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ECONOMIC ANALYSIS OF A ZERO DISCHARGE INDUSTRIAL WASTEWATER TREATMENT PROCESS

An Investigation Conducted by:

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December 1995

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

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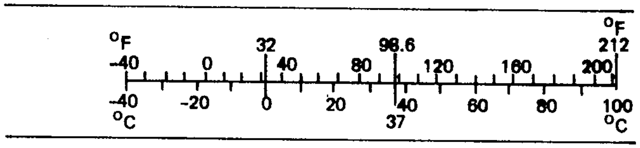
*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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13. ABSTRACT *(Maximum 200 words)*

This document reports the results of an economic analysis of advanced and emerging industrial wastewater treatment plant (IWTP) technologies. Conventional IWTPs have been capable of handling a wide range of flow rates and concentration of influent waste streams from metal plating and finishing shops. New regulations and the increase in disposal costs for solid wastes have required the Navy to focus on improving the metal removal efficiency and waste generation rates. The Navy is developing Zero Discharge Technologies for three waste steams: (1) chromium, (2) cyanide, and (3) acid/alkali cleaning wastewaters. A Zero Discharge IWTP conceptual design described in this document incorporates advanced separation technologies for metals removal and recovery, advanced oxidation processes (AOP) for mineralization of organics, and membrane separation technologies. This document reports an economic analysis of the unit processes identified in the Zero Discharge IWTP design, identification of further effluent polishing/purification methods, and an assessment of system costs for each effluent recycling option.

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Preface

On 28 September 1994, the Naval Facilities Engineering Service Center (NFESC) authorized Arthur D. Little, Inc. to initiate Delivery Order No. 0009 entitled "Economic Analysis of a Zero Discharge Industrial Wastewater Treatment Process" under Contract No. N47408-94-D-7410. This delivery order focuses on the development of innovative industrial wastewater treatment concepts, the development of an economic analysis for each concept, and comparison of the concepts to the conventional industrial wastewater treatment plant (IWTP).

1.0 Introduction

The Navy, along with other Department of Defense (DOD) and industrial organizations, faces ever-increasing regulatory scrutiny and disposal costs associated with the current methods of industrial wastewater treatment. The Navy's industrial wastewater treatment plants (IWTPs) employing conventional treatment methods produce greater than 2,000 tons of hazardous waste sludges annually. In 1992, operation of these IWTPs resulted in over 120 Notices of Violation for the U.S. Navy. The Navy is, therefore, investigating advanced and emerging IWTP technologies that will meet future treatment needs, substantially reduce the sludge produced by conventional metals precipitation techniques, and recover the value of waste by-products.

Additionally, new and more stringent regulations are being developed for the metal fabrication industries and are scheduled for promulgation by the end of 1995[1]. On 21 January 1992, as a result of a lawsuit brought by Public Citizens Inc. and the Natural Resources Defense Council (NRDC) against EPA, a Consent Decree was issued regarding the implementation of Section 304 (m) of the Clean Water Act. The result of the Consent Decree has been an increase in regulations for industrial pretreatment programs for four major industrial areas:

- Pharmaceutical manufacturing;
- Pesticide active ingredients manufacturing;
- Waste treatment; and
- *Metal products and machinery.*

Of specific interest to the Navy has been, the effluent guidelines on metal products and machinery. These guidelines, as currently defined, will apply to industries that generate wastewater during the manufacture of metal parts and metal products and during the assembly, rebuilding, repair and maintenance of such products. Metal products and machinery industries identified for regulation are shown in Table 1-1.

Table 1-1: Metal Product and Machinery Industries Identified for More Stringent Wastewater Regulations

• Household electrical equipment manufacturing	• *Ship manufacturing, rebuilding, and maintenance*
• Bus and truck manufacturing	• Industrial and electrical equipment manufacturing
• *Aircraft manufacturing and maintenance*	• Office machine manufacturing and maintenance
• Automotive repair	

In response to the increasingly stringent regulations (scheduled for implementation by the end of 1995) relating to wastewater pretreatment, the Navy has developed conceptual designs for Zero Discharge IWTPs that incorporate advanced separation technologies for metals removal and recovery, advanced oxidation processes for mineralization of organics, and membrane separation technologies to allow the effluent from the treatment system to be recycled to the industrial process.

The objective of this delivery order was to conduct an economic analysis of the conceptual Zero Discharge designs and the investigation of polishing/purification methods for alternative effluent recycling options. This objective was accomplished by:

- Conducting an order of magnitude economic analysis of the unit processes identified in the Zero Discharge IWTP conceptual design;
- Identifying further effluent polishing/purification methods that will be needed for recycling options (i.e., treated effluent used as industrial process water, cooling water, or for irrigation); and
- Assessing the impact on system costs for each effluent recycling option.

2.0 Background

Conventional IWTPs have been used for a number of years and are capable of handling a wide range of flow rates and concentrations. Because of the flexibility of the IWTP, many metal plating and finishing operators have not been concerned about the wastes each operation is generating. New regulations and the increase in disposal costs for solid wastes have required many operators to focus on improving the metal removal efficiency and waste generation rates. The Navy is developing Zero Discharge Technologies for three waste streams:

- Chromium electroplating wastewater;
- Cyanide process wastewater; and
- Acid/alkali cleaning wastewater.

Treatment of metal finishing wastes by neutralization and hydroxide precipitation of metals followed by gravity settling for separation of the metal hydroxide solids – with additional treatment steps for hexavalent chromium and cyanide – has become so widely used in the metal finishing industry that it is usually referred to as "conventional" treatment. Figure 2-1 shows the flow diagram for a conventional IWTP for electroplating wastes containing chromium and cyanides in addition to other heavy metals, acids, and alkalis.

Pollutant loading on an IWTP is often subject to wide variation. Table 2-1 presents the typical constituents found in electroplating wastewater and a corresponding range of concentrations developed by the U.S. Environmental Protection Agency (EPA) during a survey of the electroplating industry[2]. Also presented in Table 2-1 are data provided by the NFESC Project Engineer for influent data to an IWTP located at Naval Aviation Depot-North Island (NADEP-NI)[3].

In both cases, Table 2-1 shows variations between plants as well as within each plant. It is essential that the variations be understood and that the waste treatment system be sized to handle variations that cannot be eliminated. The variability in the wastewaters comes in large part from the large number of processes that generate the wastes and the inherent variability in the operation of the processes. These same factors also lead to a significant variation in the flow rate that these treatment plants have to be designed to handle.

Conventional IWTPs have been designed to handle the variability in the concentration and flow rate and have worked so well that there has been little need to change the basic operation of these system for many years. In addition, the ability of the conventional IWTP to handle the wastewater variability has allowed the operators of metal plating and finishing operations to only marginally consider the waste that each operation is generating.

New regulations and increasing costs for the disposal of sludges have required many operators of metal plating and finishing operations to focus on improving the removal efficiency of the conventional IWTP and reducing the amount of sludge that is generated. To meet these needs, the Navy has found that implementing wastewater treatment processes close to the individual operations has been very successful, and in developing the Zero Discharge Technologies, we have placed them as close to the process as to be practical and assumed that most of the high concentration wastewaters will have been treated prior to coming into the system. In some cases, where there is a synergy between

Figure 2-1: Process Flow for Electroplating Industry Conventional Integrated Wastewater Treatment

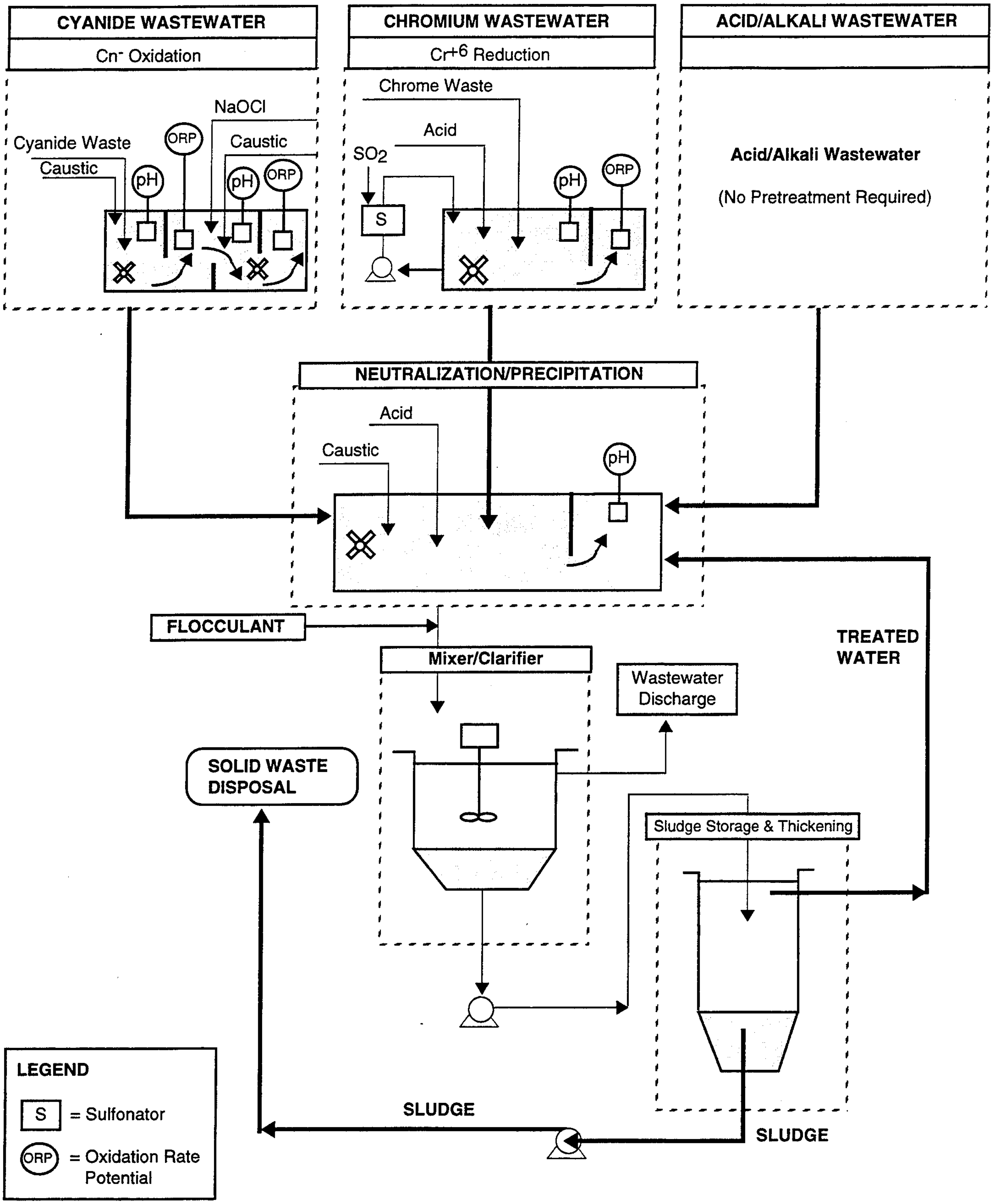


Table 2-1: Comparison of EPA Industry Standard- and NADEP-NI-Pollutant Loading Data for Integrated Wastewater Influent from Electroplating Operations

Constituent	EPA DATA Range (ppm)[2]	NADEP-NI Range (ppm)[3]
• Copper (Cu)	0.032 - 272.5	< 10
• Nickel (Ni)	0.019 - 2.954	< 10
• Chromium (Cr)		20 - 50
- Total	0.088 - 525.9	
- Hexavalent (Cr^{+6})	0.005 - 334.5	
• Zinc (Zn)	0.112 - 252.5	Not Available
• Cyanide (CN^-)		3 - 50
- Total	0.005 - 150.0	
- Amendable to chlorination	0.003 - 130.0	
• Fluoride (F^-)	0.022 - 141.7	Not Available
• Cadmium (Cd)	0.007 - 021.6	10 - 20
• Lead (Pb)	0.663 - 025.4	< 20
• Iron (Fe)	0.410 - 1482	Not Available
• Tin (Sn)	0.060 - 103.4	Not Available
• Phosphorous (P)	0.020 - 144.0	Not Available
• Silver (Ag)	Not Available	< 10
• Phenols	Not Available	< 5
• Methylene chloride	Not Available	< 5
• Total suspended solids	0.100 - 9970	Not Available

the Zero Discharge Technology and the recovery process for high concentration wastes, the recovery process has been integrated into the Zero Discharge Technology (e.g., electrolysis).

A second result of the new regulatory climate has been to try and eliminate all discharges of waste to the environment (hence the name Zero Discharge Technology). However, in some cases, we found that the elimination of all discharges caused the economics of the system to be unfavorable and in those cases the Navy may want to reconsider the strict definition of zero discharge. We have commented on this as it has occurred in the development of the economic analyses.

In order to place the Zero Discharge Technologies as close as possible to the processes, the metal plating/finishing wastewater stream was divided into three process wastestreams:

- Chromium electroplating wastewater;
- Cyanide process wastewater; and
- Acid/alkali cleaning wastewater.

Because the economic analysis is based upon a hypothetical Naval Activity, assumptions were made about the wastewater streams to form the basis for the economic analyses of advanced Zero Discharge IWTP concepts.

- The end-of-pipe IWTP will treat rinse waters and wastes generated from typical Naval metal finishing operations.

- The metal finishing operations will have source reduction technologies implemented on-line.

- The wastewater treated by the Zero Discharge Technology will be recycled back to the generating process. The quality of the water must conform to the military specifications that define the metal finishing process.

- The wastewater will be segregated into three effluent streams: cyanide-bearing wastes; chromium-bearing wastes; and acid/alkali wastes. The wastewater streams are generated 8 hours/day and 260 days/year.

3.0 Conventional Industrial Wastewater Treatment

Conventional IWTP have been used for many years to treat wastewaters from metal plating and finishing operations. Most IWTPs pretreat the cyanide and chromium wastewaters and then combine all the wastewaters and precipitate the metals as metal hydroxides. The metal hydroxide sludge is then dewatered and disposed of in a RCRA Subtitle D landfill and the treated water is released to the environment or a municipal sewer.

For the hypothetical Naval activity approximately 90 gpm of wastewater is treated. The capital cost of the system is approximately $630,000 and the annual O&M cost is $200,000. The net present value of the process, assuming a 10 year life and a 7 percent interest rate, is $2.0 million.

3.1 Industrial Wastewater Treatment Plant Description

The conventional "integrated" IWTP combines the effluents from chrome electroplating, cyanide rinse and dips, and acid/alkali cleaning into a single flow for treatment. The following discussion describes the process and the chemical reactions that occur in each unit operation. A process flow diagram is shown in Figure 2-1 and a more detailed process flow diagram showing treatment chemistry is presented in Figure 3-1. Each of the following sections relates to a corresponding block on the detailed process flow diagram.

The chromium electroplating, cyanide rinse and dip, and the acid/alkali undergo different pretreatments during the first part of the processing. However, after the initial treatment all three streams are combined during the neutralization step and become a single, integrated wastewater stream. For ease of reviewing the description of the conventional IWTP, this section has been divided into four sections:

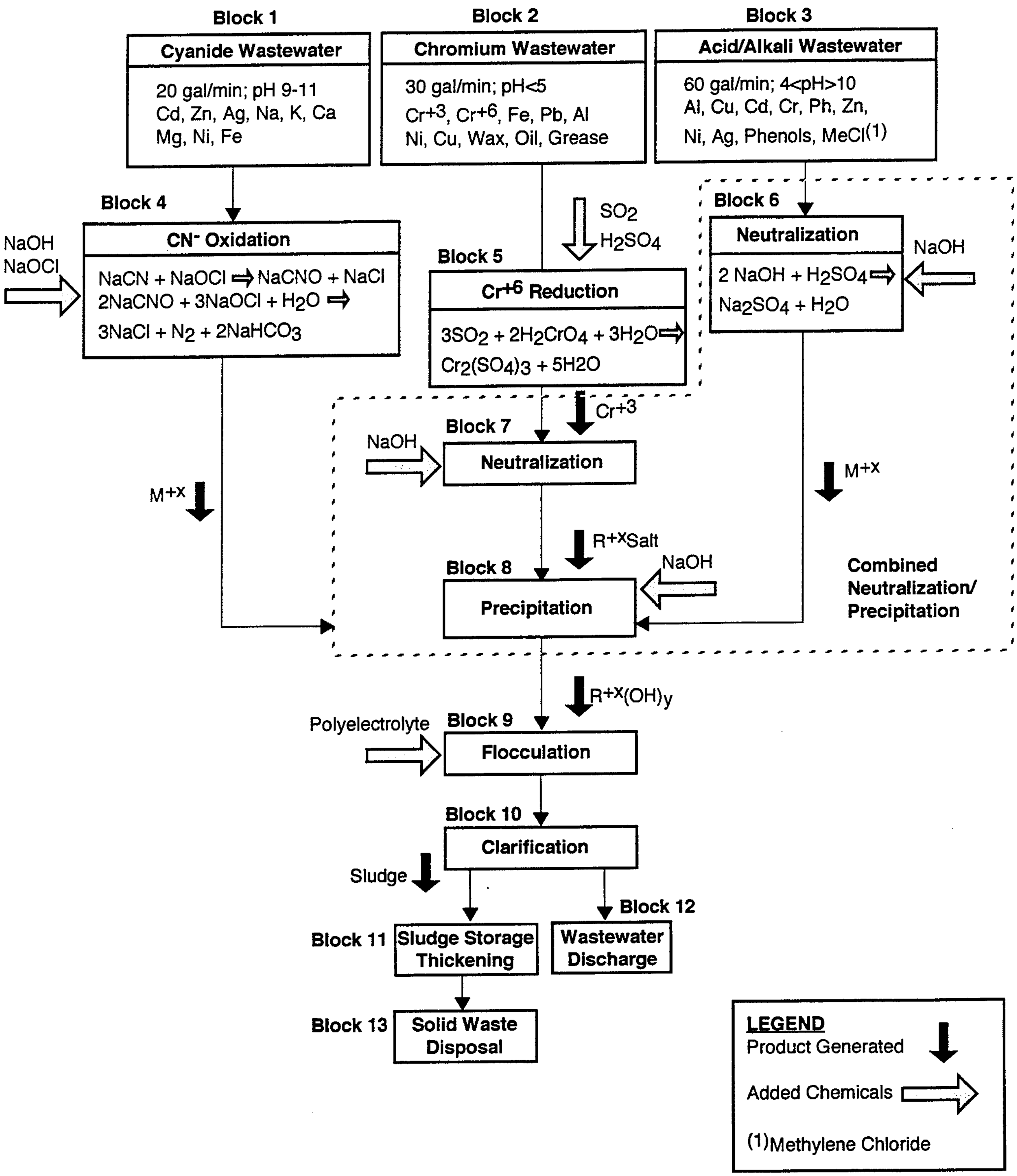
- Cyanide wastewater pretreatment;
- Chrome wastewater pretreatment;
- Acid/Alkali wastewater pretreatment; and
- Integrated wastewater treatment.

