RECOVERY OF CHROMIUM FOR WASTE STREAMS

Field Evaluation of Carbon Adsorption/Electrowinning for Recovery of Chromium

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ABSTRACT

This report discusses the evaluation of a new, patent-pending process for recovering chromium at a hard chrome plating facility. This process involves adsorption of chromium in the waste stream on granular activated carbon followed by recovery of the chromium from an acid regenerant solution by a novel electrowinning step. Test results showed that the process is capable of producing an EPA acceptable effluent from waste streams averaging 500 mg/l hexavalent chromium. The pilot test was conducted at Jersey Chrome Plating in Pittsburgh, PA, in the fall of 1989.

ACKNOWLEDGMENTS

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INTRODUCTION

Environmental regulatory pressures have brought to the forefront the serious problem of hazardous waste generation and disposal. For example, commercial landfill volumes in 1986 totaled 3.5-4.0 million t/y. Roughly 25% of all the materials disposed of in such commercial hazardous waste landfills in 1986 will ultimately be banned from landfills in the future. This will result in approximately 825,000 - 1,000,000 t/y of new hazardous waste demand on alternative disposal or recovery methods (1). These stringent EPA regulations affect the entire industrial community and especially those involved with metal plating or metal finishing. Specifically, chromium which is on EPA's hazardous materials list is one of the more costly metals to treat and dispose of properly. It is listed with the "EPA-Primary Drinking Water Standards" with acceptable discharge limits set at 0.05 mg/l for hexavalent chromium and 1.7 mg/l for total chromium for drinking waters. Such limits reflect EPA health based concerns regarding human toxicity of consumed chromium. Consequently, chromium related industries such as hard chrome plating and tin mill processing are especially hard pressed to find economical solutions to waste treatment and sludge disposal problems. These industries are seeking a strategy to comply with regulatory guidelines and at the same time effectively reduce the cost of the associated waste treatment.

In response to this need, Lewis Engineering Services, a service company, has developed the novel, integrated ENVIRO-CLEAN PROCESS for the reclamation of metals such as chromium from process and waste water streams.

The ENVIRO-CLEAN PROCESS consists of two steps: First the heavy metal influent solution is processed through a granular activated carbon system which removes the heavy metals and produces an EPA acceptable effluent. The second step recovers the metals from the carbon system using an electrolytic technique. This patent-pending process produces an EPA-acceptable effluent, recovers the heavy metal, and generates no sludge! Through the assistance of a Ben Franklin Challenge Grant, the process was tested in the laboratory for over a year. On the basis of the favorable results obtained, a decision to proceed with the further development of the process was made. The purpose of this new program was to evaluate the process on a larger scale in an industrial setting.

Funding and support for the additional work was provided by:

1. Ben Franklin Technology Center of Western Pennsylvania
2. Calgon Carbon
3. EPRI Center for Materials Production
4. Elkem Metals
5. Lewis Engineering Services

In addition, Jersey Chrome Plating in Lawrenceville, Pa., offered their facilities as a site for this program.

Section 2

BACKGROUND

Present state-of-the-art technology for chromium "clean-up" involves pH adjustment of the waste stream to about 4.5, followed by chemical reduction of hexavalent chromium to trivalent chromium using sulfur dioxide or sodium meta-bisulfite. The trivalent chromium is precipitated using lime and/or sodium hydroxide into a sludge for land disposal at a superfund site. However, with the imposition of RCRA regulations, chromium-based sludges are considered toxic, and land disposal practices are becoming prohibitively expensive to the industrial client (2).

A number of recovery processes are being marketed to address chromium recovery options. The three leading processes are (1) evaporation, (2) ion exchange, and (3)reverse osmosis. Each process has disadvantages which have hindered its commercial development. A brief discussion of these options and their disadvantages follows.

> EVAPORATION - Recovery is accomplished by boiling off sufficient water from the collected rinse stream to concentrate the stream for return to the operation. This is a very energy-intensive process, and its cost effectiveness is questionable. The cost of evaporator equipment is high and maintenance is required. Also impurity buildup is a major problem, and additional unit processes such as ion exchange or activated carbon may be required to remove other impurities.
>
> ION EXCHANGE - A major drawback of ion exchange is that when the resin is exhausted, its reprocessing generates significant volumes of waste solution which adds to the overall waste treatment loading and complicates the operation of the waste treatment system. Also resin life is very sensitive to high metal concentrations and impurity fouling. Ion exchange resins are limited in their ability to recover a wide range of metal species and normally require two separate units - one for cations and one for anions. Each system would have its own regenerating solutions with resulting waste streams.
>
> REVERSE OSMOSIS - The major limitation of commercial reverse osmosis systems is the inability to maintain membrane performance. Fouling and gradual deterioration of membranes can reduce the processing capacity of the unit and require frequent membrane replacements. The recovery solutions must be in a restrictive pH range to ensure reasonable membrane life. Moreover, these membranes are not suitable for treating

solutions having high oxidation potentials, or for concentrating dilute solutions.

The process was developed as an alternate recovery technique which overcomes the disadvantages of the present processes. It involves the adsorption and concentration of chromium onto a bed of granular activated carbon followed by recovery of the chromium from the subsequent regenerant with an electrolytic metal recovery (EMR) process which produces a chromium oxide product. This process produces an EPA-quality effluent, no hazardous waste is generated, and a salable by-product is recovered.

How the Process Works

In the process, the waste stream is treated to adjust its pH to within a range of 4-5 to facilitate removal of chromium on the adsorption media. Passing this stream through the activated carbon media produces an EPA-acceptable effluent for final discharge. Periodic regeneration of the adsorption media by a sulfuric acid stripping solution is required to remove the chromium from the surface of the adsorption media which can then be reused. The stripping solution is returned to a separate storage tank where it can be used to regenerate other adsorption units or can be sent to the EMR cell when it is loaded with chromium. The stripping solution is processed through the EMR cell where electrowinning takes place and a chromium oxide is deposited on inert cathodes. This blue-green powdery deposit is easily removed from the cathode and is an inert by-product. The electrolysis also regenerates the stripping solution which can then be reused for repeated stripping cycles, minimizing overall chemical consumption.

Potentially various liquid streams such as pickling acids, plating operation rinse waters, and spent printed circuit board etching solutions could be treated by this process. The system is not inhibited by organics, but the solution chemistry must be adjusted and controlled to maximize the metal recovery capability of the system for each particular waste stream. The system is designed to treat segregated (single metal component) streams but certain multi-metal streams can also be treated.

Disclosure statements (3,4) have been filed with the U.S. Patent Office regarding the process documentation of the electrolytic metal recovery unit. A patent application was filed July 28, 1989, detailing the innovative steps into an overall recovery process (5).

Section 3

TEST EQUIPMENT

The equipment used at the Jersey Chrome trial was assembled from generally available standard items and is shown in Figure 1. A schematic diagram of the test unit is shown in Figure 2. The sizing of the unit was based on previous laboratory tests, and a description of the pilot plant components is presented below.

Feed System - The feed system consisted of a 50-gallon (190 liters) polypropylene tank, a chemical metering pump, agitator with impeller, and a pH control system. The pH controller included a pH probe, acid or base feed, internal metering pump, and LED read out.

