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Environmental Protection Technology Series

Regeneration of Chromated Aluminum Deoxidizers

Office of Research and Development
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December 1973

REGENERATION OF CHROMATED ALUMINUM DEOXIDIZERS

Phase I Report

By

Harry C. Hicks, Senior Research Engineer
Robert A. Jarmuth, Project Director

Project 12070 HEK
Program Element 1B2036

Project Officer
Dr. Hugh B. Durham
Heavy Industrial Sources Branch
Grosse Ile, Michigan 48138

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

ABSTRACT

Large quantities of chromium compounds are disposed of annually through discard of spent aluminum deoxidizer solutions. Regeneration, rather than discard, of these concentrated solutions is a significant contribution to antipollution efforts.

The regeneration concept involves oxidation of trivalent (depleted) chromium to hexavalent (active) chromium at an electrode of a dc rectifier. This step requires that an electrical circuit be maintained within the solution, yet movement of dissolved metals must be restricted to specific areas. Infinite lifespan of the solution also implies separation and removal of aluminum and other metals that are dissolved in the deoxidizing process.

Technical activities of the project involve:

- Testing, evaluation, and development of diaphragm and electrode materials of regeneration
- Development of design information for separation and removal equipment

Performance activities of the project involve:

- Pilot scale-up and demonstrations to verify the dependability of evolved technical information
- Evaluation of the regeneration process economics

The objectives of the program were met and it is concluded that the concept of regenerating chromated aluminum deoxidizers is a feasible and practical method for significantly reducing the quantity of discarded toxic chromium compounds and conserving chromium metal resources.

This report, which has been assigned Boeing document number D6-22251-8 for internal use, was submitted in fulfillment of phase I, project number 12070 HEK, between the Environmental Protection Agency and the Boeing Commercial Airplane Company.

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SECTION I

CONCLUSIONS

Regeneration of chromated aluminum deoxidizers is feasible, practical, and economical. Electrolytic reoxidation of chromium plus removal of dissolved metals is more efficient in the conventional dichromate-sulfuric deoxidizer than in proprietary deoxidizers and can result in a cost savings to the operator.

The useful life of proprietary chromated deoxidizers can be appreciably extended by electrolytic reoxidation of the chromium, thereby minimizing disposal of concentrated chromates. Removal of dissolved metals in some of these deoxidizers requires additional investigation to resolve residual technical problems.

SECTION II

RECOMMENDATIONS

During the progress of this project, a chemically inert, electrically conductive diaphragm was developed to isolate chromate ions. Development of fabrication techniques and service life were not within the scope of this program and were not optimized. Therefore, it is recommended that further work be done to improve this diaphragm in terms of lower fabrication cost and longer service life.

It is also recommended that the process for regeneration of dichromate-sulfuric deoxidizers as described in this report be encouraged for use by heavy industrial metal finishers.

It is further recommended that electrolytic reoxidation be implemented for proprietary deoxidizers wherever economically and/or environmentally feasible.

Because simple crystallization is not practical for some deoxidizers, it is suggested that other techniques for removing dissolved metals, such as reverse osmosis or precipitation, be evaluated.

SECTION III

INTRODUCTION

BACKGROUND

Chromium-containing chemical compounds have long been recognized as a major contributor to water pollution problems because of the high toxicity of chromium's ionic forms and the prevalence of chromium in a wide variety of industrial processes. Approximately 10% of the total U.S. chromium consumption is in the chemical industries (in excess of 50,000 tons annually). Nearly one-third of this is used for paint pigments and hence can be considered as nonpolluting, as are the metallurgical and refractory uses.

Metal surface treatments and corrosion control measures also use a large quantity of chromium, estimated at 30,000 tons annually. In this metal-finishing industry, chromated processing solutions are used extensively to treat aluminum surfaces during various operations such as anodizing, conversion coatings, prepaint preparation, welding, and adhesive bonding. A specific process commonly referred to as deoxidizing of aluminum (a part of a cleaning cycle) is of special interest. Chromated aluminum deoxidizing solutions have a relatively high concentration of chromium in the hexavalent state, and this chromium is used up in three ways: (1) a minute amount remains on the surface of the aluminum as a complex chemical conversion coating; (2) a somewhat larger amount is lost by drag-out into rinse waters; and (3) high concentrations are lost when the processing solution is discarded for various nonfunctional reasons. It is predicted that for many technical and economic reasons, chromated aluminum deoxidizers will continue to be used.

The loss described in item 3 is the problem to which the efforts of this project were directed. A concept for a regeneration process was devised to extend the useful life of the chromated deoxidizers. The advantages of the regeneration process described in this report are:

- Environmental
    - Major reduction in the quantity of chromium-containing effluent
    - Conservation of chromium resources

- Industrial
    - Reduction in the requirements of treatment plants
    - Increased production through reduced downtime
    - Lower processing costs
        - Reduction of chemical additions
        - Reduction of quality control costs
        - Elimination of dumping and recharging costs
    - Increased process reliability

Preliminary research work has proved that it is feasible to regenerate spent deoxidizer solutions rather than discard them. Thus it is possible, by applying chemical engineering technology, to maintain the acceptable performance of chromium-containing solutions indefinitely. By making this technology available to all metal finishers, a significant contribution to antipollution efforts can be made.

SCOPE

The engineering techniques developed in this project involve regeneration of active chromium compounds by electrolysis plus removal of undesirable metals by crystallization and separation. A deoxidizer consisting of sulfuric acid and sodium dichromate was selected for this investigation for two reasons: (1) the initial composition is known exactly, and (2) the workload and performance of this solution within the facilities of the project contractor are critical and precisely controlled.

PROJECT OBJECTIVES

The objectives of this work are to develop equipment information and establish the operating conditions for the continuous regeneration of a sodium dichromate-sulfuric acid aluminum deoxidizer solution and evaluate this technology for other commercially available chromated aluminum deoxidizers. Successful regeneration can be realized by: (1) electrochemical oxidation of trivalent chromium to hexavalent chromium, (2) removal of dissolved aluminum and trace metals, and (3) addition of chemicals to keep the solution within

required limits. The following are specific tasks to be accomplished during this project:

- Determine electrochemical characteristics of the materials selected.
- Acquire additional laboratory experimental data for the oxidation of chromium and the removal of dissolved metals.
- Construct a pilot plant regeneration system and operate to verify previous data.
- Evaluate use of regeneration equipment on proprietary aluminum deoxidizers.
- Scale up a process to simulate production installation.
- Provide a technical report of the project.

TECHNICAL APPROACH

A previous research and development program demonstrated the feasibility of electrolytic oxidation of trivalent chromium to the hexavalent state, together with precipitation of dissolved aluminum as aluminum sulfate. Work was done in a divided tank, with anode and cathode chambers separated by a porous ceramic membrane. The porous ceramic worked well in the laboratory, but it is undesirable for large-scale industrial use because of fragility, short life, and high cost.

Initial tests in this new program were made on a laboratory scale to obtain data on alternate diaphragm material, electrode performance, current efficiency versus current density, mass transport, and solids separation. The data obtained allowed a 227-liter sodium dichromate-sulfuric acid ($Na_2Cr_2O_7$-H_2SO_4) regeneration system to be assembled and tested.

Dissolved aluminum can be crystallized as aluminum sulfate [$Al_2(SO_4)_3$-$18H_2O$] and removed. Trace metals, principally copper, zinc, magnesium, iron, and manganese, which are found in the aluminum alloys being treated, slowly accumulate in solution and methods for their removal were tested. The pilot system was operated until it was shown that oxidation and metal removal can be regulated to maintain the solution within desired functional limits.

Another phase of this work tested the regeneration techniques and equipment on three proprietary chromated aluminum deoxidizers. Finally, 2200 liters of $Na_2Cr_2O_7$-H_2SO_4 deoxidizer was operated for production verification. Regeneration equipment for this unit

was designed, installed, and operated under simulated production conditions and quality assurance surveillance.

SECTION IV

TECHNICAL DISCUSSION

The program consists of seven tasks, as detailed in the following sections.

TASK I–DIAPHRAGM EVALUATION

Testing of materials was conducted to obtain a membrane that is resistant to $Na_2Cr_2O_7$-H_2SO_4 solution and will permit adequate ion transport to maintain electrolysis rates at lowest power (IR) drop through solution. Dacron, polyester, polypropylene, Dynel, and acid-washed long fiber asbestos (supported by a polypropylene screen) were tested. The test assembly is illustrated in figure 1. Schematic arrangement was according to figure 2.

Samples of commercially available synthetic fibers were procured as follows:

Woven polypropylene	Two samples
Woven Dynel	Two samples
Nonwoven polypropylene felt	One sample
Nonwoven Dacron felt	One sample
Nonwoven polyester	Two samples

Material Preparation

The selected materials were prepared in the following manner:

- Asbestos

  The asbestos diaphragm was prepared by pouring a weighed slurry of acid-washed asbestos fiber onto a polypropylene screen fastened to a vacuum box. Water was drawn off with vacuum and the asbestos membrane was removed from the supporting screen.

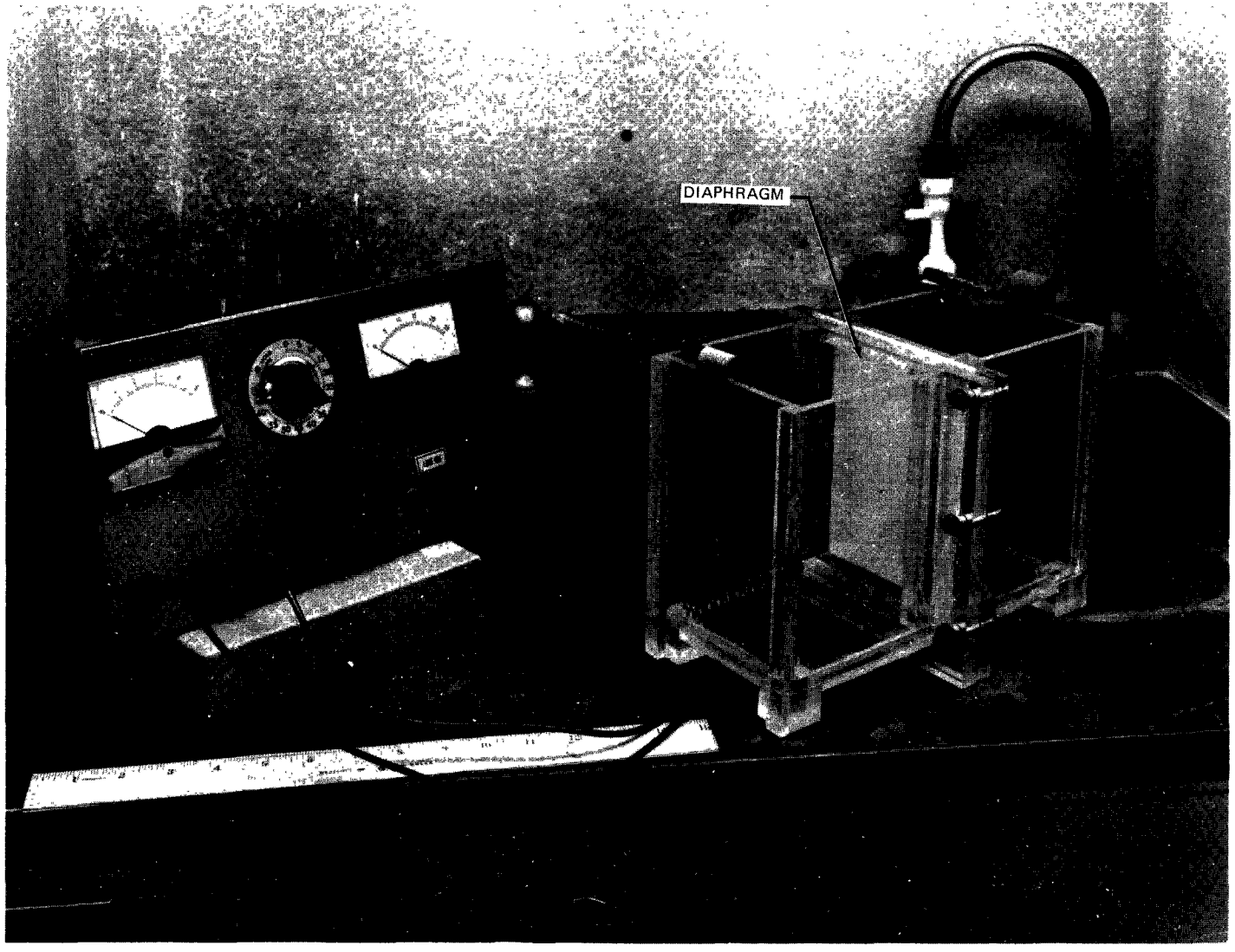


Figure 1. Diaphragm test cell

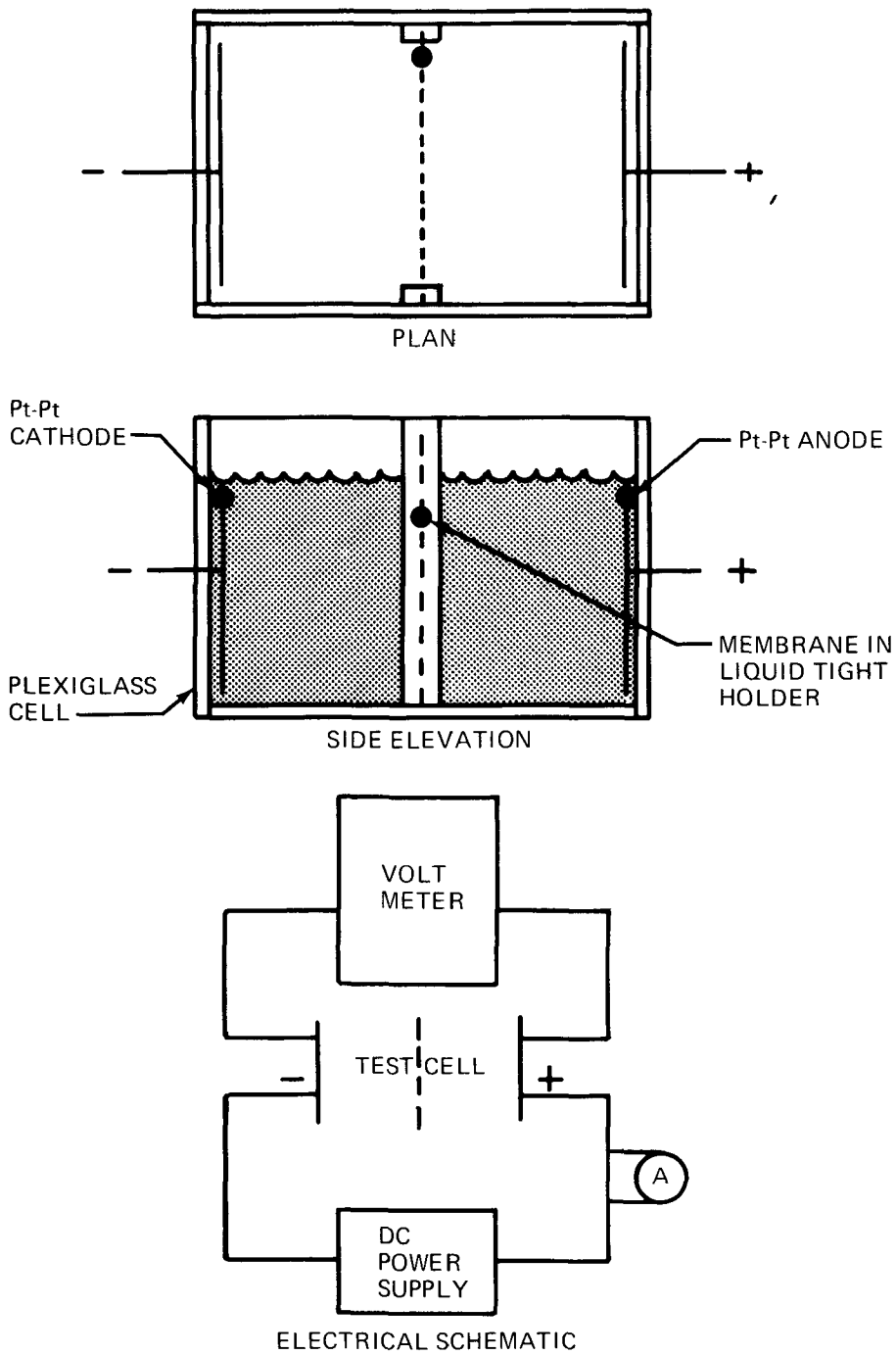


Figure 2. Diaphragm test cell schematic

- Synthetic fibrous materials

  These materials were washed and dried to remove sizing and lubricants used in manufacture.

Asbestos was investigated and set aside because of inherent difficulties in obtaining acceptable diaphragm shapes without the incorporation of soluble binder material with the asbestos fibers (see fig. 3). Further investigation of this material will be conducted only if alternate materials prove to be unsatisfactory. It is apparent that uniformity and consistent permeability can be more easily obtained with off-the-shelf synthetic fiber material.

Membrane Testing

Samples of the synthetic fibers were soaked in a sodium dichromate-sulfuric acid deoxidizer solution ($Na_2Cr_2O_7$-H_2SO_4) for 240 hr at 82°C. Weight loss, dimensional changes, and solution concentration changes were determined. Results are shown in table 1. During the progress of the test, a supplier of synthetic fibers furnished a sample of another material, Orlon felt, for evaluation. This sample was exposed to the sulfuric acid-sodium dichromate deoxidizer solution at 71° C. Severe degradation of the fiber occurred after 3 weeks of exposure. The Orlon material is therefore judged to be unsatisfactory.

Table 1. MEMBRANE CHEMICAL RESISTANCE

Sample no.	Description	Material change		Solution change	
		Weight loss, %	Dimension loss, %	Hexavalent chrome loss, %	Sulfuric acid loss, %
1	Woven polypropylene	3.5	0	73	12
2	Woven Dynel	2.4	0	40	5.5
3	Woven polypropylene	12.0	0	99	18
4	Woven Dynel	4.1	0	65	10
5	Polypropylene felt	2.1	0	99	15
6	Dacron felt	3.5	0	94	13
7	Polyester film	0.7	0	7	2
Control		–	–	–	–

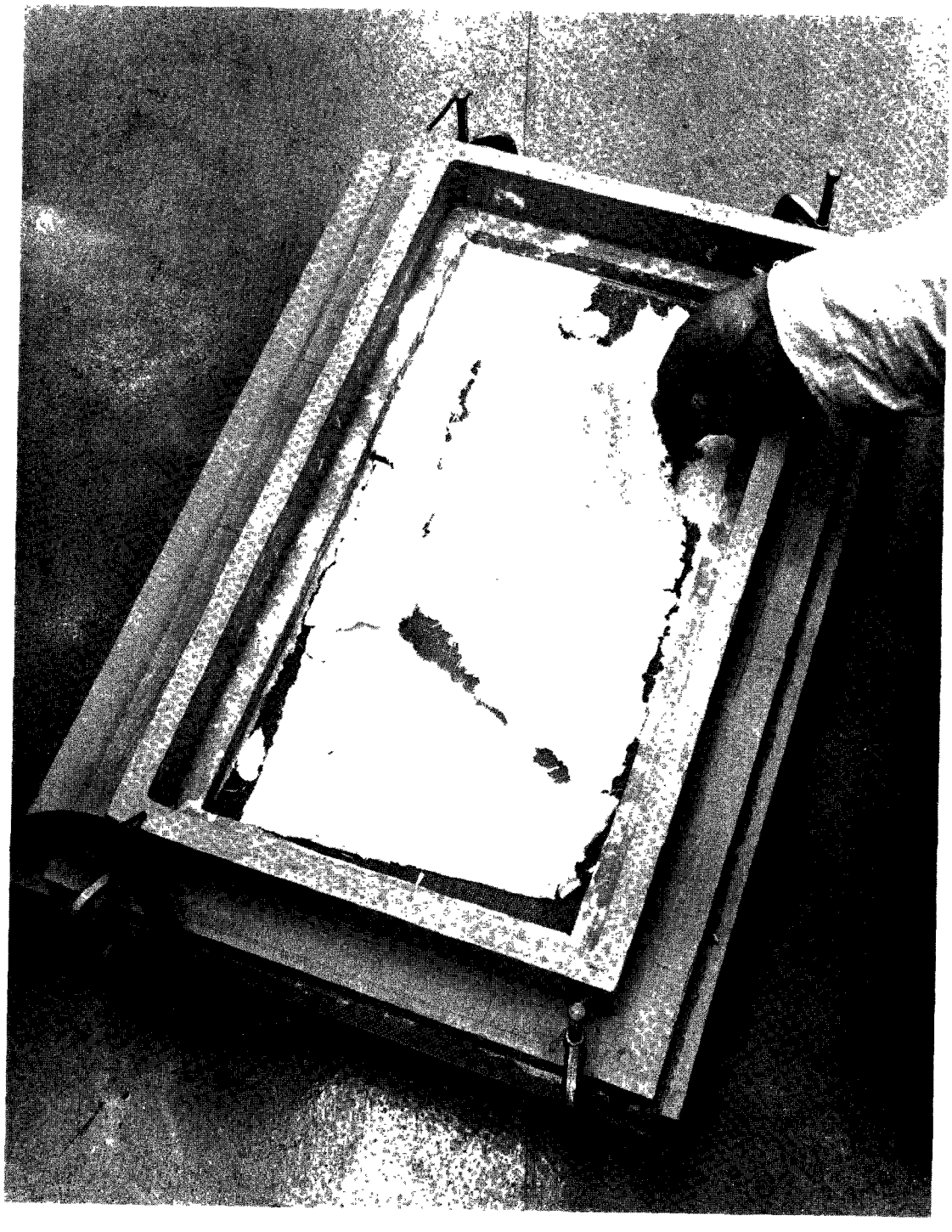


Figure 3. Asbestos diaphragm

Samples of the polypropylene felt, Dacron felt, and polyester material were installed in the diaphragm test cell. The test cell was contained in a constant-temperature bath (fig. 4) while electrical readings were determined. Electrical conductivity data were collected by filling one side of the cell with $Na_2Cr_2O_7$-H_2SO_4 deoxidizer. The other side of the cell was filled with sulfuric acid only. Electrode plates with platinum black were inserted, and voltage readings were made at several amperage levels at steady-state conditions. Data are presented in table 2.

Table 2. MEMBRANE ELECTRICAL CONDUCTIVITY

Current, amp		Potential, V				
		Polypropylene (1-3 cfm)[a]	Dacron (17 cfm)[a]	Polyester (6 layer)	Polyester[b] (12 layer)	Polyester[b] (15 layer)
Increasing amperage	1.0	1.6	Dichromate bleed-through; test discontinued	1.7	2.3	2.6
	2.0	1.9		2.0	3.0	3.6
	3.0	2.1		2.3	3.6	4.75
	4.0	2.3		2.6	4.4	6.2
	5.0	2.5		3.0	5.0	8.5
Decreasing amperage	4.0	2.3		2.6	4.4	5.8
	3.0	2.1		2.4	3.7	4.6
	2.0	1.9		2.1	3.0	3.5
	1.0	1.6		1.75	2.3	2.6

[a]Vendor's permeability data [b]Pressure-temperature laminate

It was observed very early that all materials under evaluation were much too porous to prevent diffusion of the dichromate ion into clear sulfuric acid. The least permeable material, rated by its vendor at 1 to 3 cfm (air) by ASTM test method D737, allowed too much diffusion. Since the polyester material is the most chemically resistant (reference table 1), efforts were made to decrease its permeability by laminating techniques. This laminated polyester was the diaphragm material used for continuing process development. Throughout the remainder of the project, the designation J5D will refer to a diaphragm consisting of multiple layers of this Dupont 2024 Reemay nonwoven polyester.

In addition to the above tests, a J5D diaphragm and a single layer of the J5D laminate were subjected to 3 months' continuous exposure to the dichromate-sulfuric deoxidizer at 71° C. Small particles of fiber flaked off and some swelling occurred with the laminate. Otherwise, the polyester appeared unaffected. This qualitative test was sufficiently encouraging to warrant continuing development and testing of the J5D diaphragm.

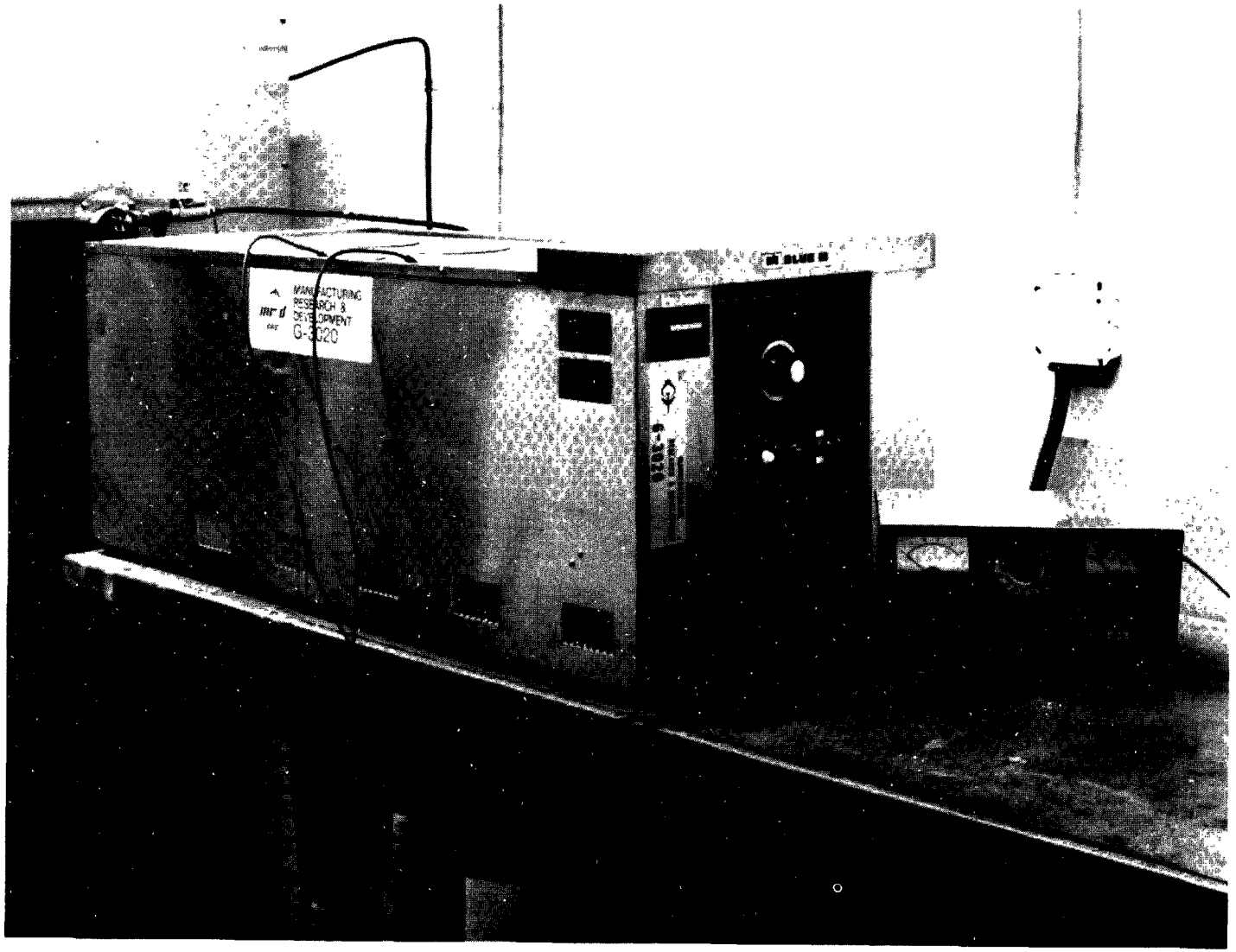


Figure 4. Constant-temperature bath and rectifier

A quantity of 15- by 20-cm J5D diaphragms were fabricated in the hydraulic press illustrated in figure 5 and were subjected to testing in the diaphragm test cell.

Test Procedure—Membranes were tested according to the following procedure:

1) Coat platinum electrodes with platinum black and insert in cell. Place cell in 71° C constant-temperature bath.

2) Fill cell with $Na_2Cr_2O_7$-H_2SO_4 solution.

3) Insert membrane in holder and immerse in beaker filled with $Na_2Cr_2O_7$-H_2SO_4 solution maintained at 71° C. Soak for 1 hr.

4) Remove membrane and holder, shake off excess solution, and insert in test cell. Allow to reach thermal equilibrium at 71° C.

5) Adjust solution to level.

6) Turn on direct current power supply and increase to predetermined level as indicated on ammeter.

7) Run cell for 5 min, adjusting to maintain constant amperage.

8) Read potential, E, between electrodes with voltmeter.

Discussion—The potential, E, obtained from item 8 above will be directly proportional to the resistance of the membrane to ion passage. E_c is the total potential across the cell and can be separated into:

$$E_c = E_r + N_a + N_c + IR$$

where:

E_r = algebraic sum of the reversible potentials of anode and cathode

N_a and N_c = polarization of anode and cathode, respectively

IR = voltage drop due to resistance of solution

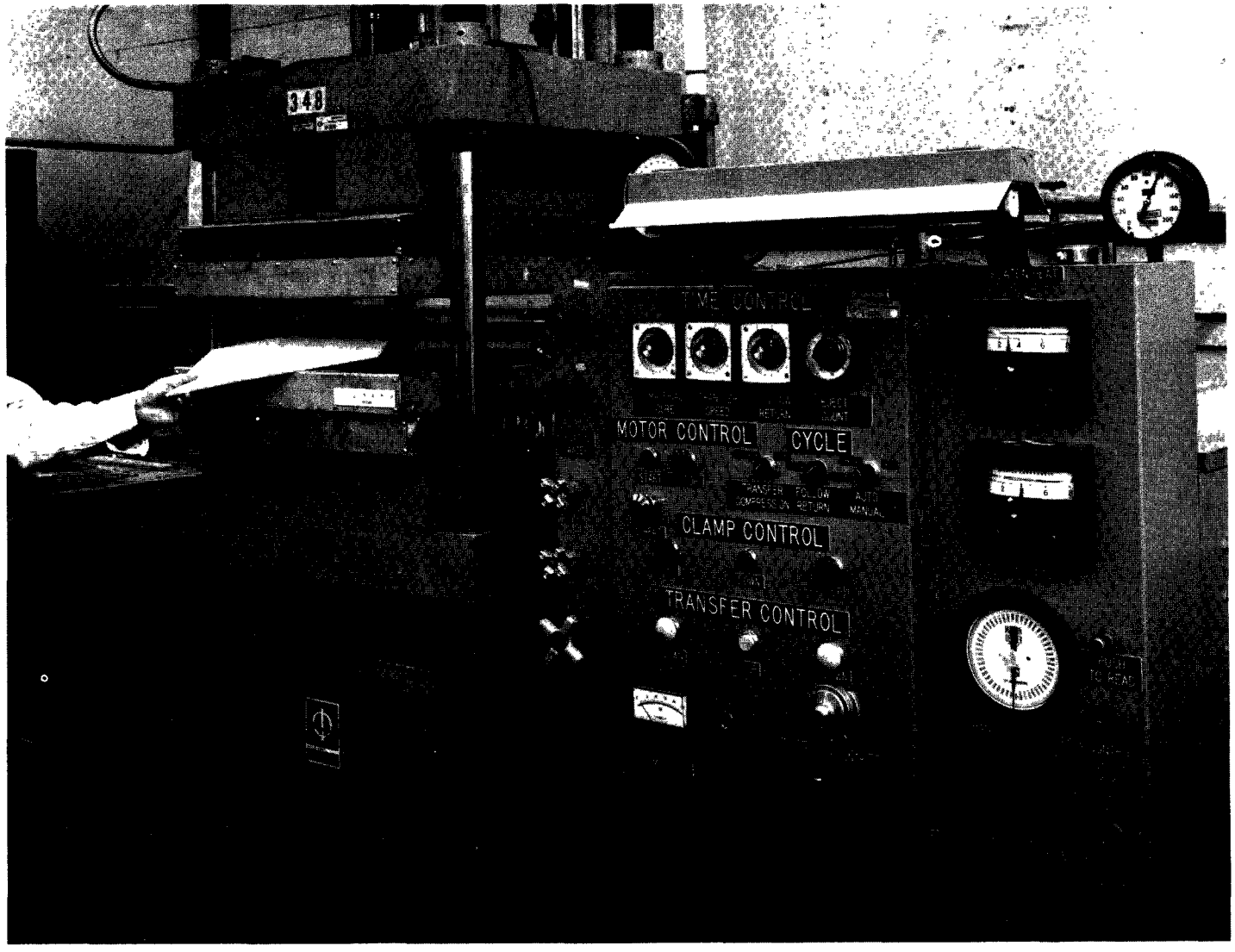


Figure 5. Hydraulic press

Under carefully controlled test conditions, $E_r + N_c$ can be kept approximately constant. The use of platinum-black electrodes helps to keep N_a and N_c at a low value and therefore make IR a higher percentage of E_c. Thus, $E_r + N_c = K$.

The IR drop through the solution can be expressed as:

$$I(R_s + R_m)$$

where:

I = amperage

R_s = solution resistance

R_m = membrane resistance

With constant amperage and identical solutions for each test, $IR_s = K_2$; therefore,

$$E_c = K_1 + K_2 + IR_m$$

$$E_c = K + IR_m$$

$$\frac{E_c - K}{I} = R_m$$

Voltage and current data were collected in the diaphragm test cell to determine the electrical resistance of the fabricated J5D diaphragm. Figure 6 illustrates the collected data.

Data from this test established the linear relationship between voltage and current. Thus the values for K_1 and K_2 in the equation $E_c = K_1 + K_2 + IR_m$ can be eliminated algebraically. The resistance due to the diaphragm system is calculated directly. This resistance is 0.61 ohm for 135.5 sq cm of J5D through the range of 1.0 to 5.0 amp. This is equivalent to a maximum current density of 3.69 amp/sq dm through the diaphragm and up to 1.72 amp/sq dm on the electrodes. A regeneration current up to 2.5 amp/l can be used in the anode and cathode chambers.

Since the chemical resistance and electrical performance of the J5D diaphragm proved to be satisfactory, a preliminary functional test was desirable to predict the capability of the diaphragm to maintain separation of ions under operating loads for a longer period of time

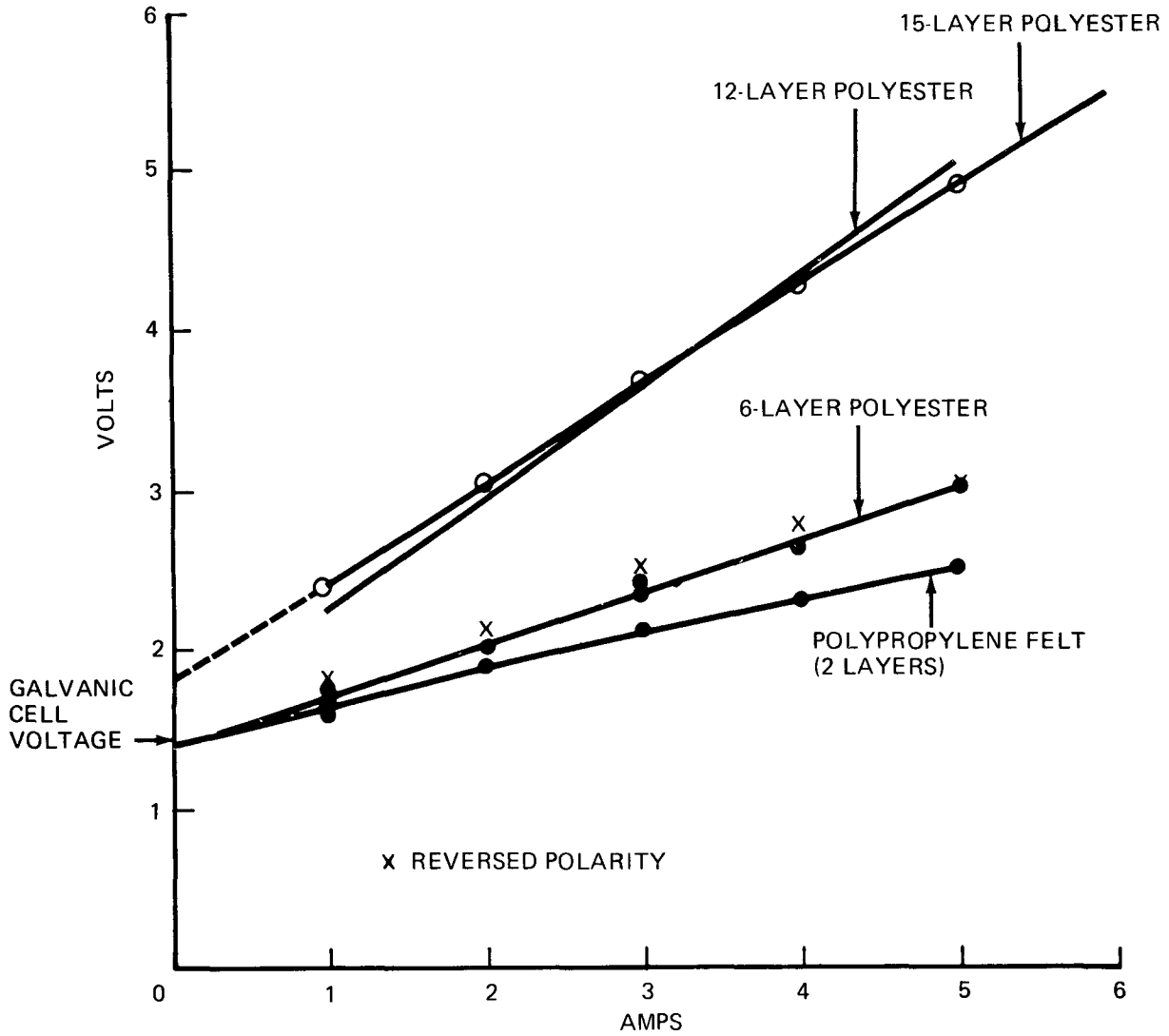


Figure 6. Diaphragm test cell electrical resistance

than had been used previously. Therefore, the diaphragm test cell was set up with a J5D diaphragm, sulfuric-dichromate deoxidizer in the anode chamber, and sulfuric acid only in the cathode chamber. The cell was operated for 4 hr at 4.0 amp and 4.5 V.

The chemical analyses are given in table 3. A small but proportional increase in concentration occurred due to water evaporation during the test. No visual degradation of solutions or diaphragm occurred. Analyses for trivalent chromium verify that regeneration did occur. The results of this test encouraged continued use of the J5D diaphragm. All other diaphragm materials tested had less chemical resistance and allowed bleed-through of dichromate ion, and consequently were rejected from further consideration.

Table 3. ELECTRODE EVALUATION CELL ANALYSES

Test no.	Chamber description	Analyses, gm/l			
		Sulfuric acid	Active chromate	Total chromate	Trivalent chrome
J5D-1	Cathode at start	39.3	None	None	None
J5D-2	Cathode at finish	40.0	None	0.01	None
J5D-3	Anode at start	40.8	4.6	4.6	0.028[a]
J5D-4	Anode at finish	41.6	4.6	4.6	0.017[a]

[a]Reduction of trivalent chromium in the anode chamber indicates an expected regeneration of chromium.

TASK II–ELECTRODE EVALUATION

Anode Material Selection

Ample references can be found in the literature that metallic lead (Pb) anodes give the highest current efficiency for the oxidation of Cr^{+3} to $Cr_2O_7^{-2}$. Tests were made on Pb-7%Sn and Pb-6%Sb to obtain the material that gives the best compromise of current efficiency and resistance to attack by the solution.

1) Determine stability of Pb, Pb-7%Sn, and Pb-6%Sb in $Na_2Cr_2O_7$-H_2SO_4 solution by electrolysis at maximum amperage for 400 hr.

2) Determine current efficiency of Pb, Pb-7%Sn. and Pb-6%Sb anodes in $Na_2Cr_2O_7$-H_2SO_4 solution for the reaction $2Cr^{+3} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e$.

   - Connect annodes in series to obtain some value of amperes. A schematic diagram of the test cell is shown in figure 7.

   - Electrolyze for a total of 400 hr in $Na_2Cr_2O_7$-H_2SO_4 solution using a 2-hr on/2-hr off cycle. Test in a 227-liter solution to minimize effects of concentration changes.

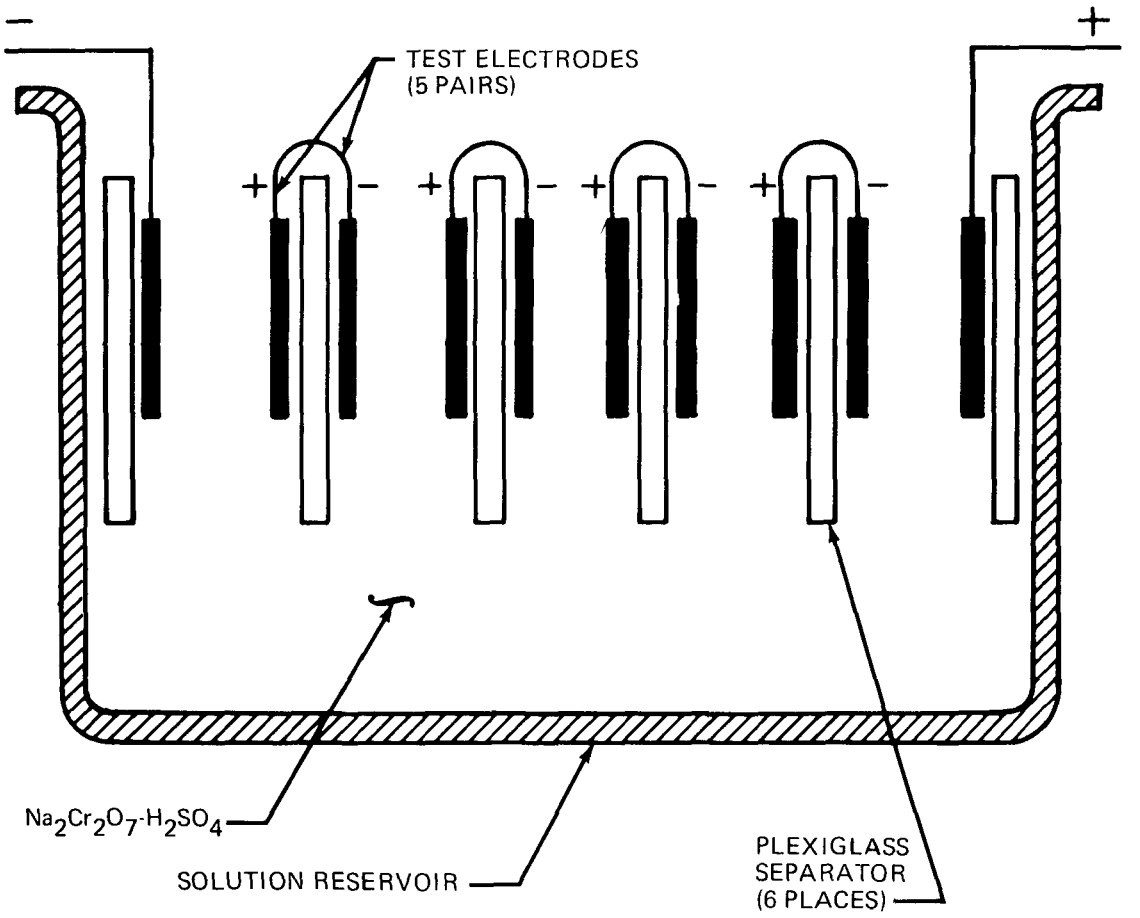


Figure 7. Electrode evaluation schematic

- Evaluate test by:

  Weight change
  Appearance (scale, cracking, etc.)

