may be removed by carbon treatment which would result in deterioration of the stabilization of the plating bath. Beneficial organic additives such as complexing agents and stabilizers need to be replenished if carbon treatment is used. This would require analyses for the specific organic compounds or other laboratory tests to determine the amount of replenishment needed. Carbon treatment should be used only when recommended by the EN vendor. Some vendors contacted during this project do not recommend carbon treatment and said that it is not in general use in industry.

If carbon treatment is selected, the type of carbon must be carefully chosen. A pure form of carbon that does not contain sulfur or other contaminants must be used (Aleksinas, 1990). Residual carbon can be left in the bath solution from carbon treatment. This residual carbon can cause considerable deposit roughness and dullness.

The only depot to report the use of carbon treatment was SAAD. Personnel at SAAD indicated that the EN-plating solution may become contaminated with oils and other organics. The bath is occasionally treated by carbon filtration to remove these contaminants.

4.5 In-Tank Treatment

Methods of waste treatment for spent EN solutions are described in the literature; however, a comprehensive discussion is not within the scope of this project (Capaccio, 1989; Kunces, 1985; Ying 1986). EN solutions are often treated with hydroxide precipitation in wastewater

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treatment plants, but many nickel complexes can interfere with precipitation of the nickel. Nickel discharges are regulated under site-specific NPDES permits.

Vendors of EN solutions often cite in-tank treatment of EN solutions involving controlled plate-out or deliberate decomposition of the solution as the preferred methods for reducing the amount of EN solution that must be shipped off site for treatment or disposal. For deliberate decomposition, the pH of the bath is increased to 8 or 9 and excess sodium hypophosphite is added to the bath while the temperature is maintained at operating conditions. This results in the formation of insoluble nickel compounds throughout the bath, depleting the solution of its nickel content. Palladium chloride may be added to initiate the chain decomposition reaction. The precipitated nickel can then be separated from the solution by decanting or filtration, and the solution may be amenable to treatment in the industrial wastewater treatment plant. One disadvantage to the uncontrolled decomposition process is that it may leave a black smut on the walls, requiring that the tank be cleaned. The precipitated product may also have little commercial value.

As an alternative to uncontrolled decomposition, many EN vendors recommend controlled plate-out of the nickel. In this process, the pH and hypophosphite of the solution are again increased. Material with a large surface area is then inserted into the solution to provide a catalytic surface for plating; this material may be nickel powder, steel mesh, or even scrap items such as nails or screws.

Some EN suppliers market an additive containing concentrated sodium hypophosphite, stabilizers, and accelerators to use for controlled plate-out. The stabilizers prevent the solution in general from decomposing as the pH is raised so that plating occurs only on the catalytic surface. Accelerators increase the speed of the reaction.

Costs for uncontrolled decomposition were estimated by one vendor to be about $0.20/gal of spent EN solution. Plating onto nickel powder or steel wool costs $0.25 to $0.85 per gallon (based on two vendor quotes). Costs for treatment with proprietary waste additives ranges from $0.45 to $2.00 per gallon (based on two vendor quotes). One vendor reported that nickel powder which has been used for controlled plate-out can be sold to a scrap dealer or smelter for $2/lb, whereas steel wool plated with nickel can be sold for $1/lb.

Vendors indicated that the nickel concentration of the spent EN solution can be reduced to 5 ppm using these plate-out methods. Some vendors indicated that the solution could be polished with ion exchange and/or treated in a wastewater treatment plant, depending on the effectiveness of the plate-out method and local NPDES discharge limits.

Different EN chemistries may be amenable to plate-out to different degrees, depending on the nickel complexing agent (nickel bound to strong complexing agents will be more difficult to plate). One vendor, Fidelity Chemical Products, indicated that its EN processes use weaker chelating agents (carboxylic acids); nickel in these solutions may be more amenable to plate-out than solutions with stronger complexing agents.

Because of the complex and proprietary nature of EN solutions, users should contact vendors to determine the waste treatment procedures that may be applicable for specific chemistries. In addition, depots must consider the state-specific limitations or permits that may apply to in-tank treatment.

5.0 Evaluation of Waste Minimization Technologies

This section presents a technical and economic evaluation of the decontamination and waste minimization technologies described in Section 4. The evaluation focuses on determining whether the waste minimization technologies identified are suitable for implementation at Army depots with current operations. The evaluation, therefore, may not be applicable to future operations at Army depots or operations at other industrial or Federal facilities.

5.1 Technical Evaluation

Table 5-1 presents a summary of waste minimization technologies that are potentially applicable to EN-plating solutions. The technologies have been divided into the following categories:

- Technologies for orthophosphite removal.
- Other contaminant-specific technologies.
- Selected other waste minimization technologies.

The scope of this project focuses primarily on decontamination technologies. The other waste minimization technologies listed in Table 5-1 have been chosen as a basis for comparison because they are some of the more frequently used waste minimization methods at Army depots or because they offer significant potential for waste reduction. The table does not include chemistry considerations because this evaluation assumes that the proper chemistry has been chosen and that the bath is well maintained; otherwise, the technologies discussed in this section would be less effective.

