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Evaluation of Electrodialysis for Chromic Acid Recovery and Purification at Corpus Christi Army Depot

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A large quantity of hazardous waste is generated during the maintenance, repair, and overhaul of a wide variety of military equipment at Army depots. Some of this waste is generated by the use of chromic acid solutions for chromium electroplating and the application and removal of chromate conversion coatings. Hazardous waste results when metal contamination builds up in the solutions to such a degree that the solutions must be disposed of as hazardous waste. Removal of this metal contamination should result in a lengthened bath life and reduced hazardous waste generation.

As part of its pollution abatement and environmental control mission, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is pursuing R&D projects to assist depots in meeting the Army goal of a 50 percent reduction in hazardous waste by the end of 1992 compared with 1985 baseline levels. In one project, USATHAMA purchased, installed, operated, and evaluated an electrodialysis system on two chromic acid process solutions at Corpus Christi Army Depot (CCAD) in Corpus Christi, Texas. The objective of this task was to evaluate the system's ability to remove metal contamination and oxidize trivalent chromium (an impurity) to hexavalent chromium (chromic acid).

In the first phase of testing, the equipment was installed on a chromic acid stripping solution used for removing chromate conversion coatings from magnesium transmission parts. This solution had become spent after several weeks of use, and the objective of this phase was to rejuvenate the solution for reuse. Samples were collected over a period of 44 days and analyzed for various metal contaminants. The system was successful in removing a significant quantity of metals from the chromic acid solution, and may have been successful in reducing trivalent chromium concentrations. A hole in the electrodialytic membrane, however, caused sulfate contamination of the chromic acid solution, which resulted in damage to parts being processed. Bench-scale testing demonstrated that the sulfates could be precipitated with the addition of barium carbonate. A potential mode of operation is to install and operate the electrodialysis cell on a holding tank of a spent solution, then add barium carbonate to remove any sulfate contamination. Operation on an in-line chromic acid stripping solution is not recommended unless the catholyte formulation can be modified.

In the second project phase, the equipment was installed on a hard chromium electroplating tank, which is less susceptible to sulfate contamination. The objective of this phase was to continuously purify the solution while it was being used to process parts. Samples were collected over a period of 90 days and analyzed for various metal contaminants. The system was successful in significantly reducing concentrations of metal contaminants, including trivalent chromium. Sufficient data were not gathered, however, to verify the expected benefits of the system, which are reduction of hazardous waste, reduction of part rejects, reduction of sludge buildup, and an increase in plating efficiency. Long-term monitoring is necessary to verify these benefits.

Analytical results indicated that metals removed from the process solutions were transported through the membrane and precipitated in the catholyte solution. The resulting sludge must be disposed of as a hazardous waste because of its chromium content. Two concerns with this catholyte solution were the volume of waste generated and the presence of hexavalent chromium, which could create additional wastewater treatment requirements. To minimize the waste volume, the spent catholyte could be pumped through the waste pretreatment plant or filtered, rejuvenated with the appropriate chemicals, and recycled. A sludge dewatering system would further reduce waste generation. The presence of hexavalent chromium can be addressed by reformulating the catholyte powder, adding additional reducing agent to a spent catholyte, batch treating with an alkaline reducing agent, treating the catholyte in the chromium reduction process in the waste pretreatment plant, and/or recycling the catholyte solution to the extent possible.

Recommendations are provided in this report regarding the best use of the purchased electrodialysis cell that remains at CCAD, additional problem areas that need to be pursued, future projects regarding electrodialysis and chromic acid solutions, and followup with CCAD personnel.

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SECTION 1

INTRODUCTION

1.1 Background

U.S. Army depots throughout the country maintain, repair, and overhaul a wide variety of military equipment, including tanks and other vehicles, engine components, electronic communication shelters, and helicopters. A large quantity of hazardous waste is generated during these operations. As part of its commitment to environmental compliance, the U.S. Army has established a goal of 50 percent reduction of hazardous waste by 1992 relative to 1985 baseline figures. Electroplating waste is one of the six major waste streams targeted by the Depot Systems Command (DESCOM) for reduction at Army depots.

The hazardous waste generated by these depots includes several types of chromic acid solutions resulting from chromium electroplating, application of chromate conversion coatings, and chromium stripping operations. To assist the Army in achieving its waste minimization goals, USATHAMA and its contractor, IT Environmental Programs, Inc. (ITEP) (formerly PEI Associates, Inc.) conducted surveys of eight major Army depots to identify potential research and development projects targeting waste reduction. As a result of these surveys, electrodialysis was identified as a potential method of recovering and purifying chromic acid solutions. These solutions currently become contaminated with metals (including trivalent chromium) and must be disposed of periodically as hazardous waste. Electrodialysis can potentially remove contaminant metals and oxidize trivalent chromium to hexavalent chromium, which is the active form in chromic acid solutions, and thereby extend the lives of the solutions while reducing the generation of hazardous waste.

The project discussed in this report was conducted at Corpus Christi Army Depot (CCAD). This depot has been designated as DESCOM's Center of Technical Excellence (CTX) for chromate conversion coatings. CCAD staff are responsible for recommending the best available technologies for minimizing hazardous waste from these types of operations. The project was conducted at CCAD because of its CTX responsibilities and the desire of its staff to evaluate the potential of implementing a closed-loop chromic acid recovery system.

1.2 Objective

The objective of this test program was to test the ability of a commercially available electrodialysis unit to recover and purify contaminated chromic acid solutions at CCAD. A complete electrodialysis system was purchased from a vendor and installed at the depot. The system was tested and evaluated both in batch and continuous modes of operation.

For evaluation of batch rejuvenation capabilities, the following items were checked:

1) Rate of contaminant metal removal (as a function of time and metal concentration).

2) Ability of the unit to oxidize trivalent to hexavalent chromium.

3) Determination of which metals migrate into the catholyte solution and which precipitate as hydroxides.

4) Ability of the rejuvenated solution to be reused for processing parts.

5) Effect of the unit on chloride concentrations.

6) Method of proper disposal of the spent catholyte solution.

For evaluation of the continuous purification capabilities of the system, the following items were addressed:

1) Ability of the system to continuously purify an operational chromic acid solution.

2) Effect of the unit on the buildup of contaminant metals in the bath.

3) Determination of which, if any, metals concentrate in the solution because they are not transported into the catholyte solution.

1.3 Technical Approach

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

Task 1. Visits to eight major Army depots to assess types and quantities of waste generated and to identify waste minimization R&D needs. Based on these visits, three projects were chosen for development, including the one presented in this report.

Task 2. Visits to CCAD to discuss project plans and to obtain depot staff input and support for the project. Vendors were contacted to identify available electrodialysis systems. A literature review was conducted to evaluate existing information on electrodialysis and other potentially competing technologies.

Task 3. Characterization of a chromic acid bath in use at CCAD. ITEP and USATHAMA conducted visits to the depot to sample the chromic acid solution, which was then analyzed for concentrations of potential contaminants. This effort was necessary to select and size a recovery unit.

Task 4. Performance of on-site testing at CCAD. A Test Plan and Accident Prevention Safety Program Plan were prepared before on-site testing was conducted.[1,2] The equipment was initially installed on a spent chromic acid solution that had been used to strip chromate conversion coatings from magnesium parts and was tested for its ability to rejuvenate the solution for reuse. The equipment was subsequently installed on a chromic acid solution used in electroplating hard chromium onto steel parts and tested for its ability to maintain bath quality continuously. Additional efforts were undertaken to test other solutions and concepts on a small scale in the laboratory.

Task 5. Evaluation of data from the test program to determine the ability of the electrodialysis system to rejuvenate and purify chromic acid solutions for the purpose of achieving a reduction in hazardous waste generation.

1.4 Report Organization

The remaining sections of this report present discussions regarding initial waste and process characterization (Section 2), selected equipment (Section 3), and the test program (Section 4). Section 5 presents the test data, and Section 6 contains an evaluation of these data. Section 7 presents conclusions and recommendations.

SECTION 2

PROCESS DESCRIPTIONS AND WASTE CHARACTERIZATION

2.1 Chromic-Acid Waste at Depots

During metal pretreatment and finishing operations, Army depots use a variety of process solutions that contain chromic acid. These operations include functional (hard) chromium electroplating; chromate conversion coatings on aluminum, cadmium, steel, and magnesium; removal of chromate conversion coatings; and anodizing. After a period of use, these solutions become contaminated with metals and other impurities that are introduced into the system. Metals may be carried into the solution on parts treated in other process or rinse tanks, or they may be introduced by dissolution of metals that compose the parts, tanks, tank liners, or bus bars. In addition, hexavalent chromium, the form of chromium that constitutes chromic acid, is reduced to trivalent chromium, an impurity.

Various negative impacts result from this buildup of metals and trivalent chromium. A buildup of contaminants in solutions used to remove older chromate conversion coatings may reduce the removal rate and cause quality problems such as the smutting of parts. Buildup of impurities in chromium plating baths causes plating quality problems and a decrease in bath conductivity and plating efficiency.

As a result of bath contamination, the process solutions frequently become spent and must be disposed of. These spent solutions are classified as hazardous wastes because of their corrosiveness and toxic metal content. Reducing the contamination in these baths should lengthen their lives and thereby cause a reduction of hazardous wastes.

In addition to chromic acid tanks, Army depots use a wide variety of other acids, including hydrochloric, sulfuric, and phosphoric acids. These acids can also become spent as the result of the accumulation of contaminant metals and end up as hazardous waste. Some of these acid solutions contain sodium dichromate, in which the hexavalent chromium is reduced. These solutions are thus candidates for recovery by the removal of these metals or by the oxidation of trivalent chromium.

All of the chromic acid process tanks are followed by rinse tanks. Solution carried out of the tank on parts (drag-out) is removed from the parts by the rinse water, which is treated in an industrial wastewater treatment plant (IWTP). The metals are usually precipitated with lime, which creates a sludge that is hazardous because of its chromium content. This IWTP sludge is a major chromium-containing waste at many depots. Also, the scrubber water for the ventilation in many depot plating shops contains chromium, which ultimately results in additional quantities of sludge from the IWTP that must be disposed of. Although this waste stream was not studied under the current project, the results of such a study might be useful for justifying a closed-loop system in which the chromium is recovered and returned to the process tank.

2.2 Selection of Test Solutions at CCAD

Table 2-1 presents the overall quantities of hazardous waste generated at CCAD in calendar year 1990. This table indicates that chromic acid, chromate conversion coating (Alodine) rinse water, and chromium-contaminated sludge are major contributors to the total quantity of hazardous waste. Table 2-2 presents the quantities of hazardous waste generated by specific process lines and solutions in the plating shop in 1987 (the latest year for which data are available). This table indicates that the chromic acid tanks on the I-line are the largest generators of hazardous wastes. Other chromic acid solutions in the plating shop generate only small quantities of hazardous waste. Table 2-2 should be used only to estimate relative quantities of waste generated by plating shop operations. It should not be used as an up-to-date source of hazardous waste generation rates.

TABLE 2-1. CCAD HAZARDOUS WASTE GENERATED IN CALENDAR YEAR 1990[a]

Waste description	Quantity generated	
	Gal	lb
Cleaning		
Varsol	10,331[b]	0
Trichloroethane	9,473	0
Alkaline waste hydroxide	6,672	814
Mg hydroxide cleaning compound	1,436[c]	0
Cleaning compound	1,097	0
Still bottoms	909	0
Varsol still bottoms	208	0
Painting		
Paint waste liquid	17,389	7,651
Paint sludge	421	0
Sump sludge; paint solid	0	312
Paint rags/paper wipes/ filters/vac. bags	0	4,659
Paint stripping		
Glass beads	0	545,578
Glass bead filters	0	3,793
Alkaline waste paint stripper	208	0
Plating		
Alodine rinsewater	66,615[d]	0
Spent chromic acid	14,182	0
Ammonium bifluoride	1,664	1,226
Ammonium nitrate oxidizing agents	1,250	0
Nitric Acid	842	0
Chromic acid sludge from Scrubber 4	420	0
Sulfuric acid	133	0
Metalworking		
Cutting oil	859	0
Fuel		
Waste oil	18,515	0
Fuel	604	1,723
TOTALS	133,250	564,033
Industrial waste treatment		
Chromium sludge		280,000[e]

[a] Some minor waste streams have not been included in this list.

[b] 8,621 gal recycled on site.

[c] 500 gal treated in IWTP.

[d] 57,444 gal treated in IWPTP.

[e] CY 1988 data.

TABLE 2-2. FREQUENTLY DISPOSED PLATING SHOP WASTE BY IWMS[a]

Line	Description of waste solution	Quantity, gal/yr[b]
A	Spent sulfuric acid	200
	Spent chrome plating solution	100
B	Spent sodium hydroxide	740
	Spent corrosion removing compound	200
C	Chromate conversion coatings	0
D	Spent sodium dichromate	470
	Spent nitric acid	465
E	Spent nitric acid	460
	Spent hydrochloric acid	235
	Spent chromic acid	230
	Spent silver solder leach	170
F	Spent iridite	190
G	Spent alkaline rust remover	1,600
	Spent alkaline cleaner	975
	Spent hydrochloric acid	1,260
	Spent ammonium nitrate	470
	Spent trichloroethane	660
H	Spent nickel strike	130
	Spent sulfuric acid	240
I	Spent magnesium alkaline cleaner	2,430
	Spent magnesium dichromate	1,475
	Spent ammonium bifluoride	1,510
	Spent chromic acid	3,760
K	Spent trichloroethane	1,060
	Waste wax	135
	Preservation waste oil	250
M	Spent enplate (nickel plating)	180
	Spent sulfuric acid	50

[a] Source: Foster Wheeler Enviresponse. Environmental Management Plan, Phase I. Qualitative Characterization of Hazardous Waste Streams, Corpus Christi Army Depot, for U.S. Army PBMA, Picatinny Arsenal. March 1989.

[b] Quantity generated in 1987, IWMS records (latest data available).

A chromic acid tank on the I-line used for stripping chromate conversion coatings from magnesium parts was initially selected for full-scale testing under this test program. A hard-chromium plating tank on the A-line was subsequently chosen for full-scale testing. Also, a chromate conversion coating tank on the C-line and a nitric acid stainless steel passivation tank on the E-line were chosen for small-scale testing. Each of these process solutions is discussed in subsequent subsections.

2.3 Chromic Acid Stripping

2.3.1 Process Description

The initial testing under the experimental program was conducted on a chromic acid solution used for removing chromate conversion coatings, primarily from magnesium transmission parts. The solution is contained in Tank I-3, whose dimensions and materials of construction are provided in Table 2-3. A ventilation hood vents the mist from the tank to a scrubber. This tank is heavily used and is the largest generator of hazardous waste in the plating shop (see Table 2-2).

TABLE 2-3. DATA FOR TANK I-3

Width:	4 ft
Length:	3 ft
Height:	3.5 ft
Capacity:	269 gal
Tank composition:	Mild steel
Liner composition:	Lead/antimony (7% antimony) alloy
Parts processed:	Magnesium transmission parts
Operating temperature:	200°F
Agitation:	Filtered, low-pressure air
Chromic acid concentration:	16-32 oz/gal

Tank I-3 is part of the magnesium line in the plating shop, which consists of the following operations:

- Alkaline cleaning
- Rinse
- Chromic acid stripping
- Rinse
- Bifluoride activation
- Rinse
- Chromate conversion coating

Parts are vapor degreased with 1,1,1-trichloroethane before being processed in the plating step.

A fresh solution in Tank I-3 contains approximately 500 pounds of chromium trioxide. The CCAD laboratory periodically analyzes the solution for chromic acid concentration and recommends the quantity of chromium trioxide needed for makeup. The target concentration of chromic acid is 16 to 32 ounces per gallon of solution.

After being used to process parts, Tank I-3 gradually becomes contaminated with tramp metals and particles of paint that may not have been removed during the abrasive blasting operation that occurs before the part reaches the plating shop. Hexavalent chromium (as chromic acid) is reduced to trivalent chromium, which becomes another impurity. The contaminant metals include those that dissolve from the part (magnesium) or the tank (lead) and those that are introduced when tap water is accidentally added to the tank.

As the solution becomes contaminated, several problems appear. The rate of chromium removal decreases, which results in increased processing time and decreased production. Also, a gray smudge remains on some parts after they are processed in a contaminated solution. This smudge generally can be removed by spraying with water; in some cases, however, manual scrubbing with a wire brush is required.

When it is no longer effective in removing chromate conversion coatings from parts, the solution is disposed of as a hazardous waste. Analytical criteria are not used to determine when a bath should be disposed of. The frequency of disposal varies greatly with the depot workload and ranges from approximately 1.5 to 11 weeks between tank changeouts.

2.3.2 *Chemical Characterization of Chromic Acid Stripping Solution*

In the initial phase of the experimental program, Tank I-3 was sampled on three separate occasions. Samples were collected 2 days after a fresh solution was formulated, during the midlife of another solution, and 2 days before disposal of a spent solution. The purpose of these sampling efforts was to determine the contaminants in the solution that might contribute to bath depletion. These analyses also provided data needed to size the chromic acid recovery/purification equipment to be used for testing, to select the parameters to be analyzed for the test program, and to determine the contamination profile of the tank over time (i.e., to determine if the metal contaminants actually increase over time and contribute to bath depletion).

On May 22, 1990, a sample was collected from a chromic acid solution after 2 days of use. This sample represents concentrations of contaminants in a relatively fresh bath. On February 7, 1990, a sample was collected from a bath that had been operated for 5.5 weeks; this solution was eventually disposed of after 11 weeks (the longest bath life in 1990.) On May 16, 1990, a sample was taken from a solution 2 days before its disposal. This sample represents a solution that is spent or no longer useful. These samples were not taken of the same solution at different times; they were collected from three different solutions at different stages of use.

Table 2-4 presents the analytical results for the three sets of chromic acid solutions. (Because of the high concentrations of chromium they contained, the samples were diluted before their analysis, and some of the resulting detection limits are higher than the theoretical capabilities of the instrumentation.) The major multivalent metal contaminants of the bath were magnesium, aluminum, iron, cadmium, calcium, lead, and zinc. These analyses indicate that almost all of the chromium was in the hexavalent form, even when the solution was spent. The spent solution contained a lower amount of hexavalent chromium than the other solutions did; however, the concentration was still within specifications. The spent solution also contained a detectable amount of thorium, a radioactive element. (Thorium is a component of several parts processed at CCAD.) Organic contamination was low (<0.1 ppm).

TABLE 2-4. ANALYTICAL RESULTS OF CHROMIC-ACID SAMPLES FROM TANK I-3 CORPUS CHRISTI ARMY DEPOT[a]

Parameter	5/22/90 (2 days of use)[b]	2/7/90 (midlife)[c]	5/16/90[d] (2 days before disposal)
Chromium, mg/L	135,000; 138,000[e]	133,000; 139,500[f]	123,000; 121,000[e]
Hexavalent chromium, mg/L	136,000; 136,000[e]	133,000; 147,000[f]	117,000; 122,000[e]
pH, S.U.	1.25	<0.2[g]	1.23
TS, mg/L	300,000	300,000	271,000
TSS, mg/L	630	326	1,700
TDS, mg/L	260,000	269,000	253,000
Chloride, mg/L	<75[h]	<52,000[i]	340[h]
Fluoride, mg/L	11.3	75.5	68
Sulfate, mg/L	1,760	<870[j]	<1,200[j]
TOC, µg/L	21.7	85.7	61.9
TOX, µg/L	<10.0[g]	<1000[k]	32
Metals, mg/L[m]			
Aluminum	145	332	591
Antimony	8.58	<29[g]	<22[g]
Arsenic	0.0490	0.0670	0.297
Barium	3.14	2.84	6.48
Beryllium	5.40	<0.1[g]	2.22
Cadmium	10.5	32.3	105
Calcium	28	NA[n]	115
Cobalt	4.97	23.9	16.5
Copper	<0.8[g]	<1.0[g]	2.73
Iron	43.6	36.8	150
Lead	95.7	41.6	93
Magnesium	692	2,270	4,000
Manganese	5.45	19.7	58
Mercury	<0.0009[g]	<0.0006[g]	<0.0009[g]
Nickel	<5[g]	<10[g]	88.7
Potassium	o	2,730	o
Selenium	<0.008[g]	<0.008[g]	<0.008[g]
Silicon	10.4	NA[n]	20.3
Silver	5.01	<0.6[g]	2.82
Sodium	196	211	267
Thallium	63.9	31.4	33.9

(continued)

TABLE 2-4 (continued)

Parameter	5/22/90 (2 days of use)[b]	2/7/90 (midlife)[c]	5/16/90[d] (2 days before disposal)
Thorium	<5[g]	<5.3[g]	6.47
Vanadium	3.99	34.6	<3[g]
Zinc	13.4	NA[n]	101
Total contaminant metals[p], mg/L	1,335	3,180[q]	5,660

[a] Tank I-3 is the chromic-acid stripping tank for magnesium parts that will be studied during the current project. The three sets of laboratory data below were obtained from different solutions.

[b] Analyzed on a solution after 2 days of use.

[c] Analyzed on a solution after 5.5 weeks of use; solution was disposed of after 11 weeks.

[d] Analyzed on a solution 2 days prior to disposal; represents a spent solution.

[e] Analyzed in duplicate.

[f] Analyzed on two samples. Each of the total chromium values are averages of two analyses.

[g] Not detected. The value given is the detection limit for the analyte.

[h] These samples were analyzed by ion chromatography in accordance with EPA Method 300.0.

[i] The chloride test is pH sensitive and involves a titrimetric endpoint color change. Due to the highly acidic, highly colored nature of these samples, a dilution was necessary prior to analysis. Detection limits have been adjusted accordingly.

[j] The sulfate test is a pH-sensitive, spectrophotometric method. A dilution was necessary prior to analysis, which resulted in the high detection limit.

[k] Because of the acidic nature of the samples, a dilution was made prior to analysis, which results in the high detection limit.

[m] For all metals except arsenic, mercury, and selenium, a 1:100 dilution was necessary to analyze the samples due to a matrix interference. This was the smallest dilution that could be made where the interference had a minimal effect on the analyses. The detection limits have been adjusted accordingly.

[n] NA = Not analyzed. Calcium, silicon, and zinc were not analyzed on the 2/7/90 sample. This was the first sample of the three to be analyzed; at that time, a more limited list of metals was selected for testing.

[o] Potassium could not be quantified due to spectral interferences.

[p] Includes all metals other than chromium and potassium.

[q] For comparison with the other two analyses, metals that were not analyzed were assumed to be the average of the other two analyses.

As expected, some metals increased in concentration with each progressive stage of the solution quality (fresh, midlife, and spent). The concentrations of the following metals generally increased with the life of the solution: aluminum, arsenic, barium, calcium, cadmium, copper, iron, magnesium, manganese, nickel, silicon, sodium, thorium, and zinc.

2.4 Hard-Chromium Electroplating

Eight tanks in the plating shop are used to electroplate functional (hard) chromium coatings. Chromium plating involves the electrodeposition of chromium metal onto a surface. Decorative chromium plating is performed to achieve a desirable appearance, whereas hard chromium plating is designed to restore dimensions of undersized parts or to improve resistance to wear, abrasion, heat, or corrosion. Plated thicknesses of hard chromium plating usually range from 0.1 to 20 mils (1 mil = 0.001 in.); however, greater thicknesses are sometimes plated.

Tank A-9 was chosen for full-scale operation of the electrodialysis system after testing on the chromic acid stripping solution was completed. This tank has a 456-gallon capacity, contains 30 to 40 oz per gallon of chromic acid and 0.30 to 0.40 oz per gallon of sulfuric acid, and is operated at 131°F. Most of the parts processed are composed of steel.

As the tank is used, the solution becomes contaminated with tramp metals such as copper, iron, lead, nickel, and trivalent chromium. This contamination reduces the conductivity and plating efficiency of the plating solution; thus, a higher voltage is required to maintain current density. Also, some plating shops report that metal contaminants cause various defects in parts, such as differences in roughness.

At the CCAD plating shop, the metal impurities create a sludge that occasionally must be removed by pumping the entire solution through a cheesecloth filter into a temporary container and then returning the solution to the plating tank. This procedure is conducted once or twice a year when plating quality problems are noted in a given bath. Depot personnel have reported that this operation may generate a couple of drums of hazardous waste per year, but quantitative data are not available.

Appendix A contains a summary of the tracking sheets used to monitor parts processed in the chromium plating tanks during calendar year 1990. These sheets contain information on the number and kind of parts processed and the number and type of part defects for each tank. It should be noted that many of the defects recorded on these sheets do not necessarily result from the buildup of metal impurities; for example, a dull chromium coat is usually attributed to operating the plating bath at too high a temperature. The plating baths themselves do not become spent and are not generally disposed of.

The data shown in Tables 2-1 and 2-2 and other information obtained from depot personnel indicate that the hard-chromium electroplating tanks on the A-line do not generate significant quantities of hazardous waste. The major waste generated by chromium plating operations is the sludge resulting from the treatment of chromium-contaminated rinse water. Reduction of this hazardous waste stream would entail removing the chromium from the rinse water before it reaches the wastewater treatment plant by a technology such as ion exchange. An electrodialysis cell could then be used to recover the solutions used to regenerate the ion exchange resins. A cell would also be placed in the plating tank to reduce the buildup of impurities that frequently results in a closed-loop system.

Tank A-9 was chosen for full-scale study to develop data in support of a possible future closed-loop recycling system and to determine the effect of the electrodialysis unit on the solution quality. The solution was chosen before quantitative data were received on waste generation and part rejection rates. The immediate potential benefits offered by this tank are an increase in (or maintenance of) plating efficiency, prevention of sludge buildup, and a reduction of part rejects caused by metal impurities.

Also, the lower temperature (131 °F) would permit the design of an electrodialysis system for solutions that are lower than the 200 °F of the chromic acid stripping solution. Such a system would likely be less expensive than the high-temperature unit.

2.5 Chromate Conversion Coatings

Chromate conversion coatings are used for both aluminum (Alodining™) and cadmium (Iriditing™) parts. For application of a chromate conversion coating, parts are immersed in a chromic acid solution that may contain some oxidizing salts. This action creates a chemical attack that dissolves some surface metals and forms a protective film containing complex chromium compounds. Chromate conversion coatings are used to provide corrosion protection.

Table 2-1 indicates that Alodine solutions were some of the largest generators of hazardous waste in 1990. The Depot Systems Command (DESCOM) has designated CCAD as the Center of Technical Excellence (CTX) for chromate conversion coatings. As such, it is responsible for identifying and recommending methods to reduce this hazardous waste.

Tank C-3 at CCAD is an Alodine tank with a capacity of 448 gallons. The solution contains 1 oz of Alodine 1200® per gallon of solution and is operated at room temperature. Table 2-2 indicates that Tank C-3 did not generate any hazardous waste in 1987; however, other Alodine tanks at CCAD and other depots do generate significant quantities of hazardous waste. For example, a solution disposed of once a year by the Air Frames Cleaning Shop reportedly generates 1800 gallons of hazardous waste. The solution in Tank C-3 was tested on a miniature scale during this project to develop data for a potential closed-loop system and to indicate if the cell would be effective on a solution that is used and disposed of more frequently. In addition, chromate conversion coatings require a different type of electrodialysis cell, and testing was conducted on Tank C-3 to determine the capabilities of this other type of cell.

2.6 Nitric Acid Passivation

Tank E-10 is used for nitric acid passivation of stainless steel parts. Stainless steel parts are immersed in a solution of nitric acid to dissolve particles of smeared or embedded iron that may exist on the part as a result of forming, machining, tumbling, lapping, or other processing operations. This treatment restores the original corrosion-resistant surface by forming a thin, transparent, oxide film.

Tank E-10 has a 224-gallon capacity, consists of 20 to 50 percent nitric acid and 3 percent sodium dichromate, and is operated at 130°F. The tank solution is disposed of four to six times a year when the hexavalent chromium is reduced to trivalent chromium, which is indicated by a color change.

A brief qualitative demonstration was conducted on a miniature scale to determine if the cell would oxidize the trivalent chromium to hexavalent chromium. The results of this test would indicate the potential for using electrodialysis to reduce the waste from this process.

SECTION 3

TECHNOLOGY AND EQUIPMENT SELECTION

3.1 Technology Selection

This test program was conducted to evaluate equipment for recovering and purifying chromic acid solutions as a means of achieving significant waste reduction. Several technologies from different vendors were considered for decontaminating the process solutions. The following criteria were used to select a technology and the associated equipment for the test program:

1) The equipment should reduce waste generated by operations using chromic acid solutions.

2) The system should be easy to maintain and minimize interferences with depot operations.

3) The system should have the potential to be incorporated with other technologies to provide a closed-loop recycling system. This closed-loop system would recover chromium from rinse water and return it to the process solution while maintaining pure bath quality.

4) The equipment and test program should meet USATHAMA's emphasis on evaluating emerging, commercially available technologies.

5) The equipment should be flexible enough to be tested on a variety of process solutions with a reasonable potential for meeting waste reduction goals.

The purification or recovery of chromic acid solutions requires two separate mechanisms:

1) The contaminant metals (such as magnesium, iron, aluminum, and copper) must be removed from the chromic acid solution.

2) Trivalent chromium must be oxidized to hexavalent chromium. A less desirable alternative is to remove the trivalent chromium from the chromic acid solution.

Three technologies were considered for purification or recovery of chromic acid solutions at CCAD. The following are brief descriptions of these technologies:

Ion Exchange--In ion exchange, a cationic resin is used to remove the metal impurities, including trivalent chromium. Generally, however, concentrated solutions must be cooled and diluted before ion exchange so that the resins are not destroyed. The solution would then have to be concentrated for reuse. The ion exchange column must be backwashed with an acid, which generates a concentrated waste stream. The disadvantages of ion exchange are its high waste volumes that require treatment or disposal, a loss of chromium due to trivalent chromium removal as opposed to oxidation to hexavalent chromium, and the limited life span of the resin. The operating parameters of ion exchange are generally well known.

Electrolysis--In simple electrolysis, or dummying, two electrodes are placed in a chromic acid tank with a large anode-to-cathode ratio. This configuration oxidizes trivalent to hexavalent chromium, but does not remove the contaminant metals. In a similar process, a device known as a porous pot can be placed in the chromic acid tank or an adjoining tank. The porous pot is the most common device used in chromic acid purification. The porous pot contains a ceramic membrane separating the chromic acid solution (anolyte) from a catholyte. When the porous pot is activated, the trivalent chromium is reoxidized to hexavalent chromium, and the cations are electrically driven through the pores of the pot into the catholyte, where some of the cations are deposited on the cathode. The membrane is not ion-selective, and the transport of cations occurs only as a result of the electrical driving force. The porous pot is labor-intensive because it may require daily catholyte changes and any metals deposited on the cathode must be removed frequently. The unit may also generate a significant volume of chromium wastes.

Electrodialysis--As opposed to electrolysis, electrodialysis uses a cation-selective membrane to control the transport of cations from the anolyte (chromic acid solution) to the catholyte. In electrodialytic units that use an acidic catholyte, electroplatable cations are deposited on the cathode; other cations remain in solution as soluble salts. As the salt concentration increases, the voltage must also be increased to maintain the current density, and the solution must eventually be replaced. The metals deposited on the cathode must be removed frequently to prevent burnthrough of the membrane. Therefore, this is a potentially labor-intensive process that generates chromium-bearing wastes.

A newer electrodialysis process, manufactured by Ionsep Corporation, Inc., uses a caustic catholyte. In this unit, cations entering the catholyte are precipitated as metal hydroxides. Precipitation of the cations prevents a loss of conductivity and eliminates the buildup of a deposit on the cathode. The unit generates a sludge much like that generated by an industrial wastewater treatment plant and must be disposed of as a hazardous waste. The catholyte solution potentially can be filtered and reused or treated in a conventional industrial wastewater treatment plant. The unit reportedly requires minimal labor for operation.

A recent paper describes studies that were conducted with the porous pot technology and the caustic electrodialytic process.[3] The electrodialysis unit had a higher removal rate for iron and copper (the only two metals studied) and produced a much smaller volume of waste.

Because the purpose of this project is to research and develop an emerging technology that can significantly reduce waste and be easy to maintain, the caustic electrodialysis unit appeared to be the best choice for testing. Ionsep Corporation, Inc., of Wilmington, Delaware, is the only manufacturer. The equipment is covered under Patent Nos. 4,325,792; 4,439,293; 4,636,288; 4,652,351; and 4,684,453. Other patents are pending. This equipment was purchased for installation at CCAD to conduct the test program.

3.2 Description of Commercial Electrodialysis Technology

Figure 3-1 presents a schematic of the Ionsep electrodialysis cell. The cell consists of an anode immersed in an anolyte solution, a cathode immersed in a catholyte solution, and a cation-permeable membrane separating the two solutions. When voltage is applied, the positive charge created at the anode drives the cations through the membrane. The rate of ion transport can be varied by varying the cell voltage. Trivalent chromium will be oxidized to hexavalent chromium or transported across the membrane with other cations. Hexavalent chromium is not transported across the membrane because it is present in an anionic form (as chromate). Electrolysis of water occurs at the anode to produce oxygen gas and hydrogen cations;

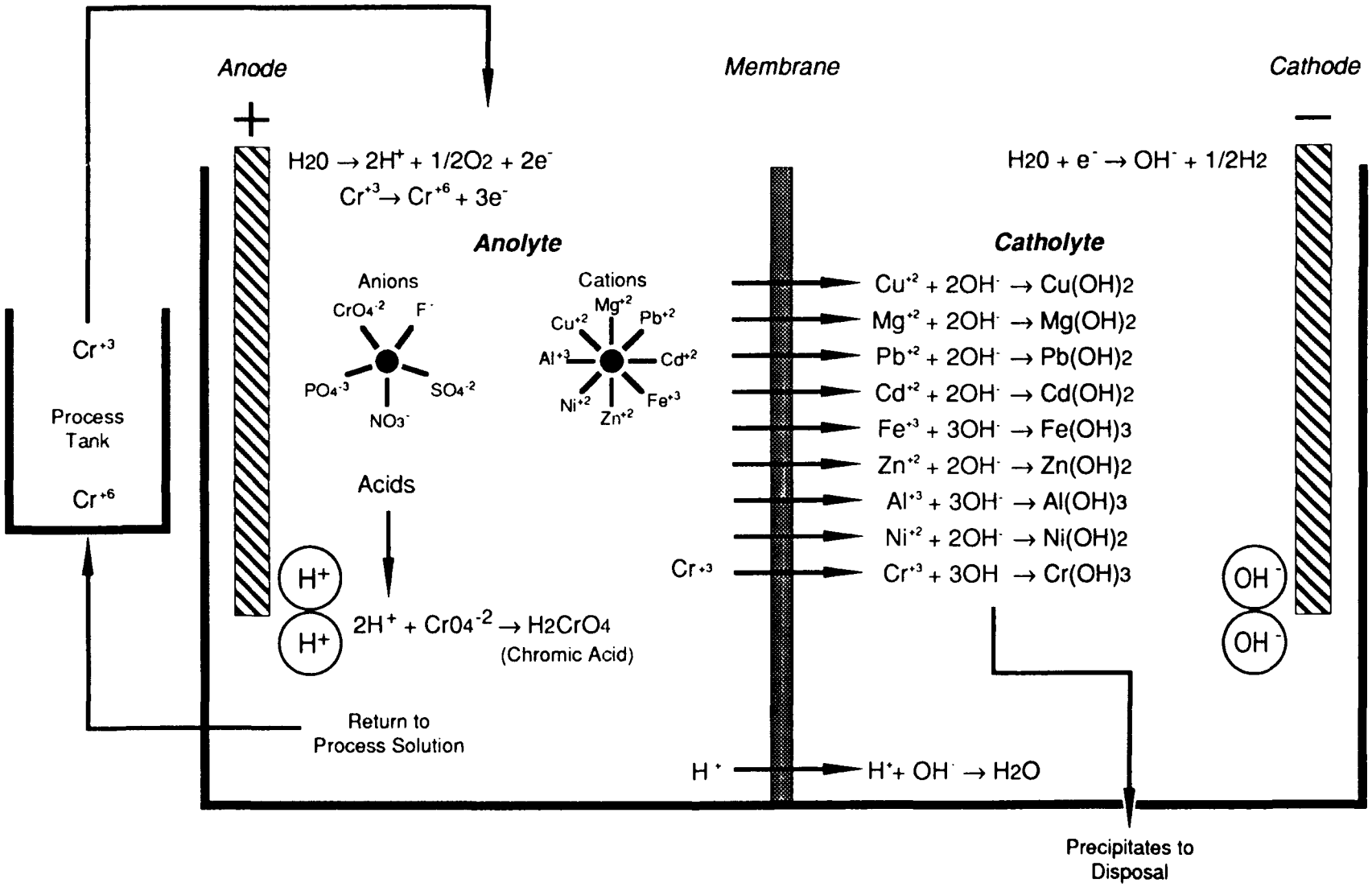


Figure 3-1. Schematic of two-compartment electrodialysis cell.

the hydrogen ions combine with chromate anions to regenerate the chromic acid (H_2CrO_4). Some hydrogen ions are also transported across the membrane. The electrolysis of the water will cause the anolyte solution to lose water during operation.

When in the catholyte, multivalent cations react with hydroxyl ions (OH^-) to form insoluble hydroxides, which precipitate. (In other electrodialysis units, the metals plate out on the cathode.) The catholyte solution contains about 10 weight percent sodium carbonate/sodium sulfate with a small amount of sodium metabisulfite to reduce the small quantity of hexavalent chromium that may cross the membrane. The hydroxyl ions are continuously formed at the cathode by the electrolysis of water, which also forms hydrogen gas. The catholyte solution will lose water from the electrolysis to hydrogen gas and hydroxyl ions, but it will gain water from the recombination of hydrogen and hydroxyl ions. Overall, the catholyte will tend to gain water.

The overall function of the electrodialysis unit is to remove the metal contaminants from the chromium acid solution while reforming chromic acid. This process should result in longer bath life, less variable chromic acid concentration, less makeup of chromic acid, and decreased generation of hazardous waste.

Chromate conversion coatings usually contain sodium as part of their formulation. In a two-compartment cell (Figure 3-1), the sodium would be transported across the membrane into the catholyte and eventually cause an increase in pH that could damage the membrane. In addition, the fluoride ion in solutions containing hydrofluoric acid could be oxidized to fluorine gas at the anode. A three-compartment cell is therefore used for solutions that contain hydrofluoric acid or significant quantities of sodium. Figure 3-2 presents a schematic for a three-compartment cell for solutions containing significant sodium concentrations. For hydrofluoric acid solutions, the solution itself would be placed in the middle (reactor) compartment.