3.1.1 Cyanide Wastewater Pretreatment (Block 1 and 4, Figure 3-1)

The cyanide wastewater stream, based on the hypothetical Naval Activity, has a typical flow rate of 20 gallons per minute (gpm) and has a basic pH of 9 to 11. The wastewater is maintained at a basic pH to prevent the reaction of the cyanide with mineral acids that produce hydrogen cyanide (HCN), a colorless and toxic gas. Typical contaminants include cadmium, zinc, silver, sodium, potassium, calcium, iron, and magnesium.

A contaminant that is sometimes present in the cyanide rinse water is nickel. Nickel contamination usually results when chemical-storage drums used to store the cyanide-process chemicals were previously used to store chemicals used for nickel plating operations. The presence of nickel can be a concern because nickel cyanide forms a very stable cyanide complex that is difficult to treat. For purposes of this study, it is

Figure 3-1: Process Schematic for Conventional Integrated Wastewater Treatment System that Shows Treatment Chemistry



assumed that good materials management programs will be implemented, and that they will eliminate the nickel contamination in the cyanide line.

The preliminary step in the treatment of cyanide wastewater is the "destruction" of the "free cyanide" by oxidation with sodium hypochlorite (NaOCl) or chlorine gas (Cl_2). When sodium hypochlorite is added in excess of the stoichiometric requirements and the wastewater stream is heated, the free cyanide is eliminated (as determined by chemical tests), but small amounts of complexed cyanide have been found to remain in the solution when analyzed by EPA Method 335.2[4]. The presence of the remaining complexed cyanide in the process solution is of concern when the wastewater treatment operation is enclosed in a recirculating ventilation room that is small in size. The concern is based on the addition of acid to the wastewater which would break the complex and form HCN. Following discussions with the NFESC Project Engineer, this concern was eliminated based on the assumption that the wastewater treatment systems would be operated in the open-air.

The cyanide complexes are oxidized per the following reactions. The oxidation reagent is usually chlorine, which can be introduced into the system by adding chlorine gas or sodium hypochlorite. In this case, NaOCl was selected because of the hazards of storing and handling gaseous Cl_2.

When sodium hypochlorite is introduced as the oxidant, the typical first stage reaction is:

- $NaCN + NaOCl \longrightarrow NaCNO + NaCl$

and in the second stage:

- $2NaCNO + 3NaOCl + H_2O \longrightarrow 3NaCl + N_2 + 2NaHCO_3$

Continuous systems use two series-connected reaction tanks. In the first stage, the pH is adjusted between 9 and 11 using an alkali such as caustic or lime. The pH in the second reaction chamber is controlled at approximately 8.5. An excess of sodium hypochlorite is added to ensure the complete oxidation of all available cyanide. Demand for the hypochlorite in the first stage is determined by measuring the oxidation rate potential (ORP). The reaction time needed is approximately 25 to 30 minutes in each stage.The cyanide stream is maintained at a pH of 9 to 11 by adding caustic (NaOH) to prevent the formation of HCN.

After the CN is oxidized the wastewater is pumped to the precipitation tank for subsequent processing with the chromium and acid/alkali wastewater streams, which will be discussed in Section 3.1.4.

The difficulty with cyanide oxidation in the development of zero discharge technologies is the addition of a significant concentration of dissolved solids to the wastewater. In the conventional IWTP, the increase in dissolved solids is not a concern; however, for zero discharge technologies the water is intended for recycle to the process and dissolved solids will continue to increase as the water is reused. Because of this issue, a zero discharge technology would have to include a unit operation to remove the dissolved solids. In general zero discharge technologies need to minimize the amount of solids that are added to the water during treatment.

3.1.2 Chromium Wastewater Pretreatment (Block 2, 5, and 7, Figure 3-1)

The chromium wastewater stream (shown as Block 2, Figure 3-1) is acidic with a pH of 5 or less and has a typical flow rate of 30 gpm. Common contaminants include iron, lead, aluminum, nickel, copper, and organic materials such as waxes, oils, and greases. Granular activated carbon units are used to remove the organic materials, which may interfere with subsequent processing.

The chromium wastewater is initially treated in a chromium reduction unit, the acidic effluent neutralized with sodium hydroxide to a basic pH, and fed into the integrated wastewater stream in the precipitation tank, where all three wastewater streams (chromium, cyanide, and acid/alkali) are treated as a single stream.

Chromium complexes are usually present in electroplating wastewater as trivalent chromium (Cr^{+3}) and hexavalent chromium (Cr^{+6}). The first step in treating the chromium electroplating wastewater is the reduction of the Cr^{+6} to Cr^{+3}. In a subsequent treatment processes, metal cations are converted to insoluble metallic hydroxides to remove them from the water stream. Cr^{+6} does not form an insoluble hydroxide, thus it cannot be precipitated out of solution. Therefore, all chromium cations must be converted to Cr^{+3} to ensure its subsequent removal by precipitation.

Reduction is usually performed by reacting Cr^{+6} with gaseous sulfur dioxide (SO_2) or a solution of sodium bisulfite ($NaHSO_3$). The net reaction using sulfur dioxide is:

- $3SO_2 + 2H_2CrO_4 + 3H_2O \longrightarrow Cr_2(SO_4)_3 + 5H_2O$

Because the reaction proceeds rapidly at low pH, an acid is added to control the chromic acid wastewater pH between 2 and 3. Gaseous sulfur dioxide is metered continuously into the reaction tank to satisfy the reduction demand based on the concentration of Cr^{+6}.

The acidic wastestream from the chromium reduction unit is fed into a neutralization tank, where the acidic solution is neutralized with sodium hydroxide prior to mixing with the other waste streams (Block 7, Figure 3-1). The acidic pH (2 to 3) of the chrome wastewater stream after chromium reduction will react violently with the higher pH wastewaters found in the precipitation tank; therefore, the chrome wastewater stream is neutralized prior to combining the streams.

3.1.3 Acid/Alkali Wastewater Pretreatment (Block 3 and 6, Figure 3-1)

The acid/alkali wastewater stream results from various washing/metal cleaning operations. It has the widest variation in pH, with a pH of 4 to 10, and the largest flow of the three waste streams. The typical flow rate is 60 gpm, and the typical metallic contaminants are aluminum, copper, cadmium, lead, zinc, nickel, and silver. This wastestream also contains phenols and methylene chloride as contaminants.

The methylene chloride and phenols are largely digested in the various acid/base reactions, and remain in the wastewater in low concentrations. However, increasingly stringent regulations on the discharge of these "refractory" compounds into publicly owned treatment works (POTWs) raises a concern under the new wastewater regulations that target some Navy operations. The Zero Discharge techniques evaluated in this study assume that the refractory compounds have to be eliminated also.

The only pretreatment required for this wastewater stream is the neutralization of the pH, shown in Block 6, Figure 3-1, prior to the precipitation of the metallic cations in the subsequent precipitation step (Block 8).

3.1.4 Integrated Wastewater Treatment (Blocks 7/8 to 13, Figure 3-1)

In this phase of the treatment, the wastewater from the chromium, cyanide, and acid/alkali processes are combined following the specialized pretreatments required to produce a solution of metal cations in a neutral aqueous solution (Block 8). All subsequent treatments are designed for the treatment of the integrated wastewater stream.

Precipitation of Metal Hydroxides (Block 8, Figure 3-1). The mixed waste streams from the acid/alkali metal cleaning and plating operations are combined in the neutralization/precipitation tank with the effluent from the chromium reduction and cyanide oxidation steps. Because the heavy metals are soluble at low pH (acidic) conditions in the wastewater, the pH is adjusted to a range of 7.5 to 9.5. In this pH range, the minimum solubility of a mixture of metals is reached and the metals precipitate as hydroxides.

Single-stage, continuous neutralizers – where an alkali such as lime ($Ca[OH]_2$) or caustic soda ($NaOH$) is fed into a single reaction vessel – are usually adequate for electroplating operations. If, however, the wastewater is subject to rapid changes in flow rates or pH, a multistage neutralizer is required. In the multistage units, most of the alkali is added in the first vessel to increase the pH to 6.

Final pH adjustments of the wastewater are made in the remaining reaction vessels to promote precipitation and to enhance the settling characteristics of the metal hydroxides. To maintain adequate pH control, the retention time for typical neutralization/precipitation systems is 10 to 30 minutes. A system using lime usually requires more retention time, as the time required for completely dissolving the lime retards the response of the system to the reagent addition.

Flocculation (Block 9, Figure 3-1). To enhance the settling characteristics of the suspended solids, flocculating agents – such as polymers, alum, or ferrous sulfate – are added in a mixing chamber before the flocculator. In the flocculator, the wastewater is agitated gently to allow the solids to flocculate. The wastewater is then discharged to the clarifier.

Clarification (Block 10, Figure 3-1). Metal hydroxides and other insoluble pollutants are removed from the wastewater by gravity settling. The solids removal efficiency depends on the settling rate of suspended solids in the wastewater feed.

Typically, some of these solids settle very slowly because of their small size and their slight density difference compared with the water. Because economical design of the clarifier limits the retention time in the settling chamber, some level of suspended solids will appear in the overflow. The overflow from the clarifier will be discharged to the environment or sent to a municipal sewer.

Sludge Handling (Block 11, 13-Figure 3-1). The solids from the clarifier are typically discharged to sludge holding tanks at solids concentrations of 0.5 to 3 percent; overflow from the tank is recycled to the clarifier. Usually metal hydroxide solids will concentrate to approximately 3- to 5-percent solids in these tanks if given adequate time.

Further concentration of the thickened sludge is performed using mechanical dewatering equipment. Centrifuges, rotary vacuum filters, belt filters, and filter presses have been used to dewater metal hydroxide sludge. For metal hydroxide sludges where lime has been used to precipitate the metals the solids concentration can be raised to between 10 and 20 percent. However, the applicability of a particular dewatering device for a specific sludge, and the degree of cake dryness the device will achieve, can only be determined by bench-scale testing with the intended feed material. The water from the dewatering operation would be sent back to the precipitation tank for treatment.

After the sludge has been dewatered it must be sent off-site for disposal. In this study, we have assumed that the sludge can be disposed of in a RCRA Subtitle D landfill.

3.2 Economic Analysis of Conventional Integrated Wastewater Treatment

The conventional integrated wastewater treatment facility is included as a basis for comparison, since an "order-of-magnitude" cost is relative. For purposes of this study, site preparation costs are not included. The costs given are order-of-magnitude (+100/-50 percent) and include the capital costs of the systems (Table 3-1). Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the conventional IWTP would be approximately $630,000 and the annual O&M costs would be $200,000. The net present value of the process, assuming a 10 year life and a 7 percent interest rate would be $2.0 million. The most sensitive aspect of the cost analysis is the disposal cost for the sludge and the consumable process chemical costs. If either of these were to increase significantly, the cost of the conventional system would also be increased significantly.

Table 3-1: Economic Analysis of Conventional Integrated Wastewater Treatment

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
Chromium Reduction Unit (continuous system rated at 30 gal/min)	ea	72,000	1	$72,000
Cyanide Oxidation Unit (continuous system rated at 20 gal/min)	ea	125,000	1	$125,000
Neutralization/Precipitation (single-stage continuous system rated at 110 gal/min)	ea	84,000	1	$84,000
Flocculation/Clarification Unit (continuous system rated at 110 gal/min)	ea	93,000	1	$93,000
Sludge Storage Tank (5,000 gal)	ea	13,000	1	$13,000
Belt Filter Press for sludge dewatering	ea	100,000	1	$100,000
Total Equipment Cost				$487,000
Installation Cost		30% equipment cost		$146,100
Total Installed Cost				$633,100
O&M Costs[a]				
Operating labor (8 hr/day)	hr	18.00	2080	$37,000
Supervision (4 hr/day)	hr	22.00	1040	$23,000
Maintenance		6% equipment cost		$22,000
Chemical cost[b]				$35,000
Sludge disposal cost	ton	150	500	$75,000
Utilities (electricity)	KWhr	0.06	120,000	$7,000
Total Annual Cost				$199,000
Net Present Value[c]				

Capital Cost	O&M Cost	Discount Factor	Total NPV
$633,100	$199,000	7.0236	$2,030,696

a *Annual operation is assumed to be 260 days/yrs.*

b *See Table A-1 and Figure A-1. Chemical amounts calculated on demand rates.*

c *NPV is calculated based on a 10 year equipment life and a 7% interest rate.*

4.0 Advanced Concepts for Treating Chrome Electroplating Wastewater Streams

Two zero discharge concepts were evaluated for the treatment of chrome-bearing wastewater:

- Ion exchange separation of the metals with electrodialytic recovery of the chromic acid and the regenerant chemicals used to recharge the ion exchange columns; and

- Ion exchange separation of the metals with electrolytic recovery of the metals.

The ion exchange/electrodialytic process has the advantage of recovering the highly toxic chromium from the wastewater as chromic acid, which is reused in the chrome plating process. The acid and base used to recharge the ion exchange columns are regenerated for reuse. Compared to conventional wastewater treatment, this process produces a reduced volume of metallic hydroxide sludge. Two methods of handling the sludge were evaluated for cost benefits: (1) disposal as a hazardous waste or (2) hydrometallurgical treatment of the sludge to render the waste non-hazardous. The hydrometallurgical treatment resulted in an annual 12 percent savings over disposal of the waste as a hazardous material.

The ion exchange/electrolytic recovery of the metallic contaminants has two distinct advantages over the ion exchange/electrodialytic wastewater treatment process: (1) in addition to the recovery of the chromic acid and ion exchange recharging chemicals, virtually all water is recovered for reuse in the process; and (2) there is no sludge generated during this process that has to be disposed of or treated.

Both systems are roughly equivalent in capital costs and have O&M costs that are within ± 10 percent of each other. Of the three wastewater streams evaluated (i.e., chrome, cyanide, and acid/alkali), the chrome-bearing alternative wastewater treatments come the closest to meeting zero discharge requirements.

Concept	Capital Cost	Annual O&M Cost		Total NPV
Ion Exchange/ Electrodialysis	$190,000	Option 1- Hazardous Waste Disposal	$124,820	$1.1 million
		Option 2- Hydrometallurgical Treatment of Waste Sludge	$109,827	$0.96 million
Ion Exchange/ Electrolysis	$199,800	No options required	$114,828	$1.0 million

Chrome electroplating uses chromic acid, $H_2Cr_2O_7$, as the base chemical for electroplating chromium onto substrates. The ability to plate substrates with a consistent coating, i.e., without pits, bumps and of a uniform thickness requires the maintenance of a uniform plating bath chemistry. Maintaining a sufficient concentration of the chromic acid, where chromium is in the hexavalent state (Cr^{+6}), is critical to the successful electroplating process.

Chromic acid electroplating baths are contaminated by the trivalent chromium (Cr^{+3}) formed by reduction of the chromic acid and other heavy metals (Al, Zn, Cu, Ni, Fe) that dissolve from materials being plated. As a result the quality of the bath solution deteriorates and a portion of the solution has to be removed to replenish the bath quality. The spent bath solution becomes a liquid waste in the wastewater stream.

Whenever possible, platers rinse plated parts using a stagnant dragout tank and countercurrent cascade rinses. These rinse waters are added back to the plating tank to minimize discharge and disposal of chemicals into the plating wastewater. However, returning the rinse water and chemicals to the plating tank contributes to the build-up of contaminants in the plating bath. The other liquid wastes come from sources such as water from the floor, eluants from the regeneration of the pretreatment system, and filter water from the conventional precipitation process.