Table 5-2 is a summary of the constituents and contaminants that are controlled by each waste reduction method. The table is designed to show the degree of applicability of each of the technologies. The first three orthophosphite-removal technologies (DOE/Martin Marietta, Stapleton, and Okuno) are potentially the most widely applicable because each addresses orthophosphite, sodium, sulfate, and, to some extent, heavy metal contamination. These technologies would be expected to be used in conjunction with methods for proper control of hydrogen ion concentration, particulates, and basic chemistry. On the other hand, filtration, electrolysis, and carbon treatment address single contaminants (particulates, metals, and organics, respectively) and do not remove the by-products and contaminants (orthophosphite, sodium, and sulfate) that are an inherent part of an EN operation.

Table 5-1
Summary of Waste Minimization
Technologies For Electroless-Nickel Plating Solutions[a]

Technologies for Orthophosphite Removal

Technology	Vendors/Researchers
Ion exchange Precipitation	DOE/Martin Marietta
Chemistry using nickel hypophosphite Precipitation	Stapleton Technologies
Electrodialysis	Okuno Chemical Industries
Ion exchange	IBM Corporation
Ferric chloride precipitation	

Other Contaminant-Specific Decontamination Technologies

Filtration[b]
Electrolysis[b]
Carbon treatment[b]

Selected Other Waste Minimization Techniques

Automatic analysis and control[b]
Rapid cooling[b]
Dust covers[b]
Contaminant prevention[b]

[a] Does not include chemistry considerations.

[b] In use at some Army depots.

Table 5-2
Constituents and Contaminants Controlled by Waste Reduction Technologies

	Bath Parameter/Contaminant Affected								
	Ortho-phosphite	H^+	Na^+	SO_4^{2-}	Par-ticulates	Heavy Metals	Organics	Basic Chemistry	Tem-perature
Technologies for Orthophosphite Removal									
DOE/Martin Marietta	X		X[a]	X		X			
Stapleton Technologies	X		X[a]	X		X[b]			
Okuno Chemical Industries	X		X	X		X			
IBM Corporation	X		X	X					
Ferric Chloride Precipitation	X								
Other Contaminant-Specific Decontamination Technologies									
Filtration					X				
Electrolysis						X			
Carbon Treatment							X		
Selected Other Waste Minimization Techniques									
Automatic Analysis and Control		X						X	
Rapid Cooling	X[c]								X
Dust Covers					X				
Contaminant Prevention			X	X	X	X	X		

[a] Affects sodium by avoiding its use in replenishment chemicals.

[b] Has the potential for removing some heavy metals.

[c] Reduces rate of buildup.

Table 5-3 presents a summary of the technologies discussed in Section 4; it also includes information on selected other waste minimization methods. The following text discusses the criteria for evaluation and provides applicable examples. Points common to several technologies are also discussed.

The primary rationale for each technology evaluated is presented in Table 5-3. For each decontamination technology, the rationale for its use relates to its ability to remove various contaminants. The reasons for using automatic monitoring and control systems is that these systems maintain the bath chemistry within the optimum range and provide records of analyses and chemical additions. The primary rationale for using rapid cooling, dust covers, and contaminant prevention relates to the ability of these techniques to prevent contamination rather than removing it once it has occurred.

Table 5-3 also presents the capital cost of each option, where available. These costs were provided by technology vendors. The costs of developing technologies such as the DOE/ Martin Marietta process are only preliminary estimates, and the costs of a full-scale system may be different from those presented in this table. A cost range in this column indicates either a range provided by the vendor, or multiple quotes from several vendors.

Because the ultimate objective of any of these technologies is waste reduction, a consideration of side streams generated by the waste minimization technologies themselves is important. The total waste reduction for an EN operation with a waste minimization technology would be given by the decrease in EN solution waste minus the waste generated by the waste reduction technology. Waste streams are listed in the fourth column of Table 5-3. As shown in this table, any technology that uses precipitation will generate a sludge that must be disposed of as a hazardous (as claimed by Stapleton) or nonhazardous (as claimed by Martin Marietta) waste. Technologies that use ion exchange will generate either spent ion exchange resins or waste liquid solutions from regeneration of the resins. Electrodialysis generates waste solutions that are used as conductive liquids and a liquid waste stream containing the contaminants removed from the EN solution. Other side waste streams may include spent carbon or filter bags.

The developmental status (presented in Table 5-3) is important because a well-developed technology that has been proven to reduce waste is more preferable for implementation than a

Table 5-3
Summary Table for Technology Evaluations
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Technology	Primary Rationale for Use	Capital Cost	Waste Streams	Stage of Development	Effect on Plating Chemistry	Other Disadvantages
IOE/Martin Marietta (Ion exchange, precipitation)	• Removes ortho- phosphite, sodi- um, sulfate, and heavy metals	$25,000	• Calcium and mag- nesium sludges • Regeneration so- lutions for ion exchange	• Laboratory	• May introduce cal- cium and magnesium ions into bath, which could have a harmful effect on bath chemistry	• Dilution by wash waters • Large amount of chemical usage • Analyze individual compounds for re- plenishment • Complex operations • Must regenerate ion exchange resins
Stapleton Tech- nologies (Pre- cipitation)	• Removes ortho- phosphite, sodi- um, sulfate, and heavy metals	$20,000 - $27,000	• Precipitated sludge	• Production units are available; one is in- stalled	• Unknown	• Frequent, manual analyses • Dilution by wash waters • Proprietary chemis- try • Sole source procure- ment since chemicals and purification unit are sold as a package • Analyze individual compounds for re- plenishment
Okuno Chemical Industries (Electrodialy- sis)	• Removes ortho- phosphite, sodi- um, sulfate, and possibly some heavy metals	NA[a]	• Anodic cell solu- tion • Cathodic cell so- lution • Condensated solu- tion	• Laboratory testing; one full-scale unit is in operation in Japan	• Some valuable con- stituents (nickel, hypophosphite, chelating agents) could be lost	• High concentration of orthophosphite after treatment • Electrodialysis has low electrical effi- ciency at low ion concentrations

Refer to footnotes at end of table.

