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REGENERATION OF CHROMATED ALUMINUM DEOXIDIZERS - Improved Diaphragm Fabrication and Performance

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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REGENERATION OF CHROMATED ALUMINUM DEOXIDIZERS

Improved Diaphragm Fabrication and Performance

By

Harry C. Hicks, Donald F. Sekits
Manufacturing Research and Development
Boeing Commercial Airplane Company
Seattle, Washington 98124

Grant No. S803064

Project Officer

Hugh B. Durham
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient control methods be used. The Industrial Environmental Research Laboratory, Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes a regeneration process which maintains continuous operation of a chemical processing solution for aluminum. Continuous regeneration minimizes chemical additions, stabilizes solution effectivity, and eliminates periodic dumping of toxic concentrated solutions. The regeneration process can be utilized by those members of the metal finishing industry who are involved in surface finishing of aluminum products. Additional information regarding this project can be obtained from the Industrial Pollution Control Division, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

"Regeneration of Chromated Aluminum Deoxidizers–Phase I," report number EPA-660/2-73-023, U.S. Government Printing Office, dated December 1973, provides the development information for the regeneration concept from theory through pilot scaleup testing. A laminated ion-selective diaphragm was developed during phase I as a necessary part of the electrolytic process. Phase II was initiated to improve the diaphragm fabrication techniques and performance.

Fabrication operations were optimized and improved diaphragms were tested in newly designed test equipment. Pilot scaleup tests were conducted to verify performance of the newer diaphragms. Fabrication improvements were made in terms of less material, lower laminating pressures, and shorter hydraulic press time. These improvements resulted in a lower cost diaphragm with increased electrical current-carrying capacity and no sacrifice in function. An alternate, newly marketed diaphragm material by E. I. DuPont called Nafion 36-3089 was also tested. In comparison to the laminated diaphragms, the service life of Nafion appears to be longer with comparable regenerating performance but with higher installation cost and some sacrifice in ruggedness.

The pilot scaleup electrolytic regeneration equipment was installed in a shop production tank and successfully operated for 4 months. The pilot operation maintained the hexavalent chromium content under widely varying workloads and at an operational cost savings.

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 resources.

This report was submitted in fulfillment of Phase II, grant number S803064-01, between the United States Environmental Protection Agency and the Boeing Commercial Airplane Company. This report covers the period November 1, 1973 to October 31, 1975.

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LIST OF ABBREVIATIONS AND SYMBOLS

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
Pg	Membrane permeability
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
$E_1, E_2 — E_x$ $I_1, I_2 — I_x$	A series of data points 1 through "x"

ACKNOWLEDGMENTS

The support of Equipment Engineering, Quality Control, Operations, and Manufacturing Research and Development of the Boeing Commercial Airplane Company is gratefully acknowledged.

John M. Watkins, Jr., Plastics Department, E. I. duPont de Nemours and Company, provided valuable technical assistance in the evaluation of membranes.

SECTION I

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 45 400 metric 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 use a large quantity of chromium, estimated at 27 200 metric tons annually. In this metal-finishing industry, chromated processing solutions are used extensively to treat aluminum surfaces prior to operations such as anodizing, conversion coatings, painting, welding, and adhesive bonding. A specific process commonly referred to as deoxidizing of aluminum (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 (by electrolytic oxidation of trivalent chromium and dissolved-metals removal by crystallization) 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 phase I of this project involve regeneration of active chromium compounds by electrolysis plus removal of undesirable dissolved metals by crystallization and separation. A deoxidizer consisting of sodium dichromate and sulfuric acid 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 facility of the project contractor are critical and precisely controlled.

Phase II of the project was undertaken to develop better fabrication techniques for the membrane used in the electrolytic section of regeneration, and to test and evaluate the improved membrane for lower cost and improved performance.

PROJECT OBJECTIVES–PHASE II

The objectives of phase II were to investigate methods of diaphragm fabrication that would reduce cost and flowtime without impairment of diaphragm function.

Other objectives were to evaluate recent commercially developed alternate membrane materials for use in this regeneration process, and subject improved and new materials to pilot testing in order to verify equal or improved performance.

An economic analysis of the improved diaphragms was also planned and presentations of the details of the project were scheduled for two EPA-sponsored national conferences.

TECHNICAL APPROACH

Efforts during the previous phase of this grant produced a diaphragm that effectively impeded migration of the dichromate ion from the anode section to the cathode chamber. At the same time, the diaphragm allowed electrical current to pass to complete the circuit for reoxidization of trivalent chromium at the anode surface. The material used for the diaphragm was 100% polyester fabric by DuPont, designated Reemay 2024. To produce a laminated structure with very low permeability, 60 layers of this material were subjected to elevated temperature and pressure. The process for fabrication was lengthy, required very high pressures (140 kg/cm^2), and occupied a hydraulic press for up to 8 hr for one 15- by 20-cm diaphragm.

Since there are other configurations of 100% polyester fabrics commercially available, the technical approach was to isolate the variables of diaphragm fabrication, establish the individual effects of these variables on fabrication performance, and establish the least costly method of fabrication consistent with suitable diaphragm performance. The acceptance criteria were permeability of the diaphragm to dichromate ion and electrical conductivity per unit area. Both woven and nonwoven polyester fabrics were scheduled for investigation for equivalent or better performance. Recently, other proprietary materials have become available. Some of these materials were obtained and tested for chemical resistance, permeability, and electrical conductivity. Finally, the most promising diaphragms were selected and pilot scaleup operations were performed to establish production suitability. The final test was a 3-month operation in a 220-liter tank, followed by a 4-month-test period in a shop production tank of 8700 liters.

SECTION II

CONCLUSIONS

Regeneration of chromated aluminum deoxidizers is feasible, practical, and economical, and results in a cost saving to the operator. The useful life of this type of deoxidizer can be extended appreciably, thereby minimizing disposal of concentrated chromium salts. From phase I of this project it has been shown that regeneration system effectiveness is more efficient in the conventional dichromate-sulfuric deoxidizer than is some proprietary solutions. From phase II, improved diaphragms for the electrolytic section of regeneration have been tested and proved satisfactory.

Suitable diaphragms for production use can be made using either 30 layers of DuPont Reemay 2024 or 10 layers of Reemay 2470, when properly laminated. Permeability of the diaphragm is satisfactory with either material when a laminating pressure of 70 kg/cm^2 is used for 30 min at 150°C followed by a rapid cooling time of 10 min to 38°C. A conditioning presoak of 3 days at 70°C in the deoxidizer is necessary to achieve long-term performance. Another DuPont product, Nafion, is a readymade perfluorosulfonic acid diaphragm material that has been tested and shows equivalent regeneration performance.

SECTION III

RECOMMENDATIONS

During phase I of this project, electrolytic regeneration of chromated aluminum deoxidizers was demonstrated to be feasible and practical for production use. It was also shown that dissolved metals which build up in the deoxidizer solution can be effectively removed by crystallization and separation. The process of regeneration was shown to be a cost-saving procedure. In phase II, improved diaphragms were developed, pilot and production tested, and proved to be satisfactory. Therefore, it is recommended that the process for regeneration of dichromate-sulfuric deoxidizers as developed in this project be encouraged for use by industrial metal finishers.

SECTION IV

TECHNICAL DISCUSSION

Phase II consisted of eight tasks as detailed in the following subsections.

TASK I–OPTIMIZE PRESS FABRICATION

Phase I performance for a Reemay 2024 diaphragm made with 60 plies laminated in a hydraulic press at 150 kg/cm^2 and held at 150°C for 4 hr was the standard for continuing work. Using these conditions, 30- and 60-ply diaphragms were fabricated and permeability and electrical resistances were measured. At the start, a test apparatus (Figure 1) was fabricated for determining permeability. Using this apparatus, it was found that more than 24 hr were required to establish permeability for each test diaphragm.

In order to shorten the laboratory test time, a greater hydraulic head was added to the permeability test apparatus. Figure 2 illustrates this first revision. In this setup, appreciable column height differences could be maintained. This difference in hydrostatic head did not appreciably change the test time for permeability. Therefore, electrodes were installed in each chamber to add electro-osmotic pressure. This step reduced individual diaphragm test time to 4 hr. The final test apparatus configuration is illustrated in Figure 3.