Table 4-1 shows the data provided by the NFESC Project Engineer for the chrome-bearing wastewater stream.

Table 4-1 NFESC-Provided Contaminant Concentrations and Flow Rates in Chromium-Bearing Wastewater

Contaminant	Concentration (ppm)
Chromium (Total Cr)	< 50
Lead (Pb)	< 10
Copper (Cu)	< 10
Nickel (Ni)	< 10
Potential Contaminants	
Sodium (Na)	Data Not Provided But Expected to Be Present
Potassium (K)	
Calcium (Ca)	
Iron (Fe)	
pH	< 5
Flow Rate	30 gpm

In selecting advanced treatments for the chrome-bearing wastewater, the following goals are desired:

- Reoxidation of the Cr^{+3} to usable chromic acid;
- Continuously removing the metal impurities (cations) at the rate they enter the bath while maintaining the bath at the preferred level of metal impurities, i.e., 4-7 g/l;

- Maintaining the ratio of chromic acid to sulfate and other catalysts;
- Controlling the level of undesirable chemicals to within acceptable limits;
- Permitting the maximum reuse of chemicals in the rinse;
- Requiring no waste treatment of the chemicals;
- Producing zero waste; and
- Producing a plating that conforms to the applicable military specification.

Two advanced concepts were selected for evaluation on chrome-bearing wastewaters that have the potential of meeting some or all of the desired goals. Both concepts use ion exchange coupled with different electroanalytical processes for constituent recovery.

- Ion Exchange/Electrodialysis
- Ion Exchange/Electrolysis

The *ion exchange/electrodialysis concept* uses ion exchange separation of the metals with recycle of the process water and chromic acid and regeneration of charging chemicals for the ion exchange columns using electrodialysis. This concept produces a small amount of concentrated brine and metallic hydroxide sludges as waste by-products.The sludge is produced at a reduced amount over conventional treatment. Two options are provided for treatment of the sludge: (1) disposal of the sludge as a hazardous waste; and (2) hydrometallurgical treatment of the sludge to render it non-hazardous[5]. Treatment of the sludge, as opposed to disposing of the sludge as a hazardous waste, resulted in an estimated 12 percent annual savings. This number will continue to grow as the cost of hazardous waste disposal increases. The literature search revealed another promising option for treating the sludge using electrolysis to remove the toxic metals[6]. However, insufficient data was available to conduct a cost/benefit analysis for this option.

This system has a capital cost of $251,000 and an annual operating and maintenance (O&M) cost of $125,000 (disposing of the generated sludge as a hazardous waste) or an annual O&M cost of $110,000 (treating the sludge using a hydrometallurgical technique). The net present value, calculated over 10 years using a 7 percent interest rate, resulted in $1.1 million for the system that included waste disposal vs. $1.0 million for the system that included sludge treatment.

The *ion exchange/electrolysis concept* uses ion exchange separation of the metals followed by electrolysis of the cation exchange regenerant and electrodialysis of the anion exchange regenerant to recover useable materials. This process produces only a small volume of concentrated brine for disposal as a waste by-product. This system has a capital cost of $256,000 with an annual O&M of $115,000. The net present value, using the same assumptions of ten year life and a 7 percent interest rate, is $1.0 million.

This system has a capital cost that is approximately 4 percent higher than the ion exchange/electrodialysis concept, but an annual O&M cost that is 8 percent lower than the ion exchange/electrodialysis concept that disposes of sludge as a hazardous waste. The cost/benefit of producing no sludge (resulting in elimination of disposal or treatment costs) in the ion exchange/electrolytic concept is offset by higher electricity consumption of the electrolytic recovery unit (ERU). However, this electrolysis system produced the smallest amount of hazardous waste (a small volume of concentrated brine). The operating site liability is minimized and operator protection from the handling of hazardous wastes is maximized with the electrolysis system.

Electrodialysis, electrolysis, and ion exchange have been used extensively in full-scale metals processing wastewater treatments. There is sufficient experience with these systems to utilize them without significant further development effort. The benefits of the use of these systems are the minimization (electrodialysis) or elimination (electrolysis) of hazardous sludge wastes. The benefits are the cost savings realized in the reuse of the chromic acid and water in the electroplating process and regeneration of the sulfuric acid and sodium hydroxide used to regenerate the ion exchange columns. The reuse of process chemicals becomes increasingly more important as the cost of process chemicals has escalated annually since 1974.

Further capital cost savings can be realized by determining if the final water polish is required for re-use of the water in the electroplating process. The final water polish has a capital cost of $115,000 (advanced reverse osmosis and evaporator).

Almost all advanced wastewater treatment systems will generate some sludge, although at significantly reduced volumes. Significant annual operational cost savings may be realized by evaluating the use of advanced sludge treatments, i.e., hydrometallurgical or electrolytic treatments. In plating processes where the capital investment is significant and the equipment still has sufficient operating life so as not to warrant replacement, treatment of the sludges generated (thus producing wastes that are non-hazardous) by advanced techniques may be cost-effective.

4.1 Chrome Electroplating Wastewater Treatment Using Ion Exchange and Electrodialysis

The treatment of chrome-bearing wastewaters using ion exchange and electrodialysis has been used successfully to produce chromium plated surfaces that comply with military specifications. The process is commercially available and is in use at several Department of Defense (DOD) facilities, shown in Table 4-2. The process flow schematic for this option is shown in Figure 4-1. The individual steps in the process are discussed in the following sections.

4.1.1 Overview of the Process

Figure 4-1 shows the process flow diagram for the ion exchange/electrodialysis process. The organic contaminants in the wastewater stream are removed using granular activated carbon (GAC). These organics can interfere with the subsequent ion exchange process.

The process uses ion exchange to separate and concentrate the cationic and anionic species from the wastewater stream. Electrodialysis is used to convert the cationic species to metallic sludge and regenerates sulfuric acid from the waste stream to reuse as a regenerant for the cation exchange column. The decatonated eluant from the cation exchange column is pumped to the anion exchange column, where the anionic species are exchanged for OH^-. The eluant from the anion exchange column produces water that is reused in the cascade rinse tank. Electrodialysis is used to regenerate sodium hydroxide, which is used to regenerate the anion exchange column, and chromic acid, which is re-used in the chrome plating bath.

Table 4-2: DOD Facilities Using Ion Exchange/Electrodialysis Wastewater Treatment (Partial List)

DOD Facility	Description	Date Installed
U.S. Army Depot, Corpus Christi, TX	Electrodialytic Chrome Plating Bath Purification Process	September 1990
U.S. Navy, Norfolk, VA	Electrodialytic Chrome Acid Bath Purification Process	October 1990
U.S. Air Force GO/CO (Government Owned/ Contractor Operated) F-16 Facility, Ft. Worth, TX	Electrodialytic Chrome Rinse Water Purification Process Plus Ion Exchange	July 1992
U.S. Army Depot, Ft. Worth District, Corpus Christi, TX	Closed Loop Chrome Rinse Water Purification Process Plus Ion Exchange	August 1992
U.S. Air Force, Kelly Air Force Base, San Antonio, TX	Electrodialytic Nitric Acid Nickel Strip Purification Process	February 1995

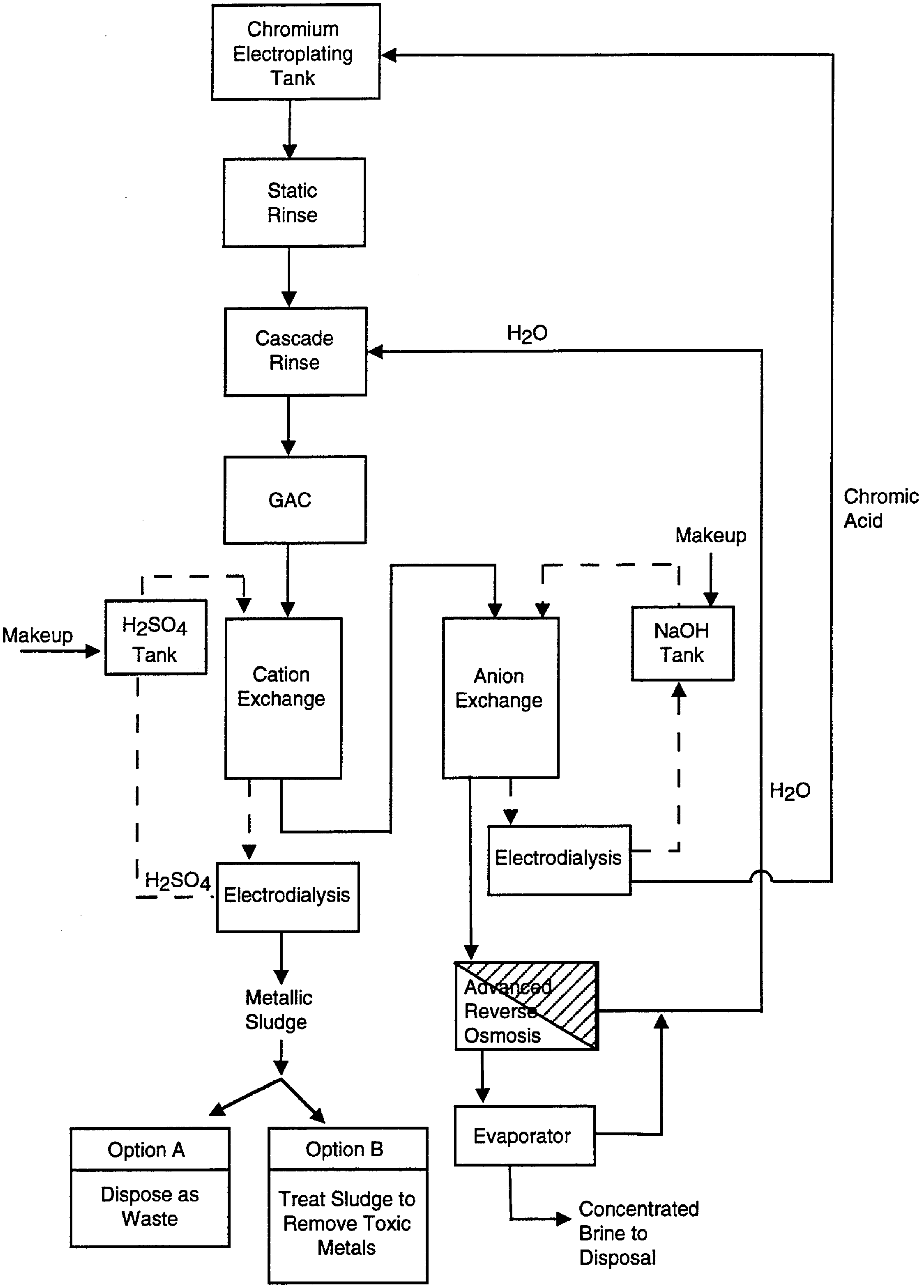
The metallic sludge generated can be handled in two ways:

- Disposal as a conventional hazardous waste; or
- Treat the sludge, using a hydrometallurgical method, to remove the metallic contaminants. This allows the sludge to be treated as a non-hazardous waste.

Ion Exchange Process[7-10] Prior to using ion exchange to remove the ionic contaminants from the plating bath, the following batch process must be employed:

- Shutdown of the plating process;
- Removing the solution from the plating tank;
- Cooling the solution;
- Diluting the solution; and
- Removing organic contaminants with GAC before the ion exchange step.

Figure 4-1: Chromium Wastewater Treatment Using Electrodialysis and Ion Exchange



Cooling and diluting the plating bath solution minimize damage to the ion exchange resin and filtering is necessary to keep the solution flowing through the resin bed. Carbon adsorption has been found to be an effective method to remove the highest level of organics. The contaminated rinse wastewaters can be pumped to the ion exchange columns with no pretreatment.

The contaminated solutions are pumped through the ion exchange columns. When the loading on the ion exchange bed reaches its maximum, the bed is taken off line and regenerated using sulfuric acid (H_2SO_4) for the cation exchange column and sodium hydroxide (NaOH) for the anion exchange column.

Cation Exchange Operation. The rinse and the spent plating bath wastewaters are pumped to a strong cation exchanger, where the metals are retained on the column. Once the plating solution is pumped through the cation exchange column, the resin must be regenerated with sulfuric acid to exchange the metallic contaminants retained on the resin with hydrogen ions. The regenerant stream, that now contains the metallic contaminants, is pumped through a two-compartment electrodialysis cell to remove the cationic species as sludge.

Anion Exchange Operation. The eluant from the cation exchange column is pumped to a strongly basic anion exchange column. The use of strongly basic anion exchange resins is recommended to minimize Cr^{+6} leakage (<1 mg/l) [7]. The chromate anion (and other anionic contaminants) are exchanged for OH^- from the anion exchange column to produce deionized water for reuse in the cascade rinse tanks.

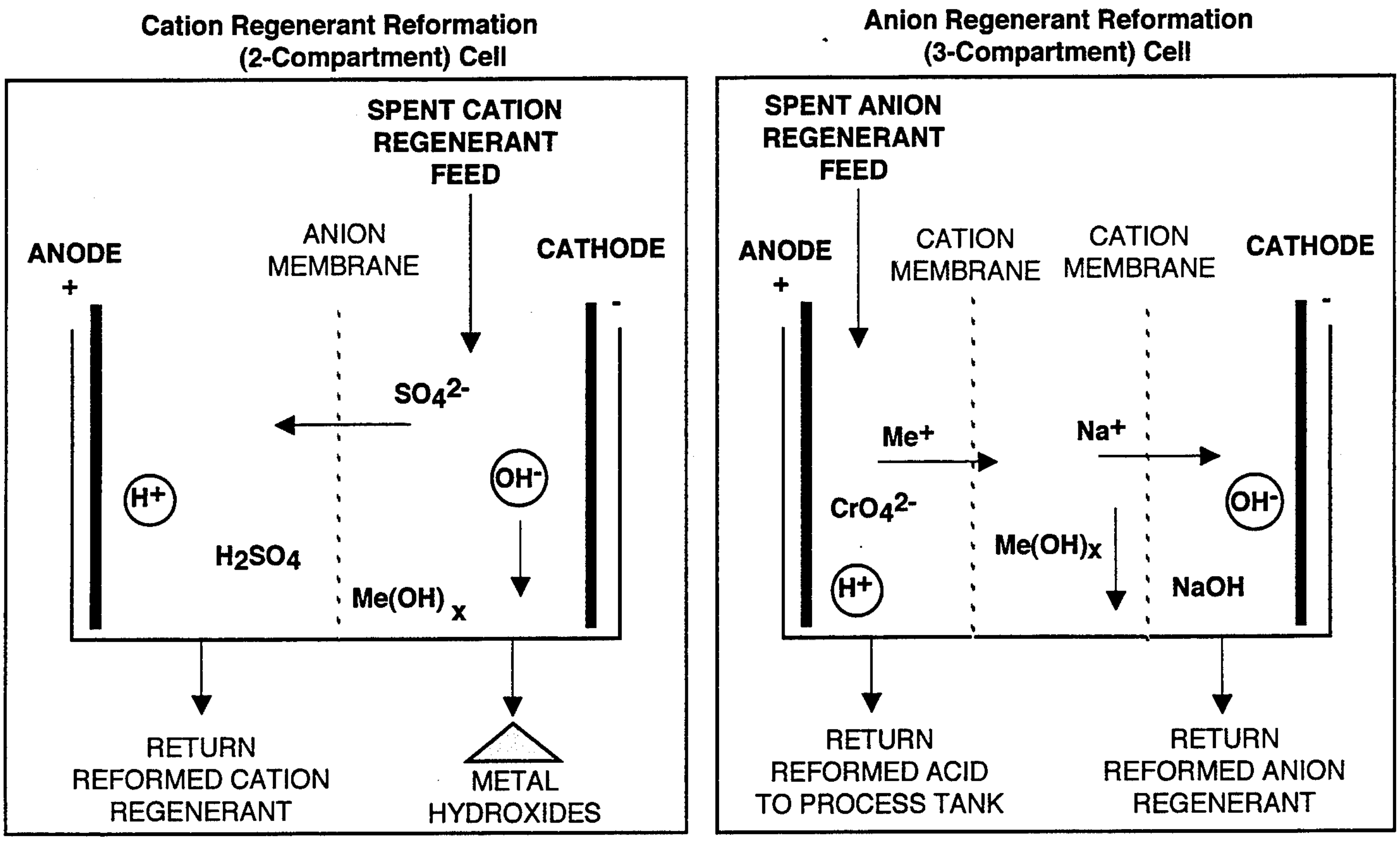
Once the anion exchange resin is exhausted, the resin is regenerated using NaOH where the retained anionic contaminants are eluted from the column. This eluant is pumped through a three-compartment electrodialysis cell to produce chromic acid for re-use in the chrome plating bath and NaOH that is used to regenerate the anion exchange column.

Electrodialysis. Two types of electrodialytic cells are used in the treatment of chrome-bearing wastewaters: a cation regenerant reforming cell (two-compartment) and an anion regenerant reforming cell (3-compartment cell). An illustration of these cells is shown in Figure 4-2.