Cathode Material Selection

The major cathode reaction is the reduction of H^{-2} to H (i.e., $2H^+ + 2e = H_2$). Reduction of $Cr_2O_7^{-2}$ to Cr^{+3} and deposition of dissolved metals are also possible. Cathodes of low hydrogen overpotential are desired to operate the cell with the lowest power cost.

1) Determine stability of cathodes in H_2SO_4 solution. Use same evaluation scheme as for anodes.

2) Determine polarization curves for Ni, Pb, Cu, CRES, and Duriron cathode material in H_2SO_4 solution. Use Anatrol model 4200 research potentiostat for determinations.

Electrode Chemical Resistance

Seven materials were arranged in a 227-liter tank of sulfuric-dichromate deoxidizer, as illustrated in figure 8. The materials were positioned so that only lead (Pb) and lead alloys were anodic, and the other metals were cathodic. Such an arrangement provided a possibility for anodic discrimination between commercially pure lead (Pb), lead-tin (Pb-Sn), and lead-antimony (Pb-Sb) materials in addition to evaluation of cathodic materials.

A dc rectifier was set up to impose 30 amp on the circuit with an instrument to register operating time. A time controller to provide a 2-hr on/2-hr off cycle was used. The total test time was 400 hr. At the end of this time the setup was disassembled and the electrode materials were examined.

Upon examination of the anode materials, no differences could be detected among the various lead alloys. For cathode materials, the copper and the nickel were completely dissolved. The Duriron was slightly etched. No effect could be seen on the stainless steel (AISI 316) or the lead.

Electrode Current Efficiency

The H-cell (figs. 9 and 10) was set up with sulfuric-dichromate in the anode chamber, sulfuric acid only in the cathode chamber, and a J5D diaphragm between the chambers. A quantity of trivalent chromium (as chromous sulfate) was added to the anode chamber for regeneration. Conditions of the test (current and time) were set to introduce slightly more than enough current to theoretically regenerate 1 gm of trivalent chromium to hexavalent chromium. The anode chamber was sampled every 15 min and analyzed for hexavalent and trivalent chromium.

Although analyses for the different valences of chromium are difficult, the collected data correlated quite well. The results are illustrated in figure 11. There appears to be a very slight advantage in selecting the Pb-7%Sn alloy for the anode material because the rate of regeneration (slope of curve) is steeper at low trivalent chromium content.

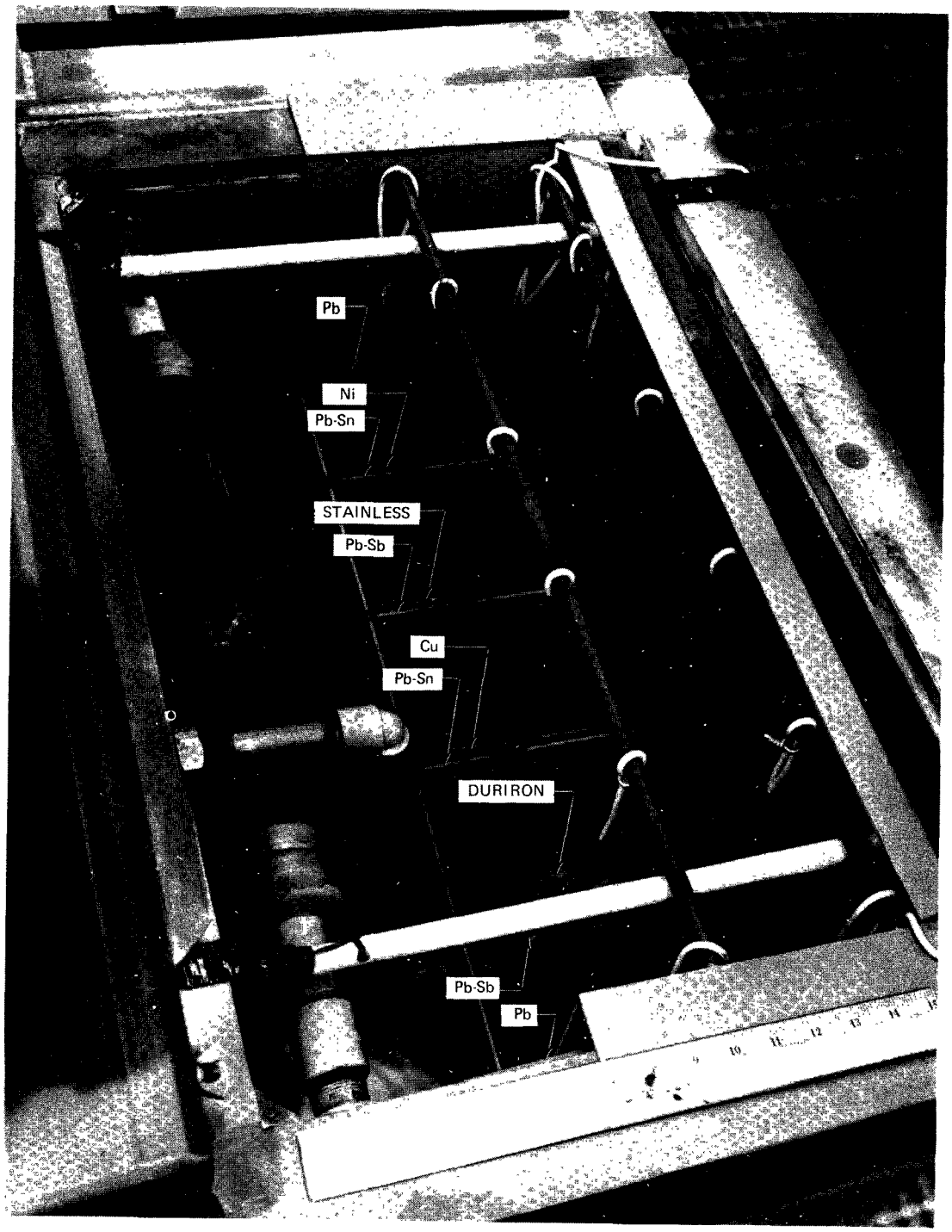


Figure 8. Electrode chemical resistance test

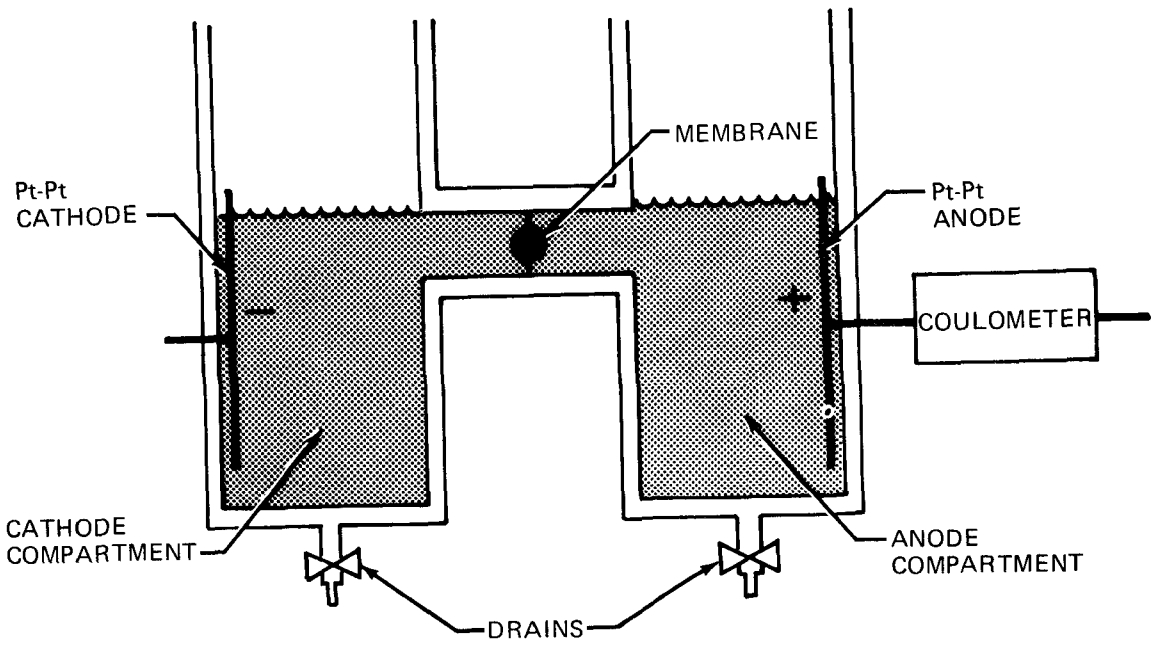


Figure 9. H-cell cross section

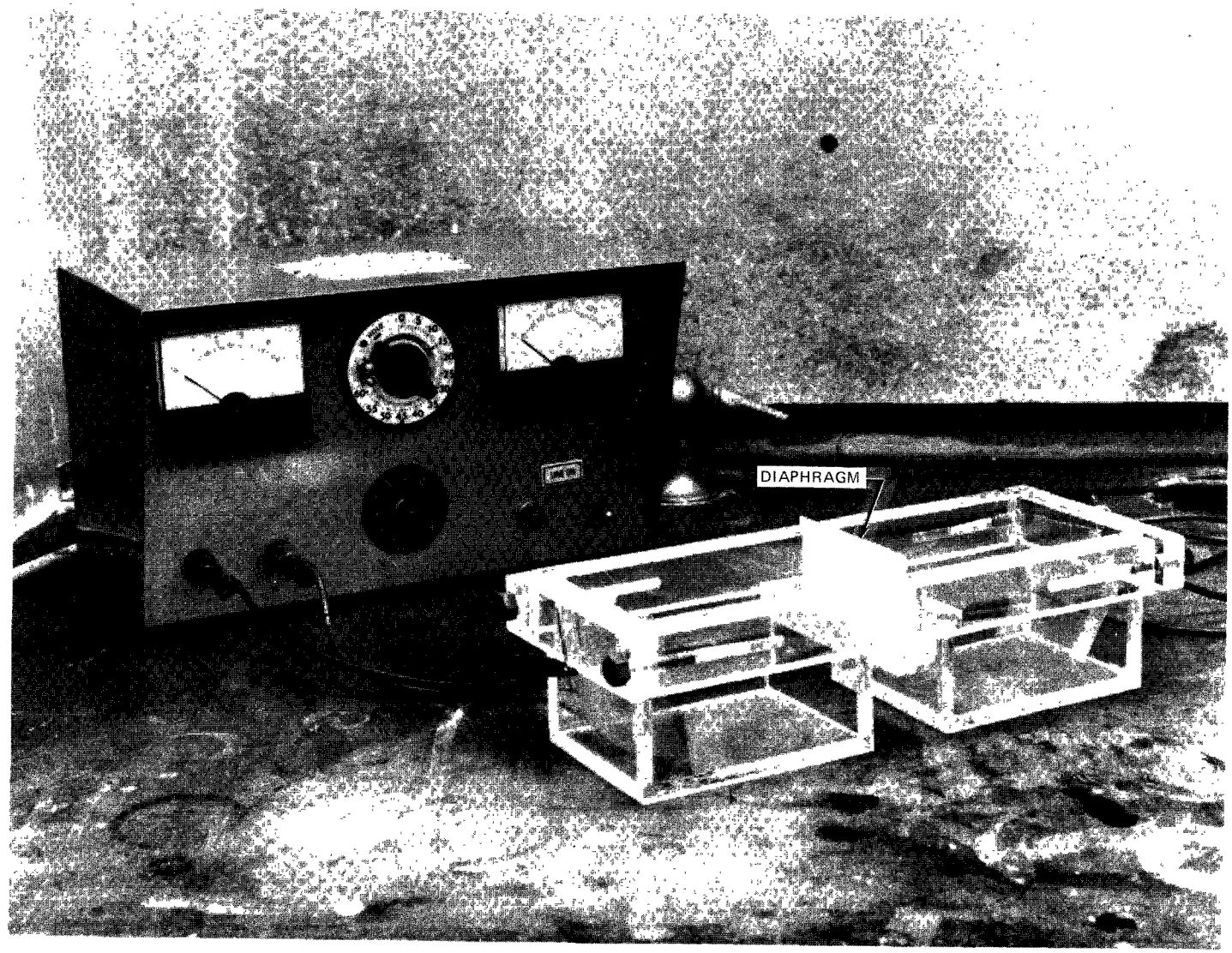


Figure 10. H-cell

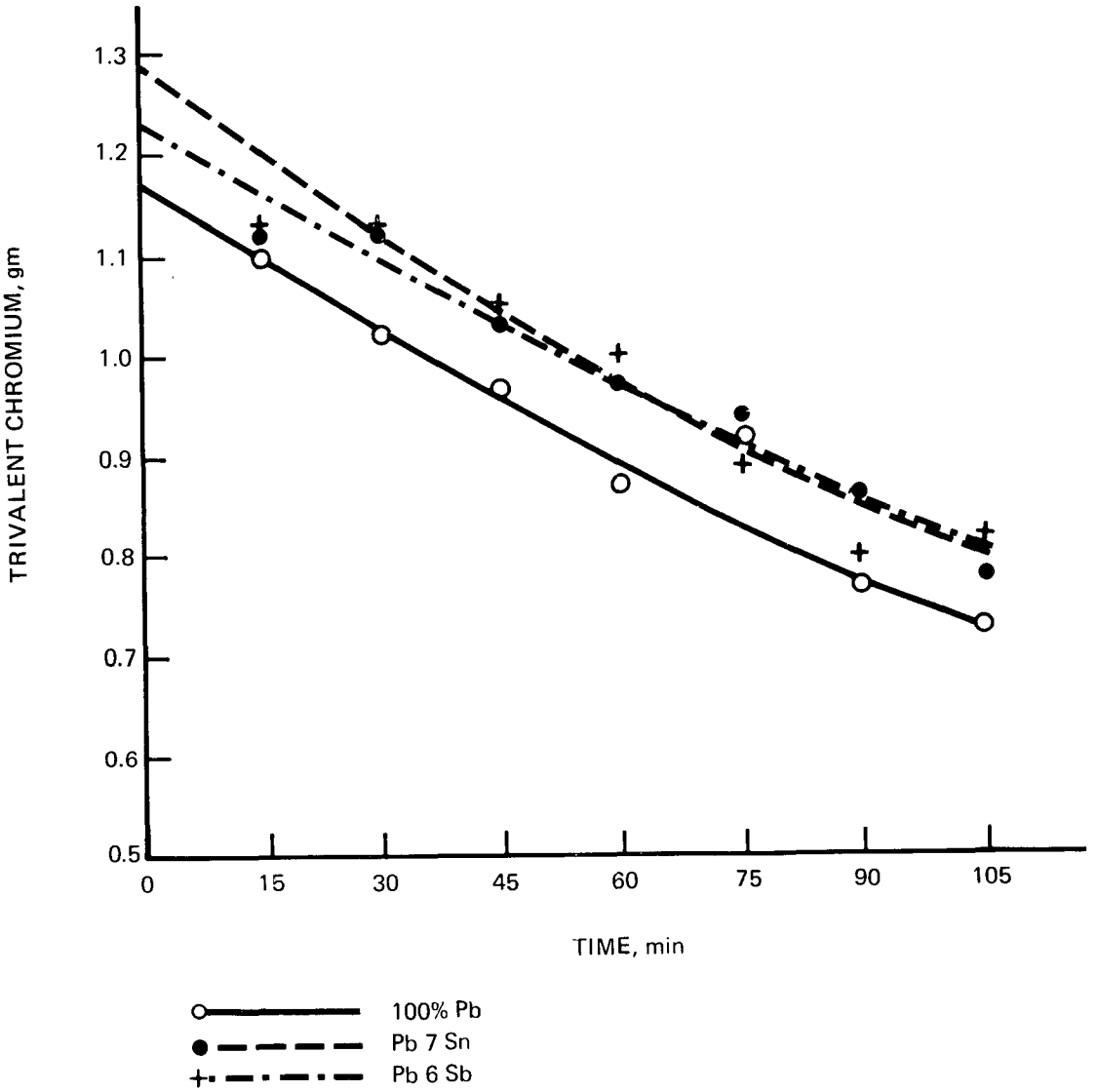


Figure 11. Anode current efficiency test

During the test run, a small leak developed around the gasket area of the H-cell. The cathode chamber was analyzed for total chromium at the end of each run. Calculations verified that this leak contributed less than 1% error to the test.

Since the electrolytic regeneration is nonlinear, efficiencies must be calculated for specific test conditions. For this test run, the regeneration efficiency is calculated on the basis of total weight of trivalent chrome oxidized to hexavalent chrome for a period of 93 min. Electrode efficiencies are calculated at: pure Pb, 38%; Pb-6%Sb, 38%; Pb-7%Sn, 45%.

Polarization of Cathode Materials

Electrodes of nickel, stainless steel, copper, lead, and Duriron (see fig. 12) were made for the Anatrol potentiostat. The setup for these tests is illustrated in figure 13. Polarization curves obtained from the potentiostat are shown in figures 14 through 18. Data extrapolated from these curves are given in table 4.

Since both nickel and copper dissolved during the 400-hr chemical resistance test, it is unwise to consider these materials as cathode candidates. In terms of energy consumption, stainless steel is the most desirable cathode material, followed by lead and Duriron. Electrode selection is stated in the summary for this section.

TASK III–LABORATORY DETERMINATION OF OPERATING PARAMETERS

The purpose of task III was to determine conditions that allow system operation to maintain the $Na_2Cr_2O_7$-H_2SO_4 solution within process limits.

Mass Transport Through J5D Diaphragm

The procedure for the mass transport test was as follows:

1) Identify ion species involved in transport of amperage through cell. A schematic of the H-cell used in transport tests is shown in figure 9.

2) Estimate changes to be expected in anode and cathode compartments because of ion transport.

3) Estimate changes to be expected in solution through removal of H^+ (as H_2) and SO_4^{-2} as $Al_2(SO_4)_3$-$18H_2O$.

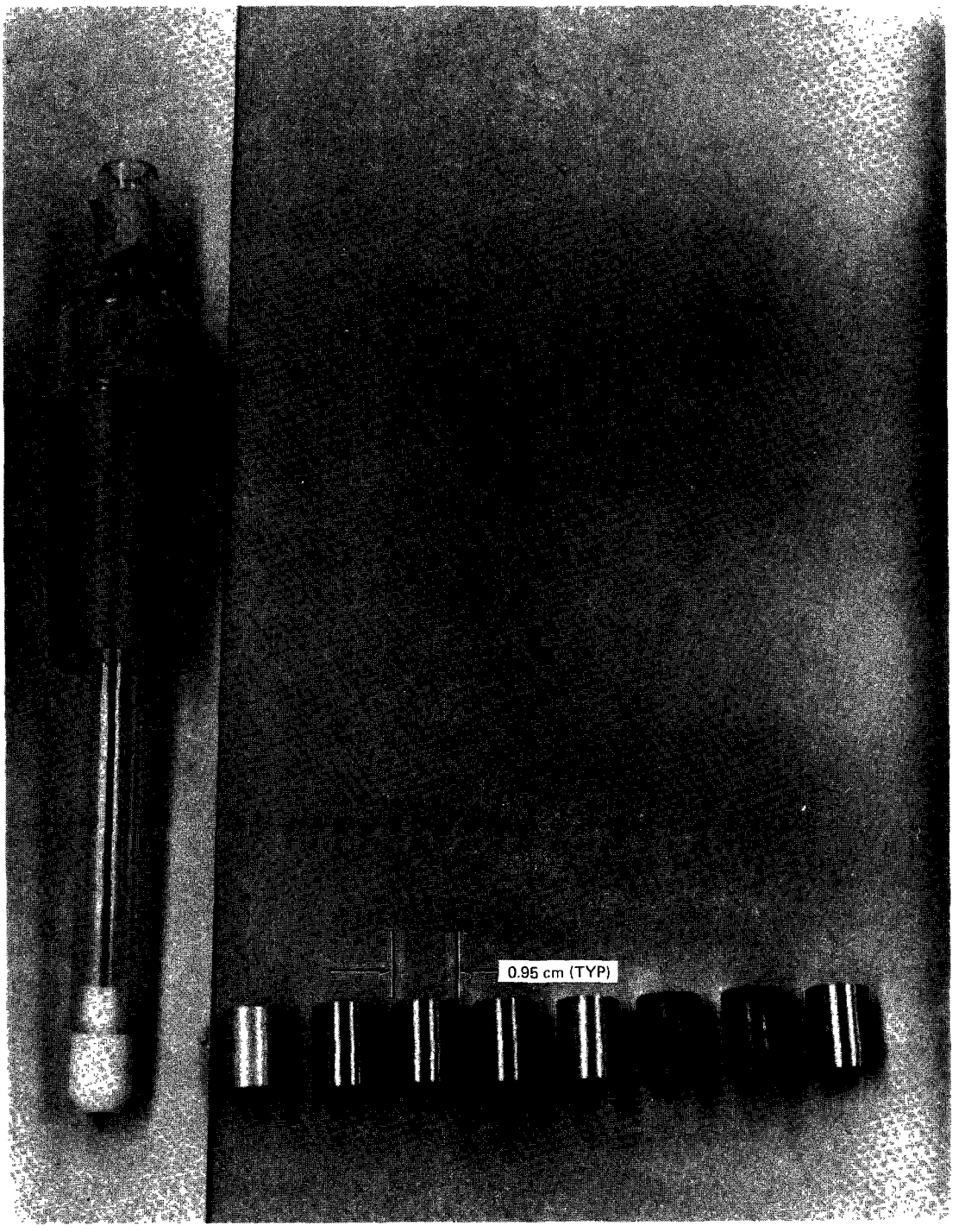


Figure 12. Potentiostat electrodes

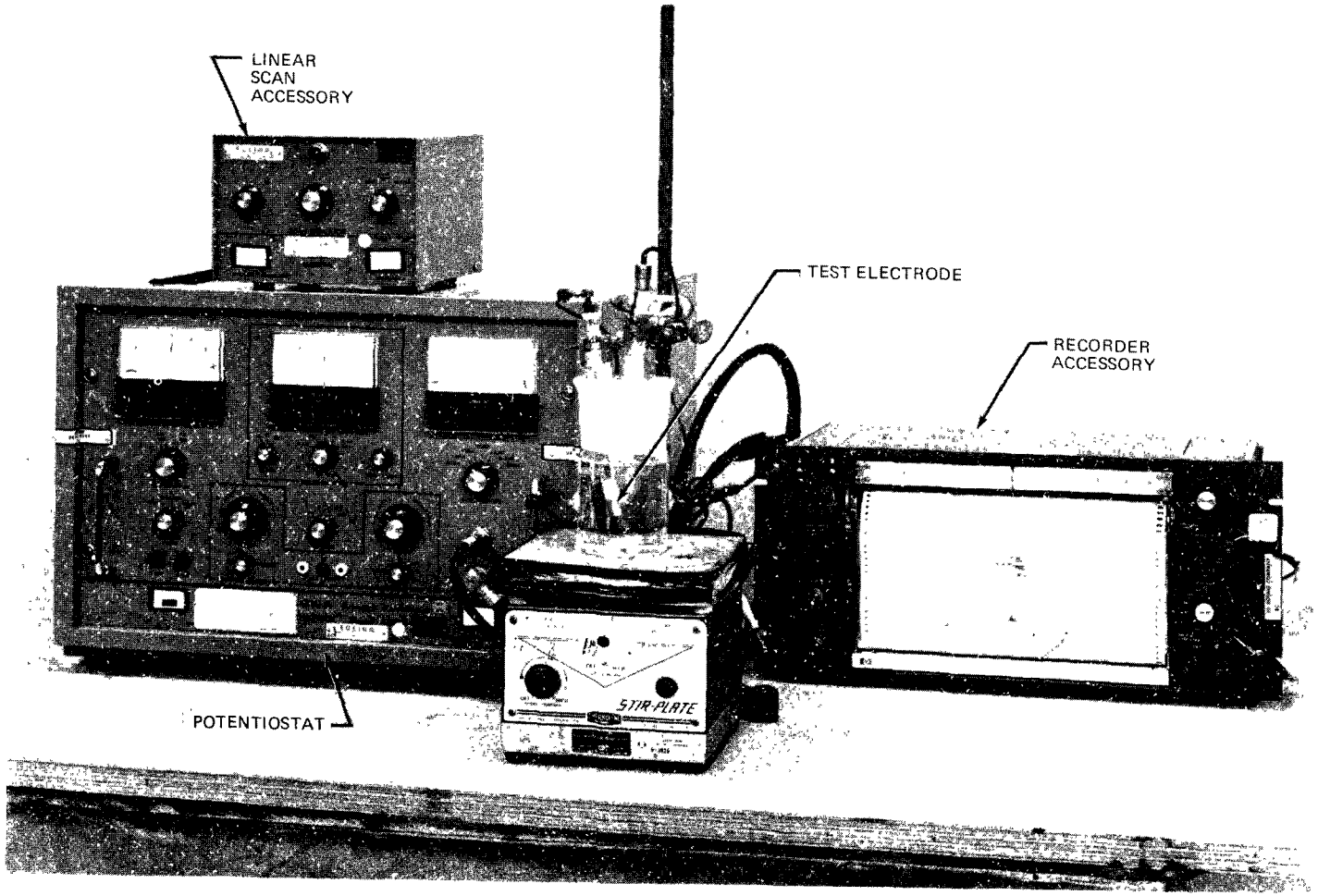


Figure 13. Potentiostat and accessories for polarization curves

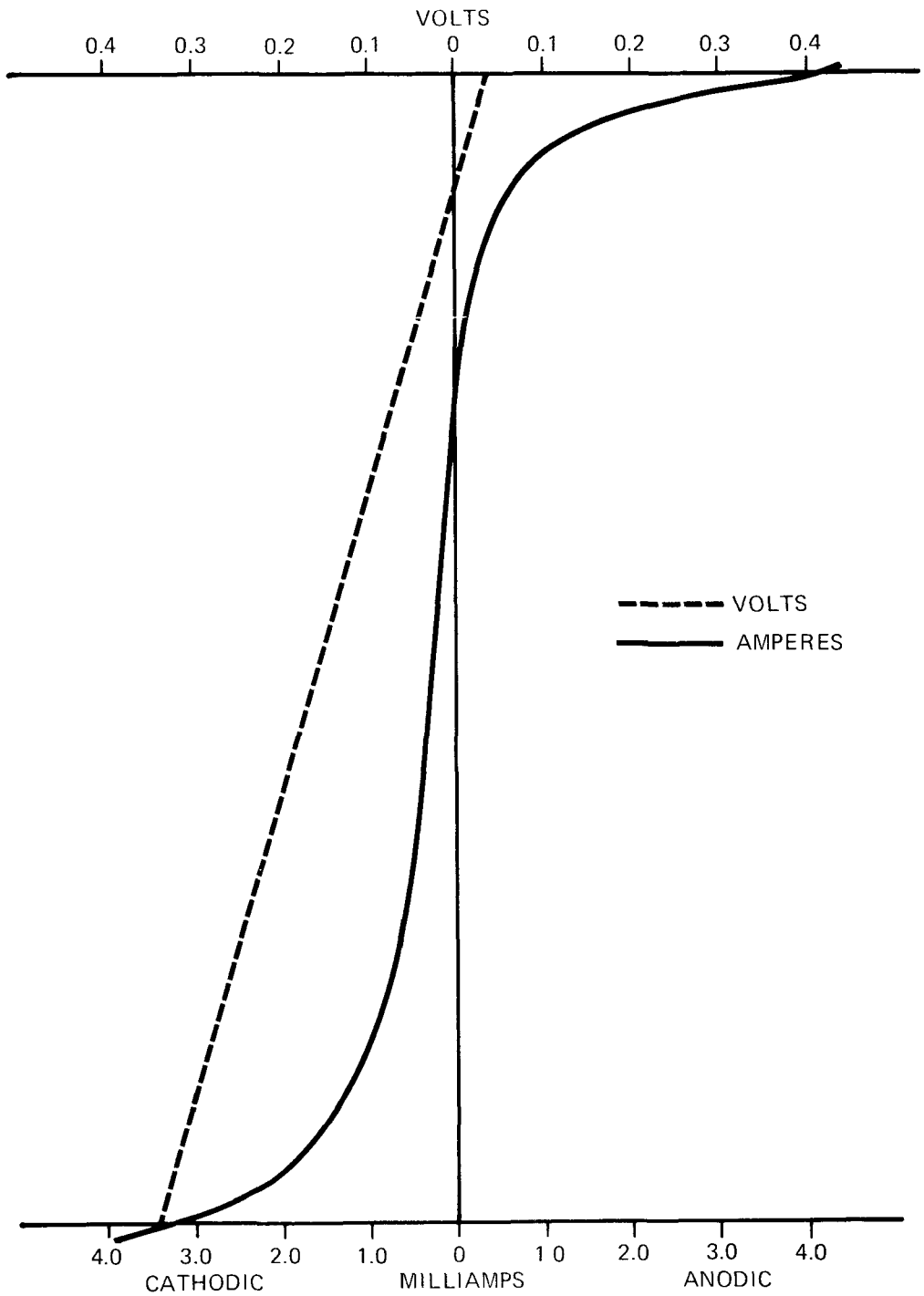


Figure 14. Polarization curve—nickel

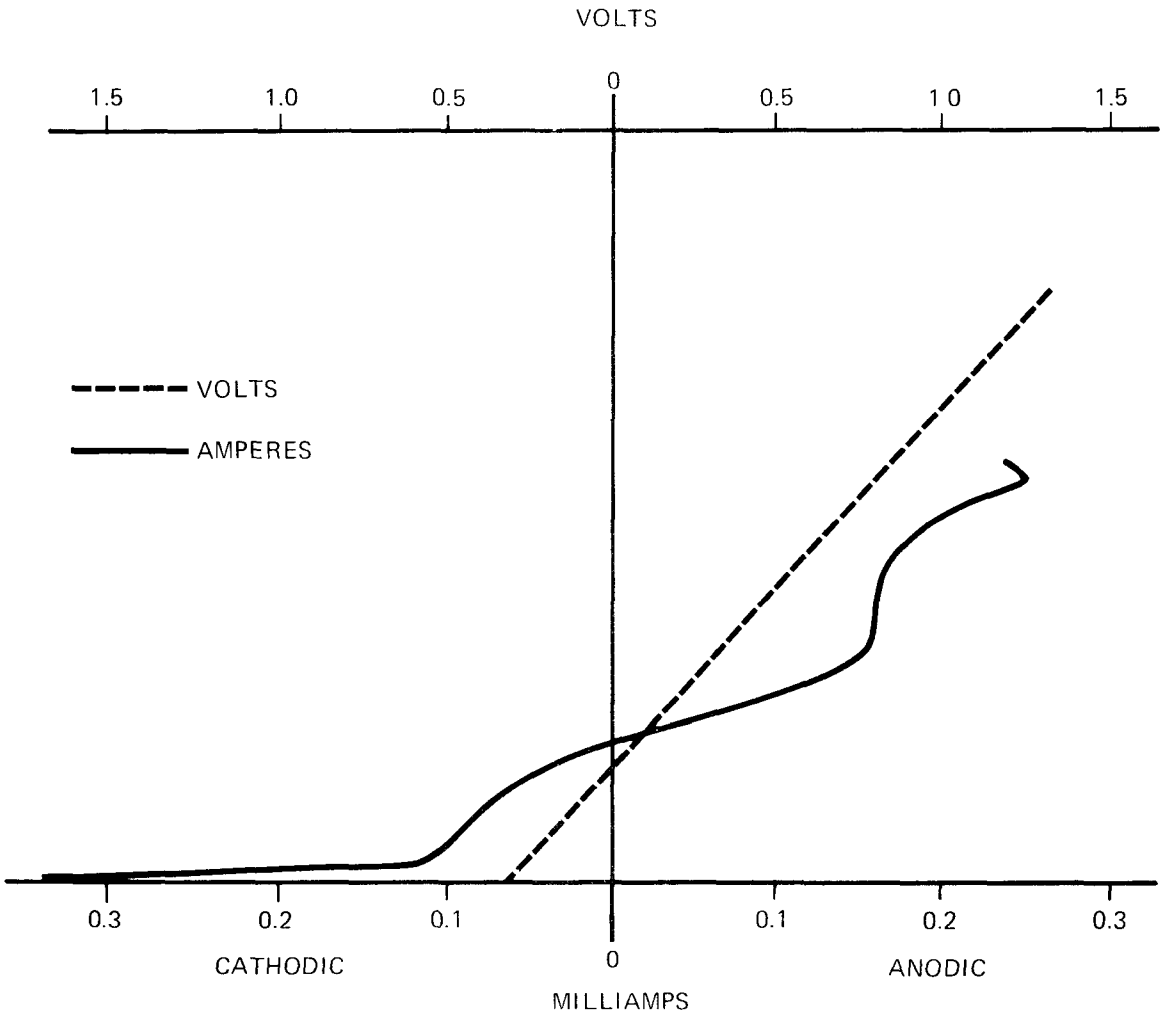


Figure 15. Polarization curve–stainless steel

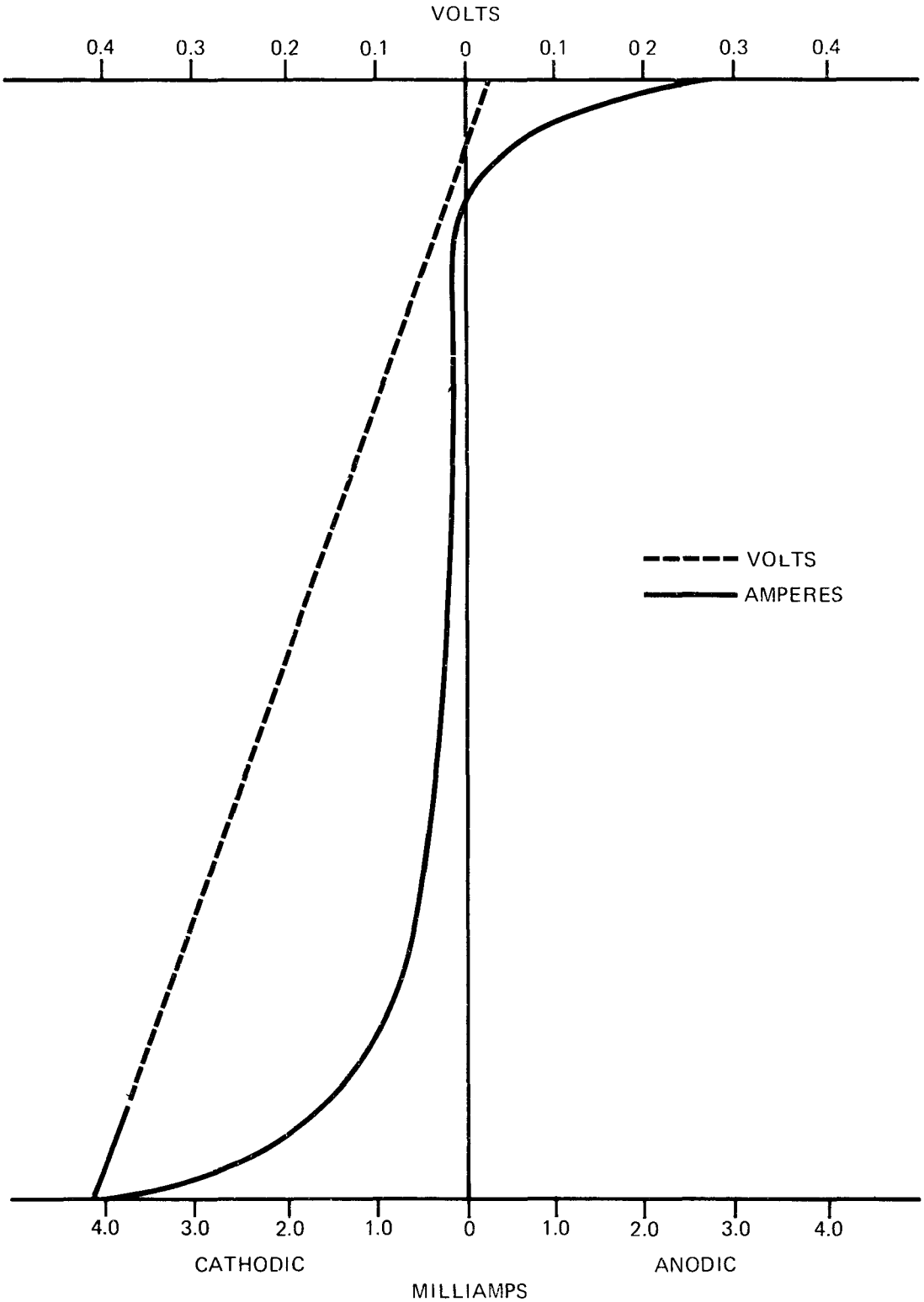


Figure 16. Polarization curve—copper

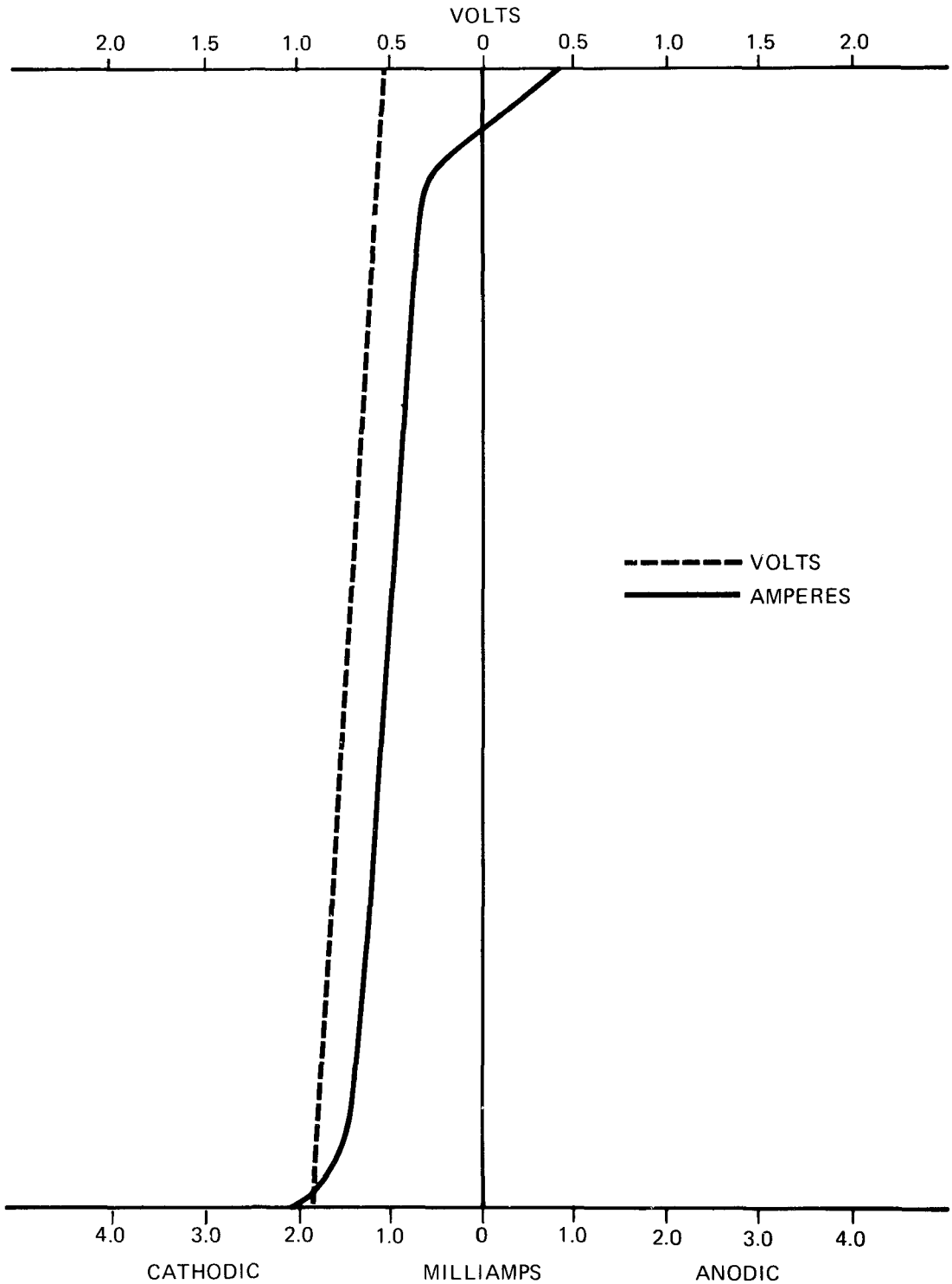


Figure 17. Polarization curve—lead

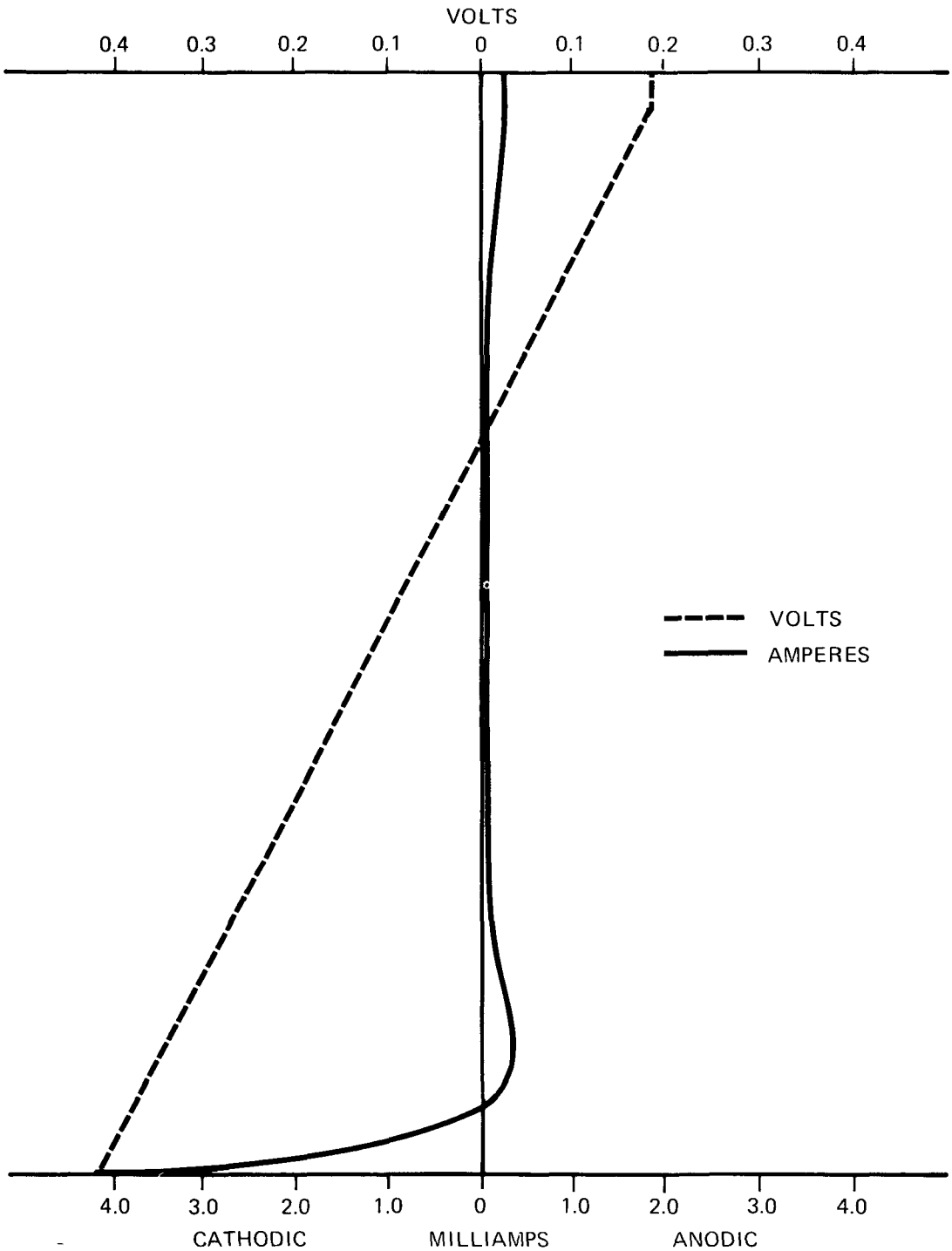


Figure 18. Polarization curve—Duriron

Table 4. ELECTRODE POLARIZATION

Metal	Hydrogen overvoltage, V	Decomposition potential, V	Test electrode		
			Current[a]	Current density[b]	Power[c]
Nickel	0.31	0.56	–	–	–
Copper	0.26	0.63	–	–	–
Duriron	0.60	0.61	3.8	0.0796	0.048
Lead	0.79	1.19	1.4	0.0280	0.033
Stainless	0.25	0.74	1.6	0.0323	0.024

[a]Milliamps at decomposition potential

[b]Amps per square decimeter at decomposition potential

[c]Watts per square decimeter at decomposition potential

The H-cell was set up with a J5D diaphragm, sulfuric-dichromate deoxidizer in the anode chamber, and sulfuric acid only in the cathode chamber. In addition, metal ion contaminants equivalent to a worked production bath were introduced into the anode (deoxidizer) chamber.