Table 5-3 (continued)
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Technology	Primary Rationale for Use	Capital Cost	Waste Streams	Stage of Development	Effect on Plating Chemistry	Other Disadvantages
IBM Corporation (Ion exchange)	• Removes ortho-phosphite, sodium, and sulfate	NA	• Regenerating solutions	• Laboratory; no experiments since 1987	• Loss of nickel on resins • Loss of hypophosphite	• Analyze individual compounds for re-plenishment • Dilution by water rinse
Ferric chloride precipitation	• Removes ortho-phosphite	NA	• Insoluble ortho-phosphite complex	• Limited: only one reference	• Introduces hydro-chloric acid • Removes some hypo-phosphite	• Limited data available
Filtration	• Removes particulates	b	• Particulates • Filter bags	• Standard equipment on EN-plating solutions	• None	• Applicable only for particulate removal, not other contaminants
Electrolysis	• Removes heavy metals	NA[c]	• Plated metal	• Well developed	• Nonselective; could plate out some nickel • May reduce concentration of hypophosphite and stabilizers	• Applicable only for heavy metal removal
Carbon treatment	• Removes organics	NA[c]	• Spent carbon	• Well developed	• Organic compounds such as complexing agents and stabilizers may be removed • Can contribute sulfur or other contaminants into bath • Residual carbon can be left in the bath	• Applicable only for organic con-tamination

Refer to footnotes at end of table.

Table 5-3 (continued)
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Technology	Primary Rationale for Use	Capital Cost	Waste Streams	Stage of Development	Effect on Plating Chemistry	Other Disadvantages
Automatic monitoring and control	• Maintains bath chemistry within optimum range • Provides records of analyses and chemical additions • Reduces labor for analysis and replenishment	$3,000 - 10,000	• None	• Commercially available	• Maintains bath chemistry within optimum range	• Does not remove contaminants
Rapid cooling	• Prevents continuing electrochemical reaction and contaminant buildup when parts are not being processed	NA	• None	• Cooling coils are commercially available	• Reduces rate of electrochemical reaction	• Does not remove contaminants
Dust covers	• Prevents contamination by airborne dust	NA [b]	• None	• Standard item on EN-plating baths	• None	
Contaminant prevention	• Prevents contamination from entering the tank	Varies	NR [d]	NR	• None	• Does not address contaminants that are byproducts of the plating reaction

[a] NA = Not available.
[b] Usually specified in the cost of a basic EN process.
[c] Considered minimal.
[d] NR = Not relevant.

technology for which only laboratory-scale studies have been conducted. The costs and operating data for a well-developed technology are also likely to be more accurate and complete. The technologies for orthophosphite removal shown in the table have generally been developed only to a laboratory stage. In the case of ion exchange at IBM, the technology has not been developed further since the initial results were published in 1987. Stapleton indicates that one production unit has been installed, with several more scheduled for installation by summer 1992. Okuno has installed a full-scale electrodialysis system at a plating facility in Japan. Therefore, of the technologies that remove orthophosphite, only the Stapleton and Okuno systems are potentially ready for immediate implementation on an EN solution. Because of the limited number installed, however, only vendor-supplied data and claims are available for determining the effectiveness of these technologies.

The detrimental effects associated with implementing a given waste minimization technology may include introduction of other contaminants into the bath or removal of valuable constituents from the solution. For example, the DOE/Martin Marietta process may introduce calcium and magnesium ions into the bath; one reference reports that these ions may harm deposit quality, although the Martin Marietta researchers did not find any negative effects in laboratory testing. Carbon treatment can contribute sulfur or other contaminants into the bath, and residual carbon could contaminate the solution. These effects are also summarized in Table 5-3.

Several of the technologies could result in a loss of valuable constituents from the plating bath. For example, laboratory testing of the Okuno electrodialysis process indicated that nickel, hypophosphite, and chelating agents were reduced in concentration. The IBM ion exchange research indicated loss of hypophosphite and nickel. Electrolysis is nonselective and could plate out some nickel. Excessive use of electrolysis could also reduce the concentration of hypophosphite and stabilizers. Carbon treatment is designed to remove organic contaminants, but it could also remove valuable organic constituents such as complexing agents and stabilizers. Finally, the ferric chloride precipitation process generates hydrochloric acid in the solution.

A technology need not be rejected solely because of harmful effects on plating chemistry if the effects can be counteracted. Valuable constituents removed can be added during the

normal replenishment cycle; however, the additional chemical purchases required must be considered in the economic analysis of the technology.

Finally, Table 5-3 presents other disadvantages of each technology. One disadvantage frequently listed is that individual compounds must sometimes be analyzed for replenishment. The normal current depot procedure is to analyze only for nickel and pH. Hypophosphite, complexing agents and stabilizers are not routinely analyzed and are added in a certain ratio to the quantity of nickel added. Many of the decontamination technologies, however, may affect concentrations of hypophosphite, complexing agents, and stabilizers; analysis of these compounds would be required, thereby significantly increasing the analytical labor required to support the EN operation.