Cation Regenerant Reforming Cell. The two compartment cell, used for cation regenerant reformation, treats the eluant from the cation exchange column and converts this eluant to sulfuric acid. The sulfuric acid is recirculated to a holding tank, where it is later used to regenerate the cation exchange column.

This cell has two compartments: an anolyte compartment having an anode and a catholyte compartment having a cathode, with the two compartments separated by an ion permeable membrane. The regenerant (eluant from the cation exchange column in the form of $Me^{+x}[SO_4]_x$) is placed into the catholyte compartment and an anolyte is placed in the anolyte compartment. The membrane selectively allows the $SO_4^=$ ion to migrate into the anolyte compartment where sulfuric acid (H_2SO_4) is formed. The metallic contaminants

Figure 4-2: Electrodialytic Cells



Cation Regenerant Reformation (2-Compartment) Cell

Anion Regenerant Reformation (3-Compartment) Cell are converted into the hydroxide form, which is insoluble in aqueous basic solutions, and the metallic hydroxides are precipitated as a sludge.

Anion Regenerant Reforming Cell. The three compartment cell, used for anion regenerant reformation, treats the regenerant from the anion exchange column and converts this eluant to sodium hydroxide (NaOH) and chromic acid ($H_2Cr_2O_7$). The NaOH is returned to a holding tank where it is later used to regenerate the anion exchange column.

The anion regenerant feed is placed into the anolyte cell, where the metal ions (Me^{+x}) selectively migrate into the middle compartment in a basic media. The $CrO_4^{=}$ is converted to chromic acid in the anolyte compartment, which is used to replenish the chrome plating tank. The alkali metal cations selectively migrate into the catholyte compartment to form NaOH, which is then used to regenerate the anion exchange column. The chromic acid that is returned to the electroplating process tank must have a minimum concentration of 80 g/l Cr^{+6} of solution to allow for direct recycling in the chrome plating baths[11].

The chromic acid that is returned to the electroplating process tank must conform to the following tri-service specifications:

- MIL-S-5002D - Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapons Systems; and
- QQ-C-320B - Federal Specification, Chromium Plating (Electrodeposited).

Advanced Reverse Osmosis. The sensitive nature of chromium electroplating, combined with the high dissolved solids in the process water and the presence of residual contaminants, requires that the treated process water be polished prior to being recycled to the chromium processes. This requirement can only be safely eliminated following sufficient laboratory testing to verify that elimination of the final polish step will not compromise military specification requirements for the chrome plating process.

The polishing method selected is advanced reverse osmosis (ARO) combined with an evaporation step. Conventional reverse osmosis (RO) is a pressure driven membrane separation process. The feed is separated under pressure (400 to 800 lb/in^2) into a purified "permeate" stream and a concentrate stream by selective passage of water through the microscopic pores of the semipermeable membrane.

The operating principle is a physical filtration separation. The porous membrane has a critical pore size to allow water molecules to pass through the filter, while retaining and concentrating the larger metal cations and cyanide anions. The process can produce a permeate that has a total dissolved solids concentration as low as 5 to 10 mg/L.

The major limitation of commercial RO systems has been its inability to maintain membrane performance. Fouling and gradual deterioration of membranes has reduced the processing capacity of the unit and required frequent membrane replacements. Feed solutions have to be in a pH range between 2.5 and 11 to ensure reasonable life for commercially available membranes and the membranes do not completely reject certain species, such as non-ionized organic wetting agents.

ARO has overcome many of these deficiencies. ARO uses filters made from composite materials that have finer pores, operate under pressures to 1,500 psi, and are not subject to attack by strong acids. In many cases operators of ARO units have found that they produce significantly less concentrate than conventional RO systems and the ARO systems have operated for up to two years without downtime. These differences (i.e., reduced cost of membrane replacement, reduced maintenance and downtime on the system, and reduced cost of hazardous waste concentrate disposal and handling) can save up to $35,000 a year in recurring maintenance and disposal costs[12].

The concentrate from the ARO unit is sent to the evaporator where the dissolved solids are further concentrated prior to being sent off-site.

***Sludge Treatment*.** The only waste that is generated during this process is the metal-containing sludge from the cation regenerant electrodialytic cell. The generated sludge can be treated in two ways: (1) conventional disposal as a hazardous waste; and (2) hydrometallurgical treatment of sludge[5].

Conventional disposal as a hazardous waste. The cost of disposal is off-set by the reduction in chrome processing costs by re-use of the chromic acid. However, the cradle-to-grave liability for the hazardous waste still resides with the site operation.

Hydrometallurgical treatment of the sludge. The wastes generated by the chrome electroplating process are classified as F006 wet sludges under the Resource Conservation and Recovery Act (RCRA). The sludges are wet slurries containing varied amounts of solids in suspension. The free water content may be as high as 75-80 percent. The sludges are processed as "non-zinc containing". If the sludge contains zinc, it must be processed differently.

The typical composition of "non-zinc containing" sludges from chrome plating are shown in Table 4-3. The treatment process uses evaporation to remove the excess water from the sludge and electrowinning to remove copper, lead and tin. The copper, lead and tin have a marginal recovered value as pure metal. The remaining liquor can be recirculated to the three-compartment electrodialytic cell to produce NaOH that is sufficiently pure to regenerate the anion exchange column.

The nickel is converted to the sulfate form, using sulfuric acid. As the nickel sulfate crystallizes out of solution, the nickel sulfate salt is decanted, filtered, washed and shipped to nickel producers. The percent nickel in the salt varies between 23 and 25 percent. The liquor from the filtration is sulfuric acid with a concentration of about 75 percent. This acid can be recycled back through the electrodialytic cell to remove remaining metal ions and, subsequently, to recharge the cation exchange resin.

Table 4-3: Contaminant Concentrations in Non-Zinc Containing Sludges from Chrome Electroplating Waste

Metallic Contaminant	Concentration
Copper	1-2 percent
Nickel	8-10 percent
Tin	0.1 percent
Lead	0.1 percent
Iron	Negligible
Chromium	1-2 percent
Zinc	Negligible
Cadmium	Negligible

The hydrometallurgical treatment of the wastes is labor and capital intensive and is not cost-effective for low-flow plating processes. The process is offered by Recontek, Inc. as a recycling service to the metals processing and electronics industries; a much more economical alternative that adds cost for disposal but produces a Zero Discharge concept with minimized hazardous waste liability for the site operation.

The economics of off site hydrometallurgical treatment of chrome plating sludges are shown in Table 4-4.

4.1.2 Economic Analysis of Chromium Plating Wastewater Treatment Using Ion Exchange and Electrodialysis

For purposes of this study, site preparation costs are not included for the ion exchange/ electrodialysis concept. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems. Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the Ion Exchange/ Electrodialysis system would be approximately $251,000 and the annual O&M costs would be $125,000 if the sludge is disposed as a hazardous waste or $110,000 if the waste is treated using hydrometallurgical treatment as a service from a supplier (Table 4-5). An annual savings of about $15,000 per year is realized by sludge treatment. The net present value of the process, assuming a 10 year life and a 7 percent interest rate, would be $1.1 million for the system that disposes of the sludge as a hazardous waste and $1.0 million for the system that hydrometallurgically treats the sludge.

The cost analysis discounts the chemical cost for the chromic acid reused in the plating process and includes an estimate for the annual cost of disposal of the sludge as a hazardous waste and the brine. The systems as proposed in this section have been installed and operated on wastewater streams similar to the stream considered for the Navy or provided as services to Navy customers. Because the system has been installed on similar streams the capital and O&M costs should be reliable preliminary estimates.

Table 4-4: Economics of Hydrometallurgical Treatment of Chrome Plating Sludges

Assume a 20 ton lot of sludge		
Processing fee per ton $300		
	$300 x 20 tons=	$6000
Discharge fee		$150
Analysis fee		$100
Penalties		
Iron	378 lbs @ 0.10/lb=$38.00	
Chromium	129 lbs @ 1.00/lb=$129.00	
Cadmium	103 lbs @ $2.00/lb=$206.00	
		$373
Total Fees		$6623
Recovered metal credits		
Copper	679 lbs @51% @$1.40	$485
Nickel	516 lbs @51% @$8.00	$2105
Lead	174 lbs @34% @$0.40	$24
Total Recovery Value		$2614
Net Cost to Customer per lot		$4009
Net Cost to Customer per ton		$200.45

The most sensitive aspect of the cost analysis is the labor costs for operating the process. Ion exchange and membrane systems are known to be labor intensive and if the total labor requirement were to double the O&M costs would increase by approximately 35 percent.

Table 4-5: Summary of Economic Analysis for Ion Exchange/Electrodialysis Treatment of Chromium Wastewaters

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
GAC Unit (continuous system rated at 30 gpm)	ea	$3,000	1	$3,000
Cation/Anion Exchange System with two Electrodialysis Cells (500 amp ea.)	ea	$75,000	1	$75,000
Advanced Reverse Osmosis (continuous system rated at 30 gpm)	ea	$90,000	1	$90,000
Evaporator (continuous system rated at 20 gph)	ea	$25,000	1	$25,000
Total Equipment Cost				$193,000
Installation Cost		30% of equipment cost		$57,900
Total Installed Cost				$250,900
O&M Costs[a]				
Operating labor (12 hr/day)	hr	$18	3120	$56,160
Supervision (4 hr/day)	hr	$22	1040	$22,880
Maintenance		6% of equipment cost		$11,580
Resin Replacement	annual	$400	2	$800
GAC Disposal	unit	$4,000	1	$4,000
Chemical cost[b]	ton	$85	10	$850
Brine Disposal[c]	ton	$150	1.0	$150
Utilities (electricity)	KWhr	$000.12	120,000	$14,400
Sludge Disposal (As Hazardous Waste)	ton	$1200	15	$18,000
Sludge Disposal (Hydrometallurgical Treatment)	ton	$200.45	15	$3007

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Total Annual Cost (Option 1)				$124,820
Total Annual Cost (Option 2)				$109,827
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor		Total NPV
Option 1 Waste Disposal				
$250,900	$124,820	7.0236		$1,127,585
Option 2 Waste Disposal				
$250,900	$109,827	7.0236		$1,022,281

Notes for Table 4-5

a Annual operation is assumed to be 260 days/year.

b See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate. chemical usage was discounted for reuse of chromic acid.

c The quantity of brine generated is based on a 1% reject from the RO and 10% residual brine from the evaporator.

d NPV is calculated based on a 10 year equipment life and a 7% interest rate.

4.2 Chrome Electroplating Wastewater Treatment Using Ion Exchange and Electrolytic Metal Recovery[13]

The treatment of chrome-bearing wastewaters using ion exchange and electrolysis is equivalent in capital cost to the ion exchange/electrodialysis technique discussed in Section 4.1, but this technique produces no sludge, resulting in an annualized savings of $3,000 to $18,000 per year over the ten year life of the equipment. The process does produce a small amount of brine as a waste, equal to the ion exchange/ electrodialysis process.

The process is commercially available, but its use on DOD facilities has not been documented. The process flow diagram is shown in Figure 4-3. The individual steps in the process are discussed in the following sections.

4.2.1 Overview of the Process

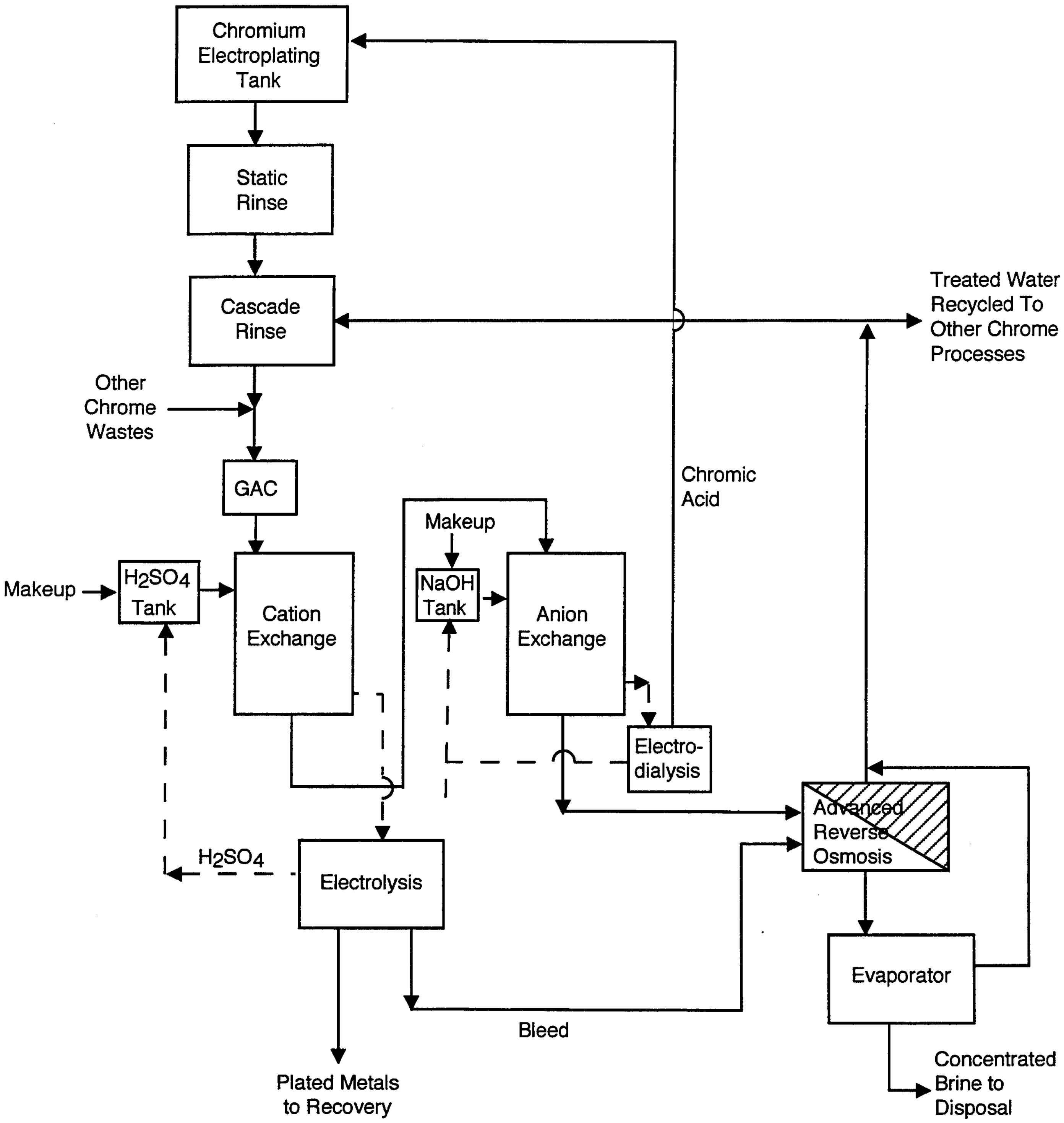
Figure 4-3 shows the process flow diagram for the ion exchange/electrolysis process. The organic contaminants entrained in the wastewater stream are removed using GAC. These organics can interfere with the subsequent ion exchange process.

The process uses ion exchange to separate and concentrate the cationic and anionic species from the wastewater stream. The process is identical to the ion exchange/ electrodialysis system discussed in Section 4.1, except an electrolytic recovery unit is used in place of the cation regenerant reformation cell. The electrolysis cell plates out the metals (as a metal mixture) rather than producing $Me^{+x}OH_x$ sludge. The plated metals can be sent to an off-site metals recovery supplier for recovered value. The eluant stream from the cation exchange resin contains $Me^{+x}(SO_4)_x$. The Me^{+x} is reduced to the metallic form (Me^{+0}); the $SO_4^=$ is converted to H_2SO_4, which is pumped to a holding tank and used in the subsequent batch operation to regenerate the cation exchange column. The anion exchange process and subsequent reformation of chromic acid and NaOH (used to regenerate the anion exchange column in a subsequent batch operation) is virtually identical to the process described in Section 4.1.

There are two distinct advantages of this system over the electrodialysis system described in Section 4.1:

- Virtually all process water is treated and recycled for use, thus reducing the cost of water consumption for make-up of the rinse tanks. The previous process did not reutilize the water from the cation exchange eluant, producing instead metal hydroxide where the site operation had to pay to remove the water during the treatment of the sludge generated. A rigorous cost benefit analysis should include this savings as a benefit.
- There is no sludge generated during this process that has to be disposed of or treated during subsequent operations. The metal by-products of the plating process can be sent to an off-site supplier for recovery for any small metal economic value.

Figure 4-3: Chromium Wastewater Treatment Using the Ion Exchange and Electrolysis



Similarly to the previous chrome-waste bearing treatment concept, the chromic acid is recovered for reuse in the plating bath and the regenerants for the cation exchange column (H_2SO_4) and anion exchange column (NaOH) are regenerated and reused. The only waste produced is a small amount of brine that results from the final polish treatment that allows the water to be reused.

Similarly to the previous treatment concept, the use of a final polishing technique for the water, if reused to produce military specification plating finishes, is not considered optional without sufficient laboratory testing to verify the water quality without the final polish. Advanced reverse osmosis and a final evaporation step are used as the most economical method to produce the smallest volume of waste with the highest water quality.