One long-term HAZMIN goal expressed by CCAD personnel is the implementation of a closed-loop recycle system on chromium rinse water and chromic-acid process tanks. Figure 3-3 presents a diagram of a closed-loop chromium-recovery system that uses the electrodialysis technology. In this system, two ion exchange columns remove the cations and anions from the rinse water, and the clean water is

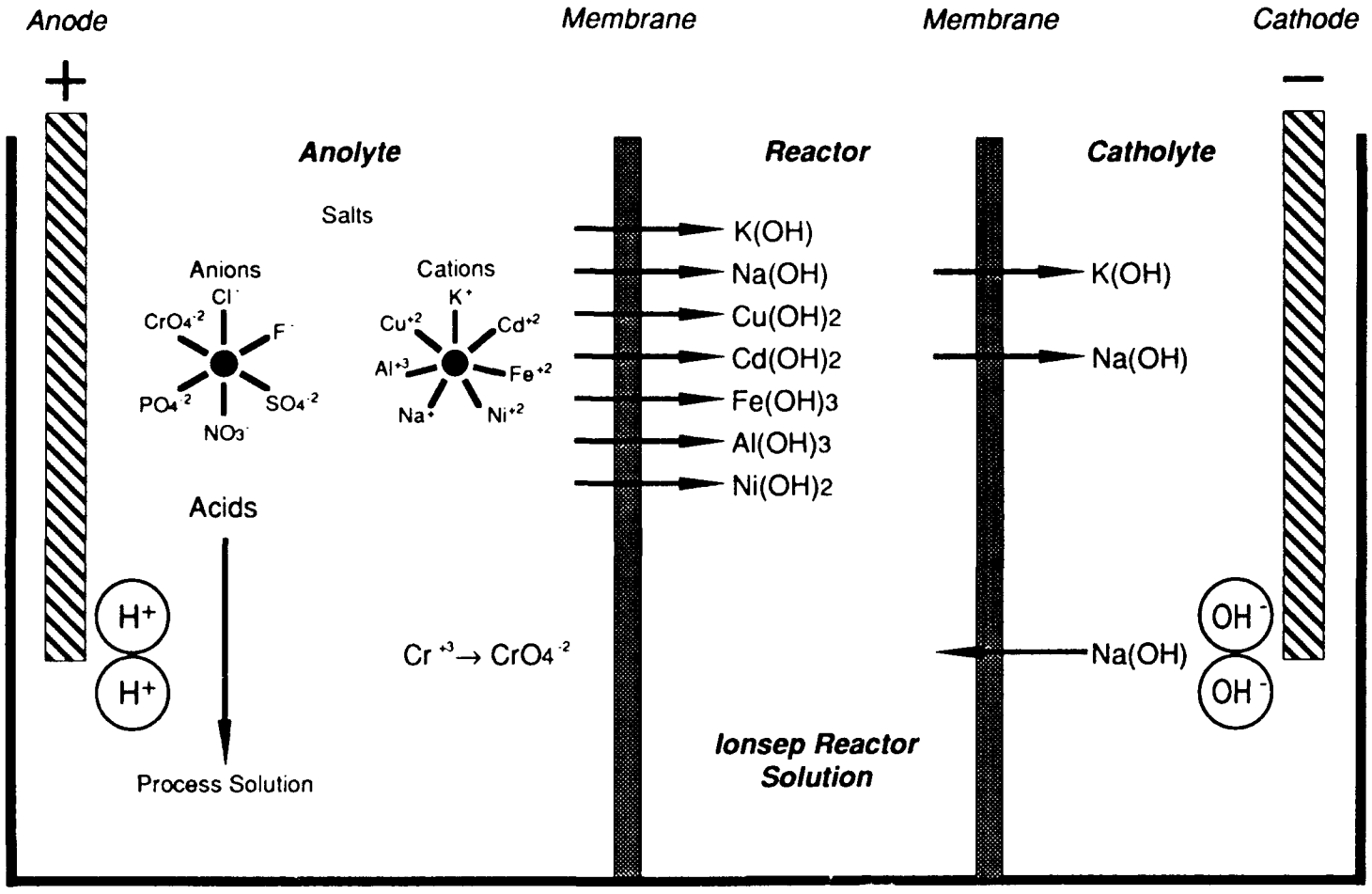


Figure 3-2. Schematic of three-compartment Ionsep electrodialysis cell.

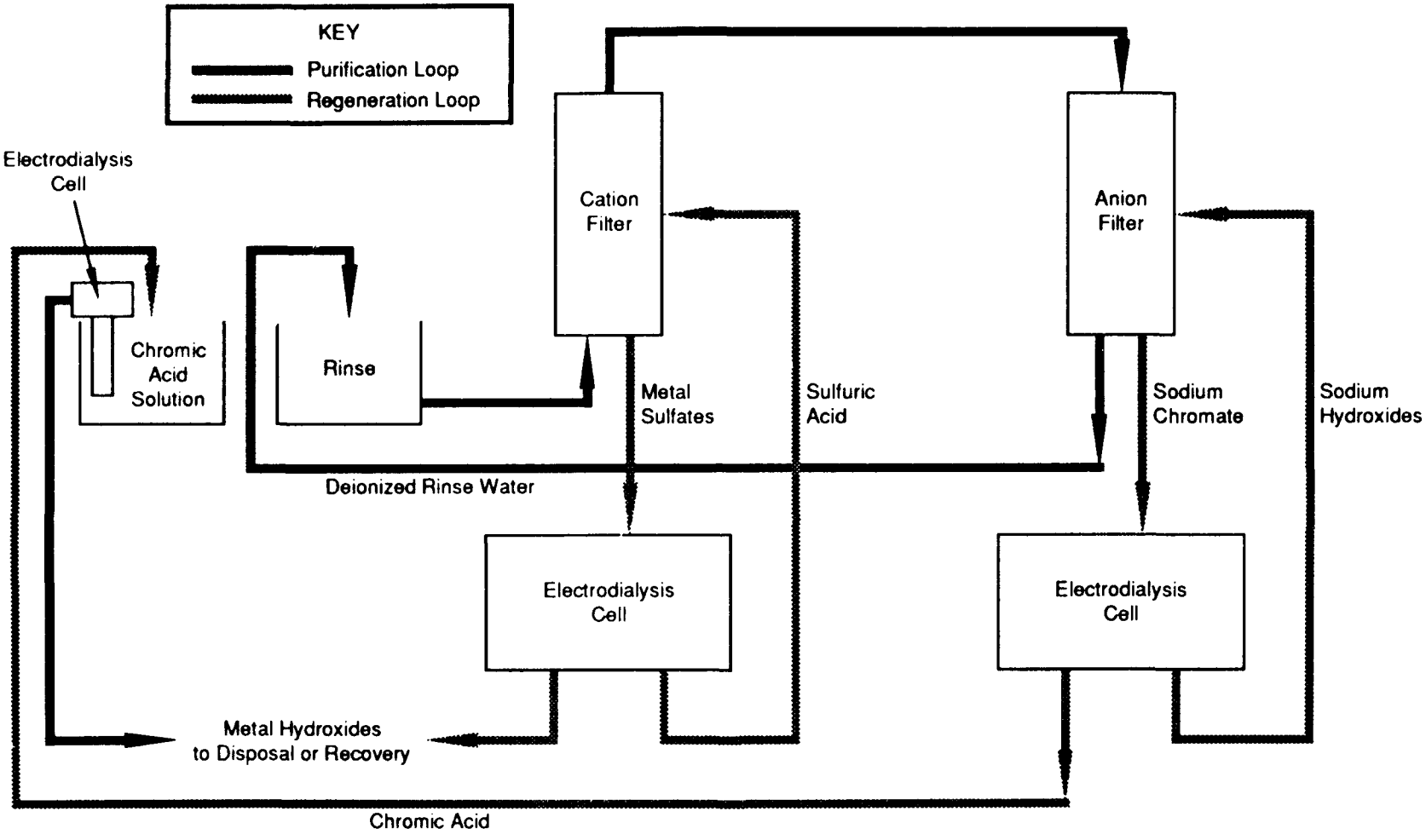


Figure 3-3. Closed-loop electrodialysis system for recovery of chromium.

then recycled to the rinse tank. The cation resin is regenerated with sodium hydroxide, and the anion resin is regenerated with sulfuric acid. The resulting regenerant solutions can be processed in different electrodialysis units that separate the salt solutions into sodium hydroxide and sulfuric acid for reuse in the regeneration process. The unit would remove metal contaminants and oxidize trivalent chromium to hexavalent chromium so the resulting chromic acid could be reused in the process tank. This system would use an additional electrodialysis cell in the plating tank itself to prevent the buildup of contaminants that frequently results from the use of closed-loop technologies.

3.3 Equipment Required for Electrodialysis

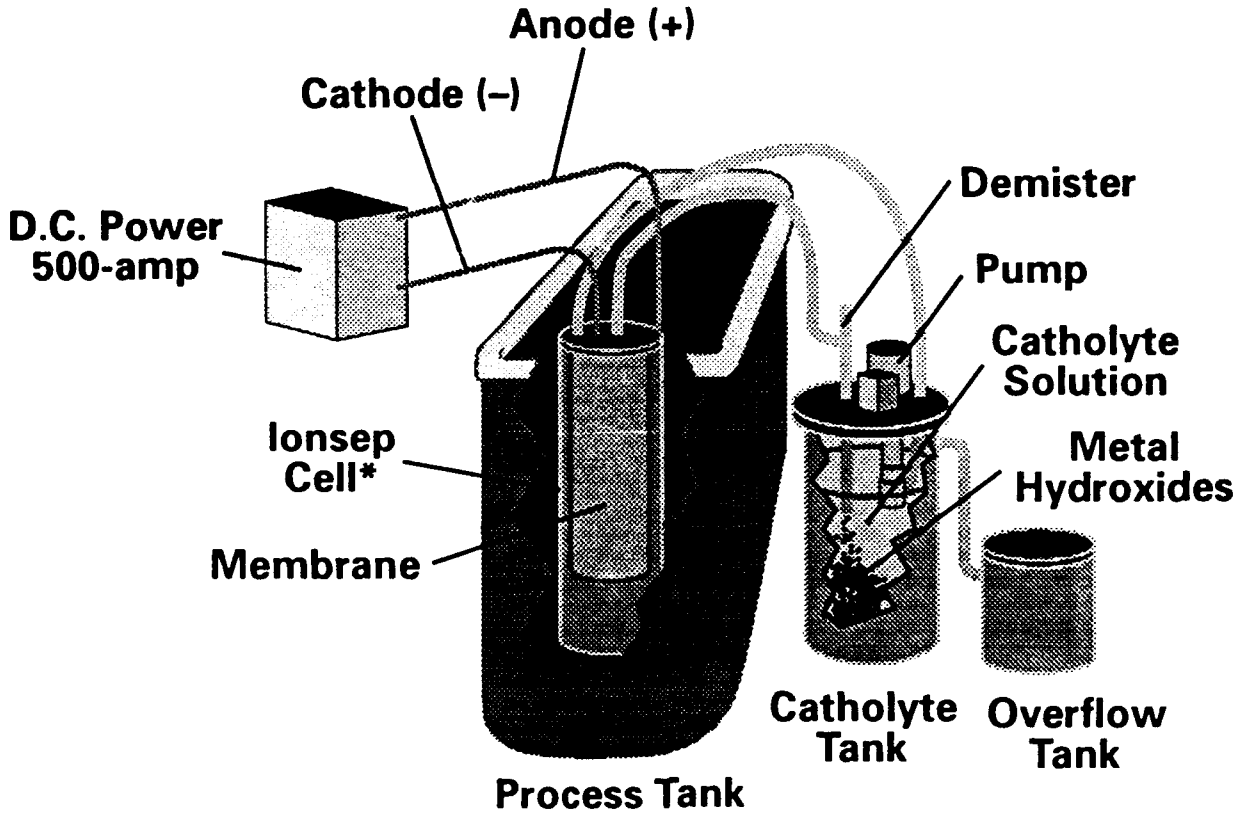
Figure 3-4 presents a diagram of the Ionsep Electrochemical Cell. This cell, which is packaged in a small cylindrical shape, is designed to be immersed directly in the process solution. The anode surrounds the membrane, and the cathode is a cylinder inside the membrane. For this project, the cell was placed in a titanium pipe for protection (this is not shown in Figure 3-4). Cations pass through the membrane and into the catholyte solution. This solution is circulated to a 55-gallon drum, where the hydroxides precipitate; the catholyte liquid is then pumped back to the interior of the cell. The high anode-to-cathode surface area provides oxidation of trivalent to hexavalent chromium. The catholyte tanks and rectifier are placed outside of the process tank. The materials of equipment for this project were specified for a concentrated chromic acid environment at high temperatures (over 200°F).

The system purchased from Ionsep consisted of the following equipment:

- Ionsep 6040 Electrochemical Two-Compartment Cell 26400 (Reference Nos. IAS-400-TCTM1-PP and ICS-630-TM1-324-N); nominal operating amperage of 400 amps; 2.5-ft^2 membrane; manufactured under U.S. Patent Nos. 4,654,137 and 4,750,525

- Titanium holder for the cell

- Rectifier, 500 amps; supply power is 460V/3PH/60HZ; 0 to 12 VDC and 0 to 500 amp output; occupies a space 28 in. high x 22 in. wide x 18 in. deep



*Ionsep Electrochemical Cell manufactured under U.S. Patent No. 4,654,137

Figure 3-4. Ionsep Electrochemical Cell.

- 55-gallon stainless steel catholyte tank 22 in. in diameter and 42 in. high. Stainless steel was necessary because one chromic acid solution used for testing was operated at a temperature in excess of 200°F

- Catholyte pump: Serfilco E 1/2 SCL pump assembly IPS-1055

- 7.5-gallon Nalgene overflow tank

- Stainless steel mist eliminator 2 in. in diameter for removing liquid droplets entrained in catholyte gases

- 5/8-in. EPDM hose, specified to withstand the chromic acid environment of more than 200°F.

SECTION 4

EXPERIMENTAL PROGRAM

4.1 Overview

The test program consisted of several activities performed with various solutions. Table 4-1 presents the matrix of activities for each of the solutions tested. The initial solution selected for testing was that in the chromium stripping tank (Tank I-3). The tank was sampled during initial visits to the depot and analyzed for potential contaminant metals. The solution was subsequently tested on a miniature, two-compartment electrodialysis cell supplied by the manufacturer. Full-scale equipment was purchased and installed on a holding tank (Tank I-20) containing a spent solution; the objective of this test phase was to rejuvenate this solution for reuse. Upon receipt of the results of this test phase, laboratory-scale testing was conducted on the etching rate of the rejuvenated solution and on what effect adding barium carbonate had on sulfate concentration and the etching rate.

After batch testing of the chromic acid stripping solution, a hard-chromium electroplating tank was selected for continuous purification. The electrodialysis unit was installed on Tank A-9, which was used to process parts while the unit was in operation. The purpose of this test phase was to evaluate the ability of the electro-dialysis equipment to purify a solution continuously while in operation. In addition, an alternate method for analyzing trivalent chromium concentrations was used when difficulties were experienced in obtaining accurate results from previous testing. Two methods of reducing hexavalent to trivalent chromium in the catholyte solution were evaluated.

TABLE 4-1. TEST MATRIX FOR ELECTRODIALYSIS EXPERIMENTAL PROGRAM

Solution	Initial characterization	Minicell testing	Full-scale testing	Etch testing and $BaCO_3$ addition	Cr^{+6} reduction	Alternate Cr^{+3} analysis
Chromic acid stripping (Tank I-3)	✓	✓ (2-compartment)	✓ (Batch-wise rejuvenation)	✓		
Chromium electroplating (Tank A-9)			✓ (Continuous purification)		✓	✓
Chromate conversion coating (Tank C-3)		✓ (3-compartment)				
Nitric acid passivation (Tank E-10)		✓ (Qualitative only)				

After the full-scale testing was completed, qualitative minicell testing was conducted on two additional solutions. A chromate conversion coating solution was tested in a three-compartment minicell to determine the applicability of this system in rejuvenating these types of solutions. In addition, a nitric acid solution used for passivation of stainless steel parts was tested on a miniature scale to determine qualitatively the ability of the cell to oxidize trivalent chromium to hexavalent chromium.

Each of these processes is discussed in more detail in the subsections that follow.

4.2 Chromic Acid Stripping Solution

The first phase of the experimental program entailed testing the ability of electrodialysis to rejuvenate a spent chromic acid stripping solution. The solution was sampled and analyzed for a lengthy list of metals (as described in Subsection 2.3.2).

4.2.1 Minicell Testing

A brief, initial test of the electrodialysis system was conducted with a small electrochemical cell supplied by the vendor. A picture of the minicell is provided in Appendix B, Figure B-1. This minicell, a small-scale version of the larger system, allowed the concepts of the electrodialysis unit to be tested in the laboratory. The two compartments are separated by a cation-permeable membrane, and each holds about 25 to 30 mL of either the solution to be rejuvenated or the catholyte. The sample used was collected during the midlife of a solution in use at the depot. A total of 106 mL of chromic acid solution and 100 mL of catholyte were tested in four runs. The runs averaged 4 hours each with the cell operating at 8 volts and an amperage of 0.3 to 0.4 (the amperage increases as metal contaminants are removed). Solutions of catholyte and chromic acid from the four runs were composited separately to give sufficient solution for analysis. The chromic acid solution and catholyte were subsequently analyzed for the following metals, which had shown significant concentrations during initial testing: aluminum, barium, cadmium, calcium, cobalt, copper, iron,

lead, magnesium, manganese, potassium, sodium, and zinc. Results of this testing are given in Subsection 5.1.1.

4.2.2 Full-Scale Testing

After the initial testing was completed, a spent chromic acid solution from Tank I-3 was pumped to a holding tank (Tank I-20), which was fitted with a hood for ventilation, and the electrodialysis unit was attached. Photographs of the equipment are shown in Appendix B, Figures B-2 and B-3. The objective of this test phase was to rejuvenate the spent solution and then return it to the operating tank for reuse. Samples of the process solution (anolyte) and the catholyte were collected periodically and analyzed for selected metals and other potential contaminants. Tables 4-2 and 4-3 present the analytical matrix for the anolyte and catholyte for the batch rejuvenation phase of the experimental program, and Table 4-4 defines the parameter categories. The solution was sampled with greater frequency near the beginning of testing because the electrochemical cell removes metals at a higher rate when the metal concentrations are highest, and therefore the concentrations change more rapidly.

In addition to sampling the process tank, the catholyte solution was sampled to determine which metals migrated into the solution and which precipitated as a sludge. The freshly made catholyte solution was sampled and analyzed for the complete parameter list. When the first catholyte solution was spent, the catholyte was sampled and filtered, and both the liquid and sludge fractions were analyzed for the critical parameters and all metals. Over the course of the test program, additional samples representative of the entire catholyte matrix were collected and analyzed.

4.2.3 Selection of Analytical Parameters

As shown in Tables 4-2, 4-3, and 4-4, the analytical list was divided into several categories of parameters based on rationale for and frequency of analysis. These categories are further described in the subsections that follow.

TABLE 4-2. ANALYTICAL MATRIX AND SAMPLING FREQUENCY FOR BATCH REJUVENATION TESTING, ANOLYTE (numbers refer to frequency of analyses)

Parameter[a]	Beginning solution	Week 1	Week 2	Week 3		Final solution	Total analyses
				Before membrane leak	After membrane leak		
Critical parameters							
Total chromium	1	4	1	1	1	1	9
Hexavalent chromium	-	4	1	1	1	1	8
Primary contaminant metals	1	4	1	1	1	1	9
Metals before and after membrane leak	1	0	0	1	1	1	4
Other metals, >1 mg/L	1	0	0	0	0	1	2
Potential problem contaminants							
Thorium	1	0	0	0	0	1	2
Chlorides	1	4	1	1	1	1	9
Sulfate	0	0	0	0	0	1	1
Visual samples	1	4	1	1	1	1	9

[a] See Table 4-4 for definitions.

TABLE 4-3. ANALYTICAL MATRIX AND SAMPLING FREQUENCY FOR BATCH REJUVENATION TESTING, CATHOLYTE (numbers refer to frequency of analyses)

Parameter[a]	Beginning	First spent catholyte		Other catholyte samples			Total analyses for catholyte		
		Liquid	Sludge	Representative samples	Liquid	Sludge	Liquid	Sludge	Representative samples
Critical parameters									
Total chromium	0	1	1	2	0	0	1	1	2
Hexavalent chromium	0	1	1	1	2	2	3	3	1
Primary contaminant metals	1	1	1	2	0	0	2	1	2
Metals before and after membrane leak	0	0	0	0	0	0	0	0	0
Other metals, > 1 mg/L	1	1	1	0	0	0	2	1	0
Potential problem contaminants									
Thorium	1	1	1	0	0	0	2	1	0
Chlorides	0	0	0	0	0	0	0	0	0
Sulfate	0	0	0	0	0	0	0	0	0
Visual samples	1	1	1	1	2	0	4	1	1

[a] See Table 4-4 for definitions.

TABLE 4-4. DEFINITIONS OF PARAMETER CATEGORIES

Parameter category	Individual analytical parameters	
	Batch rejuvenation of chromic acid stripping solution	Continuous purification of chromium electroplating solution
A. Critical parameters	Cr, Cr^{+6}, Al, Fe, Mg, Zn	Cr^{+6}, Cu, Fe, Ni, Pb
B. Primary contaminant metals (a subset of critical parameters)	Al, Fe, Mg, Zn	Cu, Fe, Ni, Pb
C. Metals analyzed before and after membrane leak[a]	Ca, Cd, Mn, Na, Ni, Pb, Tl	NA[b]
D. Other metals >1 mg/L[c]	Ag, Ba, Be, Ca, Cd, Co, Cu, K, Mn, Na, Ni, Pb, Sb, Si, Tl, V	Ag, Al, Ba, Be, Ca, Cd, Co, Mg, Mn, K, Na, Sb, Si, Tl, V, Zn
E. Potential problem[d] contaminants	Th, Cl, SO_4	NA

[a] In addition to Group B.

[b] NA = not applicable.

[c] Includes Group C.

[d] Analyzed at different frequencies.

Critical Parameters

The critical parameters were those that were essential for achieving the primary objective of this test phase--to evaluate the electrodialysis system for its ability to rejuvenate spent chromic acid solutions. The critical parameters were chosen to be total and hexavalent chromium and a group of primary contaminant metals. The primary contaminant metals were those present in the highest concentrations in the chromic acid solution and, thus, the primary contaminants that the electrodialysis system was designed to remove. These metals were selected from the initial characterization, which involved the analysis of several metals (see Subsection 2.3.2). Based on the concentrations in the initial characterization samples, four multivalent metals were chosen: aluminum, iron, magnesium, and zinc. Total chromium was also analyzed so that the trivalent chromium concentration could be determined by the difference between the hexavalent and total chromium concentrations. The four primary contaminant metals represented approximately 83 percent of the total contaminant metals (excluding potassium and trivalent chromium) determined from the three samples collected and analyzed during the initial characterization. Table 2-4 presents the concentrations used in determining these percentages. Because zinc was inadvertently not analyzed during the midlife sample, the concentration of this sample was assumed to be the average of the fresh and spent solutions for the purpose of selecting the primary contaminants.

Metals Associated With Membrane Leak

Metals other than the primary contaminants were analyzed before and after a membrane leak that occurred during the first phase of the project to provide additional data on the effect of the membrane leak on the process solution. These metals, which represented those present in the next highest concentrations after the primary contaminants in the initial characterization samples, were cadmium, calcium, lead, manganese, nickel, sodium, and thallium.

Other Metals >1 mg/L

Other metals were analyzed on the first and last samples to assess the effect of the electrodialysis system on their concentrations and to determine whether they migrated into the catholyte solution. These metals (which were defined as those metals at concentrations less than the primary contaminant metals but greater than 1 mg/L during any of the three initial sampling events and which include the metals associated with the membrane leak) were antimony, barium, beryllium, cadmium, calcium, cobalt, copper, lead, manganese, nickel, potassium, silicon, silver, sodium, thallium, and vanadium.

Potential Problem Contaminants

Thorium and chlorides were two contaminants depot personnel identified as potential problems. Thorium is a radioactive element present in some magnesium transmission parts. During the initial characterization, the thorium concentration in the spent solution approached 6.5 mg/L (because this value is so close to the detection limit of 5 mg/L, this result should be viewed as an estimate). Depot personnel indicated that a concentration of 30 mg/L would require disposal of the solution as a radioactive hazardous (i.e., mixed) waste. A high concentration of thorium in the catholyte sludge could cause a disposal problem. Personnel had identified that a potential buildup of chlorides in the chromic acid solution could etch parts. Total chlorides were thus analyzed during this first phase of testing to determine three things: 1) whether they could be problem contaminants, 2) their buildup rate, and 3) what effect the electrodialysis system has on chloride concentrations. Sulfates were analyzed on the last sample, when it was determined that they leaked into the process solution via a hole in the membrane.

Visual Samples

Samples of the chromic acid solution and catholyte were collected on a regular basis in test tubes and saved throughout the length of the project. The purpose of

these samples was to obtain a visual indication of how the color of the solution (which varies with contaminants such as trivalent chromium) varies over time.

4.2.4 Operational Monitoring of Electrodialysis Equipment

During the test program, the electrodialysis equipment was monitored to evaluate the effect of operational parameters on the metal removal rate. Figure 4-1 presents the operations log used for this task. The two important parameters of the system are voltage and amperage. The operations log also included space for noting any activity affecting the operation of the test equipment, including adjusting the voltage, changing the catholyte solution, performing equipment maintenance, or equipment shutdown.

4.2.5 Additional Laboratory Testing

During the full-scale testing, a membrane leak occurred that introduced sulfates into the chromic acid stripping solution (described in more detail in Section 5). This contamination resulted in an attack on the magnesium parts by the sulfuric acid that was formed. A laboratory test was devised to treat the solution with barium carbonate to precipitate the sulfates. This method involved using magnesium strips to test the etching rate of the solution before and after treatment with barium carbonate. A fresh batch of chromic acid solution was used as a control. An overall schematic of the experiment is shown in Figure 4-2. The experimental equipment included a reaction flask with a condenser in a heating mantle.

4.3 Hard-Chromium Electroplating

The second phase of testing involved continuous purification of a hard-chromium electroplating bath. The hard-chromium plating solution was selected after the use of the electrodialysis equipment on the chromic acid stripping solution failed to produce a solution that could be reused (as discussed in Section 5). The objective of this test phase was to remove contaminants from the plating bath and to oxidize trivalent chromium to hexavalent chromium while simultaneously processing parts. Another purpose of the test was to provide a long-term assessment of membrane

Electrodialysis Operations Log

Corpus Christi Army Depot

PEI Associates, Inc. **Page No.** ____

Recommended operating voltage 7 volts **Maximum amperage** 425 amps

Checklist: Perform the following steps at 0700, 1700, and 2400 hours.

1. Check that rectifier is on.
2. Check that catholyte is circulating through the sight glass.
3. Record the voltage and amperage on this log sheet. **Do not exceed** 425 amps or 7 volts. If the amperage is over or close to 425 amps, adjust to 400 amps. Record the voltage and amperage before and after any changes.
4. Check the liquid level in the overflow tank. Pump out this tank every day or two. When pumping out the overflow tank, reduce the voltage to 3 volts.
5. Check the liquid level in Tank I-20 and add water if necessary. The voltage should be reduced to 3 volts whenever the tank lid is opened.
6. Change the catholyte solution when the amperage has dropped below 300 amps at 7 volts, or change once per week.

Date	Time	Voltage	Amperage	Activity*

* For example, adjusted voltage, changed catholyte solution, equipment maintenance, shutdown, collection of sample.

Figure 4-1. Electrodialysis operations log.

M 37694 C 8/90 5

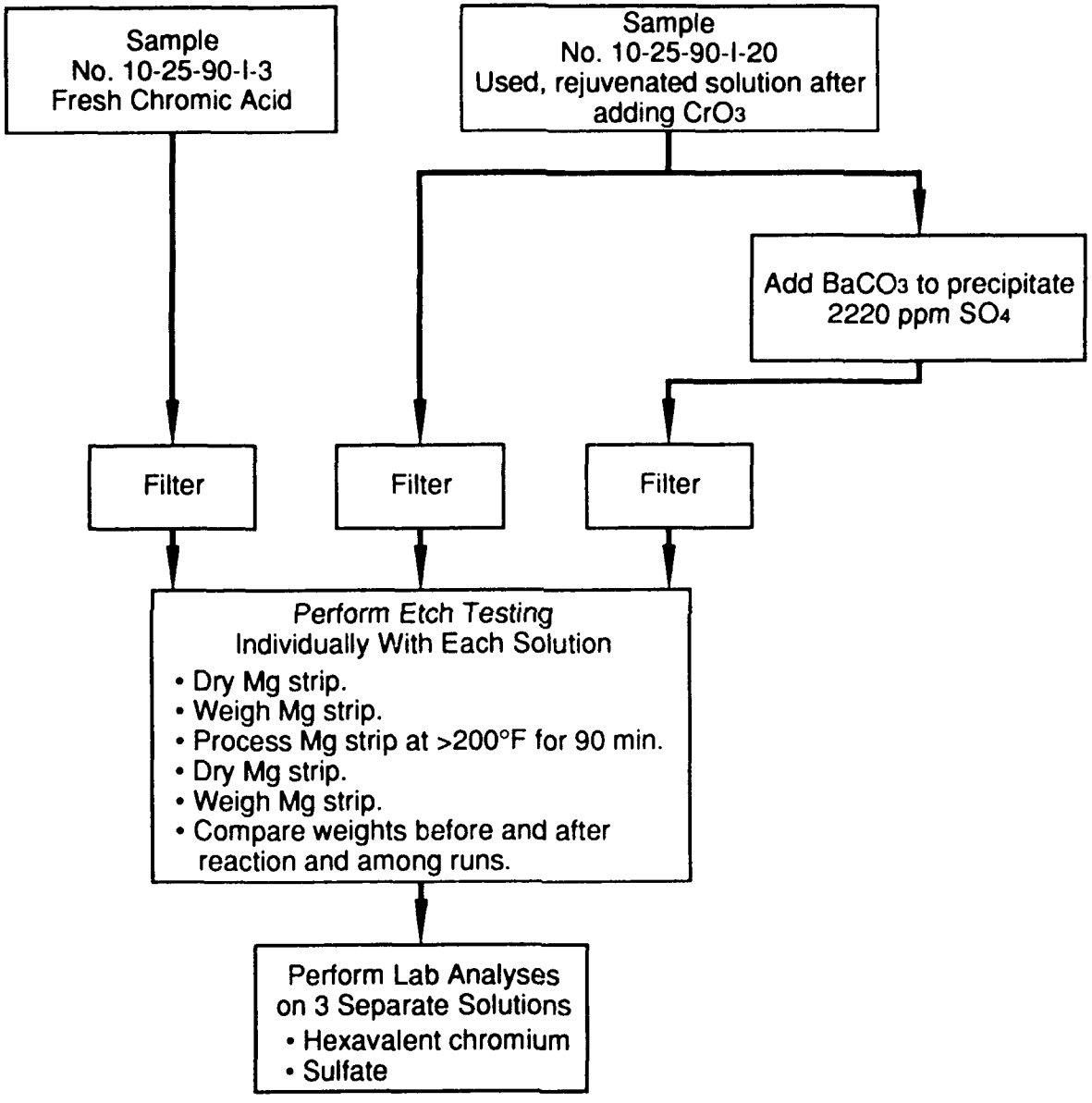


Figure 4-2. Schematic of etch testing on magnesium strips.

integrity. The advantages of this approach are that plating efficiency is maintained, sludge is removed on a continuous rather than batch basis, and plating quality may be improved.

For this phase of the test program, the electrodialysis unit was installed on Tank A-9 in the chromium electroplating area. Photographs of the installed equipment are shown in Appendix B, Figures B-4 and B-5. Samples were collected periodically and analyzed for metals. In addition to the process tank, the catholyte solution was sampled to determine which metals migrated into the solution and which precipitated as a sludge. Table 4-5 presents an analytical matrix showing when the samples were collected and the parameters for which they were analyzed. The parameter categories were defined in Table 4-4.

4.3.1 Selection of Analytical Parameters

As shown in Tables 4-4 and 4-5, the analytical list was divided into two categories of parameters based on frequency of analysis. The first and last samples were analyzed for a comprehensive list of metals to indicate which metals were removed by the sytem and which ones accumulated over the length of operation. All other samples were analyzed for a smaller list of metals chosen because they were expected to be present as contaminants in high concentrations. These included copper, iron, lead, and nickel, which are present in most chromium plating operations because of drag-in and dissolution of copper bus bars, lead anodes, and parts composed of steel and nickel alloys. The hexavalent chromium concentration was also monitored.

4.3.2 Operational Monitoring of Electrodialysis Equipment

During this test program, the electrodialysis equipment was monitored to evaluate the effect of operational parameters on the metal removal rate. The operations log used for this task, which was similar to that used for the rejuvenation of the chromic acid solution, is shown in Figure 4-3. The two important parameters of the system are voltage and amperage. The operations log also included space for

TABLE 4-5. ANALYTICAL MATRIX AND SAMPLING FREQUENCY FOR HARD CHROMIUM ELECTROPLATING (numbers refer to frequency of sampling)

	Anolyte							Catholyte	
Parameter[a]	Beginning	Week 1	Week 2	Week 4	Week 6	Final week	Total analyses	Liquid	Sludge
Critical parameters									
Hexavalent chromium	1	2	1	1	1	1	7	1	1
Primary contaminant metals	1	2	1	1	1	1	7	1	1
Other metals	1	0	1	0	0	1	3	1	1
Visual samples	1	1	1	1	1	1	6	1	1

[a] Defined in Table 4-4.

Electrodialysis Operations Log for Chromium Plating

Corpus Christi Army Depot

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Recommended operating voltage 5.5 volts **Maximum amperage** 425 amps

Checklist: Perform the following steps at 0700, 1700, and 2400 hours.

1. Check that rectifier is on.
2. Check that catholyte is circulating through the sight glass.
3. Record the voltage and amperage on this log sheet. **Do not exceed** 425 amps or 5.5 volts. If the amperage is over or close to 425 amps, adjust to 400 amps. Record the voltage and amperage before and after any changes.
4. Check the liquid level in the overflow tank. Pump out this tank every day or two. When pumping out the overflow tank, reduce the voltage to 3 volts.
5. Check the liquid level in Tank A-9 and add water if necessary.
6. Change the catholyte solution when the amperage has dropped below 300 amps at 5.5 volts, or change once per week.

Date	Time	Voltage	Amperage	Activity*

* For example, adjusted voltage, changed catholyte solution, equipment maintenance, shutdown, collection of sample.

Figure 4-3. Electrodialysis operations log for chromium plating.

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noting any activity affecting the operation of the test equipment, such as adjusting the voltage, changing the catholyte solution, performing equipment maintenance, or equipment shutdown.

In addition to parameters monitored on the electrodialysis log, CCAD laboratory personnel measured the cathode plating efficiencies of all the hard chromium plating tanks. This testing is part of the routine CCAD procedures used to monitor the quality of the plating solutions. The efficiencies were measured before the start of testing, two months after the test program was begun, and within one week of collection of the final sample.

4.3.3 Additional Laboratory Testing

During the test program, a buildup of hexavalent chromium in the catholyte solution was identified as a potential problem that could affect catholyte treatment and disposal. Two methods were tested for reduction of hexavalent to trivalent chromium, a form of chromium that is less toxic and less expensive to dispose of.

In the first method, a small amount (0.25 lb) of sodium metabisulfite was added to the catholyte solution and the cell was allowed to continue running for 4.5 hours. Sodium metabisulfite is already present in the catholyte solution (about 0.25 lb) to reduce some of the hexavalent chromium. This chemical is also frequently used in wastewater treatment plants to reduce hexavalent chromium under acidic conditions (pH of 2 to 3). The reducing potential of the cathode combined with the sodium metabisulfite reducing agent may cause hexavalent chromium reduction at a caustic pH.

In the second method, a proprietary chemical (Kolene 6-2-3) was added to the catholyte. The vendor claims that the reagent will reduce hexavalent to trivalent chromium under alkaline conditions. A dose of 1 lb per 1000 gallons of wastewater containing 1 mg/L hexvalent chromium is recommended. A total of about 10 g was added to 450 mL of catholyte containing an unknown quantity of hexavalent chromium; this amount is sufficient to treat 185 mg/L hexavalent chromium according to vendor claims.

4.4 Additional Minicell Testing

In addition to full-scale testing of the electrodialysis equipment on the chromic acid stripping bath and hard-chromium plating solution, minicell testing was conducted on two other solutions. These solutions were a chromate conversion coating for aluminum parts and a nitric acid passivation solution for stainless steel parts. The purpose of this testing was to collect data on solutions other than those addressed in the full-scale study so as to assess the potential of the equipment to recover and purify these solutions as well.

Testing the chromate conversion coating solution required a three-compartment minicell (described in Section 3). For this test, a total of 110 mL of the chromate-conversion coating was placed in the anolyte compartment, and the cell was operated at 0.2 amp for 4 hours. Samples of the solution were collected before and after processing, and a sample of the catholyte sludge was collected after processing. All samples were analyzed for the following comprehensive list of metals: aluminum, antimony, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, silicon, silver, sodium, thallium, vanadium, and zinc.

A brief, qualitative, visual test was conducted with the two-compartment minicell on the nitric acid passivation process used for stainless steel parts. A total of 25 mL of the solution was placed in the anolyte compartment, and the cell was operated at 0.2 to 0.3 amp for 24 hours. The color of the solution was compared before and after processing to determine qualitatively if the trivalent chromium was oxidized to hexavalent chromium.

4.5 Analytical Methods

The analyses conducted during this test program were selected based on results of the initial characterization and other factors (e.g., potential problem contaminants). The rationale for selecting the parameters analyzed during this program was discussed in Subsections 4.2 and 4.3, and the analytes are listed in Table 4-4. This subsection presents the specific analytical methods that were used.

Analytical methods were taken from the third edition of the U.S. EPA's "Test Methods for Evaluating Solid Waste" (SW-846) and "Methods for Chemical Analysis of Water and Wastes" (EPA-600-4-79-020). The analytical methods are summarized in Tables 4-6, 4-7, and 4-8 for the chromic acid, catholyte sludge, and catholyte liquid, respectively.