Diaphragms were made using Reemay 2024 (15, 30, and 60 plies) and varying pressure, time under pressure, and pressing temperature. Pressures used were 35, 70, 105, 120, and 140 kg/cm^2. Test times under pressure were selected at ¼, 1, 2, 3, and 4 hr. Pressing temperatures were 93°C, 149°C, and 177°C. The resultant diaphragms were tested for permeability and electrical resistance (task III). The data are summarized in (Table 1).

TABLE 1. DIAPHRAGM PREMEABILITY AND RESISTANCE TEST DATA

Plies	Fabrication pressure, kg/cm^2	Press time, hr	Press temp, °C	Pg, $(mg/cm^2 \cdot hr) \times 10^{-4}$	Rm, $ohms/cm^2$
60	35, 70, 105, 120, 140	4	149	0 to 0.06	0.018 to 0
60	70	1/4, 1, 2, 3, 4	149	0.75 to 8.7	0.028 to 0.029
30	35, 70, 105, 120, 140	1, 4	149, 177	0.4 to 55.7	0.027 to 0
15	70	1	149	10.4	(Pg too high)

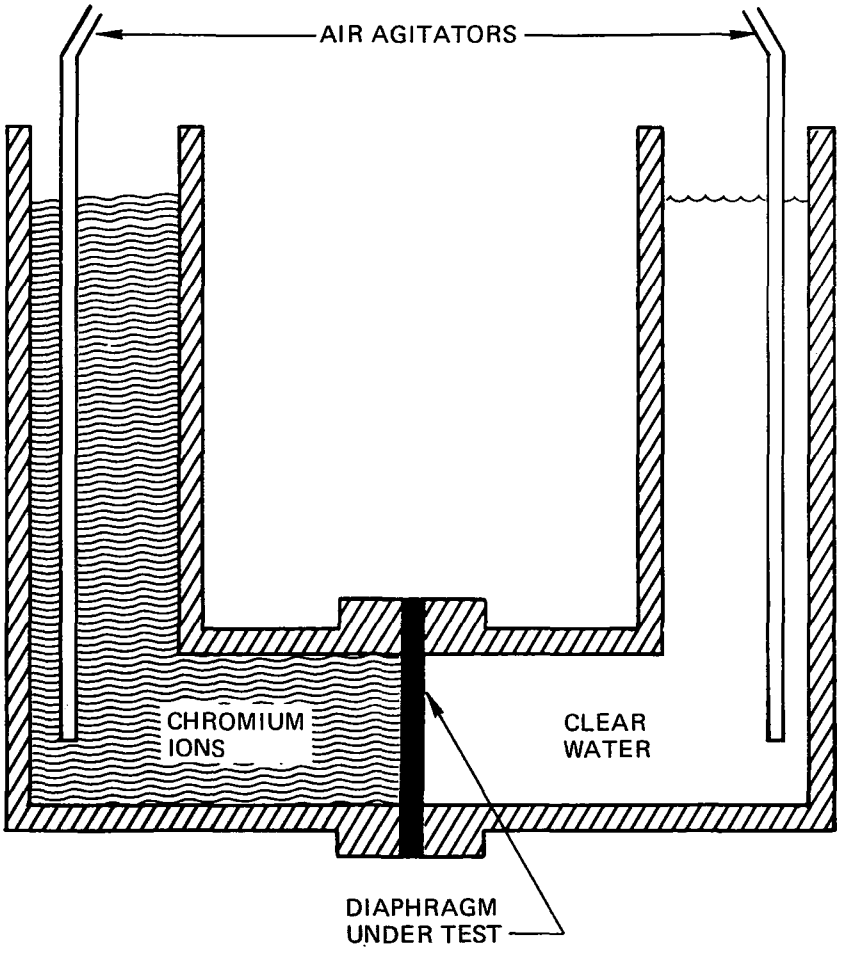

Figure 1. Diaphragm permeability test apparatus

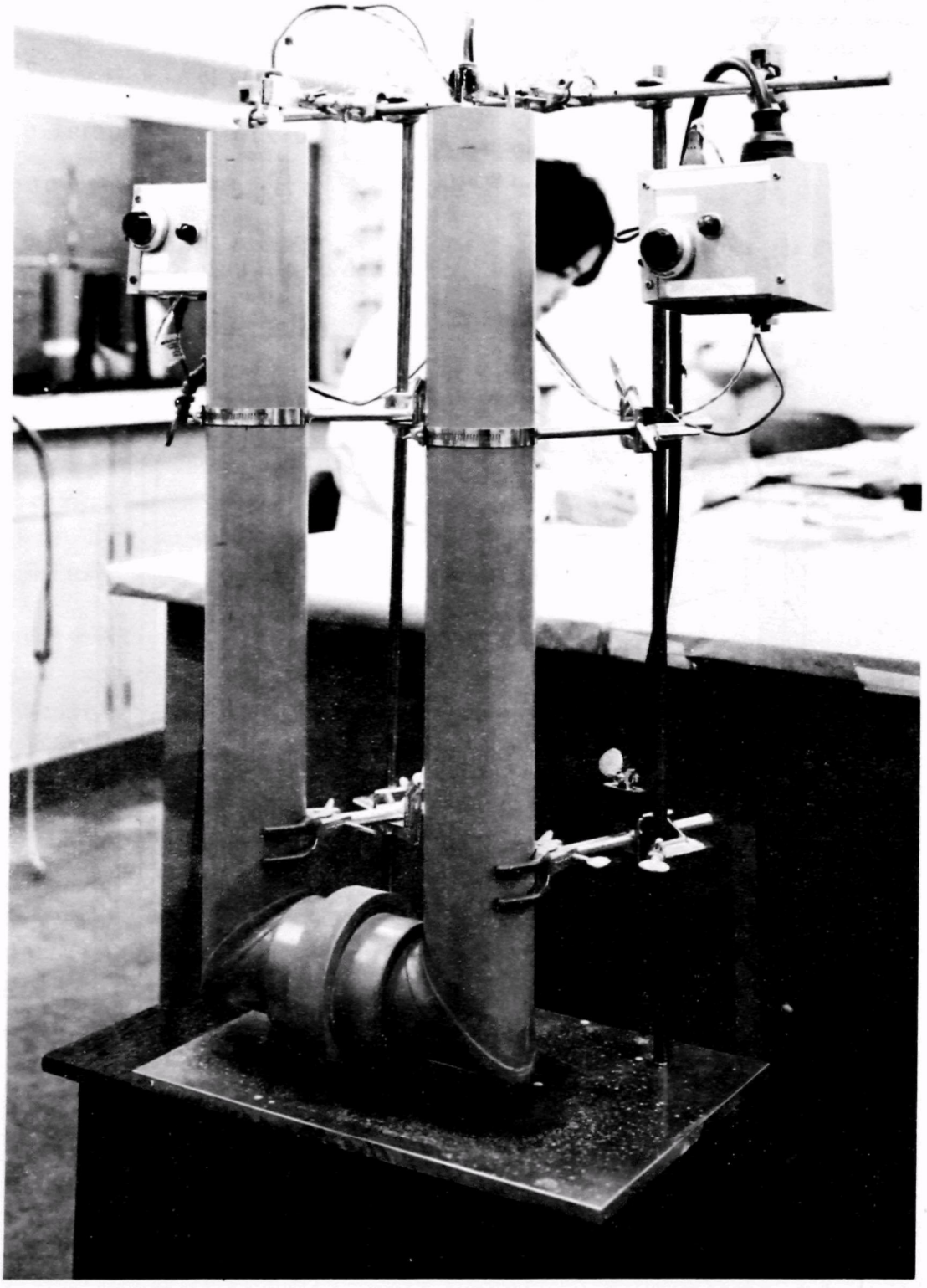

Figure 2. Diaphragm permeability test apparatus

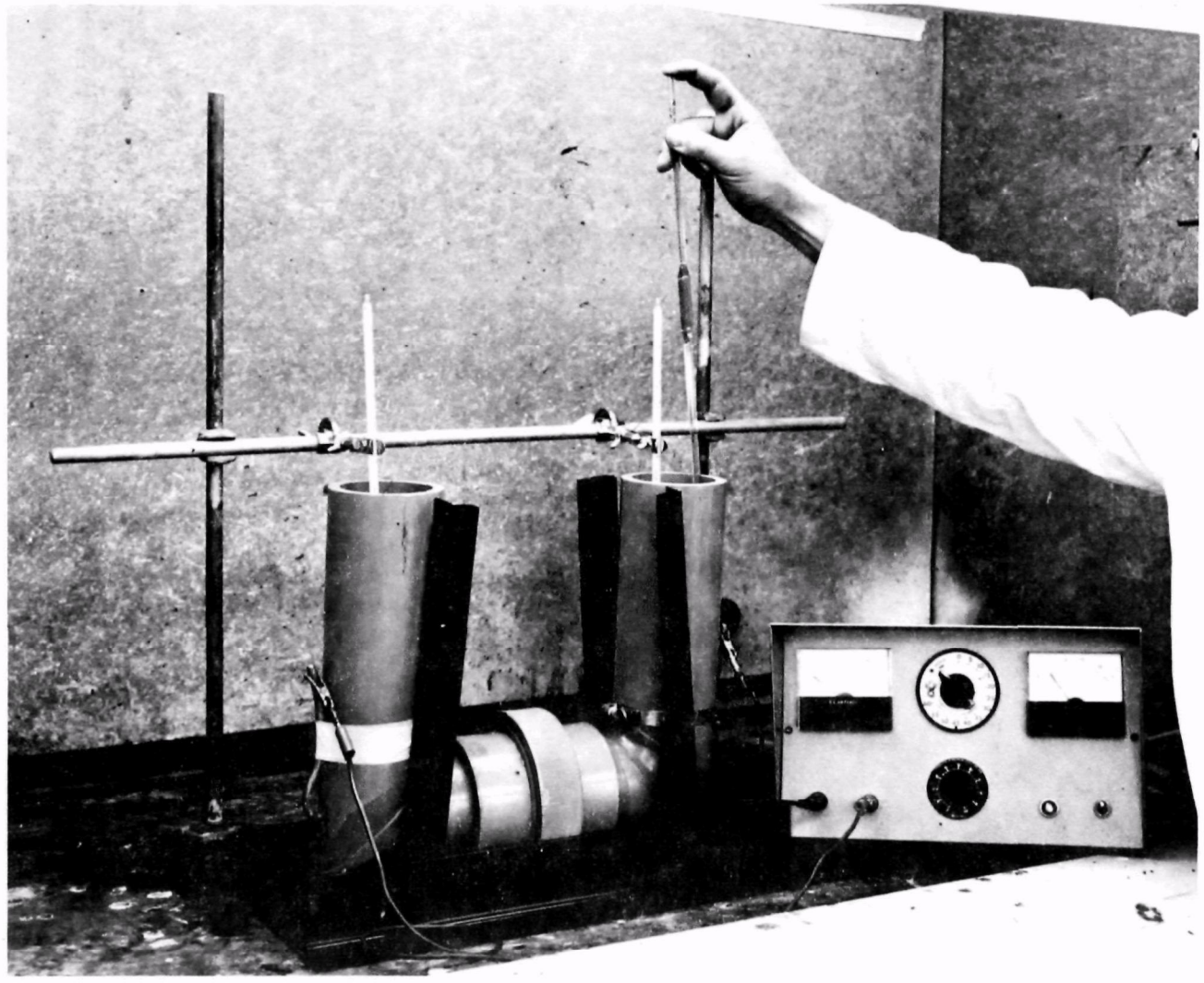

Figure 3. Diaphragm permeability and electrical test apparatus

At this stage it was also determined that a minimum soak condition of 72 hr at 70°C was necessary to stabilize the functional performance of the diaphragms. From these data, minimum diaphragm fabrication conditions are established as:

Laminating layers	30
Pressure	70 kg/cm^2
Time at pressure	1 hr
Press temperature	149°C

These conditions are considerable improvements over the phase I fabrication requirements of 60 layers, 140 kg/cm^2, and 4 hr at pressure. In addition, it was found that a rapid cooling of the press platens was beneficial to diaphragm reproducibility and visual appearance, as well as reducing the overall fabrication time. A cooling rate of 10 min from 149°C to 38°C was established for all diaphragms.

TASK II—ALTERNATE POLYESTER MATERIAL

The minimum diaphragm fabrication conditions were used to evaluate Reemay 2470, 2421, and 2408, which are crimped, nonwoven fabrics, and Reemay 2011 and 2033, which are straight-fibered fabrics similar to 2024. Six woven-polyester fabrics were also used to fabricate diaphragms under the same operating conditions. Reemay 2470 was found to be approximately equivalent to 2024 in performance, and was therefore selected for further testing. None of the woven fabrics was found to be suitable; all required much higher pressures (and thus a higher cost) to achieve adequate adhesion between layers, one material having melted at the normal press temperature. Table 2 provides a summary of the test data.