Data in table 5 indicate that the J5D diaphragm effectively inhibits transport of the major metal ion components (chromium and aluminum) of the used deoxidizer solution. The data also indicate that the minor constituents of copper, iron, zinc, magnesium, and manganese can be expected to pass through the diaphragm to some degree. It can be expected that sulfuric acid will be driven from the cathode chamber into the anode chamber. Copper, iron,and zinc should appear in a deposit on the cathode.

Removal of Dissolved Metals

The test procedure for the removal of dissolved metals was as follows:

1) Operate test cell and determine extent to which dissolved metals can be removed. Fill cell with a solution containing known amounts of Al, Cu, Zn, Fe, Mg, and Mn.

2) Inspect for electrodeposition on cathode surface.

Table 5. H-CELL MASS TRANSFER DATA

Sample	Description	H_2SO_4 gm/l	Cr^{+6} Active, gm/l	Cr^{+6} Total, gm/l	Cr^{+3}, gm/l	Al, ppm	Cu, ppm	Fe, ppm	Zn ppm	Mg, ppm	Mn ppm
HA 1	Anode chamber, start	254	9 83	10 35	0 5	20,800	380	830	326	9 2	4 75
HA-2	Anode chamber, finish	278	10 35	10 95	0 6	22,000	392	840	324	9 9	5 25
HC-3	Cathode chamber, start	287	None	None	None	None	0 15	0 70	1 72	1 47	0 65
HC-4	Cathode chamber, finish	310	None	None	None	17	0 65	1 70	2 48	1 58	1 00
CF-1	Filtered crystals of aluminum sulfate	Cr = 0 84% by weight (2 4% as $Na_2Cr_2O_7 \cdot 2H_2O$)									

3) Inspect for precipitation on cathode surface. Removal of H^+ in vicinity of cathode as $H_{2(g)}$ causes pH to increase. Precipitation of basic salts of dissolved metals can result from process.

4) Estimate material loss if cathode compartment is periodically dumped.

Preliminary work on a beaker scale was performed by dissolving aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] in a heated dichromate-sulfuric deoxidizer solution. Subsequent cooling produced insoluble solids ready for separation. The color of the crystals indicated the presence of chromium salts. A chemical laboratory analysis verified the residual chromium to be 0.84% by weight (sample CF-1, table 5).

Varying concentrations were used to establish a working range of dissolved aluminum that would lend itself well to cooling and filtration. It became apparent that a difficult crystallization and crystal separation problem existed. A concentration of aluminum sulfate below 290 gm/l requires excessive cooling capacity to produce the crystals. At a concentration of 315 gm/l, the entire volume of solution becomes a solid, immovable mass impossible to pump through a filter system. Normal quantities of minor metal constituents were added with no apparent effect on crystallization results.

Therefore, several steps were taken to reassess the details. Laboratory assemblies were made as illustrated in figure 19.

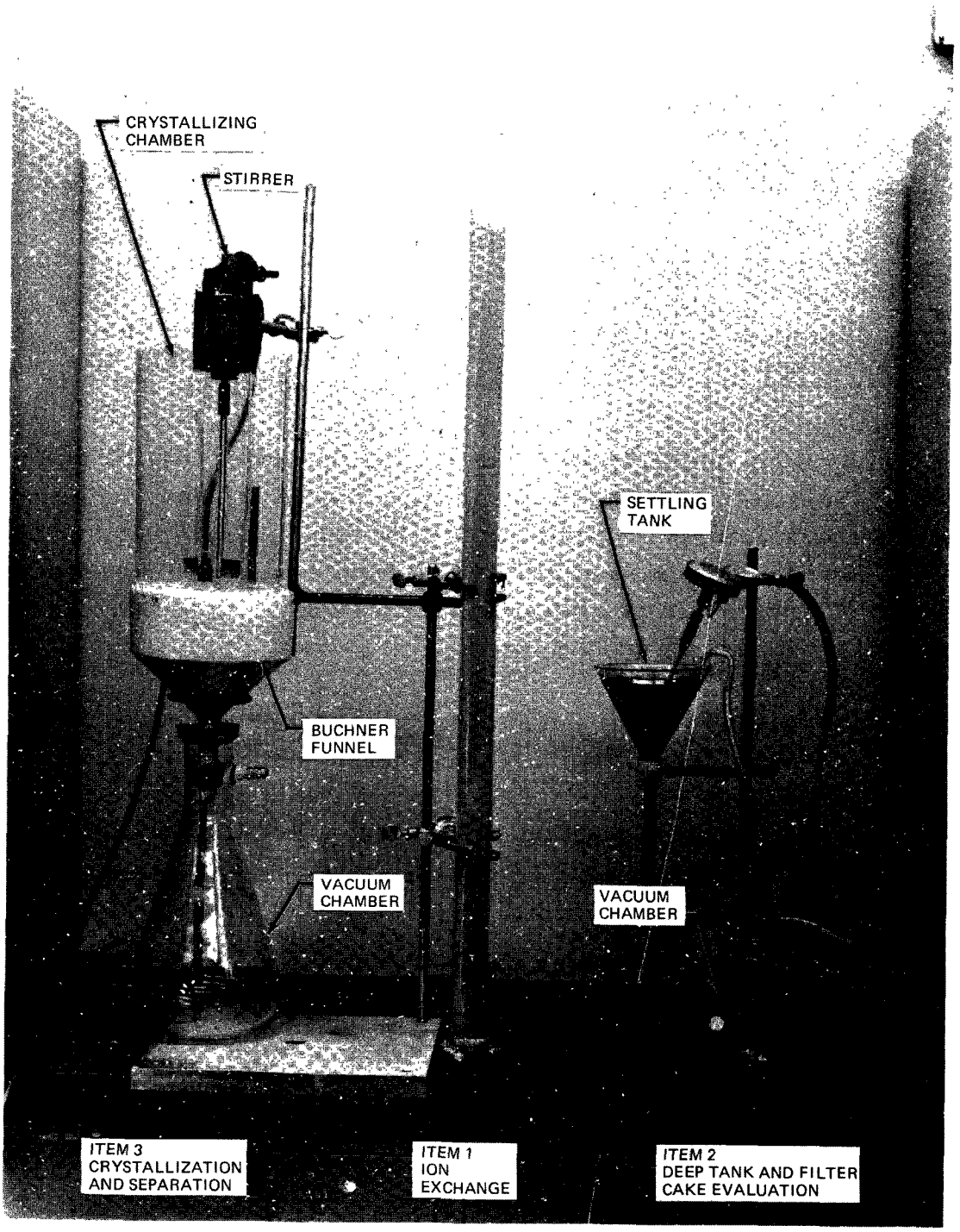


Figure 19. Laboratory metal removal evaluation

Item 1 was assembled to evaluate a backup system of ion exchange for removal of dissolved aluminum because ion-exchange beds have been successfully used to remove dissolved aluminum from chromic acid anodizing solutions. A quantity of the sulfuric-dichromate deoxidizer was passed through the regenerated bed. Results of before and after analyses are given in table 6.

Table 6. ION EXCHANGE EVALUATION
(grams/liter)

Description	Sulfuric acid	Active dichromate	Trivalent chrome	Aluminum sulfate
Beginning deoxidizer	273	30.3	0.825	173
Deoxidizer through ion exchange	260	29.0	1.20	107

From the information shown in table 6, it is apparent that development of ion exchange for recovery of dissolved metals in the strong deoxidizer would involve considerable development work. Less than half the aluminum is removed in one pass, yet the trivalent chromium content is greatly increased. This indicates degradation and consequent short life expectancy of the resin unless the oxidation potential of the deoxidizer is reduced. Further ion exchange development was withheld.

Item 2 (fig. 19) was assembled for two purposes. It was apparent that suction would be required to separate the mother liquor from the crystallized aluminum sulfate. For design purposes it is necessary to predict the maximum allowable cake thickness and the degree of vacuum required. As a result of testing, an unbroken cake of crystals 15 cm thick without the aid of a filter taxes the capability of a mechanical vacuum pump by requiring more than 700 mm of vacuum. Conversely, the mother liquor can be evacuated adequately through a 125-mm cake with less than 125 mm of vacuum.

The second test purpose of the item 2 assembly was to apply the deoxidizer solids separation problem to equivalent plating shop practices. In industrial plating shops, a common problem is the removal of carbonates from cyanide plating solutions. One procedure practiced in many areas is to transfer the problem solution to a spare tank, allow the temperature to drop, let the resultant crystals of carbonates settle out, and decant the supernatant liquid back to the plating tank. This same procedure was duplicated in item 2 on a small scale with the sulfuric-dichromate deoxidizer. Results indicate that aluminum sulfate crystals form at an extremely slow rate when slow cooling is used. Also, the aluminum sulfate crystals settle very slowly; a week or more is required for partial settling

even with vigorous stirring after crystallization. And, finally, the mother liquor cannot be removed effectively from the top of a settling because of the slow settling rate. Nor can the liquor be drawn by vacuum from the chamber bottom because of the thick bed of crystals. Therefore, this procedure was abandoned.

Item 3 (fig. 19) was assembled to gain more accurate information on the apparent problem areas of crystallization and filtration. The capacity of this setup was 7.5 liters. A heat exchanger coil of small diameter stainless steel tubing was assembled for immersion in the chamber. This provided capability for cyclic dissolving and crystallizing.

A single layer of the polyester diaphragm material was installed in the Buchner funnel to simulate a single-plate filter. A water aspirator provided suction. Later, a valve was installed between the Buchner funnel and the suction chamber. Figure 20 is a typical set of cooling curves collected from this setup.

Results of many test runs verified that:

- The workable concentration of dissolved aluminum sulfate is very narrow and lies between 290 and 315 gm/l.

- It is impractical to suction the mother liquor through a thick layer of crystals. As much as two-thirds of the liquid can be held by the crystal mass even after prolonged suction.

- It is impossible to adjust operating conditions to bring down a partial quantity of the crystals at any one cycle. The point at which small quantities of aluminum sulfate will crystallize requires refrigeration equipment for cooling. Extremes of refrigeration and reheating impose an economic burden on the process.

- A single layer of the polyester diaphragm material has adequate retention to hold the crystals. The flow resistance of the single layer is very low.

- Thick cakes of the crystals have a tendency to channel and reduce the effectiveness of suction.

- Fast cooling promotes fast crystal formation. A 10-min cooling rate from 71° to 18°C is desirable.

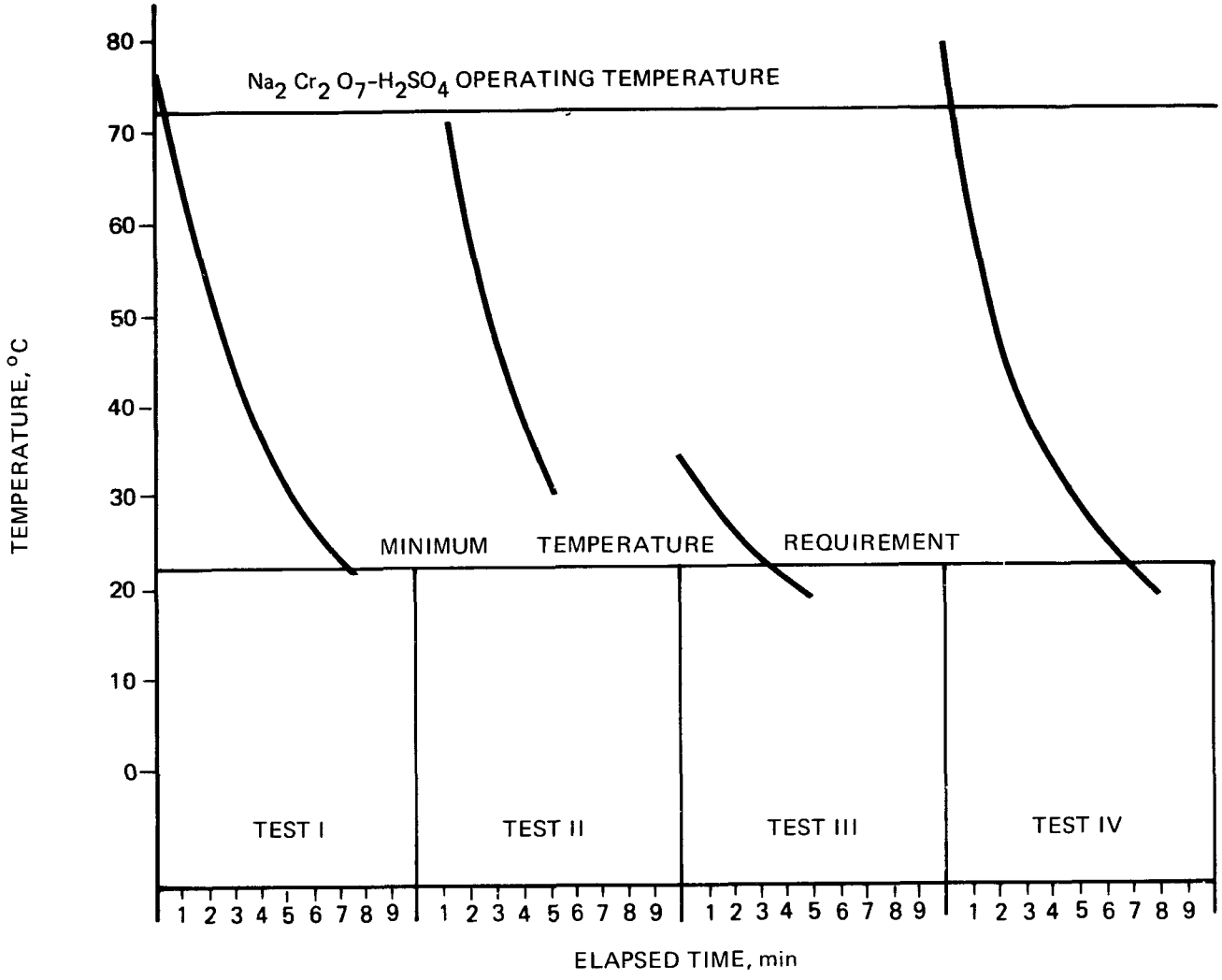


Figure 20. Solids separation cooling rate tests

- Agitation aids crystal formation and cooling rate.

- At 315 gm/l of aluminum sulfate, the cooled and crystallized solution is an immovable mass.

- Aluminum sulfate crystals cling to a chilled surface if the deoxidizer is sprayed or flowed over the cold surface. However, these crystals still retain a large volume of the mother liquor and must be evacuated.

The above results provided information for preliminary design of separation equipment for the 2200-liter preproduction tank.

Crystallizer Equipment Evaluation

A totally automated, completely continuous system was evaluated (see fig. 21). System sizing data were based on typical workload information for a full-production deoxidizer tank scaled down to the 2200-liter pilot tank size. Cost estimates for such a system indicated that continuous separation systems for a 2200-liter installation would be in excess of $4000, which was judged to be an excessive expenditure for job shop operations.

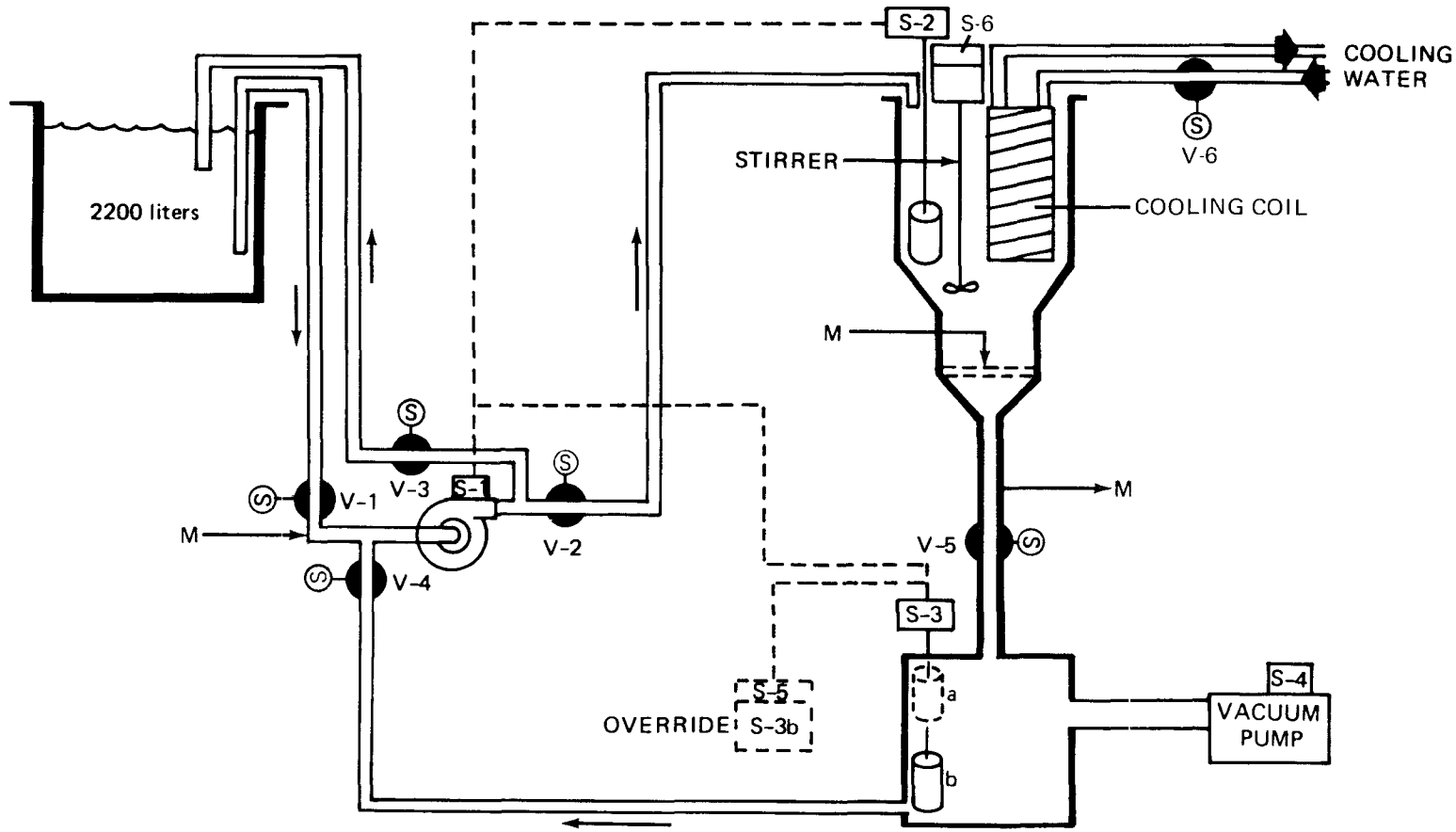
Centrifuge Evaluation

Centrifuging is a potentially effective means of removing the dissolved metals after their concentrations have increased sufficiently to allow crystallization. Therefore, the following evaluation was carried out.

A sulfuric-dichromate deoxidizer solution with 300 gm/l of dissolved aluminum sulfate was allowed to crystallize. A sample of this beginning solution is illustrated in item 1 of figure 22. A quantity of this solution (plus crystals) was processed through a commercial-size centrifuge that had both batch- and continuous-type separation capabilities.

During batch operations, only about 40% of the crystals were retained in the centrifuge bowl, while 60% passed through with the effluent (item 2 of fig. 22). Additional operations indicated that batch-type separation furnished crystals with less retained liquid than those obtained from continuous-separation operations (item 3 versus item 4 of fig. 22).

Compacting the crystals by spinning (without adding additional solution) provided somewhat drier but still unacceptable crystals (item 5 of fig. 22).



V-(x) SOLENOID-OPERATED VALVES (NORMALLY CLOSED–MANUAL OVERRIDE) } SEQUENCE
X-(x) SWITCH (NORMALLY OFF–MANUAL OVERRIDE) } TIMER CONTROLLED
M MANUALLY OPERATED WATER FLUSHING VALVE

Figure 21. Aluminum sulfate separation system schematic

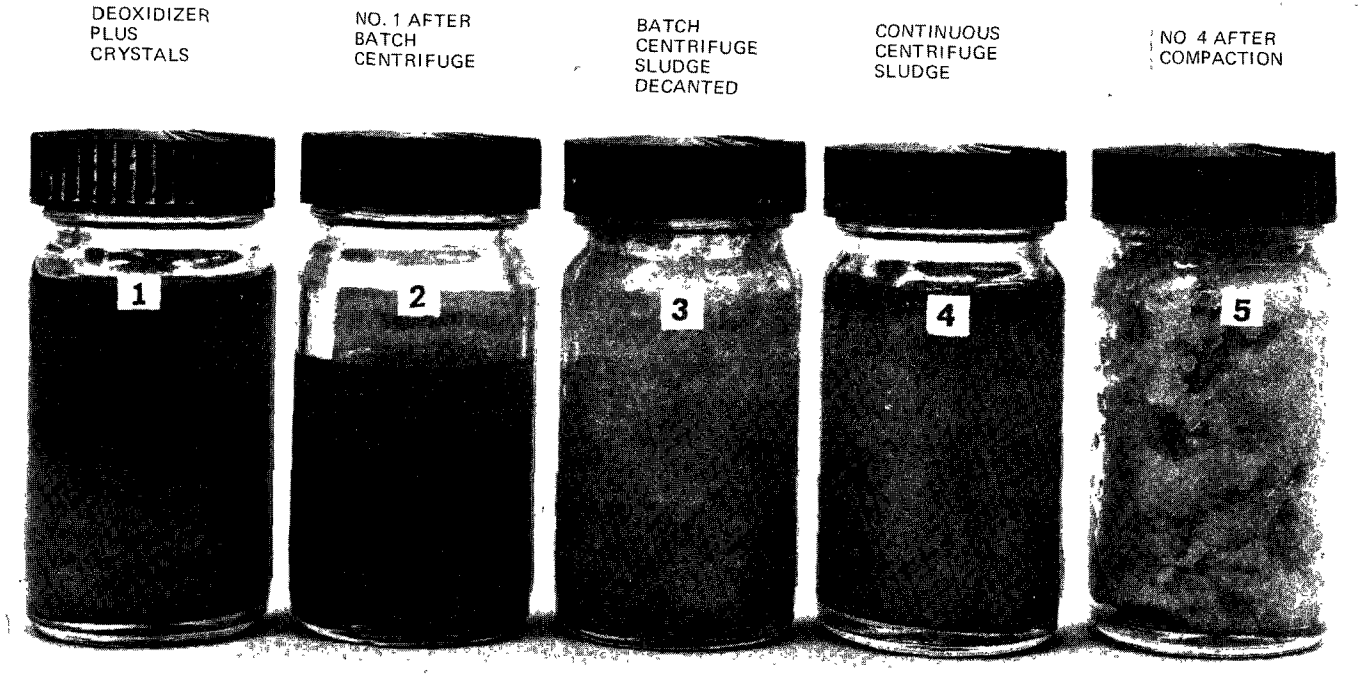


Figure 22. Display of centrifuge experimental results

A recirculating concept was then tried. Adequate dryness and solids removal were achieved by five passes of the deoxidizer volume through the centrifuge. Thus, centrifuging is technically a workable method for solids removal. However, selection of separation equipment depends not only on technical capability but also on economics, as noted later in the economics evaluation section.

Filtration Evaluation

Investigation and evaluation of conventional solids separation techniques indicated that a specialized type of filtration would most nearly satisfy the requirements of this project. A conventional cartridge-type plastics filter was tried out. The cartridges plugged up quickly, the volume of crystals limited the capacity of the filter, and the retained moisture in the crystals was very high.

Consequently, additional effort was made to adapt a laboratory-developed system for this need. The laboratory setup is illustrated in figure 23. Test data for design purposes are given in table 7. Test run 1 was made with water only and without circulation to establish basic operating data. Test run 2 was made with circulating water to establish equipment heating capabilities and ambient heat losses. To establish combined heating and cooling capabilities, test runs 3 and 4 were again made with water only. Test run 5 was made with a sulfuric-dichromate deoxidizer to determine solids separation capacity. As indicated in table 7, several test temperature plateaus were used within each test run to evaluate variations in operating conditions.

Previously evaluated systems have not provided as efficient a bulk removal as this separation system.

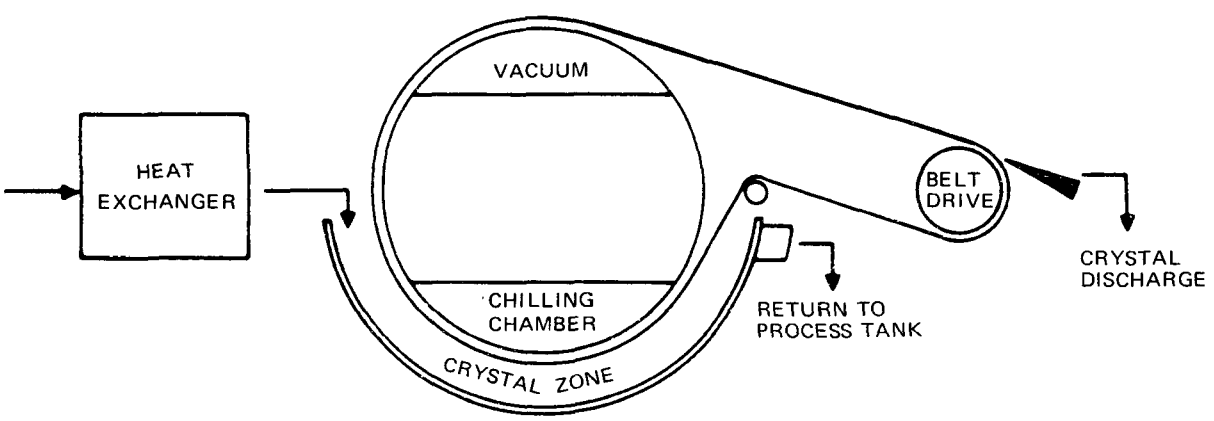


Figure 23. Setup for laboratory-developed solids separator

Table 7. LABORATORY CRYSTALLIZER EVALUATION

Items	Test run no.				
	1	2	3	4	5
Volume, ml	7000	7000	7000	7000	7000
Heat exch inlet temp, °C	45-54-66	53-66	53-66	53-70	45-90
Reservoir temp, °C	39-49-55	52	50	50-52	45-52
Crystal zone temp, °C		51	42	37-88	45-36
Chill water outlet temp, °C		—	25	19.5	24-19
Deoxidizer flow, ml/min		500	520	520	520
Belt speed, cm/min		21	23	27	23
Bulk removal, kg/hr					395
Liquid in bulk, %					48
Crystallize temp, °C					39

The following summarizes technical data for operation of the 227-liter pilot tank:

1) Deoxidizing reaction:

$$2Al + Na_2Cr_2O_7\text{-}2H_2O + 7H_2SO_4 + 9H_2O \rightarrow Al_2(SO_4)_3\text{-}18H_2O + Cr_2(SO_4)_3 + Na_2SO_4$$

2) Regeneration reaction:

$$Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O \xrightarrow{\text{6 Faradays}} Na_2Cr_2O_7 + 4H_2SO_4 + 3H_2\uparrow$$

3) Chemical and electrical consumption (227 liters):

- 315 gm/l $Al_2(SO_4)_3\text{-}18H_2O$ ≙ 95 kg crystals ≙ 7.7 kg aluminum
- Dissolving 7.7 kg of aluminum requires 42.6 kg $Na_2Cr_2O_7\text{-}2H_2O$
- Regenerating 42.6 kg $Na_2Cr_2O_7\text{-}2H_2O$ requires 23,000 amp-hr
- 23,000 amp-hr ÷ 7 hr/day ÷ 20 days/month ÷ 3 months = 54.6 amp

  -or-

  23,000 amp-hr ÷ 24 hr/day ÷ 30 days/month ÷ 3 months = 10.6 amp

4) Current densities at 45% regeneration efficiency:

Component	One-shift operation	Three-shift operation
20- by 41-cm diaphragm	7.53 amp/sq dm	1.45 amp/sq dm
25- by 61-cm electrode	3.87 amp/sq dm	0.764 amp/sq dm
227-liter deoxidizer	0.69 amp/liter	0.11 amp/liter

5) Comparative costs for a suitable cathode configuration:

100% lead	$0.379/sq dm
Pb-6%Sb alloy	$0.468/sq dm
Pb-7%Sn alloy	$1.88/sq dm
Type 316 stainless steel	$0.917/sq dm
Duriron (includes junction)	$2.78/sq dm

Copper and nickel were not priced due to total destruction of these metals in the sulfuric-dichromate deoxidizer. When this cost information is compared with electrical consumption and efficiency data collected from the potentiostat and the H-cell, the lowest priced material, 100% lead, is the logical choice for both the anode and cathode.

TASK IV–PILOT PLANT ASSEMBLY AND OPERATION

The pilot plant facility is illustrated in figure 24. The 227-liter tank was charged up and put into operation (see fig. 25), and 37 sq dm of aluminum were exposed to the solution. From 10 to 30 amp of dc current were imposed across the electrodes. In this way, aluminum dissolution and continuous regeneration were accomplished simultaneously.

Cathode chamber problems arose during the shakedown period. Chemical analyses of the tank and chamber solutions verified that an unexpectedly high mass transfer of components occurred between the chambers.

Although fabrication of the small (15- by 20-cm) polyester diaphragm developed early in the program presented no problems, equivalent low permeability in a 30- by 50-cm size was not achieved.

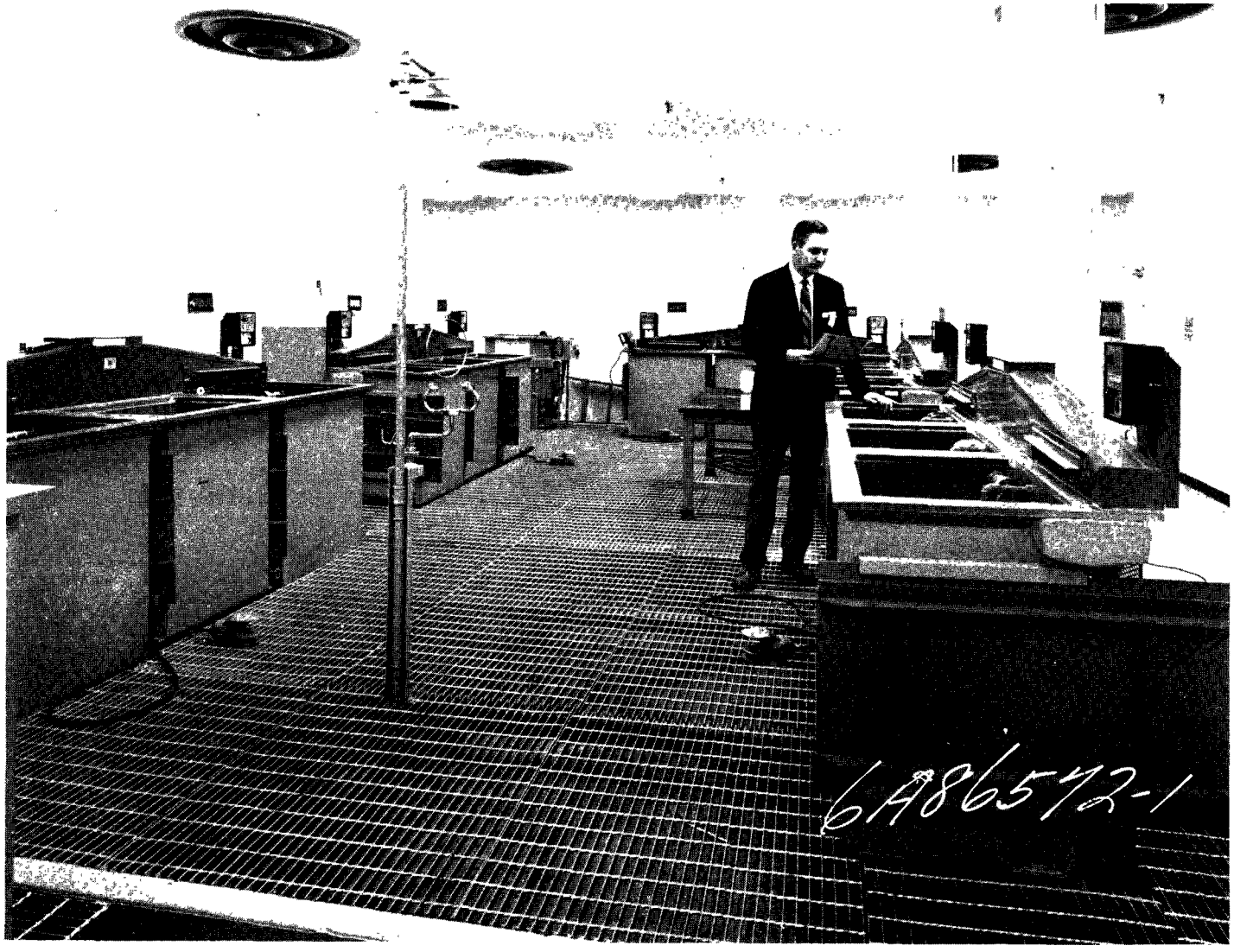


Figure 24. Pilot plant facility

Figure 25. 227-liter pilot regeneration tank and accessories

In the chamber itself, electrolytic corrosion of 18-8 stainless steel fastener was severe. Loss of sealing pressure occurred within a few days. Total fastener failure followed within a week or two, depending on fastener location.

The cathode chamber was redesigned and rebuilt. Several small diaphragms were used instead of one larger size. Titanium fasteners replaced those of stainless steel.

The pilot plant tank was recharged. Solution operating conditions were:

Sodium dichromate	31 to 37 gm/l as $Na_2Cr_2O_7 \cdot 2H_2O$
Sulfuric acid	290 to 310 gm/l as H_2SO_4
Temperature	62° to 71° C
Metal removal rate	0.00006 to 0.00016 cm/surface/hr

The rebuilt diaphragm cell was operated in the tank using various configurations of laminated polyester diaphragms. The diaphragm cell solution was sulfuric acid at 290 to 310 gm/l. Titanium fasteners performed satisfactorily. Commercial-grade lead in sheet form was used as electrode material. A dc current was imposed across the electrodes with the anode in the tank solution and the cathode in the diaphragm cell solution.

Operational performance was recorded by daily analyses for sulfuric acid, sodium dichromate, and aluminum sulfate. Hexavalent chromium was determined by conventional titration with a standardized thiosulfate solution. A specialized titrimetric method for determination of sulfuric acid and aluminum sulfate was developed to satisfy the frequency and accuracy needs of this project. The method involves titration with standardized sodium hydroxide solution to specific pH values. The calibration curves for the pH values are illustrated in figure 26.

Typical data for 2 months of operation are shown in figure 27. The early work, such as that of period A, consisted of batch-type operations. The hexavalent chromium and sulfuric acid were depleted rapidly by immersing a large area of aluminum alloy in the tank. The sheet of aluminum was then removed from the tank and the resultant trivalent chromium was electrolytically regenerated. This sequence was repeated several times.

After period A, effort was spent in determining equilibrium conditions of deoxidizing plus electrolytic regeneration and migration of chemicals through the diaphragm. Sufficient data and operating experience were gained so that only a short period of simultaneous deoxidizing and electrolytic regeneration was necessary. The data are illustrated in period B of figure 27.