Some technologies use water for washing precipitated sludges or ion exchange resins. This will result in an increase in the volume of the EN solution being treated. This disadvantage could be overcome if the additional liquid added is not greater than the amount of evaporation that would normally occur in a heated EN tank. Otherwise, an evaporator would be required to reduce the liquid content.

The primary disadvantage of the Okuno electrodialysis process is that the concentration of orthophosphite after treatment is still high (200 g/L). This concentration corresponds to a bath age (over six metal turnovers) beyond which many depots dispose of their solutions. Testing by Okuno, however, indicated that deposition speed and phosphorus content were acceptable even after 20 metal turnovers were achieved. Data regarding corrosion resistance and internal stress were not available.

The disadvantage of technologies such as filtration, electrolysis, and carbon treatment is that they only remove a single contaminant each, and none of them removes orthophosphite. Many vendors do not recommend electrolysis or carbon treatment because of their potentially harmful effects on bath chemistry. Filtration, however, should be used regardless of other waste minimization techniques implemented.

Technologies such as automatic monitoring and control, rapid cooling, and contaminant prevention may be useful for maintaining proper control of the bath and reducing contamination. However, these technologies are not designed to remove contaminants such as orthophosphite

that will inevitably build up in the bath if not removed. Thus, these technologies could provide life extension of the bath, but bath life would still be limited by orthophosphite accumulation.

5.2 Economic Evaluation

An economic analysis of the technologies listed in Tables 5-1 through 5-3 is presented in this subsection. This analysis is preliminary, as it is based on the limited data that were available. The evaluation generally considers the capital cost of waste minimization equipment, costs of waste disposal, and makeup chemical costs. Data were not available on other cost components.

The payback period (in years) of any investment can be calculated by dividing the capital cost of that investment (e.g., waste minimization equipment) by the annual income plus cost savings. This simplified method does not consider equipment life, salvage value, the time value of money, taxes, or depreciation. In the ideal case, a waste minimization method would lengthen bath life to infinity, reduce waste generation to zero, and reduce makeup chemical costs (but not replenishment chemical costs) to zero. The minimum payback period for a given equipment cost at a given depot is therefore calculated by dividing the capital cost by costs associated with waste disposal and chemical makeup.

Table 5-4 presents the payback periods for various capital costs at each of the three depots assuming 100 percent waste reduction. Calculations for SAAD are shown for both old (1991) and new (1992) contract rates. These results are shown graphically in Figures 5-1 through 5-4. In general, equipment costing more than $20,000 results in payback periods greater than 5 years even in the ideal case of 100 percent waste reduction.