Carbon Column Modules - Four plexiglass columns of 6" diameter by 6' high were skid mounted. These were complete with piping (1/2" OD tubing) and a valving system to operate the system in upflow or downflow modes and accommodate switching the positioning of the columns. Each column was filled with approximately 15 lbs. (7 kilograms) of Calgon Filtrasorb 400 carbon to a height of 55" up the column.

Regeneration Tank - A 50-gallon (190 liters) polypropylene tank was used as a recirculating tank for the acid regeneration of the GAC columns and for the EMR cell. The tank was equipped with a pH controller and a 1.5 gal/min recirculation pump.

EMR Cell

The EMR cell consisted of a custom fabricated polypropylene module (size: 3' by 1' wide by 2' deep). The cell included proprietary agitators, anodes, cathodes, and a dc power supply (150 amps @ 10 volts).

Cathodes - Two types of cathodes were provided; copper and stainless steel. The cathodes were 8" wide by 12" high by 1/4" thick. Cathode surface area was either 2 or 4 ft^2.

Anodes - Two types of lead anodes were used; lead-calcium alloy and lead-antimony alloy. The lead-calcium anodes were of a flat plate design and the lead-antimony anodes were of a grid design. The anode sizes were 8" wide by 10" high by 1/4" thick. Anode surface area was either 1.4 or 2.8 ft^2.

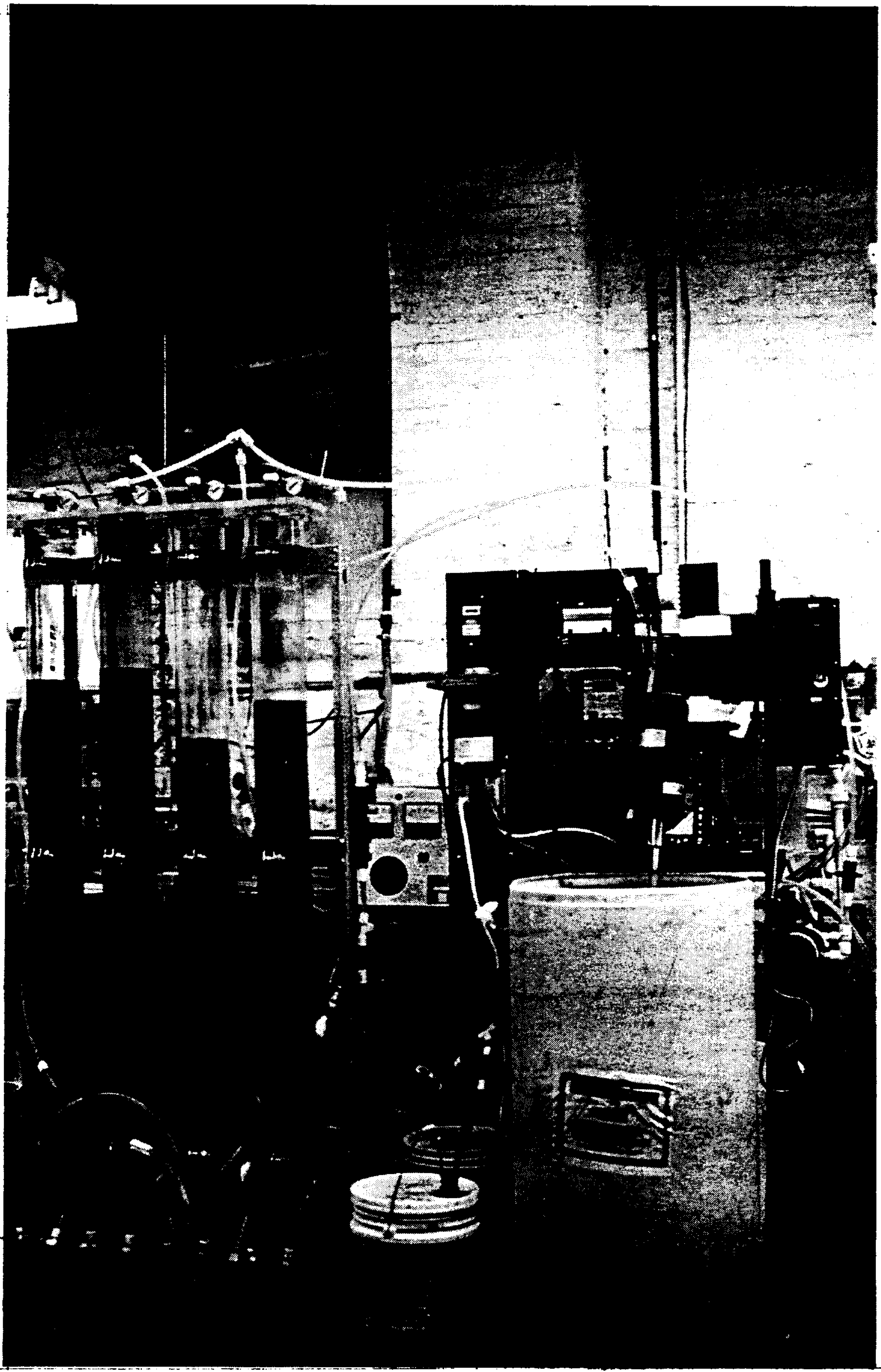

Figure 1. Demonstration unit at Jersey Chrome.