Ion Exchange Process. The ion exchange process is exactly as described in Section 4.1.1 and will not be repeated in this section.

Electrodialysis. Electrodialysis, using a three compartment cell for anion regenerant reformation and reconversion of chromic acid, is exactly as described in Section 4.1.1 and will not be repeated in this section.

Electrolysis Process. The simplest metal recovery technique is direct electrolysis which recovers the metals in their metallic form. Most metal contaminants are candidates for electrolytic recovery. The primary metallic constituents of concern in the chrome wastewater are copper, lead, and nickel in an acidic medium.

The electrolytic copper recovery process is straightforward and dates back to 1967. The ion exchange system concentrates the cations and the copper is plated at the cathode by the following reaction:

- $2Cu^+ <=> Cu^{+2} + Cu^o$

In the case of acidic copper solutions, 8000 mg/liter was reduced to 0.8 mg/liter at an overall 35 percent efficiency.

Effective results have been achieved for metal processing rinsewaters using ion exchange to produce nickel sulfate. The ion exchange provides the additional benefit of removing anions such as chloride, whose anodic reactions are undesirable. Nickel is reported to be removed to 0.01 gm/liter. The regenerated sulfuric acid stream, used to replenish the ion exchange column, will contain dilute amounts of nickel sulfate which is returned to the column for further concentration.

The electrolysis of most metal cations is optimal at a pH of 4 to 5. At this pH, the deposit is very adherent to the cathode at concentrations down to 0.01 grams per liter. The reactions that govern the stages of the electrolytic treatment of nickel are shown below. Other metal cations will be electrolyzed similarly.

- $NiSO_4$ + 2 electrons —> $Ni + SO_4^{-2}$
- H_2O —> $1/2\ O_2 + 2\ H^+ + 2$ electrons
- $NiSO_4 + H_2O$ —> $1/2\ O_2 + Ni + H_2SO_4$
- H_2O + 1 electron —> $1/2\ H_2 + OH^-$

It should be noted that pure and unbuffered nickel sulfate solutions cannot be easily electrolyzed. Electrolysis causes a continuous replacement of Ni with H ions, and the pH drops and must be constantly corrected. The electrodeposition is best carried out at or quite close to pH 2.5 where cathode efficiency and polarization are minimized. In the case of nickel solutions, a pH correction is required to repress hydrogen evolution. At 2 to 2.5 amp/dm^2, 3600 mg/liter was reduced to a level of 5 mg/liter with over 30 percent efficiency.

When a solution of cations are electrolyzed in a cell, the yield of electrolysis declines as the concentration decreases below approximately 500 mg/L. For this reason the most advanced electrolysis systems on the market contain high surface area or reticulated cathodes that offer the advantage of increasing the electrolytic yield at low metal concentrations.

An added benefit of electrolysis is the destruction of common organic materials at the anode without additional pretreatment prior to electrolysis or the subsequent reuse of the water.

Advanced Reverse Osmosis. The process of treating the water regenerated from the anion exchange column and the electrolysis cell are treated using advanced reverse osmosis and a final evaporation step. The process is identical to that discussed in Section 4.1.1 and will not be further discussed here.

4.2.2 Economic Analysis of Chromium Electroplating Wastewater Treatment Using Ion Exchange and Electrolysis

For purposes of this study, site preparation costs are not included. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems (Table 4-6). Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The installed capital cost for this system is $259,740 with an annual O&M cost of $114,828. The net present value for the system, using a 10 year life and 7 percent interest rate, was calculated to be $1.1 million.

Table 4-6: Capital and O&M Costs for the Ion Exchange and Electrolysis System

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
Equipment				
GAC Unit (continuous system rated at 30 gpm)	ea	$3000	1	$3,000
Ion Exchange System with One 3-Compartment Electrodialysis Cell	ea	$36,500	1	$36,500
Electrolytic Recovery Unit (Batch System for 100 gal)	ea	$30,000	1	$45,300
Advanced Reverse Osmosis (continuous system rated at 30 gpm)	ea	$90,000	1	$90,000
Evaporator (continuous System rated at 20 gph)	ea	$25,000	1	$25,000
Total Equipment Cost				$199,800
Installation Cost		30% of equipment cost		$59,940
TOTAL INSTALLED COST				$259,740
O&M COSTS				
Operating labor (12 hr/shift)	hr	$18	3120	$56,160
Supervision (2 hr/shift)	hr	$22	1040	$22,880
Maintenance		6% of equipment cost		$11,988
GAC Disposal	unit	$4,000	1	$4,000
Brine Disposal[c]	ton	$150	1	$150
Chemical Cost[b]	ton	$85	10	$850
Resin replacement	yr	$400	2	$800
Utilities (electricity)	KWhr	$000.12	150,000	$18,000
TOTAL ANNUAL COST				$114,828
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor		Total NPV
$259,740	$114,828	7.0236		$1,066,246

Notes for Table 4-5

a Annual operation is assumed to be 260 days/year.

b See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate.

c The quantity of brine generated is based on a 1% reject from the RO and 10% residual brine from the evaporator. Chemical usage was discounted for reuse of chromic acid.

d NPV is calculated based on a 10 year equipment life and a 7% interest rate.

5.0 Cyanide-Bearing Wastewater Treatment

Two zero discharge concepts were considered for the treatment of cyanide-baring wastes:

- Biosorption separation of the metals with electrolytic recovery of the metals; and
- Advanced reverse osmosis (ARO) of the cyanide wastewater stream followed by electrolytic recovery of the ARO concentrate.

The difficulty in developing zero discharge technologies for metal plating and finishing wastewaters is the separation of the alkali and alkaline metals from the metals with value and the separation of the alkali and alkaline metals from the process water for recycling. This problem is amplified by the addition of dissolved solids in the conventional treatment processes.

The biosorption process has the advantage in that biomaterials are strongly selective for heavy metals over alkali and alkaline metals. The disadvantage is that the cyanide must be destroyed prior to using biosorption and the cyanide oxidation process adds significant quantities of dissolved solids to the process wastewater which must be removed prior to recycling the water. Research is needed on biosorption to determine how selective the biomaterials are for heavy metals in the presence of other cations and how well the biomaterials stand up to the acid conditions of the plating wastewaters.

The ARO concept does not require the oxidation of cyanide and therefore the quantity of dissolved solids that must be removed is lower. The disadvantage of this concept is that the electrolytic recovery of the metals must be performed under alkaline conditions. Research is needed on ARO to determine the maintenance requirements in the plating environment and how well electrolytic recovery will perform at high concentrations of cations other than platable metals.

Because the ARO concept does not require the oxidation of the cyanide and is less expensive to operate than the biosorption concept (labor and biomaterials costs), the ARO concept has the economic advantage over the biosorption concept.

Concept	Capital Cost	Annual O&M Cost	Total NPV
Biosorption	$520,000	$140,000	$1.5 million
ARO	$143,000	$38,000	$0.4 million

Spent cyanide baths, eluents from cyanide rinse tanks, and wastewater streams from cyanide dips are, traditionally, one of the more difficult metal plating/finishing wastewater streams to treat. The application of a Zero Discharge Technology to this wastewater line represents significant challenges. The difficulty in recovering the metals and recycling the water is related to presence of the cyanide which reacts with acid to form HCN. Elimination of the cyanide, using traditional cyanide oxidation technologies, significantly increases the concentration of dissolved solids present in the wastewater and this concentration will continue to increase every time the process water is recycled. Zero Discharge Technologies are further complicated when the cyanide wastewater streams contain nickel because of the strong nickel cyanide complexes that are formed.

Table 5-1 shows the data provided by the NFESC Project Engineer for the cyanide-bearing wastewater stream.

Table 5-1: NFESC-Provided Contaminant Concentrations and Flow Rates in Cyanide-Bearing Wastewater

Contaminant	Concentration (mg/L)
Cyanide (CN)	< 50
Silver (Ag)	<10
Copper (Cu)	<10
Nickel (Ni)	< 10
Cadmium	< 20
Potential Contaminants	
Zinc (Zn)	Data Not Provided
Gold (Au)	
Sodium (Na)	
Potassium (K)	
Calcium (Ca)	
Iron (Fe)	
Magnesium (Mg)	
pH	9 to 11
Wastewater Flow Rate	20 gpm

Two advanced concepts were selected for evaluation on cyanide wastewaters. They are:

- Biosorption separation of the metals with metals-recovery using an electrolysis recovery unit; and
- Advanced reverse osmosis (ARO) of the cyanide wastewater stream followed by electrolytic recovery of the ARO concentrate.

The biosorption concept has the advantage that biomaterials will selectively adsorb the heavy metals and allow the alkali and alkaline metals to pass through. The concentration of the heavy metals on the biomaterial makes further processing of the acid regenerant more efficient by electrolysis. The disadvantages of the biosorption concept are that the cyanide must be oxidized and the water neutralized prior to treatment with the biomaterials. The concern, as mentioned above, is that the pretreatment steps add significant concentrations of dissolved solids to the water. These solids then must be removed prior to the water being recycled to cyanide processes to minimize the buildup of solids in the process water. To remove the dissolved solids an advanced reverse osmosis (ARO) unit is required, and a concentrated brine is produced that cannot be recycled and must be disposed of off site.

In contrast to the biosorption concept, the ARO concept does not require the oxidation of the cyanide. This concept concentrates the metals cyanide complexes and recovers them in a electrolysis unit. The concept will generate a small quantity of water (bleed stream) that needs to be disposed of, but it is expected to be smaller than the quantity generated by the biosorption concept. The bleed stream is necessary because of the presence of dissolved solids from the cyanide processes which will buildup as the process water is recycled. No dissolved solids are added in the ARO concept.

5.1 Biosorption Separation with Electrolytic Recovery of Metal Contaminants

5.1.1 Overview of the Process

Figure 5-1 shows the process flow diagram for the biosorption concept. The process utilizes the hypochlorite oxidation to eliminate the free cyanide and complexed cyanide. The cyanide-free aqueous stream is then adjusted to an acidic pH to resolubilize the metal hydroxides.

The metallic salts are passed through the biomaterial column, which functions like a cation exchange system. The metals are retained on the column and the eluant is discharged as water. The water is processed through a reverse osmosis system for final polishing and returned to the process tanks for reuse.

The biomaterials are regenerated using a countercurrent regeneration process where sulfuric acid is flushed from the bottom of the column to the top, exchanging the H+ cation for the metallic cations. The metallic cations are selectively processed by electrolysis. The recovered metals (i.e., Cd, Zn, Ag, Cu, Au, Ni) are then sent off-site to a reclamation facility.

Cyanide Oxidation. The cyanide complexes are oxidized per the following reactions. The oxidation reagent is usually chlorine, which can be introduced into the system by adding chlorine gas or sodium hypochlorite. In this case, NaOCl was selected because of the hazards of storing and handling gaseous Cl_2.

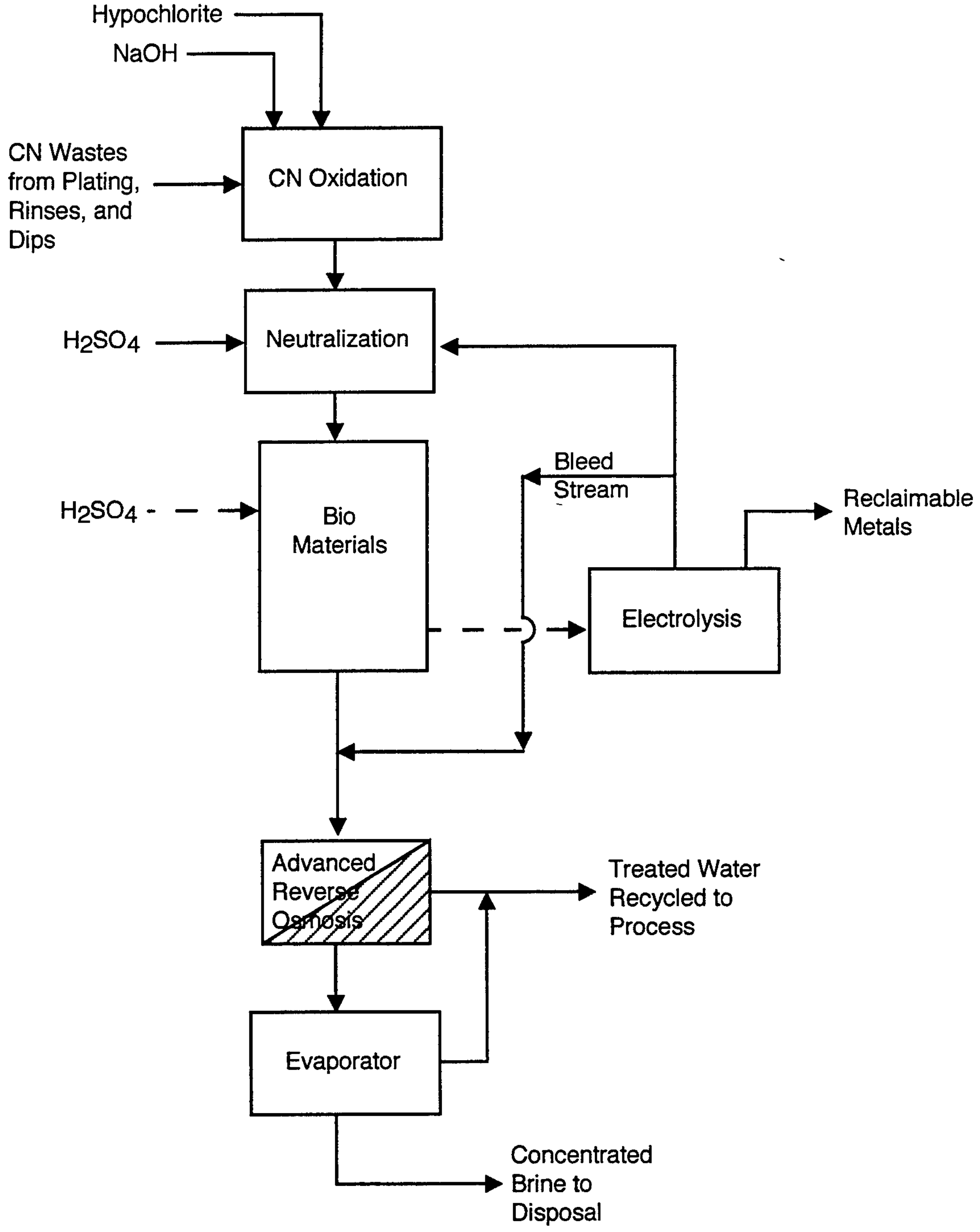
When sodium hypochlorite is introduced as the oxidant, the typical first stage reaction is:

- $NaCN + NaOCl \longrightarrow NaCNO + NaCl$

and in the second stage:

- $2NaCNO + 3NaOCl + H_2O \longrightarrow 3NaCl + N_2 + 2NaHCO_3$

Figure 5-1: Cyanide Wastewater Treatment Using Biosorption and Electrolysis



Continuous systems use two series-connected reaction tanks. In the first stage, the pH is adjusted between 9 and 11 using an alkali such as caustic or lime. The pH in the second reaction chamber is controlled at approximately 8.5. An excess of sodium hypochlorite is added to ensure the complete oxidation of all available cyanide. Demand for the hypochlorite in the first stage is determined by measuring the oxidation rate potential (ORP). The reaction time needed is approximately 25 to 30 minutes in each stage.The cyanide stream is maintained at a pH of 9 to 11 by adding caustic (NaOH) to prevent the formation of HCN.

The difficulty with cyanide oxidation in the development of zero discharge technologies is the addition of a significant concentration of dissolved solids to the wastewater. In the conventional IWTP, the increase in dissolved solids is not a concern; however, for zero discharge technologies the water is intended for reuse in the process and dissolved solids will continue to increase as the water is reused. Because of this issue, the biosorption concept treats the process water with RO prior to recycling the water to the cyanide processes. In general zero discharge technologies need to minimize the amount of solids that are added to the water during treatment.

Neutralization. After the cyanide has been oxidized the pH of the water is lowered using sulfuric acid in order to solubilize any of the metals that have precipitated during the cyanide oxidation. This operation like cyanide oxidation adds dissolved solids to the water.

Biosorption of Aqueous Metals. Biosorption is an emerging technology and to date there are not significant numbers of systems in full-scale operation. Biosorption has been considered for treatment of air and water streams for both inorganics and organics. Recently significant research and development has been completed on the use of biomaterials to remove heavy metals from contaminated groundwaters[14-16]. Biomaterials are used in a manner similar to ion exchange resins. Except instead of synthetic resins biological materials are used. A wide range of materials have been tested, but research has focused on the use of whole algae cells (both living and dead) and ligands. The advantage of these materials over ion exchange resins is that they have been found to be highly selective for heavy metals and do not retain the alkali and alkaline metals such as sodium, potassium, calcium, and magnesium. The alkali and alkaline metals are typically in solution at much higher concentrations than the metals of concern and can significantly reduce the capacity of an ion exchange resin.