TASK III—ELECTRICAL EVALUATION

The same U-tube test apparatus that was used for permeability determinations was used for the first part of the electrical evaluation. Under stabilized conditions, amperage readings were taken at predetermined voltage settings. The resistances of the individual diaphragms were isolated and calculated algebraically:

$$R_m = \frac{\frac{E_2 - E_1}{I_2 - I_1} + \text{—} + \frac{E_x - E_{x-1}}{I_x - I_{x-1}}}{X}$$

TABLE 2. POLYESTER MATERIAL TEST DATA

	Material	Pg, $(mg/cm^2 \cdot hr) \times 10^{-4}$	Rm, ohm/cm^2	Remarks
D	2470	0 to 0.65	0.023 to 0.040	OK
U	2421	1.1	0.025	OK
P	2408	0	——	Low amperage Resistance too high
O	2024	0 to 1.5	0.018 to 0.029	OK
N	2011	∞	———	Permeability too high
T	2033	21.8	———	Permeability too high
A	HG6E2D	0	0.59	Resistance too high
M	X4M7	2.2	0.03	High permeability
E	H4E6	15.7	——	High permeability
T	Z0M2	———	——	Delaminated
E	H2E0	———	——	Delaminated
K	XBHV4K2	———	——	Melted in press

Table 2 includes the diaphragm electrical resistances as determined in the equation. It should be mentioned that in many cases involving alternate materials, poor diaphragm performance such as no passage of current (infinite resistance), diaphragm delamination, or unacceptable permeability negated the need for electrical evaluation.

From examination of diaphragm breakdowns in phase I, it was surmised that electrical overloading contributed to early failures; therefore, the second part of task III consisted of determining the current-carrying capacities of the best candidate materials. The procedure involved subjecting a small, precise circle (1.27-cm diameter) of the test diaphragm to a programmed potential from 0 to 20 V over a period of 30 minutes and recording the resultant amperage. The laboratory potentiostat with its programming controller and sensing probe accessories was used (figure 4). When each diaphragm was tested in this manner, in all cases a break occurred in the current buildup prior to reaching maximum voltage. The recorded curves were reproducible and nearly the same for each material. The current-recorded area beyond the breakdown point is of added interest, and could be interpreted as being an