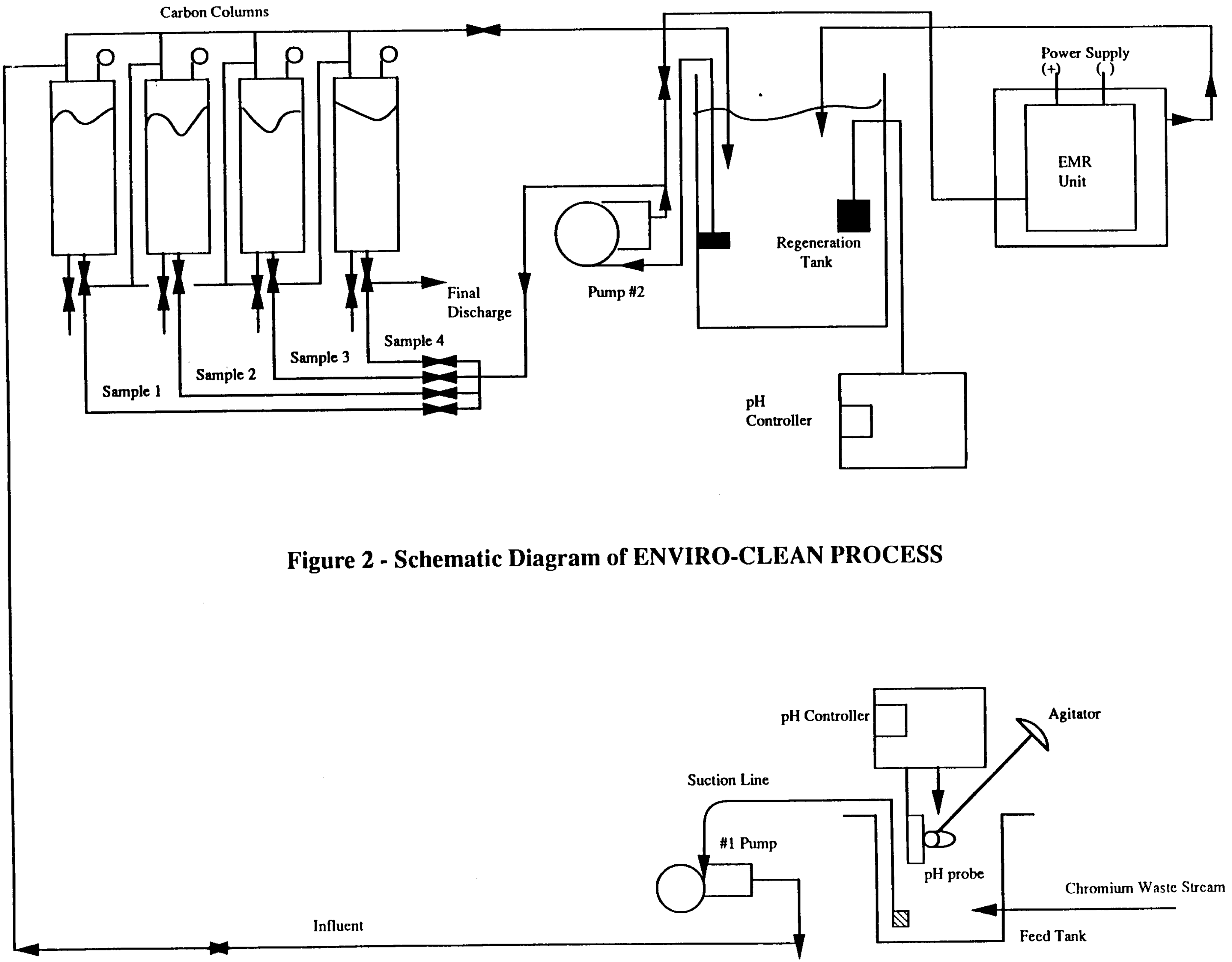

Figure 2 - Schematic Diagram of ENVIRO-CLEAN PROCESS

Section 4

EXPERIMENTAL PROCEDURES

In order to minimize the impact of this field evaluation on the normal operation at Jersey Chrome, samples of waste solution were transferred from their waste stream holding tank to the Feed Tank and treated on a batch basis. Approximately 50 gallons (190 liters) of waste stream solution were taken at one time from Jersey Chrome's holding tank and transferred to the Feed Tank for pH adjustment. This feed was pH adjusted to 4-5 using concentrated caustic soda flakes.

The Jersey Chrome solution was pH adjusted and pumped from the Feed Tank through a single GAC column at a nominal flow rate of 1.7 (6.4 L/m) gal/min. Periodic samples of the effluent were taken and analyzed. Each run was continued until "breakthrough" of the column, as evidenced by a faint yellow coloration of the effluent, occurred. If the solution in the Feed Tank was depleted before breakthrough, the run was interrupted until a new batch of waste stream solution was transferred to the Feed Tank and pH adjusted. Afterwards the run was continued until breakthrough.

After a carbon column was exhausted, it was regenerated with a sulfuric acid solution at a pH of 1.8. This solution was pumped from the Regeneration Tank at a flow rate of about 1 gal/min which fluidized the carbon bed to 50% of its original height. This stripping step was performed for 1-2 hours. An overnight soak in the same solution was added during the course of the test. After the overnight soak, the acid stripping step would be repeated. The resulting concentrated trivalent chromium/sulfuric acid solution was returned to the Regeneration Tank where it could be reused for stripping another column or directed to the EMR for chromium recovery. The column was then water washed twice with one standing bed volume of fresh city water.

The chromium/sulfuric acid solution from the acid regeneration procedure was then processed through the EMR unit. This solution was pH adjusted to 2.0 - 3.5 using caustic soda flakes, and recirculated from the Regeneration Tank through the EMR unit at a flow rate of 2-3 gal/min. The EMR unit was operated at various power settings ranging from about 6 - 10 volts and 20 - 140 amps. The cathodes were removed and the recovered product scraped off, air dried and then weighed.

The weight of the product was recorded as well as the power settings (voltage and ampere readings) and ampere totalizer reading. The electrolyzed solution was reused for the next carbon stripping cycle with the proper pH values and controls.

Also, additions of thiourea, sodium thiocyanate and sodium sulfite were made to the Regeneration Tank, to enhance plating efficiency. The GAC and EMR runs were conducted independently and separately as they would be in a commercial installation. The following variables were investigated.

GAC EXPERIMENTS VARIABLES

- Effluent Quality - hexavalent chromium < 0.1 mg/l and trivalent chromium level < 2.0 mg/l
- Effluent Chemistry - Cr, Fe, Cu, pH, conductivity, and sulfates
- Solution Parameters - temperature, color indicators, suspended solids
- Media Regeneration - number of cycles media can be regenerated and produce quality effluent
- Stripping Solution Reuse - number of cycles acid can be reused after electrolytic treatment
- Stripping Solution Volume - amount of acid needed to remove the Cr from the media

EMR VARIABLES

- Electrolytic Operation - voltage drop across cell, ampere flow, and cathode loading (grams)
- Yield - Cr percentage in recovered oxide compound
- EMR Components - evaluate the cell internals, lead and copper cathodes, mechanical drives and agitation
- EMR Solution Chemistry - monitor pH, % acid, Cr loadings (grams/liter) and addition agents
- Power Consumption - kWh per lb. of chromium
- Power Setting - current densities (amp/sq. ft.)

Section 5

RESULTS

The following are separate discussions of the results obtained from each unit operation during the field demonstration study at Jersey Chrome.

GAC COLUMNS

Chromium Removal from Waste Stream by Activated Carbon

Sixteen separate runs were conducted to evaluate the use of the GAC columns to remove chromium from the waste solutions. The tabulated experimental data taken during most of these runs are listed in Table A1 (Appendix) and the overall results are summarized in Table 1.

It should be noted that there were significant differences in the composition of the waste solutions being treated. One analysis taken on Jersey Chrome's holding tank on June 20, 1989, Table A2 (Appendix), showed a chromium content of 2700 mg/l which was totally hexavalent. Analyses of the solutions being treated during the test program varied from 442 mg/l to 990 mg/l of hexavalent Cr; 0.5 mg/l to 7.2 mg/l of Fe; and 5.1 mg/l to 13 mg/l of Cu.

It was observed that the initial runs on each column exhibited low removal capacity and high effluent pH values (6-9). It was learned that Filtrasorb 400, a coal-based product, has a high ash content. This alkaline ash was leached off the carbon surface when the hexavalent chromium contacted it resulting in high effluent pH and low chromium removal capacity. After 2-3 runs the chromium removal loadings increased, lower effluent pH values (4-5) were obtained and volume throughput increased 1.7 - 3.2 times. This resulted from processing of the acidic solution through the carbon system which ultimately prepared the activated carbon surface to maximize chromium removal. This effect is illustrated by the results of the initial runs on columns 1, 2, and 3.