After the biomaterials have reached their capacity they are regenerated in a manner similar to cation exchange resins by passing a dilute acid (usually sulfuric acid) through the media and the retained metals are released and concentrated in the regenerant. There have been some recent studies that have shown the retained heavy metals can be eluted selectively from the column by using progressively stronger acids to regenerate the biomaterials. In either case the regenerant is then treated with either electrolysis or heavy metals precipitation.

During the literature search and interviews of biomaterial suppliers, there was a mixed response to the use of biomaterials for plating wastes. Some of the research has shown good results on dilute rinsewaters from plating operations. However, the engineering personnel at Bio-Recovery Systems, Las Cruces, NM (who provide commercially available bio-recovery systems) were concerned that large volumes of water must be treated to warrant the cost of the biomaterial, and the flow rates for most plating operations are too low to make biosorption economical. Other suppliers also noted that biomaterials are sensitive to oxidation attack by very strong acids, and they have observed problems with the pH of the plating solutions.

However, because biosorption is an emerging technology and the ability to selectively absorb heavy metals would greatly advance the ability to develop a zero discharge system, it was retained as a candidate for economic evaluation for the cyanide wastewater stream.

Electrolysis. The regenerant from the biosorption column will be a concentrated solution of dissolved metals. This regenerant will be pumped to the electrolytic recovery unit where the metals will be plated out and sent off site recovery. A detailed description of the electrolytic recovery unit is presented in Section 4.2.1, Overview of the Ion Exchange Process.

After the electrolytic recovery unit has removed as much of the metal content from the regenerant as feasible, the remaining solution will be pumped to the neutralization tank where the sulfuric acid content of the water can be used to lower the pH of the water from the cyanide oxidation unit. It may be necessary to have a bleed stream from the electrolytic recovery unit in order to avoid the buildup of dissolved solids in the loop. The size of the bleed stream will be dependent on the amount of alkali and alkaline metals that are retained on the biomaterials. The lower the retention of these metals the smaller the bleed stream. The bleed will be sent to the ARO unit for treatment.

Reverse Osmosis. Reverse osmosis (RO) is a pressure driven membrane separation process. The feed is separated under pressure (400 to 800 lb/in^2) into a purified "permeate" stream and a concentrate stream by selective passage of water through the microscopic pores of the semipermeable membrane.

The operating principle is a physical filtration separation. The porous membrane has a critical pore size to allow water molecules to pass through the filter, while retaining and concentrating the larger metal cations and cyanide anions. The process can produce a permeate that has a total dissolved solids concentration as low as 5 to 10 mg/L.

The major limitation of commercial RO systems has been its inability to maintain membrane performance. Fouling and gradual deterioration of membranes has reduced the processing capacity of the unit and required frequent membrane replacements. Feed solutions have to be in a pH range between 2.5 and 11 to ensure reasonable life for commercially available membranes, and the membranes do not completely reject certain species, such as non-ionized organic wetting agents.

Advanced reverse osmosis (ARO) has overcome many of these deficiencies. ARO uses filters made from composite materials that have finer pores, operate under pressures to

1,500 psi, and are not subject to attack by strong acids. In many cases operators of ARO units have found that they produce significantly less concentrate than conventional RO systems and the ARO systems have operated for up to two years without downtime. These differences (i.e., reduced cost of membrane replacement, reduced maintenance and downtime on the system, and reduced cost of hazardous waste concentrate disposal and handling) can save up to $35,000 a year in recurring maintenance and disposal costs.

In the biosorption concept, the effluent from the biosorption column and the bleed stream from the electrolytic recovery unit will be treated in an ARO unit. The permeate from the RO unit along with the condensate from the evaporator will be recycled back to the cyanide processes.

The RO unit in this concept is not an option if the treated water is to be recycled back to the cyanide processes. The concern is the buildup of dissolved solids in the process water from the cyanide oxidation and neutralization operations. If the treated water is used in another application where it will not be recycled again it may not need to treated in the RO unit. For this analysis, however, we assumed that the water would be recycled back to the cyanide processes.

The concentrate from the RO unit is sent to the evaporator where the dissolved solids are further concentrated prior to being sent off-site.

5.1.2 Economic Analysis of Cyanide Wastewater Treatment Using Biosorption

For purposes of this study, site preparation costs are not included for the biosorption concept. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems. Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the biosorption concept would be approximately $520,000 and the annual O&M costs would be $140,000 (Table 5-2). The net present value of the process, assuming a 10 year life and a 7 percent interest rate would be $1.5 million. The most sensitive aspect of the cost analysis is the replacement of the biomaterial. Currently, most of the biomaterial suppliers are concerned about the acidic nature of the plating wastewater stream and believed that the biomaterial would have to be replaced at least once a year. Extended the life of the biomaterial from one year to two years would lower the operating costs to approximately $100,000 annually, and over the 10 year life of the system lower the NPV to 1.2 million. Therefore, any testing that is performed should further define the life of the biomaterials.

5.2 Reverse Osmosis with Electrolytic Recovery of Metal Contaminants

5.2.1 Overview of the Process

Figure 5-2 presents the flow diagram for the RO concept. This concept concentrates the metals cyanide complexes and recovers them in an ERU unit and does not require the oxidation of the cyanide. The concept will generate a small quantity of water (bleed

Table 5-2: Summary of Economic Analysis for Biosorption Recovery of Metals

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
CN Oxidation Unit (continuous system rated at 20 gpm)	ea	$125,000	1	$125,000
Neutralization Unit (continuous system rated at 25 gpm)	ea	$25,000	1	$25,000
Biosorption Column (continuous system rated at 25 gpm)	ea	$120,000	1	$120,000
Electrolytic Recovery Unit (Batch system for a 100 gal)	ea	$30,000	1	$30,000
RO Unit (continuous system rated at 25 gpm)	ea	$70,000	1	$70,000
Evaporator (continuous system rated at 20 gph)	ea	$30,000	1	$30,000
Total Equipment Cost				$400,000
Installation Cost		30% of capital cost		$120,000
Total Installed Cost				$520,000
O&M Costs[a]				
Operating labor (2 hr/day)	hr	18	520	$9,360
Supervision (1 hr/day)	hr	22	260	$5,720
Maintenance		6% investment cost		$24,000
Biomaterial Replacement	annual	75,000	1	$75,000
Chemical cost[b]	ton	85	200	$17,000
Brine Disposal[c]	ton	150	1.5	$225

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Utilities (electricity)	KWhr	0.06	120,000	$7,200
Total Annual Cost				$138,505
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor	Total NPV	
$520,000	$138,505	7.0236	$1,492,804	

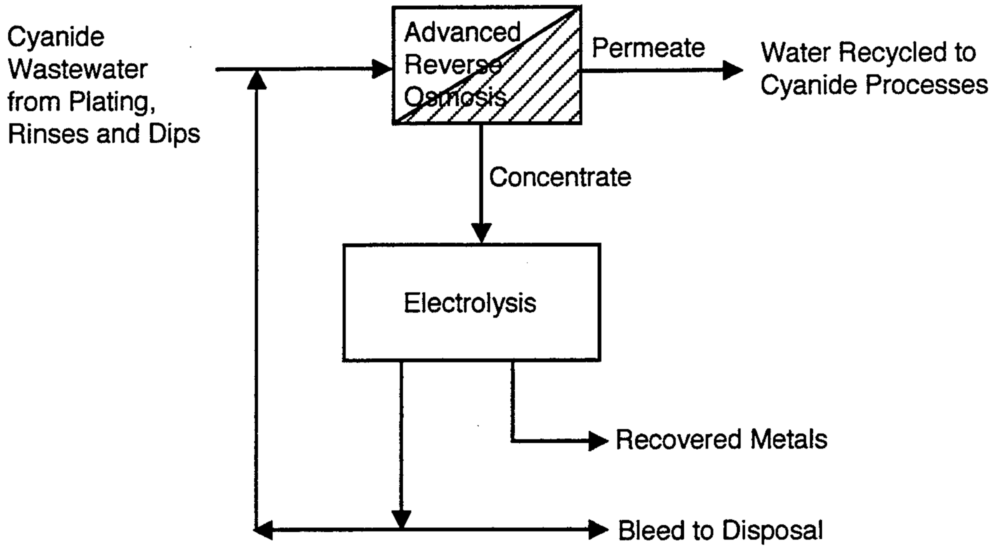
[a] Annual operation is assumed to be 260 days/year.

[b] See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate.

[c] The quantity of brine generated is based on a 1% reject from the RO and 10% residual brine from the evaporator.

[d] NPV is calculated based on a 10 year equipment life and a 7% interest rate.

Figure 5-2: Cyanide Wastewater Treatment Using Advanced Reverse Osmosis and Electrolysis



stream) that needs to be disposed of, but it is expected to be smaller than the quantity generated by the biosorption concept. The bleed stream is necessary because of the presence of dissolved solids from the cyanide processes which will buildup as the process water is recycled. No dissolved solids are added in the RO concept.

Because the concept does not acidify the wastewater prior to recovering the metals in the ERU, the concept has a significant amount of flexibility. For example, it is possible to segregate the cyanide wastewater stream and send the more concentrated wastes directly to the ERU and reduce the capacity of the RO unit or recycle a portion of the process water directly from the ERU unit. In developing our analysis, we assumed that all the water would go directly to the RO unit and only the permeate from the RO would be recycled back to the process.

Reverse Osmosis. The technologies of RO and ARO are described in Section 5.1.1 and are not repeated here. The cyanide wastewaters and a recycle stream from the ERU are pumped to the ARO unit where the dissolved solids are concentrated prior to treatment in the ERU. The permeate from the ARO is recycled back to the cyanide processes.

Electrolysis. The concentrate stream from the ARO unit will be a concentrated solution of dissolved metals. This stream will be pumped to the electrolytic recovery unit where the metals will be plated out and sent off site for recovery. A detailed description of the electrolytic recovery unit is presented in Section 4.2.1, Overview of the Ion Exchange Process.

After the electrolytic recovery unit has removed as much of the metal content from the regenerant as feasible, the remaining solution will be pumped back to the ARO unit where the remaining metal content can be concentrated. It may be necessary to bleed a portion of the concentrate stream off for disposal in order to avoid the buildup of dissolved solids in the loop. The size of the bleed stream will be dependent on the amount of alkali and alkaline metals that are present in the process water from the cyanide processes. The lower the initial concentrations of these metals the smaller the bleed stream because the ARO concept does not add any dissolved solids. The bleed will be sent off-site for disposal

5.2.2 Economic Analysis of Cyanide Wastewater Treatment Using ARO and Electrolysis

For purposes of this study, site preparation costs are not included for the ARO concept. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems. Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the biosorption concept would be approximately $143,000 and the annual O&M costs would be $38,000 (Table 5-3). The net present value of the process, assuming a 10 year life and a 7 percent interest rate would be $0.4 million. The most sensitive aspect of the cost analysis is the replacement of the membranes for the ARO unit. Currently, operators of the ARO units have found that the units need significantly less maintenance than the standard RO units; however, there is not an extensive backlog of information the operation of the ARO units. Therefore, testing would be needed to determine the required maintenance of the ARO units. An additional concern is the performance of the ERU in the presence of high concentrations of alkali and alkaline metals. These metals would be concentrated along with the heavy metals in the ARO unit.

Table 5-3: Summary of Economic Analysis for ARO with Electrolytic Recovery of Metals

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
RO Unit (continuous system rated at 30 gpm)	ea	$90,000	1	$90,000
Electrolytic Recovery Unit (Batch system for a 50 gal)	ea	$20,000	1	$20,000
Total Equipment Cost				$110,000
Installation Cost		30% of equipment cost		$33,000
Total Installed Cost				$143,000
O&M Costs[a]				
Operating labor (1 hr/day)	hr	$18	260	$4,680
Supervision (0.5 hr/day)	hr	$22	130	$2,860
Maintenance		6% of equipment cost		$6,600
Chemical cost[b]	ton	$85	200	$17,000
Brine Disposal[c]	ton	$150	0.5	$75
Utilities (electricity)	KWhr	$0.06	120,000	$7,200
Total Annual Cost				$38,415
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor	Total NPV	
$143,000	$38,415	7.0236	$412,812	

a Annual operation is assumed to be 260 days/year.

b See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate.

c The quantity of brine generated is based on a bleed stream of 1 percent of the concentrate stream.

d NPV is calculated based on a 10 year equipment life and a 7% interest rate.

6.0 Acid/Alkali-Bearing Wastewater Treatment

Two zero discharge concepts were considered for the treatment of acid/alkali wastewaters:

- Biosorption separation of the metals with electrolytic recovery of the metals; and
- Iron co-precipitation with selective precipitation and recovery of metals.

The acid/alkali wastewaters are expected to have high concentrations of dissolved solids other than the heavy metals. The first step in implementing a Zero Discharge Technology for this waste stream would be to review the wastes and segregate those wastes that have little to no heavy metals and use those wastes for pH control of other wastes where needed. Only wastes that have heavy metal concentration of concern should be combined and treated.

The biosorption process has the advantage in that biomaterials are strongly selective for heavy metals over alkali and alkaline metals. Research is needed on biosorption to determine how selective the biomaterials are for heavy metals in the presence of other cations and how well the biomaterials standup to the acid conditions of the plating wastewaters.

The overall objective of the iron co-precipitation concept is similar to the biomaterial concept which is to separate the valuable metals from solutions with high concentrations of other dissolved solids. The advantage of the iron co-precipitation concept is that the technology is based on proven fundamental chemistry, the solubilization of metals at different pHs. The disadvantage of the concept is that the control systems that are needed on a full-scale system are extensive; the labor requirements are high; and there are likely to be difficulties in selectively extracting the metals.

The biosorption concept has the economic advantage over the iron co-precipitation concept due mainly to the number of unit operations and the chemical and labor costs that are required for co-precipitation.

Concept	Capital Cost	Annual O&M Cost	Total NPV
Biosorption	$620,000	$250,000	$2.4 million
Iron Co-Precipitation	$850,000	$340,000	$3.2 million

The acid/alkali-bearing wastewater stream is the highest flow stream, with an average flow rate of 60 gpm, as compared to 30 gpm for the chrome wastewater stream and 20 gpm for the cyanide wastewater stream. Table 6-1 shows the typical contaminants and their concentrations for this stream. The data was provided by the NFESC Project Engineer. The acid/alkali stream contains the widest number of metallic contaminants, in low concentrations, and also contains methylene chloride and phenols, refractory compounds that are difficult to eliminate from the wastewater.

Table 6-1: NFESC-Provided Contaminant Concentrations and Flow Rates in the Acid/Alkali Wastewater

Contaminant	Concentration (mg/L)
Cyanide (CN)	< 3
Silver (Ag)	<10
Copper (Cu)	<10
Nickel (Ni)	< 10
Chromium (Total)	< 20
Phenols	< 5
Methylene Chloride	<5
Cadmium	< 10
Potential Contaminants	
Aluminum (Al)	Data Not Provided
Barium (Ba)	
Potassium (K)	
Magnesium (Mg)	
Zinc (Zn)	
Titanium (Ti)	
Calcium (Ca)	
Iron (Fe)	
Manganese (Mn)	
Sodium (Na)	
Cobalt (Co)	
Beryllium (Be)	
pH	4 < pH > 10
Wastewater Generated	60 gpm

The presence of the wide range of dissolved solids and the organic contamination makes the development of a Zero Discharge Technology difficult because the heavy metals have to be separated from high concentrations of alkali and alkaline metals which have little commercial value and are nonhazardous. The first step in developing a zero discharge concept for these waste streams would be to go back upstream to the operations and segregate them at their sources. Some of the waste streams may then be able to be used for pH adjustment for other streams or treated separately from the wastewaters with significant concentrations of heavy metals.

The acid/alkali wastestream is the only stream reported to contain phenols and methylene chloride. These materials, known as refractory compounds, are difficult to remove by conventional treatment technologies. Ozone (O_3) and hydrogen peroxide (H_2O_2) have been used to chemically oxidize organic and some inorganic constituents. Ozone at a high pH will react with hydroxide ions in water to generate hydroxyl radicals that can effectively treat phenolic wastes and cyanides. However, this process is not usually sufficient to remove refractory compounds like trichloroethylene (TCE), perchloroethylene (PCE), and methylene chloride.

Advanced oxidation process (AOP) employs ultraviolet (UV)-enhanced oxidations and other novel oxidation processes to promote the formation of highly reactive hydroxyl radicals to initiate oxidation reactions. AOPs are low temperature (near ambient) processes that have been developed for the treatment of dilute (tens of ppb [parts per billion] to tens of ppm) waste streams to achieve destruction efficiencies of 99+ percent. UV-enhanced AOP is effective in treating wastestreams containing TCE, PCE, methylene chloride and phenols.

However, because all DOD organizations have been tasked to eliminate the use of materials known or believed to deplete the ozone layer (TCE, PCE, methylene chloride), it was assumed that treatments for these chemicals was unnecessary and *were not* included in the cost analysis. Conventional destructions technologies can be used to treat the phenolic compounds. If this assumption is not correct, AOP must be added into the cost analysis for acid/alkali systems. A typical AOP system suited for treatment of the Navy-defined acid/alkali wastestream will cost approximately $110,000.