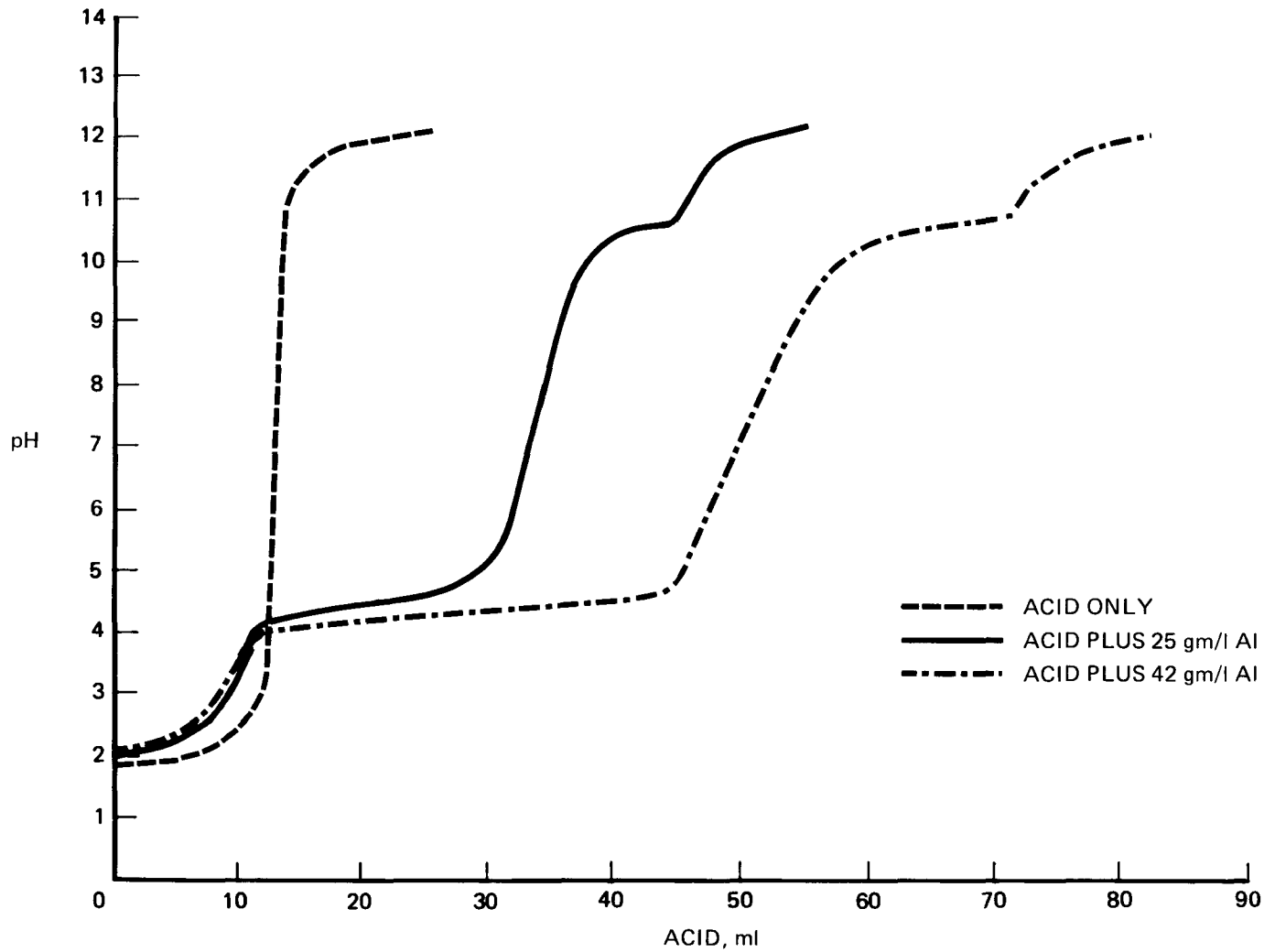


Figure 26. pH titration curves for sulfuric acid plus aluminum sulfate

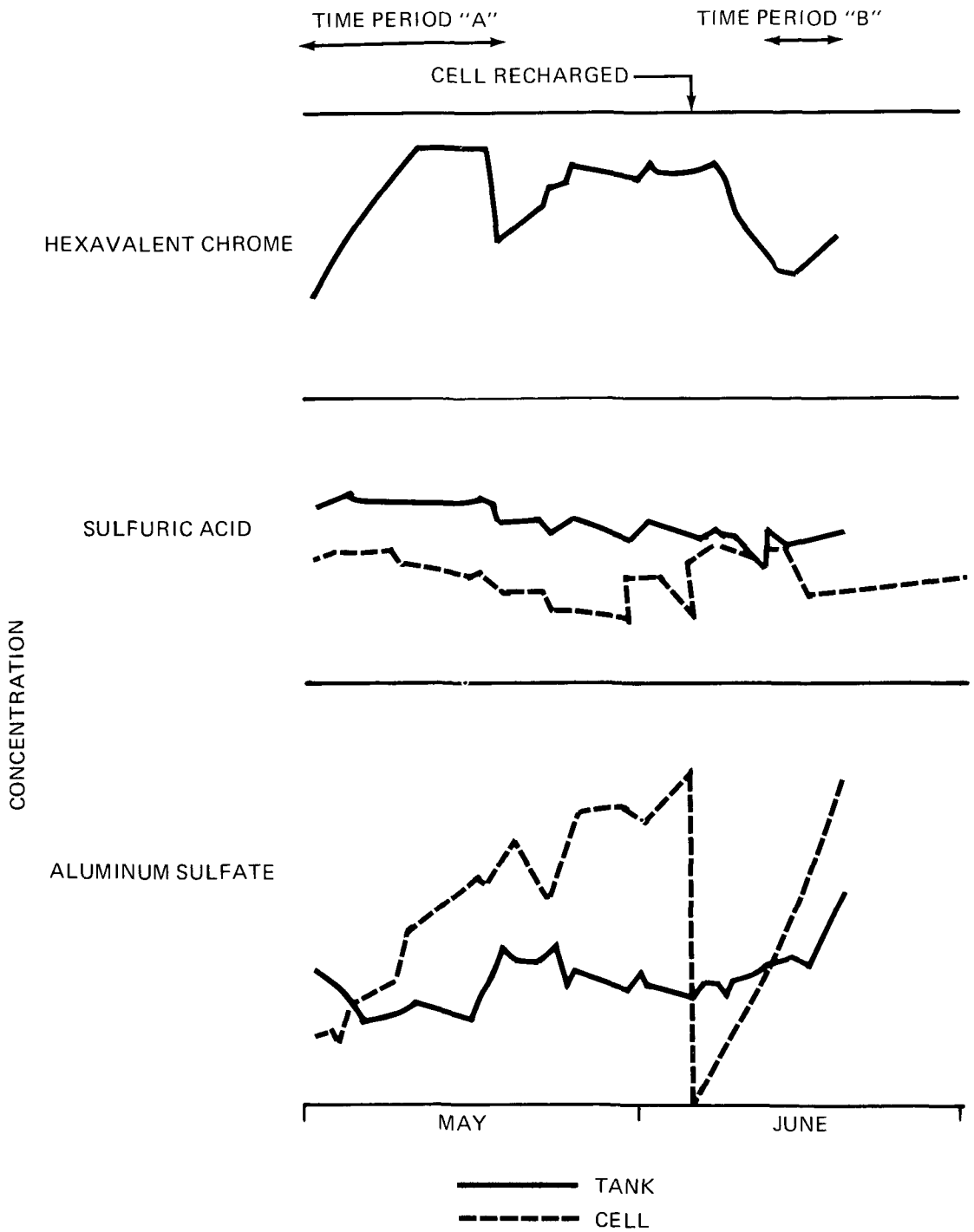


Figure 27. 227-liter pilot tank continuous regeneration analyses

It can be seen from the graphs of figure 27 that metal salts migrated into the diaphragm cell and sulfuric acid passed into the tank volume. Since the volume of the cell constitutes only about 4.5% of the total process volume, a small migration of chemicals through the diaphragm produces large concentration changes in the cell. These changes affect the regeneration efficiency and chemical concentration control. Therefore, effort was undertaken to reduce the porosity of the diaphragm.

A 130-cm water column test stand (fig. 28) was built to provide a porosity evaluation capability. A constant hydrostatic head is maintained over the diaphragm and the rate of water passing through the diaphragm as a result of this head is measured in milliliters per square centimeter per hour. Testing with this equipment indicated that porosity can be reduced by: (1) increasing the number of layers of polyester material, (2) increasing the pressure at which the layers are laminated, and (3) increasing the time at pressure. Exposure tests also indicate that excessive temperatures (such as 200°C) for a period of time tend to deteriorate the fabric. No specific time/temperature relationship has been established, however. Porosity as measured on this test stand was reduced from 220 to 2.3-4.6 ml/sq cm/hr.

Table 8 illustrates test data accumulated on the porosity test stand.

Table 8. DIAPHRAGM POROSITY

Diaphragm no.	Diaphragm code	Layers	Pressure, kg/sq cm	Temp, °C	Time, hr	Porosity, ml/sq cm/hr
			62 sq cm			
1	J5D-20STM-3	20	140	150	0.2	220
2	13 Jun-20-10/400	20	280	205	0.2	164
3	13 Jun-20-15/400	20	280	205	0.25	370
4	16 Jun-20-45/300	20	280	150	0.75	18
5	19 Jun-20-4/300	20	280	150	4.0	2
			97 sq cm			
6	J5D-20-1-22	20	280	150	3.0	50
7	J5D-20-1-25	20	280	150	4.0	25
8	J5D-20-1-21	20	280	150	5.0	17
9	J5D-20-1-25a (repressed)	20	280	150	3.0	7
10	J5D-30-1-9	30	280	150	7.0	5
11	2J5D-30	60	280	150	3.0	0
12	3J5D-20	60	280	150	3.2	2.5
13	J5D-60	60	280	150	9.0	2.3
14	J5D-60-2	60	280	150	5.7	–

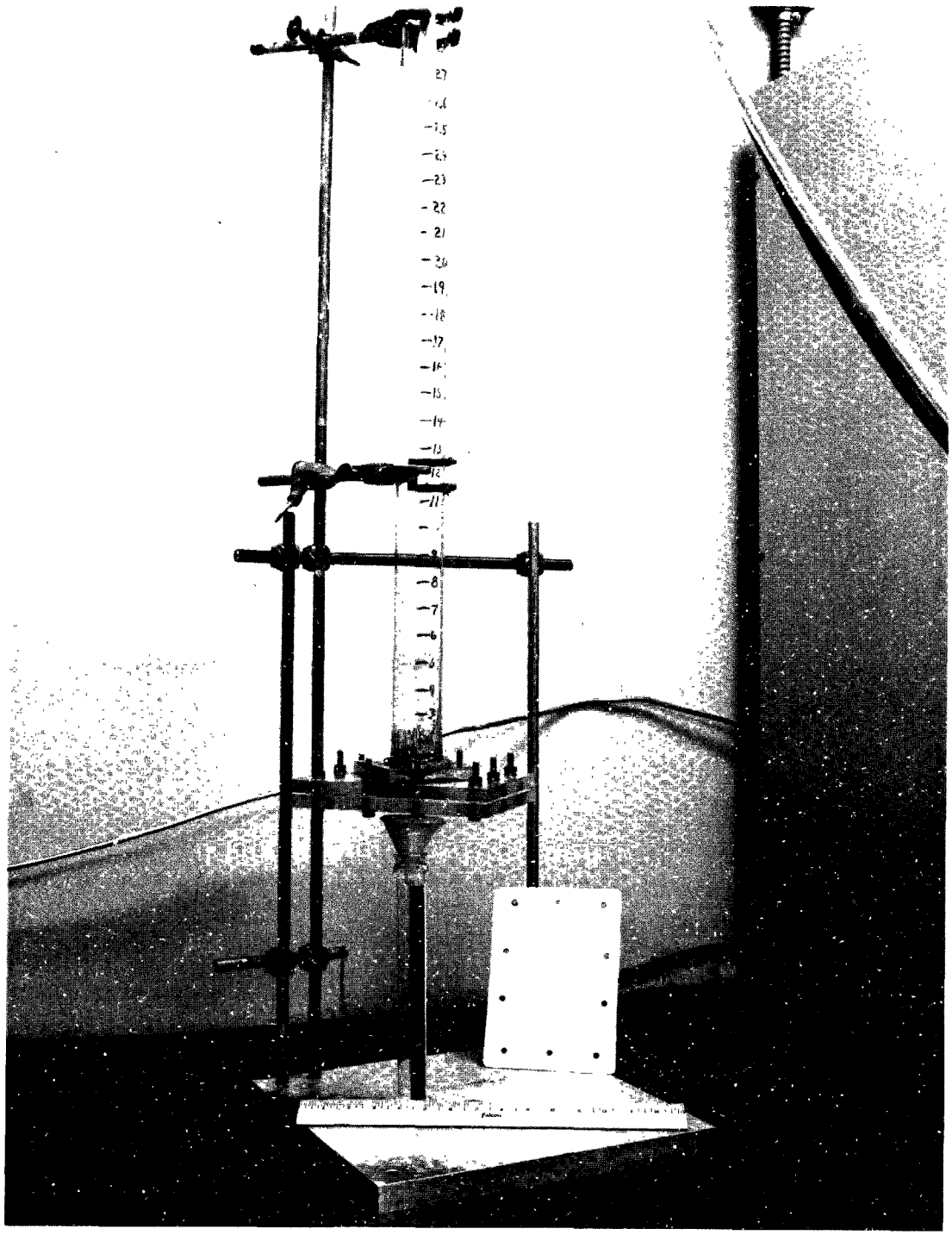


Figure 28. Test stand for diaphragm porosity evaluation

Diaphragm numbers 10, 11, 13, and 14 were selected for service testing in the 227-liter pilot tank. The tank was again recharged and, as before, operational performance of the deoxidizer regeneration was monitored by daily chemical analyses. Acceptable deoxidizing performance was judged by determining: (1) etch rates on 2024 bare and 2024 clad aluminum alloys, and (2) uniformity of etch on large areas (such as 10 to 20 sq dm) of alloys 2024 bare, 2024 clad, and 7075 bare.

Dissolved aluminum buildup for the 227-liter pilot tank was scaled down from existing production tank records. Continuous suspension of 372 sq cm of aluminum in 227 liters is equivalent to 200% of the normal cyclical load of a production tank. Therefore, this is the magnitude of the load imposed on the pilot tank.

A chart of daily analyses is given in figure 29. An explanation of the individual analyses is as follows:

1) Total chrome (tank)—This analysis is performed periodically to monitor the material balance of the system.

2) Active chrome (tank)—This analysis measures the chromium ion that is available for deoxidizing.

3) Total chrome (cell)—If chromium migrates through the diaphragm, it will exist only in the trivalent stage during regeneration because of the strong reducing conditions at the cathode. Therefore, this analysis evaluates the functional capability of the diaphragm.

4) Sulfuric acid (tank)—Additions of sulfuric acid are required to replace the acid used to form aluminum sulfate.

5) Sulfuric acid (cell)—Acid in the cell provides electrical conductivity in the cell solution. Migration into the tank through the diaphragm is expected and, therefore, additions will be required.

6) Aluminum sulfate (tank)—Analysis information provides rate and quantity of dissolved metal for eventual removal by crystallization. During pilot testing this analysis also measures the accelerated age of the test solution.

7) Aluminum sulfate (cell)—The regeneration current will drive some aluminum through the diaphragm into the cathode area.

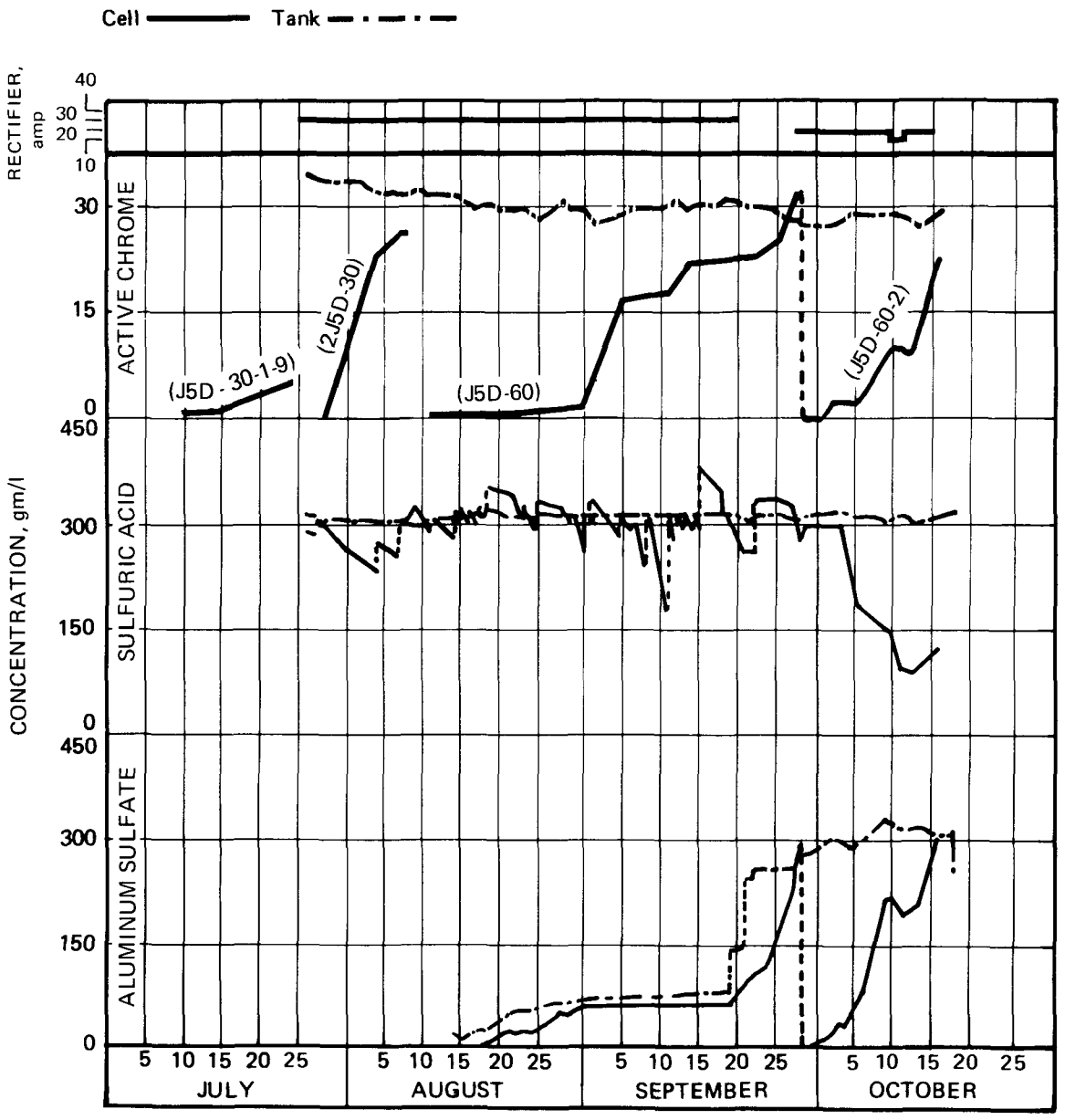


Figure 29. 227-liter pilot tank continuous regeneration—sulfuric-dichromate deoxidizer

The upper zone of figure 29 indicates the ability of the electrical system to maintain a relatively constant concentration of hexavalent chromium at 85% to 90% of the initial charge. During this test period, an area of 280 to 880 sq cm of aluminum alloy 7075 was immersed continuously. Rectifier settings were varied from 15 to 30 amp.

The middle zone of the chart illustrates the stability of the sulfuric acid in the tank and its instability in the cell. The acid in the cell was allowed to fluctuate from 225 to 375 gm/l with no detectable effect on the total system. Near the end of the test, the sulfuric acid in the cell was allowed to drop to a very low value (90 gm/l). No ill effects were noted other than a slight rise in voltage required at the rectifier (9¼ versus 11¼ V).

The lower zone of the chart records the deliberate buildup of aluminum in the tank and its migration into the cell. Note that in the best case (August 9 through 31), chromium in the cell increased from 0 to 18 gm/l while aluminum sulfate increased from 0 to 61 gm/l.

The first low-porosity diaphragm (J5D-30-1-9) was tested from July 10 through 24 without imposing electrical current. Diffusion of chromium ions occurred quickly and the diaphragm was replaced. The second low-porosity diaphragm (2J5D-30) was laminated from two previously pressed 30-layer sections that had shown some promise in preliminary evaluation. However, delamination and structural degradation occurred after 4 days of regeneration. Two 60-layered diaphragms (J5D-60 and J5D-60-2) performed quite well. The indication is that pressure time during diaphragm fabrication is important to the functional life.

Precise determination of aluminum etch rate plus visual inspection of large areas of deoxidized aluminum surfaces are used to evaluate the deoxidizer performance. Etch rates are determined by weight losses per unit of time measured on a precision laboratory balance (fig. 30). Values from 0.00093 gm/sq cm/hr at 60°C to 0.0045 gm/sq cm/hr at 71° C are considered normal.

Data from the etch rate determinations are shown in figure 31. The fluctuations in the early stages are typical of a fresh solution. For visual evaluation of deoxidizer solutions, large areas of aluminum alloys 2024 bare, 2024 clad, and 7075 bare were deoxidized for 20 min, which is twice the normal process time. The presence of pits or preferential attack in any area would be objectionable. No such defects were noted either at low- or high-aluminum content. All surfaces retained the normal, frosted appearance.

Conclusions to be drawn from this pilot test are:

- Continuous electrolytic regeneration of trivalent chromium to hexavalent chromium is not detrimental to the deoxidizing capability of the sulfuric-dichromate solution.

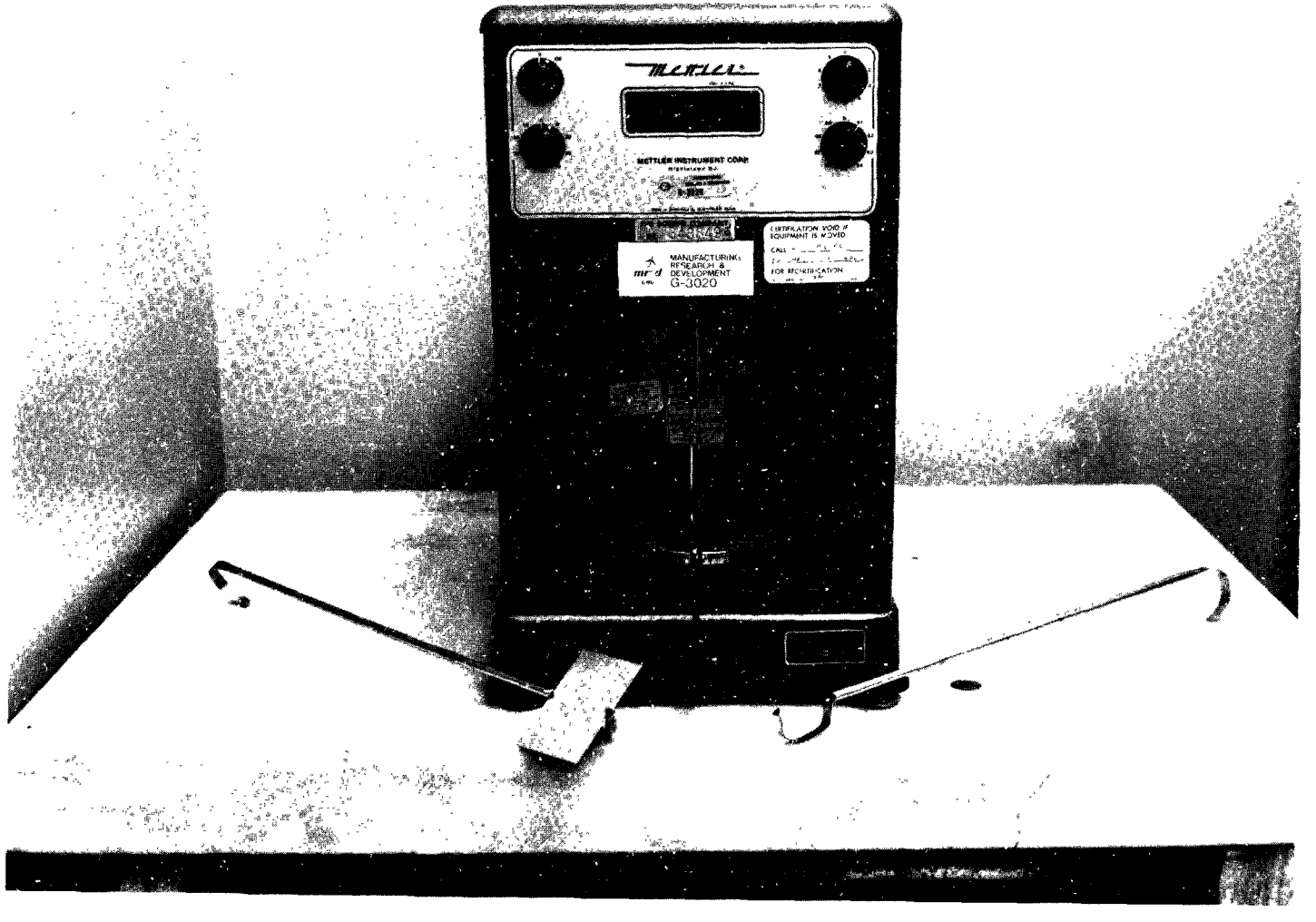


Figure 30. Precision laboratory balance

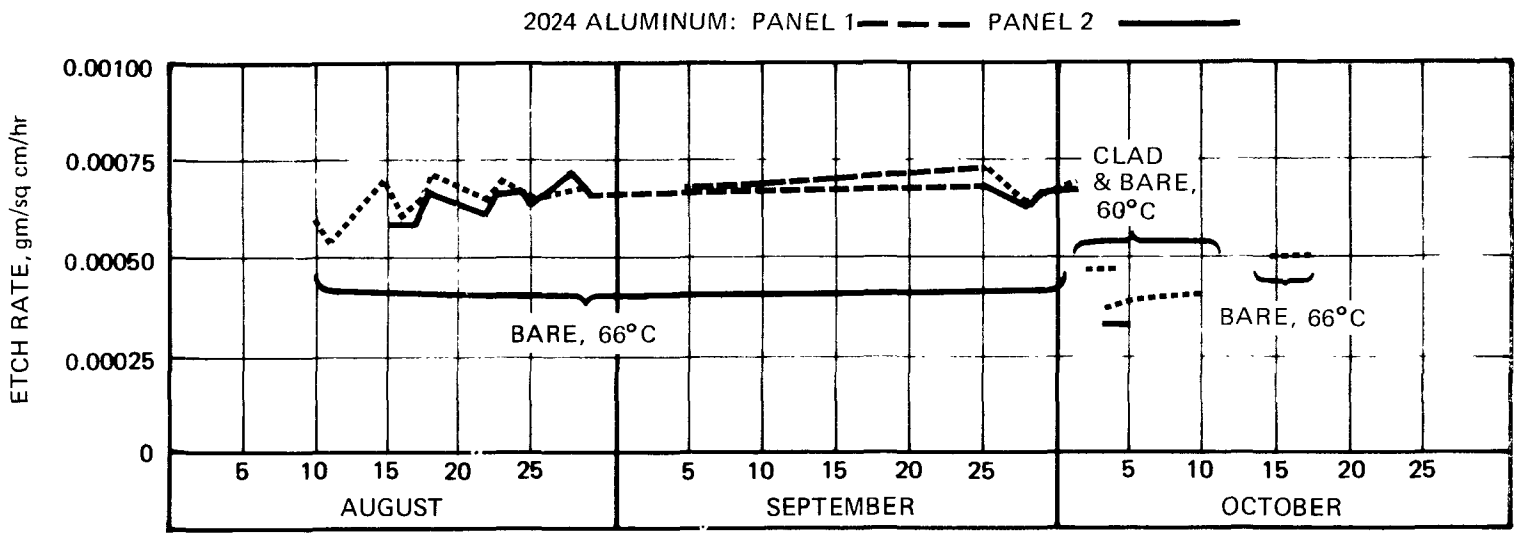


Figure 31. 227-liter pilot tank etch rates—continuous regeneration

- The concentration of hexavalent chromium can be maintained at 85% to 90% of the total chromium concentration in the deoxidizer solution.

- Chromium compounds can be retained in the oxidizing chamber of the regeneration system with a polyester diaphragm when porosity is less than 2.3 ml/sq cm/hr at 130 cm hydrostatic head.

Previous laboratory work established that a drum-type separation system is best for removal of solids from the deoxidizer solution. Additional testing has been accomplished to more accurately define size and rate requirements of equipment necessary for the 2200-liter pilot tank. A summary of these data are contained in table 9.

Table 9. DRUM FILTER EVALUATION

Items	Test no						
	1	2	3	4	5	6	7
Drum speed, rpm	1/4	1/4	1/6	1/6	1/4	1/6	1/6
Filter time, sec	88	88	132	90	88	132	132
Dewater time, sec	96	96	144	180	96	144	144
Water in cake, %	45.2	41.5	45.1	43.8	45.7	43.8	41.2
Cr in dry cake, %	2.4	2.1	2.6	1 4	2.2	4.5	4.6

A commercially available drum filter was identified by using the data from table 9. A 20- by 12-in. drum filter (50.8-cm diameter by 30.5-cm width) was the smallest marketed filter that could be located. The published characteristics of this filter were used to calculate capacities for aluminum sulfate separation and are presented in table 10.

Table 10. DRUM FILTER CAPACITY

Items	Test no						
	1	2	3	4	5	6	7
Pumping capacity, liters/sq dm/hr	15.5	14.7	3.5	2.8	4 1	1.9	1.7
Solids output, dry gm/sq dm/hr	352	366	156	151	259	142	142

The data in table 10 are applicable to the 2200-liter pilot tank operation. When capacities are compared with deoxidizer solution characteristics, the 20- by 12-in. filter would have such overcapacity that only intermittent or semi-automated solids separation would be required in conjunction with the continuous electrolytic regeneration for this operational volume.

TASK V–COMMERCIAL PRODUCTS EVALUATION

Amchem 6-16, a commercial deoxidizer produced by Amchem Products, Inc., received benchtop evaluation. This proprietary product can be mixed with either sulfuric acid or nitric acid according to the user's choice. A supply was made up using sulfuric acid according to the following analysis:

Hexavalent chromium	24 gm/l as $Na_2Cr_2O_7$-$2H_2O$
Sulfuric acid	68 gm/l

This solution was depleted by dissolving aluminum until the following analysis was reached:

Hexavalent chromium	12 gm/l as $Na_2Cr_2O_7$-$2H_2O$
Sulfuric acid	53 gm/l
Aluminum	48 gm/l as $Al_2(SO_4)_3$-$18H_2O$

Two liters were regenerated at 5 amp in the benchtop cell illustrated in figure 32. After 4 hr the hexavalent chromium rose to 16 gm/l. After 5 hr the hexavalent chromium rose to 18.3 gm/l, or about 75% regenerated. Before-and-after weighing of the lead electrodes showed no loss in weight by either electrode. This information indicates that Amchem 6-16, using sulfuric acid, is suitable for further regeneration evaluation. Since this product gives the user the choice of either sulfuric or nitric acid as the makeup acid component, continuing work requires that regeneration in the nitric acid phase also be investigated.

A partially depleted solution of Amchem 6-16, using nitric acid for makeup, was transferred to the 227-liter pilot tank. Benchtop work indicated that this formulation will dissolve both lead and lead alloys by simple immersion and by electrolytic action. This work also illustrated that 316 stainless steel was severely eroded when used as an anode. However, Duriron withstood the anodic erosion. Therefore, Duriron anodes were assembled for the 227-liter volume. Stainless steel was used for the cathode in the diaphragm cell. Diaphragms as fabricated in previous work were used for this test.

No regeneration of trivalent chromium to hexavalent chromium occurred after 1440 amp-hr were passed through the solution. The Duriron anodes were replaced with conventional precious metal plating electrodes of platinized titanium mesh overplated with platinum black to reduce hydrogen overvoltage. No regeneration of trivalent chromium occurred in 3840 amp-hr. Analytical progress results of this test are illustrated in figure 33.

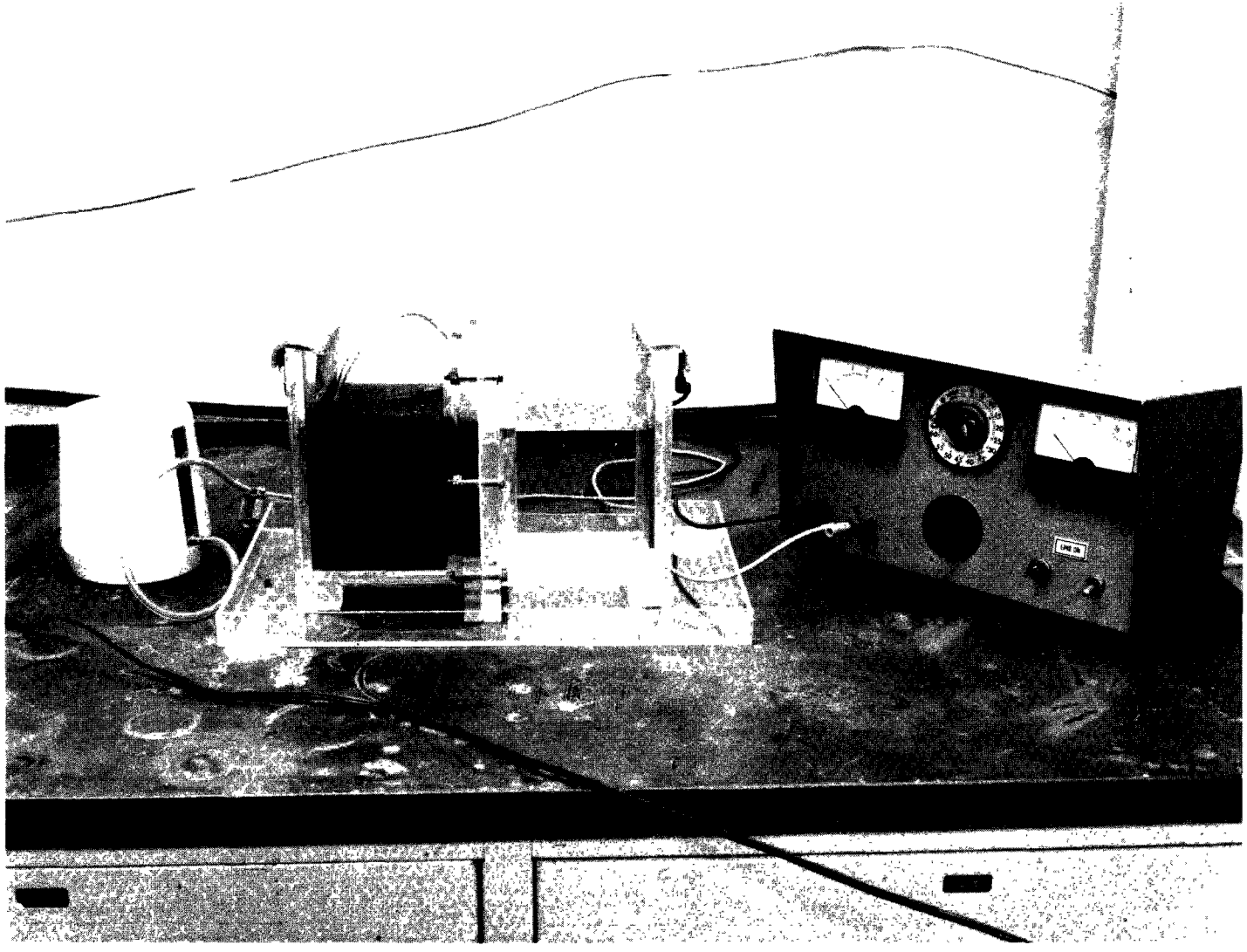


Figure 32. 2-liter cell for commercial products regeneration evaluation

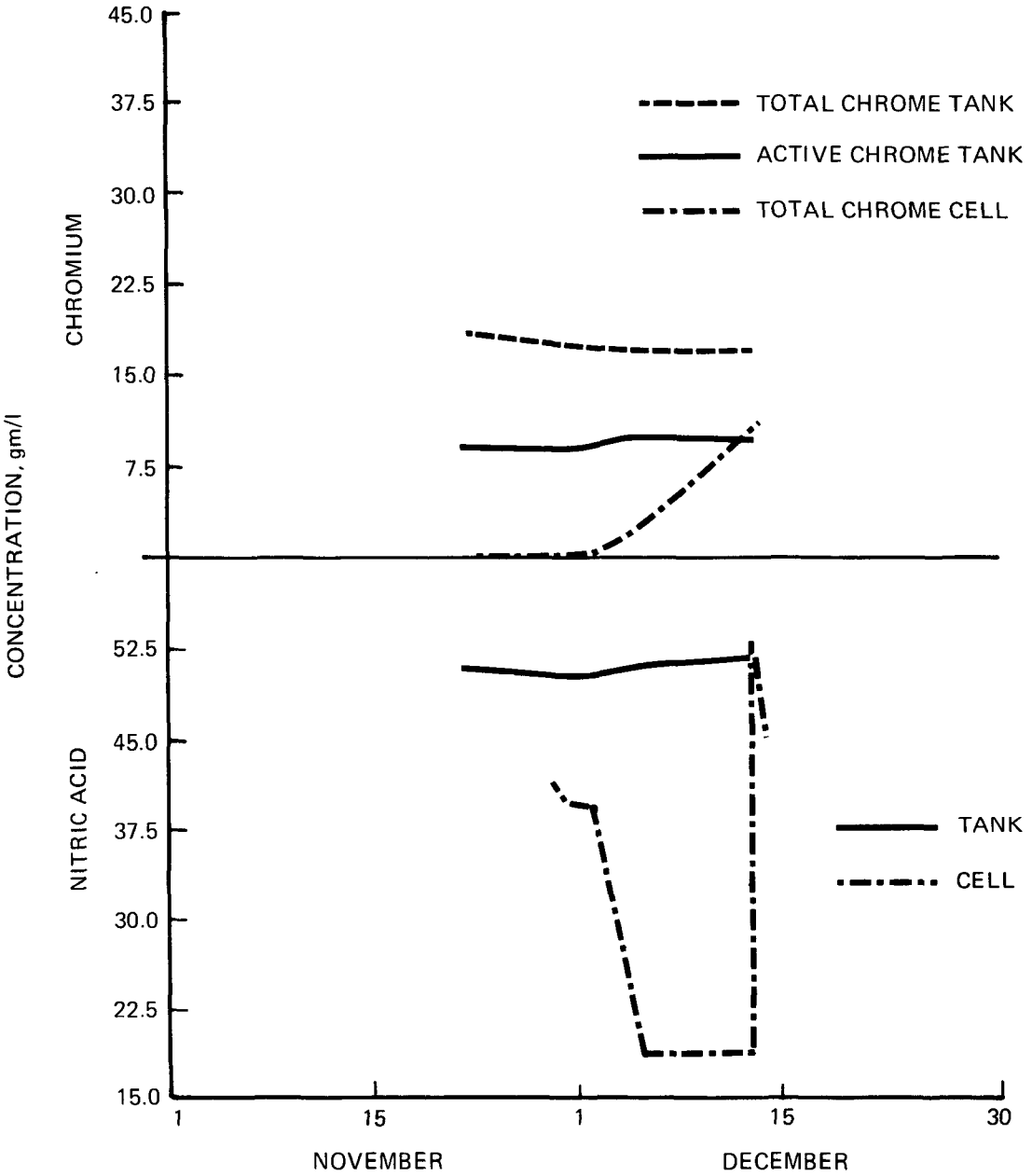


Figure 33. Regeneration of nitric-acid-based proprietary deoxidizer

At this time, further work on proprietary deoxidizers was augmented by the use of the 2-liter diaphragm cell. Regeneration operating conditions were varied as to time, temperature, concentration, and current densities. During this period, the proprietary deoxidizers evaluated were Amchem 6-16 and Smutgo 4 (manufactured by Turco Products, Inc.). Both used nitric acid as the makeup acid. Amchem 6-16 with sulfuric acid, instead of nitric, was also evaluated.

Work during this period indicated that efficient regeneration of all three materials can be accomplished if the temperature is raised to 65°C or higher, and the total chromium in terms of sodium dichromate ($Na_2Cr_2O_7$-$2H_2O$) is 22.5 gm/l or higher. This higher chromium content presents no problem industrially since hexavalent chromium is added as a solution maintenance material in normal usage. However, the elevated temperature requirement makes the regeneration process somewhat less flexible. The users of these dilute deoxidizers have the choice of using an elevated-temperature batch treatment for regeneration or investing in heating plus cooling capacity for a continuous-loop regeneration.

Each of three proprietary deoxidizers was cycled through three accelerated depletions and regenerations to verify the concept of batch regeneration at elevated temperature. Where necessary, the total chromium content was raised above 22.5 gm/l before the first depletion stage. During normal usage, all deoxidizers based on nitric acid require periodic adjustment of etch rate by the addition of a fluoride compound. This was done by additions of hydrofluoric acid. Etch rates were determined and adjusted prior to the depletion steps to ensure an optimum reduction rate of the chromium. Accelerated depletion was accomplished by immersing bare aluminum plates (alloy 2024) in the deoxidizer so that at least 4.91 sq dm/l were exposed. Hexavalent chromium content was monitored until the deoxidizer was depleted to approximately 75% of its starting concentration. The used deoxidizer was then transferred to a regeneration cell and the temperature raised above 65°C. Electrical current of 9.2 to 13.0 amp/l was imposed from a dc power supply. As regeneration proceeded, the hexavalent chromium content usually leveled off at 85% of its original makeup. At this time, regeneration was stopped, the solution cooled, the etch rate was readjusted, and the depletion step was repeated.

The results of these experiments are illustrated in figures 34, 35, and 36. The active chromium content, dc power supply output, and temperature are tracked for each proprietary deoxidizer for three full cycles of depletion plus regeneration. Active chromium is expressed as grams per liter of $Na_2Cr_2O_7$-$2H_2O$ and aluminum content is expressed as grams per liter of $Al(NO_3)_3$-$9H_2O$ or $Al_2(SO_4)_3$-$18H_2O$.