The initial run, #1, conducted on column #1 exhibited very quick breakthrough. The effluent showed yellow color and pH of 6.8 in less than 2 hours. Approximately 60 liters (15.9 gal) of rinse chromic acid had been treated. The feed pH was dropped slowly to 3.5 but the effluent pH continued to increase to a final level of pH 9.0. The run was terminated and no further sample analysis was made.

Column #1 was regenerated and run #2 started with column #1. Breakthrough occurred after 177 liters (47 gal) with 266.5 liters

TABLE 1
ACTIVATED CARBON ADSORPTION OF CHROMIUM DATA

RUN #	2	6	7	8	9	10	11	12	13	14	15	16
Variable												
Feed Concentration (mg/l)	450*	450*	450*	442*	500	500	500	500	470	480	501**	990**
pH Influent	4.2	4.3	4.4	4.25	4.1	4.2	4.2	4.2	4.2	4.3	4.3**	4.2
pH Effluent	3.2-7.4	6.5	3.5	3.1-6.8	6.3	5.6	5.6	5.0	3.1-3.6	3.0-3.4	3.6	3.4
Effluent Concentration												
Cr + 6, (mg/l)	0.0-25.0	18.0	0.01	.01-68.0	8.7	32.0	---	5.1	.02-5.6	.01-10	2.0	1.4
Cr^{TOT}, (mg/l)	2.14-25.2	18.0	1.2	9.8-69.0	8.8	33.0	---	8.5	7.5	9.4-11	17	15.6
Volume Treated (liters)	266.5	181.2	277.6	325.7	232.2	305.96	286.1	308.8	407.9	640.0	186.9	135.9
Average Flowrate (ml/min)	365	386	525	460	400	460	464	340	510	420	460	502
Carbon Weight per column #, (grams)	6356 #1	5675 #2	6583 #3	6810 #2	5448 #1	5676 #2	6356 #3	6810 #1	6356 #2	5902 #1	4994 #2	4994 #1
Chromium Absorbed (grams)	120	72.5	111	125	104.5	137.6	28.7	143.1	191.7	307.2	100.9	130.5
Carbon Loading (mg Cr^{TOT}/g carbon)	18.9	12.8	16.9	18.4	19.2	24.2	20.9	21.0	30.2	52.1	20.2	26.1

*Average Value
**Estimated Values

(70.5 gal) being processed overall. The effluent pH started at 2.5 and had an end point of 7.5. Three runs were made with the feed pH levels adjusted to 2.0, 2.5, and 4.0. Low pH effluents were noted for these runs, 3, 4, and 5, on columns 1 and 2.

The remaining test runs were conducted with the feed in the pH range of 4.2 - 4.5. The effluent from the carbon system was crystal clear and water white. Chromium was the main metal species present and trace levels of copper and iron were also present. Initially, samples of the effluent were collected every hour and analyzed. These values as listed in GAC runs 2, 7, and 8 showed hexavalent chromium levels of 0.0, 0.01, and 0.01, respectively and total chromium values of 2.1, 1.2, and 9.8, respectively (Table A1). The chromium values presented in Table 1 are effluent samples taken at breakthrough based on color indication. This explains why they are higher than the 0.1 or 10 mg/l for hexavalent or total chromium, respectively. The effluent from the carbon columns will require polishing to guarantee less than 1.7 mg/l total Cr effluent quality. Removal levels for chromium were in the 94-99% range and for copper and iron 97-99% as can be determined from Table A1.

Figure 3 shows chromium removal as a function of the volume throughput. Chromium removal was relatively independent of volume treated with the exception of runs 6, 13 and 14. Examination of the data in Table 1 shows a generally increasing carbon loading value for each column as use increased. For example, the sequential values for Column #1 were 18.9, 19.2, 21.0, 52.1, and 26.1 milligrams of chromium per gram of carbon (mgCr/gC). For Column #2 the values were 12.8, 18.4, 24.2, 30.2, and 20.2 mgCr/gC. For Column #3 the values were 16.9 and 20.9 mgCr/gC. These data suggest that the columns had not been completely conditioned, as described before, and that the increasing use of them completed conditioning of the media surface. No explanation for the lower values obtained in runs 15 and 16 can be given. However, the removal values for runs 13 and 14 approximate the range 30-40 mgCr/gC reported in the literature (6).

Acid Stripping and Carbon Regeneration

The loaded carbon columns were stripped of chromium and regenerated by recirculating sulfuric acid solution through them at a pH at 1.8. The color of the acid stripping solution upon exiting the carbon column was violet blue. The stripping step was performed for 1-2 hours.