Two processes have been proposed for treatment of the acid/alkali wastewater streams:

- Biosorption separation of the metals with electrolytic recovery of the metals; and
- Iron co-precipitation with selective precipitation and recovery of metals.

The biosorption concept has the advantage that biomaterials will selectively adsorb the heavy metal and allow the alkali and alkaline metals to pass through. The concentration of the heavy metals on the biomaterial makes further processing of the acid regenerant more efficient by electrolysis. For the acid/alkali waste stream the biomaterials selective adsorption is a significant advantage; however, there has not been sufficient research to date to determine how well the biomaterials will perform when other cations are several orders of magnitude greater than the metals of concern. If the biomaterials are not highly selective for the heavy metals in wastewaters with these characteristics, then they would be expected to perform in a similar fashion to ion exchange units.

The overall objective of the iron co-precipitation concept is similar to the biomaterial concept which is to separate the valuable metals from solutions with high concentrations of other dissolved solids. The advantage of the iron co-precipitation concept is that the technology is based on proven fundamental chemistry, the solubilization of metals at different pHs. The disadvantage of the concept is that the control systems that are need on a full-scale system are extensive; the labor requirements are high; and there are likely to be difficulties in selectively extracting the metals.

6.1 Biosorption Separation with Electrolytic Recovery of Metal Contaminants

6.1.1 Overview of the Process

Figure 6-1 shows the process flow diagram for the biosorption concept. The process utilizes granular activated carbon to remove most of the organic contaminants. The heavy metals are then removed using biosorption. The metals are retained on the column and the effluent is discharged as water. The water is processed through a reverse osmosis system for final polishing and returned to the process tanks for reuse.

The biomaterials are regenerated using a countercurrent regeneration process where sulfuric acid is flushed from the bottom of the column to the top, exchanging the H^+ cation for the metallic cations. The metallic cations are selectively processed by electrolysis. The recovered metals (i.e., Cd, Zn, Ag, Cu, Au, Ni) are then sent off-site to a reclamation facility.

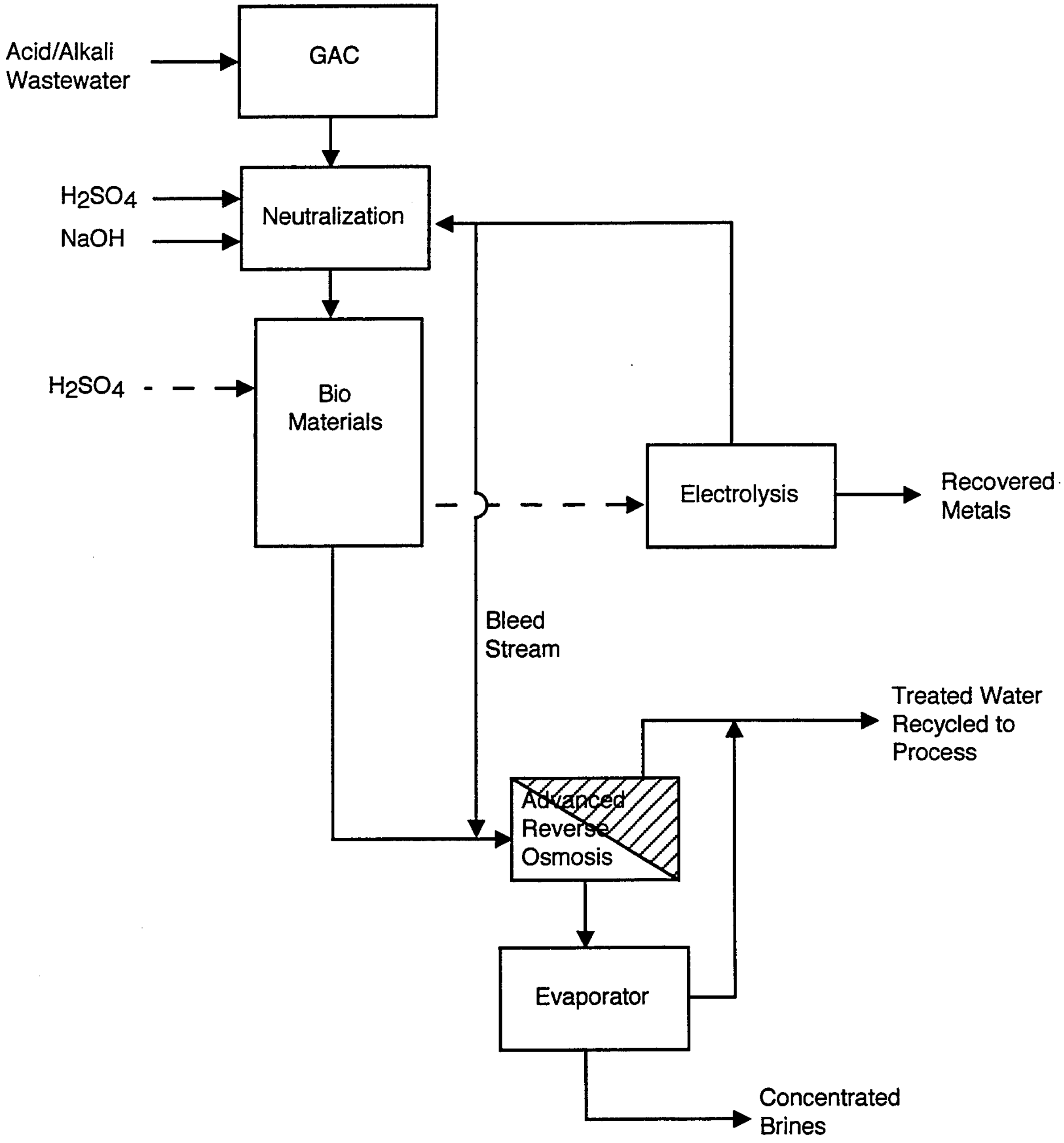
Granular Activated Carbon. The acid/alkali wastewater is expected to have significant concentrations of oil, grease, and other organic contaminants depending on the operations from which the wastewater is generated. The organics must be removed to protect down stream units and to minimize the buildup of these materials in the recycled process water.

The wastewater will be combined and passed through two GAC units in series. Each unit is expected to be approximately 1,000 lbs each to handle the hydraulic loading of the waste stream. The units would be operated such that when the lead unit breaks through it would be taken out of service and the second unit would be moved to the lead position and a clean unit would be placed in the second position.

The quantity of GAC that will be used annually is dependent on the concentration of the organics in the wastewater, but assuming low to moderate levels, approximately 8,000 lbs of GAC would be disposed of annually.

Neutralization. After the removal of the organics with GAC, the pH of the water would be adjusted with either caustic or sulfuric acid. The pH will be adjusted as little as possible to avoid adding additional dissolved solids to the water.

Figure 6-1: Acid/Alkali Wastewater Treatment with Biosorption



Biosorption of Aqueous Metals. Biosorption is an emerging technology and to date there are not significant numbers of systems in full-scale operation. Biosorption has been considered for treatment of air and water streams for both inorganics and organics. Recently significant research and development has been completed on the use of biomaterials to remove heavy metals from contaminated groundwaters[12-15]. Biomaterials are used in a manner similar to ion exchange resins except instead of synthetic resins biological materials are used. A wide range of materials have been tested, but research has focused on the use of whole algae cells (both living and dead) and ligands. The advantage of these materials over ion exchange resins is that they have been found to be highly selective for heavy metals and do not retain the alkali and alkaline metals such as sodium, potassium, calcium, and magnesium. The alkali and alkaline metals are typically in solution at much higher concentrations than the metals of concern and can significantly reduce the capacity of an ion exchange resin.

After the biomaterials have reached their capacity they are regenerated in a manner similar to cation exchange resins by passing a dilute acid (usually sulfuric acid) through the media and the retained metals are released and concentrated in the regenerant. There have been some recent studies that have shown that using progressively stronger acids to regenerate the biomaterials the retained heavy metals can be eluted selectively from the column. In either case the regenerant is then treated with either electrolysis or the heavy metals are precipitated.

During the literature search and interviews of biomaterial suppliers, there was a mixed response to the use of biomaterials for plating wastes. Some of the research has shown good results on dilute rinsewaters from plating operations. However, the engineering personnel at Bio-Recovery Systems, Las Cruces, NM (who provide commercially available bio-recovery systems) were concerned that large volumes of water must be treated to warrant the cost of the biomaterial, and the flow rates for most plating operations are too low to make biosorption economical. Other suppliers also noted that biomaterials are sensitive to oxidation attack by very strong acids, and they have observed problems with the pH of the plating solutions.

However, because biosorption is an emerging technology and the ability to selectively absorb heavy metals would greatly advance the ability to develop a zero discharge system, it was retained as a candidate for economic evaluation for the acid/alkali wastewater stream.

Electrolysis. The regenerant from the biosorption column will be a concentrated solution of dissolved metals. This regenerant will be pumped to the electrolytic recovery unit where the metals will be plated out and sent off site recovery. A detailed description of the electrolytic recovery unit is presented in Section 4.2.1, Overview of the Ion Exchange Process.

After the electrolytic recovery unit has removed as much of the metal content from the regenerant as feasible, the remaining solution will be pumped to the neutralization tank where the sulfuric acid content of the water can be used to lower the pH of the water from the acid/alkali pH adjustment unit. It may be necessary to have a bleed stream from the electrolytic recovery unit in order to avoid the buildup of dissolved solids in the loop. The size of the bleed stream will be dependent on the amount of alkali and alkaline metals that are retained on the biomaterials. The lower the retention of these metals the smaller the bleed stream. The bleed will be sent to the ARO unit for treatment.

Reverse Osmosis. Reverse osmosis (RO) is a pressure driven membrane separation process. The feed is separated under pressure (400 to 800 lb/in^2) into a purified "permeate" stream and a concentrate stream by selective passage of water through the microscopic pores of the semipermeable membrane.

The operating principle is a physical filtration separation. The porous membrane has a critical pore size to allow water molecules to pass through the filter, while retaining and concentrating the larger metal cations and cyanide anions. The process can produce a permeate that has a total dissolved solids concentration as low as 5 to 10 mg/L.

The major limitation of commercial RO systems has been its inability to maintain membrane performance. Fouling and gradual deterioration of membranes has reduced the processing capacity of the unit and required frequent membrane replacements. Feed solutions have to be in a pH range between 2.5 and 11 to ensure reasonable life for commercially available membranes, and the membranes do not completely reject certain species, such as non-ionized organic wetting agents.

Advanced reverse osmosis (ARO) has overcome many of these deficiencies. ARO uses filters made from composite materials that have finer pores, operate under pressures to 1,500 psi, and are not subject to attack by strong acids. In many cases operators of ARO units have found that they produce significantly less concentrate and the systems operate for up to two years with out downtime. These differences can save up to $35,000 a year in recurring maintenance and disposal costs.

In the biosorption concept, the effluent from the biosorption column and the bleed stream from the electrolytic recovery unit will be treated in an ARO unit. The permeate from the RO unit along with the condensate from the evaporator will be recycled back to the acid/alkali processes.

The RO unit in this concept is required if the treated water is to be recycled back to the acid/alkali processes. The concern is the buildup of dissolved solids in the process water from the cyanide oxidation and neutralization operations. If the treated water is used in another application where it will not be recycled again it may not need to treated in the RO unit. For this analysis, however, we assumed that the water would be recycled back to the acid/alkali processes.

The concentrate from the RO unit is sent to the evaporator where the dissolved solids are further concentrated prior to being sent off-site.

6.1.2 Economic Analysis of Acid/Alkali Wastewater Treatment Using Biosorption

For purposes of this study, site preparation costs are not included for the biosorption concept. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems. Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the biosorption concept would be approximately $620,000 and the annual O&M costs would be $250,000 (Table 6-2). The net present value of the process, assuming a 10 year life and a 7 percent interest rate would be $2.4 million. The most sensitive aspect of the cost analysis is the replacement of the biomaterial. Currently, most of the biomaterial suppliers are concerned about the acidic nature of the plating wastewater stream and believe that the biomaterial would have to be replaced at least once a year. Extending the life of the biomaterial from one year to two years would lower the operating costs to approximately $180,000 annually, and over the 10 year life of the system lower the NPV to $1.9 million. Therefore, any testing that is performed should further define the life of the biomaterials.

6.2 Treatment of Acid/Alkali Wastewater Using Iron Co-Precipitation and Metals Recovery by Selective Dissolution

6.1.2 Overview of the Iron Co-precipitation Treatment Method[18]

Figure 6-2 shows the process schematic for the iron co-precipitation wastewater treatment method with metals recovery by selective dissolution. The concept was selected as it is a less capital-intensive method, requiring primarily tanks instead of extensive use of expensive hardware and because it was based on well understood chemical equilibriums of metal hydroxides at different pHs.

The process uses iron, in the form of $Fe(HCO_3)$ to precipitate the metal ions out of a slightly basic solution. The Fe/metal cation solids are gravity-settled in a tank and the supernatant is treated through an ARO unit prior to recycling the water back to the processes.

The precipitated metal ions are selectively dissolved back into an aqueous solution using sulfuric acid to resolubilize the metals. After the metals are recovered individually, they can be sent to a reclamation facility to recover their value.

Table 6-2: Summary of Economic Analysis for Biosorption Recovery of Metals

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
GAC Unit (continuous system rated at 60 gpm)	ea	$3,000	2	$6,000
Neutralization Unit (continuous system rated at 60 gpm)	ea	$30,000	1	$30,000
Biosorption Column (continuous system rated at 60 gpm)	ea	$250,000	1	$250,000
Electrolytic Recovery Unit (Batch system for a 150 gal)	ea	$35,000	1	$35,000
RO Unit (continuous system rated at 60 gpm)	ea	$110,000	1	$110,000
Evaporator (continuous system rated at 50 gph)	ea	$40,000	1	$40,000
Total Equipment Cost				$471,000
Installation Cost		30% of equipment cost		$141,300
Total Installed Cost				$612,300
O&M Costs[a]				
Operating labor (2 hr/day)	hr	$18	520	$9,360
Supervision (1 hr/day)	hr	$22	260	$5,720
Maintenance		6% of equipment cost		$28,260
Biomaterial Replacement	annual	$150,000	1	$150,000
GAC Disposal	unit	$4,000	8	$32,000
Chemical cost[b]	ton	$85	200	$17,000
Brine Disposal[c]	ton	$150	4.5	$675
Utilities (electricity)	KWhr	$0.06	120,000	$7,200
Total Annual Cost				$250,215
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor		Total NPV
$612,300	$250,215	7.0236		$2,369,710

Notes for Table 6-2

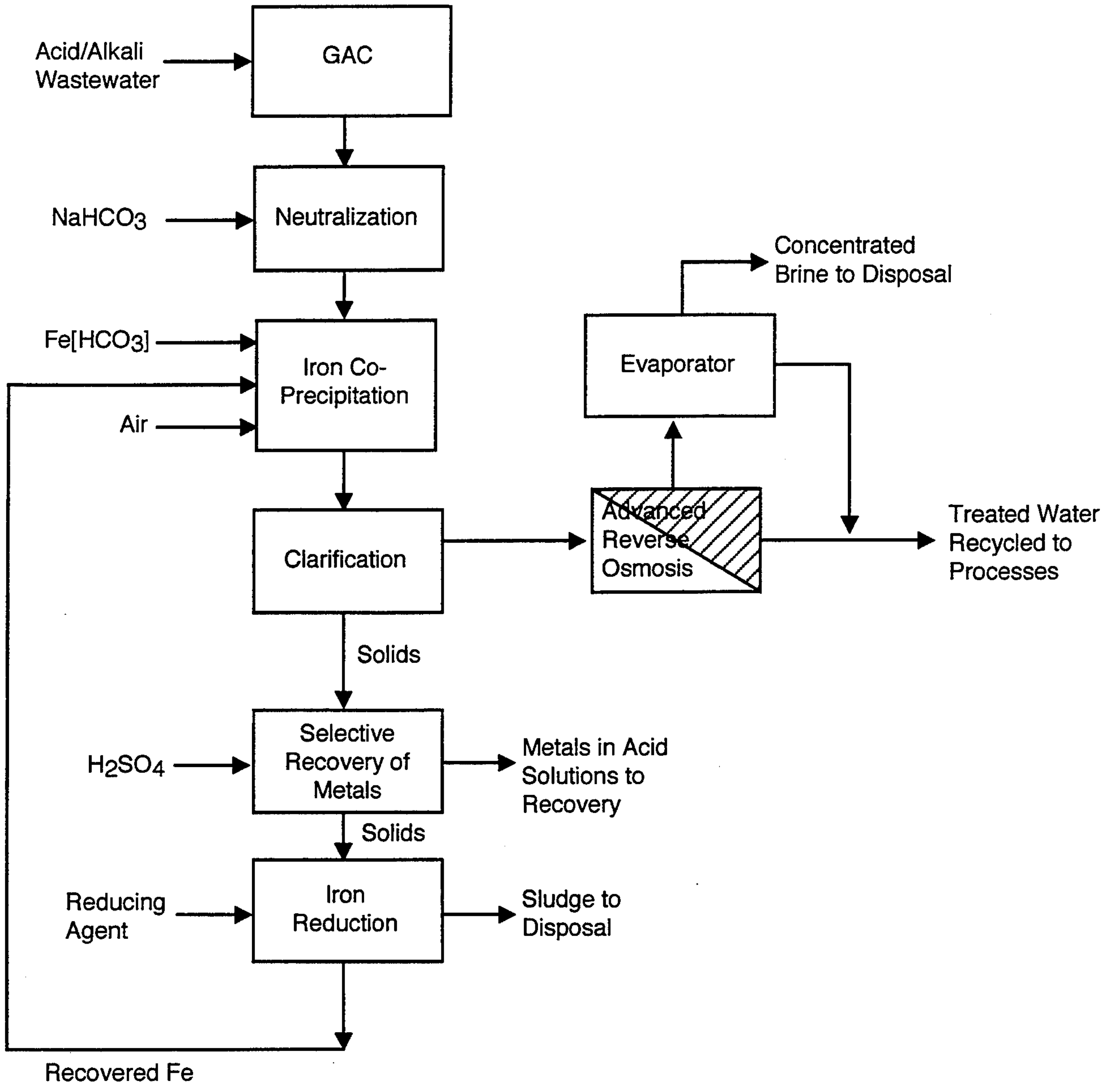
a Annual operation is assumed to be 260 days/year.

b See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate.

c The quantity of brine generated is based on a 1% reject from the RO and 10% residual brine from the evaporator.

d NPV is calculated based on a 10 year equipment life and a 7% interest rate.