The trivalent chromium content in the chromic acid solutions was measured by two different methods. During the testing involving the chromic acid stripping solution, all samples were analyzed for total and hexavalent chromium so that trivalent chromium could be determined by the difference. For these particular process samples, however, the concentrations of total and hexavalent chromium were very high (>100,000 mg/L) and the trivalent chromium concentrations were much lower (<10,000 ppm). The analytical uncertainty of the total and hexavalent chromium concentrations was greater than the concentration of trivalent chromium. Therefore, the concentration of trivalent chromium could not be determined by the difference.

For the testing involving the chromium plating solution, an electrodialytic method developed by Ionsep was used. This method is based on the use of a tracer ion in the chromic acid solution. The ratio of the tracer ion to the chromium (III) in the chromic acid solution will be equal to the ratio of the tracer ion to chromium (III) in the catholyte solution. The method is based on using an anode that does not oxidize chromium (III) in chromic acid solutions and a membrane that is permeable to cations and impermeable to chromic acid.

The cell compartments were assembled, and the respective compartments were filled with chromic acid solution and catholyte. The chromic acid solution was placed in the anolyte compartment of the cell, and the catholyte solution was added to the catholyte compartment. Electrodes were placed in the respective cell compartments, and the electrolysis process was started and continued for about 30 minutes.

The tracer ion for this project was copper, which is a major contaminant in most chromium plating baths. Copper (II) and chromium (III) pass through the membrane to the cathode compartment, where they form metal hydroxides and precipitate in the cell.

TABLE 4-6. QUALITY ASSURANCE OBJECTIVES FOR CHROMIC ACID SOLUTIONS (mg/L)

Parameter	Instrument detection limit (IDL)	Matrix	Method	Method of additions detection limit[a]	Other detection limit[b]	Precision, RPD	Accuracy, % recovery	Completeness, %
Hexavalent chromium	0.005	Liquid	7196	0.5	2.5	<20	75-125	90
Aluminum	0.016	Liquid	3010/6010	1.6	8.0	<20	75-125	90
Antimony	0.052	Liquid	3010/6010	5.2	26.0	<20	75-125	90
Barium	0.001	Liquid	3010/6010	0.1	0.5	<20	75-125	90
Beryllium	0.001	Liquid	3010/6010	0.1	0.5	<20	75-125	90
Cadmium	0.0012	Liquid	3010/6010	0.12	0.6	<20	75-125	90
Calcium	0.001	Liquid	3010/6010	0.1	0.5	<20	75-125	90
Chromium	0.003	Liquid	3010/6010	0.3	1.5	<20	75-125	90
Cobalt	0.025	Liquid	3010/6010	2.5	12.5	<20	75-125	90
Copper	0.006	Liquid	3010/6010	0.6	3.0	<20	75-125	90
Iron	0.007	Liquid	3010/6010	0.7	3.5	<20	75-125	90
Lead	0.078	Liquid	3010/6010	7.8	39.0	<20	75-125	90
Magnesium	0.002	Liquid	3010/6010	0.2	1.0	<20	75-125	90
Manganese	0.002	Liquid	3010/6010	0.2	1.0	<20	75-125	90
Nickel	0.027	Liquid	3010/6010	2.7	13.5	<20	75-125	90
Potassium	0.55	Liquid	3010/6010	55	275.0	<20	75-125	90
Silicon	0.019	Liquid	3010/6010	1.9	9.5	<20	75-125	90
Silver	0.007	Liquid	3010/6010	0.7	3.5	<20	75-125	90
Sodium	0.030	Liquid	3010/6010	3	15.0	<20	75-125	90
Thallium	0.130	Liquid	3010/6010	13	65	<20	75-125	90
Vanadium	0.005	Liquid	3010/6010	0.5	2.5	<20	75-125	90
Zinc	0.018	Liquid	3010/6010	1.8	9.0	<20	75-125	90
Thorium	0.028	Liquid	3010/6010	2.8	14.0	<20	75-125	90
Chlorides	0.200	Liquid	300.0	NA	100	<20	75-125	90

[a] If better detection limits are required, the sample will be analyzed using a smaller dilution and the method of additions.

[b] Based on IDL and dilution required for analysis.

TABLE 4-7. QUALITY ASSURANCE OBJECTIVES FOR CATHOLYTE SLUDGE (mg/kg)

Parameter	Instrument detection limit (IDL)	Matrix	Method	Method of additions detection limit[a]	Other detection limit[b]	Preci-sion, RPD	Accuracy, % recovery	Completeness, %
Hexavalent chromium	0.005	Sludge	3060/7196	0.8	3	<20	75-125	90
Aluminum	0.016	Sludge	3050/6010	80	400	<20	75-125	90
Antimony	0.052	Sludge	3050/6010	260	1300	<20	75-125	90
Barium	0.001	Sludge	3050/6010	5	25	<20	75-125	90
Beryllium	0.001	Sludge	3050/6010	5	25	<20	75-125	90
Cadmium	0.0012	Sludge	3050/6010	6	30	<20	75-125	90
Calcium	0.001	Sludge	3050/6010	5	25	<20	75-125	90
Chromium	0.003	Sludge	3050/6010	15	75	<20	75-125	90
Cobalt	0.025	Sludge	3050/6010	130	630	<20	75-125	90
Copper	0.006	Sludge	3050/6010	30	150	<20	75-125	90
Iron	0.007	Sludge	3050/6010	36	180	<20	75-125	90
Lead	0.078	Sludge	3050/6010	40	2000	<20	75-125	90
Magnesium	0.002	Sludge	3050/6010	100	500	<20	75-125	90
Manganese	0.002	Sludge	3050/6010	100	500	<20	75-125	90
Nickel	0.027	Sludge	3050/6010	140	680	<20	75-125	90
Potassium	0.55	Sludge	3050/6010	2800	14000	<20	75-125	90
Silicon	0.019	Sludge	3050/6010	96	480	<20	75-125	90
Silver	0.007	Sludge	3050/6010	36	180	<20	75-125	90
Sodium	0.030	Sludge	3050/6010	150	750	<20	75-125	90
Thallium		Sludge	3050/6010	660	3300	<20	75-125	90
Vanadium	0.005	Sludge	3050/6010	26	130	<20	75-125	90
Zinc	0.018	Sludge	3050/6010	90	450	<20	75-125	90
Thorium	0.028	Sludge	3050/6010	140	700	<20	75-125	90

[a] If better detection limits are required, the sample will be analyzed using a smaller dilution and the method of additions.

[b] Based on IDL and dilution required for analysis.

TABLE 4-8. QUALITY ASSURANCE OBJECTIVES FOR CATHOLYTE LIQUID (mg/L)

Parameter	Instrument detection limit (IDL)	Matrix	Method	Detection[a] limit	Precision, RPD	Accuracy, % recovery	Completeness, %
Hexavalent chromium	0.005	Liquid	7196	0.005	<20	75-125	90
Aluminum	0.016	Liquid	3010/6010	0.32	<20	75-125	90
Antimony	0.052	Liquid	3010/6010	1.1	<20	75-125	90
Barium	0.001	Liquid	3010/6010	0.02	<20	75-125	90
Beryllium	0.001	Liquid	3010/6010	0.02	<20	75-125	90
Cadmium	0.0012	Liquid	3010/6010	0.03	<20	75-125	90
Calcium	0.001	Liquid	3010/6010	0.02	<20	75-125	90
Chromium	0.003	Liquid	3010/6010	0.06	<20	75-125	90
Cobalt	0.025	Liquid	3010/6010	0.50	<20	75-125	90
Copper	0.006	Liquid	3010/6010	0.12	<20	75-125	90
Iron	0.007	Liquid	3010/6010	0.14	<20	75-125	90
Lead	0.078	Liquid	3010/6010	1.6	<20	75-125	90
Magnesium	0.002	Liquid	3010/6010	0.04	<20	75-125	90
Manganese	0.002	Liquid	3010/6010	0.04	<20	75-125	90
Nickel	0.027	Liquid	3010/6010	0.54	<20	75-125	90
Potassium	0.55	Liquid	3010/6010	11	<20	75-125	90
Silicon	0.019	Liquid	3010/6010	0.38	<20	75-125	90
Silver	0.007	Liquid	3010/6010	0.14	<20	75-125	90
Sodium	0.030	Liquid	3010/6010	0.60	<20	75-125	90
Thallium	0.13	Liquid	3010/6010	2.6	<20	75-125	90
Vanadium	0.005	Liquid	3010/6010	0.10	<20	75-125	90
Zinc	0.018	Liquid	3010/6010	0.36	<20	75-125	90
Thorium	0.028	Liquid	3010/6010	0.56	<20	75-125	90
Chlorides	0.200	Liquid	300.0	10	<20	75-125	90

[a] Based on a 1:20 dilution before analysis.

After electrodialysis was completed, the catholyte was removed from the catholyte compartment and filtered. The solids were collected and analyzed for copper and chromium. The chromium measured in the solids was trivalent chromium only. Trivalent chromium is membrane-permeable because it exists as a free cation, whereas hexavalent chromium is not membrane-permeable because it exists as the chromate anion.

The ratio of tracer ion to chromium in the catholyte can be calculated from the analytical concentrations. The ratio in the catholyte is equal to the ratio in the chromic acid solution. Therefore, the concentration of chromium (III) in the chromic acid solution can be calculated if the ratio of the tracer ion to chromium in the catholyte and the concentration of tracer ion in the chromic acid solution are known. This calculation is expressed in the following equation:

$$\frac{[CuA]}{[CrA]} = \frac{[CuC]}{[CrC]}$$

where [CuA] = concentration of copper in the chromic acid solution (before electrodialysis)
[CuC] = concentration of copper in the catholyte (after electrodialysis)
[CrA] = concentration of chromium (III) in the chromic acid solution (before electrodialysis)
[CrC] = concentration of chromium (III) in the catholyte (after electrodialysis), which is equal to the concentration of total chromium

SECTION 5

RESULTS

5.1 Chromic Acid Stripping Solution

5.1.1 Minicell Testing

Table 5-1 presents the results of the minicell test conducted on the spent chromic acid samples (as described in Subsection 4.2.1). The volumes of solutions after testing were 95 mL chromic acid solution and 105 mL catholyte, which represents a decrease of 11 mL and an increase of 5 mL, respectively. Approximately 10 mL of nitric acid was required to preserve the catholyte solution for metals analysis. The sludge formed in the catholyte solution was blue, and may have been the hydroxide of trivalent chromium.

5.1.2 Full-Scale Testing

During the first phase of full-scale testing, the electrodialysis equipment was installed on a 269-gallon tank of chromic acid solution that had become spent after several weeks of use. The objective of the testing was to regenerate the solution for reuse by removing contaminant metal ions and oxidizing the trivalent chromium to hexavalent chromium. During testing, the unit was operated for 593 hours and 205,000 amp-hours over 44 days. The equipment was shut down for a total of 138 hours for normal weekend shutdowns, for changing the catholyte, for replacing a leaking membrane, and for other maintenance and repair functions not directly related to the operation of the electrodialysis unit.

After about 2 weeks of testing, CCAD personnel noticed that the membrane was leaking. Loss of several gallons of catholyte solution was the first sign of this leak, which ultimately resulted in the catholyte not being circulated through the

TABLE 5-1. ANALYTICAL RESULTS OF BENCH-SCALE EXPERIMENT WITH IONSEP MINICELL ON CHROMIC ACID STRIPPING SOLUTION (mg/L)

Metals analyzed[a]	Tank I-3[b] concentration, mg/L	Processed anolyte[c] concentration, mg/L	Processed catholyte concentration, mg/L
Chromium	123,000; 121,000[d]	138,000; 140,000,[d]	895; 961[d]
Hexavalent chromium	117,000; 122,000[d]	134,000; 136,000[d]	<0.03
Trivalent chromium	2,500	4,000	928
Aluminum	591	894	202
Barium	6.48	5.90	2.31
Cadmium	105	88.5	19.8
Calcium	115	84.8	34.1
Cobalt	16.5	<4[e]	<4[e]
Copper	2.73	3.50	2.07
Iron	150	168	18.6
Lead	93	20.3	<12[e]
Magnesium	4,000	3,340; 3,450[d]	845; 883[d]
Manganese	58	59.9	7.04
Potassium	f	f	<83[e]
Sodium	267	252	63,600[g]
Zinc	101	84.3	20.4
Total concentration of contaminant metals[h]	5,506	4,804	1,170

[a] Parameters analyzed before and after the experiment were chosen because significant concentrations were found in the samples collected during initial characterization.

[b] Concentrations present prior to operation of Ionsep cell.

[c] Chromic acid solution after processing in the Ionsep minicell.

[d] Analyzed in duplicate.

[e] Not detected. The value given is the detection limit for the analyte.

[f] Potassium could not be quantified because of spectral interferences.

[g] Sodium is a component of the Ionsep catholyte.

[h] Includes all metals listed other than chromium, potassium, and sodium. Does not include metals not detected in a given analysis.

membrane and a sharp drop in the amperage. Initially, before realizing the cause of the problem, personnel tried adding water to the solution. The hole in the membrane, however, caused additional liquid to be transported from the catholyte solution into the process solution.

The data obtained from operational monitoring of the electrodialysis equipment are presented in Appendix C. Included are the date, time, voltage, amperage, number of hours shut down, cumulative hours shut down, cumulative hours of operation, and cumulative amp-hours. Also included in the data are the sample numbers and any activity such as startup, catholyte changes, or shutdowns. The amp-hours are the primary indicators of how much work the system is performing.

Tables 5-2 through 5-6 summarize the analytical data collected on the chromic acid samples during this phase of the experimental program. The parameters have been divided into five categories based on the frequency of and rationale for analysis:

1) Primary contaminants (Table 5-2).

2) Other metals that were analyzed before and after the membrane leak (Table 5-3).

3) Noncritical metals that were analyzed only on the first and last samples (Table 5-4).

4) Chromium concentrations (Table 5-5).

5) Other potential contaminants of interest (Table 5-6).

Removal rates are also presented. These data indicate removal rates of 79.0 percent for aluminum, 76.9 percent for magnesium, 72.3 percent for zinc, and 45.6 percent for iron.

All chloride concentrations were below the detection limit of 60 mg/L. Therefore, the effect of the electrodialysis equipment on chloride concentrations could not be determined.

As described in Section 3, the contaminant metals are transported into and preciptated in a catholyte solution contained in a 55-gallon drum for this project. This

TABLE 5-2. CONCENTRATIONS OF PRIMARY METAL CONTAMINANTS IN CHROMIC ACID STRIPPING SOLUTION (mg/L)

	Sample No.										
	9-6-90-1-2	9-6-90-2-2	9-7-90-1-2	9-8-90-1-2	9-10-90-1-2	9-14-90-1-2	9-20-90-I-20	10-2-90-I-20[a]	10-22-90-I-20		
	Amp-hour									Percentage reduction by 9-20-90	Overall percentage reduction
Contaminants	0	1,900	7,100	14,300	32,300	51,300	97,000	106,000	205,000		
Aluminum	649	598	564	519	443	383	267	270	136	58.9	79.0
Iron	4,410	4,070	3,910	3,830	3,610	3,390	2,990	3,250	2,400	32.2	45.6
Magnesium	3,270	3,020	2,760	2,630	2,240	1,950	1,410	1,460	756	56.9	76.9
Zinc	<4[b]	61.3	59.6	55.5	46.2	42.0	30.2	32.0	17.0	50.7	72.3[c]
Total	8,329	7,749	7,294	7,034	6,339	5,765	4,697	5,012	3,309	43.6	60.3

[a] This was the first sample taken after the membrane leak was noticed.

[b] Not detected. The concentration shown is the detection limit for the analyte.

[c] Calculated from the 9-6-90-2-2 sample.

TABLE 5-3. CONCENTRATIONS OF NONCRITICAL METALS IN CHROMIC ACID STRIPPING SOLUTION ANALYZED BEFORE AND AFTER MEMBRANE LEAK (mg/L)

	Sample No.					
	9-6-90-I-2	9-20-90-I-20	10-2-90-I-20[a]	10-22-90-I-20		
	Amp-hour					
Contaminant	0	97,000	106,000	205,000	Percent reduction by 9-20[b]	Overall percent reduction[b]
Multivalent metals						
Cadmium	63.4	28.4	30.4	15.7	55.2	75.2
Calcium	85.7	32.2	34.0	13.2	62.4	84.6
Lead	<51	<51	<0.2	<60	-	-
Manganese	104	48.4	53.7	29.4	53.5	71.7
Nickel	<10	<10	<0.02	<10	-[c]	-
Thallium	<119	<120	NA[d]	<120	-	-
Total	253	109	118	58.3	56.9	77.0
Monovalent metals						
Sodium	179	1,790	2,840	1,530	-900	-755

[a] This was the first sample taken after the membrane leak was noticed.

[b] A negative number indicates an increase in concentration.

[c] Percent removals cannot be calculated where beginning or end concentrations are nondetectable.

[d] NA = Not analyzed

TABLE 5-4. CONCENTRATIONS OF OTHER METALS ANALYZED ON FIRST AND LAST SAMPLE OF CHROMIC ACID STRIPPING SOLUTION (mg/L)

Contaminants	Sample No. 9-6-90-I-2, Amp-hour 0	Sample No. 10-22-90-I-20, Amp-hour 205,000	Overall percent reduction[a]
Multivalent metals			
Antimony	<42[b]	<50	-[c]
Barium	10.8	2.17	79.9
Beryllium	<0.7	<0.7	-
Cobalt	14.6	31.5	-116
Copper	<3	<3	-
Silicon	50.2	66.9	-33.3
Silver	<3	<3	-
Thorium	<46	<5	-
Vanadium	<5	<5	-
Total	75.6	101	-33.6
Total noncritical, multivalent metals[d]	329	159	51.7
Monovalent metals			
Potassium	4,650	4,080	12.3

[a] A negative number indicates an increase in concentration.

[b] Not detected. The concentration shown is the detection limit for the analyte.

[c] Percent removals cannot be calculated where beginning or end concentrations are nondetectable.

[d] Includes concentrations of multivalent metals from Tables 5-3 and 5-4.

TABLE 5-5. CHROMIUM CONCENTRATIONS IN CHROMIC ACID STRIPPING SOLUTION (mg/L)

	Sample No.								
	9-6-90-1-2	9-6-90-2-2	9-7-90-1-2	9-8-90-1-2	9-10-90-1-2	9-14-90-1-2	9-20-90-I-20	10-2-90-I-20	10-22-90-I-20
	Amp-hour								
Chromium concentrations	0	1,900	7,100	14,300	32,300	51,300	97,000	106,000	205,000
Total	NA[a]	108,000	109,000	111,000	109,000	103,000	118,000	121,000	99,400
Hexavalent	NA	103,000	99,400	111,000	117,000	106,000	89,100	126,000	110,000
Trivalent[b]	NA	5,000	9,600	0	-8,000	-3,000	28,900	-5,000	-10,600

[a] NA = Not analyzed.

[b] Calculated by difference. Negative numbers indicate that the hexavalent chromium result was greater than total chromium results due to analytical uncertainty in measured concentrations.

TABLE 5-6. CONCENTRATIONS OF OTHER POTENTIAL CONTAMINANTS IN CHROMIC ACID STRIPPING SOLUTION (mg/L)

	Sample No.								
	9-6-90-1-2	9-6-90-2-2	9-7-90-1-2	9-8-90-1-2	9-10-90-1-2	9-14-90-1-2	9-20-90-I-20	10-2-90-I-20	10-22-90-I-20
	Amp-hour								
Other potential contaminants	0	1,900	7,200	14,300	32,300	51,300	97,000	106,000	205,000
Chlorides	<60[a]	<60	<60	<60	<60	<60	<60	<60	NA[a]
Sulfate	NA	NA	NA	NA	NA	NA	NA	NA	2,220

[a] NA = Not analyzed.

catholyte occasionally becomes spent and must be disposed of as waste generated by the process. During the test program, the catholyte was changed six times, and approximately 300 gallons of hazardous waste and wastewater had to be treated or disposed of. (One of these changes was as a result of the membrane leak, and probably was unnecessary.) Appendix B, Figure B-6, is a photograph of catholyte sludge samples.

Tables 5-7 through 5-10 present the catholyte sludge and liquid characteristics at various phases in the test program. The results shown are from a mixture of representative sludge and filtrate samples. The parameters have been divided into four categories based on the frequency of and rationale for analysis:

1) Primary contaminants (Table 5-7).

2) Other metals (Table 5-8).

3) Total and hexavalent chromium (Table 5-9).

4) Weight percent and moisture content of the catholyte sludge (Table 5-10).

The objective of this first phase of testing was to use the rejuvenated solution in the actual processing line and operate the electrodialysis cell to purify the solution on a continuous basis. At the end of the first phase of testing, the solution was returned to process tank I-3, heated to the operating temperature of 200°F, and used to process parts. The electrodialysis unit was also installed on Tank I-3, as shown in Appendix B, Figure B-7. After a few parts were processed, the solution was found to be etching the magnesium parts as a result of the sulfates that had been transferred into the process solution during the membrane leak. As shown in Table 5-6, the sulfate concentration of this solution was 2220 mg/L. The sulfates and chromic acid are believed to have formed a pickling solution that was chemically active on the magnesium parts.

Before the Ionsep unit could be operated on Tank I-3 with a fresh, noncontaminated solution, a very small leak was noticed in the membrane seal. Despite the

TABLE 5-7. CONCENTRATIONS OF PRIMARY METAL CONTAMINANTS IN CATHOLYTE SAMPLES FROM CHROMIC ACID STRIPPING

	Sample No.				
	9-6-90-1-2(c)	9-7-90-1-2(c)	9-8-90-1-2(c)[a]		10-4-90-I-20(c)-1
	Matrix				
	Fresh catholyte, mg/L	Representative, mg/L	Sludge, mg/kg	Filtrate, mg/L	Representative, mg/L
Amp-hours from start of test program	0	7,200	12,300	12,300	119,400
Amp-hours from start of fresh catholyte	0	7,200	12,300	12,300	13,400
Contaminants					
Aluminum	<13[b]	292	2,400	122	134
Iron	9.48	918	9,450	2.14	387
Magnesium	8.16	1,470	14,700	3.57	421
Zinc	<4	35.2	268	<0.2	<9

[a] This was the first sample of spent catholyte.

[b] Not detected. Concentration shown is the detection limit for the analyte.

TABLE 5-8. CONCENTRATIONS OF NONCRITICAL METALS IN CATHOLYTE SAMPLES FROM CHROMIC ACID STRIPPING

	Sample No.		
	9-6-90-1-2(c)	9-8-90-1-2(c)	
	Matrix		
	Fresh catholyte, mg/L	Sludge, mg/kg	Filtrate, mg/L
Amp-hours from start of test program	0	12,300	12,300
Amp-hours from start of fresh catholyte	0	12,300	12,300
Other metals analyzed before and after membrane leak			
Multivalent			
Cadmium	<1[a]	254	<0.05
Calcium	75.8	507	0.242
Manganese	0.38	406	0.074
Nickel	0.544	48.2	<0.4
Monovalent			
Sodium	32,000	26,700	27,500
Other metals			
Multivalent			
Barium	0.099	7.92	<0.02
Beryllium	<0.7	<2	<0.03
Cobalt	<10	20.9	<0.4
Silver	<3	<5	<0.1
Monovalent			
Potassium	<454	1,930	18.7

[a] Not detected. The concentration shown is the detection limit for the analyte.

TABLE 5-9. CONCENTRATIONS OF TOTAL AND HEXAVALENT CHROMIUM IN CATHOLYTE SAMPLES

	Sample No.						
	9-6-90-1-2(c)	9-7-90-1-2(c)	9-8-90-1-2(c)		10-4-90-I-20(c)	10-22-90-I-20(c)	
	Matrix						
	Fresh catholyte, mg/L	Representative, mg/L	Sludge, mg/kg	Filtrate, mg/L	Representative, mg/L	Sludge, mg/kg	Liquid, mg/L
Amp-hours from start of test program	0	7,200	12,300	12,300	119,400	203,300	203,300
Amp-hours from start of fresh catholyte	0	7,200	12,300	12,300	13,400	97,300	97,300
Chromium							
Total	NA[a]	3970	NA	NA	495	NA	NA
Hexavalent	NA	NA	250	106	37.7	360	220

[a] NA = Not analyzed.

small size of this leak, a decision was made not to operate the cell on Tank I-3 during normal operations because the leak could potentially become larger over time and allow sulfates to leak into the process solution. Because this particular use of a chromic acid bath at the high temperatures used (>200°F) is apparently sensitive to sulfates, it was decided the risk of membrane failure and resulting damage to parts was too great. The membrane was replaced and installed on a tank containing a solution that would be less sensitive to sulfate leaks.

TABLE 5-10. WEIGHT PERCENT AND MOISTURE CONTENT OF CATHOLYTE SLUDGE [Sample number 9-8-90-1-2(c)]

	Sludge	Filtrate
Amp-hours from start of test program	12,300	12,300
Amp-hours from start of fresh catholyte	12,300	12,300
Weight, %	47	53
Moisture content of sludge, %	77.8	

5.1.3 Air Measurements of Chromic Acid

The tank used for the batch rejuvenation test program (Tank I-20) was initially set up with a high ventilation rate and the option of partially closing the lid (see Appendix B, Figures B-2 and B-3). The ventilation hood is shown in Figure B-8. As with plating baths, the electrodialysis cell generates oxygen gas at the anode, which sits directly in the plating solution. The gas then rises through the chromic acid solution and entrains droplets of chromic acid. During the experiment, the surface of the solution appeared to be disturbed by the gas bubbles. Chromic acid mist was also noted to be rising from the tank.

Testing was conducted with smoke tubes and Draeger tubes. When the lid was left open, the smoke indicated that eddies were formed around the cell, which would sometimes waft up and drift toward the breathing space. When the lid was placed on the tank, the smoke tubes indicated negative pressure all around the tank; the surface of the tank appeared to be agitated by the high rate of flow. With the lid closed, the

ventilation rate was so high that the chromic acid mist leaving the solution near the cell received sufficient momentum to travel the length of the tank (parallel to the vents) and hit a board placed at the opposite end. As a result of the high evolution rate of the chromic acid mist, the hood became coated with a layer of chromic acid within a few hours.

One of the vents was closed to reduce the ventilation rate when the tank lid was closed (Appendix B, Figure B-9). When smoke testing was repeated, the ventilation appeared to be adequate as long as the lid remained closed. When the lid was opened, however, smoke began rising from the tank and leaving the surface toward the breathing space. Draeger tube readings around the cell ranged from 2.5 to 5 mg/m^3; the NIOSH-recommended ceiling is 0.1 mg/m^3. It was recommended that the lid be kept closed. When it was necessary to open the lid, respirators were worn or the cell voltage was reduced to 3 V to prevent the generation of oxygen gas. The Draeger tube readings were nondetectable when the lid was closed (detection limit is 0.1 mg/m^3).

Plastic discs were added to the top of the solution to reduce the misting problem (Appendix B, Figure B-10). No mist was observed near the surface, and the chromic acid mist on the hood was markedly reduced. The Draeger tube readings ranged from 0.1 to 0.3 mg/m^3. Although this represented a marked reduction of chromic acid concentrations and would result in less chromic acid loss to the ventilation system, the concentrations were still above the 0.1 mg/m^3 ceiling. The lid was left closed for the duration of the experiment.

5.1.4 Additional Laboratory Testing

Table 5-11 presents the results of testing to determine how the addition of barium carbonate ($BaCO_3$) to a chromic acid solution contaminated by sulfates affected the sulfate concentration and etching rate. A magnesium strip lost 79.0 percent of its weight when heated at boiling for 90 minutes in the chromic acid solution contaminated with sulfates. After treatment with an excess of barium carbonate, another magnesium strip lost only 2.71 percent of its weight compared with a

TABLE 5-11. RESULTS OF ETCHING RATE TESTING

Sample No.	Description of sample	Sulfate concentration, mg/L	Hexavalent chromium concentration, mg/L	Weight of magnesium strip before $BaCO_3$ addition, grams	Weight of magnesium strip after addition, grams	Weight lost to etching, %
10-25-90-I-3	New chromic acid solution (control)	750	140,000	0.6873	0.6774	1.44
10-25-90-I-20	Spent chromic acid solution after treatment by electrodialysis	3,000[a]	120,000	0.6809	0.1429	79.0
10-25-90-I-20-Post	Sample 10-25-90-I-20 after treatment with $BaCO_3$	970	130,000	0.7164	0.6970	2.71

[a] This sample is from the same solution as sample number 10-22-90-I-20 in Table 5-6. This result is a reanalysis.

1.44 percent weight loss when immersed in the fresh chromic acid solution used as a control. The concentration of sulfate was reduced from 3,000 mg/L in the contaminated solution to 970 mg/L in the sample treated with barium carbonate (compared with 750 mg/L sulfate in the fresh chromic acid solution.)

5.1.5 Additional Data

Additional data were collected on Tank I-3 during an initial test phase. The purpose of these data was to compare the buildup of contaminants in an untreated process solution with that in a solution fitted with the electrodialysis unit. The data included the results of detailed parts monitoring and sample analysis. Because the electrodialysis unit was not installed in Tank I-3 while the solution was being used to process parts, the data could not be used to compare the contaminant buildup rate before and after the electrodialysis unit was installed. For additional characterization of the Tank I-3 process solution, the analytical data are presented in Table 5-12. The parts-processing information is not included in this report, but it is available from ITEP if needed for future projects.

TABLE 5-12. SUPPLEMENTAL DATA FOR TANK I-3

	Date				
	9/20/90[a]	9/4/90	9/5/90	9/7/90	9/12/90
Sample No.	9-20-90-I-3	9-4-90-1-1	9-5-90-1-1	9-7-90-1-1	9-12-90-1-1
Time collected	1400	1430	1630	1600	1600
pH, S.U.	0.17	0.07	0.37	0.25	0.25
Aluminum, mg/L	<13	37	57	84	143
Iron, mg/L	63	782	973	1,390	2,170
Magnesium, mg/L	4.56	210	278	416	608
Zinc, mg/L	<4	7.39	10.2	11.8	20.1
Total metals, mg/L	68	1,036	1,318	1,902	2,941
Chromium, mg/L	145,000	121,000	119,000	125,000	119,000
$Chromium^{+6}$, mg/L	122,000	127,500	115,000	125,000	107,000

[a] Fresh solution.

5.2 Hard-Chromium Electroplating

During the second phase of full-scale testing, the electrodialysis equipment was installed on a 456-gallon-capacity hard chromium plating tank, as described in Subsection 4.3. Data obtained from operational monitoring of the electrodialysis system are shown in Appendix D. During testing, the equipment was operated for a total of 1031 hours and 331,000 amp-hours by the time the last sample was collected. The equipment was shut down for 1129 hours for normal weekend shutdowns, for catholyte changes, and for other functions not directly related to the operation of the electrodialysis unit.

Tables 5-13 and 5-14 summarize the analytical data for the contaminant metals in the chromium plating tank. Table 5-13 presents the concentrations of primary metal contaminants (copper, iron, lead, and nickel), and Table 5-14 presents the concentrations of noncritical metals. These data indicate overall removal rates of 73 percent for copper, 62 percent for iron, and 59 percent for nickel. The concentration of lead increased from less than 0.2 mg/L to 18 mg/L. An average reduction of 56 percent was achieved for all other multivalent metals that were analyzed.

As described in Subsection 4.5, an alternate method using a nonoxidizing electrolytical ninicell was implemented during this phase of the test program to analyze for trivalent chromium in chromic acid solutions. Table 5-15 presents the analytical data used to calculate the trivalent concentrations in the chromium plating solution. After 260,000 amp-hours (approximately 79 percent of the total test program), the concentration of trivalent chromium was reduced from 2120 mg/L to 364 mg/L, or 83 percent. As a result of time constraints, the last sample collected was not analyzed for trivalent chromium.

5.2.1 Plating Efficiencies and Part Rejects

The cathode plating efficiencies measured by the CCAD laboratory during the test program are presented in Table 5-16. The efficiencies are given in percentages. For comparison, data are provided for the tank on which the electrodialysis unit was installed (Tank A-9) as well as for other tanks in the plating shop.

TABLE 5-13. CONCENTRATIONS OF PRIMARY METAL CONTAMINANTS IN CHROMIUM PLATING SOLUTION (mg/L)

	Sample No.							
	1-22-91-A-9	1-24-91-A-9	1-31-91-A-9	2-14-91-A-9	3-8-91-A-9	4-22-91-A-9		
	Amp-hour							
Contaminants	0	13,800	60,800	156,000	260,000	331,000	% Reduction by 2/14/91	Overall percent reduction
Copper	145	144	136	101	47	39	30.3	73
Iron	475	466	456	393	200	180	17.3	62
Lead	<0.2[a]	<0.2	<0.2	<0.2	5.6	18	--	--
Nickel	13.7	16.3	14.3	12.4	7.2	5.6	9.5	59
Total	634	626	606	506	260	243	20.2	62

[a] Not detected. The concentration shown is the detection limit for the analyte.

TABLE 5-14. CONCENTRATIONS OF NONCRITICAL METAL CONTAMINANTS IN CHROMIUM PLATING SOLUTION (mg/L)

Contaminants	Sample No. 1-22-91-A-9 Amp-hour 0	Sample No. 3-8-91-A-9 Amp-hour 260,000	Sample No. 4-22-91-A-9 Amp-hour 331,000	Overall percent reduction[a]
Multivalent				
Aluminum	34.2	10	7.5	78
Antimony	<0.09[b]	2.0	2.4	c
Barium	0.593	0.3	0.25	58
Beryllium	<0.001	<0.05	<0.05	c
Cadmium	5.51	2.6	2.0	64
Calcium	36	7.1	4.6	87
Cobalt	28.7	20	20	30
Magnesium	8.56	1.5	0.94	89
Manganese	3.61	1.5	1.2	67
Silicon	16.7	<2	<2	>88[d]
Silver	<0.005	<0.3	<0.3	c
Thallium	<0.3	12[e]	22[e]	e
Vanadium	<0.008	1.4	1.4	e
Zinc	14.7	4.2	3.5	76
Total Multivalent	149	62.6	65.8	56
Monovalent				
Potassium	7000	6200	6500	7.1
Sodium	185	220	280	-51

[a] A negative number indicates an increase in concentration.

[b] Not detected. The concentration shown is the detection limit for the analyte.

[c] Percent reductions are not calculated when the beginning concentrations are nondetectable.

[d] Calculated using a maximum final concentration of 2 mg/L (the detection limit).

[e] Detection limit = 12 mg/L

TABLE 5-15. TRIVALENT CHROMIUM CONCENTRATIONS IN CHROMIUM PLATING SOLUTION

	Sample No.					
	1-22-91-A-9	1-24-91-A-9	1-31-91-A-9	2-14-91-A-9	3-8-91-A-9	4-22-91-A-9
	Amp-hour					
Chromium concentrations	0	13,800	60,800	156,000	260,000	331,000
Total chromium in solution	135,000	137,000	144,000	148,000	120,000	130,000
Copper in solution	145	144	136	101	47	39
Copper in minicell catholyte sludge	1,190	1,150	NA[a]	NA	730	NA
Chromium in minicell[b] catholyte sludge	17,400	13,400	NA	NA	5660	NA
Trivalent chromium in[c] solution	2120	1678	-	-	364	-

[a] NA = Not analyzed.

[b] Note that total chromium concentration = trivalent chromium concentration in sludge.

[c] Calculated: concentrations of Cr^{+3} in solution = conc. total Cr in minicell catholyte sludge x conc. copper in solution ÷ conc. copper in minicell catholyte sludge.

TABLE 5-16. CATHODE PLATING EFFICIENCIES FOR CHROMIUM ELECTROPLATING TANK

	Cathode efficiency, %			
Tank number	1/14/91	1/18/91	3/13/91	4/4/91
A-1	14	--	Down[a]	Down
A-3	12	--	15	18
A-4A	16	--	Down	21
A-6	--	10	24	24
A-9[b]	--	14	22	22
A-10	--	14	20	20
A-12	--	18	17	21

[a] Tank was not operational during time of testing.

[b] The electrodialysis cell was installed in Tank A-9 on January 22, 1991.

Appendix A presents CCAD logs that record the number of parts run per tank for each month. Also presented is the number of defects per tank by type of defect. Table 5-17 summarizes the number of parts processed in Tank A-9 from July 1990 to April 1991. Also included is the number of rejects and the percent reject rate. The electrodialysis unit was installed on Tank A-9 on January 22, 1991.

TABLE 5-17. PART REJECT RATE FOR CHROMIUM PLATING SHOP

Month	% of days A-9 was in operation	Number of parts plated in A-9	Number of rejects for A-9	Percent rejection for A-9	Total parts run in plating shop	Total rejects for plating shop	Percent reject rate for plating shop
July 1990	63	141	6	4.3	745	26	3.5
August 1990	46	112	11	9.8	530	45	8.5
Sept. 1990	73	129	0	0	533	24	4.5
Oct. 1990	NA[a]	NA	NA	NA	NA	NA	NA
Nov. 1990	45	43	1	2.3	430	23	5.3
Dec. 1990	19	33	0	0	463	41	8.9
Jan. 1991	45	44	0	0	805	23	2.9
Feb 1991	66	112	1	0.0089	856	15	1.8
March 1991	46	53	0	0	502	24	4.8
April 1991	56	55	1	1.8	504	12	2.4

[a] NA = not available.

5.2.2 *Catholyte Generation*

During the chromium plating test program, the catholyte was changed two to three times; these changes generated 100 to 150 gallons of hazardous waste and wastewater. The generation of sludge was generally much lower than that during the operation on the chromic acid stripping solution, and each catholyte solution lasted a month or more. (Records may not have been accurately kept on the catholyte changes, and these data are estimated.)

Table 5-18 presents the concentrations of contaminants metals in the catholyte sludge and liquid. When these samples were collected, only a small amount of sludge had been formed. The results show up to 158,000 mg/kg of chromium in the sludge.