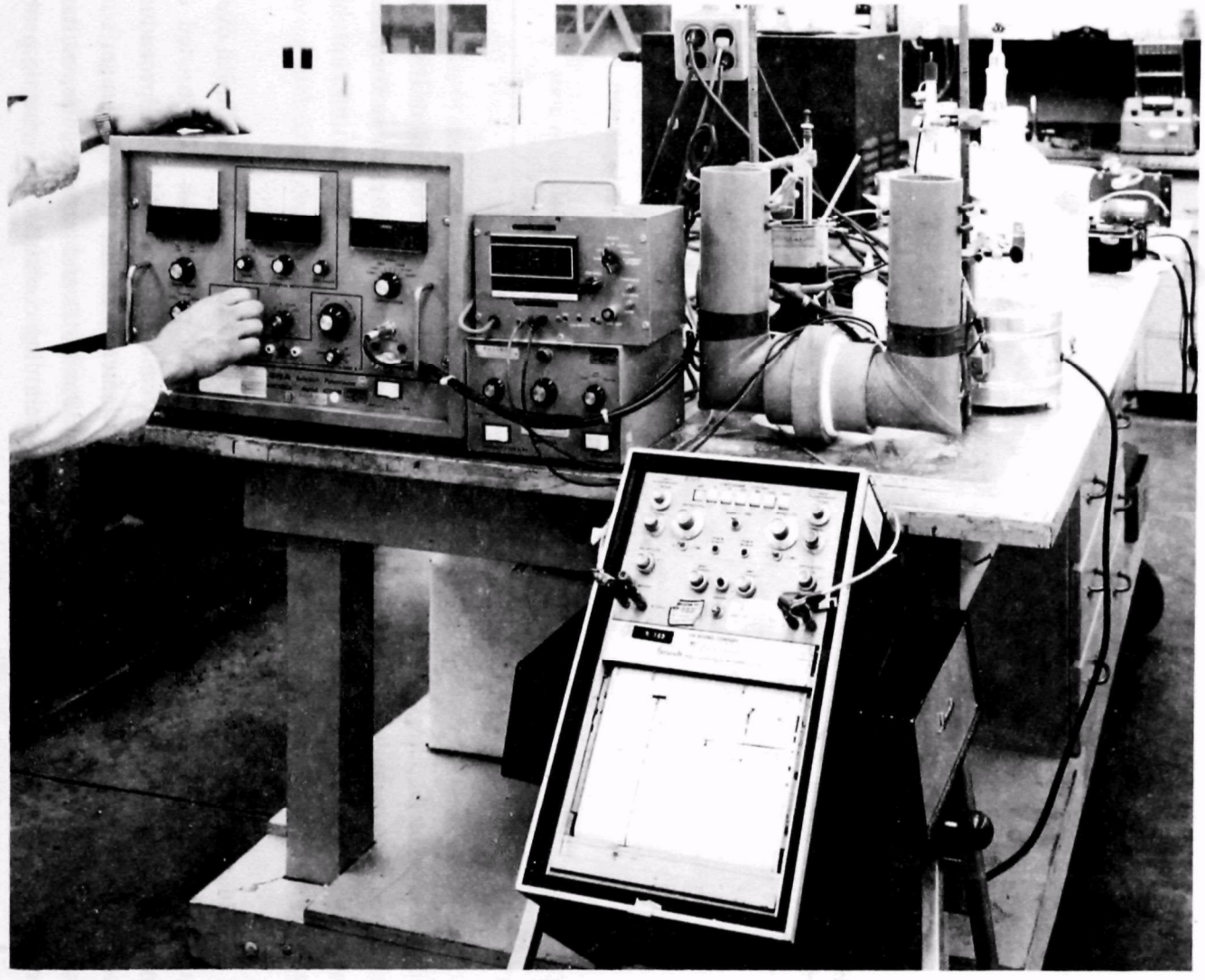

Figure 4. Potentiostat test setup for electrical evaluation of diaphragms

indication of a diffusion controlled, electrical conductivity process in a restricted opening. Posttest examination revealed a physical deterioration in each diaphragm. Figure 5 provides the recorder tracings for three diaphragm materials. Since several of the tasks in this phase were run concurrently, this figure also illustrates the current-voltage breakdown curve for Nafion, one of the materials tested in task V. From this information, a maximum of 16 amp/dm^2 was established for the durability test in task VI.

TASK IV–CALENDERING EVALUATION

Since production of the diaphragms at the present state of the art includes the use of a heated-platen hydraulic press, it is logical, in an improvement program, to inquire into alternate lower cost methods of achieving the necessary laminating pressures and temperatures. Calendering, a procedure used for hot-roll pressing of fabrics and paper, was investigated as a substitute for diaphragm fabrication. Stacks of 30 layers of Reemay 2024 were passed through heated rolls under various pressures and temperatures. Rolling speed was established at 175 rpm for a 10.2-cm-diameter roll by preliminary test runs. The fabric was passed through the rolls by themselves and also when contained between two layers of aluminum sheet stock. The thickness of the aluminum was also varied to some extent. A final diaphragm thickness of 0.215 to 0.254 cm was the objective.

In most cases, visual examination of the resultant diaphragm was sufficient cause for rejection. The diaphragms frequently were warped, smeared, and/or delaminated in the as-produced condition. A few appeared to have some of the necessary requirements of a diaphragm and subsequently were tested for permeability. None of the diaphragms passed acceptance testing; consequently, the calendering process was abandoned.

Table 3 summarizes the efforts.

TABLE 3. CALENDERED DIAPHRAGM EVALUATION

(30 Layers Reemay 2024, Roller Speed – 175 rpm)

Preheat, °C	Backing plates	Roller heat	Roller gap, cm	Diaphragm thickness, cm	Pg, (mg/cm^2. hr) x 10^{-4}	Rm, ohm/cm^2	Remarks
171	Yes	None	0.03 to 1.7	0.27 to 0.78	46.6	Not tested	Warped and too thick
None to 171	Yes	71	0.67 to 1.13	0.21 to 0.60	1.9	0.02	Warped and too thick
204	No	60	0.51 to 1.4	0.47 to 0.60	10.8	Not tested	Too thick
204	Yes	60	1.25	0.23	6.5	Not tested	Warped

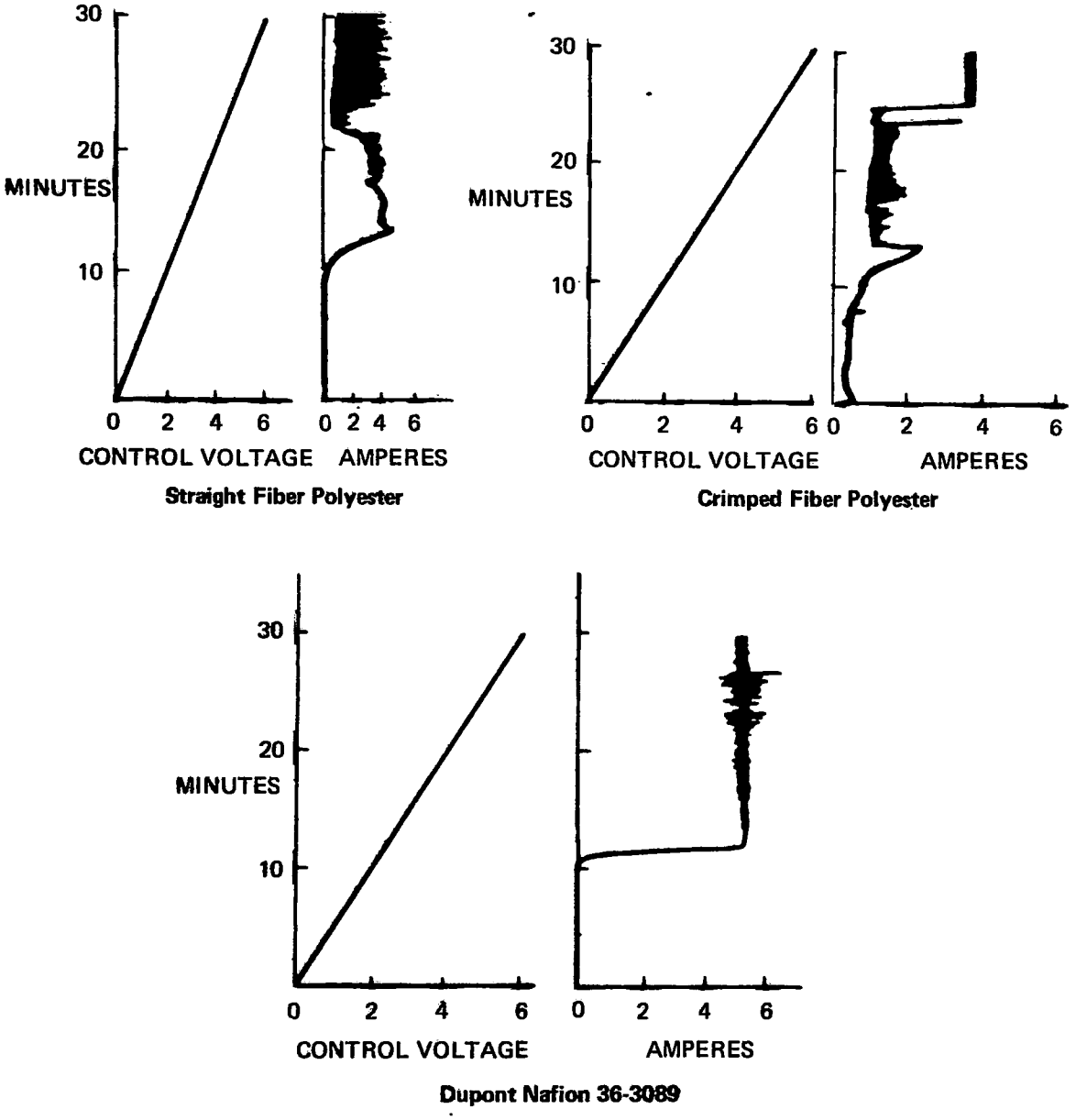

Figure 5. Electrical test data for current-carrying capacities of diaphragms

TASK V—NEW PRODUCT EVALUATION

A search of recent market developments in membranes revealed two potential candidates as alternates for the diaphragm developed during this grant. Past investigations of available diaphragms produced no material that would withstand the strong oxidizing environment of a hot deoxidizer. However, recently there has become available from several sources a Teflon semipermeable membrane and also a proprietary organic film called Nafion, marketed by DuPont. The Teflon semipermeable membrane was acquired from Southwestern Analytical Chemicals, Incorporated. The DuPont Company provided a quantity of two types of Nafion membrane.