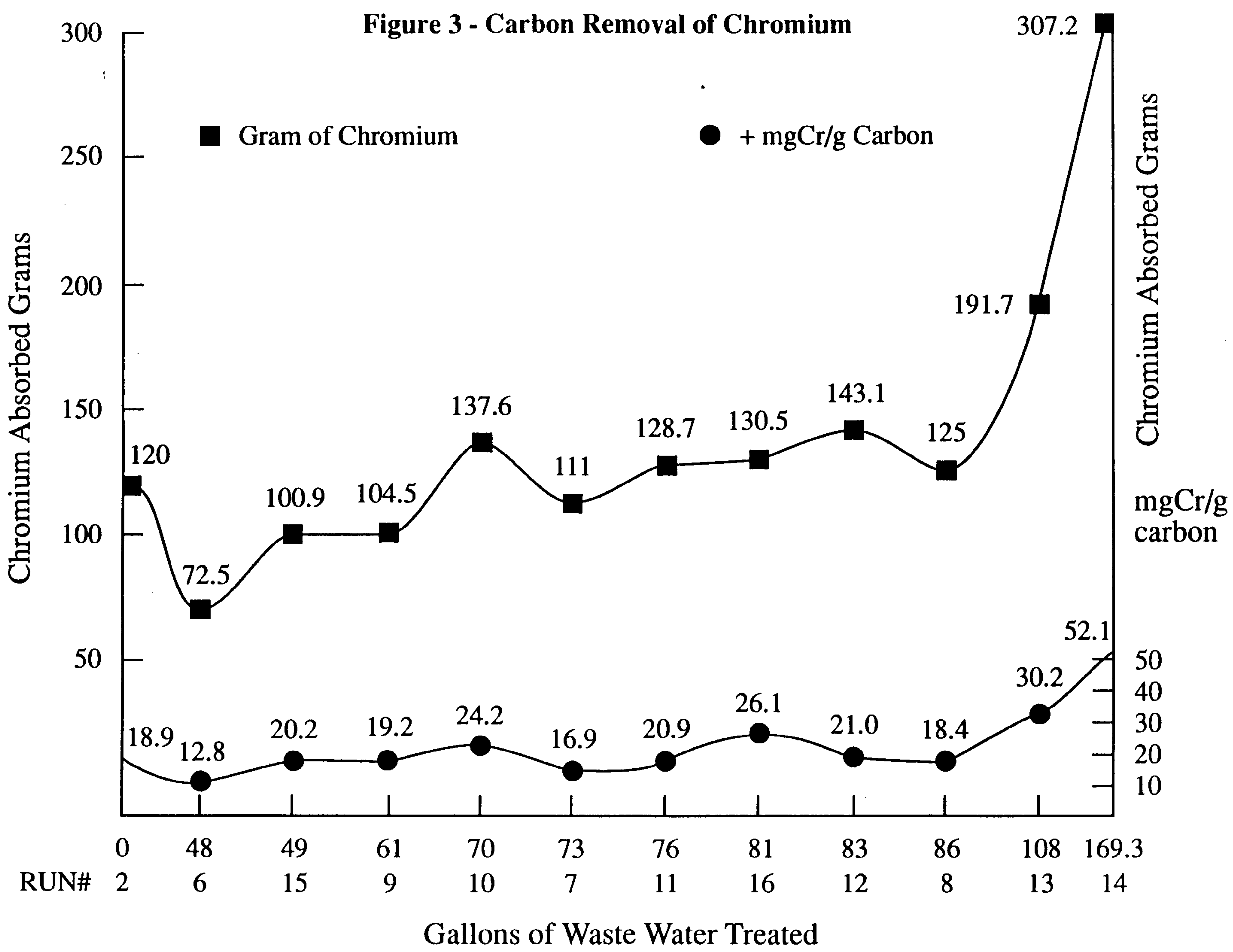

Figure 3 - Carbon Removal of Chromium

TABLE 2
ACTIVATED CARBON ACID STRIPPING

GAC Run #	2	6	8	9	13	14
Variable						
Stripping Concentrations						
Cr^{TOT}, (mg/l)	600.0	440.0	661.0	740.0	2450.0	3000.0
Cr^{+3}, (mg/l)	599.8	439.9	660.8	739.9	2446.9	2995.1
Copper, (mg/l)	---	---	---	8.6	63.0	98.0
Iron, (mg/l)	---	---	---	7.6	71.0	100.0
Stripping pH	2.1	2.1	2.3	2.3	2.1	1.9
Stripping Volume (liters)	139.9	139.9	139.9	121.0	75.6	75.6
Chromium Stripped (grams)	83.9	61.5	103.5	89.5	185.2	41.6
Chromium Adsorbed (grams)	120.0	72.5	125.0	104.5	191.7	307.2
Stripping Removal (%)	69.9	84.8	82.8	85.6	96.6	13.5

The carbon adsorption/acid regeneration cycle was performed for most of the sixteen runs. For some runs the stripping solution was used more than one time to concentrate the amount of chromium in the solution. Six different solutions were obtained by these stripping procedures. The experimental data for these stripping runs are listed in Table 2. More than 99.7% of the chromium removed from the columns was trivalent chromium. Analyses of the regenerant from GAC runs 9, 13, and 14 show that copper and iron were also removed from the waste stream by the carbon columns.

Chromium recovery percentages achieved by acid stripping the carbon column ranged from 13.5-96.6%.

GAC Rinsing

Before beginning the next chromium removal cycle, the GAC had to be water rinsed. Initially, only two water rinses were used to conserve the amount of rinse water needed after stripping the chromium from the carbon. The two water rinses recovered an average of 750 and 370 mgCr/l respectively with a maximum concentration of 900 mgCr/l. The water rinsing resulted in two separate solutions of trivalent chromium. Both solutions were violet in color with the first rinse solution being darker. The pH 6.8 rinse water, exited the carbon column at pH 2.1.

When a carbon column that was acid regenerated and water rinsed contained water overnight, a 1-2 inch blue-violet haze could be observed in the solution on the top of the carbon bed. This indicated that some additional trivalent chromium remained in the column after stripping and rinsing.

This phenomenon was further investigated in GAC runs 11 and 12 by leaving a third water rinse in the column overnight. The chromium concentrations of the three rinses are tabulated in Table A3 (Appendix) and shown in Figure 4. The chromium concentrations of the first rinse from Runs 11, 12, 13, and 16 ranged from about 560 mg/l to about 770 mg/l.

The concentrations for the second rinses from these runs ranged from about 350 to 550 mg/l. In comparison, the chromium concentrations from the third rinses for Runs 11 and 12 were about 700 and 900 mg/l, respectively.

The hexavalent chromium concentrations in the rinses were very low averaging 0.8 mg/l with nine runs at 0.1 mg/l. The trace metals of copper and iron were also present in the rinse solutions with average concentrations of 38 and 30 mg/l, respectively.