The payback periods shown in Table 5-4 and Figures 5-1 through 5-4 are dependent on several factors. The first factor is the assumption of 100 percent waste reduction. Because data are not available on the specific quantity of waste reduction achievable by each technology, the waste reduction rates can only be estimated. Figures 5-1 through 5-4 present the relationships for capital costs versus payback periods for 100, 75, 50, 25, and 10 percent waste reduction. The payback period for a waste reduction of less than 100 percent is calculated by dividing the payback period at 100 percent by the percent reduction. For example, a technology resulting in a waste reduction of 50 percent will yield a payback period twice that of the
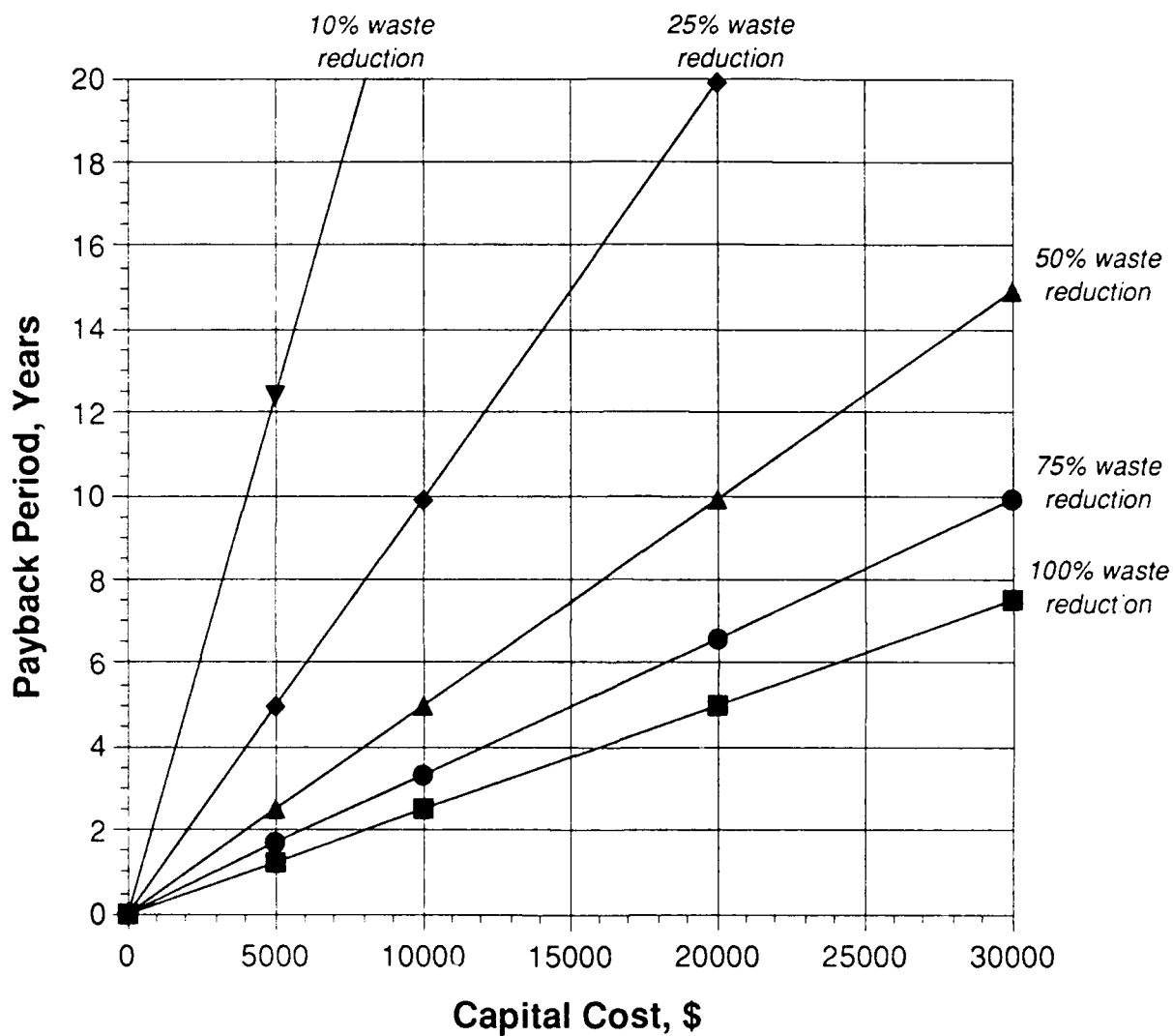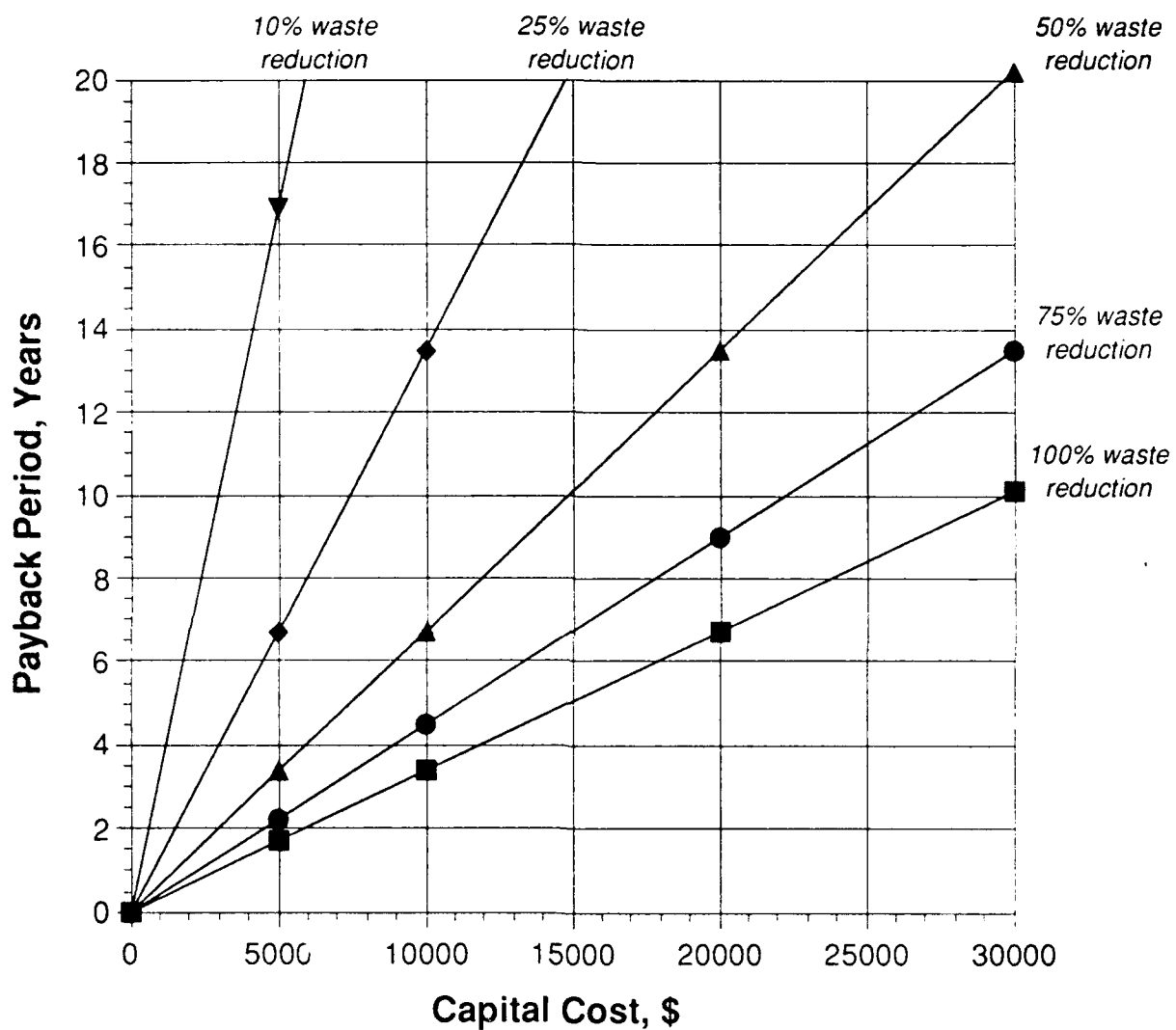
Figure 5-1.
Payback Period Versus Capital Cost
for Selected Waste Reduction
Percentages at CCAD.