The Teflon membrane provided low permeability, but no appreciable electrical current could be forced through. The material was rejected as unsatisfactory for this reason. Both types of Nafion membrane material provided encouraging results. Consequently, Nafion 36-3089 was selected for pilot scaleup evaluation.

Table 4 provides U-tube test results from the new product evaluation effort.

TABLE 4. NEW PRODUCT MEMBRANES TEST DATA

Material name	Material number	Volts	Watts	Pg, $mg/cm^2 \cdot hr \times 10^{-4}$	Rm, ohm/cm^2
Teflon	236	10.0	0	0.44	∞
Nafion	XR-480	7.2	31.7	0.33	0.020
Nafion	36-3089	7.0	34.3	0.29	0.017

TASK VI—PILOT VERIFICATION

Three diaphragm materials were selected for pilot scaleup durability testing. These were Reemay 2024, Reemay 2470, and Nafion 36-3089. A three-section cathode chamber was fabricated as illustrated in figure 6. Because of the improvements in diaphragm fabrication techniques resulting from work in phase II, it was possible to produce larger sized diaphragms with the available press capability. After each larger sized diaphragm was fabricated, permeability was measured in at least three different areas. It was found that permeability varied widely between the areas, and permeability was roughly proportional to thickness. Therefore, the press platens were examined for flatness. Such a wide variation

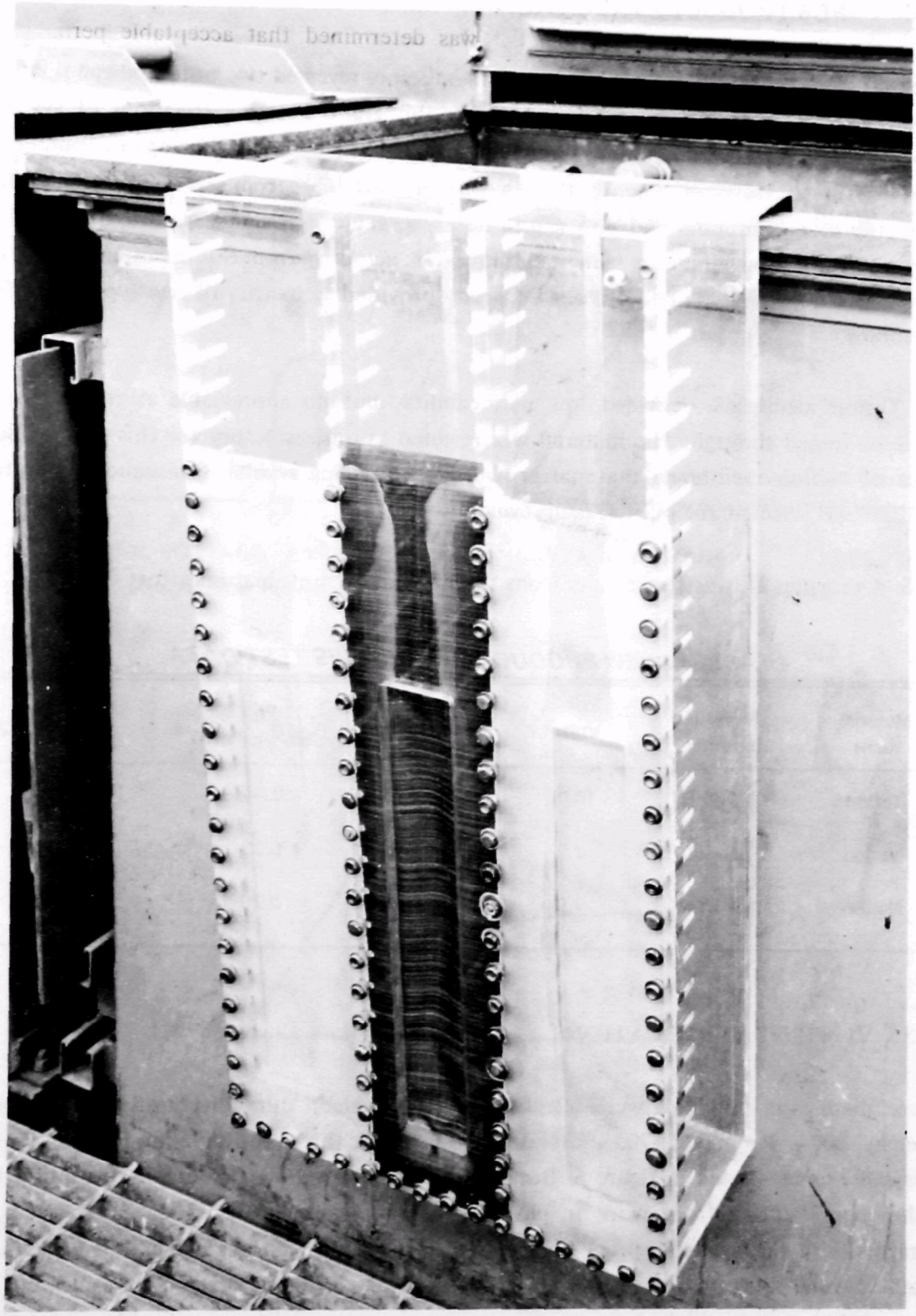

Figure 6. Three-section cathode chamber for 220-liter pilot tank

in platen gap was found that the platens were removed from the press and reground. Additional diaphragms were made and it was determined that acceptable permeability could be obtained when diaphragms were fabricated in areas where the platen gap did not vary greater than 0.25 mm.

Acceptable large diaphragms, each with an exposed area of 2.34 dm^2, were installed in the three-section cathode chamber and the chamber was placed in a 220-liter pilot tank containing a dichromate-sulfuric deoxidizer at 63°C. An electrical load of 13 A/dm^2 was imposed on each diaphragm. Periodic analyses for chromium migration into the cathode chamber were made. The complete pilot installation is shown in figure 7.

The 220-liter pilot tank was operated continuously for 2 months without shutdown except for periodic examination of components. The collected data verify that dichromate migration into the cathode chamber was effectively prevented, that electrical conductivity was high, and that the improved Reemay diaphragms, as well as the Nafion material, resisted the corrosive environment. Resistance measurements were made in the pilot tank and the results are shown in table 5.

TABLE 5. MATERIAL RESISTANCE MEASUREMENTS IN PILOT TANK

Material	Electrical resistance, ohm/cm^2
Reemay 2024	0.0207
Reemay 2470	0.0215
Nafion	0.0186

After an additional month of pilot operations, results were sufficiently encouraging to warrant a longer term of exposure. A shop production tank containing 8700 liters of the dichromate-sulfuric deoxidizer was selected for further exposure tests. This solution was new in April 1974. At the time of installation of the regeneration equipment, dissolved aluminum content had risen to 13 800 ppm. Since this aluminum content is well below the concentration at which crystallization becomes feasible, no metals separation equipment was installed.