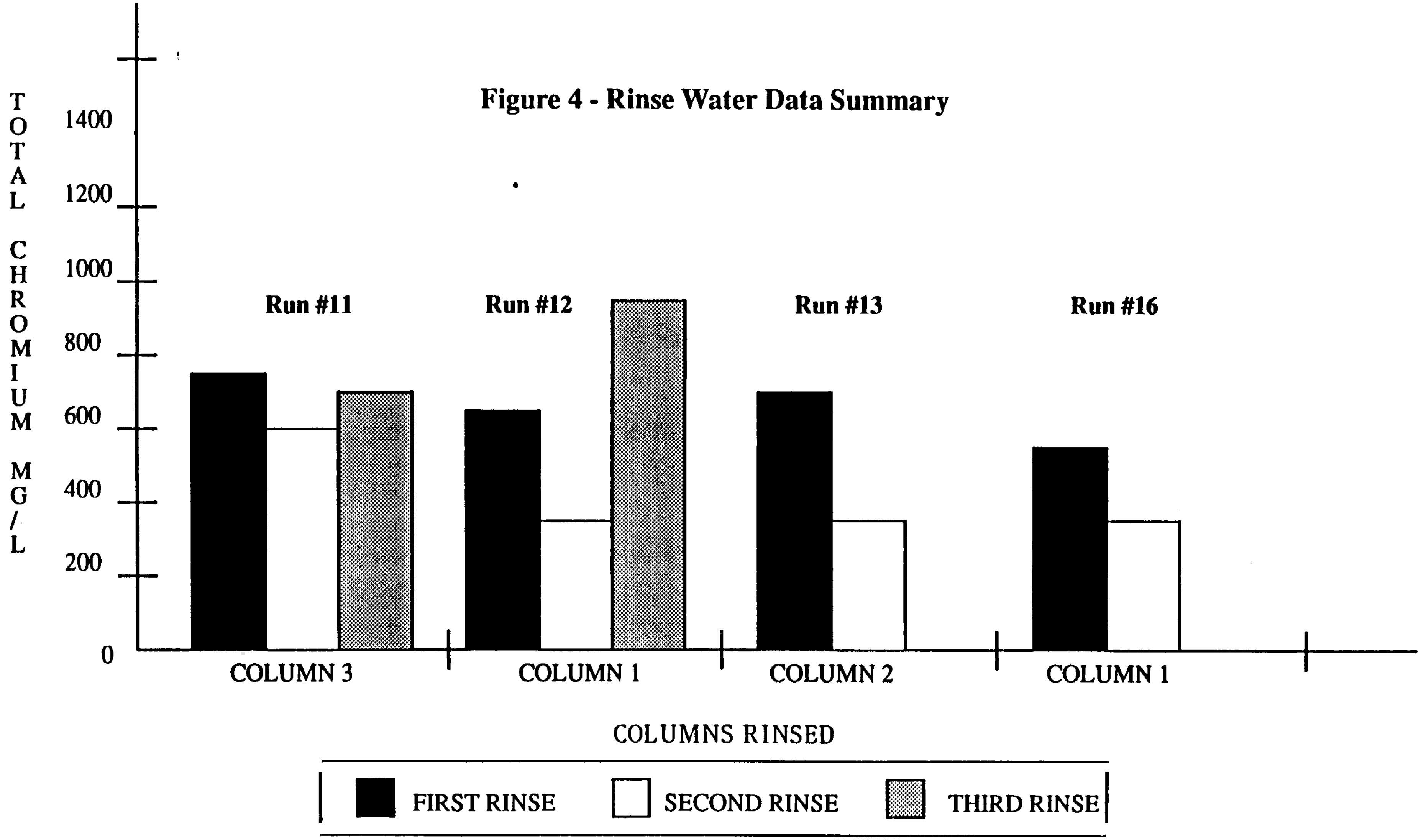

Figure 4 - Rinse Water Data Summary

Electrolytic Metal Recovery

The stripping procedures described above produced six solutions which could be processed in the EMR unit. A total of nine EMR runs were made from five of these solutions. These concentrated trivalent chromium/ sulfuric acid solutions from the acid regeneration procedure were pH adjusted to 2.0-3.5, and processed in the EMR unit to recover the contained chromium. The EMR unit was operated at various power settings ranging from about 6-10 volts and 20-140 amps. Each recovery run lasted about 4 hours. The experimental data from the nine EMR runs are reported in Table A4 (Appendix) and summarized in Table 3. During the early runs, it was observed that very little cathode deposit was obtained at less than 7 volts. This observation suggests the existence of a threshold voltage or current density. It was also observed that higher voltages did not significantly increase the rate of deposition. This suggests a need for greater mass transport to the cathode. On this basis, the preferred operating conditions for the remaining runs were about 7-7.5 volts and 120-140 amperes.

It was also observed that there was very little, if any, deposit on the lower portion of the cathode which extended below the anode. This is a further indication that deposition does not occur at low current densities.

The deposit on the cathodes in the cell was a loose and powdery form of chromium oxide as shown in Figure 5. A typical deposit after removal from the cathode by scraping is shown in Figure 6. The weights of the cathode deposits were recorded for each run and on some runs the weights were recorded on an individual cathode basis. The recovered product weights ranged from 7.2-78.7 grams. After weighing, the material from each run was stored in a common container.

Most of the cathode deposits were a blue-green slate color. Two deposits, however, were green. Analysis of these different colored recovered product samples are presented in Table 4.

The EMR solutions contained copper and iron after stripping the activated carbon columns. A mass balance was performed and based on chromic acid feed concentrations, the trivalent/sulfuric acid solutions for the EMR runs contained over two times as much copper as removed by the carbon. It appears that the copper cathodes were etched by the EMR solution and caused the higher copper concentrations. Iron concentrations were also present at levels higher than feasible based on a mass balance. The source of the iron contamination was uncertain.

TABLE 3
SUMMARY OF ELECTROLYTIC METAL RECOVERY DATA

Variable	Time (Hrs.)	Cr^{TOT} (mg/l) Initial	Final	% Cr Recovered	Chromium Recovered, g	Average Current (amp)	kWh	Avg. Deposition Rate (g/h.)	Avg. Chromium Yield (g/kWh)
EMR RUN #									
A	6.5	661	623	5.7	5.3	5.0	1.66	0.81	6.38*
F	3.6	2050	1650	19.5	48.4	33.0	2.97	13.44	16.30
G	1.9	1650	1600	3.0	6.1	40.0	0.80	3.21	7.63
I	2.6	2030**	1650	10.2	35.2	30.0	1.69	13.54	20.83

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[*] EMR contained only 2 cathodes; average recovery rate calculated assumed 4 cathodes.

[**] Starting concentration of solution was 3000 mg/l but 35.9 liters of water with 500 mg/l of Cr^{+3} was added to fill the hydraulic circuit.

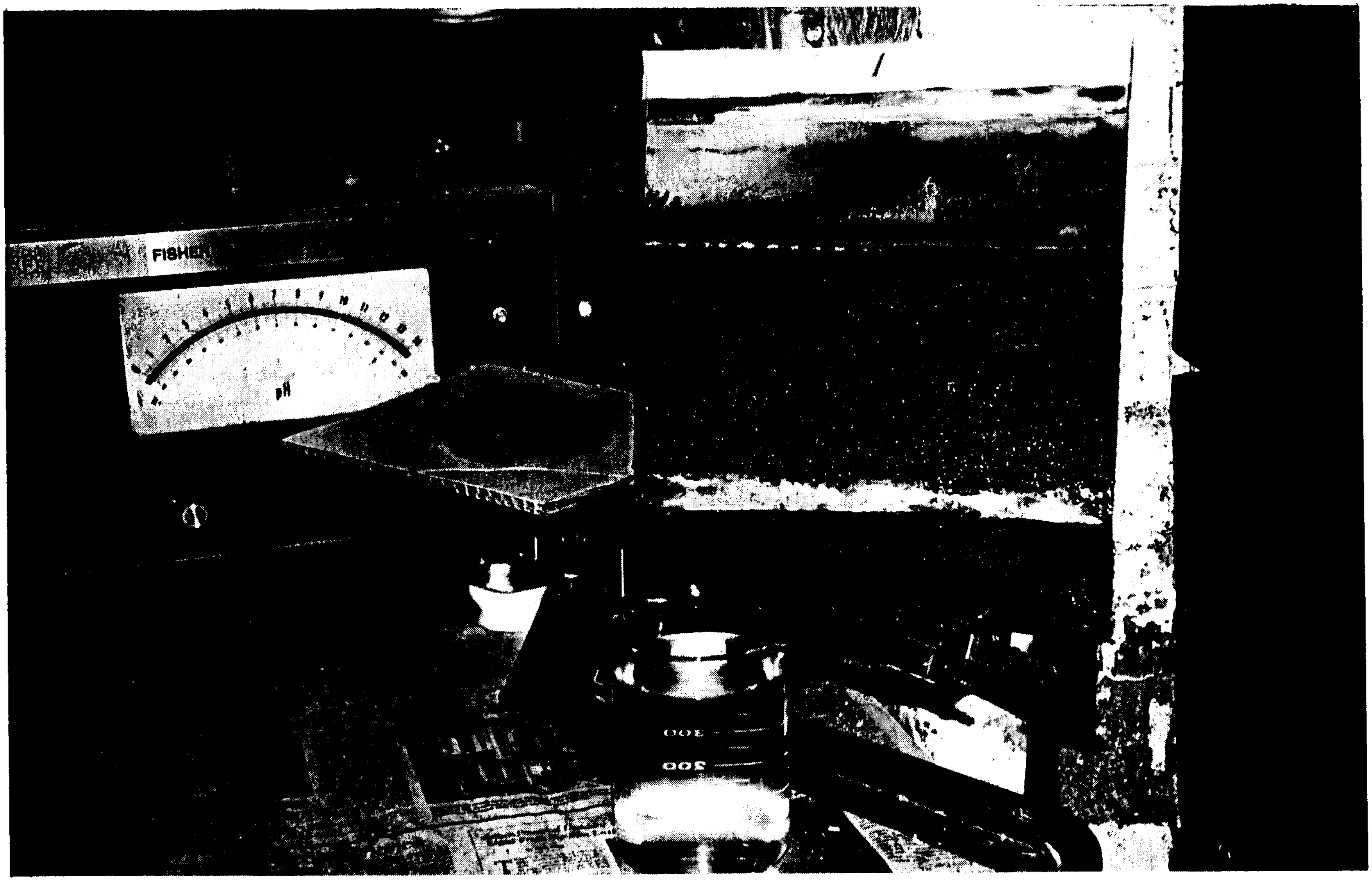


Figure 5. Catliode as removed from cell.