TABLE 5-18. CONCENTRATIONS OF CONTAMINANT METALS IN CATHOLYTE FOR CHROMIUM ELECTROPLATING

	Sample No.	
	1-25-91-C2[a]	1-25-91-C2[a]
	Matrix	
	Liquid, mg/L	Sludge, mg/kg
Primary contaminants		
Hexavalent chromium	35[b]	270[a]
Chromium	53.4	158,000
Copper	<0.006[c]	14,500
Iron	<0.02	11,800
Lead	<0.2	<20
Nickel	<0.02	2,050
Noncritical contaminants		
Aluminum	23.2	<6
Antimony	<0.09	<17
Barium	<0.001	80.9
Beryllium	<0.001	<0.3
Cadmium	<0.002	611
Calcium	0.463	5,740
Cobalt	<0.02	<4
Magnesium	<0.002	962
Manganese	<0.002	373
Potassium	<1	<200
Silicon	<0.04	497
Silver	<0.005	<0.1
Sodium	25,300	48,900
Thallium	<0.3	<50
Vanadium	<0.008	<2
Zinc	<0.008	1,640

[a] After treatment with sodium metabisulfite for hexavalent chromium reduction.

[b] Before treatment with sodium metabisulfite (Sample No. 1-25-91-C1). One sample measured 810 mg/L hexavalent chromium.

[c] Not detected. The concentration shown is the detection limit for the analyte.

Table 5-19 presents hexavalent chromium concentrations in catholyte samples collected at different times during the chromium plating test program. These data indicate that hexavalent chromium tends to build up in the catholyte over time. As described in Subsection 4.3.3, two methods were tried to reduce the hexavalent to trivalent chromium. Doubling the sodium metabisulfite concentration resulted in an 87 percent reduction of hexavalent chromium, from 35 to 4.5 mg/L.

TABLE 5-19. HEXAVALENT CHROMIUM CONCENTRATIONS IN CATHOLYTE SOLUTIONS FROM PLATING TEST PROGRAM

Sample number	Sample description	Hexavalent chromium concentration, mg/L	Percent reduction after treatment[a]
1-23-91-C	Liquid fraction, after 3400 amp-hrs	5.3	-
1-25-91-C	Liquid fraction, after 22,200 amp-hrs	35	-
1-25-91-C2	Liquid fraction, after adding 0.25 lb sodium metabisulfite and spinning cell for 4.5 hours	4.5	87
1-25-91-C2	Sludge fraction	270	-
4-22-91-C1	Liquid fraction	810	-
4-22-91-C2	Liquid fraction, after treatment with alkl-aine proprietary alka-line reducing agent	320	60

[a] Doses were not optimized.

When the alkaline reducing agent was added to a catholyte sample, a green sludge was quickly formed. When the sludge settled with time, the liquid fraction of the catholyte remained yellow, which indicated that insufficient reagent was added for complete chemical reduction. Nevertheless, addition of the chemical at the dosage selected resulted in a 60 percent reduction in hexavalent chromium concentration, from 810 to 320 mg/L.

5.3 Additional Minicell Testing

During the operation of the three-compartment minicell on the chromate conversion coating (described in Subsection 4.4), very little gasing occured at the electrodes and very little sludge was formed. The cell was operated for 4 hours at only 0.2 amp even though the cell was operated at 12 volts (by comparison, the two-compartment cell operated at 0.3 to 0.4 amp at 8 volts).

Table 5-20 presents the data collected for this experiment. Metal concentrations did not decrease significantly when the analytical margin of error was taken into account. Most of the metal concentrations in the catholyte analyzed after processing could have resulted from the catholyte powder or water used to make the solutions. The process did not generate sufficient sludge for analysis, and the catholyte concentrations shown are for a representative sample.

A nitric acid passivation solution was also qualitatively tested in a two-compartment minicell (as described in Section 4.4). After 24 hours of operation, no color change was observed in the solution.

5.4 Quality Assurance/Quality Control Results

The results of the analytical quality assurance/quality control procedures are presented in Tables 5-21 through 5-25. Table 5-21 presents the QA results for standard reference solutions. All results fell within the range of acceptable data.

The detection levels achieved for selected samples are shown in Table 5-22. Many of the metals analyzed during testing of the chromic acid stripping solution (Samples 10-22-90-I-20 and 9-8-90-1-2(c), filtrate) did not achieve the target detection levels (Tables 4-6 through 4-8). However, the achieved detection levels were close to the target levels and did not affect data quality. All other samples listed in Table 5-22 achieved the target detection levels.

Tables 5-23, 5-24, and 5-25 respectively present matrix spike and matrix spike duplicate data for the chromic acid stripping test phase, chromium plating test phase, and for hexavalent chromium during the chromic acid stripping test phase. Most data

TABLE 5-20. ANALYTICAL DATA FOR THREE-COMPARTMENT MINICELL TEST ON CHROMATE CONVERSION COATING TANK C-3

Metal	Chromate conversion coating before processing in minicell, mg/L	Chromate conversion coating after processing in minicell, mg/L	Catholyte after processing in minicell, mg/L
Aluminum	84.1	86.6	<0.3
Antimony	<50	<50	<0.8
Barium	<0.4	<0.4	<0.007
Beryllium	<0.7	<0.7	<0.02
Cadmium	7.83	7.1	<0.02
Calcium	16.9	34.1	7.5
Chromium	3,400	3,460	0.098
Cobalt	<10	<10	<0.2
Copper	<3	<3	<0.06
Iron	583	578	<0.2
Lead	<60	<60	<1
Magnesium	14.8	15.9	14.9
Manganese	0.9	1.05	<0.02
Nickel	<10	<10	<0.2
Potassium	456	525	97.0
Silicon	269	319	4.46
Silver	<3	<3	<0.05
Sodium	1,530	1,480	22,000
Thallium	<2	<2	<3
Vanadium	<5	<5	<0.08
Zinc	8.6	6.25	<0.08

TABLE 5-21. QUALITY ASSURANCE RESULTS FOR STANDARD REFERENCE SOLUTIONS

Analyte	Theoretical value, mg/L	Percent Recovery	
		Sample No. 10-22-90-I-20	Sample No. 3-8-91-A-9 and 4-22-91-A-9
Aluminum	1	100	105, 99.3
Antimony	2	98.9, 94.5	97.7, 99.2
Barium	1	103, 101	106, 106
Beryllium	1	94.1, 97.2	91.8, 93.0
Cadmium	1	92.7, 90.9	97.1, 94.7
Calcium	1	102	106, 103
Chromium	1	94.8, 94.4	99.4, 95.6
Cobalt	1	95.7	95.9, 98.2
Copper	1	92.4, 88.0	95.9, 94.3
Iron	1	101	89.1, 89.6
Lead	2	101, 98.8	98.5, 98.1
Magnesium	1	103	101, 100
Manganese	1	105	105, 105
Nickel	1	94.1, 96.8	96.0, 98.1
Potassium	25	94.3	95.7, 97.5
Silicon	1	90.3	--
Silver	1	81.8	105, 102
Sodium	2	96.0	101, 100
Sulfate	4	98.2, 93.2, 93.5, 98.2	--
Thallium	2	91.7	84.0, 95.0
Thorium	4	102	-
Vanadium	1	97.7, 102	95.6, 95.0
Zinc	1	94.8, 100	92.2, 91.6

TABLE 5-22. DETECTION LEVELS ACHIEVED FOR SELECTED SAMPLES

	Sample No.						
	10-22-90-I-20	1-22-91-A-9	3-8-91-A-9	9-8-90-1-2(c)	9-8-90-1-2(c)	1-25-91-C2	1-25-91-C2
	Matrix						
Analyte	Chromic acid solution, mg/L	Plating solution,[a] mg/L	Plating solution, mg/L	Catholyte filtrate, mg/L	Catholyte sludge, mg/kg	Catholyte filtrate, mg/L	Catholyte sludge, mg/kg
Aluminum	20	0.03	2	0.6	26	0.03	6
Antimony	50	0.09	0.2	2	83	0.09	17
Barium	0.4	0.001	0.05	0.02	0.7	0.001	0.2
Beryllium	0.7	0.001	0.05	0.03	2	0.001	0.3
Cadmium	2	0.002	0.1	0.05	3	0.002	0.5
Calcium	0.6	0.001	0.05	0.02	2	0.001	0.3
Chromium	0.006	0.006	0.3	--[b]	--	0.006	2
Cobalt	10	0.02	1	0.4	19	0.02	4
Copper	3	0.006	0.3	0.2	6	0.006	2
Iron	6	0.02	0.6	0.3	12	0.02	3
Lead	60	0.2	6	3	102	0.2	20
Magnesium	0.8	0.002	0.1	0.04	2	0.002	0.4
Manganese	0.8	0.002	0.1	0.03	2	0.002	0.3
Nickel	10	0.02	1	0.4	19	0.02	4
Potassium	500	1	50	19	908	1	200
Silicon	2	0.04	2	0.7	33	0.04	7
Silver	3	0.005	0.3	0.1	5	0.005	0.1
Sodium	20	0.04	2	0.7	34	0.04	7
Thallium	120	0.3	12	5	239	0.3	50
Thorium	5	---	---	2	92	--	---

(continued)

TABLE 5-22 (continued)

	Sample No.						
	10-22-90-I-20	1-22-91-A-9	3-8-91-A-9	9-8-90-1-2(c)	9-8-90-1-2(c)	1-25-91-C2	1-25-91-C2
	Matrix						
Analyte	Chromic acid solution, mg/L	Plating solution,[a] mg/L	Plating solution, mg/L	Catholyte filtrate, mg/L	Catholyte sludge, mg/kg	Catholyte filtrate, mg/L	Catholyte sludge, mg/kg
Vanadium	5	0.008	0.04	0.2	9	0.008	2
Zinc	5	0.008	0.4	0.2	9	0.008	2

[a] Analyzed with the 1-25-91-C2 filtrate sample.

[b] Not analyzed.

TABLE 5-23. MATRIX SPIKE/DUPLICATE RECOVERY DATA FOR CHROMIC ACID STRIPPING TEST PHASE

	Sample No. 10-2-90-I-20						
Analyte	Amount added, g	Sample[a] amount, g	Matrix spike (MS) concentration, mg/L	Percent[b] recovery	Matrix Spike Duplicate (MSD) concentration, mg/L	Percent recovery	Relative percent difference[c] (RPD)
Aluminum	25	27.0	47.6	83	48.8	87	3
Cadmium	25	3.04	28.2	101	27.3	97	3
Calcium	25	3.39	27.0	94	26.0	90	4
Iron	25	325	349	93	359	133	3
Lead	50	ND	49.2	98	45.7	91	7
Magnesium	25	146	172	105	173	110	1
Nickel	25	ND	22.3	89	22.6	91	2
Sodium	50	284	348	127	335	102	4
Thorium	50	ND	46.1	92	42.4	85	1
Zinc	25	3.20	26.0	91	26.5	93	2

[a] A 1:10 dilution was prepared, spiked, and digested for analysis.

[b] Percent recovery = (Conc MS (or MSD) - Sample Amt)/Amt Added) x 100

[c] RPD = ((Conc MS - Conc MSD)/(Conc MS + Conc MSD)/2)) x 100

TABLE 5-24. MATRIX SPIKE/DUPLICATE RECOVERY DATA FOR CHROMIUM PLATING TEST PHASE

	Sample No. 1-22-91-A-9						
Analyte	Amount added, g	Sample[a] amount, g	Matrix spike (MS) concentration, mg/L	Percent[b] recovery	Matrix spike duplicate (MSD) concentration, mg/L	Percent recovery	Relative percent difference (RPD)[c]
Chromium IV	10	5.43	15.3	99	15.5	101	1
Aluminum	25	3.42	23.9	82	24.1	83	1
Antimony	50	ND	41.5	83	42.0	84	1
Barium	10	0.06	8.74	87	8.89	88	2
Beryllium	10	ND	8.31	83	8.20	82	1
Cadmium	25	0.55	23.2	91	23.6	92	2
Calcium	25	3.60	23.3	79	23.5	80	1
Cobalt	25	2.87	21.2	73	20.7	72	2
Copper	25	14.5	34.8	81	35.4	84	2
Iron	25	47.5	67.1	78	67.9	81	1
Lead	50	ND	46.2	92	44.8	90	3
Magnesium	25	0.86	22.1	85	21.7	83	2
Manganese	10	0.36	8.52	82	8.52	82	0
Nickel	25	1.37	22.6	85	22.7	85	0
Potassium	50	699	663	d	695	d	5
Silicon	10	1.67	9.74	81	11.9	102	20
Silver	10	ND	7.26	73	6.31	63	14
Sodium	50	18.5	70.6	104	71.2	105	1
Thallium	50	ND	39.7	79	41.8	84	5
Vanadium	25	ND	20.6	83	20.2	81	2
Zinc	28	1.47	23.4	88	23.2	87	1

[a] A 1:10 dilution was prepared, spiked, and digested for analysis.

[b] Percent recovery = (Conc. MS (or MSD) - Sample Amt)/Amt added) x 100

[c] RPD = [(Conc. MS - Conc. MSD)]/(Conc. MS + Conc. MSD)/2)) x 100

[d] Inappropriate spike level.

TABLE 5-25. POST DILUTION MATRIX SPIKE/DUPLICATE RECOVERY DATA FOR HEXAVALENT CHROMIUM DURING CHROMIC ACID STRIPPING PHASE

Client Sample ID	Amount added, g	Sample[a] amount, g	Matrix spike (MS) concentration, mg/L	Percent[b] recovery	Matrix spike duplicate (MSD) concentration, mg/L	Percent recovery	Relative percent difference (RPD)[c]
9-4-90-1-1	10	6.27	15.7	94.7	15.8	95.8	0.7
9-6-90-2-2	10	10.3	20.1	97.8	20.0	97.3	0.3
9-10-90-1-2	10	5.87	15.8	99.8	15.8	99.3	0.3
9-12-90-1-1	10	5.37	16.7	113	16.6	112	0.3
9-14-90-1-2	10	5.25	15.1	98.6	15.2	99.1	0.3

[a] A 1:10 dilution was prepared, spiked, and digested for analysis.

[b] Percent recovery = (Conc. MS (or MSD) - Sample Amt)/Amt added) x 100

[c] RPD = [(Conc. MS - Conc. MSD)]/(Conc. MS + Conc. MSD)/2)) x 100

were in the target percent recovery range of 75 to 125 percent and achieved the target precision of <20 percent. The only exceptions for the accuracy were iron on Sample No. 10-2-90-I-20, and cobalt and silver on Sample No. 1-22-91-A-9. Also, precision for silicon was slightly over the target value of <20 percent.

SECTION 6

EVALUATION OF RESULTS

This section presents an evaluation of results with regard to meeting the objectives stated in Section 1 of this report.

6.1 Chromic Acid Stripping Solution

6.1.1 Minicell Testing

Table 6-1 presents the results of mass balance calculations based on the analytical data provided in Table 5-1 for minicell testing. For determination of a mass balance on the system before and after operation, the volume changes that occurred during the experiment were taken into account. Because of the electrolysis of water, the anolyte solution decreased in volume from 106 mL to 95 mL during processing. The volume of the catholyte solution increased from 100 mL to 106 mL. In addition, approximately 10 mL of nitric acid was added for preservation of the sample.

The mass balance calculations include the amount of metals (in milligrams) in the starting anolyte, processed anolyte, and the final catholyte solution (the starting amount in the fresh catholyte was assumed to be negligible). The total amount of metals in the catholyte and anolyte after processing should be equal to the amount in the starting anolyte.

The table shows the percentage of metals removed from the anolyte solution, which was calculated based on the starting and final concentrations in the anolyte. It also shows the percentage of metals migration into the catholyte, which was calculated based on the starting anolyte concentrations and the ending catholyte

TABLE 6-1. MASS BALANCE CALCULATIONS FOR THE IONSEP MINICELL EXPERIMENT ON CHROMIC ACID STRIPPING SOLUTION

Parameter	Amount in starting anolyte, mg[a]	Amount in processed anolyte, mg[b]	Amount in ending catholyte solution, mg[c]	Total amount of metals in catholyte and anolyte after processing, mg	Metal removal from anolyte, %[d]	Migration into catholyte, %[e]
Chromium	12,932	13,205	107	13,312	-2.1	0.8
Hexavalent chromium	12,667	12,825	0	12,825	-1.2	0.0
Trivalent chromium	265	380	107	487	-43.4	40.3
Aluminum	62.6	84.9	23.2	108	-35.6	37.1
Barium	0.687	0.561	0.266	0.827	18.3	38.7
Cadmium	11.1	8.41	2.28	10.7	24.2	20.5
Calcium	12.2	8.06	3.92	12.0	33.9	32.1
Cobalt	1.75	<0.38[g]	<0.16	<0.54	NA[h]	NA
Copper	0.289	0.333	0.238	0.571	-15.2	82.4
Iron	15.9	16.0	2.14	18.1	-0.63	13.5
Lead	9.86	1.93	<1.38	<3.31	80.4	NA
Magnesium	424	323	99.4	422	23.8	23.4
Manganese	6.15	5.69	0.810	6.50	7.5	13.2
Potassium	i	i	i	i	NA	NA
Sodium	28.3	23.9	7,314	7,338	15.5	NA
Zinc	10.7	8.01	2.35	10.4	25.1	21.9
Total contaminant metals[k]	555	456	135	589	17.8	24.3

[a] Amount in starting anolyte = concentration (see Table 5-1, column 2) x volume (0.106 L).

[b] Amount in processed anolyte = concentration (Table 5-1, column 3) x volume (0.095 L). The original volume of 106 mL decreased to 95 mL during the experiment.

[c] Amount in ending catholyte solution = concentration (Table 5-1, column 4) x volume 0.115 L). The original volume of 100 mL increased to 105 mL during the experiment; 10 mL of concentrated nitric acid was used for preservation of the sample.

(continued)

TABLE 6-1 (Continued)

[d] Metal removal from anolyte = (column 2 - column 3)/column 2 x 100%. Negative values indicate an increase in concentration (i.e., analytical uncertainty).

[e] Migration into catholyte = column 4/column 2 x 100%.

[f] Calculated by the difference between total and hexavalent chromium.

[g] Not detected. The value given is the detection limit for the analyte.

[h] NA = not applicable.

[i] Potassium could not be quantitated due to spectral interferences.

[j] Sodium is a component of the ionsep catholyte.

[k] Includes all metals listed other than chromium, potassium, and sodium. Does not include metals not detected in a given analysis.

concentrations. These two values should be similar in quantity because the metals removed from the anolyte should migrate to the catholyte.

These results indicate that between 18 and 24 percent of the contaminant metals were removed from the anolyte and transported to the catholyte during the experiment. The maximum removal or migration rates for the major contaminant metals were 37.1 percent for aluminum, 24.2 percent for cadmium, 33.9 percent for calcium, 13.5 percent for iron, 80.4 percent for lead, 23.8 percent for magnesium, and 25.1 percent for zinc. A significant amount of trivalent chromium (comparable to magnesium) was transported across the membrane and precipitated as a hydroxide rather than being oxidized to hexavalent chromium. The vendor noted that the trivalent chromium is transported across the membrane because of the dead space between the anode and the membrane. The larger membrane on a full-scale system should be more efficient in oxidizing the chromium because of the agitation around the membrane. The results also indicate that hexavalent chromium did not migrate into the catholyte.

A comparison of the amount of metals in the starting anolyte with the total amount of metals in the catholyte and anolyte after processing indicates that a mass balance was achieved on all metals except aluminum, cobalt, copper, and lead. These are also the metals that contain the greatest discrepancies between the metal removal from the anolyte and the migration into the catholyte. Based on the amounts in the starting anolyte, 106 percent of the metals were accounted for after processing in the minicell.

The minicell experiment demonstrated that metal removal from the chromic acid stripping solution was feasible, and that hexavalent chromium was not transported across the membrane. Based on these results, a full-scale system was purchased for installation.

6.1.2 Full-Scale Testing

Figure 6-1 is a graph of the primary contaminant metal concentrations in the chromic acid solution during operation of the electrodialysis cell. The multivalent

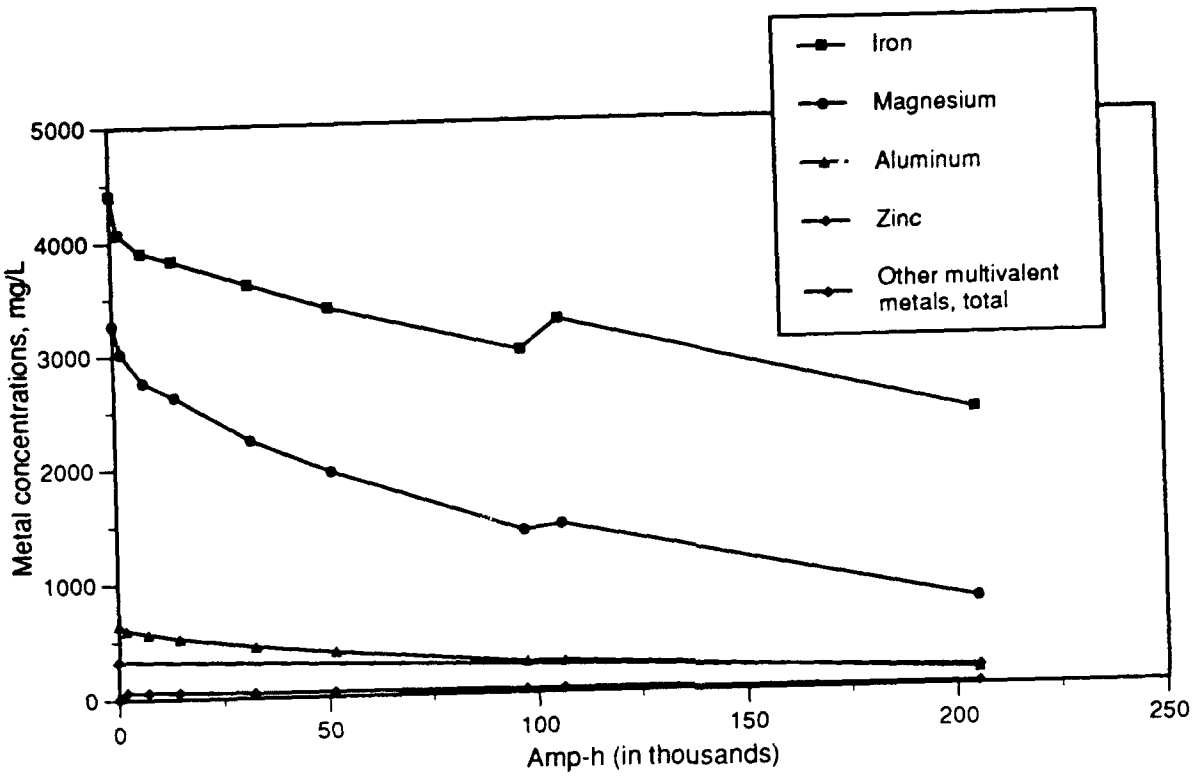

Figure 6-1. Concentration data for major metal contaminants in chromic acid stripping solution.

metals that were not primary contaminants are shown as a total. These data were taken from Tables 5-2 through 5-4. As expected, the concentration of metals decreased with increasing amp-hours, which indicates that the metals were transported across the membrane into the catholyte solution. Over the period of testing (205,000 amp-hours), 60.3 percent of the major metal contaminants were removed, and 51.7 percent of the other detectable multivalent metals were removed. The removal rates for the four primary contaminant metals were 79.0 percent for aluminum, 45.6 percent for iron, 76.9 percent for magnesium, and 72.3 percent for zinc. The only metals that did not show an increase in percentage removal were those that were lower in concentrations and closer to their individual detection levels, which may have caused higher analytical uncertainties. The concentration of sodium also increased as a result of the membrane hole and the leak of catholyte into the process solution. Both the data and graph show that the efficiency of the electrodialysis process decreases with decreasing metal concentration: 72 percent of the metals removed during testing were removed during the first 47 percent of amp-hours.

In addition to metal contaminant removal, the other criterion for evaluating the success of the electrodialysis unit was oxidation of the trivalent chromium to hexavalent chromium. All samples were analyzed for total and hexavalent chromium, and trivalent chromium was determined by the difference. Table 5-5 showed the concentrations of total and hexavalent chromium, along with the calculated trivalent chromium concentration. For these particular process samples, the concentrations of total and hexavalent chromium were very high (>100,000 mg/L), whereas the trivalent chromium concentration was much lower (<10,000 mg/L). Therefore, the analytical uncertainties of the total and hexavalent chromium concentrations were greater than the trivalent chromium concentration. Table 5-5 showed that the analytical result for hexavalent chromium was sometimes greater than the total chromium result, which is physically impossible. Thus, the concentration of trivalent chromium could not be determined by the difference.

Despite the fact that the trivalent chromium could not be quantified, visual evidence indicated a reduction in trivalent chromium concentrations. A fresh solution of

chromic acid is typically bright red, and the solution turns black over time as the trivalent chromium concentration increases. During the test program, the beginning spent solution was black; by the end of testing, the solution was the bright red color of a fresh solution, which indicates that significant amounts of trivalent chromium may have been oxidized to hexavalent chromium or transported across the membrane. This is indicated in Figure B-11 in Appendix B, which shows the appearance of a solution turn from bright red to black as it becomes contaminated (first five test tubes on left), then from black to bright red again as the solution was rejuvenated (four test tubes on right).

When the "rejuvenated" chromic acid stripping solution was returned to Tank I-3 for reuse, it was used to process parts and appeared to be effective in removing old chromate conversion coatings. It was eventually determined, however, that sulfates introduced into the process solution from the catholyte as a result of a membrane leak were attacking the magnesium parts. Data from a vendor catalog suggested that the chromic acid solution with this added amount of sulfates formed a good pickling solution, which resulted in the chemical attack on parts. This type of attack is more likely in a solution such as this because of the high temperatures involved (>200°F). Although another major membrane leak was not likely to occur, the sensitivity of this particular solution to sulfates was too great to risk part damage. This initial attempt at rejuvenating the chromic acid stripping solution was therefore not successful.

The metal concentrations listed in Tables 5-2 and 5-3 reflect the consequences of this membrane leak. All metals increased slightly in concentration between a sample taken just before the leak was noticed (Sample No. 9-20-90-I-20) and a sample taken after the equipment was shut down and before a new membrane was installed (Sample No. 10-2-90-I-20). Apparently, some of the metals that had been electrotransported into the catholyte leaked back into the process solution. [This can also be seen in Figure 6-1, which shows an increase in metal concentrations (mainly iron) between 97,000 and 106,000 amp-hours.] In particular, the concentration of sodium increased dramatically, from 179 to 2,840 mg/L from the start of the test program until after the membrane leak was noticed. The catholyte is composed primarily of sodium

sulfate and sodium carbonate. It is noteworthy that the sodium concentration increased by a factor of 10 before the leak was noticed (Table 5-3). This confirms one depot engineer's observation of a red slug of chromic acid passing through a catholyte site glass when the equipment was first turned on and indicates that the membrane hole probably occurred during the assembly, transport, or installation of the equipment. Apparently, the hole became larger over time through abrasion caused by the catholyte and sludge circulating over the membrane's surface.

In addition to sodium, the membrane leak would have added carbonates and sulfates to the process solution. The carbonates would react with the chromic acid and form carbon dioxide gas; however, the sulfates would remain in the process solution. Table 5-6 indicates that approximately 2,220 mg/L of sulfates were in the last sample and a later reanalysis showed 3,000 mg/L (Table 5-11); the CCAD lab reported a similar amount. The initial characterization of the chromic acid solution indicated 1,760 mg/L of sulfates in a relatively fresh solution; however, analyses on other solutions indicated less than 1,000 mg/L. The original analysis is now suspected to have been erroneous.

After the membrane leak was repaired, the equipment continued to run for a number of amp-hours approximately equal to the number before the leak was noticed. The last sample for the first phase of testing was then taken and analyzed.

Although the chromic acid stripping solution could not be rejuvenated by the electrodialysis unit without further treatment, the testing of the etching rate and barium carbonate addition showed that the solution could be rendered reusable by the addition of barium carbonate. Table 5-11 indicates that the addition of barium carbonate to the sulfate-contaminated solution reduced the weight loss due to etching from 79.0 to 2.71 percent compared with a weight loss of 1.44 percent for a fresh chromic acid solution. The addition of barium carbonate also decreased the sulfate concentration from 3,000 mg/L to 970 mg/L compared with 750 mg/L for a fresh chromic acid solution. These data are shown graphically in Figures 6-2 and 6-3. Thus, a theoretical mode of operation is as follows: install the electrodialysis unit on the chromic acid

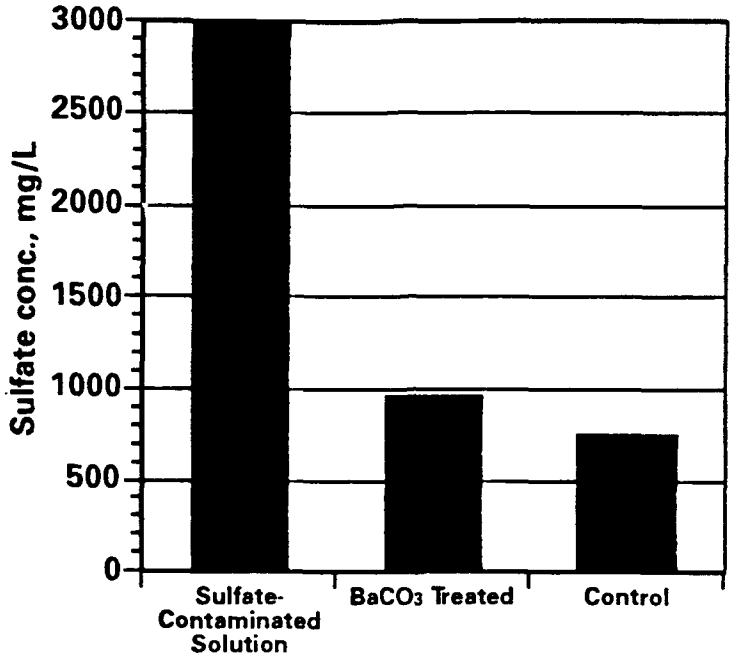

Figure 6-2. Sulfate concentrations of contaminated and treated chromic acid stripping samples.

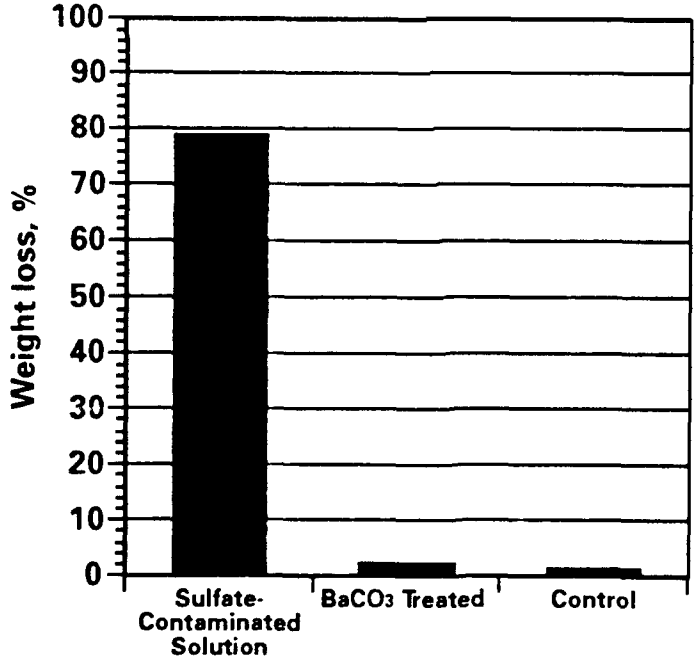

Figure 6-3. Weight loss of a magnesium strip in contaminated and treated chromic acid stripping samples.

stripping solution being used to process parts, monitor sulfates and parts quality frequently (at least daily, and possibly with every batch of parts), and then add barium carbonate when necessary. The following is a more practical method: batch-treat a spent solution of chromic acid in the holding tank, analyze for sulfates, add the required amount of barium carbonate for sulfate precipitation, and then pump the rejuvenated solution back to the operating tank through a filter to remove the barium sulfate sludge.

Three potential solutions to the membrane leak are: 1) Improve membrane integrity, 2) Change the system configuration, and 3) Change catholyte composition. Ionsep has attributed the two membrane failures to poor quality control by their former suppliers of the Nafion™ membrane and formation of the membrane tube. The membranes are now purchased directly from the manufacturer (DuPont), and Ionsep makes all tubes. Ionsep continues to work with membrane suppliers to find a membrane with no diffusion of anions from the catholyte to the process solution or hexavalent chromium from the process solution to the catholyte.

Changing the system configuration would entail reversing the cathode and anode (and the catholyte and anolyte) so that the catholyte (rather than the anolyte) is pumped through the center of the cell. Thus, if any leak occurred, the pump pressure would cause the process solution to leak into the catholyte rather than vice versa.

Finally, the vendor has indicated that they have developed a new catholyte solution that contains carbonate ions in place of the sulfate ions. In the event of a leak, the carbonate ion would form carbon dioxide gas. Using this catholyte would allow continuous in-line rejuvenation of Tank I-3. A test could be conducted with the modified catholyte to verify the vendor's claim.

As shown by the Draeger tube concentrations of airborne chromic acid (Section 5.1.3), proper ventilation must be taken into account when an electrodialysis system is installed on a tank that is not designed for large amounts of chromic acid mist. The Draeger tube concentrations measured in the first phase of the experimental program were up to 50 times those of the NIOSH-recommended ceiling. The addition of plastic disks helped reduce the concentrations significantly, and a tank lid was installed to

increase the linear flow rate across the surface of the tank. Installing a mist eliminator directly on the electrodialysis unit may prove useful on these types of tanks. This would ensure against the escape of excess chromic acid mist from the tank environment. A mist eliminator would also prevent the loss of chromic acid through the ventilation; chromic acid lost in this manner ultimately winds up in the IWTP, where it must be treated, resulting in the generation of hazardous sludge.

6.2 Hard-Chromium Electroplating

Figure 6-4 is a graph of the primary metal contaminants in the chromium plating solution (excluding lead), and Figure 6-5 is the same graph but includes the concentrations of trivalent chromium. The metals that were not primary contaminants are shown as a total. Lead is not shown because concentrations were below the detection level (0.2 mg/L) in four out of six samples. Over the period of testing (331,000 amp-hours), an average of 62 percent of the primary contaminant metals were removed (73 percent for copper, 62 percent for iron, and 59 percent for nickel). The trivalent chromium concentration was reduced by 83 percent after the first 260,000 amp-hours. A total of 56 percent of the noncritical metals were removed. The concentration of lead increased from a nondetectable concentration to 18 mg/L. The concentration of sodium increased by 51 percent, from 185 to 280 mg/L. The metal removal rate was slower at the beginning of testing, with only 33 percent of the reduction in primary metal contaminants occurring in the first 47 percent of the amp-hours.

The metal-removal data indicate that the electrodialysis unit was successful in achieving a significant reduction of metal concentrations, including trivalent chromium, even though some parts were being processed in the tank during the test period. Over the period of testing, the appearance of the solution changed from the black color of a contaminated solution to the bright red color of a fresh solution, as shown in Figure B-12 in Appendix B.

On the basis of the data collected, the percentage reduction in trivalent chromium concentrations that occurred because of oxidation rather than transport

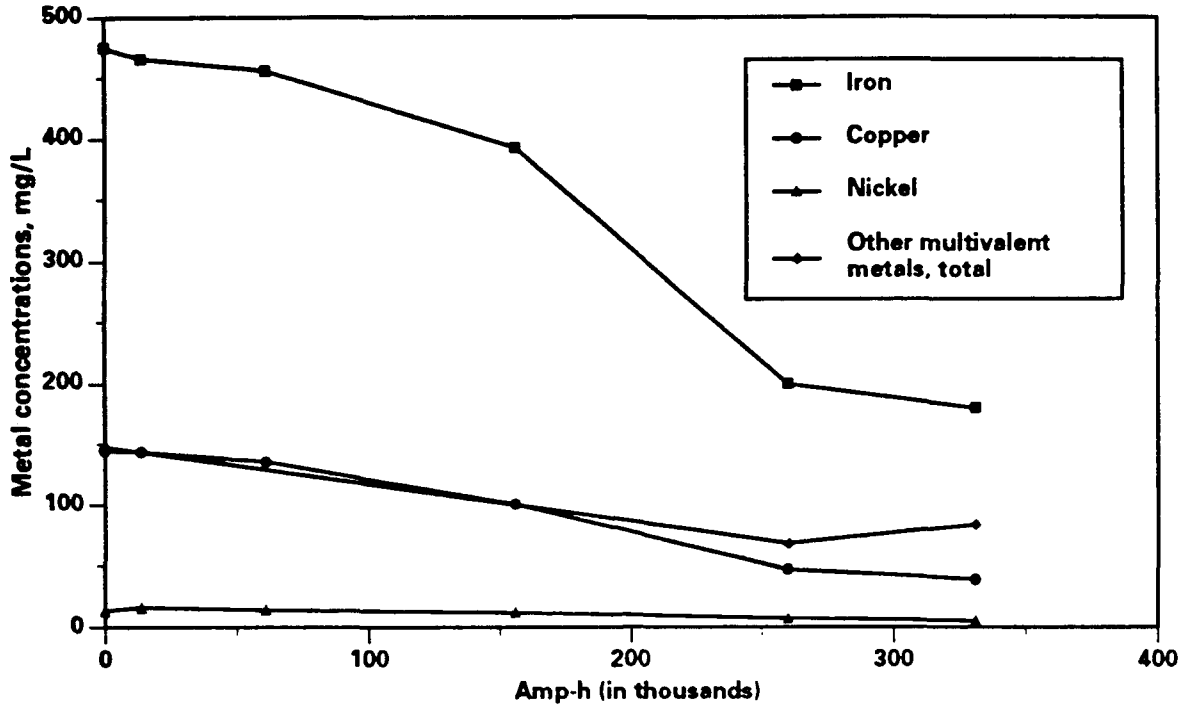

Figure 6-4. Concentration data for metal contaminants in chromium plating solution.