Using the data from phase I of this project, it was calculated that 111 amperes of direct current (16 A/dm^2) would be adequate to maintain a constant hexavalent chromium level and offset the reduction of chromium caused by the average workload. An existing constant-

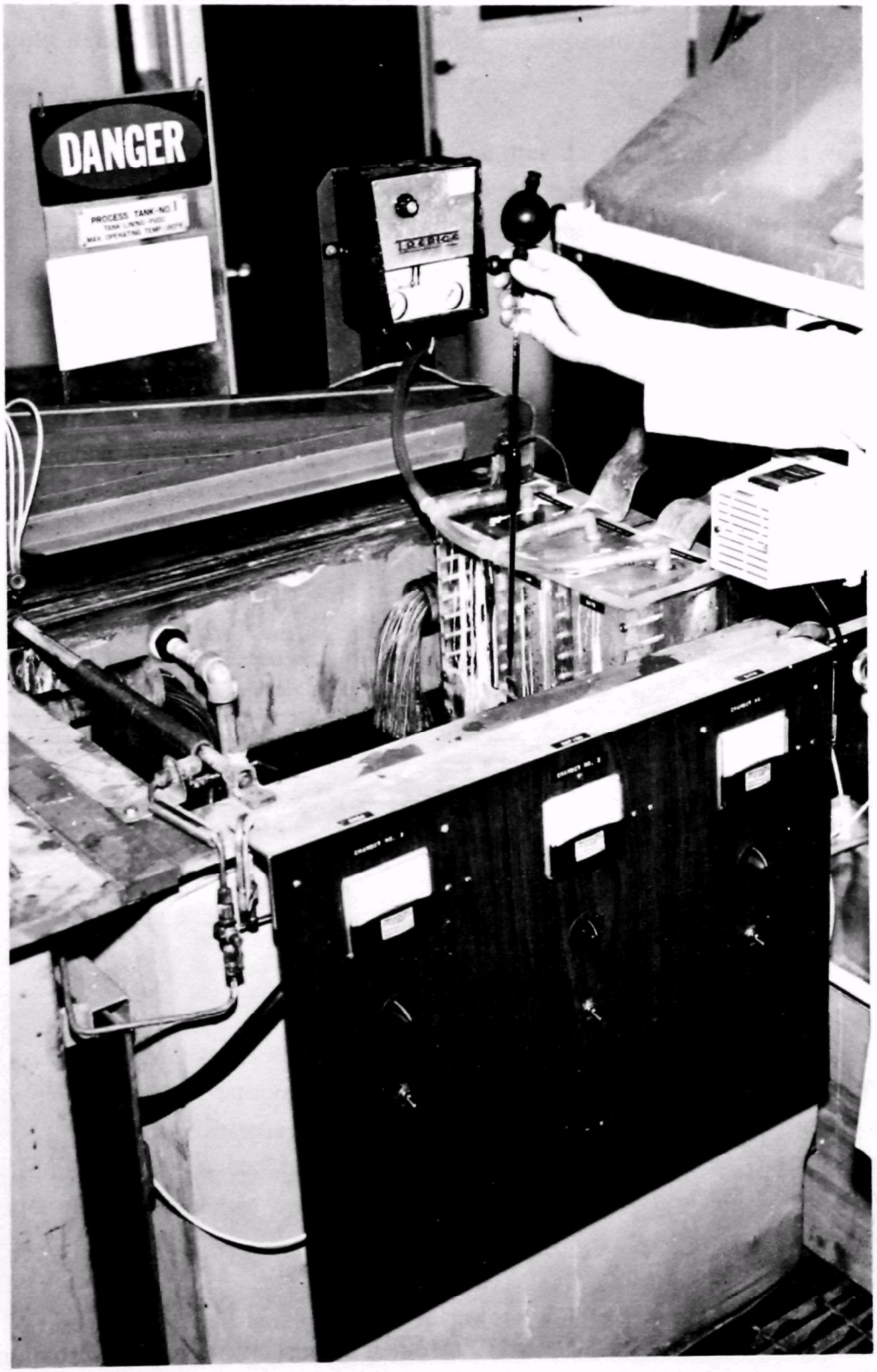

Figure 7. Pilot tank for testing regeneration diaphragms

voltage-controlled dc power supply was used. From this basic starting point, it was determined that the pilot tank cathode chamber could be used with the existing diaphragm sizes. A maximum cathode area of 1160 cm^2 was used. A sheet lead (Pb) anode area of 5750 cm^2 was selected. The anode was suspended at one end of the tank and the cathode chamber was placed at the other end, approximately 6.7 meters away. Instrumentation not normal to a production installation was added for monitoring during this test period. A two-channel recorder monitored voltage and amperage at the dc power supply. A digital ampere-hour meter registered energy consumption for data reduction. Figures 8, 9, and 10 illustrate the shop installation.

Since it had been observed previously that water was lost from the cathode chamber during elevated temperature operations, a metering pump with a 227-liter water reservoir was also installed to maintain liquid level at the cathode.

The sulfate ion was driven through the diaphragm as well as the hydroxyl ion by the electro-osmotic pressure. Therefore, daily additions of sulfuric acid were made as required by chemical analyses.

After 2 months of operation, the data verified that all operating parameters had been stable and predictable for this installation. The water was replaced with a 10% sulfuric acid solution, which was metered into the cathode chamber. This improvement eliminated the daily manual additions of acid.

A comparison of analytical records for the deoxidizer solution illustrates the advantage of the electrolytic regeneration process. Prior to installation, this 8700-liter solution consumed an average of 68 kg of sodium dichromate per month. During the test run of 4 months, no additions of sodium dichromate were made. The analysis for hexavalent chromium remained constant. The amount of sulfuric acid consumed was stoichiometrically equivalent to the amount of aluminum metal dissolved. The aluminum content rose from 13 800 ppm in late February to 16 700 ppm at the end of May. Figure 11 summarizes the regeneration performance.

The diaphragms were examined at the time the sulfuric acid metering was initiated. It was found that both the Reemay 2024 and 2470 were deteriorated to the extent that replacement was required. Two new Reemay 2024 diaphragms were installed. The Nafion diaphragm was left in place. Thus, the Reemay material endured 6 months of regeneration at 13 to 16 A/dm^2. This compares to approximately twice the current-carrying capacity of the original diaphragms for the same service life.