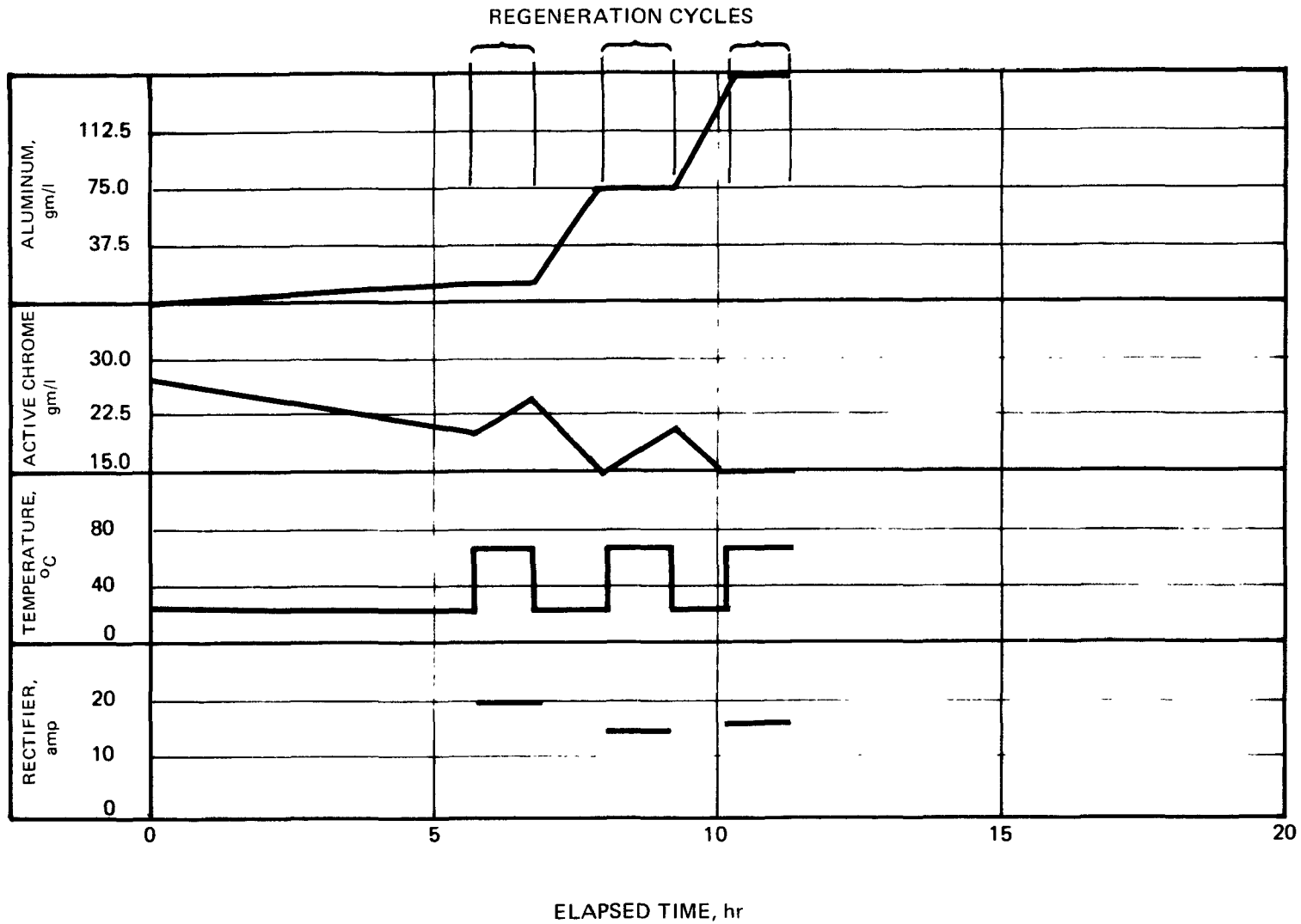


Figure 34. Regeneration of Amchem 6-16 (HNO_3)

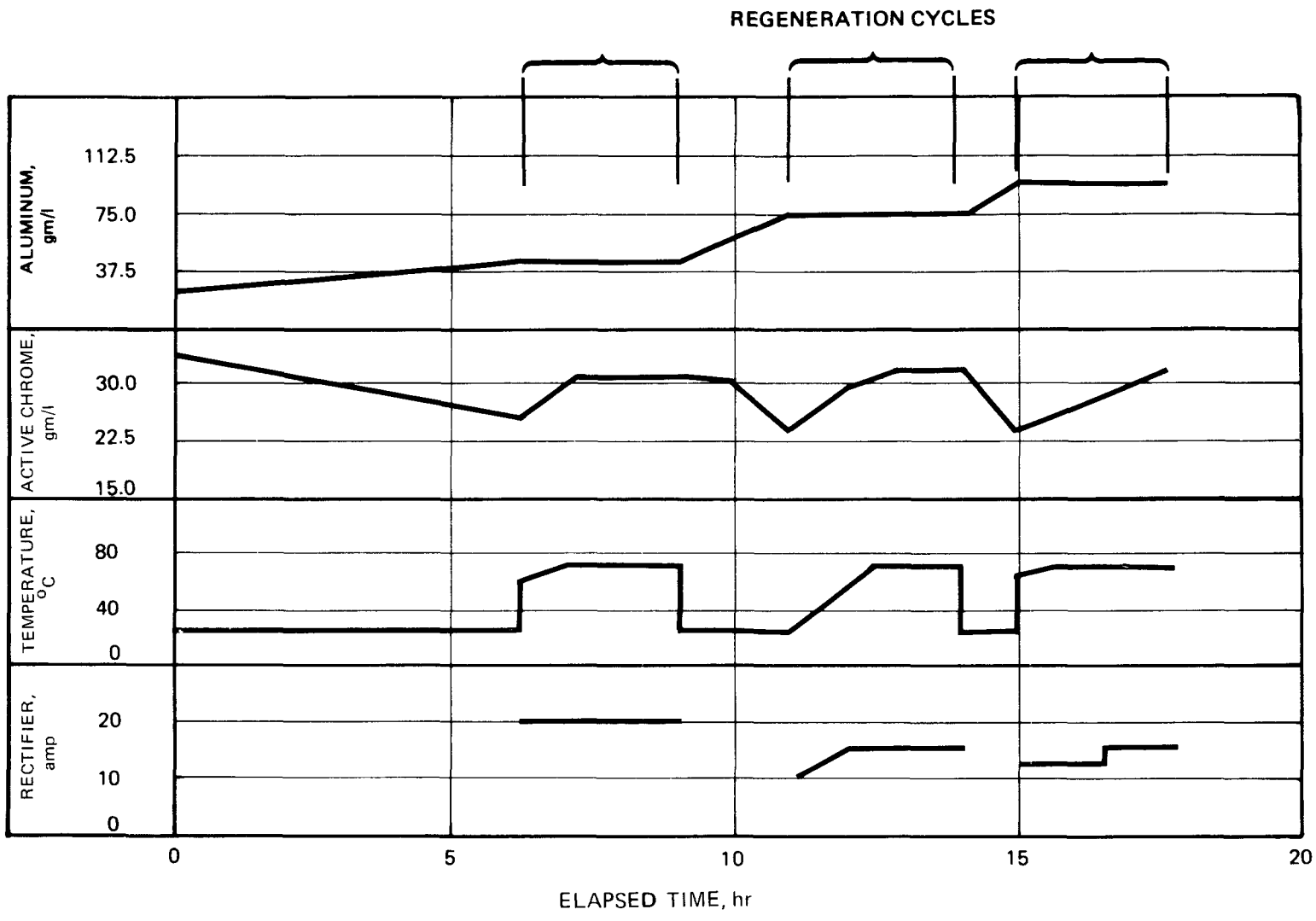


Figure 35. Regeneration of Smutgo 4 (HNO_3)

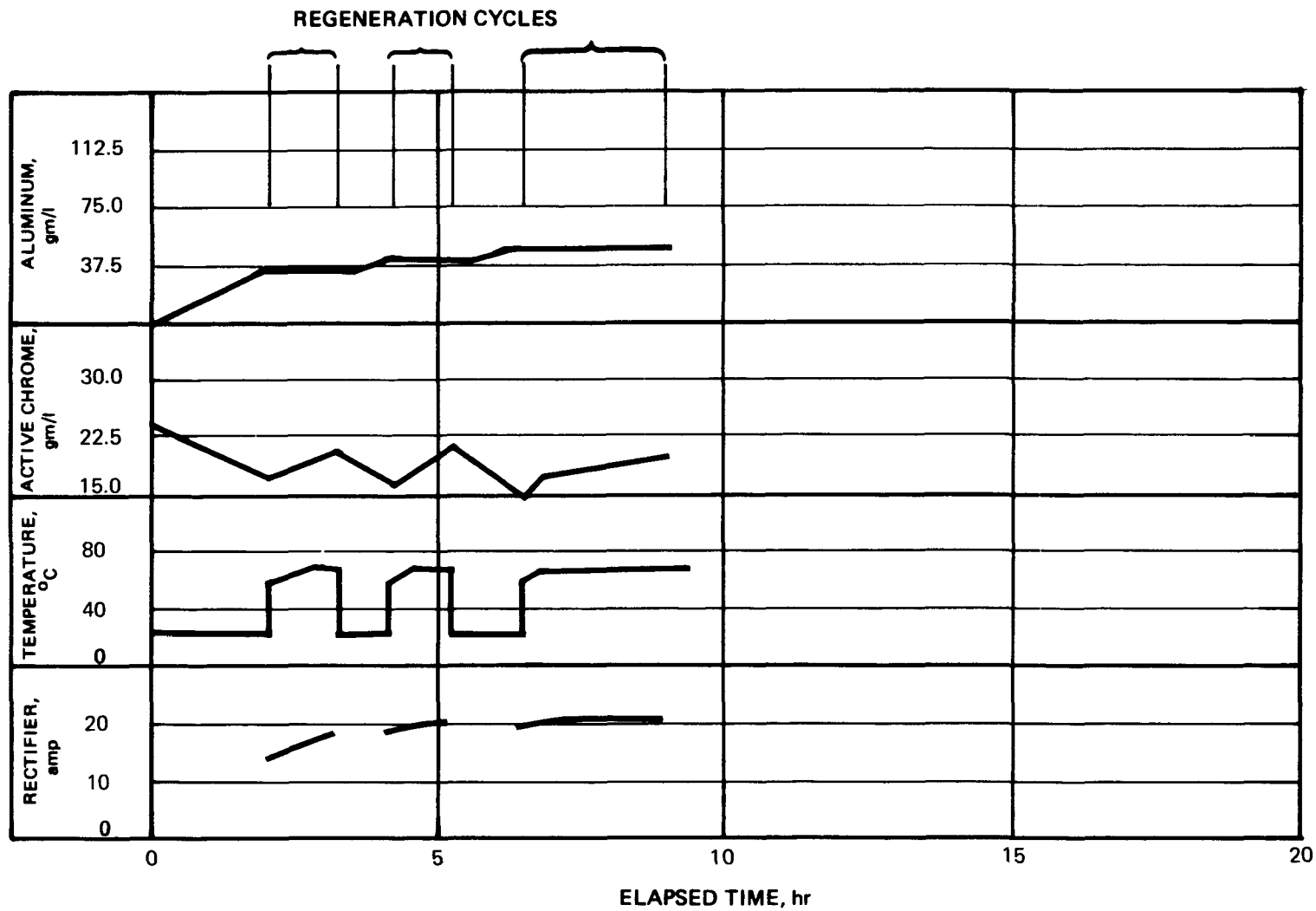


Figure 36. Regeneration of Amchem 6-16 (H_2SO_4)

Information from observations and from data during this evaluation is summarized as follows:

1) Regeneration can be accomplished to 85% of the total chromium content provided this total exceeds 22.5 gm/l of $Na_2Cr_2O_7$-$2H_2O$ and the temperature during regeneration is 65°C or higher.

2) Electrical conductivity of the solution increases with increased temperature.

3) Increasing quantities of dissolved aluminum appear to inhibit the maximum level of regeneration.

4) Smutgo 4 (HNO_3) responded better to regeneration than the other two proprietary deoxidizers. This may be due to its inherently higher chromium content. No attempt was made to evaluate the other deoxidizers by adding more chromium.

5) Regeneration efficiency of these dilute deoxidizers is in the range of 10% as calculated from the ampere-hour data.

6) Electrode material is a problem for deoxidizers containing nitrate and/or fluoride ions. Platinum gauze proved to be satisfactory in the test cell.

   A much less expensive arrangement of stainless steel plated with gold performed satisfactorily for about 30 min before the coating flaked off. (This was a preliminary, nonprogrammed test to seek a direction of effort since platinized titanium anodes failed in test due to severe erosion.)

7) As the concentration of copper builds up in the deoxidizer due to dissolving copper-bearing aluminum alloys, the copper ions migrate through the diaphragm and deposit on the cathode. The deposition of copper on the cathode is beneficial because it reduces the formation of copper smut on critical aluminum surfaces during deoxidizing.

8) Satisfactory deoxidizing of an aluminum surface continues even after the third regeneration as long as the deoxidizer etch rate is adjusted–a normal production practice.

A literature search revealed very little information about solubilities of aluminum nitrate or aluminum fluoride formulations, particularly in the presence of chromium and fluoride compounds. Therefore, a preliminary investigation was made to determine the amount of aluminum nitrate required to saturate Amchem 6-16 (HNO_3). It was found that 840 gm of $Al(NO_3)_3$-$9H_2O$ dissolved in a liter of the deoxidizer. In a representative tank line for precleaning prior to anodizing, 840 gm/l of dissolved $Al(NO_3)_3$-$9H_2O$ represents 4 to 5 years of production. This high solubility indicates that it is impractical to use simple ambient temperature crystallization for removal as was done in the previous work of this program. The deoxidizer is quite viscous at high salt content, and the capability of the deoxidizer to perform its normal function is questionable. A different approach to dissolved metals removal is needed, but additional work was not done along this line. However, early in the program it was shown that an ion-exchange resin was rapidly degraded by a deoxidizer.

TASK VI–PRODUCTION DEMONSTRATION

For this phase of the work, a 2200-liter preproduction tank was charged with a sulfuric-dichromate deoxidizer. A cathode cell of plexiglass was fabricated to contain seven 15- by 20-cm J5D diaphragms of 60 layers each (fig. 37).

The tank was filled with a partially depleted solution of sulfuric acid-sodium dichromate deoxidizer. The analysis of this solution was as follows:

H_2SO_4	266 gm/l
$Na_2Cr_2O_7$-$2H_2O$	15.5 gm/l
Cu	5.9 ppm
Zn	7.7 ppm
Fe	20.2 ppm
Mn	2.4 ppm
Mg	3.75 ppm

The solution was depleted until the hexavalent chromium was near zero. Electrolytic regeneration was initiated and progress was monitored by daily analyses, as illustrated in figure 38.

As can be seen from the upper section of the figure, regeneration leveled off at 15 to 30 gm/l of active (hexavalent) chromium. Since the regenerated concentration was well below the available amount that could be generated, this became an area of concern.

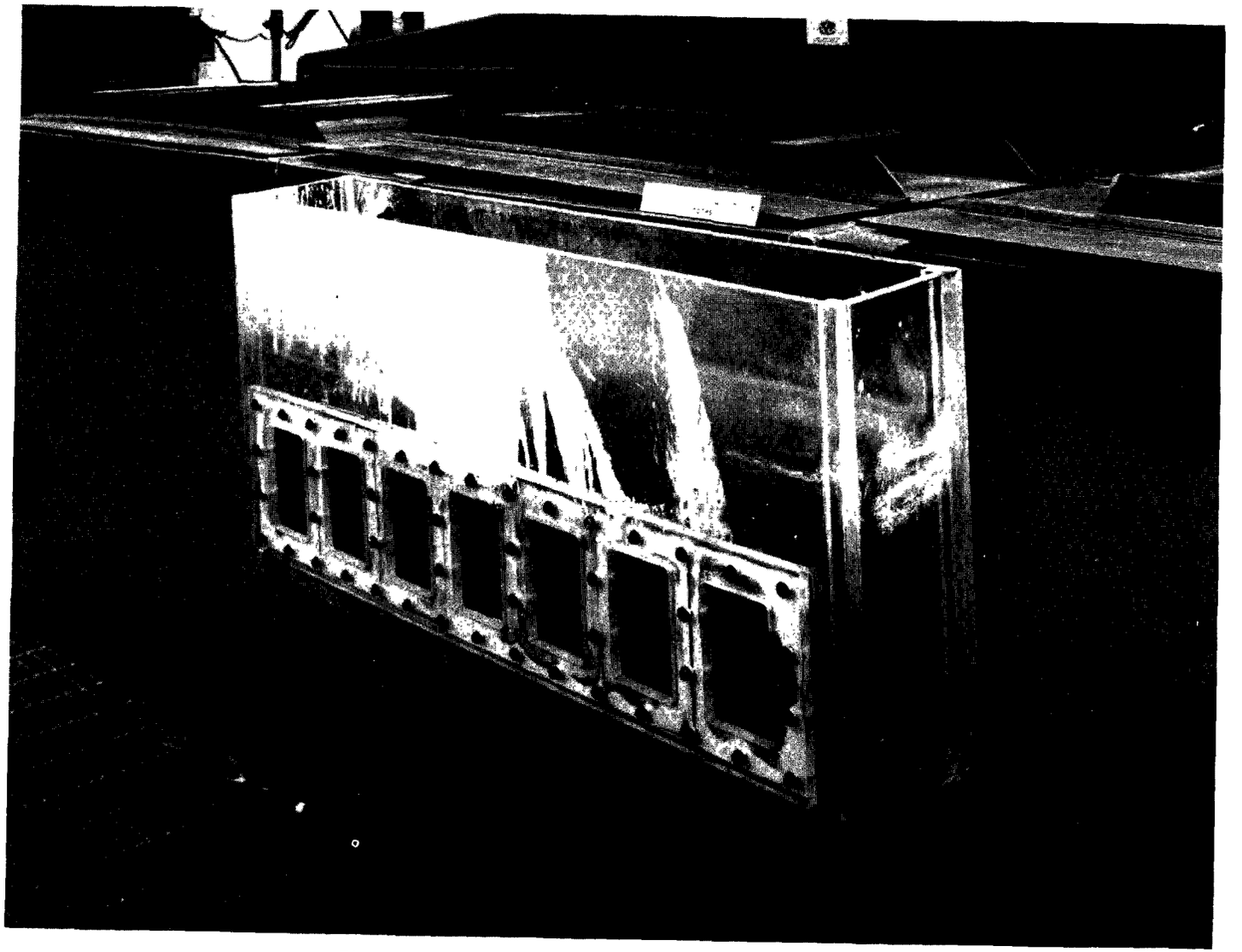


Figure 37. Diaphragm cell for preproduction tank

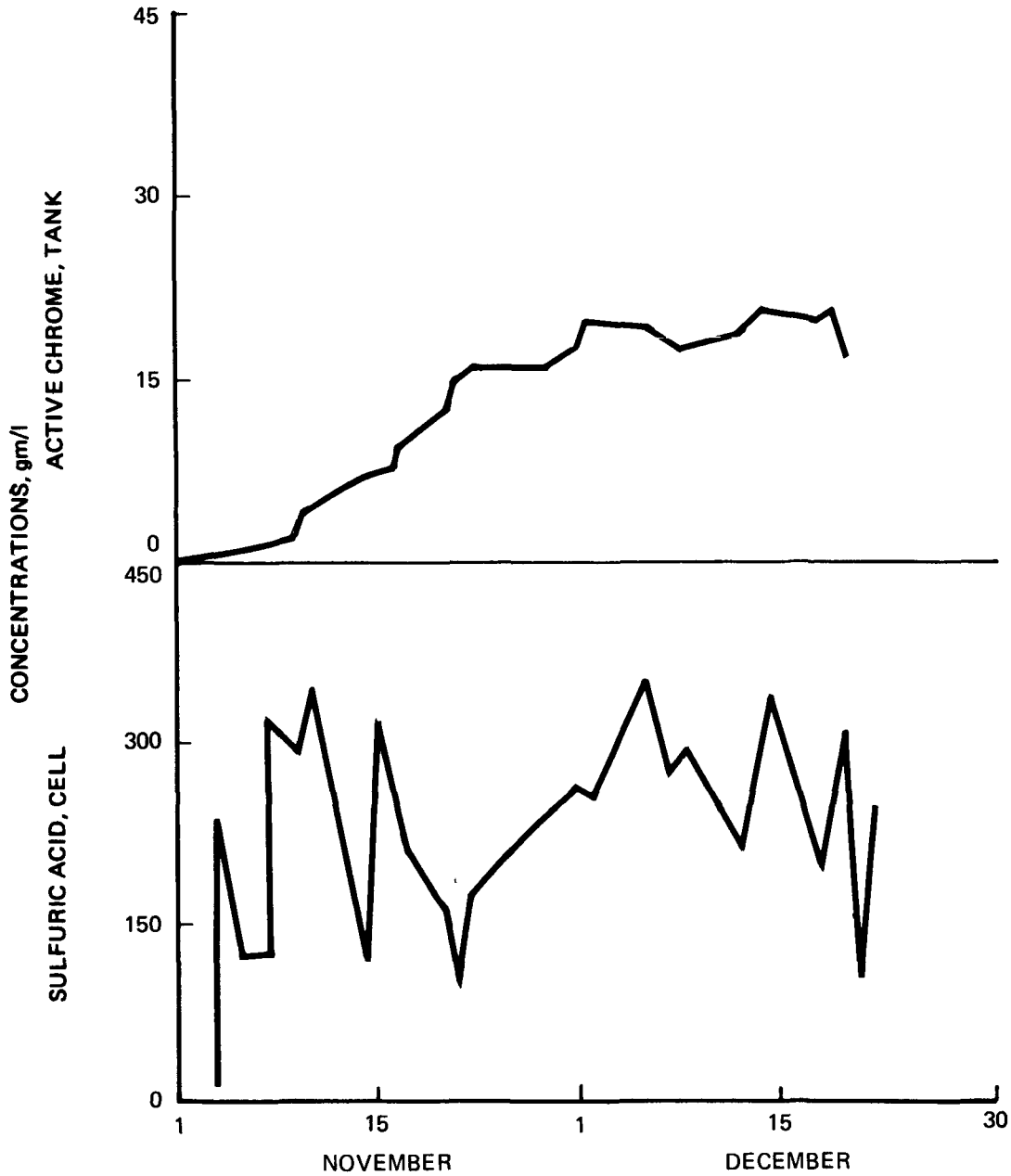


Figure 38. Regeneration in preproduction tank

The solution was cooled, pumped into a spare tank, and allowed to settle. The original tank was cleaned out and inspected. This examination provided the explanation for the low efficiency of regeneration. The tank lining is composed of carbon brick. In the areas of the electrical flux paths between anode and cathode, each brick became a dipole, i.e., one end of each brick is anodic, the other end is cathodic. The dipole phenomenon is confirmed by the fact that the anodic end of each brick was severely eroded. For further confirmation, the filter cake was analyzed at 3.2% insoluble solids, which were carbonlike in appearance. Thus, much of the regenerating current was wasted.

To correct the problem, the sensitive areas of the tank lining were insulated with 0.25-in. (0.635-cm) thick rigid plastic. It is recommended that carbon brick not be used as a tank lining material when electrolytic regeneration is planned.

The cooled and settled deoxidizer solution was decanted into the original tank, and the solids removal evaluation was continued.

An Ametek, Inc., 20- by 12-in. (50.8- by 30.5-cm) drum filter system was installed at the 2200-liter tank. The equipment assembly is shown in figure 39. String discharge was selected for the first trial. In this discharge system, polypropylene string loops are spaced on 0.5-in. (1.27-cm) centers around the drum surface and over idling rollers. The cake is formed on the drum, lifted off by the strings, and discharged over an idling roller, as illustrated in figure 40.

A severe drop in filter output, traceable to plugged cloth on the filter, emphasized the carbon contamination problem. As the carbon filled the pores of the filter cloth, the cake became increasingly thinner and wetter, and would no longer lift off the drum for discharging. This zero output occurred within 1 hr of startup. In addition, the strings showed a tendency to climb on top of the cake after a few drum revolutions, which also reduced cake liftoff. As a remedy, after the deoxidizer solution was decanted, the string discharge was replaced with a scraper discharge. This discharge method proved to be satisfactory and was used for the remainder of the test period (see fig. 41).

The aluminum content of the deoxidizer was raised to 330 gm/l (expressed as $Al_2(SO_4)_3 \cdot 18H_2O$). Batch- and continuous-type runs were made for salts removal. Three different types of cloth were tried on the drum, and drum speeds were varied within the range of the equipment. The drum speed dial control setting was calibrated (fig. 42) for accurate determination of drum rpm.

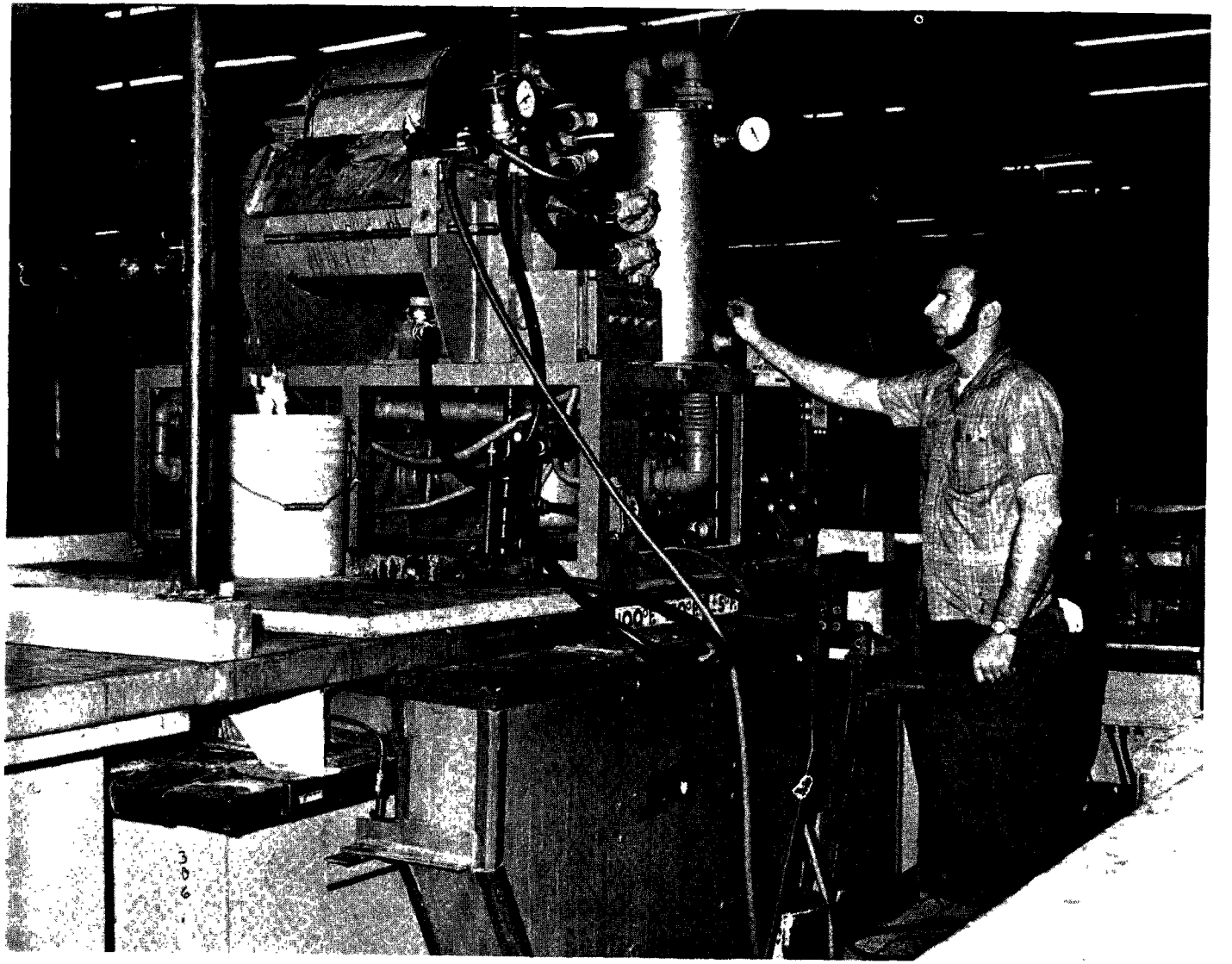


Figure 39. Drum filter installed at preproduction tank

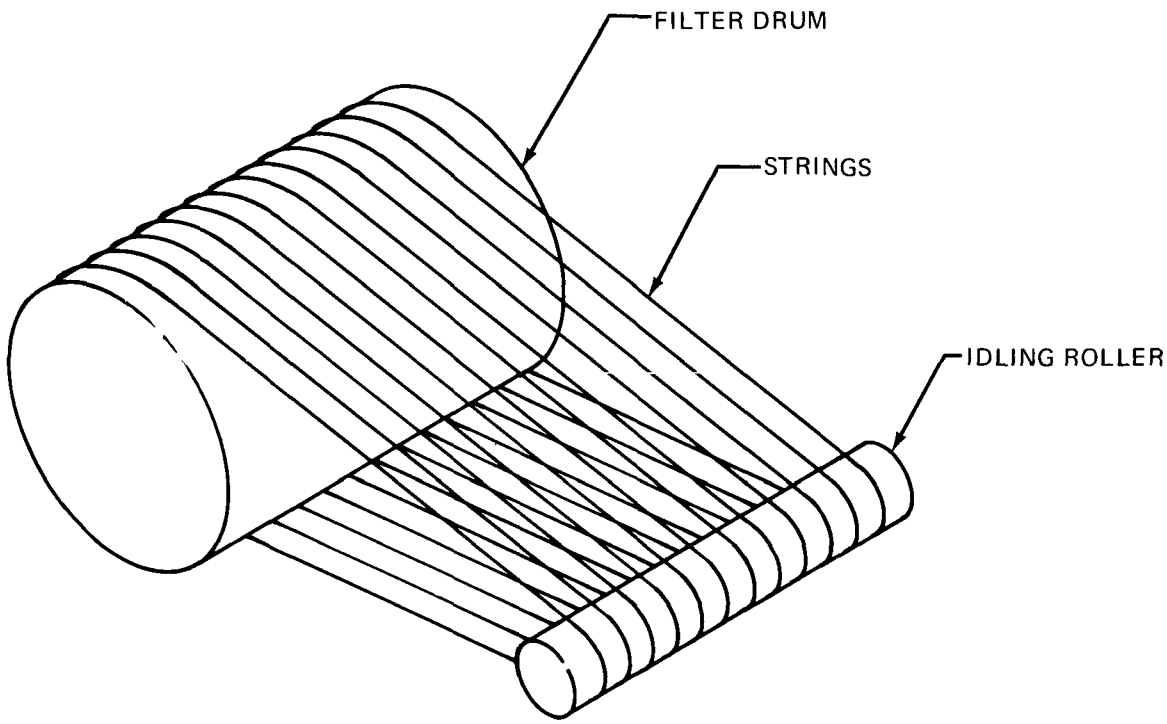


Figure 40. Details of drum filter system

The following information was obtained from the drum filter evaluation:

1) Crystallized aluminum sulfate can be removed effectively from the deoxidizer solution with a drum filter.

2) The rate of removal is dependent upon the drum speed (fig. 43). Optimum removal rate is over a broad range of drum speeds. This flexibility is advantageous for industrial applications.

3) Moisture retained by the cake can be held at 30% to 40%. The least amount of retained moisture can be achieved by adjusting operating conditions for minimum practical cake thickness and maximum drum vacuum. Visual observations indicate that the amount of retained moisture varies with the crystal size. However, no attempt was made to investigate this aspect.

4) The amount of chromium lost by the solids removal technique can be held at less than 4% and is related to the amount of moisture retained in the cake. The relationships between drum speed, retained moisture, and retained chromium are illustrated in figure 44.

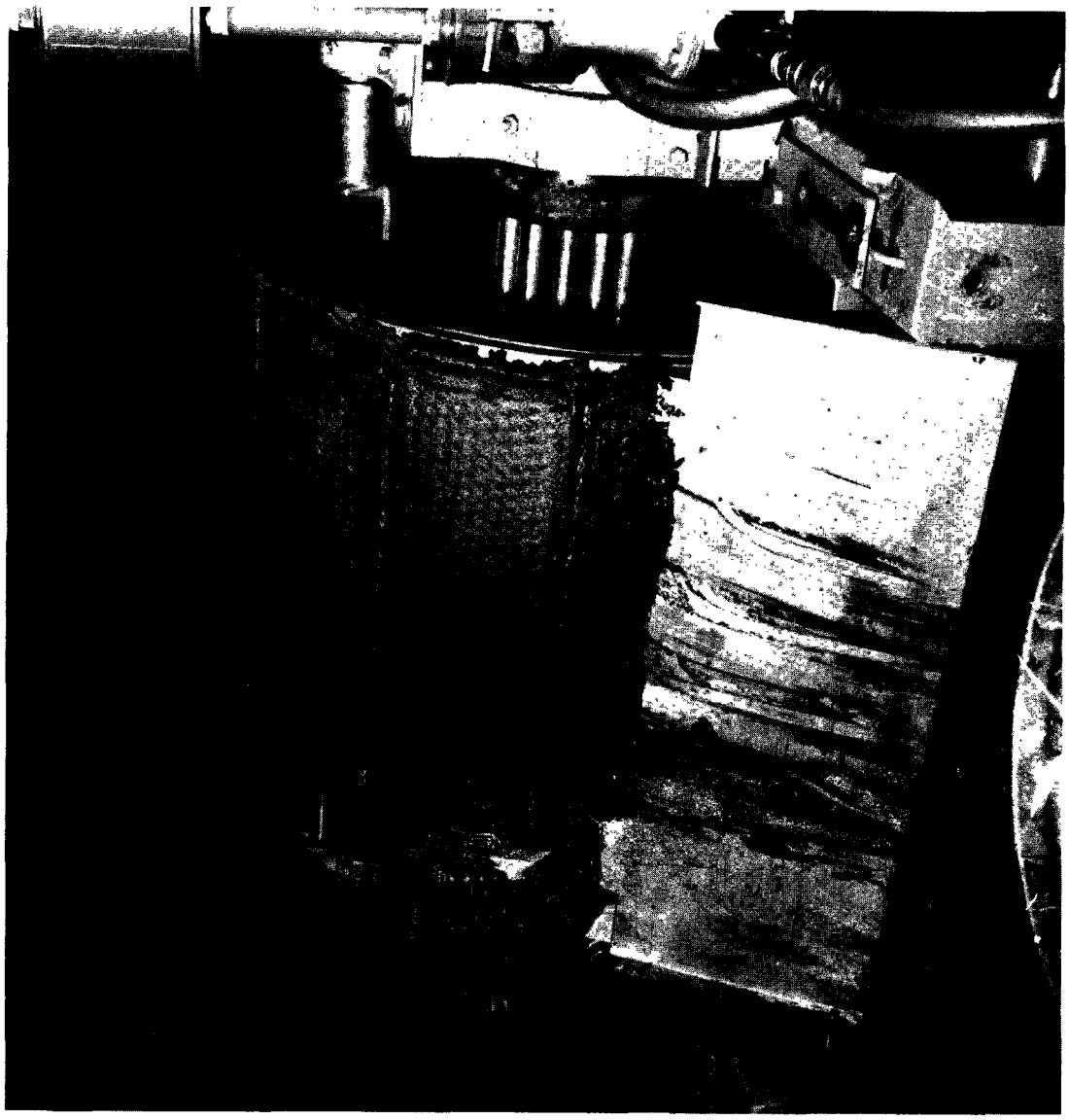


Figure 41. Scraper discharge on 20- by 12-in. (50.8- by 30.5-cm) drum filter

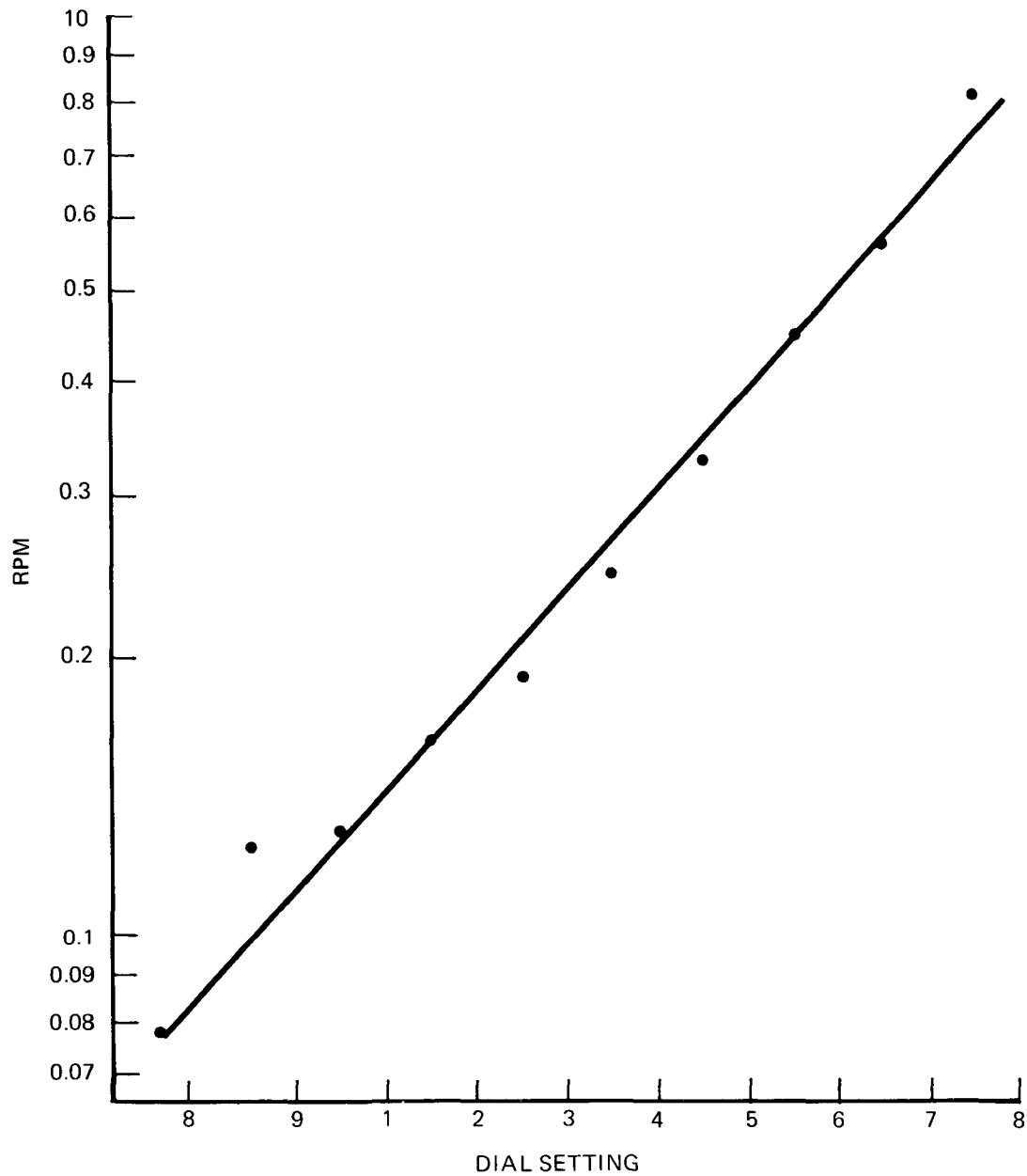


Figure 42. Drum filter evaluation—drum speed calibration

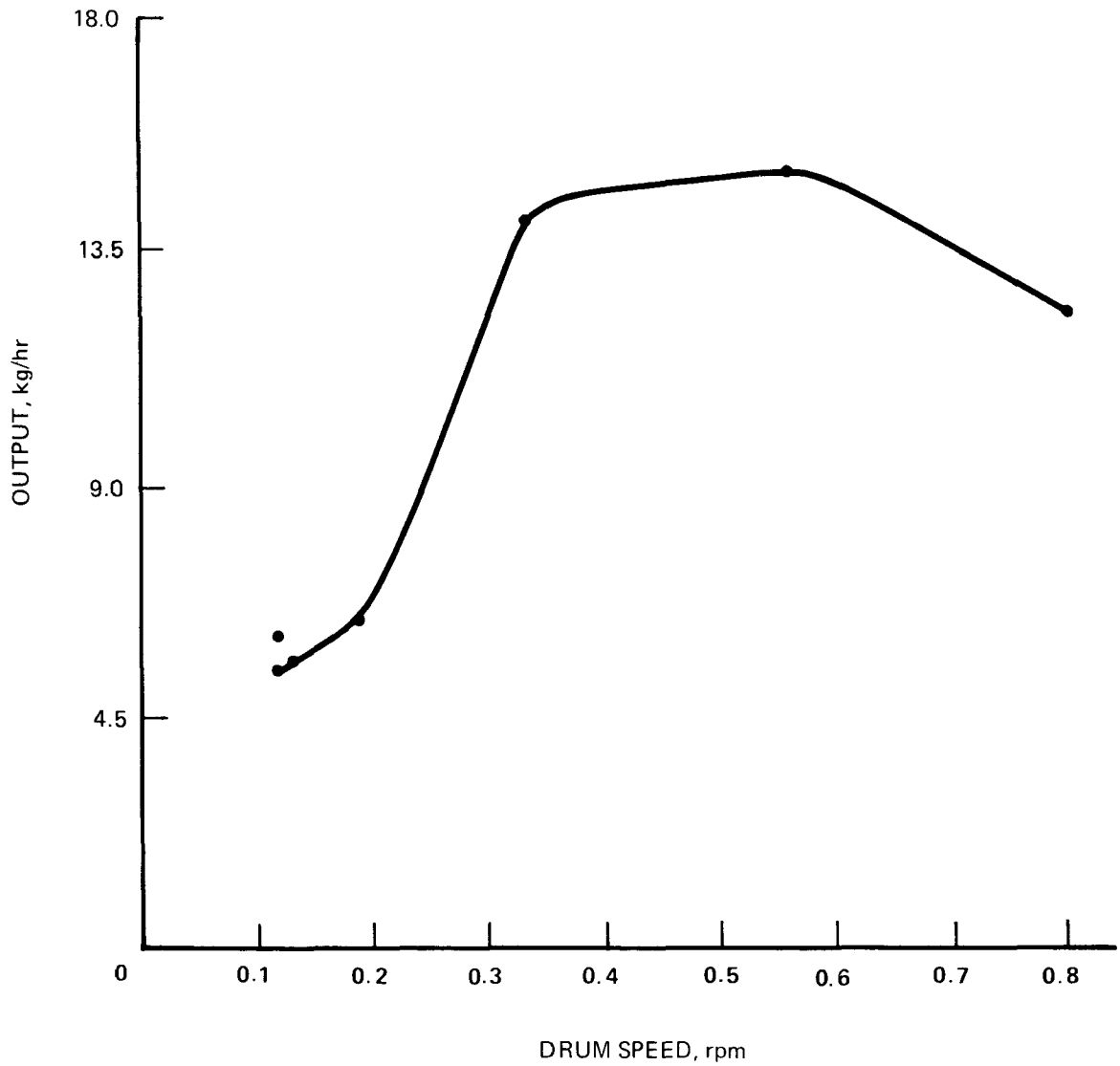


Figure 43. Drum filter evaluation—drum speed versus output

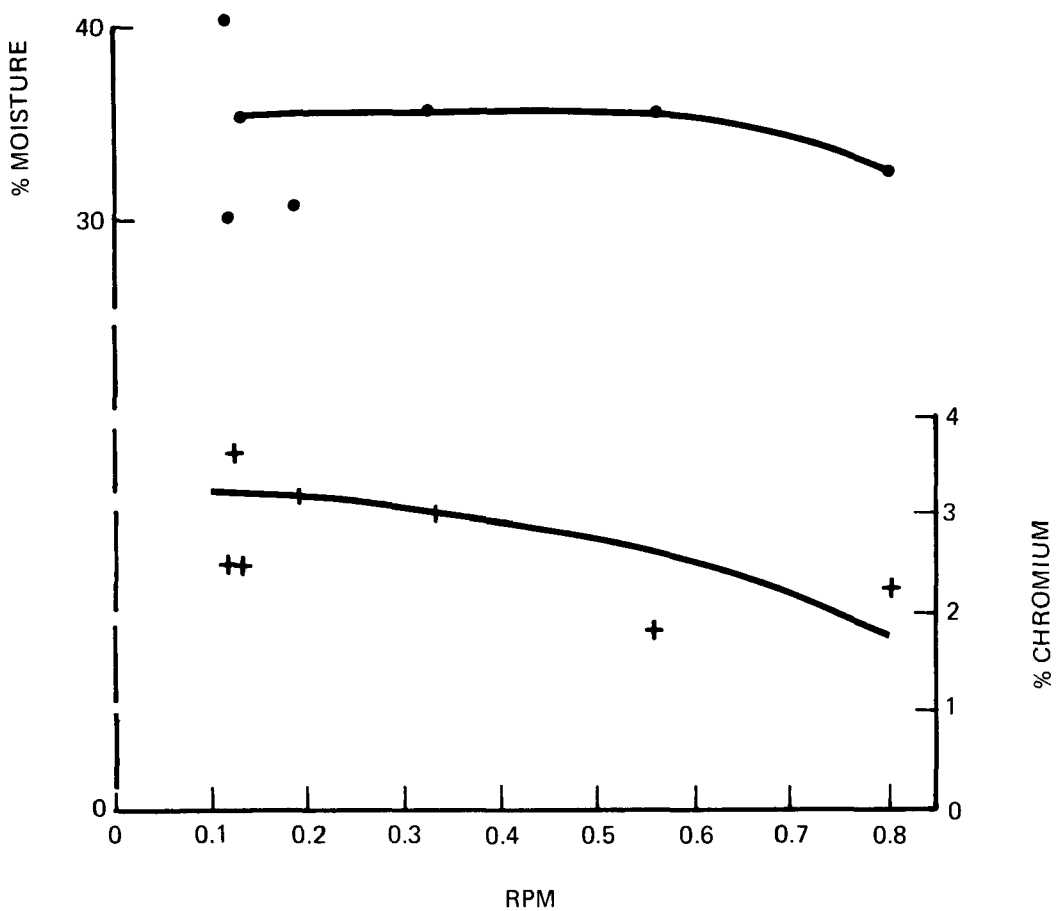


Figure 44. Drum filter evaluation—drum speed versus cake moisture and chromium

5) Crystallized aluminum sulfate can be removed either by batch operation or by continuous operation of the drum filter. The removal capacity of the smallest available commercial drum filter is such that batch operations are desirable for all except very large tank volumes.