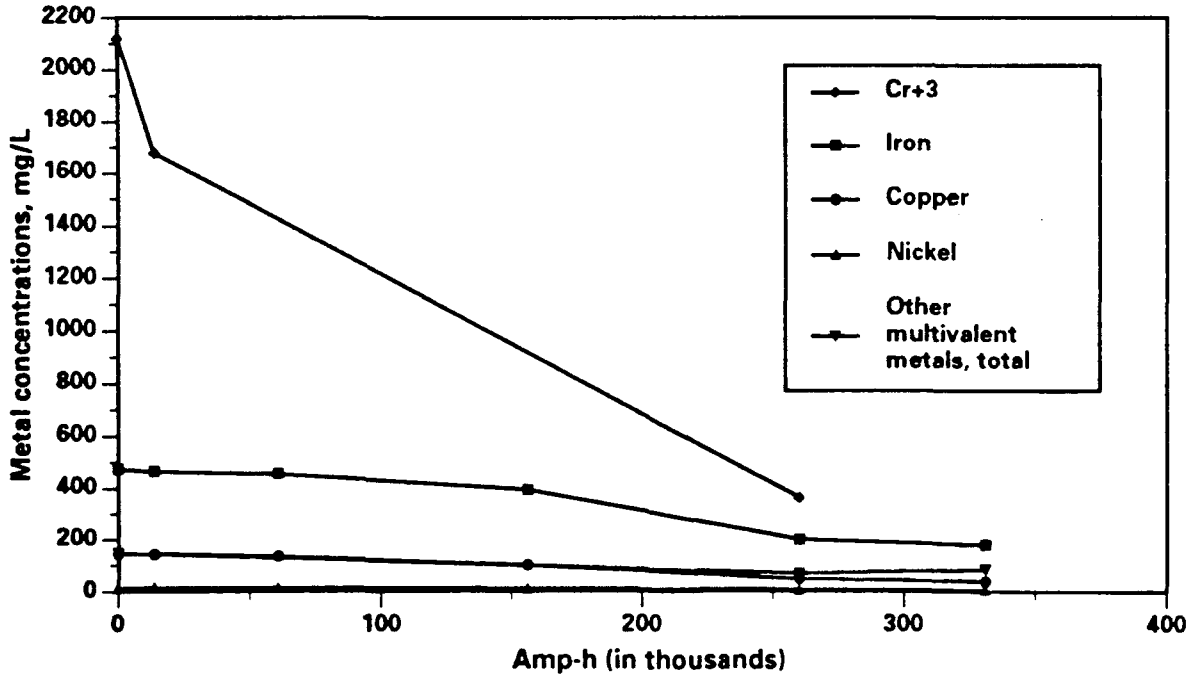

Figure 6-5. Concentrations of metal contaminants in chromium plating solution, including trivalent chromium.

through the membrane cannot be determined. The high reduction in trivalent chromium concentration (83 percent after 260,000 amp-hours) compared with other metals (a high of 73 percent for copper after 331,000 amp-hours) may indicate at least some trivalent chromium oxidation. However, the high chromium concentration in the catholyte sludge (158,000 mg/kg) indicates significant transport across the membrane (although the total quantity of sludge from which this particular sample was taken was low).

Plating Efficiencies and Part Rejects

The chief function of the electrodialysis unit is to reduce concentrations of contaminant metals and trivalent chromium. The ultimate benefit of the system, however, would be derived from increasing the plating efficiency of the bath, reducing the number of reject parts, reducing the amount of labor required to remove sludge from the plating tank, extending the tank life, or from otherwise reducing the amount of waste generated by the process tank.

Plating efficiencies were given in Table 5-16. Although the plating efficiency of Tank A-9, which was fitted with the electrodialysis cell, increased significantly during the test program (from 14 to 22 percent), the plating efficiencies of most other tanks also increased during the test program even though they were not fitted with the electrodialysis unit. For example, the measured efficiency of Tank A-6 increased from 10 to 24 percent. None of the tanks showed a decrease in efficiency as a result of use and, presumably, an increase in metal contamination. None of the solutions was replaced during the test program. The results show an overall consistency between the last two sets of results, although the first set is significantly lower. On the basis of these results, the increase in plating efficiency for Tank A-9 cannot be credited to the electrodialysis unit and may be due to the uncertainty in the efficiency test. Therefore, conclusions cannot be drawn regarding the effect of the electrodialysis cell on the cathode plating efficiency of Tank A-9. Longer-term monitoring may be necessary.

Table 5-17 lists the number of parts processed from July 1990 through April 1991; the electrodialysis unit was installed on January 22, 1991. This table generally

showed a low amount of reject parts even before the electrodialysis unit was installed (e.g., September - January). It should be noted that reasons are not always provided for reject parts on the original SPCs, nor do all tank problems result in parts that are rejected. For example, in July 1990, a defective activator was suspected after six parts were rejected, but the follow-up action is not recorded on the SPCs. In September, several instances of plating roughness were observed, but no resulting reject parts were recorded. Finally, Tank A-9 was inoperational for most of December due to overheating, but this problem did not result in any record of rejected parts. Based on these data, the effect of the electrodialysis unit on part reject rates cannot be determined. Furthermore, it is not clear that part rejects were a problem prior to installation of the electrodialysis cell, nor that the primary problems with the tank were related to metal contamination. Longer-term monitoring of the part reject rates for the tanks and an increase in the volume of data collected are necessary to draw definite conclusions regarding the effect of the electrodialysis unit.

When the electrodialysis unit was initially installed, Tank A-9 had an iron concentration of 475 mg/L and a trivalent chromium concentration of 2,120 mg/L. For comparison, the starting concentration of iron in the chromic acid stripping solution tested in the first phase of the test program was 4,410 mg/L. According to one reference (3), plating baths begin to cause quality problems at iron concentrations of 4,000 mg/L, and some baths have been operated successfully up to 10,000-15,000 mg/L. Copper concentrations may also have an impact on plating quality. The relatively low iron and trivalent chromium concentrations in Tank A-9 at the beginning of testing may help explain why part rejects as a result of metal contamination may not have been a problem during the period covered in Table 5-17.

The hard-chromium electroplating tank was initially selected to reduce waste generated by the process, as waste minimization was the primary goal of this project. This reduction could have been effected by lengthening the life of the tank, by reducing the amount of sludge requiring periodic removal, or by reducing the number of rejects processed (which would contribute additional chromium to the IWTP and require additional chemical processing). The plating tanks, however, are not generally

disposed of in their entirety and so do not directly generate large quantities of hazardous waste. According to plating shop personnel, the amount of sludge generated by the plating tanks is also relatively small (perhaps 100 gallons of sludge results from eight plating tanks during a year). The metal salts likely to form this sludge would be transported into the catholyte, where they would form a sludge requiring disposal; although this would decrease the need for manual sludge removal and increase the convenience of operation, it may not decrease the overall waste generation. Finally, as discussed above, available data suggest that part rejects are not a large problem, and rejects that do occur may be the result of operational problems with the tank rather than metal contamination. For these reasons, it is not clear from the data collected that the electrodialysis process will result in a direct reduction in waste from the plating tank.

Although electrodialysis was successful in removing contaminant metals and reducing trivalent chromium concentrations in the chromium plating bath, data collected during this project are inconclusive as to the effect of the electrodialysis unit on reducing hazardous waste, reducing part rejects, reducing sludge buildup, and increasing plating efficiency. The CCAD laboratory chemist has noted that chemical analyses of sulfates has appeared to be more consistent since the system was installed (perhaps because metals are not precipitating as sulfates). To achieve more than anecdotal evidence of the ultimate benefits of the system, a longer term monitoring program needs to be implemented and pursued to increase the volume of data necessary for drawing definite conclusions. This program would focus on maintaining records relating to operation and benefits of the system, and would include:

- Maintaining the electrodialysis log.
- Recording catholyte changes.
- Monitoring plating efficiency of all plating baths.
- Compiling chemical analyses of all plating baths and recording the results in a project-specific notebook.

- Maintaining quantitative records on sludge removal from all plating tanks.
- Continuing to monitor part rejects, the suspected cause of these rejects, any action taken, and the results of this action.

The electrodialysis unit will be more useful in the future if a closed-loop recycling system is installed for the plating tanks and associated rinse waters. In a closed-loop system, metal contaminants would be removed from the rinse water and returned to the plating solution rather than being treated in the wastewater treatment plant. The buildup of contamination would be greater than it is now, and an electrodialysis unit in the plating tank would keep this contamination under control. The closed-loop system would result in significant waste reduction because it would reduce the amount of chromium-contaminated wastewater treated at the IWTP and, ultimately, the resulting hazardous sludge. The chromium and other metals would be removed from the wastewater by ion exchange. Additional electrodialysis units would be used to recover the ion-exchange regenerant solutions, which would otherwise result in large quantities of hazardous waste.

Another method of achieving the most usefulness out of the present electrodialysis system would be to ensure that the tank fitted with the system is more heavily used. Table 5-17 indicated that Tank A-9 was used on 19 to 73 percent of all days in a given month. CCAD personnel have also suggested that the reverse-current etching conducted in each plating tank before the actual plating could all be conducted in one tank. The etch process probably contributes a high degree of metal contamination to the process solution, and performing this operation in a tank fitted with the electrodialysis unit would decrease contamination in all the plating tanks in the shop.

6.3 Catholyte Generation

Laboratory analyses of catholyte samples from testing of the chromic acid stripping and chromium plating solutions indicated that the metals removed from the process solutions were transported into the catholyte (Tables 5-7 through 5-9 and Table 5-18). Furthermore, a large percentage of the metals were precipitated as hydroxides and the liquid portion did not have a significant metals content.

Approximately 300 gallons of hazardous waste and wastewater were generated during the 205,000 amp-hours of the chromic acid stripping test program. The sludge was brown, which indicates that high amounts of iron precipitated as a hydroxide. The catholyte consisted of approximately 47 weight percent sludge, 78 percent of which was moisture. Therefore, only about 10 percent of the total catholyte was solid material. Because the catholyte sludge contains significant quantities of cadmium and chromium, it may have to be disposed of as a hazardous waste.

Operation of the electrodialysis cell on the plating solution created a significantly lower volume of waste, from 100 to 150 gallons for 331,000 amp-hours (records may not have been kept accurately). The greenish-blue appearance of the sludge indicated the presence of the hydroxides of copper, chromium, and nickel. The relatively high chromium concentration (158,000 mg/kg) would likely require disposal of the sludge as a hazardous waste.

To ensure that the operation of the electrodialysis cell leads to an overall reduction in hazardous waste, the amount of catholyte disposed of must be minimized. Decanting, filtration, or other liquid-solid separation techniques could significantly reduce the sludge volume requiring disposal. The liquid could then be recycled or treated at the wastewater treatment plant.

One problem encountered with the spent catholyte during the test program involved the hexavalent chromium concentration in both the liquid and sludge phases (see Tables 5-9 and 5-19). The presence of this element was confirmed by the greenish-yellow color of the liquid phase. Hexavalent chromium can enter the catholyte as a metal complex or by diffusion through the membrane. It could also enter the catholyte when the chromium plating solution is splashed onto the catholyte tank or the demister.

The hexavalent chromium content of the liquid and sludge phases of a spent catholyte means that it would require treatment in an IWTP to reduce the hexavalent to trivalent chromium. Hexavalent chromium is generally reduced by the addition of a reducing agent, such as sodium metabisulfite, under acidic conditions. Because the catholyte is alkaline, the liquid would require acidification before chromium reduction.

To obtain the most efficient operation and use of treatment plant chemicals, a spent catholyte would be pumped directly to the basic precipitation section of the IWTP to avoid acidification of the alkaline liquid. A significant hexavalent chromium content, however, would require acidification and reduction.

The two methods described in Subsections 4.3.3 and 5.2.2 were successful in significantly reducing hexavalent chromium concentrations. Adding more sodium metabisulfite to the catholyte drum while the cell continued to operate resulted in an 87 percent reduction in hexavalent chromium concentration, from 35 to 4.5 mg/L; adding the alkaline reducing agent resulted in a 60 percent reduction, from 810 to 320 mg/L. The amount of alkaline reducing agent added was sufficient to reduce only 185 mg/L of hexavalent chromium as calculated by using the vendor's formula. Because the chemical doses were not equivalent, these results should not be compared directly. Additional testing could be performed with chemical doses that further reduce the hexavalent chromium concentrations.

On the basis of the results of this project, the vendor or depot personnel need to address the hexavalent chromium concentrations in the catholyte. Ionsep has indicated success in eliminating hexavalent chromium concentrations in the catholyte of systems used by other companies. Four potential methods of addressing this issue are:

1) Reformulation of the catholyte powder to include additional reducing agent (sodium metabisulfite);

2) Addition of more sodium metabisulfite to the 55-gallon drum if hexavalent chromium is detected in a spent catholyte;

3) Batch-treatment of the catholyte for hexavalent chromium by using an alkaline reducing agent; or

4) Work with personnel at the IWTP to determine if the spent catholyte can be treated directly in the chromium reduction process despite its alkalinity.

Recycling the catholyte liquid by sludge filtration would reduce the magnitude of this problem, but would not eliminate it because the sludge would still contain hexavalent chromium and require treatment.

Additional work also needs to be performed to decrease the overall amount of catholyte sludge disposed of or treated, and to decrease the amount of labor required to pump out the spent solutions and make up fresh solutions from the catholyte powder. The two approaches to solving this problem are an automatic closed-loop recycling system and recycling using the existing equipment. These options are described below.

Ionsep currently offers closed-loop catholyte recycling systems for middle- to large-size electrodialysis systems. For the closed-loop operation, small adjustments must be made in the pH and chemical concentration. The available closed-loop systems offer catholyte filtration, catholyte recycling, and catholyte composition control. In a larger system consisting of a centralized catholyte tank to service several plating baths (e.g., all eight tanks in the chromium plating shop), the catholyte could be stored in a tank with a conical bottom. The sludge could then be pumped directly off the bottom to a filter press.

Another option for decreasing the amount of catholyte to be treated or disposed of is to modify the procedures and equipment currently used. For example, a spent catholyte solution could be filtered, the sludge disposed of, the pH of the liquid adjusted with sodium bicarbonate (which is more efficient than acid adjustment), and the liquid reused. Two catholyte tanks could also be used -- one for operation, and one for solids settling. The solids could then be pumped out and the filtrate chemically adjusted.

The optimum solution to the labor required to make up and dispose of the catholyte is a semiautomatic catholyte recycling system. For this scenario, a pump and small filter press would be installed on the bottom drain of the 55-gallon drum. When the sludge buildup reaches a significant level (as indicated by a decrease in amperage), the catholyte would be pumped through the filter press and returned to the drum. The sludge would be removed periodically from the filter press. When the

catholyte liquid itself becomes spent, it could be readjusted with makeup chemicals or pumped through the filter press directly to the IWTP. This method would result in increased catholyte use, less waste being sent to the IWTP, and fewer makeups of the catholyte solution. It would also result in less labor being required than the current practice of manually pumping the spent catholyte solution from the drum to a temporary holding tank for later disposal.

Although some concerns arose during this test program regarding the hexavalent chromium concentrations in the catholyte, treatment of the catholyte liquid, and disposal of the catholyte sludge, each of these issues can be readily addressed by continuing contacts with the vendor or through small modifications of the existing equipment or procedures. The hexavalent chromium concentrations could be addressed easily through coordination with Ionsep to reformulate the catholyte powder, or by the addition of reducing agents to the spent catholyte. The treatment and disposal problems associated with the catholyte could be reduced by installation of a recycling system that minimizes sludge volume and allows reuse of the catholyte liquid. Further developments by the vendor may warrant following.

6.4 Ease of Maintenance

One of the criteria for success during this project was ease of maintenance of the electrodialysis system. The cathode section of the cell must be removed from the unit whenever the system is shut down so the cathode and anode are not damaged (in the absence of electricity, the cell acts as a battery). As a result of problems created by a large hole in the first membrane and very small hole in the second membrane, significant labor was required to return the membranes to the manufacturer and then to reinstall the new membrane section. This problem should be reduced somewhat, however, as the integrity of the membrane improves as a result of further experience and improved development by the vendor.

During the chromic acid stripping solution test program, the catholyte was made up from a powder and disposed of six times. This procedure involved a fair amount of labor caused by pumping the catholyte to a holding tank, making up a new

solution from the powder, and disposing of the spent catholyte. Because the hard-chromium plating solution was less contaminated, the catholyte was changed only two to three times over the 3 months of testing. This problem could be significantly reduced by installation of a semiautomatic catholyte recycling system, as described in Subsection 6.3.

6.5 Summary of Options

Figure 6-6 presents a summary of options available for tank selection, operational mode (batch versus continuous), and catholyte recycling and treatment for the current electrodialysis equipment. These options were described in Subsection 6.3 and are summarized below.

Tank Selection and Operational Mode

- A chromic acid stripping solution or chromium plating solution could be chosen.
- If a chromic acid stripping solution is chosen, a batch mode operation could be selected for rejuvenation or a continuous mode selected for in-line purification.
    - If in-line purification is selected, the current catholyte or a modified catholyte formulation could be used.
        - Use of the current catholyte for in-line purification of the chromic acid stripping solution is not recommended.
        - Use of a modified catholyte would require additional monitoring and testing.
    - If the unit is operated on a spent chromic acid stripping solution for batch rejuvenation, the treated solution should be analyzed for sulfates and treated with barium carbonate if necessary.
- If the cell is operated on the chromium plating solution for in-line purification, long-term monitoring is necessary to verify that the desired benefits are achieved.

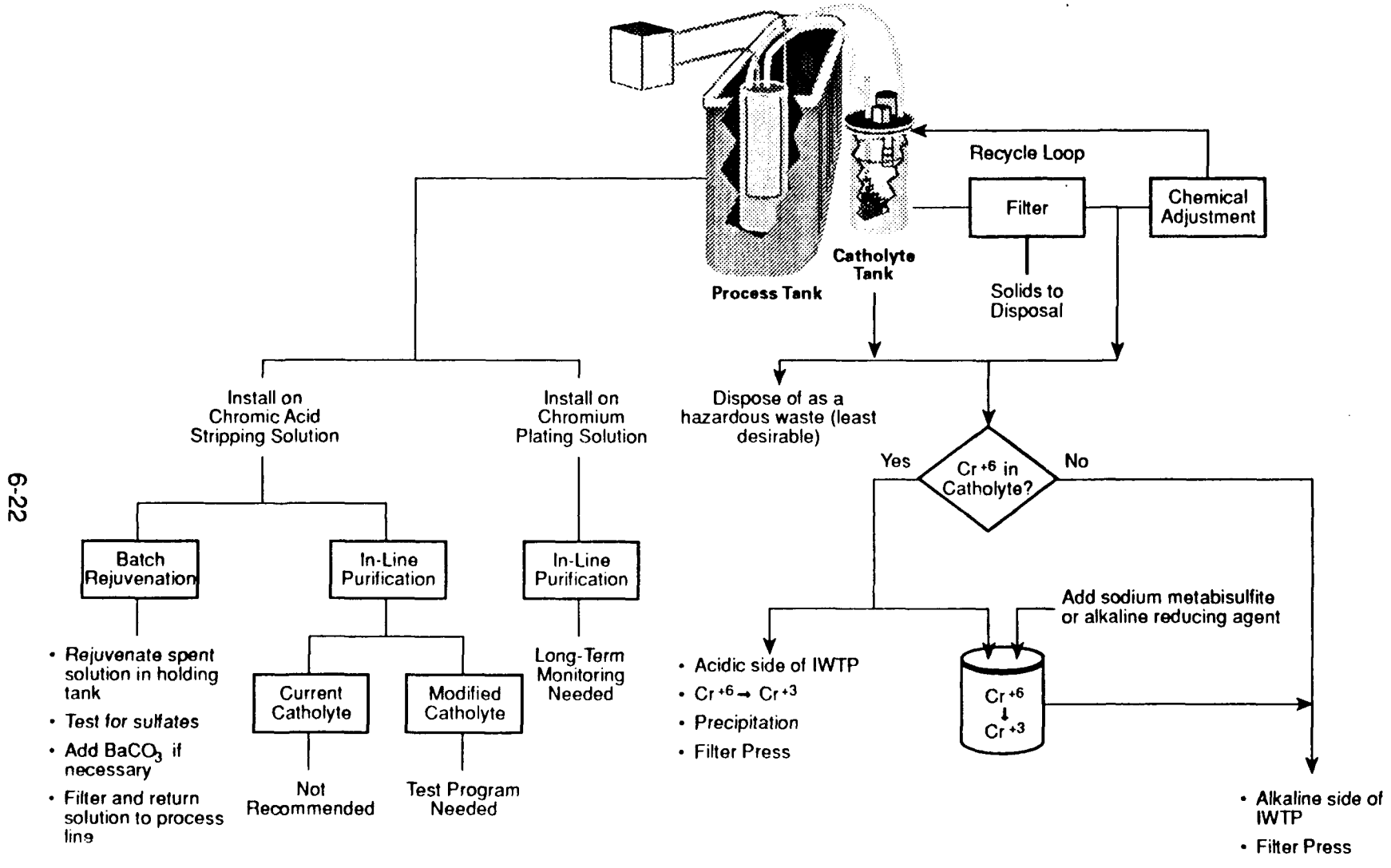

Figure 6-5. Options for tank selection, operational mode, and catholyte recycle/treatment.

Catholyte Recycling/Treatment

- The catholyte solution could be recycled by filtering and adjusting the pH and chemical composition.
- The solution could be disposed of in its entirety (this is the least-desirable option).
- The solution could be treated through the ITWP.
    - If hexavalent chromium is not in the catholyte, it can be pumped to the alkaline side of the IWTP.
    - If the catholyte contains hexavalent chromium, it must be treated further.
        - Reduction of hexavalent chromium could occur in the acidic side of the IWTP.
        - Chromium reduction could also occur in the catholyte drum itself under alkaline conditions, with the resulting solution being pumped to the IWTP.

6.6 Additional Minicell Testing

The results of the test program for the chromate conversion coating solution were inconclusive (Table 5-20). Very little activity was observed with the three-compartment cell, and the amperage was low despite high voltage. The analytical data did not indicate any significant transport of metals across the membrane. Repeating the test over a longer operating period could result in higher metal removals and a more definitive evaluation of the three-compartment cell.

The minicell test for the nitric acid solutions was also inconclusive because no readily observable color change occurred. For a more conclusive test, the minicell must be operated long enough to produce a color change and must be produced in sufficient volume to allow quantitative analysis of trivalent chromium oxidation.

SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Based on the results presented in Section 5 and the evaluations presented in Section 6, several conclusions can be drawn regarding the applicability of the electrodialysis system for rejuvenating and purifying chromic acid solutions. The system was successful in removing a significant quantity of metals from the chromic acid solutions, and it may have been successful in oxidizing trivalent to hexavalent chromium. In the batch rejuvenation of the chromic acid stripping solution, however, the leakage of sulfates into the solution through a membrane hole resulted in damaged parts when the solution was used on an operational tank. With the current design and catholyte formulation, the electrodialysis system should not be used on operational process tanks that may be sensitive to sulfate contamination because it cannot be guaranteed that the membrane will not leak. The testing with barium carbonate, however, demonstrated that the solution can be successfully rejuvenated by treatment with barium carbonate after use of the electrodialysis cell even in the unlikely event of a recurring membrane leak.

Although electrodialysis significantly reduced contaminant metal and trivalent chromium concentrations in the chromium plating solution, sufficient data were not gathered during this project to verify the expected results of the system. These results are: reduction of hazardous waste, reduction of part rejects, reduction of sludge buildup, and an increase in plating efficiency. Long-term monitoring of the system is needed to verify these benefits. The electrodialysis unit could produce greater benefits if installed on a closed-loop recycle system or on a tank that is more heavily used.

The system's vendor has also indicated that a catholyte has been developed that would not contaminate the process solution even in the event of a membrane leak. This catholyte could allow operation of the unit on a continuous basis directly on the in-line chromic acid stripping tank. Because the materials of construction for the purchased system were chosen for use at high operating temperatures, an in-line chromic acid stripping tank would be the most effective use of the current equipment.

Analytical results of the catholyte sludge indicated that the majority of metals precipitated as hydroxides. The sludge must be disposed of as a hazardous waste because of its chromium content. The spent catholyte could be pumped through the waste pretreatment plant or filtered, rejuvenated with the appropriate chemicals, and recycled. The presence of hexavalent chromium in the catholyte liquid and sludge creates concerns in regard to liquid treatment or sludge disposal. This issue can be addressed by reformulating the catholyte powder, adding more reducing agent to a spent catholyte, batch treating with an alkaline reducing agent, treating the catholyte in the chromium reduction process in the wastewater pretreatment plant, and/or recycling the catholyte solution to the extent possible. This issue should be resolved by coordination among the vendor, CCAD engineers, and wastewater pretreatment plant personnel.

Catholyte recycling minimizes the waste and wastewater generated by the electrodialysis process. Catholyte recycling would be much easier if a semiautomatic system consisting of a pump and small filter press were installed.

The results of the three-compartment minicell test with the chromium conversion coating and the nitric acid passivation test were inconclusive.

7.2 Recommendations

Based on the data collected during this project, several recommendations can be made regarding the best use of the electrodialysis cell that will remain at CCAD, additional problem areas that need to be pursued, future projects, and follow-up with CCAD personnel. These recommendations are as follows:

- Long-term monitoring should be conducted on the effectiveness of electrodialysis in reducing waste generation, sludge buildup, part rejects, and increasing the plating efficiency for the chromium plating operation. The membrane integrity should also be monitored.

- CCAD should continue monitoring the electrodialysis system as specified in Subsection 6.2.

- The electrodialysis unit should be tested on the in-line chromic acid stripping tank with the new catholyte developed by the vendor to prevent sulfate contamination of the process solution. The chromic acid stripping solution remains the single largest chromic acid waste stream, with the greatest opportunity for significant reduction of hazardous waste.

- As an alternative to testing a new catholyte, the first phase of the experimental program involving batch testing on the chromic acid stripping solution should be repeated. The rejuvenated solution would be analyzed for sulfates, and barium carbonate would be added if necessary to precipitate the sulfates. This testing would indicate if the membrane leak is likely to be a persistent problem and would also indicate the feasibility of using electrodialysis in combination with the addition of barium carbonate for complete rejuvenation of a spent chromic acid solution for reuse.

- An automatic catholyte recycling system should be installed, including a pump and small filter press. The 55-gallon drum should be piped directly to the IWTP for disposal of the spent catholyte.

- A method should be developed to eliminate the hexavalent chromium concentrations in the catholyte solution, or the catholyte should be pumped to the chromium reduction process in the wastewater pretreatment plant.

- When future electrodialysis systems are to be installed on tanks that are not designed for ventilation of chromic acid mist, the equipment should be designed to include a mist elimination system.

- Additional analytical methods are needed for the testing of concentrated process solutions, especially trivalent chromium.

- Additional data, including costs, are needed on comparable technologies such as electrolysis, electrodialysis systems with an acidic catholyte, and the porous pot.

- Additional testing could include evaluating other comparable technologies; testing a three-compartment cell on a chromate conversion coating in the Air Frames Cleaning Shop, which generates 1800 gallons of chromic acid waste a year; and testing a closed-loop system on the chromate-conversion coating or hard-chromium electroplating tanks.

- An evaluation should be made of solutions other than the high-temperature chromic-acid bath for stripping chromate conversion coatings that would be less sensitive to sulfate contamination.

REFERENCES

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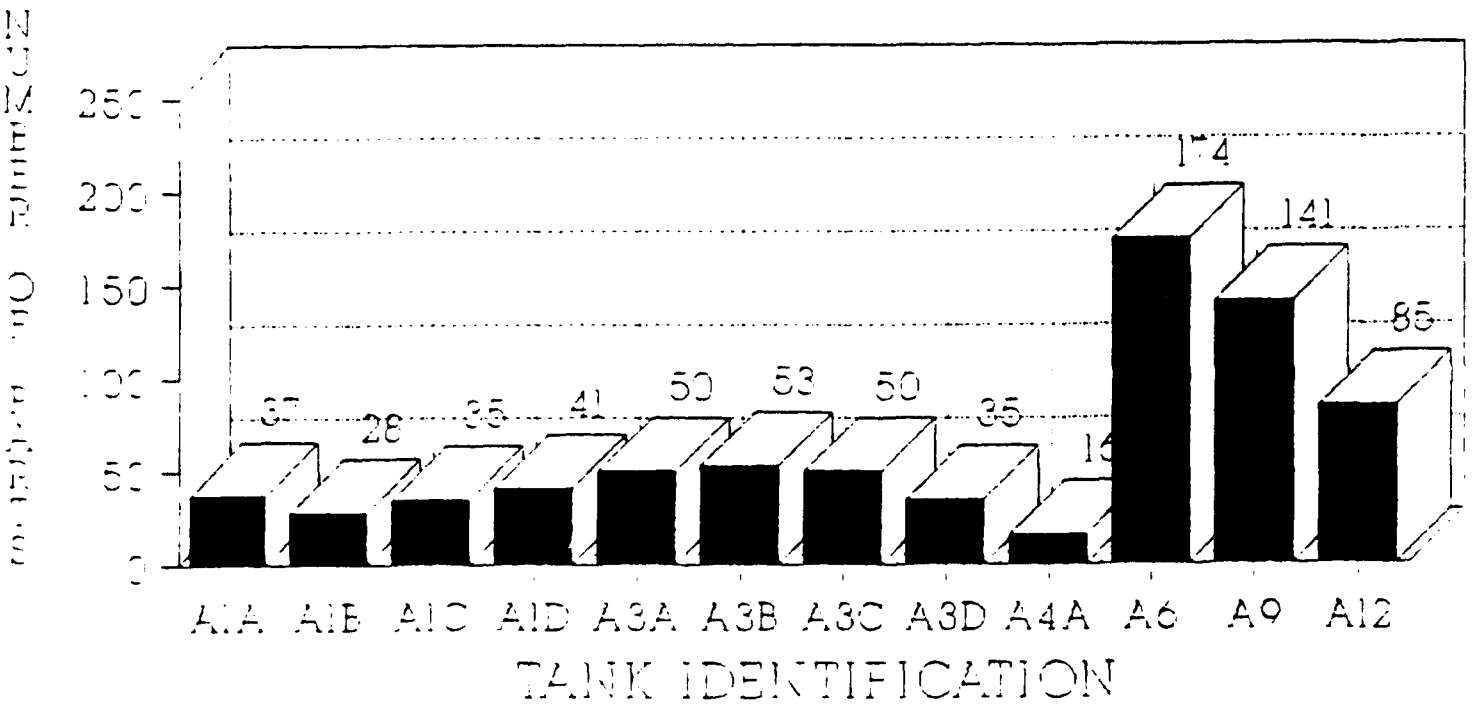
2. Accident Prevention Safety Program Plan for Evaluating a Chromic Acid Recovery/Purification Electrodialysis System at Corpus Christi Army Depot. IT Environmental Programs, Inc. (formerly PEI Associates, Inc.), under contract to USATHAMA. August 1990.

3. Cushnie, G. C., Jr., and W. Anderson. Removal of Metal Cations From Chromium Plating Solution. Paper presented at the 10th AESF/EPA Conference on Environmental Control, January 23-25, 1989, Orlando, Florida.

APPENDIX A

CHROMIUM PLATING SHOP LOGS

CHROME SHOP
TOTAL NUMBER PARTS RUN
JUL 2 THRU AUG 4



CHROME SHOP
DEFECTS BY TANK/TYPE
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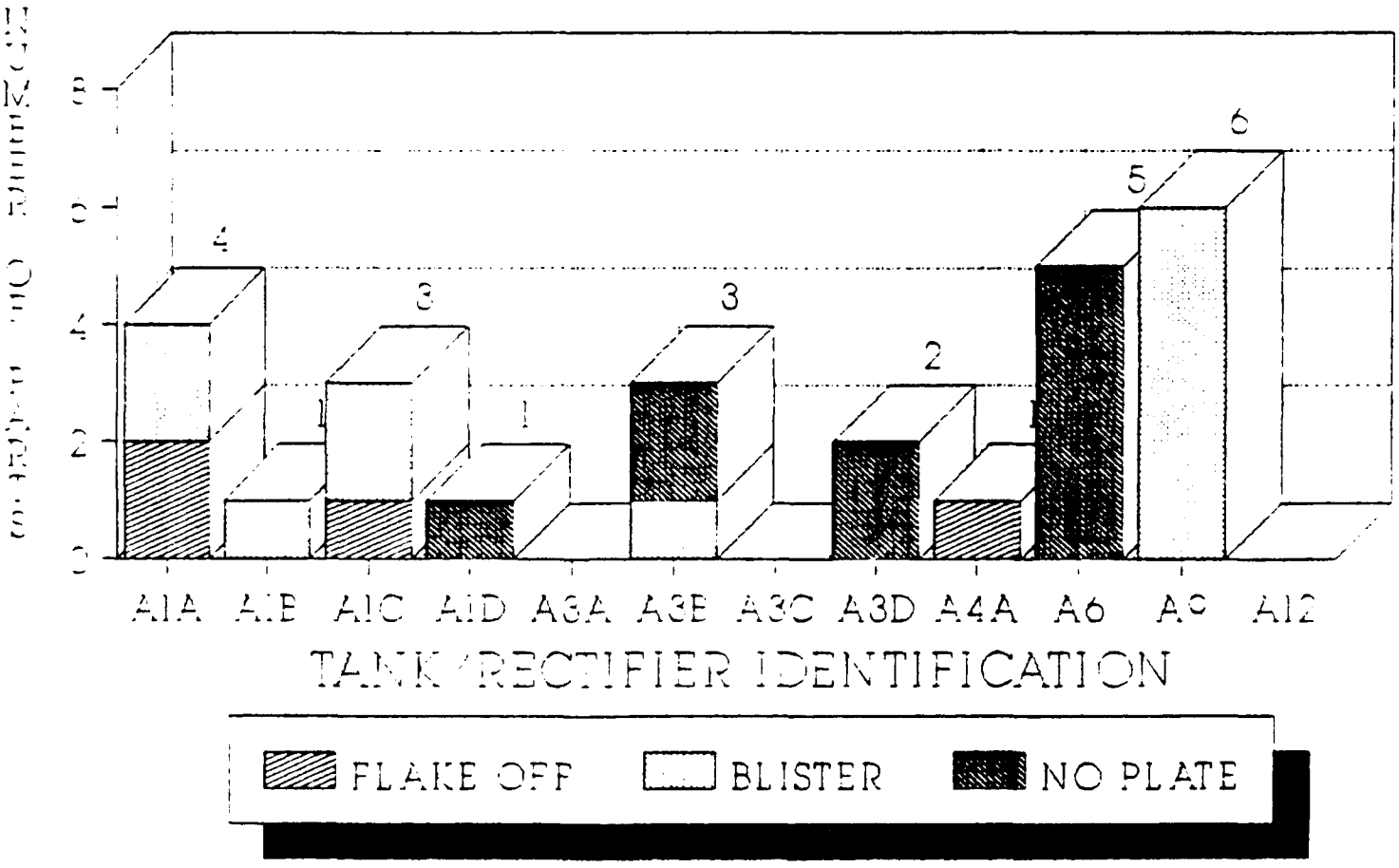

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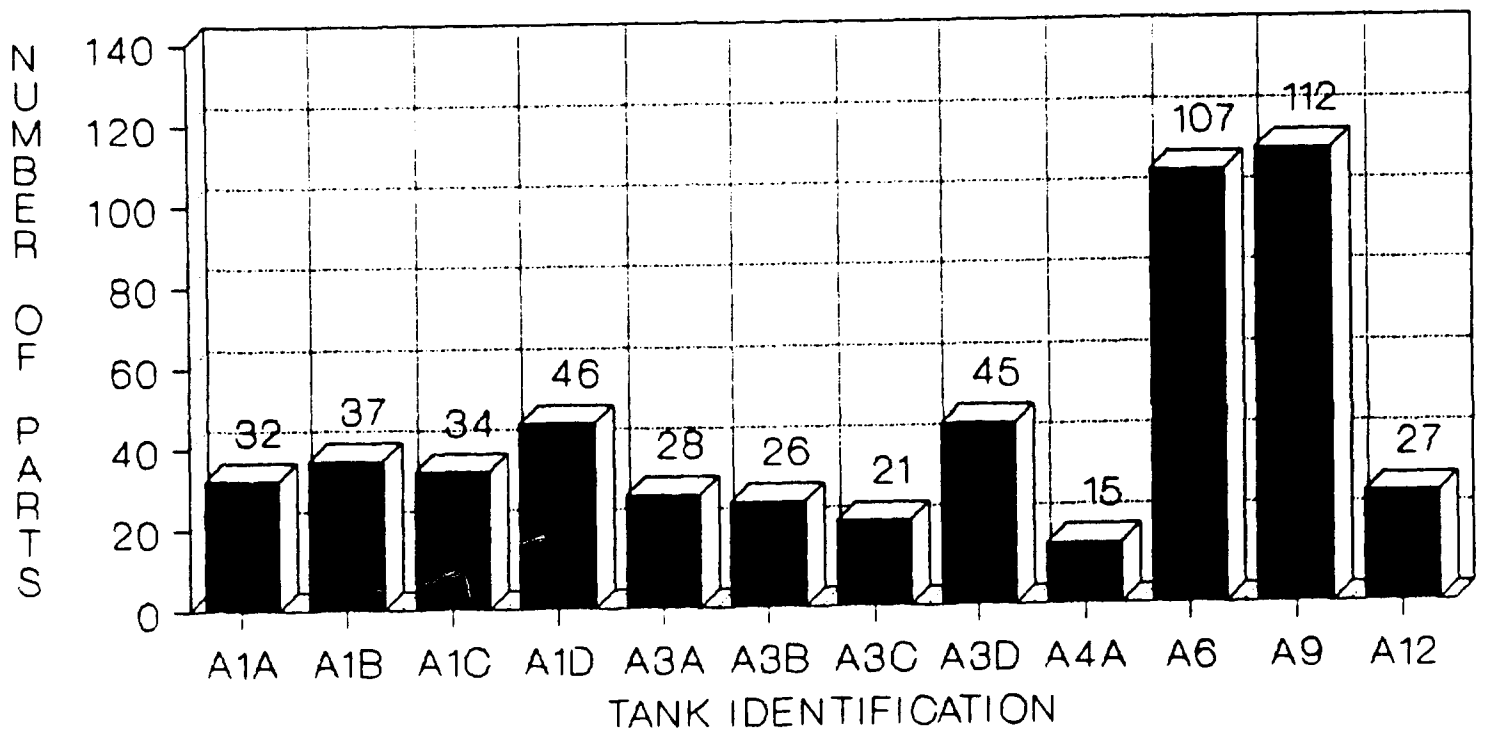
AUG. 8 THRU AUG 31