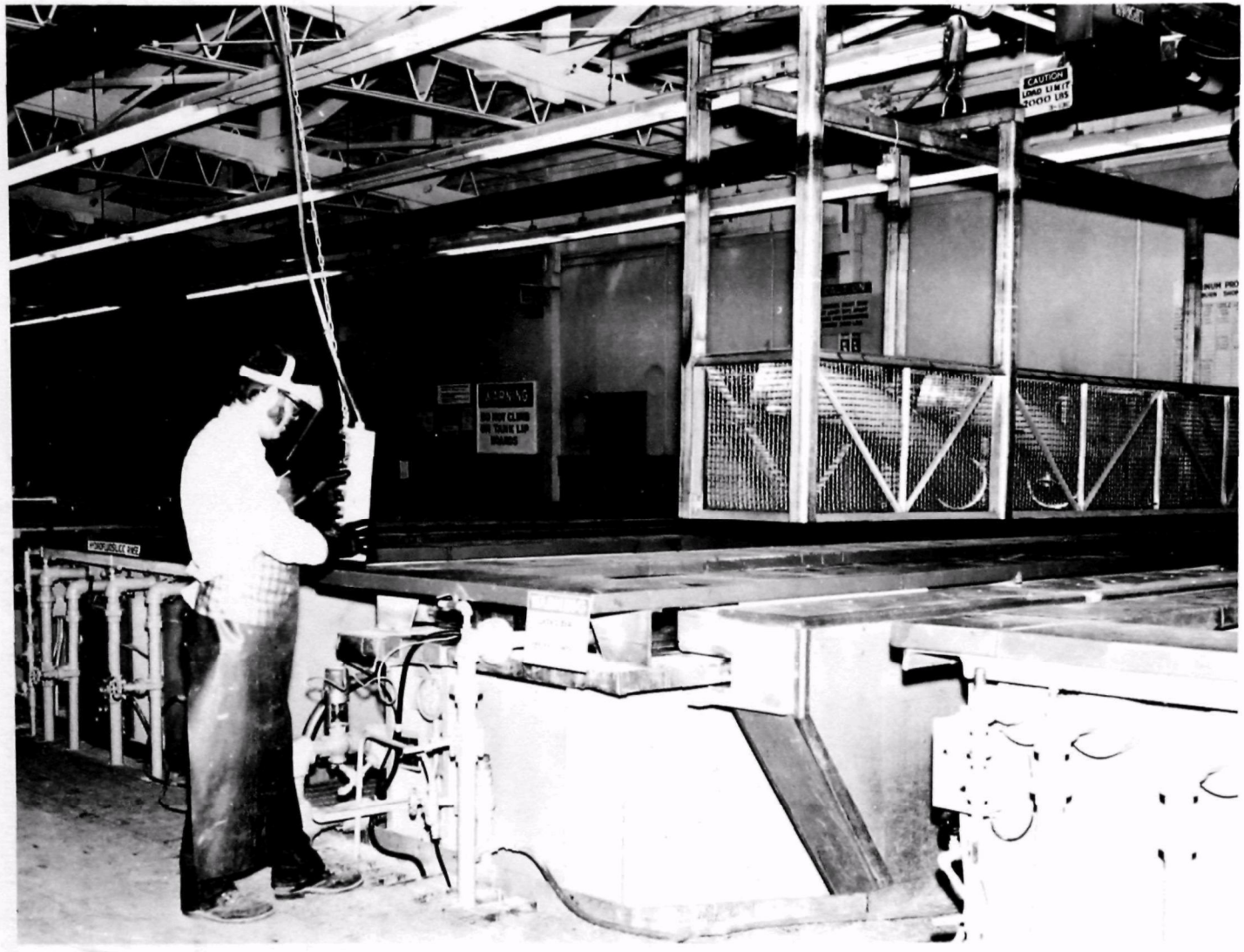

Figure 8. 8700-liter deoxidizer tank with regeneration equipment installed

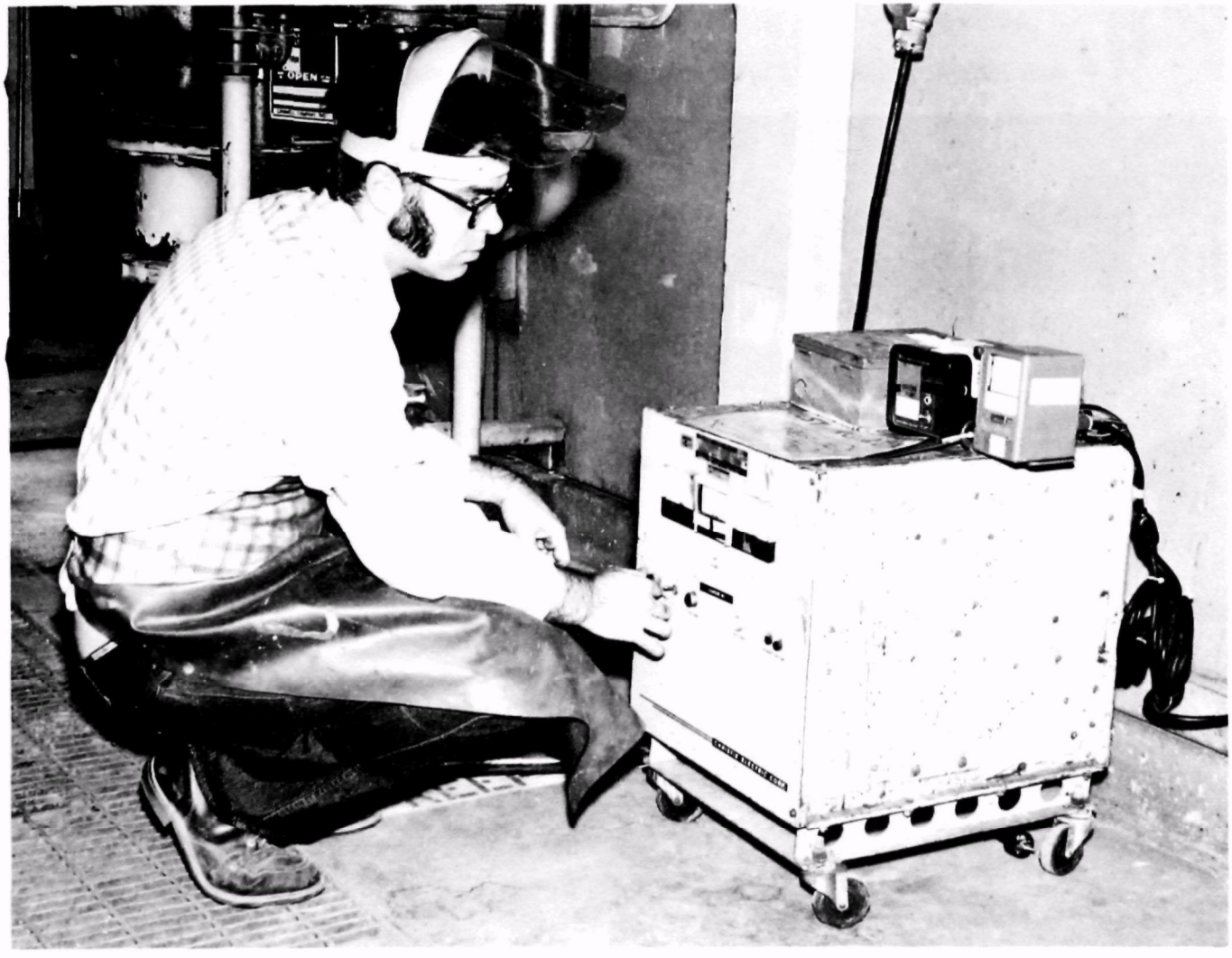

Figure 9. D.C. power supply and recording instrumentation used with 8700-liter deoxidizer