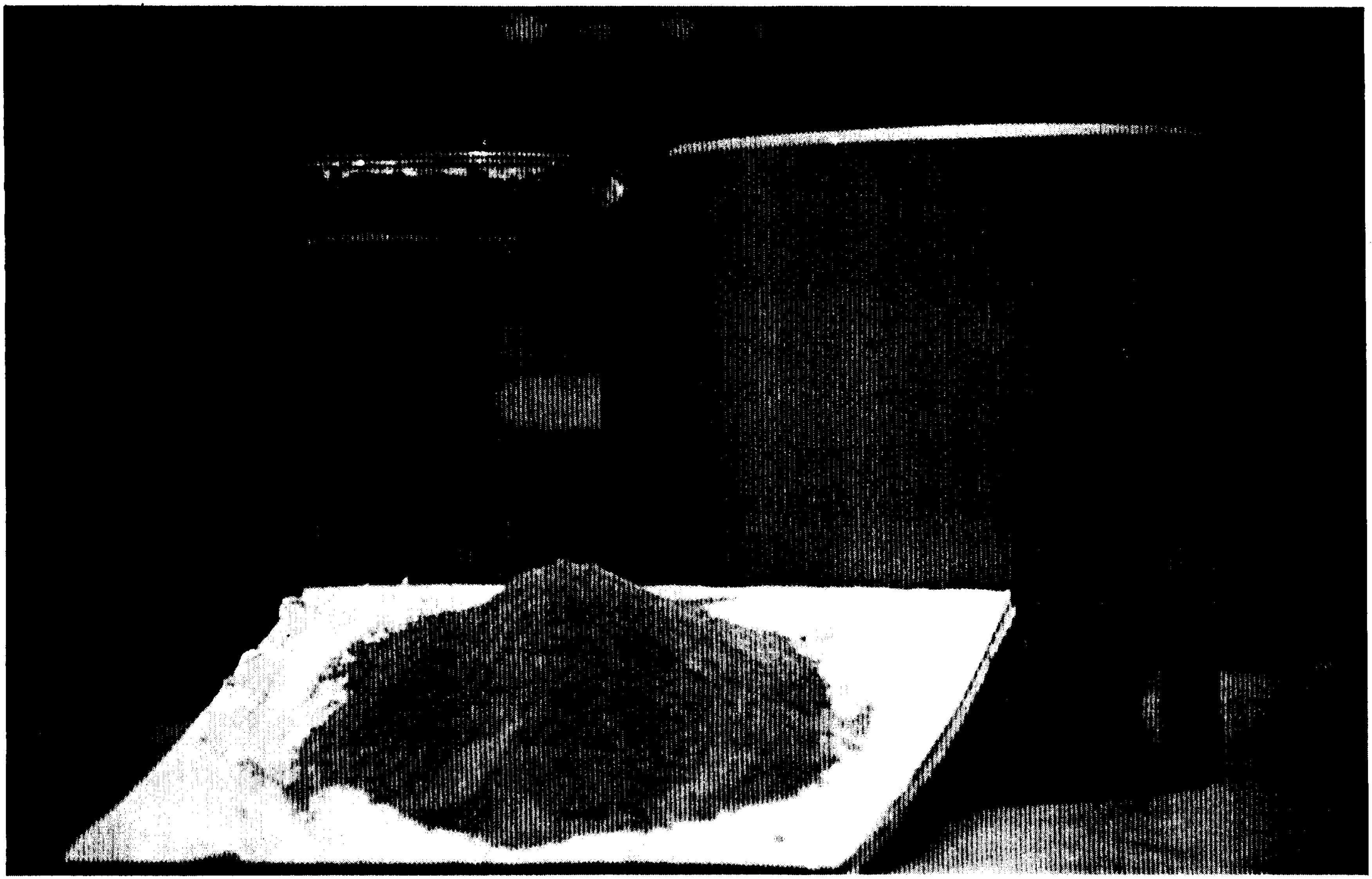


Figure 6. Recovered cathode deposit.

Table 4 - Cathode Deposit (WT %)

Sample	Total Chromium	Copper	Iron	Lead
Blue Color (1)	36.7	21.0	8.0	8.3
Blue Color (2)	27.5	13.7	5.5	7.5
Green Color	12.6	43.0	12.4	10.3