6) Coarse weaves of olefin, polypropylene, or polyester woven fabrics are satisfactory for the drum filter cake retaining cloth.

A summary of the drum filter evaluation is as follows:

Equipment	20- by 12-in. (50.8- by 30.5-cm) drum filter with scraper
Effective drum area	3677 sq cm
Maximum removal rate	15 kg/hr wet cake

Moisture in cake	35% by weight
Chromium in dried cake	1.85% by weight
Equivalent aluminum metal removed from deoxidizer	0.80 kg/hr

This last value of 0.80 kg/hr equilibrates to a range of 172 to 460 sq m/hr of deoxidized aluminum parts depending on the effective etch rate of the deoxidizer at time of processing. The calculation is based on the usual immersion time of 10 min/cycle.

The inclusion of residual chromium in the dried salts indicates that consideration should be given to the loss of chromium in the filter cake. In the chemical reaction that takes place during deoxidizing, 1 kg of aluminum reduces 3.49 kg of chromium from hexavalent to trivalent. Therefore, at the maximum rate of removal during which 0.797 kg of dissolved aluminum is removed from the deoxidizer per hour, 0.18 kg of chromium is also removed. Thus, 6.5% of the total chromium metal required for deoxidizing will be carried out in the cake.

The impact of the regeneration process is more simply made by saying that a process that formerly consumed 3 kg of chromium per unit of time will now consume slightly less than 0.4 kg in the same unit of time.

In the continuing work of production demonstration, maintenance problems on the 2200-liter preproduction tank severely hampered the accumulation of continuous regeneration data progress. Failures of the tank level control system made it necessary to replace the deoxidizer solution several times. Dc power supply problems delayed data accumulation. The tank lining continued to deteriorate the solution.

This last item, when finally identified, was measured quantitatively for rate of chromium reduction and was used to advantage for calculating rates of regeneration as well as regeneration system loading. The quantitative data were collected by eliminating all other variables and tracking hexavalent chromium content as a function of time.

In the final simulated production run with the 2200-liter tank, the chromium reduction loading was equivalent to 5 sq cm of aluminum per liter suspended in the solution continuously. This is equivalent to almost three times the normal loading in a typical production sulfuric-dichromate deoxidizer tank line.

The dc power supply was set at 225 amp. The electrical load in the tank volume was 0.1 amp/l and 6.6 amp/l in the diaphragm cell. This vigorous electrical activity promoted

migration of sulfuric acid from the cell into the tank. Consequently, all acid additions were made in the cell. The quantity of acid added over an extended period of time approximated the quantity of acid required for chemical reaction in dissolving the aluminum.

The actual amperage produced by the dc power supply fluctuated with the acid concentration of the cell. Therefore, an ampere-hour meter was included in the equipment setup and ampere-hours were recorded.

Performance of the regeneration was monitored by analyses for active chromium reported as $Na_2Cr_2O_7$-$2H_2O$. Figure 45 illustrates the active chromium monitoring analyses. The intermittent graph lines illustrate regeneration attempts during and between equipment failure periods. The final confirming regeneration run is graphed for the period April 3 to 13. The period from April 13 through 19 is a reconfirmation test of the quantitative effect of the deteriorating tank lining.

Table 11 illustrates reduction of data that establish the electrical efficiency of a sulfuric dichromate deoxidizer.

Table 11. ELECTRICAL EFFICIENCY

Date, 1973	Regenerated chromium, kg metal	Current required, amp-hr	Current used, amp-hr	Efficiency, %
22 Feb	2.15	3,320	4,280	78
20 Mar	1.86	2,880	3,310	87
22 Mar	2.65	4,090	4,670	88
28 & 29 Mar	3.68	5,670	6,185	91
4 & 5 Apr	2.09	3,227	3,884	83
6 - 9 Apr	6.09	9,400	10,878	86
10 - 12 Apr	4.83	7,450	10,413	72
13 Apr	1.01	1,920	2,440	79
				Average: 83

The polyester diaphragm assembly in the 2200-liter pilot tank performed satisfactorily for approximately 5 months in the sulfuric-dichromate deoxidizer, which was held from 60° to 71° C most of the time. The electrical load through the diaphragm was low ranging, from 0 to 10 amp/sq dm. During the final confirmation run, the electrical load on the diaphragm system increased to 30-36 amp/sq dm. Near the end of this final run, chromium migrated heavily into the cathode chamber. This migration is considered to be caused by a diaphragm

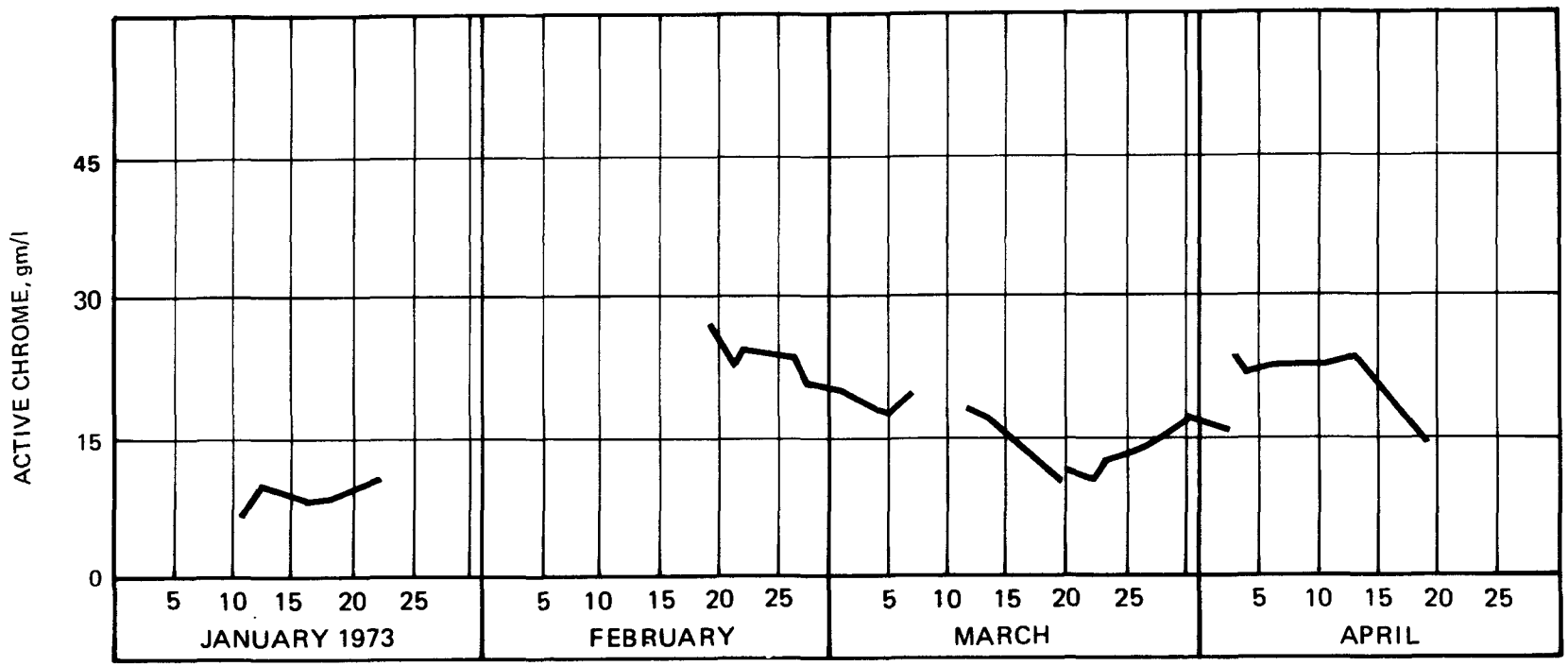


Figure 45. Electrolytic regeneration preproduction tank

failure. Electrical current density thus appears to be a factor in the service life of the diaphragm.

This concludes the technical work and data collection requirements of the program.

TASK VII–ECONOMIC EVALUATION OF REGENERATION

The following baseline costs have been used for economic evaluation of the regeneration process. For application of this information to specific installations, local costs in each area should be determined for each plant and the values proportioned accordingly. Quantities shown in table 12 are expressed in British rather than metric system units because of common industry usage at the present time.

Table 12. REGENERATION PROCESS ECONOMICS

Cost item	Baseline period 2nd Quarter 1973
Equipment amortization	*10 years*
Electrical cost	13¢ per 100,000 BTU
Water cost (purchase)	10¢ per 100 cubic feet
Water cost (dispose)	10¢ per 100 cubic feet
$Na_2Cr_2O_7 \cdot 2H_2O$ (tech)	$30.95 per cwt
H_2SO_4 (tech), 66° Be	$ 5.15 per cwt
Chromated salts disposal (1% as Cr^{+6})	$ 3.62 per cwt
Deoxidizer disposal	12¢ per gallon
100 A, 30 V rectifier, installed	$500
1,000 A, 30 V rectifier, installed	$5,000
20- by 12-in. drum filter, installed	$11,044
12- by 6-in. drum filter, installed	$7,000
12- by 5-in. centrifuge, installed	$5,475
Regeneration accessories, 600 gallons (2,200 liters) (cathode chamber, electrodes, level control, diaphragms)	$660
Regeneration accessories, 6,000 gallons (22,000 liters) (cathode chamber, electrodes, level control, diaphragms)	$1,195

In assessing the impact of regeneration of chromated aluminum deoxidizers, a departure from product weight reporting is necessary. Metal-finishing processes are unique in that they are surface related and not proportional to pounds of product throughput. Therefore, in relating costs and production rates, this task will state values based on areas (such as square decimeters) of aluminum processed.

Effect on Waste Volume and Characteristics

Implementation of this regeneration process will reduce the sporadicity of plant waste effluent that is normally due to periodic dumping of concentrated solutions. As a result of regeneration, it is reasonable to assume that the chromated deoxidizer need never be changed, or at the most—in the case of some proprietary formulations—changed only every 4 or more years. Thus, the total amount of plant effluent containing chromium compounds can be greatly reduced, and the effluent is expected to be more uniform in concentration and character per unit of time.

Effect of Reuse

The added benefits of regeneration are immediately obvious:

- Capital investment in waste treatment facilities can be lower because it is no longer necessary to size the facility to handle the periodic heavy overloads.

- This same waste facility can be more easily automated because of the lack of annual surges of high concentrates.

During the period of testing and production simulation in this regeneration program, no detrimental effects caused by continual reuse of the chromium compounds could be detected on the deoxidized surfaces. Thus, continual regeneration of chromated aluminum deoxidizers will contribute to preservation of chromium resources.

Effectiveness of Treatment

The electrolytic section of regeneration is a wholly self-contained system since the reoxidation of the chromium occurs within or adjacent to the aluminum processing tank. When dissolved aluminum concentration reaches the point at which separation procedures should be implemented (estimated at 1 year), the waste product (salts of various metals) is sufficiently dry to be used as a chrome-bearing, solid fill material. Under the most effective conditions encountered in this program, chromium metal constituted about 1% of the dried salts weight. In very large installations, metals recovery operations may be considered.

Capital Costs

Capital costs are based on regeneration equipment sized to meet the workload throughput of a deoxidizer tank that has been monitored for several years. Workload information has been extrapolated to other tank sizes proportionally to tank volumes, as shown in table 13.

Table 13. CAPITAL EQUIPMENT COSTS

2,200-liter (600-gal.) deoxidizer tank	
Rectifier (100 A, 30 V), installed	$ 500.00
Centrifuge (12- by 5-in.), installed	5,475.00
Regeneration accessories, installed	660.00
Total capital	$ 6,635.00
22,000-liter (6,000-gal.) deoxidizer tank	
Rectifier (1,000 A, 30 V), installed	$ 5,000.00
Drum filter (20- by 12-in.), installed	11,004.00
Regeneration accessories, installed	1,195.00
Total capital	$17,239.00

Maintenance

Maintenance costs for the types of equipment described in this report are generally low compared with those for other chemical processing facilities. Maintenance of a centrifuge is usually considered as being higher than that for other types of separation equipment. The diaphragm cost as stated in this report is abnormally high because the diaphragm is in the early stages of development. A 15- by 20-cm unit cost is estimated at $30 and presently has a maximum of 6 months' service life.

Yearly maintenance cost for the 2200-liter regeneration equipment is estimated at $620. Yearly maintenance cost for a 22,000-liter system is estimated at $1380.

Operating Costs, Regeneration Versus Nonregeneration

2200-liter Deoxidizer—During the first year, electrical cost for the rectifier is $6.39 per month. After dissolved metals separation is implemented, add: 1) $4.73 per month for electricity for centrifuge, 2) $10.54 for cooling to crystallize, 3) $4.38 for reheating, and 4) $3.34 per month for disposal of removed solids. Total operating costs under full regeneration conditions are $29.28 per month.

This figure is contrasted to nonregenerated deoxidizer costs of: 1) $23.65 per month for addition of chemicals, 2) $6.00 per month for prorated dumping charge, and 3) $14.15 per month for prorated new solution makeup charge. Total nonregeneration cost is $43.80 per month.

22,000-liter Deoxidizer—During the first year, electrical cost for the rectifier is $63.90 per month. After dissolved metals separation is implemented, add: 1) $13.77 per month for drum filter electrical cost, 2) $21.08 for cooling to crystallize, 3) $8.55 for reheating, and 4) $38.67 per month for disposal of removed solids. Total operating costs under full regeneration conditions are $145.97 per month.

This figure is contrasted to nonregenerated deoxidizer costs of: 1) $93.29 per month for addition of chemicals, 2) $60.00 per month for prorated dumping charge, and 3) $141.50 per month for prorated new solution makeup charge. Total nonregenerated cost is $249.79 per month.

In summary, regeneration operating costs can be related to the area of aluminum processed according to table 14.

Table 14. REGENERATION COSTS PER UNIT AREA

Item	Electrolytic only, ¢ per sq dm[a]	Total regeneration, ¢ per sq dm[a]
2,200-liter tank volume		
Capital	-0.0115	-0.1531
Maintenance	–	-0.0014
Operating	+0.1035	+0.0402
	+0.0920	**-0.1143**
22,000-liter tank volume		
Capital	-0.0115	-0.0398
Maintenance	–	-0.0003
Operating	+0.0639	+0.0412
	+0.0524	**+0.0011**

[a]+ indicates a cost savings; – indicates a cost

No calculation relating regeneration of deoxidizers to product value increase has been attempted because of the wide variations encountered when attempting to relate product value to product surface area. It is well to note, however, that this cost analysis indicates that regeneration of chromated aluminum deoxidizers can be cost effective.

Waste Load—The waste load is calculated in terms of grams of chromium metal in plant waste effluent per square decimeter of aluminum processed, as shown in table 15.

Table 15. WASTE LOAD PER UNIT AREA

Tank volume, liters	Nonregenerated waste, gm Cr/sq dm/month	Regenerated waste, gm Cr/sq dm/month
2,200	0.0660	0.00041
22,000	0.0660	0.00053

Note: These values do not include chromium lost by dragout.

SECTION V

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SECTION VI

LIST OF INVENTIONS

Ion Selective Membrane, Boeing patent disclosure 71-0238, EPA case no. WQO-70-73 (c).

SECTION VII

GLOSSARY

$Cr^{III}, Cr^{+++}, Cr^{+3}$	Trivalent oxidation state of chromium
Cr^{VI}, Cr^{+6}	Hexavalent oxidation state of chromium (also expressed as $Cr_2O_7^{-2}$)
E,V	Potential, volts
E_c	Total potential measured between anode and cathode
E_r	Reversible electrode potential
(g)	Gas
I or A	Current, amperes
I_{eff}	Current efficiency
i	Current density, amperes per square foot
N_a	Anode polarization, volts
N_c	Cathode polarization, volts
R	Resistance, ohms
R_m	Membrane resistance
R_s	Solution resistance
Dichromate sulfuric	An aluminum deoxidizer whose makeup chemistry consists of only the dichromate ($Cr_2O_7^{-2}$) ion plus sulfuric acid

SECTION VIII

APPENDIX

TASK I

DIAPHRAGM EVALUATION

DATA SHEETS

LABORATORY REPORT

NO. R-6725-51-1412

Purpose: Test Model: _____ Date: 10-6-71

To: H. Hicks Org'n. 7-7310 Part No. _____

Subject: Regeneration of Chromates

Source: Environmental Protection Agency, Water Quality Office Reinsp. Req. ~

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material: Filter Media Evaluation Spec. BAC 5765, Solution 10

☒ Chem. Lab. Job 1270 ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ 12070 HEK

Reference: C.C. to:

Boeing Program Authorization No. 632-083
Work Order No. 5-66967-7322-632083

Phase I: Diaphragm Evaluation

Sample 1	Polypropylene Polymax B, style 222-00900, by National Filter Media Company
Sample 2	Dynel style 182-003-00, by National Filter Media Company
Sample 3	Polypropylene Polymax B, style 222-001-00, by National Filter Media Company
Sample 4	Dynel style 182-004-00, by National Filter Media Company
Sample 5	100% Polypropylene, item 342-1903, Troy Mills, Inc.
Sample 6	100% Dacron, item S-4, Troy Mills, Inc.
Sample 7	Filter paper, 6-pt SC, Dennison Mfg. Company

Above 7 samples were immersed 240 hours at 82°C in a covered 100-ml aliquot of BAC 5765, solution 10.

Results are tabulated on attachment

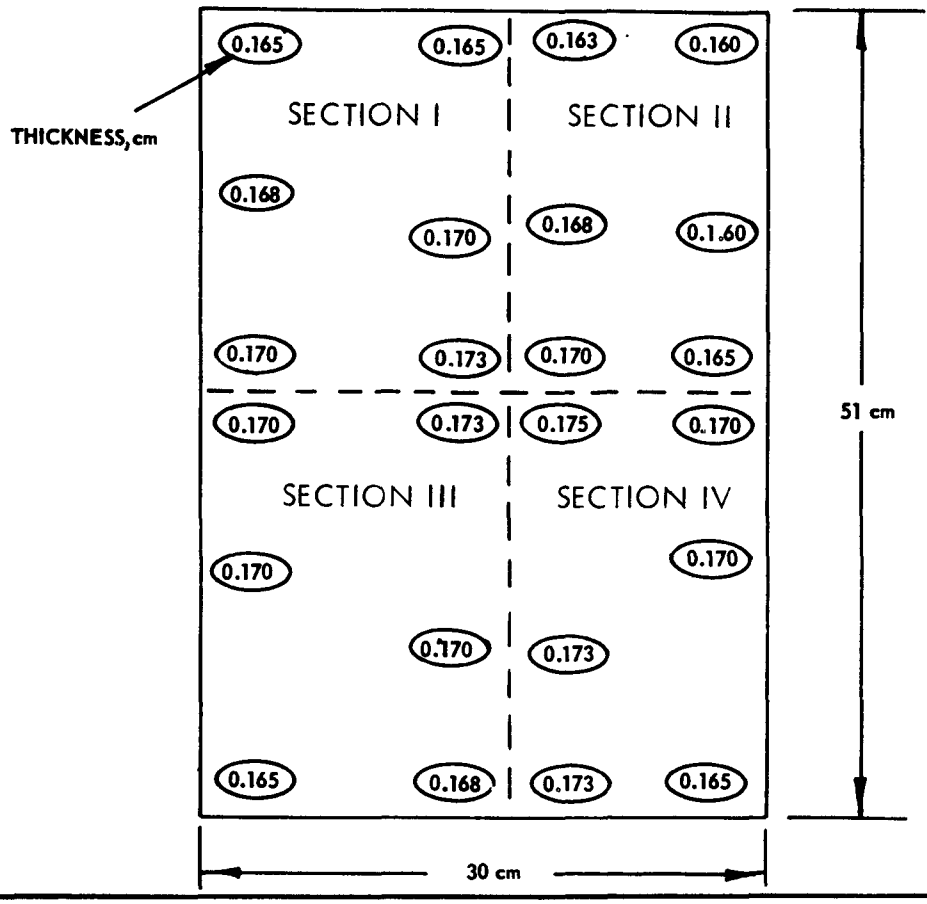
Prepared by: Leo Hagen Approved by: M. Minak Org'n. R-6725

AD 2847A 6-4600

DIAPHRAGM EXPOSURE TEST (START - STOP)

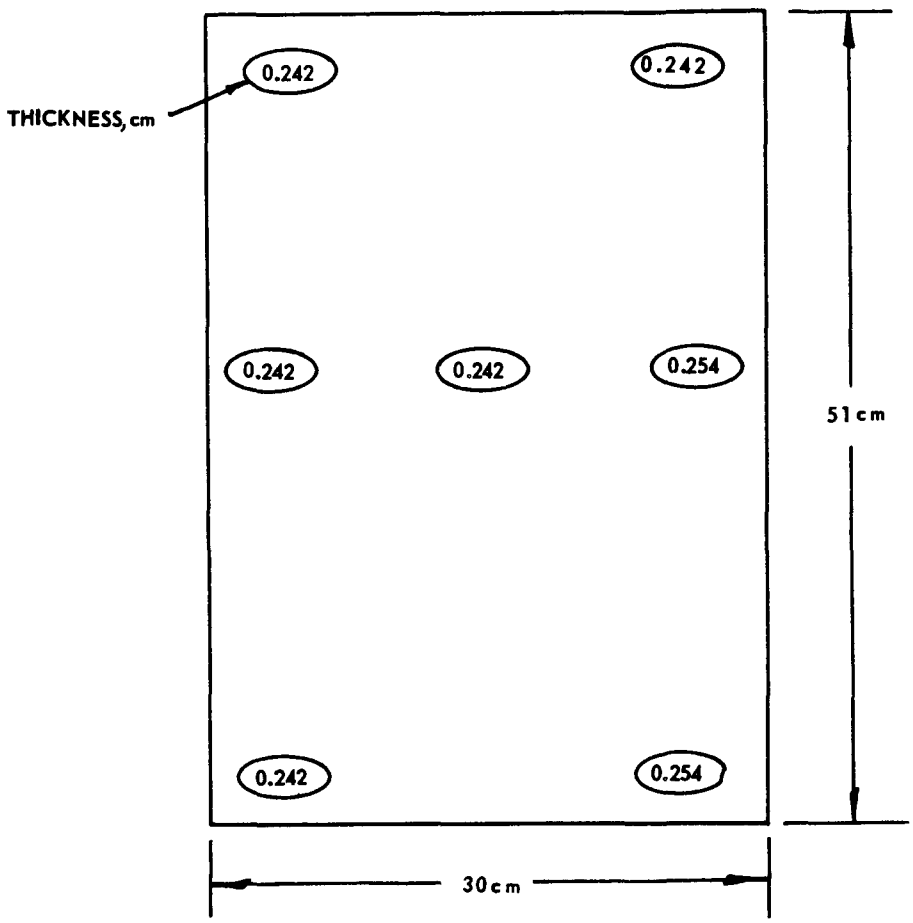
Material	Weight		Diameter		$Na_2Cr_2O_7 \cdot 2H_2O$			H_2SO_4	
	gm	% loss	cm	% loss	gm/l	Solution color	% loss	gm/l	% loss
Sample 1– Polypropylene	6.172 -5.952		13.6 -13.6		36.4 -9.8			280 -248	
	0.220	3.5		0	26.6	Yellow	73	32	12
Sample 2– Dynel	7.254 -7.080		13.8 -13.8		36.4 -21.7			280 -265	
	0.174	2.4		0	14.7	Brown	40	15	5.5
Sample 3– Polypropylene	6.859 -6.030		13.6 -13.6		36.4 -0.4			280 -230	
	0.829	12		0	36.0	Green	99	50	18
Sample 4– Dynel	7.546 -7.237		13.8 -13.8		36.4 -12.8			280 -251	
	0.309	4.1		0	23.6	Green	65	29	10
Sample 5– Polypropylene	8.551 -8.341		13.4 -13.2		36.4 -0.2			280 -238	
	0.210	2.1		0	36.2	Blue	99	42	15
Sample 6– Dacron	9.255 -8.935		13.4 -13.4		36.4 -2.2			280 -242	
	0.320	3.5		0	34.2	Green	94	38	13
Sample 7– 6-pt SC	1.029 -0.959		13.7 -13.7		36.4 -33.8			280 -274	
	0.070	0.7		0	2.6	Brown	7	6	2
Control 1	0				36.4	Brown		280	
Control 2	0				36.4	Brown		280	

J5D LAMINATED DIAPHRAGM THICKNESS — 15 LAYERS



LAMINATION SEQUENCE	
ELAPSED TIME, MIN.	CONDITION
0	51 TONS APPLIED, HEAT TURNED ON
9	BOTTOM PLATEN AT 149° C
11	TOP PLATEN AT 149° C
42	HEAT OFF, COOLING AIR ON, 46 TONS
58	PLATENS AT 93° C, RELIEVED PRESSURE
62	REMOVED DIAPHRAGM

J5D LAMINATED DIAPHRAGM THICKNESS — 20 LAYERS



LAMINATION SEQUENCE	
ELAPSED TIME, MIN.	CONDITION
0	51 TONS APPLIED, HEAT TURNED ON
9	BOTTOM PLATEN AT 149° C
11	TOP PLATEN AT 149° C
42	HEAT OFF, COOLING AIR ON
58	PLATENS AT 93° C, RELIEVED PRESSURE
62	REMOVED DIAPHRAGM

DIAPHRAGM ELECTRICAL RESISTANCE–POLYESTER, 6-PT SC (SIX LAYERS)[a]

Amperes		Volts	Observations
		Run 1	
Increasing amperage	1.0	1.7	Gassing at both electrodes at all conditions. Dichromate bleeds thru diaphragm into H_2SO_4. Dichromate reduced (visually) in cathode chamber.
	2.0	2.0	
	3.0	2.3	
	4.0	2.6	
	5.0	3.0	
Decreasing amperage	4.0	2.6	
	3.0	2.4	
	2.0	2.1	
	1.0	1.75	
		Run 1-1[b]	
Increasing amperage	1.0	1.8	Gassing at both electrodes at all conditions. Extended time necessary to reach first steady state after polarity reversed. Dichromate in H_2SO_4 appears (visually) to be reoxidized.
	2.0	2.1	
	3.0	2.5	
	4.0	2.75	
	5.0	3.0	
Decreasing amperage	4.0	2.75	
	3.0	2.5	
	2.0	2.1	
	1.0	1.8	

[a]Dennison Company

[b]Electrodes worked at 4.0 amp for 15 min after first run. Polarity at electrodes reversed and test repeated for second run.

DIAPHRAGM ELECTRICAL RESISTANCE–100% POLYPROPYLENE (TWO LAYERS)[a]

Amperes		Volts	Observations
		Run 2	
Increasing amperage	1.0	1.6	Some bleed-thru of dichromate into cathode chamber.
	2.0	1.9	
	3.0	2.1	
	4.0	2.3	Test temperature: 67°C
	5.0	2.5	
Decreasing amperage	4.0	2.3	
	3.0	2.1	
	2.0	1.9	
	1.0	1.6	

[a]Troy Mills, 100% Polypropylene, No. 342-1903

DIAPHRAGM ELECTRICAL RESISTANCE—100% POLYESTER[a]

Amperes		Volts	Observations
		Run 3, 15-layer laminate	
Increasing amperage	1.0	2.6	Required about 15 min of soak time to wet thru the diaphragm and establish conductivity. Diaphragm stopped dichromate bleed-thru.
	2.0	3.6	
	3.0	4.75	
	4.0	6.2	
	5.0	8.5	Temperature: 69° C.
Decreasing amperage	4.0	5.8	
	3.0	4.6	
	2.0	3.5	
	1.0	2.6	
		Run 4, 12-layer laminate	
Increasing amperage	1.0	2.3	Bleed-thru of dischromate observed after test run.
	2.0	3.0	
	3.0	3.6	
	4.0	4.4	Temperature: 69° C.
	5.0	5.0	
Decreasing amperage	4.0	4.4	
	3.0	3.7	
	2.0	3.0	
	1.0	2.3	

[a]Dennison Company, No. 024

DIAPHRAGM ELECTRICAL RESISTANCE—100% POLYESTER (15-LAYER LAMINATE)[a]

Amperes		Volts	Observations
		Run 5	
Increasing amperage	1.0	2.60	Preconditioned by holding at 4 amp for 15 min. Stabilized for 5 min at each setting. Temperature: 66° C.
	2.0	3.48	
	3.0	4.32	
	4.0	5.12-5.10	
	5.0	5.86-5.88	
Decreasing amperage	4.0	5.05	
	3.0	4.23	
	2.0	3.43	
	1.0	2.58	
		Run 6	
	4.0	4.97	Second conditioning by holding at 4 amp for 15 min.
	5.0	5.68	
		Run 7	
Increasing amperage	1.0	2.43	Third conditioning by holding at 4 amp for 15 min. Resistance continues to drop. Temperature: 66° C.
	2.0	3.12	
	3.0	3.76	
	4.0	4.40	
	5.0	5.00	
	4.0	4.36	
		Run 8	
Increasing amperage	1.0	2.41	After four preconditioning periods of 4 amp for 15 min each, diaphragm is now considered stabilized.
	2.0	3.04	
	3.0	3.66	
	4.0	4.25	
	5.0	4.85	
Decreasing amperage	4.0	4.25	
	3.0	3.65	
	2.0	3.04	
	1.0	2.41	

[a]DuPont Reemay, No. 2024

TASK II

ELECTRODE EVALUATION

DATA SHEETS

POTENTIOSTAT PROBE DATA

Identification Number	Description	Diameter, cm	Length, cm	Exposed Area, cm^2
D-1	Duriron AS1101-7	0.947	1.268	4.83
D-2	Duriron AS1101-7	0.934	1.234	---
C-3	Copper, commercial	0.955	1.272	4.89
C-4	Copper, commercial	0.955	1.298	---
P-5	Lead, commercial	0.955	1.300	---
P-6	Lead, commercial	0.953	1.288	4.93
N-7	Nickel, commercial	0.951	1.289	---
N-8	Nickel, commercial	0.957	1.294	---
S-9	316 Stainless steel	0.958	1.288	--
S-10	316 Stainless steel	0.953	1.265	4.86

ANODE CURRENT EFFICIENCY DATA

Time, min	Volume, ml	Cr^{+6}, gm/l		Corrected Cr^{+6}, total gm		Corrected Cr^{+3}, total gm
		Active	Total	Active	Total	
Lead Anode (commercially pure)						
Start	500	11.8	14.2	5.93	7.10	1.17
15	490	11.8	14.1	5.81	6.91	1.10
35	470	11.8	14.0	5.58	6.60	1.02
45	460	11.8	13.95	5.45	6.42	0.97
60	450	11.8	13.8	5.34	6.21	0.87
75	440	11.9	13.9	5.19	6.11	0.92
90	430	11.8	13.7	5.10	5.87	0.77
105	420	11.8	13.6	4.98	5.71	0.73
Tin-lead anode (7% Sn-93% Pb)						
Start	510	34.4	41.6	6.13	7.42	1.29
15	500	34.1	40.4	5.95	7.07	1.12
30	490	34.2	40.6	5.85	6.97	1.12
45	480	34.6	40.6	5.80	6.83	1.03
60	470	34.6	40.4	5.68	6.65	0.97
75	460	34.2	40.0	5.50	6.44	0.94
90	440	34.2	39.65	5.38	6.24	0.86
105	430	34.2	39.4	5.26	6.04	0.78
Antimony-lead anode (6% Sb-94% Pb)						
Start	510	34.4	41.1	6.13	7.33	1.20
15	500	34.4	40.8	6.01	7.14	1.13
35	490	34.6	41.2	5.93	7.06	1.13
45	480	34.6	40.8	5.80	6.85	1.05
60	470	34.6	40.6	5.68	6.68	1.00
75	460	34.4	39.9	5.53	6.42	0.89
90	450	34.2	39.3	5.38	6.18	0.80
105	440	33.8	39.1	5.20	6.02	0.82

TASK III

OPERATING PARAMETERS

DATA SHEETS

H-CELL OPERATION FOR MASS TRANSFER DATA

Time	Temperature, °C	Amperes	Volts
10:05	32	0	23
10:10	49	1.5	12.5
10:20	57	1.5	10.75
10:30	66	1.5	9.5
11:25	70	1.5	8
1:20	70	1.5	8.5
2:05	70	1.5	8.5

H-CELL ANALYSES

Sample no.	Description	H_2SO_4, gm/l	Hexavalent chromium, gm/l		Cr^{+3}, gm/l	Al, ppm	Cu, ppm	Fe, ppm	Zn, ppm	Mg, ppm	Mn, ppm
			Active	Total							
HA-1	Anode chamber start	254	9.83	10.4	0.52	20,800	380	830	326	9.2	4.75
HA-2	Anode chamber end	278	10.4	10.9	0.60	22,000	392	840	324	9.9	5.25
HA-3	Cathode chamber start	287	None	None	None	None	0.15	0.70	1.72	1.47	0.65
HA-4	Cathode chamber end	310	None	None	None	17	0.65	1.70	2.48	1.58	1.00

LABORATORY REPORT

NO. R-6725-51-1450

Purpose _____ Model _____ Date 11-11-71

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Tank 6, Dept. 6-7310, Regeneration of Chromium

Source Renton MR&D Lab Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material _____ Spec. BAC 5765, Solution 10

[XX] Chem. Lab. 1305 [ ] Sonic _____ [ ] Met. Lab. _____ [ ] Mechanical _____

[ ] X-Ray _____ [ ] Mag/Penetrant _____ [ ] _____

Reference: C.C. to:

12070 HEK project

Sample pulled 11-02-71. Results are as follows:

Sample	$Na_2Cr_2O_7 \cdot 2H_2O$, gm/l	Total chrome, gm/l	Δ chrome, gm/l	Cr^{+++}, gm/l
J5D2	34.2	34.8	0.6	0.2
J5D3	Omitted	0.3	Omitted	0.1
J5D4	34.2	34.6	0.4	0.1
Tank no. 6	32.0	33.0	1.0	0.3

Sample	H_2SO_4, gm/l
J5D1	295
J5D2	306
J5D3	300
J5D4	312
Tank no. 6	287

Prepared by _____ Approved by _____ Org'n. _____

AD 2847A

6-4800

LABORATORY REPORT

NO. R-6725-51-1510

Purpose _____ Model _____ Date 1-20-72

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Solutions X-1 and X-2

Source Renton MR&D Lab Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material _____ Spec. BAC 5765, Solution 10

☐ Chem. Lab. _____ ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ _____

Reference: C.C. to:

R-6725-51-1500

Analyses on 12/2, 12/3, and 12/6 show the following results:

X-1	273 gm/l H_2SO4
X-2	260 gm/l H_2SO4
X-1	30 gm/l $Na_2Cr_2O_7 \cdot 2H_2O$
X-2	29 gm/l $Na_2Cr_2O_7 \cdot 2H_2O$
X-1	0.8 gm/l Cr
X-2	1.2 gm/l Cr

Analyses 1-19-72

Aluminum in X-1 = 13,900 ppm

Aluminum in X-2 = 8,600 ppm

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6725

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ALUMINUM SULFATE CRYSTAL FORMATION — TEST 1

Aluminum sulfate gm/l	Cooling rate, min from 82° to 38°C	Observation temperature, °C	Observed crystals
150	1.5	32	None
150		27	
165		32	
165		27	
165		22	
180		43	
180		22	
195		38	
195		21	
210		38	
210		21	
225		38	
225	1.5	21	None

ALUMINUM SULFATE CRYSTAL FORMATION — TEST 2

Aluminum sulfate, gm/l	Temperature drop, °C	Elapsed time for temperature drop, min	Observed crystals
150	66 - 38	1.5	None
150	38 - 23	5	
150	23 - 23	5	
165	66 - 38	1.25	
165	38 - 23	5	
165	23 - 23	5	
180	66 - 38	2	
180	38 - 23	5	
180	23 - 23	5	
225	66 - 38	1.5	
225	38 - 23	8	None

LABORATORY-SIZE CRYSTALLIZER COOLING RATE — RUNS 1-6

Low Agitation	
Time	Temperature, °C
Run 1	
9:31	78
32	64
33	54
34	43
35	37
36	31
37	27
38	23.5
39	21.5
40	19.5
Run 2	
10:10	70.5
11	58
12	47
13	38
14	31
Run 3	
10:30	34
31	29
32	26
33	23
34	21
35	19

High Agitation	
Time	Temperature, °C
Run 4	
1:15	79
16	59
17	48
18	39
19	32
20	28
21	25
22	22
23	20

Time, min	Temperature, °C	
	Run 5	Run 6
Start	65	67
0.5	50	53
1.0	40	43
1.5	32	36
2.0	26.5	30.5
2.5	22.5	26
3.0	20	22.5
3.5	17.5	19.5
4.0		18.5
4.5		16.5

LABORATORY-SIZE CRYSTALLIZER COOLING RATE — RUNS 7-9

Time, min	Run 7 (311 gm/l alum sulfate	Run 8 (297 gm/l alum sulfate)	Run 9 (304 gm/l alum sulfate)
Start	84.5	42.5	89
0.5	72	39.5	77.5
1.0	62	36	68.5
1.5	54	33	60.5
2.0	46.5	30	54.5
2.5	41	27.5	48.5
3.0	36.5	25.5	44
3.5	32	23.5	40
4.0	29	22	36.5
Agitator on			
4.5	26	21.5	33
5.0	23.5		30.5
5.5	21		28
6.0	19.5[a]	21	26
6.5	18		24
7.0		20	22.7
7.5			21.5
8.0		19[a]	20
8.5			19[a]
9.0			18.5
9.5			17.5
10.0			17
10.5			16.5
11.0			15.5
11.5			15
12.0			14.5

[a]Crystallization occurs

LABORATORY-SIZE CRYSTALLIZER COOLING RATE — RUNS 10 & 11

Time, min	Temperature, °C	
	Run 10 (289 gm/l alum sulfate)	Run 11 (289 gm/l alum sulfate with vigorous agitation)
Start	43	45
0.5	39.5	
1.0		39
1.5	32	
2.0	28	32
2.5	28.5	
3.0	23.5	27
3.5	22	
4.0	20.5	22.5
4.5	19	
5.0	Cooling water and stirrer off	19.5
6.0	↓	17.5
7.0		16
8.0		15
9.0		14
9.5	19	
10.0	Air agitator on	13[a]
18.0	18.5	
	18[a]	
19.0	17	

[a]Crystallization occurs

LABORATORY-SIZE CRYSTALLIZER - ALUMINUM SULFATE REMOVAL EQUIPMENT
(Water Used in Solution Chamber)

Item	Test Run				
	1 [a]	2 [b]	3 [c]	4 [c]	5 [c]
Reservoir Volume, ml	7000	7000	7000	7000	7000
Heat exchanger inlet temp °C	45-54-66	53-66	53-66	53-70	45-90
Reservoir temp, °C	39-49-55	52	50	50-52	45-52
Upper chamber temp, °C		51	42	37-38	45-36
Chilled water outlet temp, °C			25	19.5	24-19
Chilled solution flow, ml/min		500	520	520	520
Belt speed, cm/min		20.8	22.9	26.7	22.9
Solids removed total, kg/hr					393
Crystallize temp, °C					39

[a] Circulating pump not operating

[b] Circulating pump operating

[c] Circulating pump operating, cooling water used

LABORATORY REPORT

NO. R-6725-51-1516

Purpose _____ Model _____ Date 2-2-72

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Analysis

Source R&D BAC 5765, Solution 10 Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material Cr-1 and Cr-2 Spec. _____

☐ Chem. Lab. Aerospace ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ _____

Reference: C.C. to:

Analysis of $Al_2(SO_4)_3 \cdot 18H_2O$ on R&D tank:

Cr-1 = 2.3% by weight

Cr-2 = 2.5% by weight

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6725

AD 2847A

6-4800

LABORATORY-BUILT BELTED DRUM PRODUCT ANALYSIS

Assay of solids removed by belt (not dried)

Solution	Weight, gm	% of total
Aluminum sulfate	19.6	40.2
Sulfuric acid	12.7	26.1
Sodium dichromate	11.2	23.0
Water	5.2	10.7

Weight analysis of solids removed by belt

Item	Weight, gm	Liquid loss
Gross weight	27.3433	
Tare weight	12.7837	
Net solids	14.5596	
Gross weight	27.3433	
Vacuum dried weight	20.3119	
Weight loss	7.0314	48.3%
Vacuum dried weight	20.3119	
Alcohol washed weight	17.8355	
	2.4764	17.0%
		65.3% total

LABORATORY TEST DATA FOR CENTRIFUGE OPERATING CONDITIONS

DATA

Type Liquid: acid-water pH: acid Process Temp: Ambient ☒ Other ☐ °F

Type Solids: crystals Quantity Material Received: approx. 9.5 liters

Remarks: See second sheet for material preparation procedure.

Procedure: Samples taken before processing, after one pass, three passes, five passes and sludge samples before and after compaction.

MACHINE(S) USED

☒ 125-F Barrett clarifuge

☐ 125-F with accelerator

☒ Lab centrifuge (test tube)

Flow Rate: 4 gpm

TEST RESULTS

Sample no.	Sampling done	Solids in 10-ml sample, ml	% of solids by volume	Remarks	% Moisture	% CrO_3
1	As received	5.1	51			
2	1 pass	0.9	9			
3	3 passes	0.04	0.4			
4	5 passes	0	0			
5b	Sludge			Before compaction	29	0.4
5a	Sludge			After compaction	23	0.45

NOTE: Samples are spun at maximum speed in lab centrifuge for 1 minute unless otherwise noted.

*Solids are ☒ Scoopable ☐ Screwable ☐ Undeterminable (explain below)

☒ Not Scoopable ☐ Not Screwable ☐ Other

REMARKS: *Solids are scoopable before the 5-minute compaction and not scoopable thereafter.

CONCLUSIONS & RECOMMENDATIONS: The clarifuge does an excellent job of recovering all crystals from this chemical solution.

We have found the weight of the compacted crystals to be 1.5 kg/l, which means the customer could acquire his 9 kg of crystals in two batches. The solids are easily removed from the bowl by hand and whatever crystals or liquid that remain can easily be flushed from the clarifuge since the solution is water soluble.

This solution had no effect on the CRES clarifuge or its hoses.

LABORATORY TEST DATA FOR CENTRIFUGE OPERATING CONDITIONS (Concluded)

MATERIAL PREPARATION PROCEDURE

The necessary ingredients were mixed and dissolved at the temperature of 71° C for 5 minutes. The container was then allowed to cool to ambient temperature for 2 hours before processing.