Figure 6-2: Acid/Alkali Wastewater Treatment with Selective Metal Recovery



Granular Activated Carbon. The acid/alkali wastewater is expected to have significant concentrations of oil, grease, and other organic contaminants depending on the operations from which the wastewater is generated. The organics must be removed to protect down stream units and to minimize the buildup of these materials in the recycled process water.

The wastewater will be combined and passed through two GAC units in series. Each unit is expected to be approximately 1,000 lbs each to handle the hydraulic loading of the waste stream. The units would be operated such that when the lead unit breaks through it would be taken out of service and the second unit would be moved to the lead position and a clean unit would be placed in the second position.

The quantity of GAC that will be used annually is dependent on the concentration of the organics in the wastewater, but assuming low levels, approximately 8,000 lbs of GAC would be disposed of annually.

Neutralization. After the removal of the organics with GAC, the pH of the water would be adjusted with either caustic or sulfuric acid. The pH will be adjusted as little as possible to avoid adding additional dissolved solids to the water.

Iron Co-Precipitation. The effluent from the neutralization unit will be at a pH of approximately 7. The iron will be added to the wastewater as iron carbonate ($Fe[HCO_3]_2$) along with sparged air. Iron is highly reactive, is a strong reducing agent, and oxidizes readily in moist air. It dissolves in nonoxidizing acids (sulfuric and hydrochloric) and in cold, dilute nitric acid. The reaction below shows the oxidation of the iron bicarbonate in the moist air stream to an iron oxide, carbon dioxide gas, and hydroxyl ion minimizing the introduction of additional dissolved solids.

- $3Fe(HCO_3)_2 + 2\,O_2 \longrightarrow Fe_3O_4 + 6CO_2 + 6\,OH^-$

As the iron oxide precipitates out of the basic solution, the metal cations are adsorbed onto the iron oxide. This co-precipitation process occurs more rapidly and eliminates a higher percentage of the cations in the solution than simply forming the metal hydroxide in a basic solution.

The solids (iron oxide and metal hydroxides) are allowed to gravity settle in a tank, where the liquid portion (water) is removed for further treatment. The solids are then treated to the selective recovery of the metal cations.

Selective Recovery of Metal Ions. The precipitated solids are transferred to a reaction vessel where the metals are selectively recovered by incrementally increasing the pH of the solution. The metals will redissolve based upon their solubility in the acid solution. Table 6-3 shows the solubilities of the metals in a basic (pH 8) solution. The least soluble metal in the basic solution will be the first metal to be removed from the solids during treatment with the acid. As each metal is selectively solubilized the solution is decanted from the reaction vessel. The dissolved metals can be further treated by evaporation to remove the liquid and then sent to a reclamation facility. Or they can be sent to the reclamation facility in the liquid form.

The solution containing the iron would be treated in order to recover and recycle the iron to the co-precipitation step.

This operation would need to be proven in laboratory and pilot studies. Specifically, it is unclear whether a process could be designed and operated for a wastewater stream with such a large range of metals. An additional concern is the increased labor that would be required for the operation.

Table 6-3: Solubility of Metals when Precipitated at pH 8.0 as Hydroxides

Metal	Solubility (mg/l)
Iron	2.2×10^{-15}
Tin	1.7×10^{-11}
Mercury	6.0×10^{-9}
Copper	1.4×10^{-3}
Zinc	7.8×10^{-1}
Nickel	1.2×10^{2}
Lead	2.5×10^{2}
Silver	2.2×10^{3}
Cadmium	2.8×10^{3}

Reverse Osmosis. The effluent from the co-precipitation unit will be treated in a reverse osmosis unit. The permeate from the RO unit along with the condensate from the evaporator will be recycled back to the acid/alkali processes.

The RO unit in this concept is required if the treated water is to be recycled back to the acid alkali processes. The concern is the buildup of dissolved solids in the process water from the neutralization stages. If the treated water is used in another application where it will not be recycled again it may not need to treated in the RO unit. For this analysis, however, we assumed that the water would be recycled back to the acid/alkali processes.

The concentrate from the RO unit is sent to the evaporator where the dissolved solids are further concentrated prior to being sent off-site.

6.2.2 Economic Analysis of Acid/Alkali Wastewater Treatment Using Iron Co-Precipitation

For purposes of this study, site preparation costs are not included for the iron co-precipitation concept. The costs given are order-of-magnitude (+100/-50 percent) and include the capital cost of the systems. Installation costs are given as a percentage of the capital cost. Start-up, training, manuals, project management, and contingency budgeting are not included. Capital and operating and maintenance (O&M) costs were obtained from supplier quotes and from current literature.

The results of the cost analysis indicated that the capital cost for the biosorption concept would be approximately $850,000 and the annual O&M costs would be $340,000 (Table 6-4). The net present value of the process, assuming a 10 year life and a 7 percent interest rate would be $3.2 million. The most sensitive aspect of the cost analysis is the labor required to ensure that the metals are recovered individually. The concern surrounds the need to change the pH of the solution very precisely and this would require the use of a sophisticated control system.

Table 6-4: Summary of Economic Analysis for Iron Co-Precipitation Recovery of Metals

Item	Units	Unit Cost (1995$)	# Units	Total Cost
Capital Costs				
GAC Unit (continuous system rated at 60 gpm)	ea	$3,000	2	$6,000
Neutralization Unit (continuous system rated at 60 gpm)	ea	$30,000	1	$30,000
Fe Precipitation Unit (continuous system rated at 60 gpm)	ea	$200,000	1	$200,000
Clarifier (continuous system rated at 60 gpm)	ea	$110,000	1	$110,000
Selective Recovery Unit (continuous system rated at 60 gpm)	ea	$160,000	1	$160,000
RO Unit (continuous system rated at 60 gpm)	ea	$110,000	1	$110,000
Evaporator (continuous system rated at 50 gph)	ea	$40,000	1	$40,000
Total Equipment Cost				$656,000
Installation Cost		30% of equipment cost		$196,800
Total Installed Cost				$852,800
O&M Costs[a]				
Operating labor (6 hr/day)	hr	$18	1600	$28,800
Supervision (3 hr/day)	hr	$22	800	$17,600
Maintenance		6% of equipment cost		$39,360
Chemical cost[b]	annual	$250,000	1	$250,000
Brine Disposal[c]	ton	$150	4.5	$675
Utilities (electricity)	KWhr	$0.06	80,000	$4,800
Total Annual Cost				$341,235
Net Present Value[d]				
Capital Cost	O&M Cost	Discount Factor		Total NPV
$852,800	$341,235	7.0236		$3,249,498

Notes for Table 6-4

a Annual operation is assumed to be 260 days/year.

b See Table A-1 and Figure A-1 for chemical costs. Chemical rate is calculated based on demand rate.

c The quantity of brine generated is based on a 1% reject from the RO and 10% residual brine from the evaporator.

d NPV is calculated based on a 10 year equipment life and a 7% interest rate.

7.0 Summary and Recommendations

The economic evaluations of the treatment technologies resulted in two immediate conclusions:

- The cost of chemicals used for wastewater treatment has increased dramatically and will probably continue to increase; and
- The cost and liability associated with sludge disposal has increased significantly and will probably continue to increase.

From an economic viewpoint, the preferred technologies for wastewater treatment will utilize little or no chemicals and will minimize or eliminate the production of hazardous wastes.

Table 7-1 presents a summary of the economic evaluations for the three wastewater streams. The net present value (NPV) was calculated assuming a 10 year equipment life and a 7 percent interest rate.

Table 7-1: Summary of Economic Evaluations of Advanced Wastewater Treatment Technologies

Wastewater Stream	Treatment Technology	Capital Costs	O&M Costs	NPV $ (Million)
Conventional Integrated Wastewater Treatment	Chemical	$633,100	$199,000	$2.0
Chrome-Bearing Wastewater	Ion Exchange/ Electrodialysis (Sludge Disposal)	$250,900	$124,820	$1.1
	Ion Exchange/ Electrodialysis (Sludge Treatment)	$250,900	$109,827	$1.0
	Ion Exchange/ Electrolysis	$259,740	$114,828	$1.1
Cyanide-Bearing Wastewater	Biosorption/Electrolysis	$520,000	$138,505	$1.5
	ARO/Electrolysis	$143.000	$38,415	$0.4
Acid/Alkali-Bearing Wastewater	Biosorption/Electrolysis	$612,300	$250,215	$2.4
	Iron co-precipitation	$852,800	$341,235	$3.2

The chrome- and cyanide-bearing wastewater treatments had NPV's that were about 50 percent less (on average) than the NPV for conventional wastewater treatment. The acid/alkali-bearing wastewater treatments had NPVs that exceeded that for conventional water treatment by an average of 140 percent. This is caused by the high cost of biomaterial replacements for the biosorption process and the high labor requirements and the extensive need for automated controls on the iron co-precipitation process.

The process that appeared the most attractive for cyanide, and possibly, the acid/alkali wastewater treatment is ARO/electrolysis. The capital investment is modest and the O&M is very low.

Integrated Wastewater Treatment

The sensitivity of the plating and cleaning processes, as well as the fact that advanced technologies are designed for very specific processes, discourages the concept of proposing an integrated wastewater treatment concept. There are synergies between the cyanide and acid/alkali wastestreams and the methods that can be used to treat the water. However, the chrome plating process does not appear to be easily integrated into an advanced integrated wastewater treatment concept. ARO coupled with electrolytic metals recovery could, potentially, be used with both the cyanide and acid/alkali wastewater streams.

Concepts Requiring Laboratory Validation

During the course of this evaluation, a number of concepts were identified that had promise; however, laboratory validation was felt required prior to the construction of a demonstration project or a pilot plant. These are concepts where limited data on actual "in-service" use on similar processes was available.

ARO/Electrolysis. There is one reported case where ARO was used to treat the wastewater from a chromate conversion coating process with no other treatment technology. The features of ARO (higher efficiency of contaminant removal caused by improved membrane design)have led to good results in treatment. The permeate, without further polishing, is fed back to the rinse tank. The concentrate is still undergoing evaluation for reuse in the conversion coating without further treatment. This process is used on the manufacturer of the U.S. Navy F-18E/F fighter aircraft. The system has been in operation for two years, saving 1,500,000 gallons of water annually and precluded the necessity to construct a $250,000 water treatment facility. ARO has a low labor cost associated with its operation and uses no chemicals during the processing.

Biological Treatments. Biological treatment does not appear economically feasible for treatment of metal processing wastewaters at this time. Its primary application was in the treatment of enormous quantities of contaminated groundwater. However, new research is emerging that expands the usefulness and versatility of this technology. While it does not appear economical at this time, it is certainly a technology to monitor for future results.

Sludge Treatment. The treatment of sludges that contain hazardous pollutants (heavy metals) is gaining in popularity, as it provides significant relief from the "cradle-to-grave" ownership of hazardous wastes. The treatment can be hydrometallurgical (available as a system cost or provided as a service by a supplier) or electrolytic treatment of the sludge.

Sludge treatment can prove beneficial as each zero discharge system produces a small amount of wastes that must be disposed of as hazardous. Alternatively, the approach of treating the sludge rather than employing expensive, sophisticated, and advanced wastewater treatments may be more cost-effective in some circumstances.

Electrolysis. Of all the techniques evaluated, electrolysis appears to have the highest potential for producing closest to a zero discharge wastewater treatment system.

References

1. "Pretreatment Rules Impact Industry, POTWs", Environmental Protection, October, 1994, pp. 20-67.

2. Environmental Pollution Control Alternatives: Economics of Wastewater Treatment Alternatives for the Electroplating Industry, U.S. Environmental Protection Agency, EPA 625/5-79-016, June 1979.

3. Development Document for Proposed Existing Source Pretreatment Standards for the Electroplating Point Source Category, U.S. Environmental Protection Agency, EPA 440/1-78-085, Feb.1978.

4. Memorandum from NFESC Project Engineer, Ms. Jennie Koff, to Mr. Ric Bowen, Arthur D. Little, Jan. 18, 1995.

5. Rajcevic, H. P., "A Hydrometallurgical Process for the Treatment of Industrial Wastes", Plating and Surface Finishing, July 1990, pp. 22-25.

6. Wiaux, J.P., and Nguyen, T, and Titalyse, S.A., "Recovered Value from Electroplating Waste", Metals Finishing Journal, November, 1993, pp. 85-92.

7. Liberti, L. And Petruzzelli, D., "Discussion of: A Process to Improve the Regenerated Effluent Concentration of Ion Exchange", Ion Exchange, pp 406 - 415.

8. Urbanski, T. S., Chmielewski, A. G., Kazmierczak, T., Kierat, Z, Flak, M., and Szmander, H., "An Electrochemical Oxidation and Ion Exchange Method for Recovery of Chromium", Metal Finishing Journal, pp 55-59 (November, 1993).

9. Ion Exchange for Pollution Control, Calmon, C. Gold, H., and Prober, R., eds, CRC Press, Inc., Boca Raton, FL.

10. Giordana, T. J., Ledwig, C., and Rickles, S., "Use of Solution Rejuvenation and Process Modifications to Minimize Metal Stripping Waste", 9th Annual Aerospace Hazardous Materials Management Conference, Denver, CO (28-30 September 1994).

11. Reinhard, F. P., "Utilization and Practical Application of Ion Exchange - A Critical Review", 14th Annual AESF/EPA Conference on Environmental Control for the Surface Finishing Industry, pp. 197-203 (1993).

12. Osterman, R., Private Conversation, Northrop-Grumman Advanced Reverse Osmosis System Used on U.S. Navy F-18 E/F Manufacturing, 1995.

13. Wiaux, J-P., Oberflache-Surface, No. 7, July, 1988, pp. 21-26, 167-177.

14. Torma, A. E. and Apel, W. A., "Recovery of Metals from Dilute Effluent Streams by Biosorption Methods", Residues and Effluents - Processing and Environmental Considerations, The Minerals, Metals & Materials Society, 191, pp. 735-743.

15. Daarnall, D. W., Gabel, A., Torresdey, J., "AlgaSORB® A New Biotechnology for Removing and Recovering Heavy Metals Ions from Groundwater and Industrial

Wastewater", Proceedings of the 1989 A&WMA/EPA International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control, 1989, pp. 113-124.

16. USEPA, "Removal and Recovery of Metal Ions from Groundwater", SITE Superfund Innovative Technology Evaluation, Emerging Technology Bulletin, February 1992.

17. Baldwin, P. C., "Electrolytic Plate-Out of Scrapped Cyanide Copper Baths", Metal Finishing, November, 1993, pp. 13-14.

18. Eckenfelder, Jr., W. W., Principles of Water Quality Management, CBI Publishing Co., Boston, MA, 1980, p. 477.

Appendix A: Basis for Economic Evaluations

Table A-1: 1995 Cost of Chemicals

Chemical	1995 Cost [a]
NaOH (98% equivalent)	$1.23/lb
NaOCl	$1.55/lb
H_2SO_4	$75.00/ton
$Ca(OH)_2$	$83.50/ton
Ca(O) Quicklime	$83.50/ton
Cl_2	$215/ton
FeS	$0.82/lb
HCl (28% HCl)	$78.00/ton
Sodium Bisulfite ($NaHSO_3$)	$28.50/100 lbs
Sodium Carbonate ($NaHCO_3$)	$20.80/100 lbs
Sodium Hypochlorite (NaOCl)	$1.55/lb
Na_2S	$113/ton
SO_2	$230/ton
H_2SO_4	$85/ton
Quadrol Complexing Agent[b]	$28.80/gram

[a] *Prices from Chemical Marketing Reporter, February 27, 1995.*

[b] *Sigma Chemical Catalog, 1994.*

Figure A-1 Sample of Method Used to Calculate Chemical Usage and Costs