Figure 5-2.
Payback Period Versus Capital Cost
for Selected Waste Reduction
Percentages at RRAD.

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Figure 5-3.
Payback Period Versus Capital Cost for
Selected Waste Reduction Percentages
at SAAD, 1991 Contract Rates.

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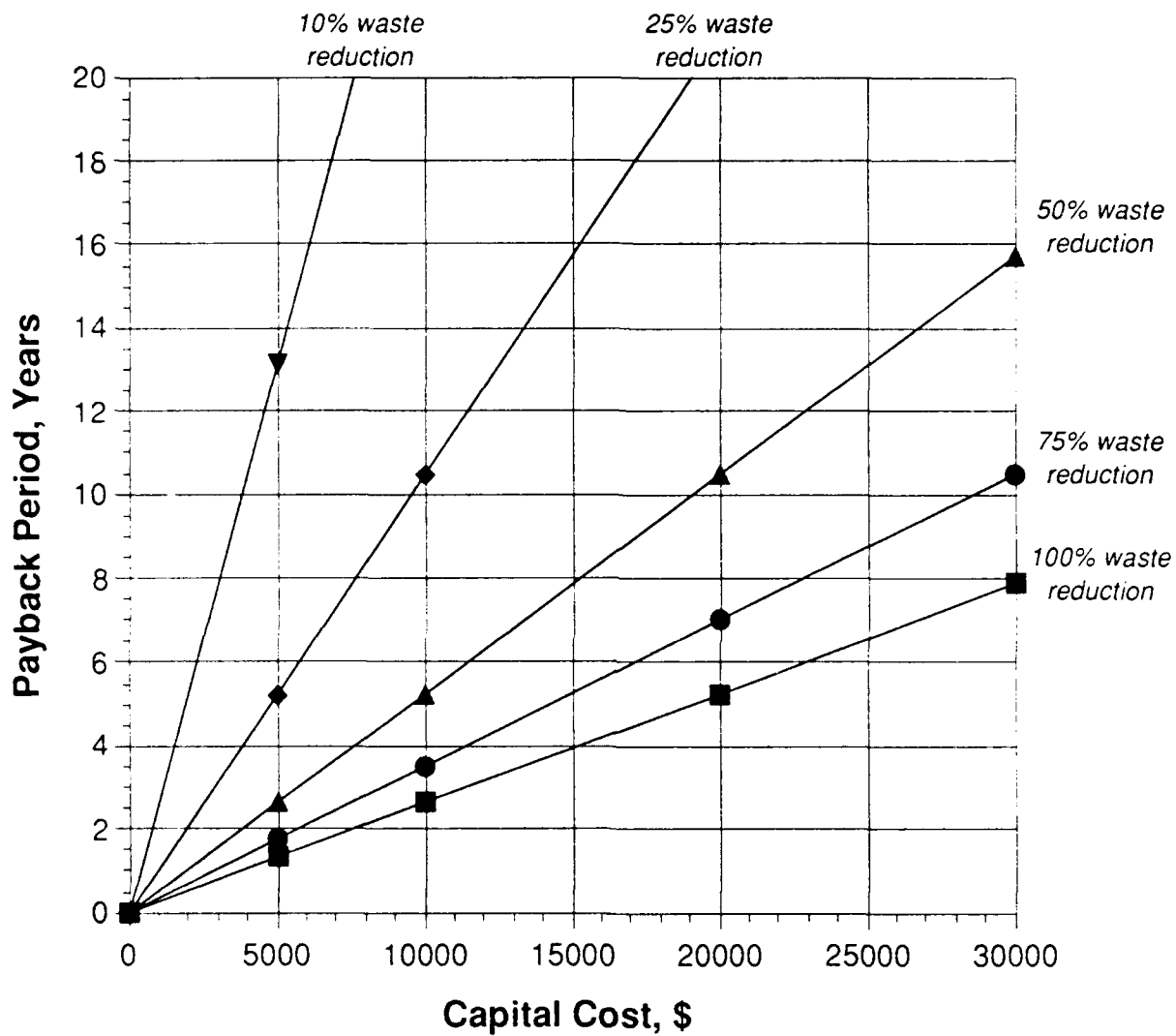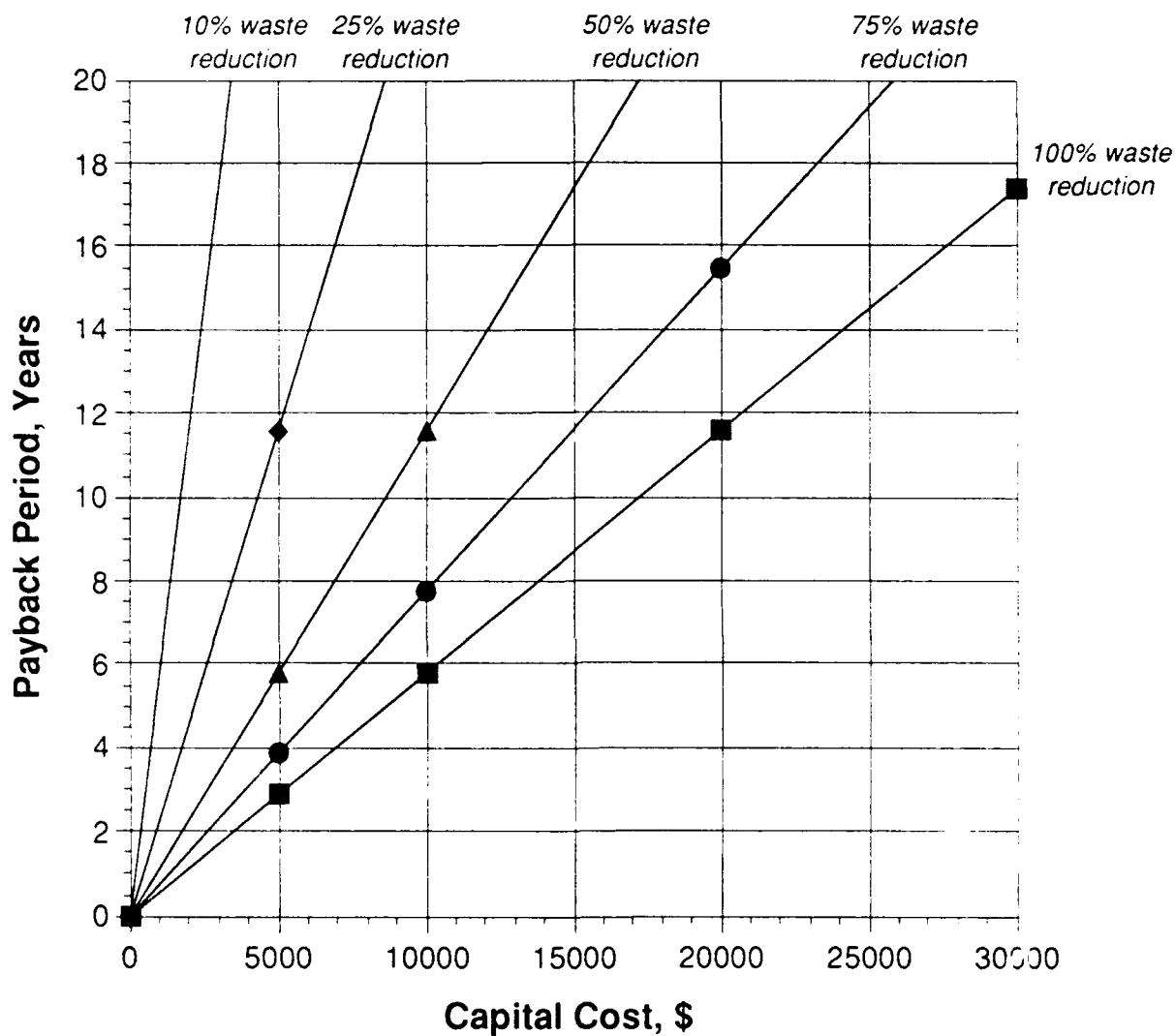
Figure 5-4.
Payback Period Versus Capital Cost for
Selected Waste Reduction Percentages
at SAAD, 1992 Contract Rates.