The batch as we mixed it:	Aluminum sulfate	2.24 kg
	Sodium dichromate	0.21 kg
	Sulfuric acid	2.21 liters
	Water	4.88 liters

The weight of 1 gallon of compacted crystals:

500 ml of compacted crystals = 1.625 lb
1000 ml = 1.057 qt
946 ml = 1 qt
3784 ml = 1 gal.

Crystals weigh 12.298 lb/gal. or 1.47 kg/l

LABORATORY REPORT

NO. R-6725-51-1580B

Purpose _____ Model _____ Date 04-14-72

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Analysis of Chromium Regeneration

Source Pilot Tank 6-7310 Research Laboratory Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material 12070 HEK Project Spec. BAC 5765, Sol. #10

[X] Chem. Lab. _____ [ ] Sonic _____ [ ] Met. Lab. _____ [ ] Mechanical _____

[ ] X-Ray _____ [ ] Mag/Penetrant _____ [ ] _____

Reference: C.C. to:

Environmental Protection Agency
5-66967-7322-632083

ANALYSIS	CELL 04-05-72	CELL 04-06-72
H_2SO_4	221 gm/l	223 gm/l
Total $Na_2Cr_2O_7 \times 2H_2O$	4.1 gm/l	5.7 gm/l
Active $Na_2Cr_2O_7 \times 2H_2O$	0 gm/l	0 gm/l
Chromium (trivalent)	1.5 gm/l	2.0 gm/l
Aluminum	35 gm/l	55 gm/l

ANALYSIS	TANK 04-05-72	TANK 04-06-72
H_2SO_4	270 gm/l	275 gm/l
Total $Na_2Cr_2O_7 \times 2H_2O$	31 gm/l	30 gm/l
Active $Na_2Cr_2O_7 \times 2H_2O$	24 gm/l	25 gm/l
Chromium (trivalent)	2.6 gm/l	2 gm/l
Aluminum	102 gm/l	100 gm/l

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6725

AD 2847A 6-4800

LABORATORY REPORT

NO. R-6725-51-1620

Purpose _____ Model _____ Date 05-05-72

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Analysis of Chromium Regeneration Tank

Source Pilot Tank 6-7310 Research Lab. Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material 12070 HEK Project Spec. BAC 5765, Sol. #10

☐ Chem. Lab. _____ ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ _____

Reference: C.C. to:

Environmental Protection Agency
5-66967-7322-632083

ANALYSIS	CELL 04-07-72	CELL 04-10-72	CELL 04-11-72
H_2SO_4 gm/l	270	331	331
$Na_2Cr_2O_7 \times 2H_2O$	26	39.2	37
Total gm/l			
$Na_2Cr_2O_7 \times 2H_2O$	5.0	2.5	11
Active gm/l			
Aluminum Metal gm/l	2,0	4.5	4.5
Chromium +++ gm/l	7.4	7.6	9.0

ANALYSIS	TANK 04-07-72	TANK 04-10-72	TANK 04-11-72
H_2SO_4	344	336	321
$Na_2Cr_2O_7 \times 2H_2O$ Total gm/l	36	36	36
$Na_2Cr_2O_7 \times 2H_2O$ Active gm/l	26	12	6.5
Aluminum Metal gm/l	3.6	4.5	4.5
Chromium (trivalent) gm/l	3.5	8.5	10.2

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6725

AD 2847A 6-4800

LABORATORY REPORT

NO. R-6725-51-1610

Purpose _____ Model _____ Date 05-05-72

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Analysis of Chrome Regeneration Tank

Source Pilot Tank 6-7310 Research Lab. Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material 12070 HEK Project Spec. BAC 5765, Sol. #10

☐ Chem. Lab. _____ ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ _____

Reference: C.C. to:

Environmental Protection Agency
5-66967-7322-632083

ANALYSIS	CELL 05-03-72	TANK 05-03-72
H_2SO_4 gm/l	270	319
$Na_2Cr_2O_7 \times 2H_2O$ Total gm/l	27	36
$Na_2Cr_2O_7 \times 2H_2O$ Active gm/l	.8	24
Aluminum gm/Liter	34	34
Chromium (trivalent) gm/l	9	1.5

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6275

AD 2847A 6-4800

REMOVAL OF ALUMINUM SULFATE CRYSTALS WITH SOCK-TYPE FILTER

Sock type	Gross weight, gm	Tare weight, gm	Net weight gm	Dried weight, gm	Crystal weight loss, gm	Crystal % liquid
Polypropylene fiber with Dynel core	1048.4	132.4	916.0	614.1	434.3	47.5

DRUM FILTER OPERATING CONDITIONS — TESTS 1-6
Dressed Buchner Type Filter Cloth, 97 sq cm

Item	Laboratory Test					
	1	2	3	4	5	6
Sample, volume cc		200	300	100	200	200
Vacuum, cm Hg		66-71	66-71	66-71	66-71	66-71
Filtering time, sec		180	405	45	50	215
Initial dewatering rinse, sec		180	405	45	100	215
Time before cracking, sec		No cracking observed in any test run				
Discharge from cloth		Clean in all cases				
Cake thickness, cm		0.32	0.95	0.16	0.16	0.24
Clarity of filtrate		Filtrate became progressively cloudy				
Wet weight of cake, gm		19.1	31.0	9.2	10.1	18.0
Dry weight of cake, gm		11.6	24.8	5.3	5.9	11.3
H_2O removed, gm		7.5	6.2	3.9	4.2	7.3
H_2O in cake, %		39.2	20.0	42.4	41.5	39.1
Rate, kg/cm^2/hr		2.5	2.4	4.6	2.3	2.1
Volume, ml filtrate/sq cm/hr		43	29	85	77	36
Removal rate (dry cake), gm/l		56	83	53	56	56
Chrome in cake (CrO_3), %		0.95	0.88	0.99	0.90	0.93
Comments and Observations	Not valid due to vacuum leak.				Drying period double that of test 4 had no effect.	

DRUM FILTER OPERATING CONDITIONS — TESTS 1a-7a

Item	Laboratory Test						
	1a	2a	3a	4a	5a	6a	7a
Submergence, %	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Rpm	1/4	1/4	1/6	1/6	1/4	1/6	1/6
Filtering time, sec	88	88	132	90	88	132	132
Initial dewatering time, sec	96	96	144	180	96	144	144
Time before cracking, sec	None	None	None	None	None	None	None
Discharge from cloth	Clean	Clean	Clean	Clean	Clean	Clean	Clean
Cake thickness, cm	0.48	0.48	0.32	0.32	0.32	0.16	0.16
Clarity of Filtrate	Sparkling	Sparkling	Clear but precipitating	Clear but precipitating	Clear but precipitating		
Filtrate volume, cc	1600	1500	540	430	435	290	265
Wet weight of cake, gm	66.7	65.3	43.7	42.2	49.0	31.1	36.9
Dry weight of cake, gm	36.6	38.2	24.0	23.7	26.6	22.0	21.7
H_2O removed, gm	30.1	27.1	19.7	18.5	22.4	17.1	15.2
H_2O in cake, %	45.2	41.5	45.1	43.8	45.1	43.8	41.2
Rate, kg/sq dm/rev	0.23	0.25	0.15	0.15	0.17	0.14	0.14
Rate, kg/sq dm/hr	3.5	3.5	1.5	1.5	2.6	1.4	0.14
Volume, ml filtrate/sq cm/hr	156	145	35	28	42	19	17
Removal rate (dry cake), gm/l	23	26	44	53	62	75	83
Chrome in cake (CrO_3), %	2.4	2.1	2.6	1.4	2.2	4.5	4.6
Comments and Observations	String discharge ok	String discharge ok	String discharge ok	String discharge ok	String discharge limit seems to have been reached	Too thin for strings-- try roller	Carbon steel roll

LABORATORY REPORT

NO. 2-4861-0002-354

Purpose _____ Model _____ Date Oct. 18, 1972

To: Leo Hagen M/S 93-54 Org'n. R-6725 Part No. _____

Subject: Analysis of Solution #10 BAC 5765

Source _____ Reinsp. Req. _____

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material _____ Spec. _____

☐ Chem. Lab. _____ ☐ Sonic _____ ☐ Met. Lab. _____ ☐ Mechanical _____

☐ X-Ray _____ ☐ Mag/Penetrant _____ ☐ _____

Reference: C.C. to: H. Hicks 7-3141

The submitted Solution #10 samples for iron, copper, zinc, magnesium, and manganese, were analyzed by atomic absorption techniques. Aluminum was requested on two samples and was determined wet chemically.

JOB #180 10-5-72		Job #185 10-16-72	
		#1 227-1 Tank	#2 Cell (from Tank)
Fe	322 ppm	268 ppm	304 ppm
Cu	920 ppm	74 ppm	0.93 ppm
Zn	186 ppm	164 ppm	198 ppm
Mg	572 ppm	56 ppm	69 ppm
Mn	34 ppm	26.5 ppm	32 ppm
Al	21 gm/l	-	-

Job #185 Sample #3 - Sludge scraped from cathode of tank

cu	= 53.06%	Mu	= 0.002%
Fe	= 0.034%	Mg	= 0.055%
Zn	= 0.20%	Al	= 2.8%

Prepared by Bruce Smith Approved by S. D. Urban Org'n. 2-4861

AD 2847A 6-4600

TASK IV

PILOT PLANT OPERATION

DATA SHEETS

DIAPHRAGM HYDROSTATIC POROSITY

Identification[a]	First water drops, cm	Volume, ml/10 min	Porosity, ml H_2O/hr/sq cm	Remarks
J5D-20 STM-3	–	2276	559	
J5D-20 STM-2	97	390	96	
J5D-30 STM-4 (after service)	41	225	55	
13 Jun EX-20	74	1900	467	
13 Jun-20-15M400°	30	1690	415	
13 Jun-20-15M400°	53	3838	941	
16 Jun-20-45M300°	79	182	45	
19 Jun-20-4H300°	> 127	21	5	
J5D-20-1-21	> 127	280	44	Pressure failure in hydraulic press; forming time at pressure is unknown.
J5D-20-1-22	122	810	128	
J5D-20-1-25	> 127	396	63	
J5D-20-1-21a	> 127	91	14	
J5D-20-1-25a	> 127	58	9	
J5D-20-1-22a	127	120	19	
J5D-20-1-25a	64	108	17	
J5D-30-1-9	> 127	81	13	
J5D-30-1-24 (spec)	31	565	28	
2J5D-30	30	0	0	Two used 30-layer diaphragms.
3J5D-20	68	260	6	Three used 20-layer diaphragms.
J5D-30-1-7 Nov	30	236	12	
J5D-30-1-16 Nov			7	
J5D-20-1-19 Nov			356	

[a]Identification code:

J5D	-	20	-	1	-	21		16 June	-	20	-	45M	-	300°
↑		↑		↑		↑		↑		↑		↑		↑
Material		Number of cloth layers		Daily series		Day of the month	or	Date		Layers		Pressure		Temperature

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK AND CELL ANALYSES — MARCH-APRIL 1972
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Time	Temp, °C	Tank analysis						Cell analysis						Remarks
			Active chrome		Sulfuric acid		Aluminum sulfate		Total chrome		Sulfuric acid		Aluminum sulfate		
			ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	
Mar															
16	9:00	67		34.5		273		0		0.8		278		0	10 amp, 1 V
17	10:00	67		29.5		283		11 4				311		46.5	10 amp, 1 V
20	7:45		5.1	10.4	5.1	230	3.6	65.3	12.9	26.3	13.9	333	3 0	40.5	30 amp, 3.3 V; total Cr^{+6} 32.9 gm/l
22	1:00		8.6	17.5	11.5	275	3.4	57							Power supply off, total Cr^{+6} 37 7 gm/l
24	1 15	71	8.5	17.3	11.8	283	2.3	94							Power supply at 10 amp; total Cr^{+6} 36.7 gm/l
27	8.30	71	11.1	22.6	12.2	292	3.8	74			14.8	354	2.6	24	Power supply at 10 amp, total Cr^{+6} 35.2 gm/l
28	9:00	71	11.8	24	11.5	283	2.5	102			14.2	340	1.4	57	
30	9:00	71	10 45	21	9.3	223	1.5	61			15.5	113			
Apr															
3			15.0	31	16.1	308	1.6	69			20.95	401	2.9	126	
5				24		270		102		4.0		221		35	Total Cr^{+} (tank) 24 gm/l
6	1:00			25		275		101		6 0		223		55	Power supply at 30 amp
7	1:00			26		344				26		270			Power supply at 30 amp
10	8:00			12		336				39		331			Power supply at 30 amp
11	8:00			6		321				37		331			Leak in diaphragm, shut down

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK AND CELL ANALYSES
MAY-JUNE 1972
227-Liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Sample size, ml	Chamber	Active Cr^{+6} ml	Active Cr^{+6} gm/l	H_2SO_4 (pH 3.5) (a) ml	H_2SO_4 (pH 3.5) gm/l	Aluminum (pH 11.3) (b) ml	Aluminum (pH 11.3) (b-a-blank) ml	Aluminum (pH 11.3) gm/l	Total Cr, gm/l
May										
1		Tank	9.0	18	17.4	341	24.1	4.6	144	
	2.5	Cell	0	0	14.5	284	19.1	2.5	78	
2	↑	Tank	10.7	22	17.6	344	24.0	4.3	135	
		Cell	0	0	14.6	286	19.3	2.6	82	
3		Tank	11.3	23	17.8	348	24.1	4.1	131	36
		Cell	0	0	14.9	292	20.3	2.3	72	27
4		Tank	12.5	25	17.6	353	23.5	3.8	119	
		Cell	0	0	14.3	287	19.8	3.4	107	
5		Tank	13.1	26	17.2	345	22.2	2.9	91	
		Cell	0	0	14.3	287	20.0	3.6	113	
8	↓	Tank	15.7	31	17.6	345	22.9	3.2	101	36
	2.5	Cell	0	0	14.5	290	21.9	4.3	135	
9		Tank	12.8	32	13.7	344	18.1	2.7	106	
	2.0	Cell	0	0	10.9	274	17.2	4.6	180	
10	↑	Tank	13.3	33	13.7	344	18.2	218	110	
		Cell	0	0	10.9	274	17.6	5.0	196	
11		Tank	13.5	34	13.7	344	19.6	4.2	131	
		Cell	0	0	19.9	274	17.0	5.2	203	
15		Tank	13.5	34	13.5	339	18.3	3.1	122	
		Cell	0	0	10.2	257	18.0	6.1	239	
16		Tank	13.4	33	13.75	345	18.9	3.45	135	
		Cell	0	0	10.2	257	18.2	6.3	247	
17		Tank	13.3	33	13.5	339	18.5	3.3	129	
		Cell	0	0	9.9	249	17.8	6.2	243	
18		Tank	9.7	24	12.8	321	18.8	4.3	168	
		Cell	0	0	9.8	246	18.2	6.7	262	
19		Tank	10.1	25	12.7	318	18.4	4.0	157	
		Cell	0	0	9.7	243	16.8	7.2	281	
22		Tank	11.2	28	12.8	321	18.4	3.9	153	34
		Cell	1.8	5	9.5	241	17.2	5.9	231	45
23		Tank	12.0	3	12.5	314	18.1	3.9	153	
		Cell	0	0	8.9	224	17.9	6.3	246	
24		Tank	12.3	31	12.8	321	17.8	3.3	129	
		Cell	0	0	9.2	231	18.1	7.2	281	
25		Tank	12.7	32	12.9	323	18.3	3.7	145	
		Cell	0	0	9.4	236	19.0	7.9	309	
26		Tank	12.7	32	12.7	318	17.9	3.5	137	22
		Cell	0	0	9.6	236	19.4	8.1	317	
30		Tank	12.3	31	12.2	305	17.1	3.2	125	
		Cell	0	0	8.55	215	18.5	8.25	323	
31	↓	Tank	12.4	31	12.5	313	17.9	3.7	145	
	2.0	Cell	0	0	10.4	261	19.9	7.8	305	

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK AND CELL ANALYSES
MAY-JUNE 1972 (Concluded)
227-Liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Sample size, ml	Chamber	Active Cr^{+6} ml	Active Cr^{+6} gm/l	H_2SO_4 (pH 3.5) (a) ml	H_2SO_4 (pH 3.5) gm/l	Aluminum (pH 11.3) (b) ml	Aluminum (pH 11.3) (b-a-blank) ml	Aluminum (pH 11.3) gm/l	Total Cr, gm/l
Jun										
1		Tank	12.8	32	12.5	318	17.5	313	129	
	2.0	Cell	0	0	10.1	253	19.8	8.0	313	
2		Tank	12.5	31	12.4	316	17.3	3.2	128	
		Cell	0	0	9.95	254	19.8	8.15	324	
5		Tank	12.5	31	12.0	305	16.7	3.0	119	
		Cell	0	0	8.6	219	9.4	9.1	362	
		Cell[c]	0.5	1	11.1	282	13.2	0.4	16	
6		Tank	12.5	31	12.5	304	17.6	3.4	131	
		Cell	0	0	11.3	289	13.4	0.4	16	
		Cell[d]	213	6	1.9	49	3.4	0.0	0	
7		Tank	12.8	32	12.8	312	17.9	3.4	131	
		Cell	0	0	11.5	294	14.4	1.2	49	
		Cell[d]	5.8	14	5.5	141	8.1	0.9	37	
8		Tank	12.4	31	12.6	305	17.4	3.1	119	
		Cell	0	0	11.5	294	14.7	1.5	61	
		Cell[d]	7.2	18	6.9	176	10.1	1.5	61	
9		Tank	10.8	27	11.9	305	16.9	3.3	134	
		Cell	0	0	11.2	287	14.8	1.9	77	
12		Tank	9.1	23	10.9	279	16.2	3.6	146	
7 :00 a.m.		Cell	0	0	11.0	281	16.3	3.6	146	
12		2nd Tank	8.8	22	11.3	289	16.8	3.8	154	
12 :30 p.m.		Cell	0	0	11.5	294	16.8	3.6	146	
12		3rd Tank	0	0	12.3	314	18.0	4.0	162	
1 :30 p.m.		Cell	0	0	0	0	0	0	0	
13		Tank	8.4	21	12.0	307	17.5	3.8	154	
		Cell	0	0	11.5	294	17.2	4.0	163	
14		Tank	8.2	20	11.5	295	17.2	4.0	163	
		Cell	0	0	11.3	290	17.9	4.9	199	
16		Tank	8.8	22	11.7	299	18.1	317	150	
		Cell	0	0	9.5	243	17.2	6.0	244	
19		Tank	9.7	24	12.2	313	19.7	5.6	227	
		Cell	0	0	9.5	243	19.8	8.6	349	
25		Tank	11.0	27	10.55	270	12.25			
26		Tank	11.0	27	10.5	270				
27	2.0	Tank	14.1	35	12.3	315				

[a]First titration
[b]Second titration
[c]Refilled
[d]Special test

CONTINUOUS (ELECTROLYTIC) REGENERATION CELL ANALYSES — JULY-OCTOBER 1972
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972	Active Cr^{+6}		H_2SO_4 (pH 3.5)		$Al_2(SO_4)_3 \cdot 18H_2O$ (pH 11.3)			Total chrome		Additions
						Corrected				
Date	ml	gm/l	ml	gm/l	ml	ml	gm/l	ml	gm/l	
Jul										
7	nil	nil								
8	0.53	0.13								
9	0.23	0.6								
14	0.57	0.13								
21	1.6	4.0								
24	1.9	4.7								
25										
26	–	–	11.4	292						
27	0	0	11.2	287						
28	0	0	12.1	309						
31			10.3	263				3.5	8 3	
Aug										
4			9.2	236				9 4	23	38 gm/l H_2SO_4
7			10.0	256				10.4	26	5 25 gm/l H_2SO_4, raised to 305 gm/l
8			11.6	296				10.6	26	
9			12.8	327				0 02	0.04	Cell recharged
10			12.2	313				–	–	
11			11.1	284				0.4	1.0	260 gm H_2SO_4, raised to 309 gm/l
14			10.9	279	12.05	0	0	0 8	2.0	300 gm H_2SO_4, and second 300 gm H_2SO_4
15			12.1	310	13.2	0	0	0.7	1 7	160 and 300 gm H_2SO_4
16			11.55	296	12.45	0	0	1 4	3.5	145 gm H_2SO_4, and 75 cc H_2SO_4
17			11.7	300	12.7	0	0	1.5	3.7	80 cc H_2SO_4
18			12.2	313	13.4	0.8	0.54	1.3	3.5	80 cc H_2SO_4, and another 80 cc H_2SO_4
21			13.6	348	15 4	5.3	3.8	3 5	9.0	
22			12.8	328	14.3	3.0	2.2	3.6	9 0	
23			12.0	307	13.8	5.3	3.8	3.6	9.0	80 cc H_2SO_4
24			12.0	307	13.5	3.0	2 2	4 0	9.8	80 cc H_2SO_4
25			11.6	297	13.4	5.3	3.8	4.2	10.5	80 cc H_2SO_4
28			12.8	328	15 4	11	8.1	7.6	19	
29			11.8	302	14.1	9	6.5	7.3	18	
30			10.95	288	13.5	11	7.8	8 0	20	80 cc H_2SO_4
31			9.8	251	12.4	11	8.1	7.3	18	160 cc H_2SO_4, and another 160 cc H_2SO_4
Sep										
1			11.5	294					16	
5		0.2	10.8	276			92		16	160 cc H_2SO_4, 9:00 a.m.
6			11.5	294						100 cc H_2SO_4, 9:00 a m
7			11.7	300						50 cc H_2SO_4, 8:00 a.m.
8			8.9	240					18	100 cc H_2SO_4, 7 30 a.m., 320 ml H_2SO_4, 3:00 p m.

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — JULY-OCTOBER 1972
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Active Cr^{+6}		H_2SO_4 (pH 3 5)		$Al_2(SO_4)_3$ -$18H_2O$ (pH 11.3)			Total chrome		Additions	Remarks
	ml	gm/l	ml	gm/l	ml	corrected ml	gm/l	ml	gm/l		
Jul											
26	14.0	35	12 3	314	–	–	–	–	–		
27	13.9	34	12 2	313	–	–	–	–	–		
28	13 6	34	12 0	307	–	–	–	–	–		
31	13 6	34	12.0	307	–	–	–	–	–		
Aug											
4	12.9	32	11.9	305	–	–	–	–	–		Stabilizing period for new solutions and short-term 60-layer diaphragm testing.
5											
6											
7	12.9	32	11.9	305	–	–	–	13 3	33		
8	12.9	32	12.0	307	–	–	–				
9	13.2	32	12.2	312	–	–	–				
10	13.0	32	12.0	307	–	–	–				
11	12.8	32	12.1	309	–	–	–	13.1	32		
12											
13											
14	12.8	32	12.25	314	13 85	0 5	20				
15	12.7	31	12.3	314	13 75	0.35	14				
16	12 0	30	12.0	307	13.6	0.5	20			1000 ml H_2SO_4	
17	12.0	30	12.6	322	14.4	0.7	29				
18	12.2	30	12.4	317	14.2	0.7	29	13 2	32		
19											
20											
21	11.8	29	12.15	311	14.40	1 15	47				
22	12.0	30	12.10	310	14 5	1 3	53				
23	12.0	30	12.00	307	14.4	1 3	53				
24	11.6	29	11.8	302	14.2	1 3	53			900 ml H_2SO_4; 53 gm/l $Al_2(SO_4)_3$-$18H_2O$ ⇔962 gm dissolved Al	
25	11 4	28	11.9	305	14.45	1.45	59	12.9	32	900 ml H_2SO_4	
26											
27											
28	12.5	31	12.3	314	14.95	1.55	63				
29	11 9	29	12.25	314	14.95	1.6	65				
30	11.9	29	12.15	311	14.9	1.65	67				
31	11.95	29	12.15	311	14 95	1 7	69				
Sep											
1	11.3	28									
5	11 6	29		299			130		31		
6	11.9	29									
7	11.9	29									
8	11.9	29									

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — JULY-OCTOBER 1972 (Concluded)
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Active Cr^{+6}		H_2SO_4 (pH 3 5)		$Al_2(SO_4)_3$ -$18H_2O$ (pH 11 3)			Total chrome		Additions	Remarks
	ml	gm/l	ml	gm/l	ml	corrected ml	gm/l	ml	gm/l		
Sep											
11	12 2	30		250			102		25		
12	12 4	31									
13	12 1	30									
14	12 3	30									
15	12 3	30									
16	12 2	30									
17	12.4	31									
18	12 8	32									Rectifier off for Al^{+++} addition
19	12 3	31	13 2	317	16.8	2 3	88			13 5 kg $Al_2(SO_4)_3$ -XH_2O	
20											
21			12 8	306	17 95	3.85	146			13 5 kg $Al_2(SO_4)_3$ -XH_2O	
22	11 85	30	13.05	313	19 6	5 25	200			18.0 kg $Al_2(SO_4)_3$ -XH_2O	
23											
24											
25	11.70	29	13.15	315	21.3	6.85	260				Rectifier on at 9.00 a.m., 20 amp
26											
27	11 20	28	12 95	310	21 1	6 85	260	12.7	32		
28	11 1	28	12 6	302	21 3	7 4	281				
29	11 0	27	13 0	311	21 7	7 4	281	12.7	32		
30											
Oct											
1											
2	11 1	28	13 05	313	22.5	8 15	310				
3	11 3	28	13 0	311	22 35	8.05	305				
4	11 4	28	13 0	311	21 9	7 6	289				Rectifier at 28 amp
5	11 7	29	13.1	314	22 2	7 8	297				
6	11 5	29	13 1	314	22.5	8 1	308				Rectifier at 23 amp
7											
8											
9	11 3	29	12 85	308	23 1	8 95	341				
10	11 5	29	13 1	314	22 9	8 5	324				Rectifier at 20 amp
11	11 4	28	13 1	314	22 7	8 3	315				Rectifier at 15 amp
12	11 3	28	13 0	311	22 7	8 4	319				
13	10 9	27	12 6	302	22 4	8 5	323				Rectifier at 20 amp
14											
15											
16	11.9	30	13 0	311	22 5	8.2	311				
17											
18			13.3	318	21.3	6 7	254				This analysis made after cooling to ambient and analyzing supernatant
19											

CONTINUOUS (ELECTROLYTIC) REGENERATION CELL ANALYSES — JULY-OCTOBER 1972 (Concluded)
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972	Active Cr^{+6}		H_2SO_4 (pH 3.5)		$Al_2(SO_4)_3\ 18H_2O$ (pH 11.3)			Total chrome		Additions
						Corrected				
Date	ml	gm/l	ml	gm/l	ml	ml	gm/l	ml	gm/l	
Sep										
11		0 2	6.6	169			101		18	300 ml H_2SO_4, 8 00 a.m., 500 ml H_2SO_4, 3.00 p m.
12			10.8	276						200 ml H_2SO_4, 8 00 a m., 250 ml H_2SO_4, 3 00 p.m
13			11.3	290						240 ml H_2SO_4, 8 00 a.m.
14			11.4	292						300 ml H_2SO_4, 8·00 a.m.
15			11.2	287						500 ml H_2SO_4, 8 00 a m , 700 ml H_2SO_4, 3·30 p m.
18			13.5	345						No acid additive today
19			12.85	308	15.80	1.65	63	9 0	21	200 ml H_2SO_4, 8 00 a.m
22			11.0	264	15 3	3.0	114	9 2	23	300 ml H_2SO_4
25			13 95	334	18.45	3.2	122	9 9	25	
26										
27			13.1	314	20.5	6.1	232	12.3	31	
28			11.5	276	20.8	8.0	304	12.7	32	
29			11 7	281			nil		nil	
30										
Oct										
1										
2			12 5	300	14 3	0.5	19	2.7	0.75	
3			12 6	302	15.05	1.15	44	1.3	3 0	
4			10 1	242	12.4	1.0	38	0 8	2.2	
5			8 85	212	13.45	3 3	125	0.9	2.2	
6			7.6	182	11.1	2.1	80	1.2	3.0	
9			6 65	159	13 65	5.7	217	3.8	9 8	
10			5 7	137	12.7	5 7	217	4 2	10.5	
11			4.3	104	10 7	5.1	194	4 1	10.5	
12			3 9	94	10.5	5.3	201	4.4	11.3	
13			3.9	94	10 6	5.4	206	4.3	10.5	
16			5.7	137	14.9	7 9	300	9 2	23	

CONTINUOUS (ELECTROLYTIC) REGENERATION CELL ANALYSES
NOVEMBER 1972
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	H_2SO_4, gm/l	Total chrome, gm/l	Additions
Nov			
10	177		
11			
12			
13	297		
14	279		130 ml H_2SO_4
15	312		
16	308		
17	288	5	100 ml H_2SO_4
18			
19			
20	310	8	
21	310	11	

CONTINUOUS REGENERATION ETCH RATE DATA — 2024 ALLOY
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer, 30.5 sq cm Panel Area

1972 Date	Panel no.	Weight, gm		Time		Weight loss, gm	Elapsed time, min	Etch rate			Temp, °C	Remarks
		Start	End	In	Out			gm/sq in./hr	gm/sq cm/hr	(BAC) in /surf/hr		
Aug												
10	1	5.2054	5.1064	9 03 00	9:23 00	0 0990	20	0 02475	0.0038	0.00057	71	
11	1	5.1071	4.9970	8 53·00	9.18:00	0 1101	25	0 0220	0 0034	0 00052		
14	1	4 9969	4.9140	9:12·00	9 27.00	0 0829	15	0.0276	0 0043			Immersion time uncertain.
14	1	4.9144	4.8081	1:28 00	9 48·00	0.1063	20	0.0266	0.0041			
15	1	4.8083	4.6368	8.00:00	8:30·00	0.1715	30	0.0286	0 0044			
15	1	5.4108	5.3153	9:07.03	9:27 03	0.0955	20	0.0239	0 0037			
16	1	5.3159	5.2427	9:46·00	10.01·00	0.0732	15	0.0244	0 0038			
17	1	4 6373	4 5615	10.58·15	11.13 15	0.0758	15	0.0253	0.0039			
17	2	5.2428	5.1753	10:58 15	11·13.15	0.0675	15	0.0225.	0.0035			
17	1	4.5615	4.4838	11.55·00	12:10·00	0.0777	15	0.0259	0.0040			
17	2	5 1753	5.1050	11:55 00	12:10·00	0.0703	15	0.0234	0.0038			
18	1	4.4840	4 3970	9:15:15	9:30.15	0 0870	15	0 0290	0 0045			
18	2	5 1053	5.0254	9.15:15	9:30 15	0 0799	15	0 0267	0 0041			
21	1	4 3970	4.3163	10:44·00	10·49:00	0.0807	15	0.0269	0 0042			
21	2	5.0255	4.9504	10·44·00	10.49:00	0.0751	15	0.0251	0 0039			
22	1	4.3163	4.1855	8.25:00	8·50·00	0.1308	25	0.0261	0.0040			
22	2	4.9504	4.8271	8.25·00	8:50:00	0.1233	25	0.0247	0 0038			
23	1	4.1855	4.1011	8:10:10	8·25·10	0.0844	15	0 0281	0.0044			
23	2	4 8271	4.7469	8:10:10	8:25:10	0 0802	15	0.0268	0.0042			
24	1	4 1011	3.9293	7:56·15	8:27.15	0.1718	31	0.0277	0.0043			
24	2	4.7469	4.5791	7:56:15	8:27·15	0.1678	31	0.0271	0.0042			
25	1	3.9293	3.8391	7:47:00	8·04:00	0.0902	17	0.0265	0.0041			
25	2	4.5791	4.4907	7:47:00	8·04·00	0 0884	17	0.0260	0.0040			
28	1	3.8391	3.7200	8:40:00	9·01:00	0 1191	22	0 0271	0.0042			
28	2	4.4912	4.3645	8.40:00	9.01:00	0.1267	22	0.0288	0.0045			
29	1	3.7200	3.5448	7.14.00	7:46.00	0.1752	32	0 0274	0.0042			
29	2	4.3645	4 1866	7.14:00	7:46:00	0.1779	32	0.0278	0.0043			
30	1	3.5448	3.4585	8·42·00	8:58·00	0.0863	16	0.0270	0.0042			
30	2	4.1866	4.1005	8:42:00	8·58:00	0.0861	16	0.0269	0.0042			
31	1	3.4585	3.3767	7.06:00	7:21:00	0.0818	15	0.0273	0.0042			
31	2	4 1005	4.0180	7:06·00	7 21.00	0.0825	15	0.0275	0.0043			
Sep												
25	1	3.3560	3.2302	10.43:00	10:58.00	0 1258	15	0 0418	0.0065			Questionable data. Erratic readings on Mettler balance.
25	2	4.0014	3.9039	10:43:00	10:58·00	0 0975	15	0.0325	0.0050			Composite etch rate from Aug 31 to Sep 25 weights is: No 1 = 0 0295
27	1	3.2396	3.2103	2·53:00	3:08:00	0.0293	15					No. 2 = 0.0277
27	2	3.9199	3.8405	2.53.00	3·08·00	0.0794	15					
28	1	3.2105	3.1217	7:38:00	7·55:00	0.0888	17	0.0262	0 0041			
28	2	3.8407	3.7532	7 38.00	7:55 00	0.0875	17	0.0258	0 0040			
29	1	3.1221	3 0421	7:39:00	7:54:00	0.0800	15	0.0267	0 0041			
29	2	3.7535	3 6745	7.39:00	7:54:00	0.0790	15	0.0264	0.0041			

CONTINUOUS REGENERATION ETCH RATE DATA — 2024 ALLOY (Concluded)
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer, 30.5 sq cm Panel Area

1972 Date	Panel no	Weight, gm		Time		Weight loss, gm	Elapsed time, min	Etch rate			Temp, °C	Remarks
		Start	End	In	Out			gm/sq in./hr	gm/sq cm/hr	(BAC) in /surf/hr		
Oct												
2	1	3.0424	2 9623	9.32 00	9·47 00	0.0801	15	0 0267	0 0041	0.00063	71	
2	2	3 6743	3 5940	9.32·00	9·47 00	0 0803	15	0.0268	0.0042	0 00063	71	
3	1	5 2832	5 1814	9.06 00	9.33 00	0 1018	27	0.0188	0.0029	0 00043	65.5	Etch rate ran per BAC 5765 requirements.
3	2	5 2812	5 1822	9.06 00	9·33 00	0 0990	27	0 0183	0.0028	0 00042		
3	1	5.1817	5.1269	10 12 00	10.27 00	0 0548	15	0 0183	0 0028	0 00042		Same as above, with copper sulfate added
3	2	5.1826	5.1283	10.12 00	10.27 00	0 0543	15	0.0181	0.0028	0 00042		
3	1	5.1269	5.0764	10.44 30	10.59:30	0.0505	15	0.0169	0.0026	0.00037		Same as above, with ferrous sulfate added.
3	2	5 1283	5 0778	10.44 30	10.59 30	0 0505	15	0.0169	0.0026	0 00037		
3	1	5 3212	5.2690	12 53 15	1 08 15	0 0532	15	0 0178	0 0028	0 00040		Same as above, with magnesium sulfate added
3	2	5 2649	5 2139	12 53 15	1 08 15	0 0510	15	0 0171	0 0027	0 00039		
3	1	5 2690	5 2137	1 24 00	1 40.00	0 0553	16	0 0173	0 0027	0 00037		Same as above, with zinc sulfate added
3	2	5.2139	5.1593	1 24 00	1 40 00	0 0546	16	0 0171	0 0027	0 00037		
3	1	5 2137	5 1642	1 54 00	2 09 00	0 0495	15	0 0165	0 0026	0 00036		Same as above, with manganese sulfate added
3	2	5 1593	5 1102	1 54 00	2 09·00	0 0491	15	0 0164	0 0025	0 00036		
4	1	5 1656	5 1215	10 58·00	11 13·00	0 0441	15	0.0147	0 0023			
4	2	5 1114	5 0722	10 58 00	11.13.00	0 0392	15	0 0131	0 0020			
5	1	4 9798	4 9315	8 17 00	8 32 00	0 0483	15	0 0161	0 0025			
6	1	4 9322	4 8741	7 52 00	8 10 00	0 0581	18	0 0162	0.0025			
9	1	4 8750	4 8264	7 22 00	7 37 00	0 0486	15	0 0161	0 0025			
16	1	4 8268	4 7647	8 39·00	8 54·00	0 0621	15	0.0207	0.0032		71	
Dec												
4	1	5 0734	5.0409	8 16 00	8 31 00	0 0325	15	0.0108	0 0017		72 5	

CONTINUOUS REGENERATION ETCH RATE DATA — 7075 ALLOY
227-liter Pilot Tank, Sulfuric-Dichromate Deoxidizer

1972 Date	Bar no.	Area, sq cm	Weight, gm		Time		Weight loss, gm	Elapsed time, hr	Dissolved metals		Etch rate		Remarks
			Start	End	In	Out			Total, gm	gm/hr	gm/sq in/hr	gm/sq cm/hr	
Aug													
10	1	444	853.9	830 1	9 43	3 08	23 8	5 42		4.4	0 0639	0.0099	
11	1	444	830 1	800 7	7 33	2 33	30 0	7 00		4 3	0 0624	0 0097	
14	1	444	800 7	772.9	7 43	2 18	27 8	6 58		10 4	0 0614	0 0095	
	2	444	874 6	841 6	7 43	2 18	33 0	6 58	114 6		0.0757	0 0117	
15	1	421	772 9	742 1	7 48	2 48	30 8	7 0		9 93	0.0674	0 0105	
	2	444	841.6	802 9	7 48	2 48	38 7	7 0	184 1		0 0804	0 0125	
16	1	421	742 1	713 3	8 45	3 15	28 8	6 5		9.85	0.0678	0 0104	
	2	421	802.9	767 8	8 45	3:15	35 1	6 5	248 0		0 0825	0 0128	
17	1	410	713.3	690.0	9 10	3 10	23 3	6 0		8.52	0 0612	0 0095	
	2	412	767.8	740 0	9.10	3:10	27 8	6 0	299.1		0 0727	0.0113	
18	1	410	690 0	665 9	7 50	1·52	24 1	6 0	323 2	4.02	0.0633	0 0098	
	2	368	740.0	444 5	7 50	9 50(8/21)	295 5	74.0	618.7	4 00	0 0701	0 0109	Power setting 14 amp
21	2	323	444 5	376 5	10 15	7:50	68 0	21.6	686 7	3 15	0 0648	0 0100	Power setting 30 amp
22	2	297	376 5	311 0	8 00	7 15	68 5	23 75	755 2	2 88	0.0627	0 0097	
23	2	274	311 0	250 6	7 50	7.30	60 4	23 7	815 6	6.12	0.0570	0 0088	
	1	387	665 9	581.3	7 50	7·30	84 6	23 7	900 2		0 0578	0 0090	
24	1	364	581 3	499.1	7 50	9·00	82 2	25 2	982 4	5.57	0 0590	0 0092	
	2	250	250 6	192 6	7 50	9:00	58.0	25 2	1040.0		0 0634	0.0098	
25	1	341	499.1	497 4	9 30	10·10	1 7	0 66	1041 7				Bars removed for weekend
	2	218	192 6	191.4	9 30	10 10	1 2	0 66	1042 9				
28	1	323	497 4	422 6	7·35	7·10	74 8	23 4	111 7	5.71	0 0640	0.0099	Bar 2 deleted from test
	3	436	867.3	808 7	7·35	7 10	58 6	23 4	1176 3		0.0309	0 0048	
29	1	315	422.6										
	3	414	808 7	750 0	8 35	8:35	58.7	24 0	1235.0	2 45	0.0385	0 0060	
30	3	397	750 0	697 5	9.00	7 10	52 5	22 2	1287.5	2 39	0 0380	0 0059	
31	3		697.5	629 5	8 00	1 30	68.0	29 5	1355 5	5 33			
	1	314	422.6	341.4	9 25	1 30	81.2	27 1	1436 7				
Sep													
1	3		629.5	438 6	1·30	8:00(9/5)	19.09	90.5	1627 6	2 11			
5	3		438.6	393.5	8 30	8.30	45 1	24.0	1672 7	1.88			
6	3		393.5	360 9	2 00	8:00	32.6	18.0	1705.3	1.81			
8	3		360.9	239 8	7 30	7:30(9/11)	121 1	72.0	1826 4	1.68			
11	3		239.8	208 5	8 30	7 30	31.3	23.0	1857 7	1.36			
12	3		208.5	176.8	8 30	7·30	31.7	23 0	1889.4	1 38			
13	3		176.8	148.3	8 30	7 30	28.5	23 0	1917 9	1.24			
14	3		148.3	121 0	8 00	7:00	27 3	23.0	1945.2	1 19			
15	3		121.0	68.8	8 00	7.00(9/18)	52.2	71 0	1997.4	0.74			
18	3		68.8	49.7	8 00	7·00	19.1	23 0	2016 5	0.83			
19	3		49.7		8 00								
20	3			26.6		12·30							
25	1		341.3	183 5	1·50	7 30(9/29)	157.8	89 7	2174 3	1.67			
Oct													
4	1	427	868.4	761.0	11.00	9.15	107.4	46 25		0.035	2.32	0 0054	
6	1	373	761.0	582.3	9 30	2:30(10/9)	178.7	77.0		0.039	2.32	0 0061	
9	1	355	582.3	547 0	2 30	7:20	35 3	16.8		0.038	2 10	0.0059	
10	1	328	547.0	401 6	7.45	7:45(9/13)	145 4	72.0		0.040	2.02	0 0062	

TASK V

COMMERCIAL PRODUCTS EVALUATION

DATA SHEETS

pH CURVE FOR AMCHEM 6-16 (HNO_3) WITH Al $(NO_3)_3 \cdot 9H_2O$ AT 308 gm/ Al^{+++}

ml	pH	ml	pH	ml	pH	ml	pH
pH standard at 4.01		18.0	3.81	42.6	7.63	46.0	9.70
0	1.83	19.0	3.83	42.7	7.70	46.1	9.72
2.0	1.85	20.0	3.85	42.8	7.76	46.2	9.75
3.0	1.88	21.0	3.86	42.9	7.82	46.5	9.83
4.0	1.91	22.0	3.88	32.0	7.90	47.0	9.95
5.0	1.98	23.0	3.89	43.1	7.99	47.5	10.03
6.0	2.04	24.0	3.90	43.2	8.04	47.0	10.11
7.0	2.13	25.0	3.91	43.3	8.10	49.0	10.20
8.0	2.21	26.0	3.93	43.4	8.17	50.0	10.31
9.0	2.33	27.0	3.94	43.5	8.24	51.0	10.42
10.0	2.49	28.3	3.96	43.6	8.30	52.0	10.50
11.0	2.80	29.0	3.99	43.7	8.38	53.0	10.55
11.5	3.05	30.0	4.00	43.8	8.44	54.0	10.61
11.6	3.15	31.0	4.02	43.9	8.51	55.0	10.68
11.7	3.20	32.0	4.05	44.0	8.60	56.0	10.72
11.8	3.30	33.0	4.09	44.1	8.70	57.0	10.56
11.9	3.38	34.0	4.10	44.2	8.82	57.1	10.90 [a]
12.0	3.42	35.0	4.05	44.3	8.88	57.2	10.93 [a]
12.1	3.47	36.0	4.20	44.45	8.96	57.3	10.95 [a]
12.2	3.49	37.0	4.28	44.6	9.01	57.4	10.84
12.3	3.51	38.0	4.40	44.7	9.08	57.5	10.91
12.4	3.54	39.0	4.61	44.8	9.15	57.6	10.99
12.5	3.56	40.0	5.19	44.9	9.22	57.7	11.03
12.7	3.61	pH standard at 10.00		45.0	9.28	57.8	11.08
12.8	3.63			45.1	9.33	57.9	11.11
12.9	3.64	40.0	6.00	45.2	9.39	58.0	11.14
13.0	3.66	41.0	67.0	45.3	9.42	58.2	11.18
13.1	3.67	42.0	7.26	45.4	9.47	58.3	11.20
13.5	3.69	42.1	7.30	45.5	9.50	58.4	11.21
14.0	3.70	42.2	7.36	45.6	9.54	58.5	11.23
15.0	3.75	42.3	7.41	45.7	9.60	59.0	11.38
16.0	3.78	42.4	7.50	45.8	9.61	60.0	11.55
17.0	3.80	42.5	7.58	45.9	9.67	61.0	11.66

[a]These values doubtful; pH meter was unstable.