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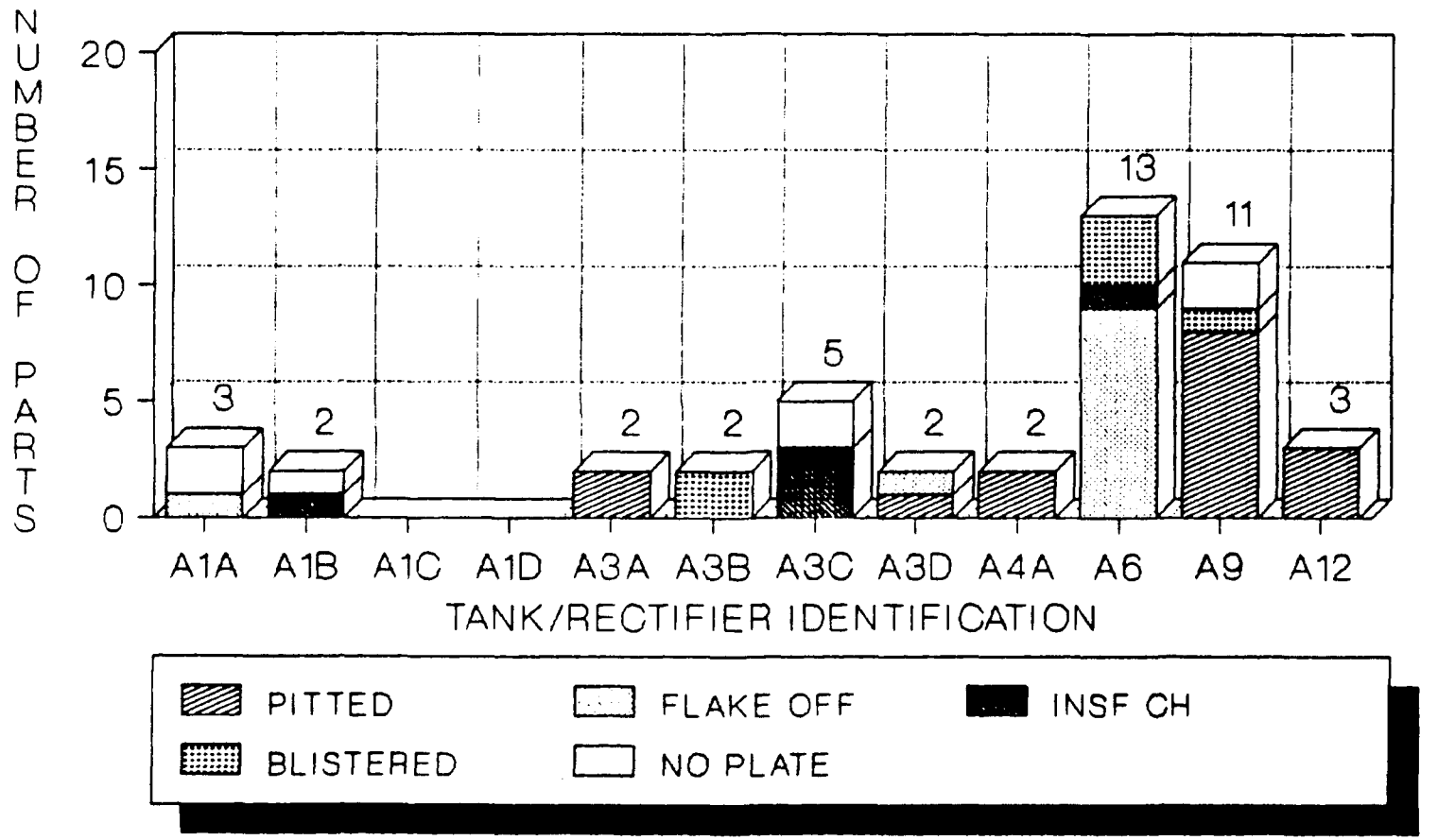

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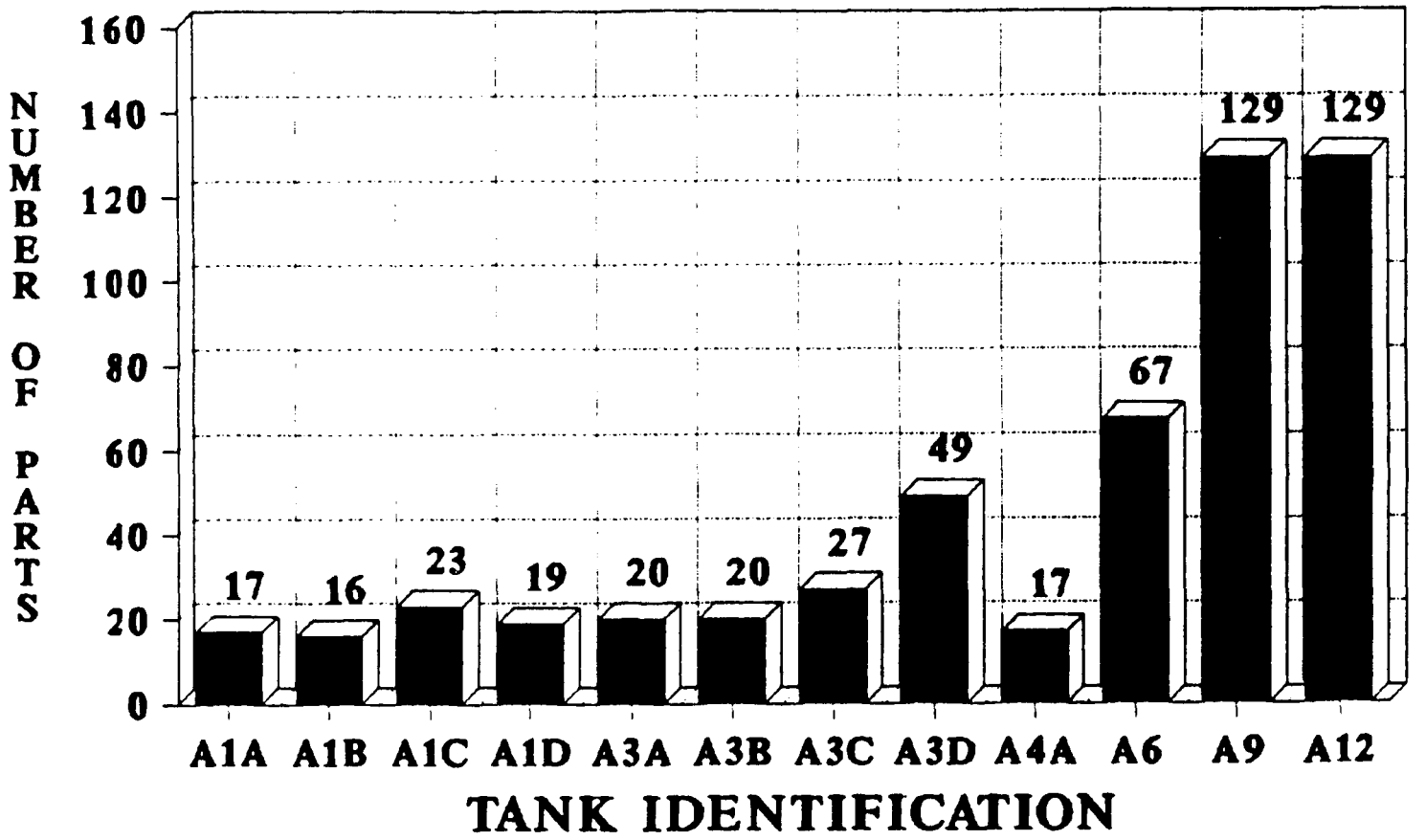

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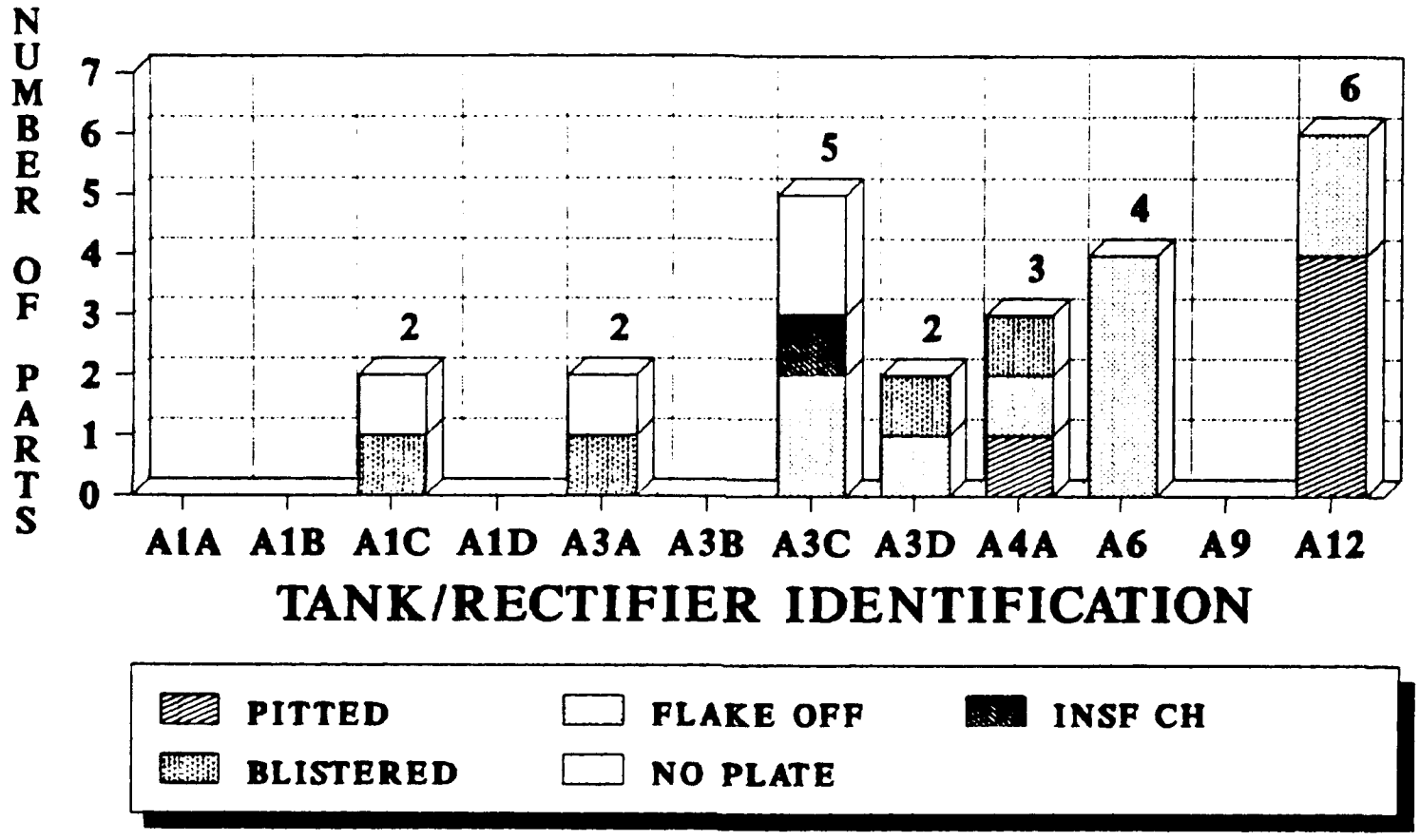

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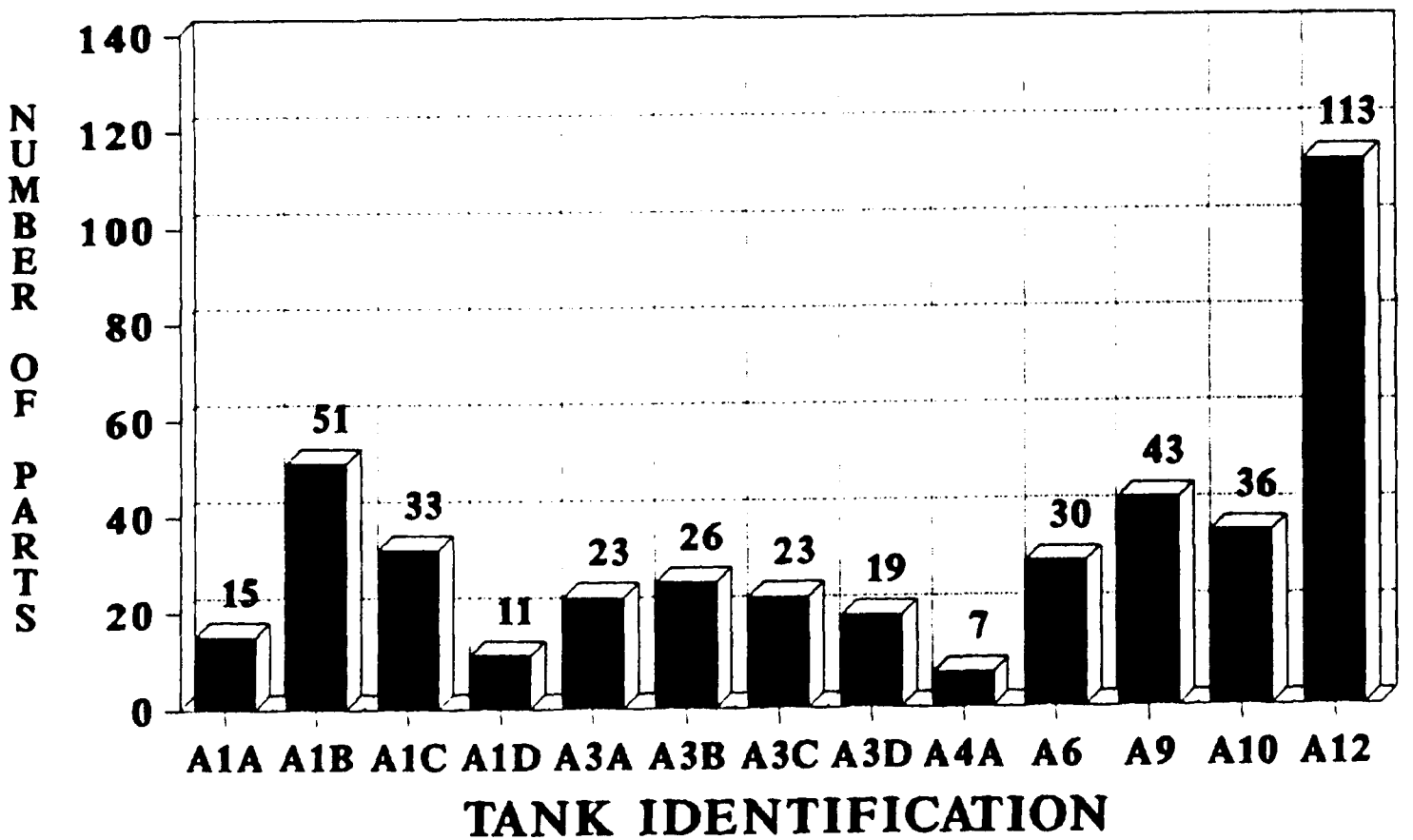

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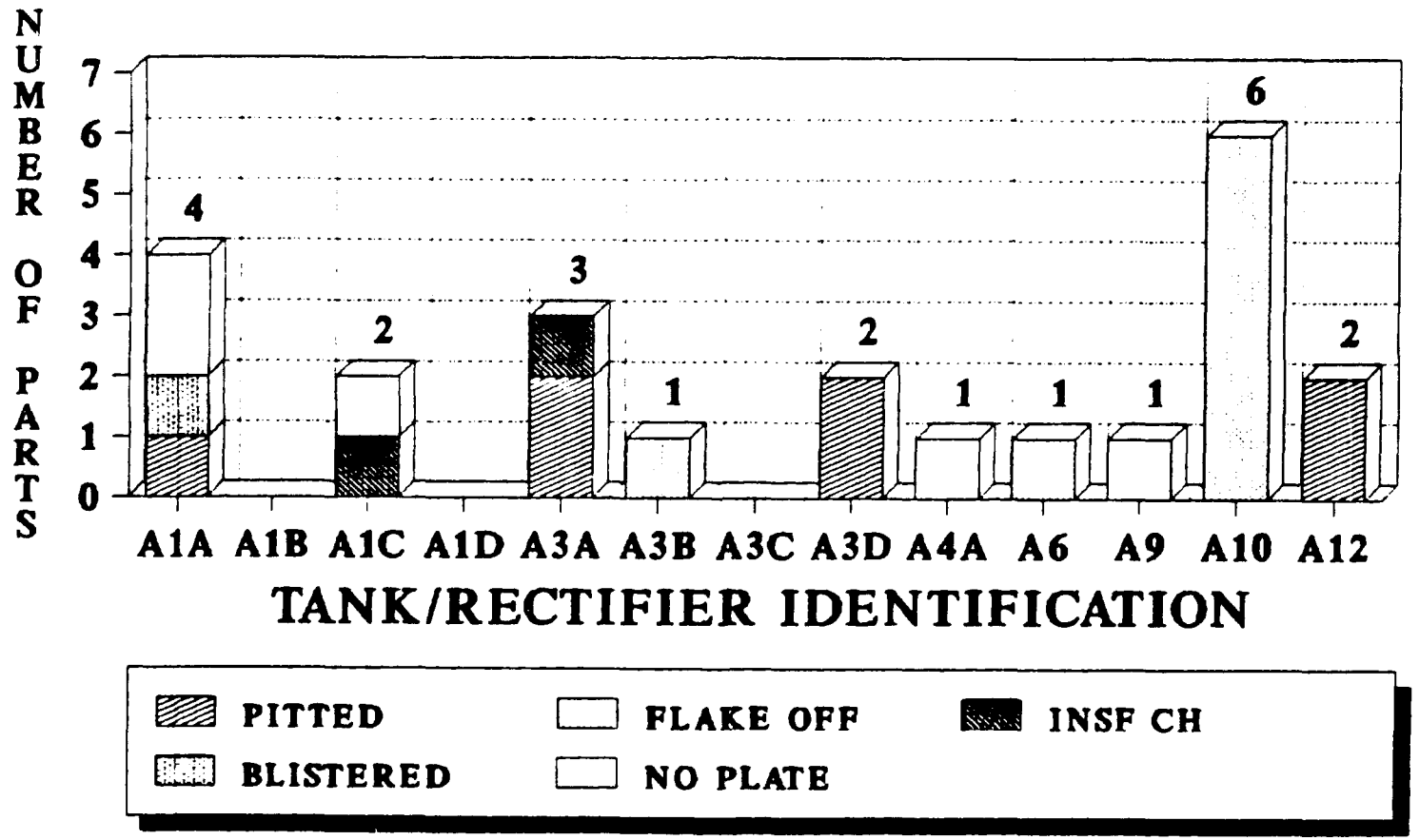

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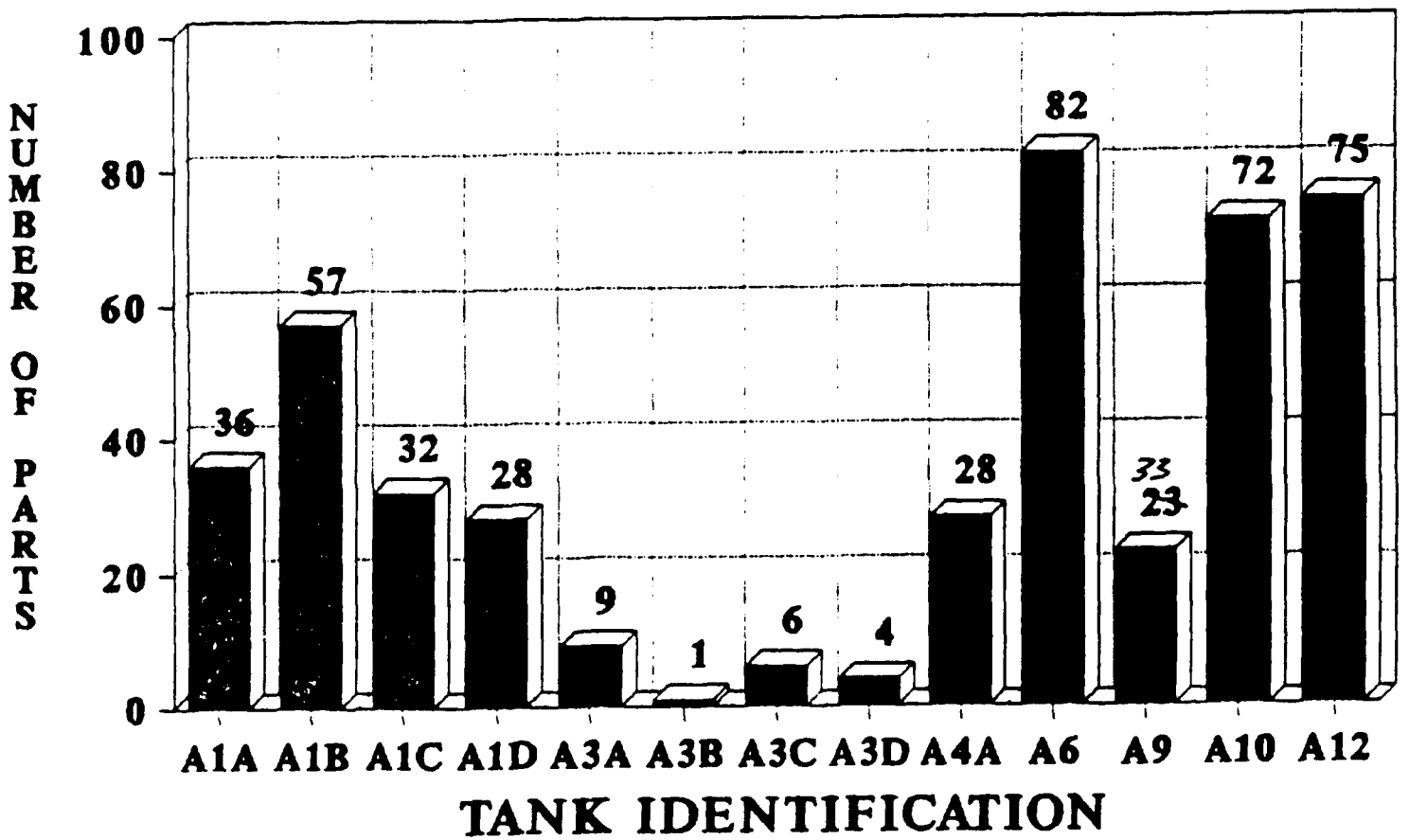

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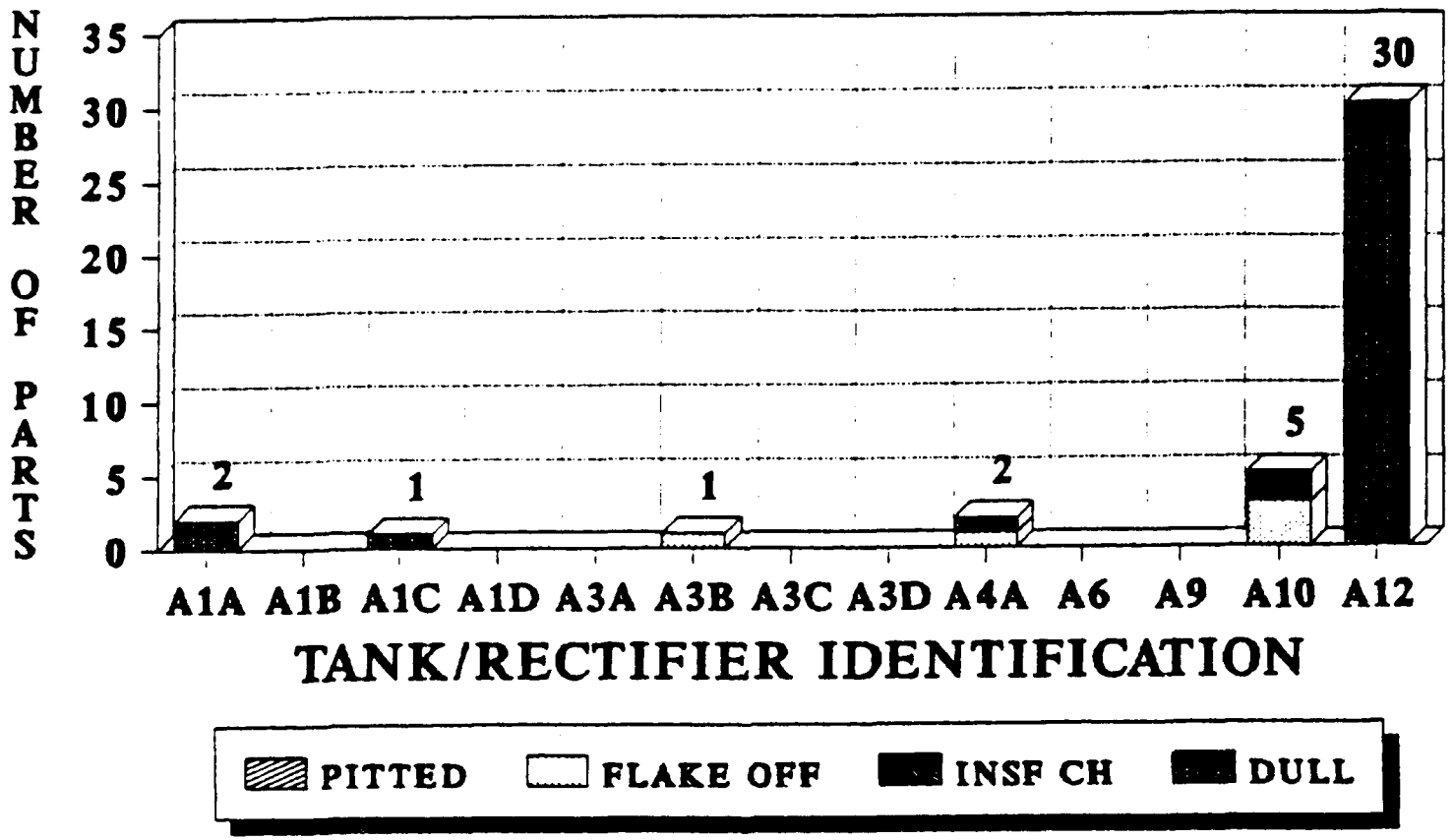

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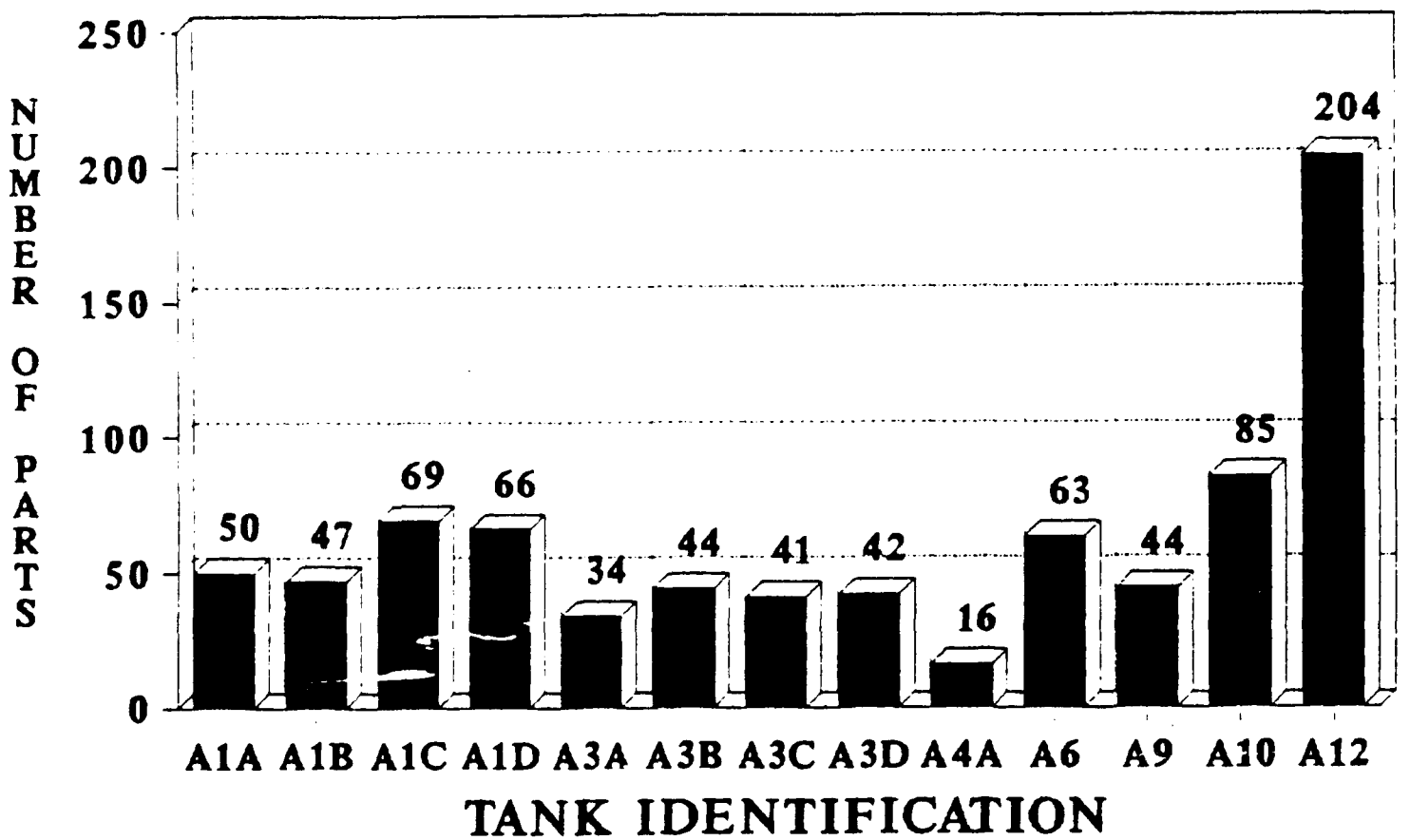

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DEFECTS BY TANK/TYPE

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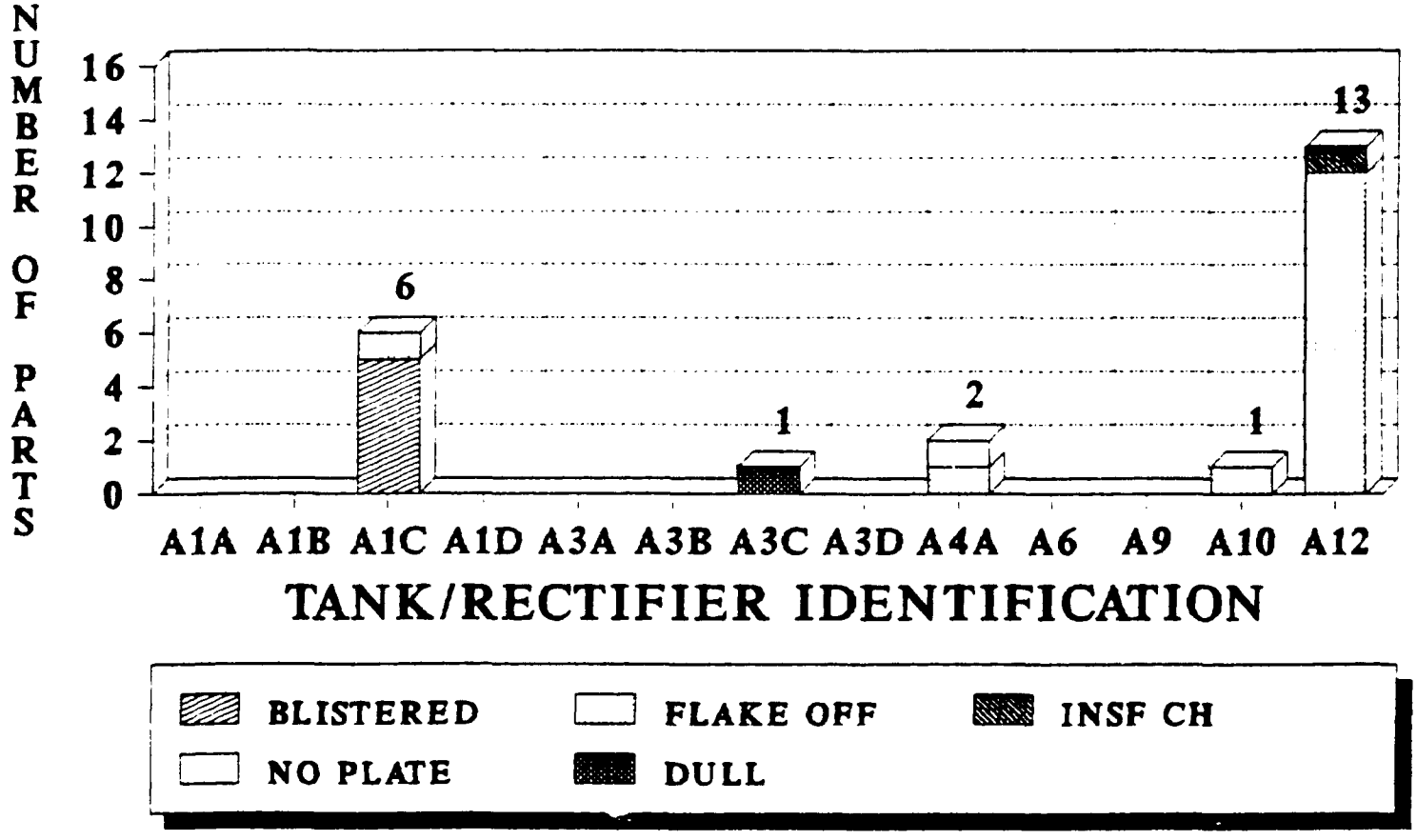

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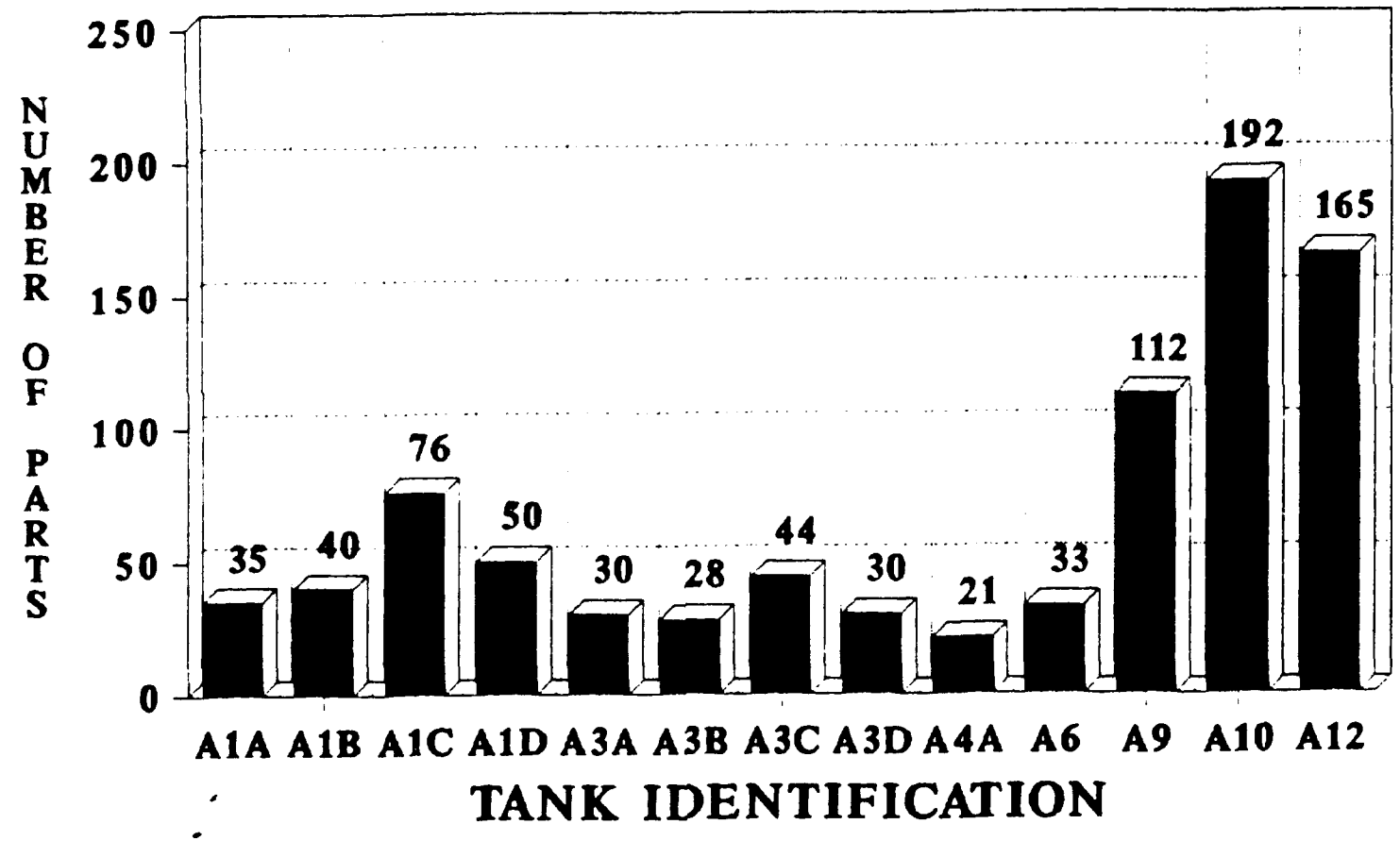