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100 percent waste reduction. This analysis assumes that the percent reduction in makeup chemicals will equal the reduction in waste disposal.

Table 5-4
Payback Period Versus Capital Costs
for 100 Percent Waste Reduction

Capital Cost, $	Payback Period for CCAD, yr	Payback Period for RRAD, yr	Payback Period for SAAD at 1991 Disposal Costs, yr	Payback Period for SAAD at 1992 Disposal Costs, yr
500	0.12	0.17	0.13	0.29
1000	0.25	0.34	0.26	0.58
5000	1.2	1.7	1.3	2.9
10,000	2.5	3.4	2.6	5.8
20,000	5.0	6.7	5.2	12
30,000	7.5	10	7.9	7

An additional factor in the cost analysis that could vary widely is the unit cost of waste disposal. CCAD and SAAD originally indicated costs of $2.20/lb and $2.50/lb ($22/gal and $25/gal), respectively, while RRAD reported waste disposal costs of $0.73/lb ($7.27/gal). In early 1992, SAAD received a new contract for disposal of EN solutions at $0.60/lb ($6.00/gal), representing a 76 percent decrease in disposal cost, and decreasing annual disposal/makeup costs by 55 percent (the makeup costs do not change). Waste minimization equipment costs of $20,000 yielded a payback period of 5.2 years under the old contract rate and 12 years under the new contract rate. Similarly, if CCAD paid the same disposal costs as SAAD's new rate, equipment costs of $20,000 would yield a payback of 14 years instead of the 5.0 years calculated using CCAD's current rate. Reducing waste disposal costs therefore could result in significant cost savings, but would also make the implementation of waste minimization technologies appear less attractive. The reduction in waste disposal cost could result from lower contract disposal costs or through alternative methods of waste disposal such as treating the EN bath by plating the nickel onto steel wool. Costs for in-tank treatment of EN by plate-out range from $0.20 to $2.00/gal (excluding the credit received for selling the plated nickel and the cost of treating the residual liquid) [Subsection 4.5], compared with the $6 to $25/gal currently paid by depots for waste disposal.

Returning to Figures 5-1 through 5-4, the "percent reduction" lines can represent waste reduction for a constant unit disposal cost, or cost reduction for given waste generation and

chemical makeup rates. Again, waste reduction of less than 100 percent or cost reduction independent of waste generation rates make waste minimization technologies less attractive.

Cost elements that would need to be considered in a more comprehensive analysis include the following: replenishment chemicals, labor for operating the EN tank, labor for analysis and additions, and labor for disposal of the solutions. Costs associated with waste minimization technologies that have been excluded because data are not available include: disposal of side waste streams, chemicals needed for operation of the decontamination technology, labor for operating and maintaining the technology, other materials such as ion exchange resins, and utilities. On the other hand, costs for rejects and poor product quality could be reduced by implementing waste minimization techniques.