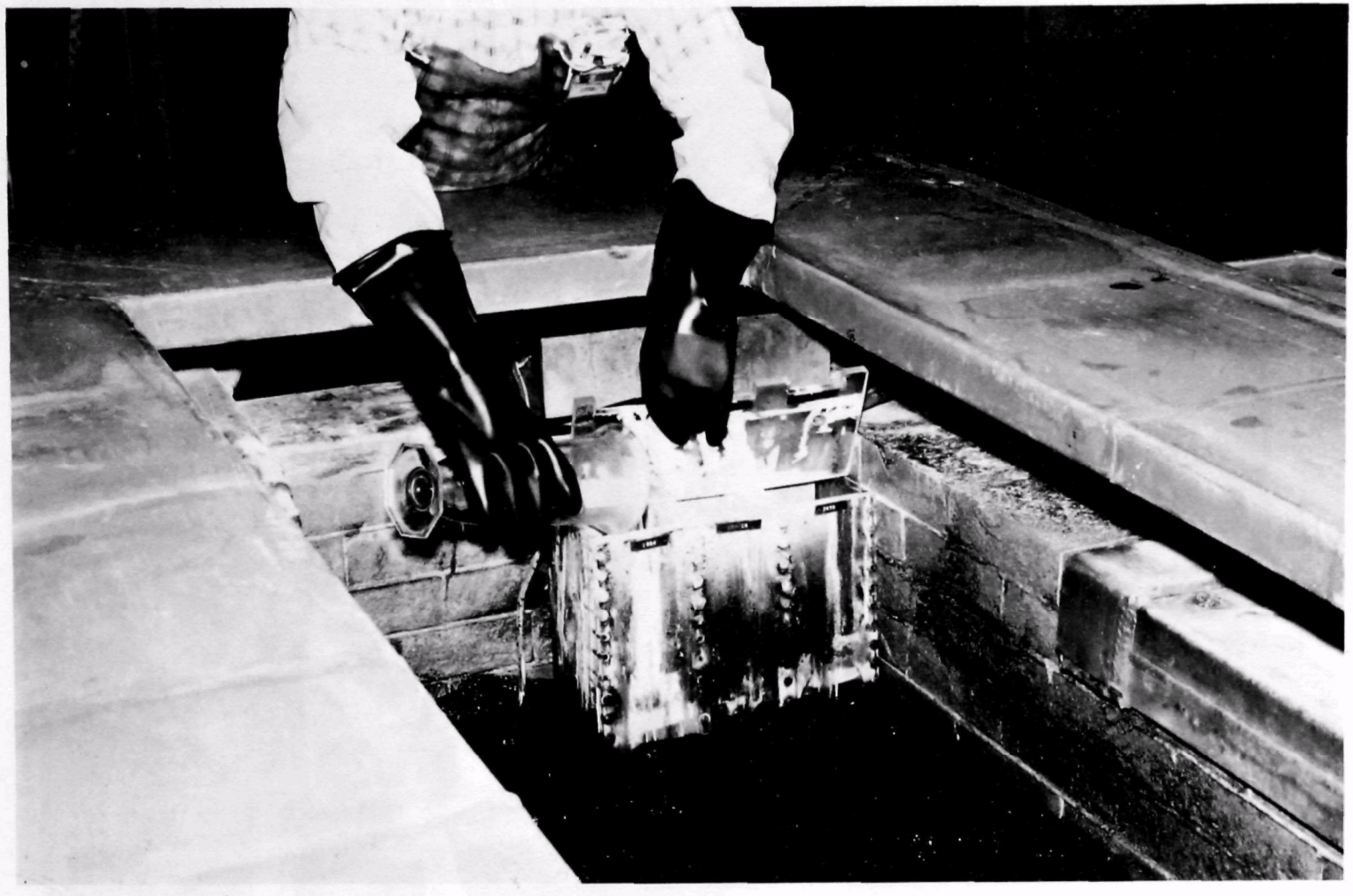

Figure 10. Regeneration cathode chamber in 8700-liter deoxidizer tank

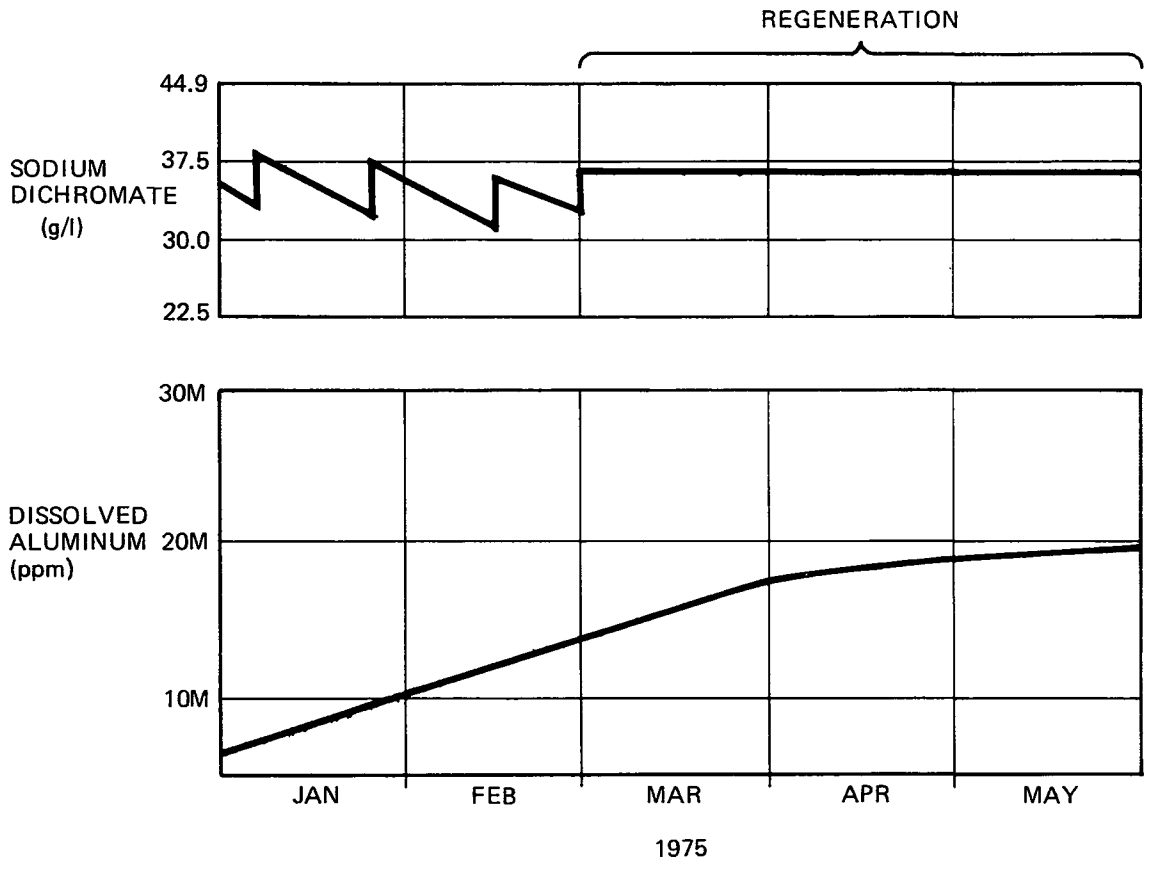

Figure 11. Regeneration performance in 8700-liter deoxidizer

Summarizing, two diaphragm materials—100% polyester resin-laminated fabric and a perfluorosulfonic acid membrane—have been identified as providing suitable electrical conductance and ionic separation for successful reoxidization of trivalent chromium.

- The polyester diaphragm utilizes low-cost material, is physically strong and rigid, and requires only simple clamping in order to seal it effectively in a cathode chamber. Its disadvantage is that it requires an elevated temperature and high pressure to achieve satisfactory lamination.

- The perfluorosulfonic acid diaphragm is ready to install as received and may have a longer service life. Its disadvantage is that it is slightly more costly, is very flexible, and requires more critical cathode chamber design for support and sealing.

TASK VII—PRESENTATIONS

Details of the regeneration project were summarized in presentations at the National Conference on Management and Disposal of Residues from the Treatment of Industrial Wastewaters sponsored by Information Transfer Inc., 6110 Executive Blvd, Rockville, Md 20852 in association with The Office of Research and Development, U.S. Environmental Protection Agency; American Institute of Chemical Engineers, and Manufacturing Chemists Association. A second presentation was made at the Second National Conference on Complete WateReuse sponsored by American Institute of Chemical Engineers and Environmental Protection Agency Technology Transfer.

TASK VIII—ECONOMIC ANALYSIS

Previously, a 15- by 20-cm, 60-ply, Reemay 2024 diaphragm was estimated to cost $30. This amounts to $10/dm^2. This charge includes labor, material, and equipment amortization. As a result of improving the diaphragm press time, material and labor have been reduced so that the polyester diaphragm cost is now $3.16/dm^2. Nafion diaphragm cost is nearly the same at about $3.25/dm^2.

Cost data have been updated from the phase I report to reflect the economics of an electrolytic regeneration in a 8700-liter deoxidizer tank (see table 6).

TABLE 6. ECONOMICS OF ELECTROLYTIC REGENERATION INSTALLATION

Cost item	Baseline period, 2nd quarter 1975
Equipment amortization	10 yr
Electrical cost	$\$1.52/10^9$ Joules
Water cost (purchase)	$\$3.53/m^3$
$Na_2Cr_2O_7 \cdot 2H_2O$ (tech grade)	$31.00 per cwt
Deoxidizer disposal	3.17¢/ℓ
150 A, 15 Vdc power supply	$650
Regeneration accessories (cathode chamber, electronics, diaphragms, metering pump)	$1057
Regeneration installation	$655

Effect on Waste Volume and Characteristics

Implementation of this regeneration process will reduce the sporadicity of plant waste effluent 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, 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 8700-liter deoxidizer tank that has been monitored for several years.

Capital equipment for electrolytic regeneration in this tank consists of one dc power supply at a cost of $650, a cathode chamber plus electrodes at $686, and a metering system at $371. The total capital cost is $1707.

Maintenance

Maintenance costs for the types of equipment described in this report are generally low compared with those for other chemical processing facilities. The diaphragm cost as fabricated in this report has been reduced, while labor rates have risen since the previous report. Yearly maintenance cost for the 8700-liter regeneration equipment is now estimated at $214.

Operating Costs, Regeneration Versus Nonregeneration

8700-Liter Deoxidizer—During regeneration, electrical cost for the rectifier and metering pump is $7.12 per month, equipment amortization is $19.68 per month, and maintenance is $17.83 per month. The total regeneration operating cost is $44.63 per month. This figure is contrasted to nonregenerated deoxidizer costs of $46.50 per month for addition of chemicals, $39.20 per month for prorated dumping charge, and $31.00 per month for prorated new solution chemicals. The total nonregeneration cost is $116.70 per month.

SECTION V

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16. ABSTRACT

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 hexavelent 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.

In the second phase of this project diaphragm fabrication techniques were refined to produce an improved diaphragm in terms of cost and performance. In addition, electrolytic regeneration equipment installed in a large production tank for six months exceeded technical and economic objectives.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Regeneration, Water Pollution, Centrifuge, Crystallization, Drum Filters, Chemical cleaning, Metal cleaning	Chromate recycle, Toxic metal control, Electrolytic reoxidation, pH titrimetry, Permeable diaphragm, Aluminum deoxidizer reuse, Chromated deoxidizer	13B

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