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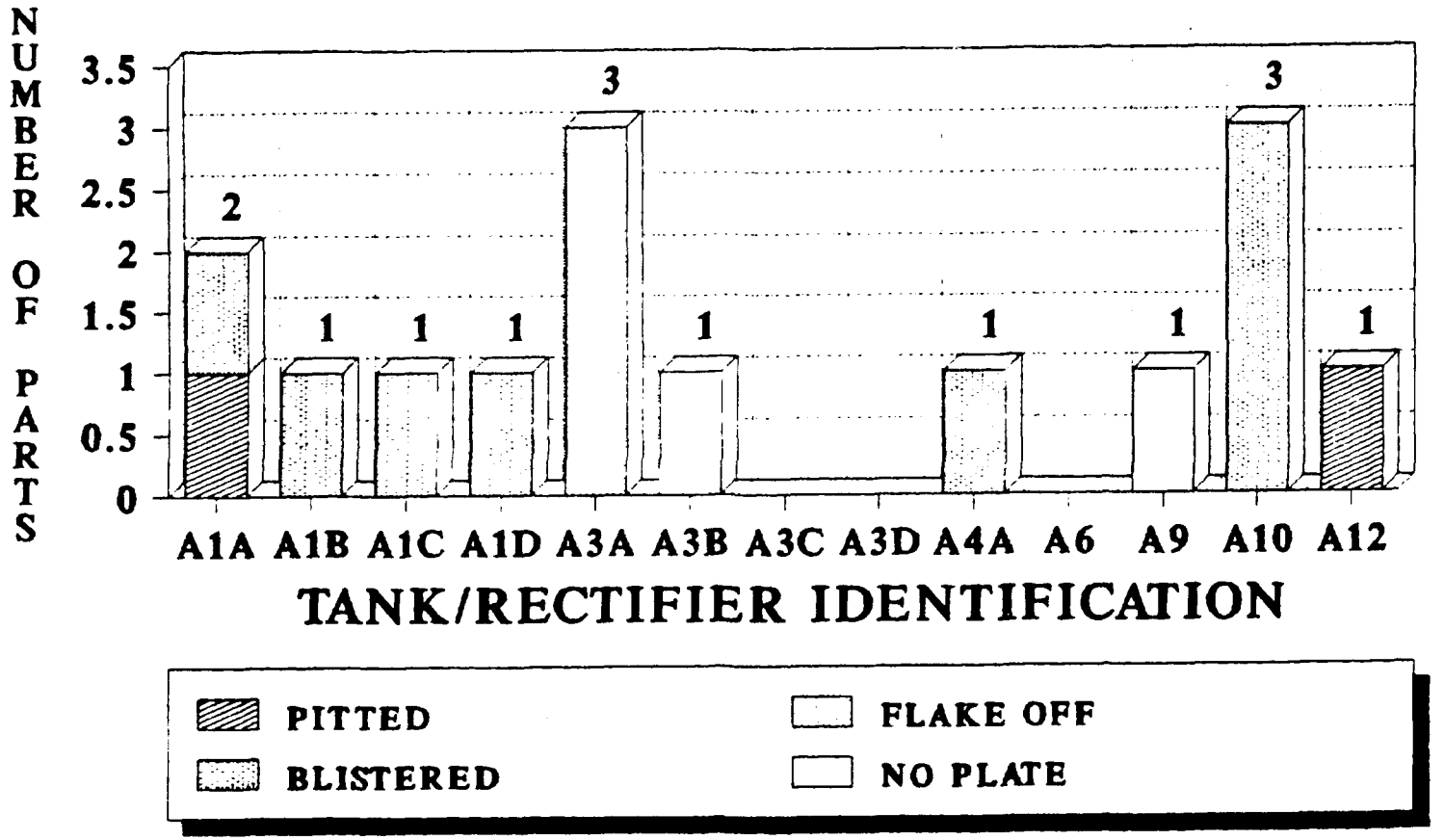

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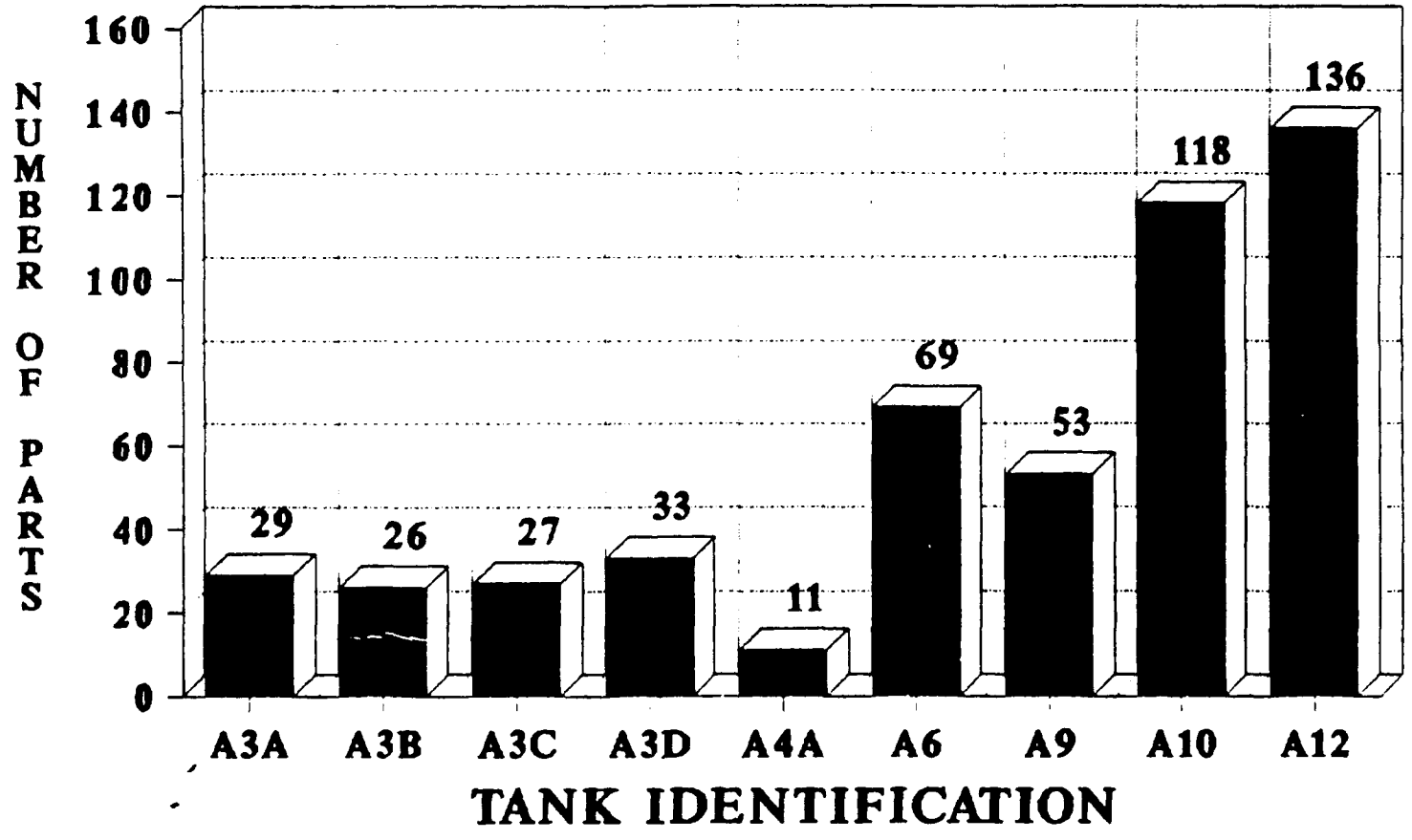

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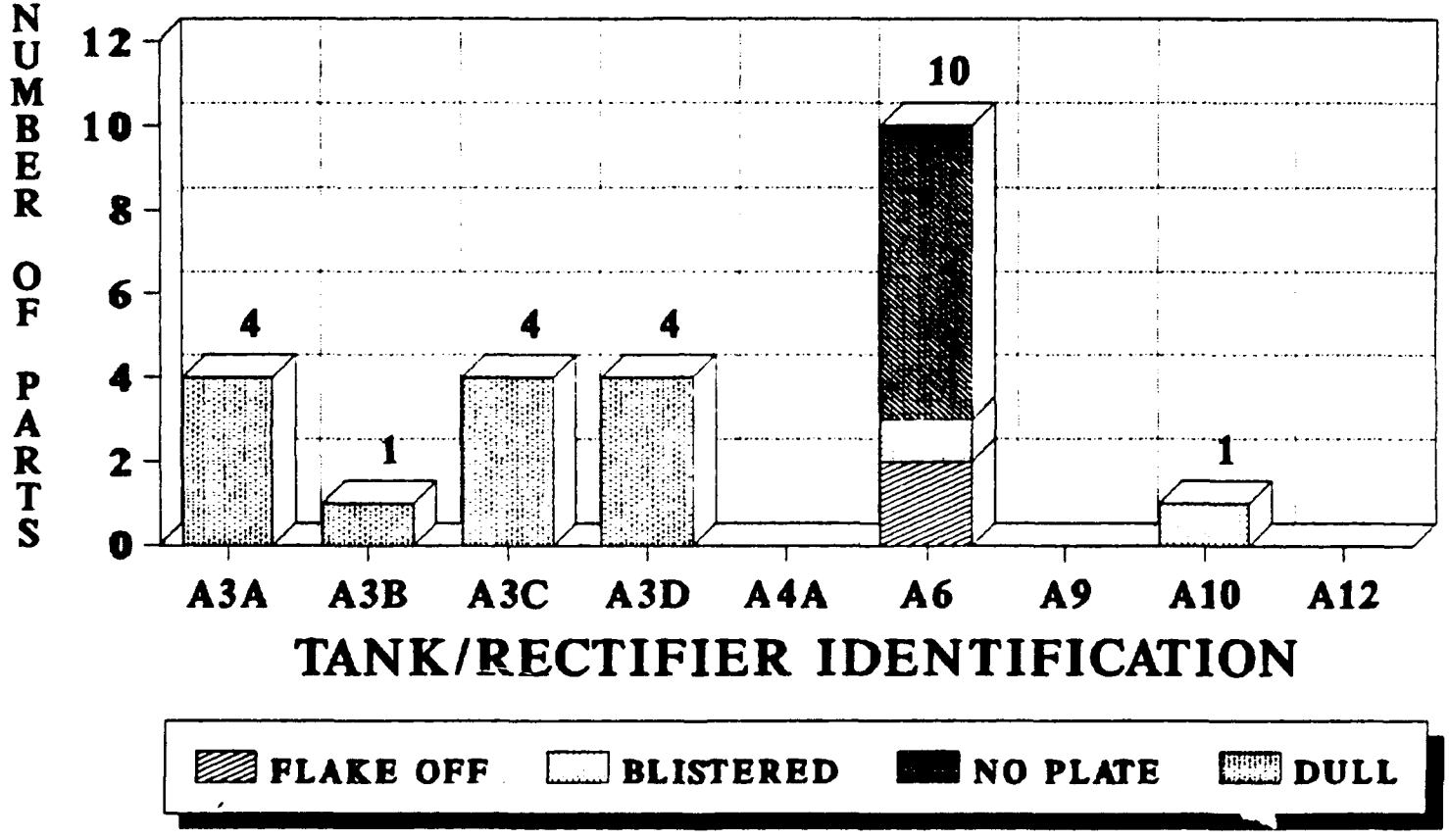
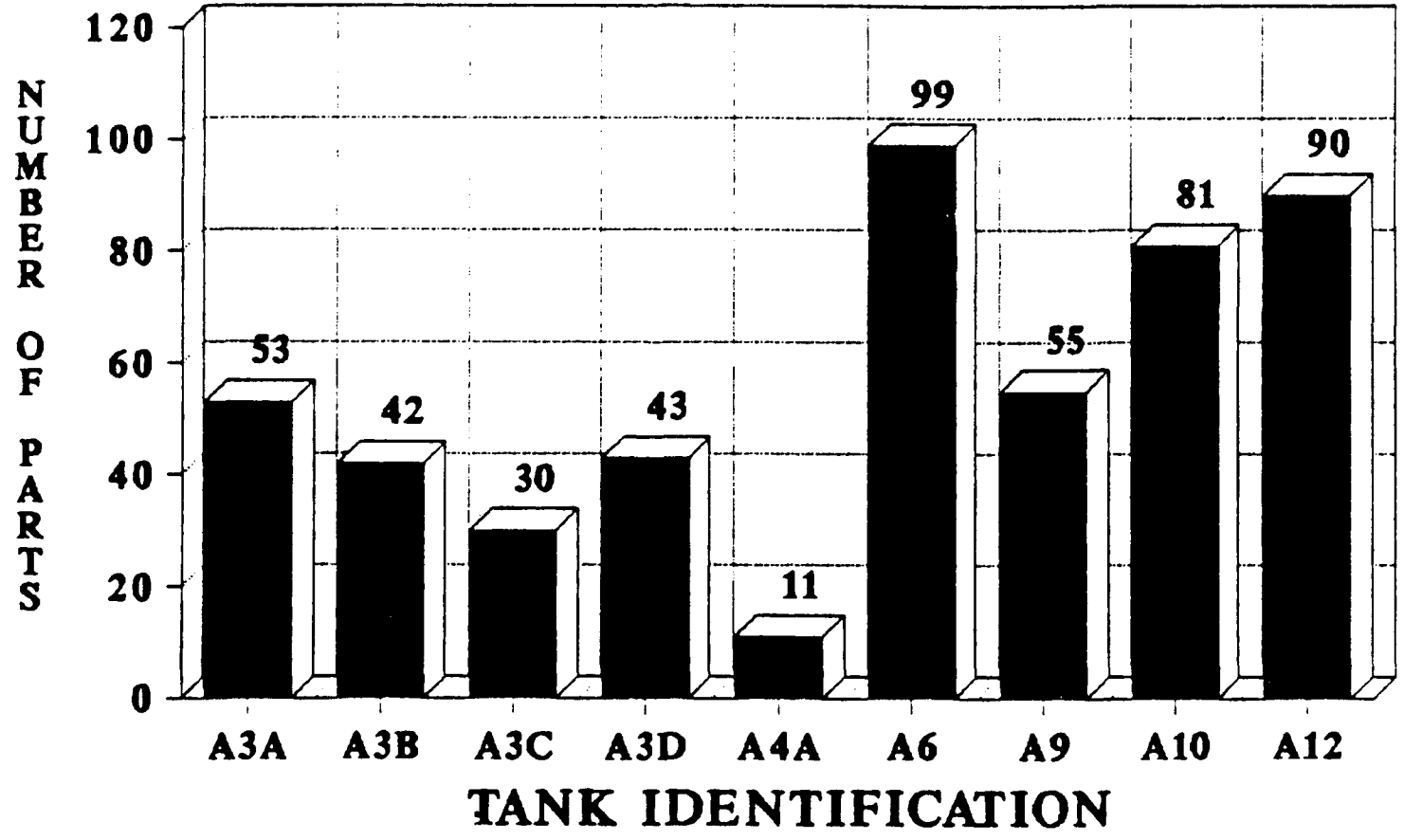
DEFECTS BY TANK/TYPE
MAR 01 THRU MAR 28 1991



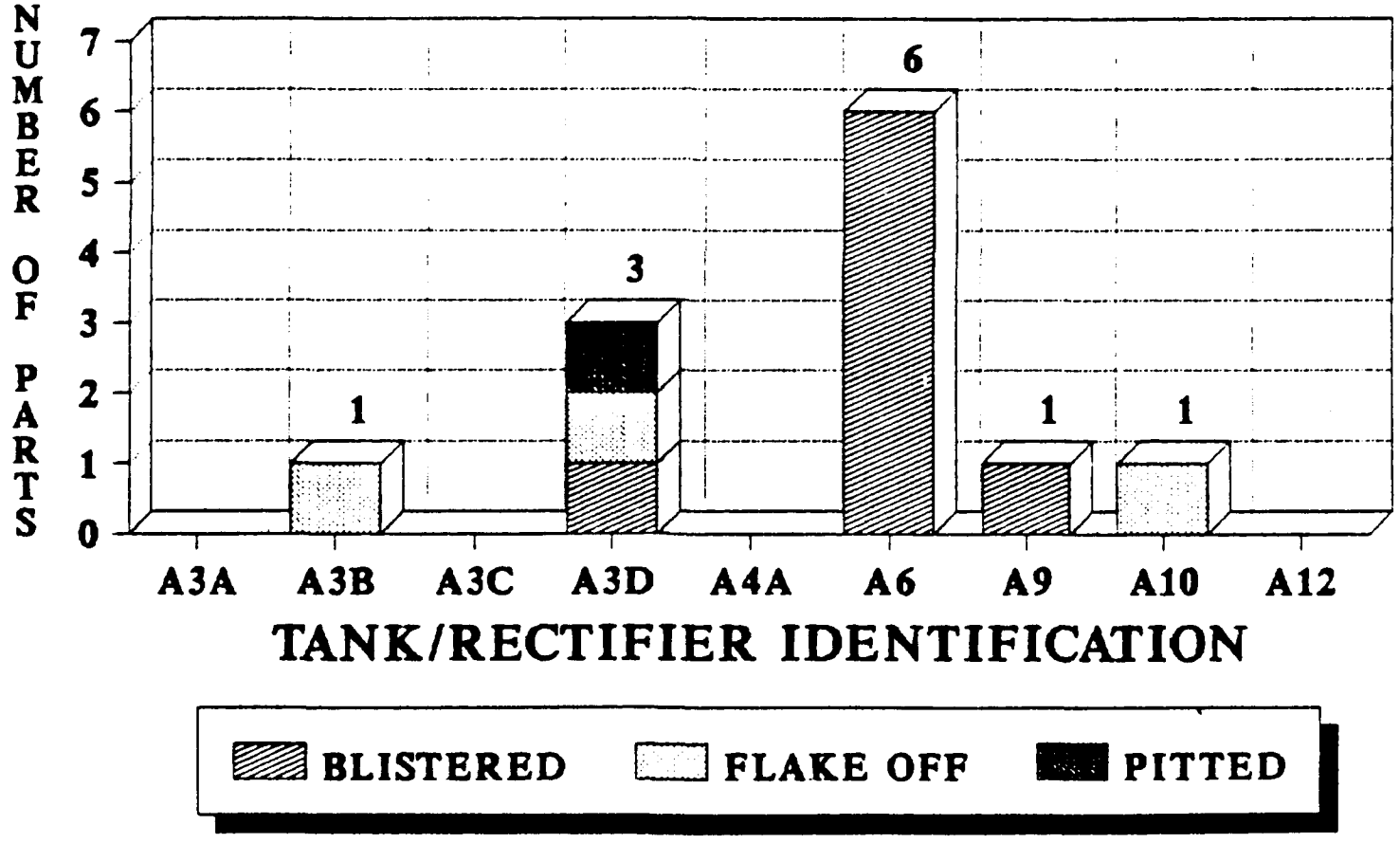
CS4MAR28

CHROME SHOP
504 TOTAL NUMBER PARTS RUN
APR 01 THRU MAY 2 1991



CS1MAY2

CHROME SHOP
DEFECTS BY TANK/TYPE
APR 01 THRU MAY 2 1991



CS4MAY2

APPENDIX B

PHOTOGRAPHS OF THE TEST PROGRAM AND ELECTRODIALYSIS SYSTEM

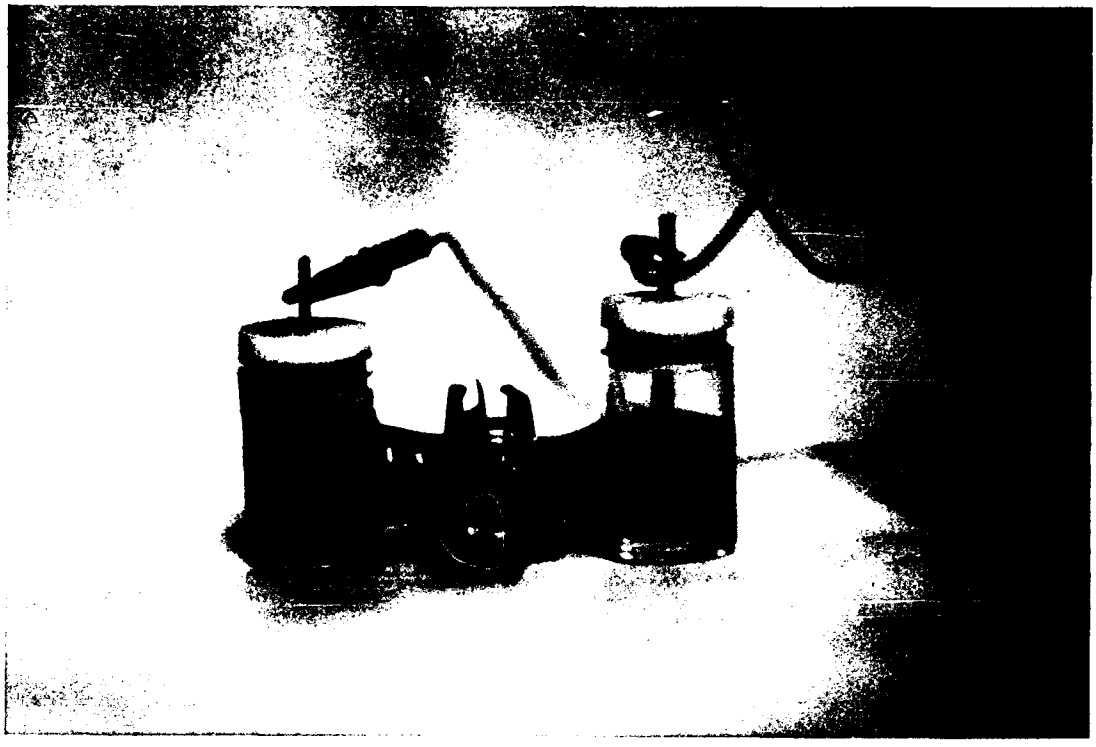


Figure B-1. Electrodialysis minicell (solution shown was not tested during this project).

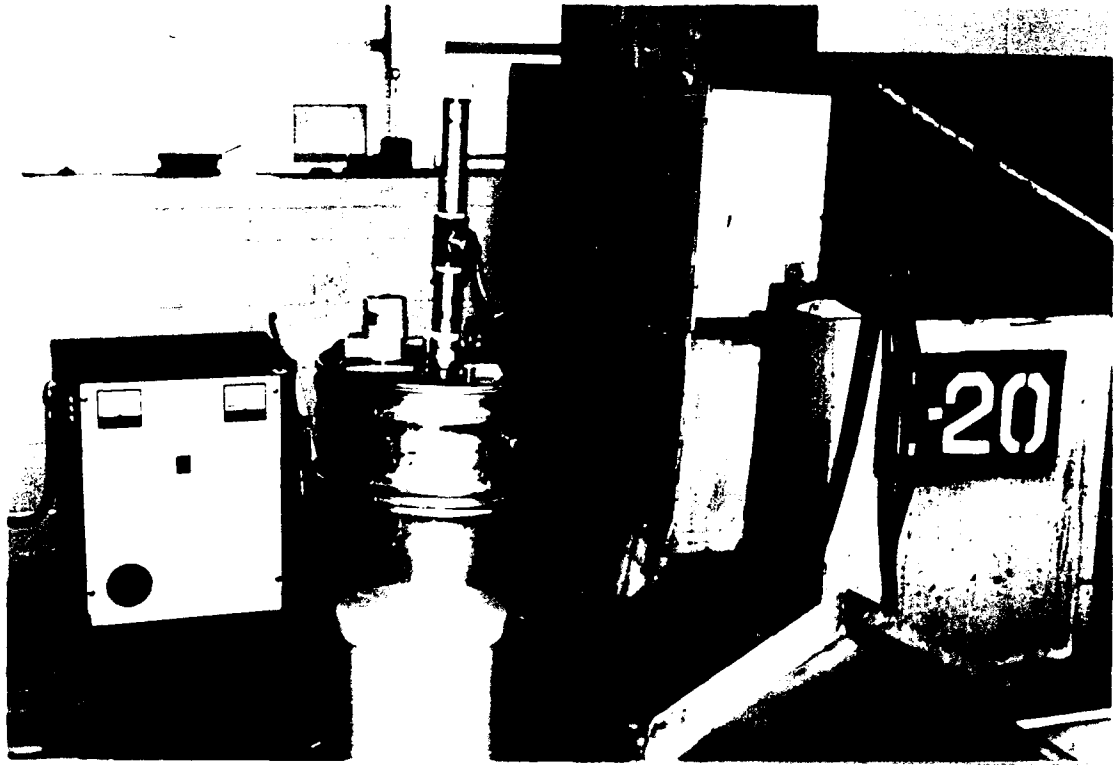


Figure B-2. Electrodialysis system installed on spent chromic acid stripping solution, Tank I-20.

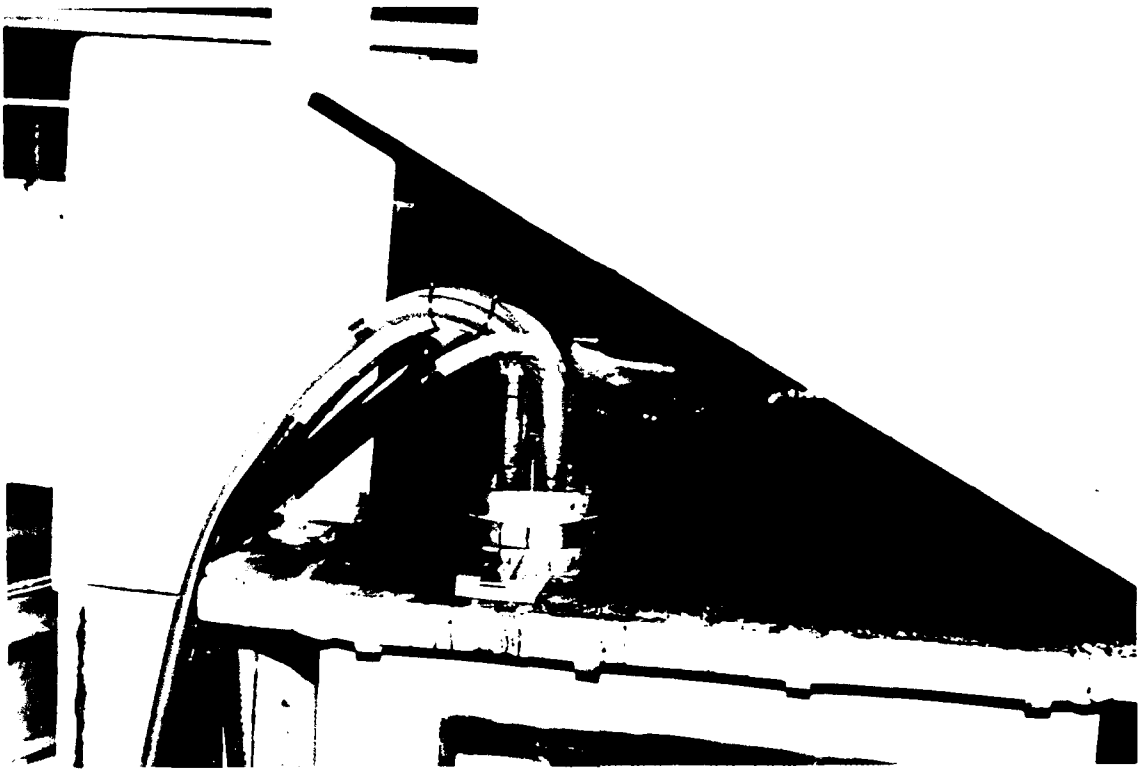


Figure B-3. Closeup of electrodialysis cell in chromic acid stripping tank.

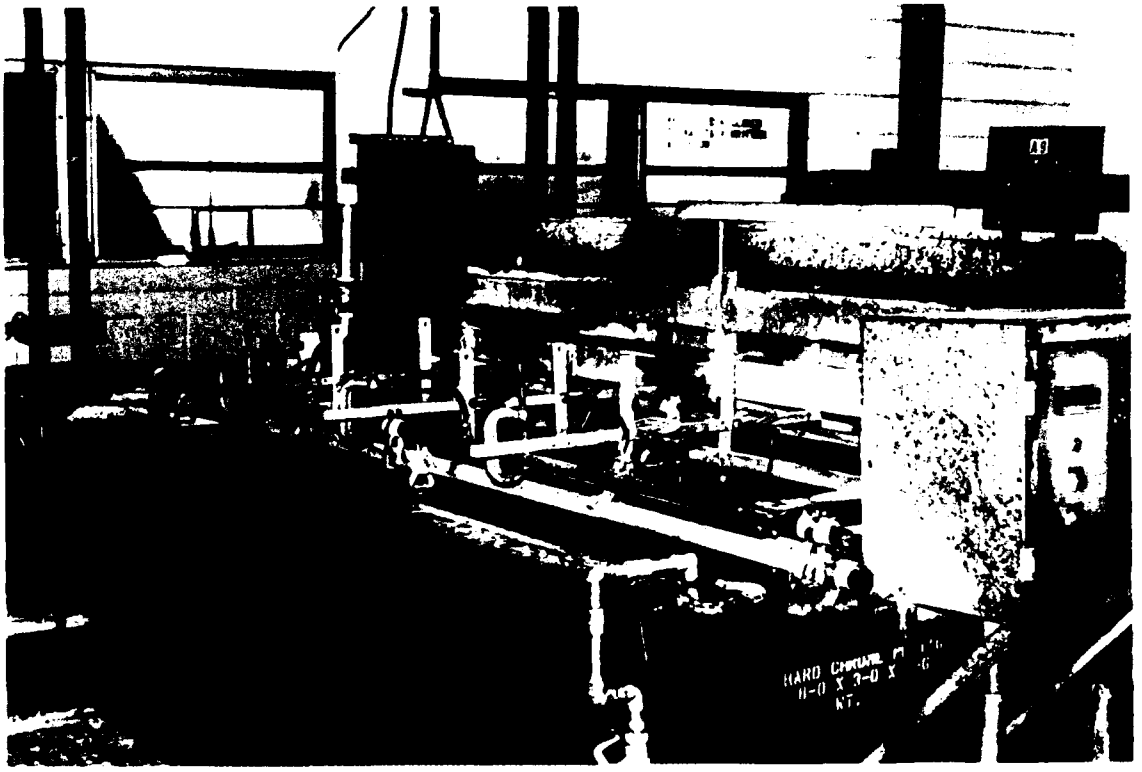


Figure B-4. Electrodialysis system installed on chromium electroplating solution, Tank A-9.

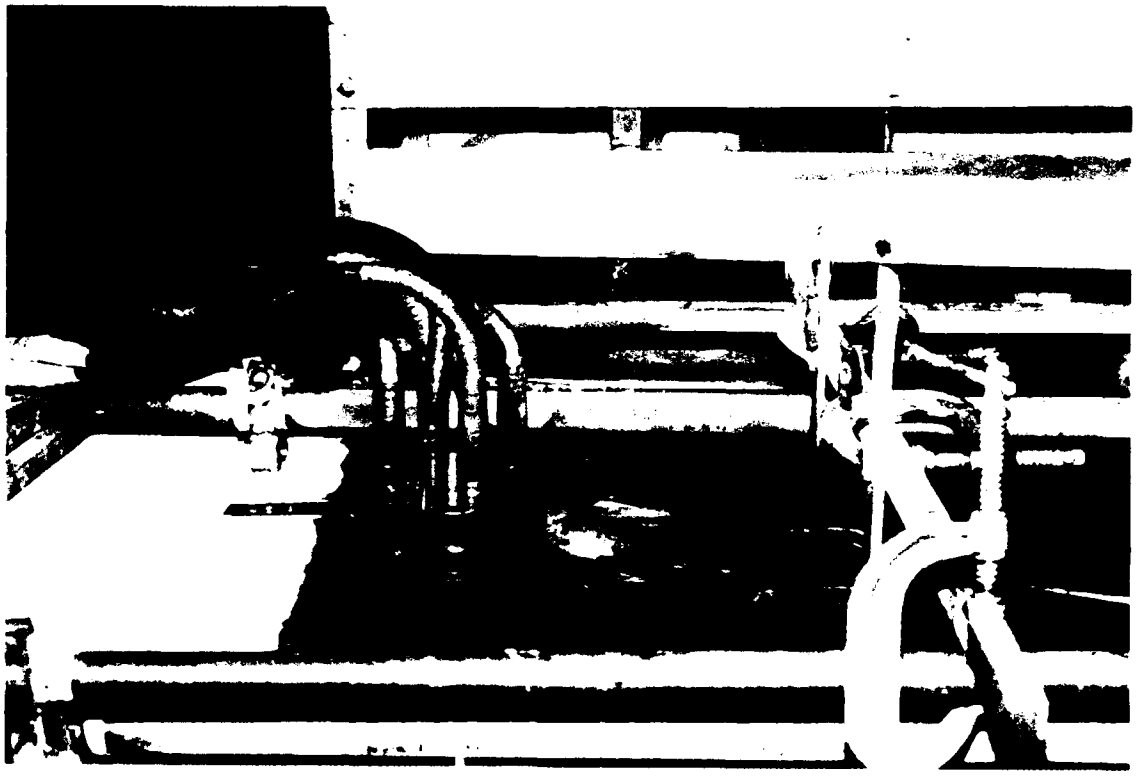


Figure B-5. Closeup of electrodialysis cell in chromium plating tank.

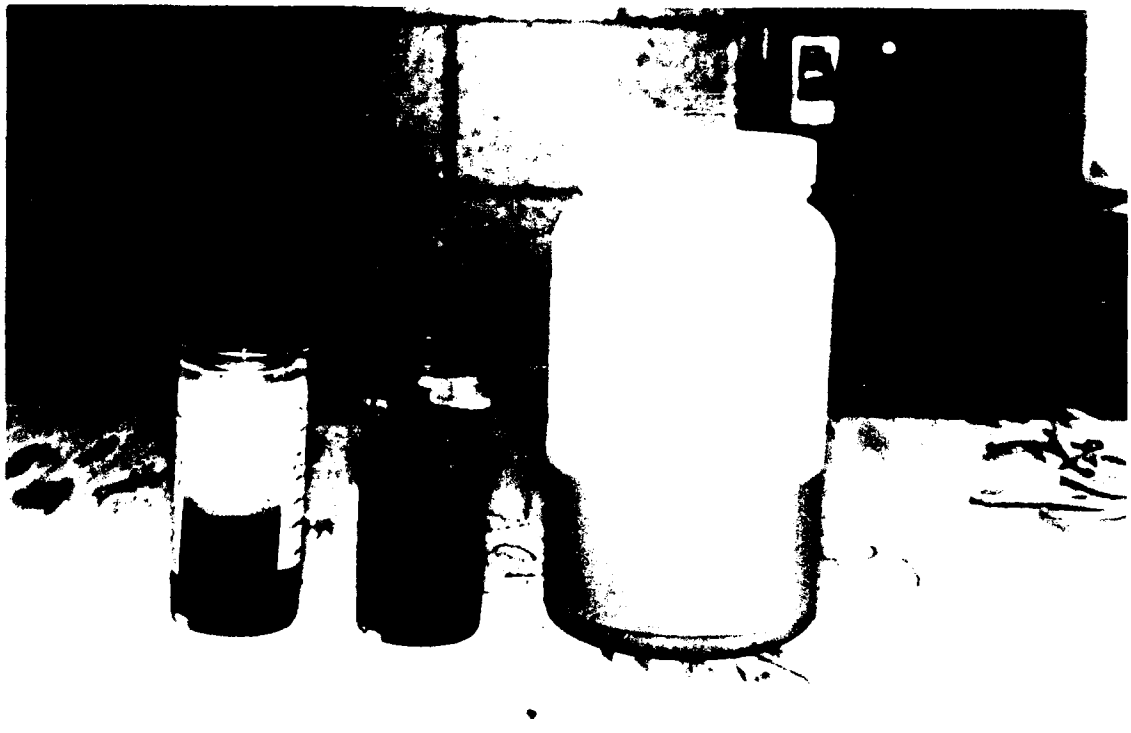


Figure B-6. Catholyte sludge from chromic acid stripping test program.

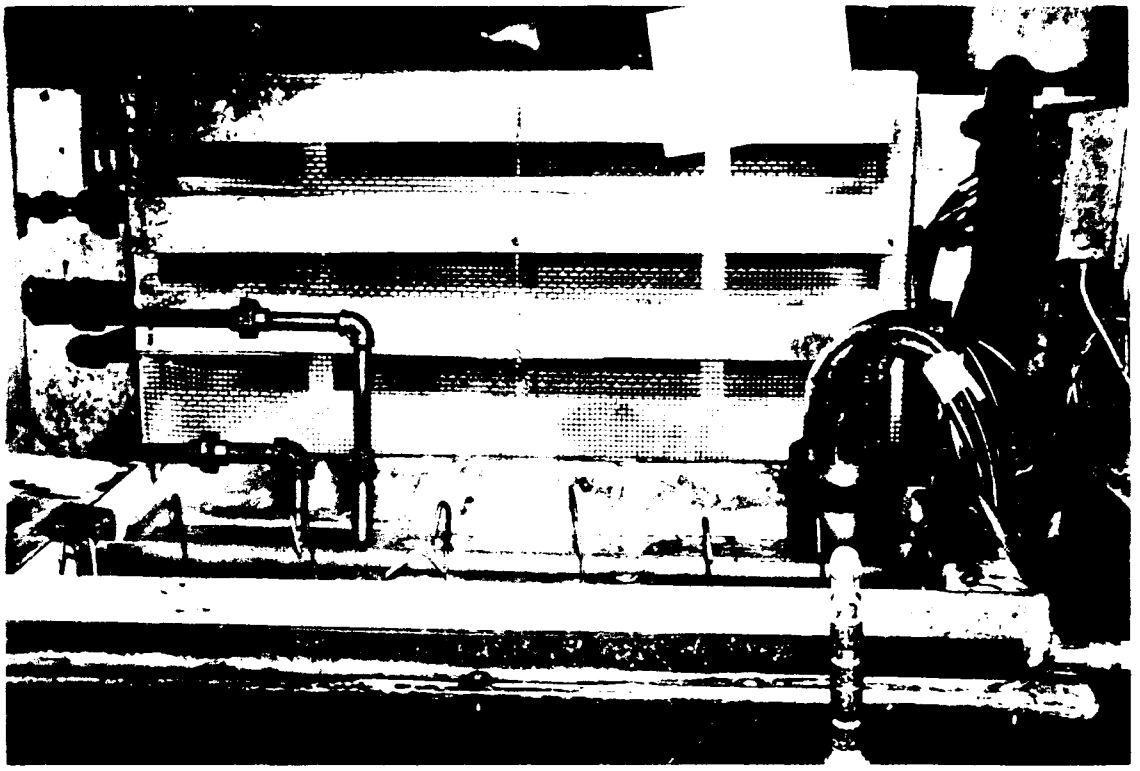


Figure B-7. Electrodialysis system installed on tank I-3.

Figure B-8. Ventilation hood for chromic acid stripping tank (tank lid was partially closed during operation).