One cost element that should be emphasized but that cannot be quantified relates to the fact that most of orthophosphite-removal technologies are only in the laboratory stage of development, or at most, have only one unit in production. Therefore, some developmental costs would be associated with purchasing a unit. In addition, implementation of a complex technology at a depot would result in some additional costs. In particular, analytical costs would be increased if individual analyses were required for hypophosphite, complexing agents, and stabilizers.

Finally, the literature is not definitive about which contaminants (orthophosphite, sodium, sulfate) cause which plating or coating problems (decreased deposition speed, decreased corrosion resistance, increased stress). Therefore, testing of plating and coating properties could be required in order to determine if an EN solution after treatment with a contamination technology still met the specific requirements of a particular facility and application. This testing would result in additional developmental costs.

Because cost elements not considered in this analysis tend to discourage implementation of comprehensive decontamination technologies, the payback periods given earlier are weighted more in favor of implementation of these technologies than a more comprehensive cost analysis would yield; i.e. the actual payback periods for implementation would likely be longer than presented in this preliminary evaluation. Additionally, the nonquantifiable benefits of waste reduction should always be considered. These include the environmental ethic, the DESCOM directive of "zero discharge," and public relations.

6.0 Conclusions and Recommendations

This section presents conclusions and recommendations based on the information and descriptions presented in earlier sections and the evaluation presented in Section 5.

6.1 Conclusions

The major conclusion of this study is that EN operations at the three Army depots evaluated generate relatively insignificant quantities of waste. The current total waste generation from these depots is estimated to be only 495 gallons (4950 pounds) per year. The total disposal cost associated with this waste is currently $5813/yr. While potential for waste minimization of this source exists, the overall impact of any change in EN operations to the Army's overall waste-generation rate will be minimal at this time.

The following additional conclusions have been reached based on information presented in this project report:

1. Spent EN solutions are not RCRA-listed or characteristic hazardous wastes. They are, however, defined as hazardous waste by the State of California and are Class 1 industrial nonhazardous waste in Texas.

2. The mechanisms responsible for solution depletion at Army depots are not well understood. Available information indicates that orthophosphite buildup is usually the limiting factor in EN bath lives because it decreases plating rate and may cause spontaneous bath decomposition. Sodium and sulfate buildup may significantly decrease coating quality by decreasing corrosion resistance and increasing the internal stress of the deposit. A successful waste minimization technology must reduce the concentration of the contaminants that contribute most to solution depletion at a particular facility.

3. The three Army depots currently using EN practice some of the common and available waste minimization techniques typical of the industry (e.g., filtration and contaminant prevention).

4. The decontamination technologies that promise the greatest percentage reduction in waste generation are in their early stages of development and are capital intensive.

5. The orthophosphite-removal technologies currently being developed require increased analysis of the EN solutions.

6. Using an ideal assumption of 100 percent waste reduction, the payback period for major decontamination technologies (capital cost of $20,000 to $30,000) is 5 to 7.5 years at CCAD, 6.7 to 10 years at RRAD, 5.2 to 7.9 years at SAAD under 1991 contract disposal rates, and 12 to 17 years at SAAD under 1992 contract disposal rates.

7. Given current waste generation rates, pursuit of the major decontamination technologies does not appear to be cost-effective for implementation at the Army depots.

8. Developing these technologies for a wider market or for a given facility with a larger waste generation rate may be economical. These results could be extended to the Air Force and Navy or potentially to other Army facilities.

6.2 Recommendations

Recommendations are made in the following areas for implementation at the Army depots:

1. Depot personnel should continue to work with vendors to select the best bath chemistry for the particular application. The goal is to achieve a stable bath with the most turnovers. For example, the vendor of the solutions used at SAAD indicated that they have developed solutions with longer bath lives that are more appropriate for the depot's applications (high priority).

2. Ensure that the "easy" waste minimization methods are implemented: prevent drag-in and dust contamination; cool the solution rapidly at the end of a shift; and minimize time spent at elevated temperatures (high priority).

3. Maintain the bath within narrow chemical ranges to provide increased bath stability; implement automatic monitoring and install a control system to provide this function and to produce good record keeping (high priority).

4. Determine if waste disposal costs can be reduced through contract mechanisms (high priority).

5. Investigate the simple decontamination techniques: electrolysis and carbon treatment. (Limitations of these techniques were provided in Sections 4 and 5.) Vendors of depot-specific solutions should be contacted regarding the appropriateness of these techniques.

6. Determine if using in-tank plate-out to recover nickel will reduce disposal cost and waste; treat resulting liquid in wastewater treatment plant. Determine if this method is allowable by State and local regulations.

7. Keep track of purification system developments. Once fully developed, they may become more economically attractive as EN is used more often to replace chromium and cadmium electroplating.

8. Develop an analytical program to determine the reasons for EN bath failure so that waste minimization methods can be targeted. Analysis of spent solutions would verify whether orthophosphite or metals are the primary cause of solution degradation.

9. Transfer the results of this project to the Navy and the Air Force so that they can determine if the technologies may be more economical for implementation at their facilities.

10. Conduct demonstration tests of automatic monitoring and control or in-tank plate-out. These techniques are commercially available, relatively inexpensive, and have significant potential for reducing waste generation.

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