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK AND CELL ANALYSES -- AMCHEM 6-16 (HNO_3)
227-liter Pilot Tank

1972 Date	Power supply, amp	Tank analysis						Cell analysis				Additions
		Total chrome		Active chrome		Nitric acid		Nitric acid		Total chrome		
		ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	
Nov												
22		2.44	30	1.22	25	6.8	2.86					
23	1.5											
24	↑											
25												
26												
27												
28	↓											
29	1.5							2 6	41	0.0	nil	
30	5.0							2 5	40	0.4	1	
Dec												
1	5.0		28	1 2	24	6 7	2.81	2.5	40	0.2	0	
2	5.0											
3	20											
4	↑	2 3	29	1 3	25	6.8	2 86	1 6	26	0 9	2	
5			29	1 3				1.2	19			
6												300 cc HNO_3 (cell)
7												
8												300 cc HNO_3 (cell)
9												
10												
11	↓											300 cc HNO_3 (cell)
12	20											
13		7.0	17	4 0	10	3.4	52	1.2	19	4.1	1 1	900 cc HNO_3 (cell)
Feb (1973)												
23		8						3.4	53			900 cc HNO_3 (cell)
26		8						2.4	38			
Mar												
5								4.0	12			

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK AND CELL ANALYSES — AMCHEM 6-16 (HNO_3)

1973 Date	Deoxidizer temp, °C	Time	Elapsed time, hr	Power supply V	Power supply amp	Tank analysis: Active chrome ml	Tank analysis: Active chrome gm/l	Tank analysis: Nitric acid ml	Tank analysis: Nitric acid gm/l	Tank analysis: Total chrome ml	Tank analysis: Total chrome gm/l	Cell analysis: Active chrome ml	Cell analysis: Active chrome gm/l	Cell analysis: Nitric acid ml	Cell analysis: Nitric acid gm/l	Cell analysis: Total chrome ml	Cell analysis: Total chrome gm/l	Remarks
Jan 30	21.5	10 25	Start	10	2.0	17.5	8 7											Used J5D-20
	21.5	10:40	0.25	10	2 7													
	24	10.55	0.50	10	3.4	17 5	8.7											
	26	11:20	0.92	10	4 0													
	35	12:13	1.8	9 4	5.0	18.1	9			28.6	14	6.5	3 0			32 7	15.8	
	41	1 25	3.0	8 5	5.0	18 9	9 3											
		1.50	3.4			18 95	9 4											
Feb 1	48	8:35	Start	8.0	5.0	18.6	9 2	16 5	50	35 0	17	7 6	3 8	11 4	35	37 0	18.2	
	44.5	9 35	1.0	7.1	5 0	19 8	9 8					4 0	2 0					
	43.0	10 35	2.0	7 1	5.0	10 3	10 1					3.1	1 5					
	41.5	12:20		6 5	5.0													Added 12.8 gm HNO_3
	41.5	12:35	4.0	6.7	5 0	20 7	10 3					4.9	2 3					
		2.15						18 1	56					1 0	3			
		2·20												15 0	46			Added 42 5 gm HNO_3
	41.0	2.35	6.0	5.5	5.0	21.9	10 9					4.1	2 1					60% regenerated
5	35.0	8:30	Start	5.6	5.0	17.1	85	15.8	49	7.2 (2)[a]	18			15 8	49		17 9	
	36 8	9:45	1 25	4 3	5.0	18 8	9 4							11 1	35			Added 3 5 ml HNO_3
	37 0	10:30	2 0	5 3	5.0	19 3	9 5							10 3	32			Added 14 7 ml HNO_3
	37.8	12:30	4.0	5 4	5.0	21.0	10.4							10 0	31			Added 30.0 ml HNO_3
	39.0	2:30	6.0	5 3	5.0	22 0	10 9							9 0	28			Added 50 0 ml HNO_3
	39 8	3:30	6 5	4 8	5 0	22.0	10 9	19 3	59	7 4 (2)	18 5			24 6	75	8.1 (2)	20 1	60% regenerated
7	46.5	8:20	Start	5 0	5.0	17 0	8 4			7 2 (2)	18							
	47 0	9:20	1 0	4.0	5 0	19 0	9 4							11 8	36			Added 25 0 ml HNO_3
	46.0	10:20	2.0	5 0	5 0	20 5	10 1							12 0	37			Added 25 0 ml HNO_3
	48 0	11:20	3 0	4.9	5.0	20 7	10 4							18 9	58			
	48.0	12:20	4.0	5.0	5.0	21 4	10.6							16 0	49			
	48 0	2:20	6.0	5 1	5.0	21 4	10 6							11 8	26			54% regenerated
23	65 5	9:25	Start	5 0	5.0	16 9	8 3							15 4	47			
	66.0	10:25	1.0	5.0	5.0	20 4	10 1							13 6	42			Added 25 0 ml HNO_3
	66 0	11:25	2 0	5 0	5 0	20 8	10 4							22 5	69			
	65 5	1:25	4 0	5.0	5 0	23 9	11 9							14 7	45			
	66 0	3:25	6.0	5 0	5 0	26 0	12 9											70% regenerated
26	65.5	9:35	Start	5 3	5 0	35 0	17 9	15 7	48					15 7	48			
	66.0	10:35	1.0	5.3	5 0	8 1 (2)	20 2			11 8 (2)	29			14 6	45			
	66.0	1:35	4 0	5 0	5 0	8 7	21 7							17 2	53			
	66.0	2:30	5 0	5 0	5 0	9 7	24 1							10 1	32			
	66 0	3:20	5.8	5 0	5 0	9 9	24 7											84% regenerated
Mar 2	66 8	8 10	Start	6 0	5 0	7 8	19 4			11 0	27			8 9	27			New J5D-20, Added 10.0 ml HNO_3
	66 2	9·10	1 0	5 7	5 0	8 4	20 9	(b)						11 9	36			Added 6 0 ml HNO_3
	66.2	10·10	2 0	5 6	5 0	8 5	21 2							12 4	38			
	67 5	11 10	3.0	5 8	5 0	8 3												
29						32 2	16 0	7 1	21 8									600 gm/l $Al(NO_3)$ added to 3500 ml, evaporated from 3500 to 1250 and raised to 2750 ml
29								8 2	25 2									Depleted from 2200-liter tank

[a]Parentheses denote sample size (ml)
[b]Leaking cell

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — SMUTGO 4

1973 Date	Phase	Deoxidizer temp, °C	Time	Elapsed time, hr	Power supply V	Power supply amp	Tank analysis: Active chrome ml	Active chrome gm/l	Nitric acid (a) ml	Nitric acid gm/l	Total chrome ml	Total chrome gm/l	$Al(NO_3)_3 \cdot 9H_2O$ (b) ml	(b-a-blank[c]) ml	gm/l	Remarks
Apr																
3	Fresh		8 15	Start			13 5 (2)	33 6	16 15 (10)	65 8	15 2 (2)	5 05	21 7	2 45	25 6	
	1st depletion		10 15	2 00			12 4	30 9	15 5 (10)	47 5						
			12 00	3 75			11 7 (2)	29 2	14 5 (10)	44 6			21 4	2 8	29 3	106 gm HNO_3 added
			2 30	6 25			10 3	25 7	16 5	50 8						24% depleted
4	1st regeneration	155	7 30	Start	16	20	10 4	26 0	16 5	50 8			24 4	4 8	50 3	
		170	8 30	7 25	15	20	12 5	31 2	18 6	57 2						
		170	9 15	8 00	15	20	12 6	31 4	18 9	58 1						83% regenerated
		171	10 15	9 00	15	20	12 7	31 7	19 5	60 0						84% regenerated
5	2nd depletion		8 05	9 00			15 7		18 8	57 8			26 8	5 1	53 3	
			9 20	9 00			13 7	34 1	16 2	50 3						
			10 20	9 00			13 3	33								After 1st regeneration
16			1 52	9 00			13 3	33								Added 1 98 ml/l 70% HF
			2 45	10 00			12 6	31								Added 0 825 ml/l 70% HF
17			9 00	10 0			12.6	31								Started 2nd phase of 2nd depletion
	2nd regeneration		10 00	11 0	2 0	1 0	10 0	25	13 9	44			24 1	7 1	75	Start regeneration
		66	11 00	12 0	12	15	11 8	29	15 9	50						Add 40 ml HNO_3 to cell, raised to 10 5V and 20 amp,
		66	11 30	12.5	11 5	15	12 4	31								cannot maintain 20 amp
			12 00	13.0	11 5	15	12 5	31								
		74	12 30	13.5	11 5	15	12 8	32								
			1 00	14 0	18	15	12 9	32	19.2							Total Cr 14 5 ml = 36 gm/l = 89% regeneration
18	3rd depletion		2 18	14 0				32								864 sq cm Al immersed = 540 sq cm/l
			3 18	15 0			9 5	24								
19	3rd regeneration	77	10 20	15 0	18	12										Used 45 gm/600 ml $NaNO_3$ instead of HNO_3 and CRES
		77	11 20	16.0	18	12	11 0	28								anode gold-plated with Hanovia Liquid Gold 3 coats
		77	11 50	16 5	18	12	11 4	28								baked at 315° C Plate flaked off quickly
20		77	9 05	16 5	12 5	15										
		77	9 35	17 0	12 5	15	12 0	30								
		77	10 05	17 5	12 5	15	12 5	31								
		71	10 50	17 75	12 5	12 5	12 5	31								Total Cr 15 1 ml = 38 gm/l = 83% regenerated
23	4th depletion	83	8 05	17 75			12 1	30								Start of 4th depletion, total chrome 14 6 ml = 37 gm/l
			10 05	19 75			5 7	14								
24	4th regeneration	65	8 15	19 75	13	13 5		14								Start of 4th regeneration, Meter reading 1580 Amp-hr 15 8
		76	9 00	20.0	12	15	7 0	17								
			10 30	21 5	12	14	7 6	19	15 8	50						Total Cr^{+6} 13 5 ml = 34 gm/l, 3180 31 8
			11 00	22.0	12	14	7.6	19								56% regenerated 3810 38 1

[a]First titration
[b]Second titration
[c]Blank = 3 1 ml
[d]Parentheses denote sample size (ml)

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — AMCHEM 6-16 (HNO_3)

1973 Date	Phase	Deoxidizer temp, °C	Time	Elapsed time, hr	Power supply		Tank analysis				Remarks
							Active chrome		Nitric acid		
					V	amp	ml	gm/l	ml	gm/l	
Apr											
3	Fresh		8:45	Start			39.2 (10)[a]	19	15.5 (10)	48	7.5 gm/l $Na_2Cr_2O_7$ $2H_2O$ added
	1st depletion		12 00	3.25			8.9 (2)	22	13.2 (10)	41	18.8-13.2-3.1 = 2.5 gm/l $Al(NO_3)_3 \cdot 9H_2O$
	1st regeneration		2.30	5.75			8 3	21	13.4	41	25% depleted, 5 gm/l HNO_3 added
5			9.05	6 75	12	20	9.9	25	15 9	49	
20	2nd depletion		9 20					25			Start of 2nd depletion
			10 45	8.17			6 1	15			
	2nd regeneration	81	10 55	Start	18	15		15			
			11.55	9 17	15	15	8 3	21	10 8		14 535 amp-hr, total Cr^{+6}= 27 gm/l, 77% regen
	3rd depletion	31	1 25	Start							
			2 25	10.17			6.2	16			
May											
1	3rd regeneration	83	7.30	Start	12	17.4		16			
			8·35	11.25			6.2	16	13 2		21.0 amp-hr

[a]Parentheses denote sample size (ml)

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — AMCHEM 6-16 (H_2SO_4)

1973 Date	Phase	Deoxidizer temp, °C	Time	Elapsed time, hr	Power supply		Tank Analysis						Remarks
							Active chrome		Sulfuric acid		Total chrome		
					V	amp	ml	gm/l	ml	gm/l	ml	gm/l	
Mar													
19	Fresh			Start			31.5	15 2	19 25	12.9	32 0	2 04	
20	1st depletion						26 8	13 3					Depleted to 87 5% of original Cr^{+6}
20	1st depletion		11 20		6 6	5.0	24 3	12 1					Depleted to 79 5% of original Cr^{+6}
22	1st regeneration		9 00		6 6	5 0	6 2 (2)[a]	15.5			8 0 (2)	2 66	77 5% Cr^{+6} — no regeneration apparent (3 hr regen)
			2 30			20.0	9 3 (2)	23 2			10 7 (2)	3 55	350 ml reduced to 1600 ml at this time 87% regen
May													
1	Fresh		8 45	Start			9 45	24	19 7	96			Total chrome 9 8 ml = 24 gm/l, add 20 ml H_2SO_4
	1st depletion		10 45	2.0			7 0	17					26% depleted
	1st regeneration	83	11 22	2.0	22	15		17	21 5	105			28 5 - 1 3 - 21 5 = 5.7 ml = 33 gm/l $Al_2(SO_4)_3\ 18H_2O$
		83	12.34	3 2	12.3	18 5	8 0	20					18 0 amp-hr
	2nd depletion		12:50	3.2									85% regenerated
			1 50	4.2			6.8	17					Start depletion
	2nd regeneration		2·40	4 55	18 3	21.3	7 3	18					16 4 amp-hr total chrome· 9 2 ml = 23 gm/l, 79% regen
			2.55	5.2			7.7	19					21 1 amp-hr, 84% regenerated
	3rd depletion		8 05	5 2			7.8	19	24 4	119			31.4 - 1 3 - 24.4 = 5 7 ml = 44 gm/l $Al_2(SO_4)_3\ 18H_2O$, total chrome 9.9 ml = 25 gm/l
			9 23	5.5			7 1	18					
	3rd regeneration		10 23	6.5	12	20	6 1	15	22 7				31.2 - 1 3 - 22 7 = 7.2 ml = 56 gm/l $Al_2(SO_4)_3 \cdot 18H_2O$
			10 53	7.0	12	21	6.4	16					9 8 amp-hr
		87	11 45	8.0	12	21	7.1	18					29 1 amp-hr
			12.13	9.0	12	21	8.0	20					38 2 amp-hr, 81% regenerated

[a]Parentheses denote sample size (ml)

CONTINUOUS REGENERATION ETCH RATE DATA — PROPRIETARY DEOXIDIZERS
77.4 sq cm Panel Area

1973 Date	Panel no.	Weight, gm Start	Weight, gm End	Time In	Time Out	Weight loss, gm	Elapsed time, min	Etch rate gm/sq cm/hr	Temp, °C	Remarks
Jan										
30	1	5.0414	5.0189	10:55	11:10	0.0225	15	0.0012	21.6	Amchem 6-16 regenerated from Jan. 29, 1973
	1	5.0200	4.9979	12:08	12:23	0.0221	15	0.0012	21.4	Amchem 6-16 from 2200-liter tank not regenerated
Feb										
2	1	4.9983	4.9639	9:59	10:24	0.0344	25	0.0011		Amchem 6-16 from 2200-liter tank not regenerated
27	2	4.7653	4.7387	7:53	8:08	0.0266	15	0.0014	19.5	Regenerated Amchem 6-16 (HNO_3) at 29 gm/l total Cr
	2	3.7387	4.7178	8:34	8:49	0.0209	15	0.0011	20.0	Not regenerated Amchem 6-16 (HNO_3) at 29 gm/l total Cr
Mar										
19	2	4.7182	4.6889	12:18	12:33	0.0313	15	0.0016	26.0	Fresh Amchem 6 (H_2SO_4) 3.78 liters
	1	4.9633	4.9296	12:29	12:44	0.0337	15	0.0018	17.0	Fresh Amchem 6 (HNO_3) 227 liters; temperature is below spec
23	2	4.6890	4.6884	12:44	12:59	0.0006	15		26.9	Fresh Amchem 6 (HNO_3) with 600 gm/l $Al(NO_3)_3 \cdot 9H_2O$
28	1	4.9307	4.9299	8:47	9:02	0.0008	15		24.0	Fresh Amchem 6 (HNO_3) with 600 gm/l $Al(NO_3)_3 \cdot 9H_2O$
Apr										
3	1	4.6884	4.6587	9:27	9:40:15	0.0297	13.25	0.0017	26.5	Smutgo 4 (Auburn)
	2	4.9302	4.8911	9.29	9:44	0.0391	15	0.0020	30.8	Amchem 6 (HNO_3) + 7.5 gm/l $Na_2Cr_2O_7 \cdot 2H_2O$
	1	4.6587	4.6442	2:36	2:51	0.0145	15	0.0007	28 9	Smutgo 4 (Auburn) after depleted 24%
	2	4.8911	4.8829	2:39	2·54	0.0082	15	0.0004	26.8	Amchem 6 (HNO_3) + 7.5 gm/l dichromate after depleted 24%
5	1	4.6450	4.6338	8:55	9:10	0.0112	15	0.0006	25.7	Smutgo 4 (Auburn) after 1st regeneration to 84%
	1	4.6338	4.6233	10:53	11·11	0.0105	18	0.0005	27.0	Amchem 6 (HNO_3) after 1st regeneration
16	1	4.6235	4.6129	9.40	9:55	0.0105	15	0.0005	23 8	Smutgo 4, after 1st regeneration, 0 33 cc/l HF added
	1	4.6129	4.6107	10:10	10:39	0.0022	20	0.0001	24.5	Smutgo 4, after 1st regeneration, another 0.33 cc/l HF added
	3	5.2425	5.2294	12:08	12:23	0.0131	15	0.0007	21.5	Smutgo 4 same as previous test except new etch rate panel used
	3	5.2294	5.1992	12:54	1:11	0.0302	17	0.0014	24.8	Smutgo 4, after 1st regeneration, another 1.32 cc/l HF added
	3	5.1992	5.1748	2.45	3:03	0.0244	18	0.0010	24.5	Smutgo 4, after 1 hr 2nd depletion, another 0.825 ml/l 70% HF added
17	3	5.1758	5.1403	8:36	8:51	0.0345	15	0.0018	30.0	Smutgo 4 after above HF addition
	3	5.1419	5.1164	2:11	2:27	0.0255	16	0.0012	31.0	Smutgo 4 after 2nd regeneration
18	3	5.1166	5.0941	7:59	7:14	0.0225	15	0.0012	22.0	Smutgo 4 after 2nd regeneration with 0 825 ml/l, 70% HF added
	3	5.0941	5.0650	12:38	12:53	0.0291	15	0.0015	21.0	Smutgo 4 after 2nd regeneration with 2nd 0.825 ml/l, 70% HF added
	3	5.0650	5 0337	1·21	1:36	0.0313	15	0.0016	20.8	Smutgo 4 after 2nd regeneration with 3rd 0.825 ml/l, 70% HF added
20	3	5.0340	4.9912	12:56	1:25	0.0428	29	0.0012	26.0	Smutgo 4 after 3rd regeneration
	3	4.9912	4.9540	1:38	1·53	0.0372	15	0.0019	26 0	Smutgo 4 after 3rd regeneration and 2 475 ml/l 70% HF added
	3	4.9558	4 9225	8:37	8:54	0.0333	17	0 0015	22.0	Amchem 6 (HNO_3), 1.65 ml/l 70% HF added after 1st regeneration (-0.002 mg)
	3	4.9234	4.8838	12 58	1:13	0.0396	15	0.0020	32 5	
	3	4.8847	4.8673	8:24	8 39	0.0174	15	0 0009		Amchem 6 (H_2SO_4) 7.5 gm/l $Na_2Cr_2O_7$ $2H_2O$ fresh

TASK VI

PRODUCTION DEMONSTRATION

DATA SHEETS

CALIBRATION OF VARIABLE-SPEED DRIVE ON DRUM FILTER

Dial reading	Minutes per revolution	Revolution per minute
17.5	1.25	0.800
16.5	1.72	0.580
15.5	2.28	0.440
14.5	3.08	0.325
13.5	4.04	0.248
12.5	5.23	0.192
11.5	6.12	0.164
9.5	7.34	0.136
8.5	8.08	0.124
7.5	12.75	0.079

CONTINUOUS REGENERATION— AMETEK DRUM FILTER EVALUATION
2200-liter Preproduction Tank, Sulfuric-Dichromate Deoxidizer

Item	Run no. 1	2	3	4	5	6	7	8	9	10	11	12
Date	12/11/72	12/11/72	12/11/72	12/11/72	1/2/73	1/2/73		1/2/73	1/8/73	1/8/73		1/8/73
Stop time	11 15	2.20	8.33	9:10	9 08	10 41		1 21	8 35	11 05		12 25
Start time	10 15	1 20	7 33	8·40	8 38	10 11	12 09	12 49	8 05	10 35		11 55
Test time, hr.	1.0	1.0	1.0	0.5	0.5	0 5		0 5	0.5	0 5		0.5
Vacuum, cm Hg	48-55	51-58	53-58	58-61	51-58	58	48-51	56-58	53-58	48-53		58-64
Cake thickness, mm	16	24	8	78	72-48	8-32		8-16	32-48	32-48		32-24
Drum speed setting	9.5	8 5	8 5	7 5	8 5	9 5	9 5	8.5	8 5	8.5		8 5
Type discharge	String	String	Scraper	Scraper	Scraper	Scraper	Scraper	Scraper	Scraper	Scraper		Scraper
Discharge air, gm/sq cm	–	–	700	700	140	140	140	140	280	350		350
Feed pumps	Overflow	Overflow	Overflow	Overflow	Overflow	Overflow	Overflow	Overflow	Overflow	Overflow		Overflow
Filter agitator setting	ON	ON	ON	ON	ON	ON	ON	ON	ON	ON		ON
Filter cloth	Polypro	Polypro	Polypro	Polypro	Polypro	Polypro	Polypro	Polypro	Reemay 2024 polyester			polyester
Deoxidizer temp, °C	24	24	29	29	24	24	24	26	26	–		26
Filtrate volume:												
Stop time	10 45	1.55	8:15 45	–	8 58.15	10 26 15	(a)	12.57 15	Not measured	10 50 22	Not measured	
Start time	10 30	1 40	8:90		8 55	10 22		10 52		10 48		
Time, min	15	15	7.75		3 25	4.25		5.25		2 37		
Weight as H_2O, gm	8638	9993	8638		8638	8638		8638		8638		
Volume as H_2O, liters	8.63	10 3	8.63		8.63	8.63		8 63		8 63		
Filtrate, liters/hr	34.6	39.9	67.0		159.3	121 9		98.8		218 8		
Cake												
Total weight, gm	5051	5100		1576	4069	964		813	2130	3155		2696
Rate, kgm/hr	4 79	5 12		3 15	8 15	1 95		1 63	4 26	6 30		5 39
Moisture, %	21.0	18.0	44 1	Not measured	36.6	37 6		36.6	32 67	30 03		40 68
Chrome (dried salt), %	3.1	3 0	2.47		0.8	0 8		0 8	2 54	3.65		2.55
Drum rpm	0.13	0.12	0.12	0 10	0 12	0.13		0 12	0.12	0.12		0 12
Remarks			Cake too wet and very small amount	Cake too wet	Batch oper from 227-liter tank, Renton lab	Batch oper from 227-liter tank, Renton lab		Cake very thin, black, graphite plugs cloth	Cloth too coarse and inflexible	Good cake		Good cake

CONTINUOUS REGENERATION — AMETEK DRUM FILTER EVALUATION (Concluded)
2200-Liter Preproduction Tank, Sulfuric-Dichromate Deoxidizer

Item	Run no 13	14	15	16	17
Date	1/8/73	1/8/73	1/9/73	1/9/73	1/9/73
Stop time	1 00	1 34	9 17	9:48	1·19
Start time	12 30	1 04	8·47	9:18	12 49
Test time, hr	0 5	0.5	0.5	0 5	0.5
Vacuum, cm Hg	64	61-64	53-58	58-61	51-58
Cake thickness, mm	16-24	16	16-40	8-16	8
Drum speed setting	9.5	2 5	4.5	6.5	7 5 (high)
Type discharge	Scraper	Scraper	Scraper	Scraper	Scraper
Discharge air, gm/sq cm	350	350	350	350	350
Feed pumps	Overflow	Overflow	Overflow	Overflow	Overflow
Filter agitator setting	ON	ON	ON	ON	ON
Filter cloth	polyester	(b)	Olefin	Olefin	Olefin
Deoxidizer temp, °C	26	26	26	26	26
Filtrate volume					
Stop time	12:45	1.26 45	9.10:10	9 42.30	1 08
Start time	12:33	1·13	9 05	9 37	1 04
Time, min	12.0	13.75	5.17	5 0	4 0
Weight as H_2O, gm	8638	8638	8638	8638	8638
Volume as H_2O, liters	8.63	8.63	8 63	8 63	8.63
Filtrate, liters/hr	43.1	37.5	100	104	129
Cake·					
Total weight, gm	2805	3328	7060	7548	6216
Rate, kgm/hr	5 62	6 66	14 1	15.1	12.5
Moisture, %	35 79	31 71	36.20	35.59	32 32
Chrome (dried salt), %	2 53	3.20	3.08	1 85	2.27
Drum rpm	0.13	0.19	0.325	0.56	0 8
Remarks					(c)

(a) Run aborted. Cake too thin. Analysis of solution shows large dilution of deoxidizer. Aluminum sulfate crystals are dissolved

(b) Polyester cloth except two sections are olefin for hole repair.

(c) Atomic absorption analysis of run 17 dried salts (% by weight)
Cr = 2.10 Cu = 0.025 Zn = 0 550
Al = 3.00 Mn = 0.015
Fe = 0 07 Mg = 0.003

Drum Speed Calibration					
Dial Setting	Test 1	Test 2	Test 3	Average min/rev	Average rev/min
7.5	1.25	1 25		1.25	0.800
6.5	1.72	1 82	1.82	1.78	0.562
5.5	2.28			2 28	0 439
4 5	3.08			3.08	0 325
3 5	4.04			4 04	0 247
2.5	5.23			5.23	0 191
1 5	6.12			6 12	0 163
9 5 (low	7.34	8 17		7.75	0 129
8 5 (low)	8.08			8.08	0 124
7.5 (low)	12.78	13.0		12.88	0 078

LABORATORY REPORT

NO. R-6725-51-1900

Purpose _____ Model _____ Date January 16, 1973

To: H. Hicks Org'n. 6-7310 Part No. M/S 92-06

Subject: Regeneration of Deoxidizer

Source Auburn - 600 Gallon Tank Reinsp. Req. /

Purchase Order _____ R.R. _____ Date Rec'd. _____ Quan. _____ Acc. _____ Rej. _____

Material 12070 HEK Spec. BAC 5765 Sol. #10

[x] Chem. Lab. _____ [ ] Sonic _____ [ ] Met. Lab. _____ [ ] Mechanical _____

[ ] X-Ray _____ [ ] Mag/Penetrant _____ [ ] _____

Reference: C.C. to

EPA 5-66967-7322-632083

Run #1 (01-04-73)	Moisture 0.6% Total Chrome *
Run #2 (01-04-73)	Moisture 0.5% Total Chrome *
Run #3 (12-18-72)	Moisture 44.1% Total Chrome *
Run #5 (01-02-73)	Moisture 36.7% Total Chrome 0.8%
Run #6 (01-02-73)	Moisture 37.6% Total Chrome 0.8%
Run #8 (01-02-73)	Moisture 36.6% Total Chrome 0.8%

*Total Chrome to be done by Atomic Absorption or Equivalent

Prepared by Leo Hagen Approved by M. Minsk Org'n. R-6725

AD 2847A

6-4800

CONTINUOUS REGENERATION TANK AND CELL ANALYSES — 2200-LITER PREPRODUCTION TANK
Sulfuric-Dichromate Deoxidizer

1972 Date	Total chrome, gm/l	Tank analysis: Active chrome, gm/l	Tank analysis: Sulfuric acid, gm/l	Tank analysis: Aluminum sulfate, gm/l	Cell analysis: Sulfuric acid, gm/l	Remarks
Jul						
12		4.31	39.6			
Sept						
25		2.07	35.4			
Oct						
30		0.12	2.3			
31		0.065	1.97			
Nov						
3		1.4			233	
6		1.0			122	
7		1.5			315	
9		2.5			297	
10		4.1			344	
12						
13[a]		6.7			173	
14		7.2			122	
15		7.7			311	
16		8.2			278	
17		9.3			217	
20		13.6			161	
21		14.9			111	
22		15.5			251	
28		16.1			226	
29		16.7			247	
30		17.6			277	
Dec						
1		19.5			264	
5		19.3			352	362 kg aluminum sulfate added
6	63.0	18.0	281	295		
7					284	91 kg aluminum sulfate added
8		17.9	284	295	293	
9						36 kg aluminum sulfate removed with drum filter
10						30.6 kg aluminum sulfate removed with drum filter

[a]Minor element analysis (ppm):
Cu = 5.9 Mn = 2.4
Zn = 7.7 Mg = 3.8
Fe = 20.2

CONTINUOUS REGENERATION TANK AND CELL ANALYSES — 2200-liter PREPRODUCTION TANK
Sulfuric-Dichromate Deoxidizer

1973 Date	Power supply amp	Power supply V	Amp-hr[a] Time off	Amp-hr[a] Meter reading	Amp-hr[a] Time on	Amp-hr[a] R/40 reading	Amp-hr[a] Cum[b]	Tank analysis Total chrome, gm/l	Tank analysis Active chrome, gm/l	Tank analysis Sulfuric acid, gm/l	Tank analysis Aluminum sulfate, gm/l	Cell analysis Total chrome, gm/l	Cell analysis Sulfuric acid, gm/l	Deoxidizer temp, °C	Remarks
Dec (1972)															
12									18 3				216		
13									19 7				270		
14									20 4				341		
15															
16													278		
17													217		
18[c]									18 9				197		
19									19 7				266		
20									16 7				161		
21													111		
22													251		
Jan															
5										202	337				
10										211	350				Tank filtrate
11									11 2	227	323		158		
12									12 2		323				
13															
14					8 49	000000									
15	75	17 5	10 19	55910	10 47	6348			11 7				263	63	
16			8 52	86219	9 18	86532			11 5				222		
17			9 12	172708	9 38	173038			11 7				263		
18			10 00	255285	10 24	255564			11 7				273		
19	75	17 5	9 17	323927	9 44	324200[d]	644 93		11 9				277		
22	90	17	9 33	559214	9 55	559455			12 8				215		
23			10 12	649216	10 35	649485								63	
24			9 58	734153	10 22	734574									
25			10 08	802736	10 41	803045	1146 81								
26			9 45	854405	10 14	854607									
29			7 10	899046	Rectifier off to dump and recharge										
30[e]															
Feb															
19									27 2				28 0		
20	75								24 8				232		
21	145	14 5	Start		7 45	917111	4280		22 7			nil	66 7	Tank = 69, cell = 56	
22	175	14.25			7 34	088180			24 1				64 5	Tank = 68, cell = 68	
			10 10	088180	2 54	131615	1315								
23			10 32	131615	1 44	304853	1720		24 0				42 8		
25							2285								
26			10 17	533258	1 18	853153			23 4						

CONTINUOUS REGENERATION TANK AND CELL ANALYSES — 2200-liter PREPRODUCTION TANK (Concluded)
Sulfuric-Dichromate Deoxidizer

1973 Date	Power supply amp	Power supply V	Amp-hr[a] Time off	Amp-hr[a] Meter reading	Amp-hr[a] Time on	Amp-hr[a] R/40 reading	Amp-hr[a] Cum[b]	Tank analysis Total chrome, gm/l	Tank analysis Active chrome, gm/l	Tank analysis Sulfuric acid, gm/l	Tank analysis Aluminum sulfate, gm/l	Cell analysis Total chrome, gm/l	Cell analysis Sulfuric acid, gm/l	Deoxidizer temp, °C	Remarks
Feb															
27			10:23	536018	1:49	539251	26	9.5	21 0				94 5		
28[f]			9·28	622206	2 35	628819	879								
Mar															
1[g]			7:20	660291	2.38	715814	867		19 6				242		
2			7:55	802619	1 30	844226	1049		19.1				173		
5					7.00	030612	1320		17.3				75 8		
6	210	13			7 50	162410		9.7	17.6						
7			8·55	371704	1 27	399680	2360		19.5			0 02			
8	190	13	8:40	534679	2 21	716296	2240								
9[h]	200		8:50	716296	1.47	751593	339								Tank shut down @ 1 45 due to float failure.
10															
11															

[a]500-amp 100-mV shunt used with meter
[b]Cumulative amp-hr corrected for shared meter use
[c]Minor element analysis (ppm):
Al = 10,000 Zn = 40
Cu = 685 Mg = 245
Fe = 805 Mn = 210
[d]94 hr, 46 min total
[e]Tank out of operation due to loss of solution. Tank pumped out and cleaned, new float valves installed
Electrical heater conduit from tank 3N isolated from rectifier leads.
[f]Accumulative amp-hr January 15 thru 28 = 10,505
[g]Minor element analysis (ppm):
Al = 5575 Mg = 35
Fe = 195 Mn = 6.1
Cu = 93 Zn = 10.5
[h]Accumulative amp-hr March 1 thru 9 = 8175

CONTINUOUS REGENERATION TANK ANALYSES — 2200-liter PREPRODUCTION TANK
Sulfuric-Dichromate Deoxidizer

1973 Date	Power supply amp	Power supply V	Amp-hr[a] Time off	Amp-hr[a] Meter reading	Amp-hr[a] Time on	Amp-hr[a] R/40 reading	Amp-hr[a] Cum[b]	Tank analysis Total chrome, gm/l	Tank analysis Active chrome, gm/l	Tank analysis Time	Deoxidizer temp, °C	Remarks
Mar												
12									17.9		73	
13									17.0		71	
14									15.3		83	No rectifier
15									14 9		140	
16									13 4		148	
17												
18												
19	200	13			3.00	756600			10 1		142	
20			10·50	888897	11 15	889707	3310		10 8		145	
21			8 53	002168	1.44	030150			7 4		140	
22			12 22	217168	12 48	217713	4670	28.4	10 1		142	
23									12.0		142	
24												
25				217713	7 00	653104	10900					
26				653104	10 30	838420	4670		13.1			
27				838420		94752	2725		14.0		143	
28			10.38	947452	10.05	070056	3035					
29			10.58	070056	9.33	196656	3150		15 4			
30			3·07	196656	9.30	216394	494		16 7			Power supply set at 100 amp for weekend, 59% regenerated
31												
Apr												
1			9 10	216394	1 03	306149	2224					
2									15.4			Reset power supply to 200 amps; add 7.5 gm/l dichromate after analysis, 37 2 sq dm alloy 2024 suspended in tank
3									22.6	10 30		
4			9.30	306149	2 08	346770	755		21 5	10 30		
5			9 45	346770	2 41	472807	3129		21 6	9 45		
6									22 4	9.45		
7												
8												
9			12.05	472807	4 03	907650	10878		22 4	9 30		
10				907650		059850	3800					
11			8:25	059850	2 50	207736	3121			10.00		
12			8·30	207736	1 03	348537	3492		23.1			
13			7 30	348537		446072	2440		23 0			Rectifier shut down at 7 45a m. to run tank lining depletion test
14												
15												
16									18.8	10.30		
17									16.9	10.30		
18												Tank volume calculated at 2200 liters
19									14 5	10·30		Preproduction tank test completed

[a]500-amp 100-mV shunt used with meter

[b]Cumulative amp-hr corrected for shared meter use

CONTINUOUS REGENERATION TANK ANALYSIS — 8-hour RUN
2200-liter Preproduction Tank, Sulfuric-Dichromate Deoxidizer

1973 Date	Power supply		Time	Elapsed time, hr	Amp-hr		Active chrome $Na_2Cr_2O_7\ 2H_2O$		Tank analysis: Sulfuric acid (pH 3.4)		Tank analysis: Total chrome $Na_2Cr_2O_7\ 2H_2O$		Aluminum $Al_2(SO_4)_3\ 16H_2O$		Remarks
	amp	V			Meter reading	per hour	ml	gm/l	ml	gm/l	ml	gm/l	ml	gm/l	
Apr 10	175	12	7 30	Start	0	–	11 4	22	11 8	232			25 9	115	Temp 63° C held steady
	215	14	8 30	1	007400	0	11 3	22	11 8	232					37 2 sq dm aluminum hung in tank
	230	15	9 30	2	014940	188	11 5	23	11 9	234	21 2	42			
	230	15	10 30	3	023740	220	11 4	22	11 85	233					
	230	15	11 30	4	035510	243	11.6	23	12 0	239					
	240	15.5	12 30	5	043210	242	11 4	22	12 0	239					
	230	15	1 30	6	052280	226	11 5	23	12 0	239					Set power supply back to 200 for last hour
	200	13	2.30	7	059850	189	11 5	23	12 0	239	21 1	42	16 36		

COMPARISON OF MINOR ELEMENT CONTENT — 22,000 -liter PREPRODUCTION SOLUTION

Element	November 13, 1972		December 18, 1972		February 22, 1973	
	ppm	% of Total	ppm	% of Total	ppm	% of Total
Fe	20.2	50	805	40	195	45
Cu	5.9	15	685	34	93	21
Mn	2.4	6	210	11	6	14
Mg	3.8	9	245	12	35	18
Zn	7.7	19	40	2	105	24

CONTINUOUS (ELECTROLYTIC) REGENERATION TANK ANALYSES — MARCH 1973
Sulfuric-Dichromate Deoxidizer

1973 Date	Exposed material	Deoxidizer temp, °C	Time	Elapsed time, hr	Power supply		Tank analysis			
							Active chrome		Nitric acid	
					V	amp	ml	gm/l	ml	gm/l
Mar 7		28.3	9:15	Start	6.2	5.0	7.1	17.7		
	None[a]	34.0	10:15	1.0	6.2	5.0	7.1	17.7		
			11:00	2.0	6.2	5.0	7.7	19.2		
			12:00	3.0	6.2	5.0	7.9	19.7		
			12:40		12.0	15.0				
		61.1	1:45	4.5	11.0	15.0	9.5	23.6		
		91.5	2:45	5.5	14.0	30.0	13.8	34.4		
7	PVC and PVDC		8:00	Start	NA	NA	7.2	17.9	7.1	17.7
			9:15	1.25	↓	↓	6.9	17.2	7.0	17.4
			10:10	2.2			6.9	17.2	6.7	16.7
			11:00	3.0			7.1	17.7	6.9	17.2
			12:00	4.0			6.8	17.0	6.7	16.7
			1:15	5.25			6.8	17.0	6.7	16.7
			6:45	22.75			6.6	16.7	6.3	15.8
			12:30	28.50	NA	NA	6.4	15.2	6.2	15.5
8	Carbon brick (plus mortar)[c]	96	12:30	Start	NA	NA	6.4	15.2	6.2	15.5
		98	7:30	19.0	NA	NA	6.4	15.2	0.2	0.5

[a]Solution regeneration verification data
[b]Total surface area = 9 sq dm/l; temperature varied from 78° - 108° C
[c]One large piece and two small pieces

REDUCTION OF HEXAVALENT CHROMIUM BY TANK LINING MATERIAL

Time	Elapsed Time, min	Titration, ml	Sodium Dichromate, gm/l
7:45	Start	11.7	230
8:15	0.5	11.6	228
8:45	1.0	11.6	228
9:45	2.0	11:45	225
10:45	3.0	11.45	225
11:45	4.0	11.50	226
12:45	5.0	11.5	226

SELECTED WATER
RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No.

2.

W

REGENERATION OF CHROMATED ALUMINUM DEOXIDIZERS

5. Report Date

6.

8. Performing Organization Report No.

Hicks, H. C. and Jarmuth, R. A.

The Boeing Commercial Airplane Company
P. O. Box 3707
Seattle, Washington 98124

12070 HEK

Type of Report and Period Covered

12. Sponsoring Organization

Environmental Protection Agency report number, EPA-660/2-73-023, December 1973.

In the metal finishing industry highly concentrated hexavalent chromium solutions are used extensively to deoxidize aluminum surfaces prior to anodizing, conversion coatings, prepaint preparation, welding and adhesive bonding. A regeneration process was conceived and tested to reduce the frequency of discarding the spent chromated deoxidizers. The engineering techniques developed in this project involve reoxidation of trivalent chromium to the hexavalent state by electrolysis thru a diaphragm plus removal of undesirable dissolved metals by crystallization and separation. Results of the accomplished work establish that regeneration of chromated aluminum deoxidizers is feasible, practical and economical.

* Chromate recycle, *Regeneration, *Electrolytic reoxidation, *Water pollution control, *Toxic metal control, Crystallization, Drum filtration, Centrifugation, Permeable diaphragms, pH titrimetry.

*Aluminum deoxidizer reuse, *Chromated deoxidizers, *Chromium reoxidation, Chemical cleaning, Aluminum etching, Aluminum cleaning, Pre-cleaning, Acid etching, Metal cleaning, Chromium resources conservation, Regeneration of chromium solutions, Hexavalent chromium, Trivalent chromium, Dissolved metals removal, Diffusion diaphragm, Metal finishing waste treatment.

19. Security Class. (Report)

20. Security Class. (Page)

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