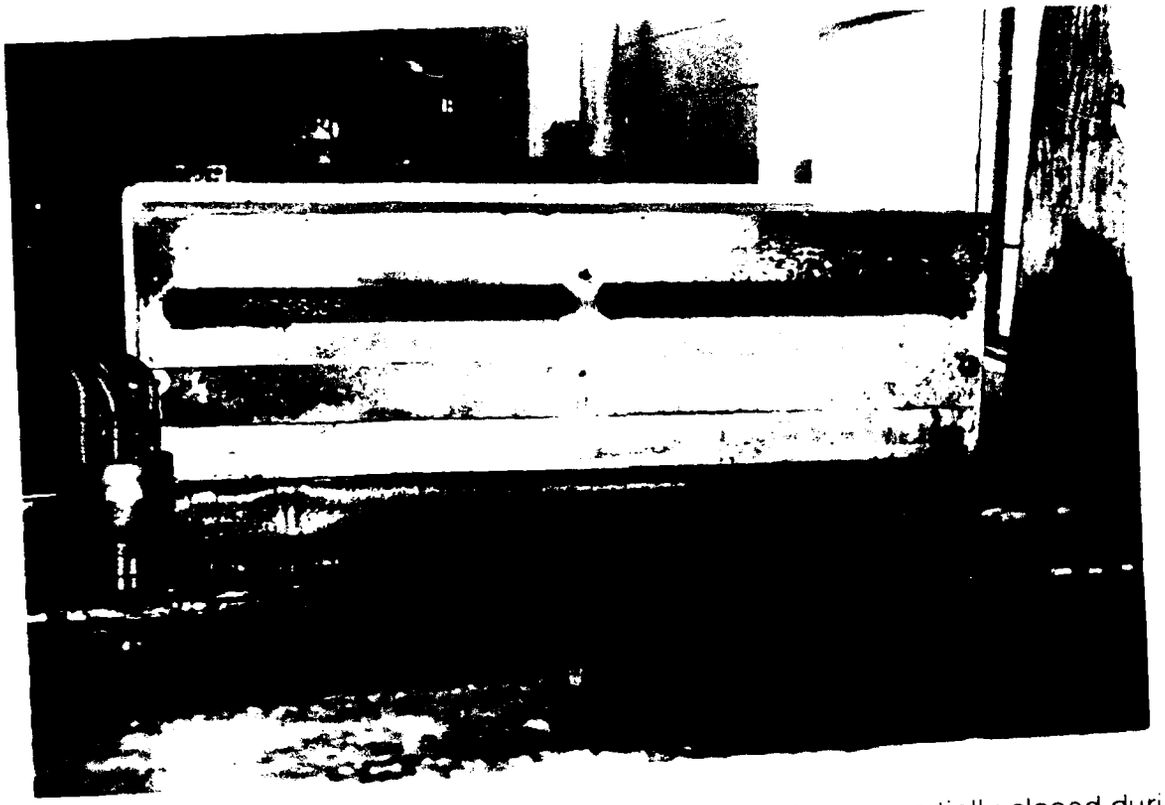


Figure B-9. Ventilation hood with one vent closed (tank lid was partially closed during operation).

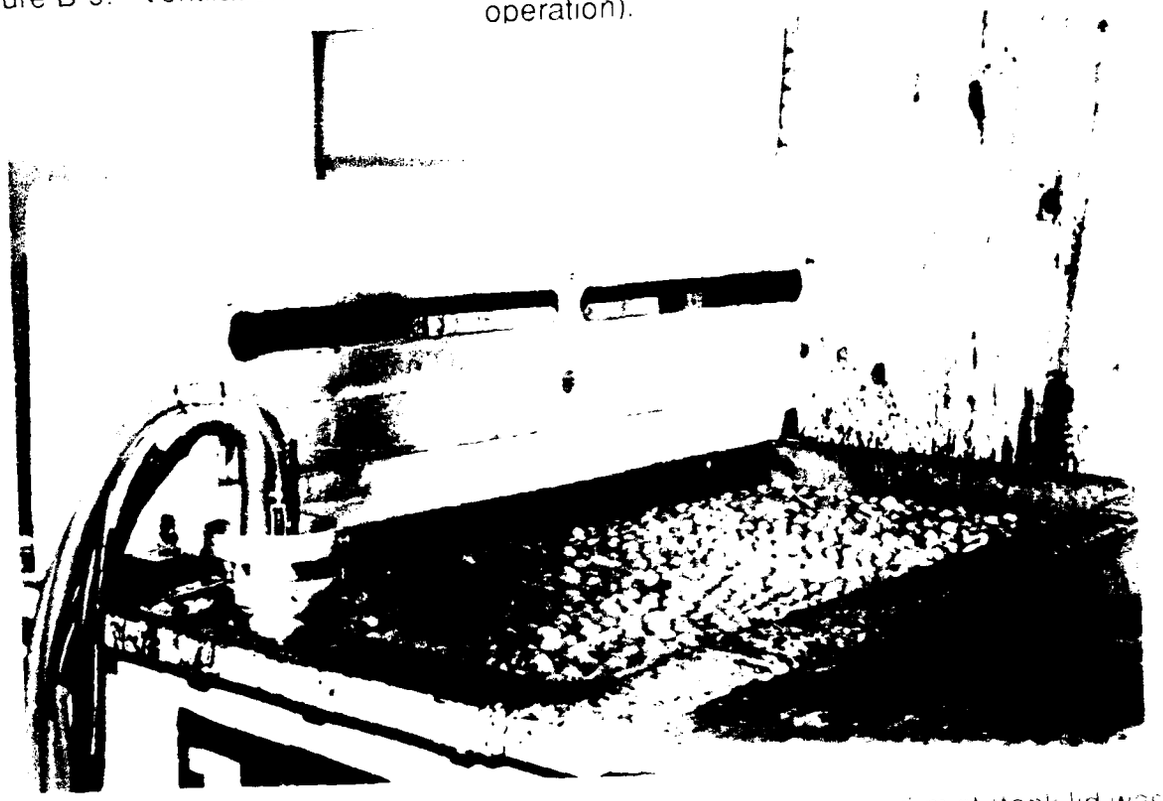


Figure B-10. Tank I-20 with plastic discs to reduce chromic acid mist (tank lid was partially closed during operation).

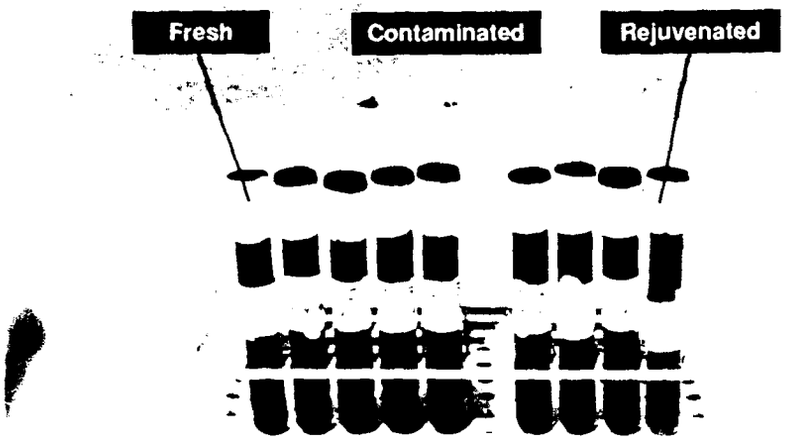


Figure B-11. Visual samples collected during chromic acid stripping test program.

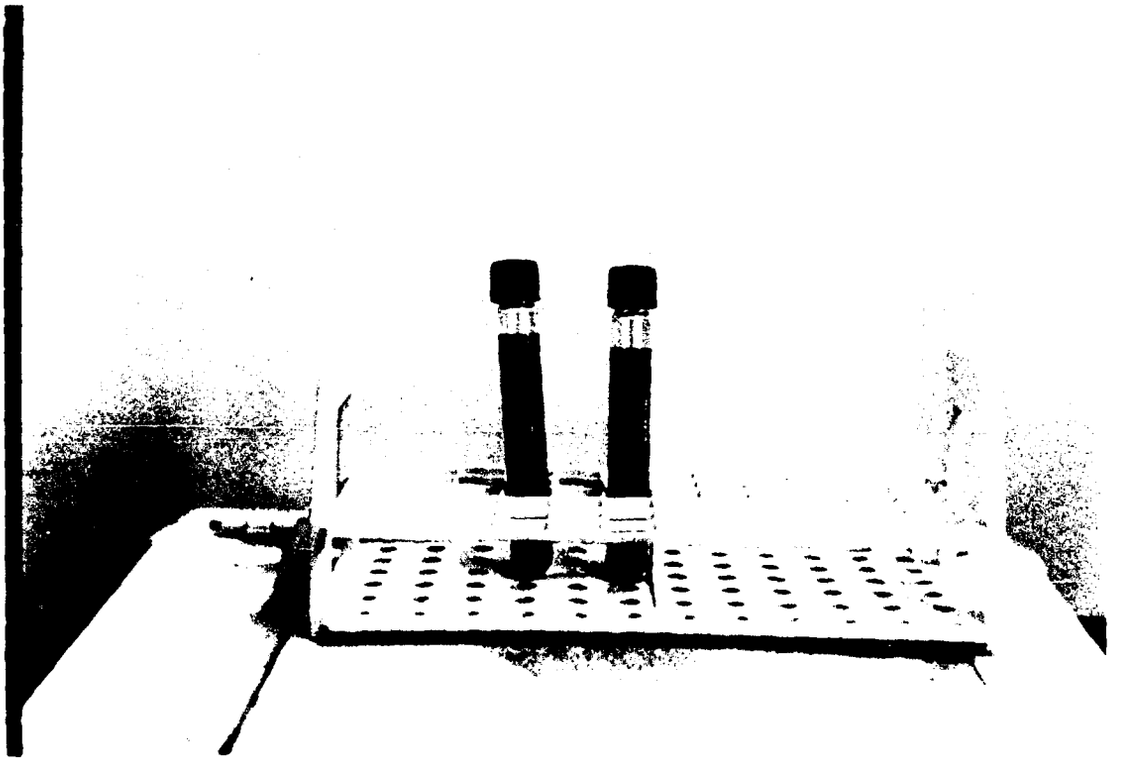


Figure B-12. Visual samples collected at beginning and end of chromium plating test program.

APPENDIX C

OPERATIONAL DATA FOR CHROMIC ACID STRIPPING

Date	Day No.	Hrs	Min.	Voltage	Amperage	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours (cumulative)	Sample No.	Activity
6-Sep	1	9	0	-	-	-	-	-	-	9-6-90-1-2 9-6-90-1-2(c)	
6-Sep	1	9	25	4.0	50	0.0	0.0	0.0			° Start-up of equipment until
6-Sep	1	9	27	4.6	88		0.0	0.0	2		voltage reaches 7 volts
6-Sep	1	9	40	5.0	95		0.0	0.3	22		
6-Sep	1	11	0	5.0	100		0.0	1.6	152		
6-Sep	1	11	0	6.0	160		0.0	1.6	152		
6-Sep	1	12	25	6.0	185		0.0	3.0	397		
6-Sep	1	12	25	7.0	265		0.0	3.0	397		
6-Sep	1	12	30	7.2	292		0.0	3.1	420		
6-Sep	1	13	25	7.0	295		0.0	4.0	689		
6-Sep	1	15	35	7.1	291		0.0	6.2	1324		
6-Sep	1	17	15	7.1	297		0.0	7.8	1814	9-6-90-2-2	
7-Sep	2	8	40	6.8	350		0.0	23.3	6801		
7-Sep	2	9	30	6.8	350		0.0	24.1	7093	9-7-90-1-2	
7-Sep	2	9	45	6.8	350		0.0	24.3	7180		
7-Sep	2	9	45	3.0	0		0.0	24.3	7180	9-7-90-1-2(c)	° Turned down voltage to
7-Sep	2	9	50	3.0	0	0.1	0.1	24.3	7180		collect sample
7-Sep	2	9	50	7.0	380		0.1	24.3	7180		
7-Sep	2	10	30	7.0	370		0.1	25.0	7430		
7-Sep	2	14	0	7.0	360		0.1	28.5	8708		
7-Sep	2	16	15	7.2	357		0.1	30.8	9514		
7-Sep	2	16	15	7.0	340		0.1	30.8	9514		
7-Sep	2	17	0	7.0	334		0.1	31.5	9767	9-7-90-2-2 (NA)*	
7-Sep	2	18	0	7.0	325		0.1	32.5	10096		
8-Sep	3	0	25	7.4	250		0.1	38.9	11941		
8-Sep	3	0	25	7.0	230		0.1	38.9	11941		
8-Sep	3	2	0	7.0	215		0.1	40.5	12294		
8-Sep	3	2	0	0.0	0		0.1	40.5	12294		° Turned off system due to
8-Sep	3	8	30	0.0	0		0.1	40.5	12294	9-8-90-1-2(c)	catholyte sludge buildup
8-Sep	3	10	20	0.0	0	8.3	8.4	40.5	12294		° Changed catholyte
8-Sep	3	10	20	7.0	360		8.4	40.5	12294		
8-Sep	3	15	40	7.0	383		8.4	45.8	14275	9-8-90-1-2	° Restarted system
8-Sep	3	16	10	7.0	385		8.4	46.3	14467		
8-Sep	3	23	0	7.0	385		8.4	53.2	17098		

Date	Day No.	Hrs	Min.	Voltage	Amperage	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours (cumulative)	Sample No.	Activity
9-Sep	4	9	30	7.0	378		8.4	63.7	21103		
10-Sep	5	6	10	7.0	350		8.4	84.3	28626		
10-Sep	5	14	0	7.0	338		8.4	92.2	31321		
10-Sep	5	17	0	7.2	329		8.4	95.2	32321	9-10-90-1-2	
10-Sep	5	17	45	7.2	327		8.4	95.9	32567		
10-Sep	5	17	45	7.0	315		8.4	95.9	32567		
10-Sep	5	24	0	7.0	280		8.4	102.2	34427		
11-Sep	6	9	50	7.2	240		8.4	112.0	36983		
11-Sep	6	9	50	7.0	230		8.4	112.0	36983		
11-Sep	6	13	35	7.0	210		8.4	115.8	37808		
11-Sep	6	16	30	7.2	200		8.4	118.7	38406		
11-Sep	6	16	30	3.0	0		8.4	118.7	38406		° Changed catholyte
11-Sep	6	17	25	3.0	0	0.9	9.3	118.7	38406		
11-Sep	6	17	25	7.0	300		9.3	118.7	38406		° Restarted system
11-Sep	6	17	35	7.0	330		9.3	118.8	38459		
11-Sep	6	17	45	7.0	335		9.3	119.0	38514		
11-Sep	6	24	0	7.0	370		9.3	125.3	40717		
12-Sep	7	8	45	6.8	370		9.3	134.0	43955		
12-Sep	7	8	45	7.0	380		9.3	134.0	43955		
12-Sep	7	9	10	7.0	400		9.3	134.4	44117		
12-Sep	7	9	15	7.0	400		9.3	134.5	44151		
12-Sep	7	9	15	0.0	0		9.3	134.5	44151		° Shut down system to repair
12-Sep	7	11	40	0.0	0		9.3	134.5	44151	9-12-90-1-2 (NA)	ventilation hood
13-Sep	8	12	0	0.0	0	26.8	36.1	134.5	44151		
13-Sep	8	12	0	7.0	375		36.1	134.5	44151		° Restarted system
13-Sep	8	13	45	7.0	408		36.1	136.3	44836		
13-Sep	8	16	15	7.0	425		36.1	138.8	45877		
13-Sep	8	16	15	6.8	400		36.1	138.8	45877		
13-Sep	8	23	0	7.0	450		36.1	145.5	48746		
13-Sep	8	23	0	0.0	0		36.1	145.5	48746		° Turned off by operators
14-Sep	9	7	10	0.0	0	8.2	44.3	145.5	48746		due to high amperage
14-Sep	9	7	10	7.0	410		44.3	145.5	48746		° Restarted system
14-Sep	9	9	40	7.0	450		44.3	148.0	49821		
14-Sep	9	9	40	6.7	400		44.3	148.0	49821		
14-Sep	9	13	30	6.6	390		44.3	151.8	51335	9-14-90-1-2	

Date	Day No.	Hrs	Min.	Voltage	Amperage	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours (cumulative)	Sample No.	Activity
14-Sep	9	13	30	6.7	400		44.3	151.8	51335		
14-Sep	9	15	35	6.8	400		44.3	153.9	52168		
14-Sep	9	23	0	6.8	415		44.3	161.3	55191		
15-Sep	10	6	55	6.8	410		44.3	169.3	58456		
15-Sep	10	13	15	6.8	400		44.3	175.6	61021		
15-Sep	10	23	0	6.8	400		44.3	185.3	64921		
16-Sep	11	6	30	6.8	400		44.3	192.8	67921		
16-Sep	11	6	30	3.0	25		44.3	192.8	67921		° Reduced voltage for weekend
17-Sep	12	6	45	3.0	5	24.2	68.5	192.8	68285		shutdown
17-Sep	12	6	45	7.0	270		68.5	192.8	68285		° Restarted system
17-Sep	12	11	45	7.0	310		68.5	197.8	69735		
17-Sep	12	24	0	7.0	310		68.5	210.1	73532		
18-Sep	13	7	10	7.0	290		68.5	217.3	75682		
18-Sep	13	10	40	7.0	280		68.5	220.8	76680		
18-Sep	13	10	40	0.0	0		68.5	220.8	76680		
18-Sep	13	11	0	0.0	0	0.3	68.8	220.8	76680		° Changed catholyte solution
18-Sep	13	11	0	7.0	400		68.8	220.8	76680		
18-Sep	13	11	40	7.0	450		68.8	221.4	76963		
18-Sep	13	11	40	6.6	400		68.8	221.4	76963		
18-Sep	13	24	0	6.4	400		68.8	233.8	81897		
19-Sep	14	7	5	6.3	400		68.8	240.8	84730		
19-Sep	14	7	5	6.4	400		68.8	240.8	84730		
19-Sep	14	16	0	6.4	400		68.8	249.8	88297		
19-Sep	14	24	0	6.4	400		68.8	257.8	91497		
20-Sep	15	7	0	6.4	400		68.8	264.8	94297		
20-Sep	15	14	0	6.4	380		68.8	271.8	97027	9-20-90-I-20	
21-Sep	16	7	10	6.4	330		68.8	288.9	103121		
21-Sep	16	7	10	7.0	390		68.8	288.9	103121		
21-Sep	16	12	5	8.2	100		68.8	293.8	104325		° Reduced amperage was
21-Sep	16	12	5	7.0	80		68.8	293.8	104325		inital sign of membrane
21-Sep	16	12	15	7.0	80		68.8	294.0	104339		leak
21-Sep	16	12	15	7.0	280		68.8	294.0	104339		° Added water to catholyte
21-Sep	16	12	45	7.0	280		68.8	294.5	104479		solution
21-Sep	16	12	45	0.0	0		68.8	294.5	104479		° Changed catholyte solution
21-Sep	16	13	20	0.0	0	0.6	69.4	294.5	104479		

Date	Day No.	Hrs	Min.	Voltage	Amperage	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours (cumulative)	Sample No.	Activity
21-Sep	16	13	20	7.0	340		69.4	294.5	104479		° Restarted system
21-Sep	16	15	0	7.0	270		69.4	296.2	104987		
21-Sep	16	18	20	7.0	340		69.4	299.5	106004		
21-Sep	16	18	20	0.0	0		69.4	299.5	106004		° Turned off system due to leaking membrane
2-Oct	27	15	30	0.0	0		69.4	299.5	106004	10-2-90-I-20	
2-Oct	27	15	30	4.0	85	261.2	330.6	299.5	106004		° Restarted system with new membrane and catholyte
2-Oct	27	16	30	4.0	90		330.6	300.5	106091		
2-Oct	27	16	30	4.5	130		330.6	300.5	106091		
2-Oct	27	17	50	4.5	135		330.6	301.8	106268		
2-Oct	27	17	50	5.0	180		330.6	301.8	106268	10-2-90-I-20(c)	
2-Oct	27	24	0	5.0	200		330.6	308.0	107439		
3-Oct	28	7	45	4.9	190		330.6	315.8	108951		
3-Oct	28	7	45	5.5	250		330.6	315.8	108951	10-3-90-I-20(c)-1	
3-Oct	28	8	45	5.5	260		330.6	316.8	109206		
3-Oct	28	8	45	6.0	310		330.6	316.8	109206		
3-Oct	28	8	45	6.0	315		330.6	316.8	109206		
3-Oct	28	9	45	6.5	370		330.6	317.8	109548		
3-Oct	28	13	30	6.4	385		330.6	321.5	110964		
3-Oct	28	13	30	6.6	400		330.6	321.5	110964		
3-Oct	28	16	15	6.6	412		330.6	324.3	112080		
3-Oct	28	16	15	6.4	385		330.6	324.3	112080		
3-Oct	28	16	25	6.4	410		330.6	324.4	112147		
3-Oct	28	16	25	6.2	380		330.6	324.4	112147	10-3-90-I-20(c)-2	
3-Oct	28	24	0	6.2	400		330.6	332.0	115104		
4-Oct	29	7	50	6.0	390		330.6	339.8	118198		
4-Oct	29	7	50	6.2	400		330.6	339.8	118198		
4-Oct	29	10	45	6.2	400		330.6	342.8	119365	10-4-90-I-20(c)-1	
4-Oct	29	14	50	6.2	400		330.6	346.8	120998		
4-Oct	29	14	50	0.0	0		330.6	346.8	120998		° Turned off for scheduled long-weekend power outage
10-Oct	35	9	10	0.0	0	138.3	468.9	346.8	120998		° Restarted system
10-Oct	35	9	10	6.0	250		468.9	346.8	120998		
10-Oct	35	9	30	7.0	350		468.9	347.2	121098		
10-Oct	35	24	0	6.1	380		468.9	361.7	126391		
12-Oct	37	7	0	6.1	380		468.9	392.7	138171		

Date	Day No.	Hrs	Min.	Voltage	Amperage	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours (cumulative)	Sample No.	Activity
12-Oct	37	8	30	6.2	400		468.9	394.2	138756		
12-Oct	37	12	30	6.2	420		468.9	398.2	140396		
12-Oct	37	12	31	6.0	400		468.9	398.2	140403		
13-Oct	38	24	0	6.1	390		468.9	433.7	154419		
14-Oct	39	7	0	6.1	390		468.9	440.7	157149		° Weekend shutdown
14-Oct	39	7	0	0.0	0		468.9	440.7	157149		
15-Oct	40	6	15	0.0	0		468.9	463.9	157149		° Restarted system
15-Oct	40	6	15	6.0	340		468.9	463.9	157149		
15-Oct	40	24	0	6.1	380		468.9	481.7	163539		
16-Oct	41	7	0	6.1	370		468.9	488.7	166164		
16-Oct	41	15	20	6.0	380		468.9	497.0	169289		
16-Oct	41	24	0	6.0	380		468.9	505.7	172582		
17-Oct	42	7	7	6.0	380		468.9	512.8	175286		
17-Oct	42	10	30	6.0	385		468.9	516.2	176580		
17-Oct	42	24	0	6.0	400		468.9	529.7	181879		
18-Oct	43	7	0	6.0	400		468.9	536.7	184679		
18-Oct	43	24	0	6.0	380		468.9	553.7	191309		
19-Oct	44	7	0	6.0	360		468.9	560.7	193899		
19-Oct	44	10	30	6.0	360		468.9	564.2	195159		
20-Oct	45	7	0	6.0	360		468.9	584.7	202539		
20-Oct	45	9	0	6.0	360		468.9	586.7	203259	10-22-90-I-20(c)	
20-Oct	45	12	0	6.0	360		468.9	589.7	204339		
20-Oct	45	14	30	6.0	360		468.9	592.2	205239		
20-Oct	45	14	30	0.0	0.00		468.9	592.2	205239		° End rejuvenation experiment
22-Oct	47	8	30	0.0	0.00	-	-	-	205239	10-22-90-I-20	° Disposed of final catholyte solution

APPENDIX D

OPERATIONAL DATA FOR CHROMIUM ELECTROPLATING

Date 1991	Day No.	Hrs	Min.	Voltage	Amperage	Hours after start	Days after start	Hrs shut down	Cum. hrs. down	Cum hrs of operation	amp-hours incremental	amp-hours (cumulative)	Sample No.	Activity
22-Jan	1	15	30	3.0	15	0.0	0.00	0.0	0	0.0			1-22-91-A-9	° Start-up of system with new membrane; collected sample
22-Jan	1	16	0	3.0	20	0.5	0.02		0	0.5	9	9		
22-Jan	1	16	0	3.5	65	0.5	0.02		0	0.5	0	9		
22-Jan	1	16	30	3.5	65	1.0	0.04		0	1.0	33	41		
22-Jan	1	16	30	4.0	115	1.0	0.04		0	1.0	0	41		
22-Jan	1	17	0	4.0	125	1.5	0.06		0	1.5	60	101		
22-Jan	1	17	0	4.5	185	1.5	0.06		0	1.5	0	101		
23-Jan	2	9	25	4.4	195	18	0.75		0	18	3119	3220		
23-Jan	2	9	25	5.0	275	18	0.75		0	18	0	3220		
23-Jan	2	10	8	5.0	278	19	0.78		0	19	198	3419		
23-Jan	2	10	8	5.5	355	19	0.78		0	19	0	3419	1-23-91-C	° Collected catholyte sample
23-Jan	2	10	45	5.5	351	19	0.80		0	19	218	3636		
23-Jan	2	10	45	5.8	400	19	0.80		0	19	0	3636		
23-Jan	2	15	50	5.8	410	24	1.01		0	24	2059	5695		
23-Jan	2	15	50	5.7	389	24	1.01		0	24	0	5695		
24-Jan	3	10	15	5.6	409	43	1.78		0	43	7348	13043		
24-Jan	3	11	25	5.7	410	44	1.83		0	44	478	13521		
24-Jan	3	12	0	5.7	410	45	1.85		0	45	239	13760	1-24-91-A-9 &	° Collected sample
24-Jan	3	13	53	5.6	395	46	1.93		0	46	758	14518	1-24-91-C (visual)	
24-Jan	3	14	45	5.6	395	47	1.97		0	47	342	14861		
24-Jan	3	16	0	5.6	395	49	2.02		0	49	494	15354		° Began processing parts
24-Jan	3	16	50	5.6	405	49	2.06		0	49	333	15688		
24-Jan	3	16	50	5.5	382	49	2.06		0	49	0	15688		
25-Jan	4	9	5	5.5	392	66	2.73		0	66	6289	21976		°1.2 gallons in overflow
25-Jan	4	9	40	5.5	385	66	2.76		0	66	227	22203	1-25-91-C	° Collected sample of catholyte
25-Jan	4	9	47	5.5	365	66	2.76		0	66	44	22247		for Cr+6; added 1/4 lb Na metabisulfite
25-Jan	4	11	10	5.5	375	68	2.82		0	68	512	22759		
25-Jan	4	12	50	5.5	379	69	2.89		0	69	628	23387		
25-Jan	4	14	10	5.5	385	71	2.94		0	71	509	23896	1-25-91-C2	° Collected catholyte sample
26-Jan	5	14	45	5.5	385	95	3.97		0	95	9465	33361		
26-Jan	5	14	45	0.0	0	95	3.97		0	95	0	33361		° Pulled cell out for weekend shutdown
28-Jan	7	7	15	0.0	0	136	5.66	40.5	41	95	0	33361		
28-Jan	7	7	15	5.5	290	136	5.66		41	95	0	33361		° Put cell back in, turned on
29-Jan	8	7	0	5.5	370	160	6.65		41	119	7838	41198		
29-Jan	8	15	30	5.5	360	168	7.00		41	128	3103	44301		
29-Jan	8	16	25	5.5	360	169	7.04		41	128	330	44631		
29-Jan	8	16	25	0.0	0	169	7.04		41	128	0	44631		° Emptied 7-gallon container
29-Jan	8	16	30	0.0	0	169	7.04	0.1	41	128	0	44631		
29-Jan	8	16	30	5.5	360	169	7.04		41	128	0	44631		
29-Jan	8	23	0	5.5	365	176	7.31		41	135	2356	46987		
30-Jan	9	7	0	5.5	368	184	7.65		41	143	2932	49919		° 1.5 gal in container
30-Jan	9	15	0	5.5	370	192	7.98		41	151	2952	52871		° 2 gal in container

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30-Jan	9	23	0	5.5	390	200	8.31		41	159	3040	55911		
31-Jan	10	8	0	5.5	375	209	8.69		41	168	3443	59354		° 3.75 gallon in container
31-Jan	10	12	0	5.5	372	213	8.85		41	172	1494	60848	1-31-A-9*	
31-Jan	10	15	15	5.5	370	216	8.99		41	175	1206	62054		
1-Feb	11	0	10	5.5	370	225	9.36		41	184	3299	65353		
1-Feb	11	2	0	5.0	375	227	9.44		41	186	683	66036		
1-Feb	11	7	0	5.5	369	232	9.65		41	191	1860	67896		° 4.75 gal in container
1-Feb	11	23	0	5.5	370	248	10.31		41	207	5912	73808		
2-Feb	12	8	0	5.5	370	257	10.69		41	216	3330	77138		
2-Feb	12	8	0	0.0	0	257	10.69		41	216	0	77138		° Took out cell for weekend
4-Feb	14	6	0	0.0	0	303	12.60	46.0	87	216	0	77138		shutdown; emptied overflow
4-Feb	14	6	0	5.5	325	303	12.60		87	216	0	77138		° Put cell back in
5-Feb	15	7	30	5.5	350	328	13.67		87	241	8606	85745		
5-Feb	15	15	30	5.5	351	336	14.00		87	249	2804	88549		
6-Feb	16	8	30	5.5	361	353	14.71		87	266	6052	94601		
6-Feb	16	14	0	5.5	370	359	14.94		87	272	2010	96611		° 4.5 gallon in container
6-Feb	16	20	45	5.5	365	365	15.22		87	279	2481	99091		
7-Feb	17	7	30	5.5	350	376	15.67		87	289	3843	102935		° 5.5 gallon in container
7-Feb	17	16	0	5.5	350	385	16.02		87	298	2975	105910		° Emptied 6.5 gallon from
7-Feb	17	23	0	5.5	360	392	16.31		87	305	2485	108395		container
8-Feb	18	3	0	5.5	360	396	16.48		87	309	1440	109835		
8-Feb	18	23	0	5.7	350	416	17.31		87	329	7100	116935		
9-Feb	19	23	55	5.7	360	440	18.35		87	354	8845	125780		
10-Feb	20	7	30	5.5	350	448	18.67		87	361	2692	128472		
10-Feb	20	15	0	5.5	350	456	18.98		87	369	2625	131097		
10-Feb	20	15	0	0.0	0	456	18.98		87	369	0	131097		° Pulled cell out for weekend
11-Feb	21	7	30	0.0	0	472	19.67	16.5	103	369	0	131097		shutdown
11-Feb	21	7	30	5.5	300	472	19.67		103	369	0	131097		° Emptied 6 gallons; put cell
11-Feb	21	15	30	5.5	333	480	20.00		103	377	2532	133629		back in
11-Feb	21	22	0	5.5	330	487	20.27		103	383	2155	135784		
12-Feb	22	8	0	5.5	320	497	20.69		103	393	3250	139034		
12-Feb	22	23	0	5.5	330	512	21.31		103	408	4875	143909		
13-Feb	23	7	0	5.5	323	520	21.65		103	416	2612	146521		
13-Feb	23	15	30	5.5	310	528	22.00		103	425	2690	149211		
13-Feb	23	21	30	5.5	330	534	22.25		103	431	1920	151131		
14-Feb	24	7	15	5.5	310	544	22.66		103	441	3120	154251		
14-Feb	24	12	0	5.5	313	549	22.85		103	445	1480	155731	2-14-91-A-9*	
14-Feb	24	22	20	5.5	320	559	23.28		103	456	3271	159002		
15-Feb	25	7	15	5.5	320	568	23.66		103	465	2853	161856		
15-Feb	25	15	15	5.5	320	576	23.99		103	473	2560	164416		° Emptied 6.5 gal. from overflow
15-Feb	25	15	15	0.0	0	576	23.99		103	473	0	164416		° Weekend shutdown
19-Feb	29	6	0	0.0	0	663	27.60	86.8	190	473	0	164416		
19-Feb	29	6	0	5.5	180	663	27.60		190	473	0	164416		° Put cell membrane back in and
19-Feb	29	9	0	5.5	240	666	27.73		190	476	630	165046		started up

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19-Feb	29	16	0	5.5	312	673	28.02		190	483	1932	166978		
20-Feb	30	1	0	5.5	320	682	28.40		190	492	2844	169822		
20-Feb	30	7	0	5.5	310	688	28.65		190	498	1890	171712		
20-Feb	30	16	0	5.5	310	697	29.02		190	507	2790	174502		
21-Feb	31	1	0	5.5	320	706	29.40		190	516	2835	177337		
21-Feb	31	7	30	5.5	310	712	29.67		190	522	2048	179384		
21-Feb	31	15	30	5.5	300	720	30.00		190	530	2440	181824		
22-Feb	32	17	15	5.5	299	746	31.07		190	556	7712	189536		
23-Feb	33	15	0	5.5	300	768	31.98		190	578	6514	196050		
23-Feb	33	15	0	0.0	0	768	31.98		190	578	0	196050		° Took cell out; emptied 6.5 gal.
25-Feb	35	7	30	0.0	0	808	33.67	40.5	230	578	0	196050		Weekend shutdown
25-Feb	35	7	30	5.5	230	808	33.67		230	578	0	196050		° Put cell back
26-Feb	36	7	45	5.5	284	832	34.68		230	602	6232	202283		
26-Feb	36	16	0	5.5	292	841	35.02		230	610	2376	204659		
27-Feb	37	0	5	5.5	280	849	35.36		230	618	2312	206970		
27-Feb	37	7	0	5.5	279	856	35.65		230	625	1933	208904		
27-Feb	37	13	30	5.5	279	862	35.92		230	632	1814	210717		
27-Feb	37	13	30	0.0	0	862	35.92		230	632	0	210717		° Turned off and emptied; added new
27-Feb	37	14	0	0.0	0	863	35.94	0.5	231	632	0	210717		catholyte solution from barrel
27-Feb	37	14	0	5.5	200	863	35.94		231	632	0	210717		° Turned on
28-Feb	38	1	0	5.5	320	874	36.40		231	643	2860	213577		
28-Feb	38	7	30	5.5	310	880	36.67		231	649	2048	215625		
1-Mar	39	1	0	5.5	300	898	37.40		231	667	5338	220962		
2-Mar	40	14	30	5.5	280	935	38.96		231	704	10875	231837		
2-Mar	40	14	30	0.0	0	935	38.96		231	704	0	231837		° Pulled cell out for weekend
5-Mar	43	0	10	0.0	0	993	41.36	57.7	289	704	0	231837		shutdown
5-Mar	43	0	10	5.5	320	993	41.36		289	704	0	231837		
5-Mar	43	7	30	5.5	335	1000	41.67		289	712	2402	234239		
5-Mar	43	14	30	5.5	340	1007	41.96		289	719	2363	236601		
6-Mar	44	0	30	5.5	340	1017	42.38		289	729	3400	240001		
7-Mar	45	0	10	5.5	340	1041	43.36		289	752	8047	248048		
7-Mar	45	7	15	5.5	335	1048	43.66		289	759	2391	250439		
8-Mar	46	7	15	5.5	350	1072	44.66		289	783	8220	258659		
8-Mar	46	12	0	5.5	350	1077	44.85		289	788	1663	260321	3-8-91-A-9*	
8-Mar	46	15	0	5.5	350	1080	44.98		289	791	1050	261371		
9-Mar	47	0	30	5.5	370	1089	45.38		289	801	3420	264791		
9-Mar	47	7	15	5.5	360	1096	45.66		289	807	2464	267255		
9-Mar	47	15	0	5.5	340	1104	45.98		289	815	2713	269967		
*9-Mar	47	15	0	0.0	0	1104	45.98		289	815	0	269967		
*19-Mar	57	23	0	0.0	0	1352	56.31	248.0	537	815	0	269967		** Shut down
19-Mar	57	23	0	3.0	20	1352	56.31		537	815	0	269967		
20-Mar	58	9	0	5.5	240	1362	56.73		537	825	1300	271267		
20-Mar	58	17	0	5.5	249	1370	57.06		537	833	1956	273223		
21-Mar	59	15	30	5.5	260	1392	58.00		537	856	5726	278950		

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*21-Mar	59	15	30	0.0	0	1392	58.00		537	856	0	278950		** Shut down; Catholyte
*25-Mar	63	8	0	0.0	0	1481	61.69	88.5	625	856	0	278950		may have been changed
25-Mar	63	8	0	5.5	285	1481	61.69		625	856	0	278950		
25-Mar	63	15	30	5.5	320	1488	62.00		625	863	2269	281218		
26-Mar	64	8	0	5.5	320	1505	62.69		625	880	5280	286498		
27-Mar	65	7	30	5.5	320	1528	63.67		625	903	7520	294018		
28-Mar	66	7	0	5.5	300	1552	64.65		625	927	7285	301303		
28-Mar	66	16	0	5.5	300	1561	65.02		625	936	2700	304003		
*28-Mar	66	16	0	0.0	0	1561	65.02		625	936	0	304003		** Shut down
*2-Apr	71	7	0	0.0	0	1672	69.65	111.0	736	936	0	304003		
2-Apr	71	7	0	5.5	330	1672	69.65		736	936	0	304003		
2-Apr	71	16	0	5.5	320	1681	70.02		736	945	2925	306928		
3-Apr	72	7	30	5.5	320	1696	70.67		736	960	4960	311888		
3-Apr	72	15	30	5.5	305	1704	71.00		736	968	2500	314388		
*3-Apr	72	15	30	0.0	0	1704	71.00		736	968	0	314388		** Shut down
*15-Apr	84	8	30	0.0	0	1985	82.71	281.0	1017	968	0	314388		
15-Apr	84	8	30	5.5	290	1985	82.71		1017	968	0	314388		
15-Apr	84	16	30	5.5	310	1993	83.04		1017	976	2400	316788		
16-Apr	85	11	0	5.5	300	2012	83.81		1017	995	5643	322431		
16-Apr	85	17	0	5.5	300	2018	84.06		1017	1001	1800	324231		
17-Apr	86	7	30	5.5	300	2032	84.67		1017	1015	4350	328581		
17-Apr	86	16	30	5.5	300	2041	85.04		1017	1024	2700	331281		
*17-Apr	86	16	30	0.0	0	2041	85.04		1017	1024	0	331281		** Shut down
*22-Apr	91	8	0	0.0	0	2153	89.69	111.5	1129	1024	0	331281		
*22-Apr	91	8	0	5.5	295	2153	89.69		1129	1024	0	331281		
22-Apr	91	14	30	5.5	295	2159	89.96		1129	1031	1918	333198	4-22-91-A-9	
23-Apr	92	7	0	5.5	295	2176	90.65		1129	1047	4868	338066		
24-Apr	93	7	11	3.0	0	2200	91.65		1129	1071	3567	341633		

* Information was not recorded by depot personnel; operations shown are estimated.