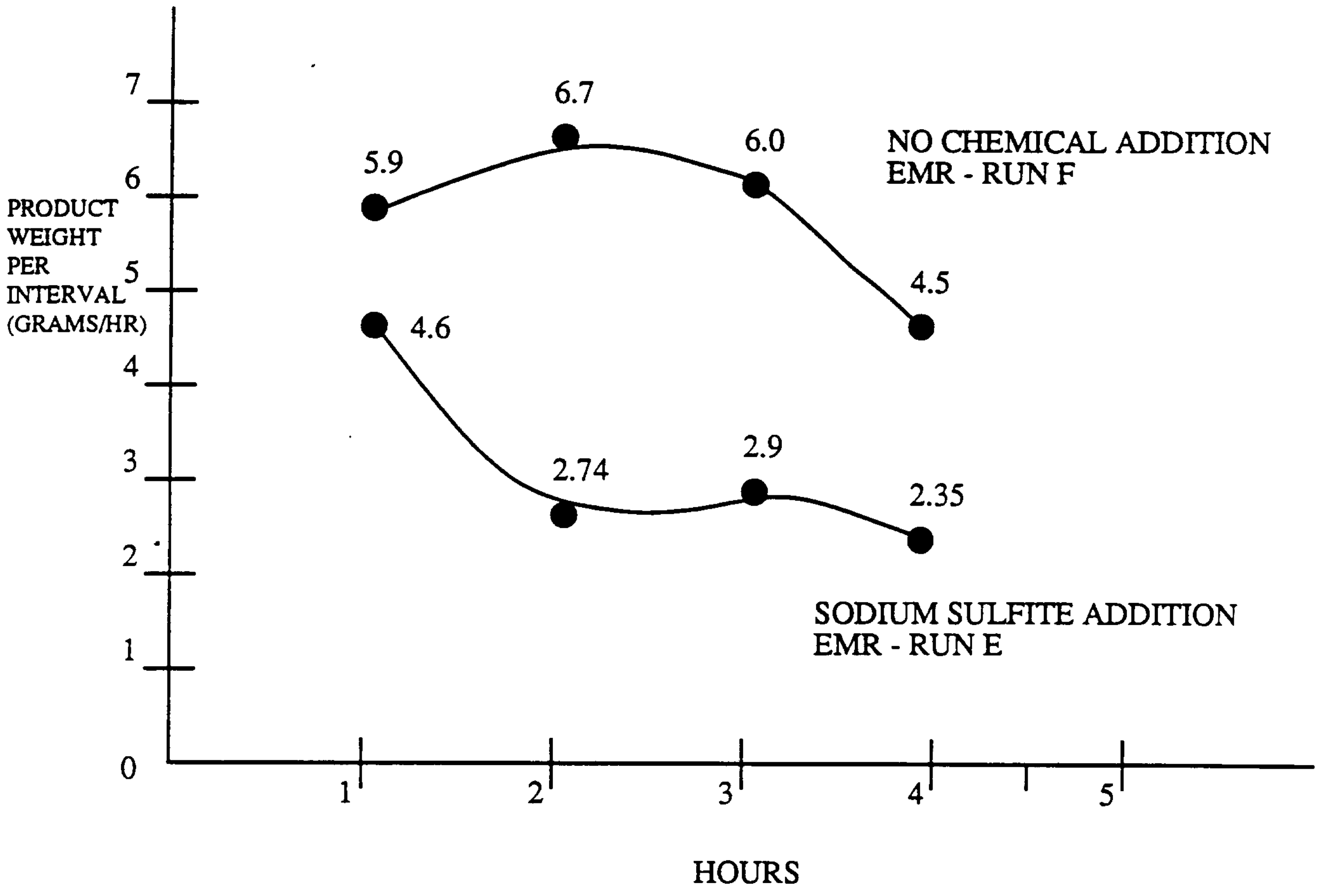
Solution Additives

The EMR solution was oxidized during the runs as evidenced by a greenish-yellow color of the solution. In three of the early runs, sodium sulfite was added to the EMR solution to prevent oxidation of the trivalent chromium. Additions in the range of 10-300 mg/l were made. Large additions reduced the hexavalent chromium as indicated by a change in the solution to a predominantly blue color, but these had a negative effect on the process. After the additions, current flow would remain constant or decrease and the weight of recovered product was insignificant.

This effect was investigated by periodically replacing the cathodes during runs and obtaining product weights for several time intervals throughout the runs. The resulting data for run E with sodium sulfite additions and run F without any additions are shown in Figure 7. For both runs the deposition rate for the first hour of recovery was high. For run E, the average hourly deposition rate for cathodes withdrawn after 2, 3, and 4 hours dropped significantly indicating a marked decrease in deposition rate. For run F, however, the hourly rate remained high for the first three hours and decreased after four hours. As a result of these data the use of sodium sulfite was discontinued.

The effects of two plating additives, sodium thiocyanate and thiourea, were also evaluated. Additions of 10-40 mg/l were made. Sodium thiocyanate was used most of the time. The following observations were made: (1) cathode deposits appeared wetter or shinier and (2) the electrical current reading increased 5-10 amps after a chemical addition was made, and electrical efficiency was increased by 15.9%. The impact of this addition on plating efficiency will require more investigation. Small quantities of the additive were used so this area has promise.

Figure 7 - Effect of Sodium Sulfite On Product Deposition Rate



Chromium Recovery

Solution analyses were performed on four of the EMR runs to calculate the amount of chromium metal recovered on a mass balance basis. These calculations are shown in Table 3. The calculated recoveries range from 5.3 to 48.4 grams which correspond to recovery of 5.7 to 19.5% of the chromium contained in the initial EMR solutions.

The average rate of chromium removal is also shown in Table 3 to normalize the difference in the length of the runs. These values ranged from 0.81 for Run A to 13.54 g/hr for Run I. However, as shown above, the deposition rate decreased with time so the value for Run A is understated. Nevertheless, these calculations show that the deposition rate was higher for those solutions with higher initial chromium concentrations.

The average current for these runs was calculated from the amphere-hour meter readings and the length of the run. These calculations show that the lowest deposition rate was obtained for Run A which also had the lowest current (5 amperes for the given cathodes). The current densities for the other runs were similar. Of those, Runs F and I had similar initial concentrations and similar deposition rates. Run G had a much lower deposition rate and it is proposed that the low rate is the result of the high ratio (40%) of hexavalent chromium to trivalent chromium in the initial solution.

Power Consumption

Table 3 shows the average yield of chromium metal per kWh. These values reflect the trends shown for the deposition rates. The highest yields obtained were 16.3 and 20.8 g/kWh for Runs F and I, respectively. These values represent the average for the length of the run and are understated because, as indicated by Figure 7, the deposition rate decreases with time.

CONCLUSIONS

The results of the program conducted at the Jersey Chrome Plating Company indicated that this new, patent-pending process can be used to recover chromium from industrial wastewater. The granular activated carbon columns effectively removed chromium from the wastewater. Simultaneously, quantities of copper and iron were also removed by the activated carbon system. The columns were successfully regenerated and the resulting regenerate solution was processed in an electrolytic metal recovery unit. Chromium oxide deposits were produced with a chromium metal yield of about 16 to 21 g/kWh. These deposits contained residual quantities of copper and iron.

Section 7

RECOMMENDATIONS

On the basis of this program, it is recommended that the following areas be considered for further studies.

1. Improved column design and use to increase chromium loading.
2. Improved column regeneration to increase the concentration of chromium in the regenerate.
3. Improved agitation to increase mass transport in the Electrolytic Metal Recovery process.
4. Prevention of trivalent chromium oxidation in the Electrolytic Metal Recovery process.
5. Evaluation of improved anode-cathode materials.
6. Evaluation of the effect of residual impurities on the economic value of the recovered product.
7. Perform an economic analysis of the process.

Section 8

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APPENDIX

EXPERIMENTAL DATA

TABLE A1
ADSORPTION REMOVAL DATA

RUN #	Date	Volume Liters	TOT CR	HEX CR	Copper	Iron	pH	Flowrate ml/min	Column #
#2	8-25-89							365	#1
Feed			450.0*	400.0*	-	-	4.2		
eff #1			2.1	0.0	-	-	3.2		
eff #2		266.5	1.1	0.0	-	-	3.6		
eff #3			25.2	25.0	-	-	4.2		
eff #4			162.4	162.1	-	-	7.4		
#6	8-28-89							386	#2
Feed			450.0*	400.0*	-	-	4.3		
eff #1		181.2	18.0	18.0	-	-	6.5		
#7	8-30-89							525	#3
Feed			450.0*	400.0*	-	-	4.4		
eff #1		277.6	1.2	0.01	-	-	3.5		
#8	9-6-89							460	#2
Feed (1)			384.0	384.0	-	-	4.25		
Feed (2)			500.0	450.0	4.9	0.5	4.2		
eff #1			9.8	0.01	<0.1	<0.1	3.1		
eff #2		325.7	69.0	68.0	0.1	0.1	6.8		
#9	9-11-89							400	#1
Feed			500.0	450.0	-	-	4.1		
eff #1		232.2	8.8	8.7	0.1	0.1	6.3		
#10	9-13-89							460	#2
Feed			500.0	450.0	-	-	4.2		
eff #1		305.9	33.0	32.0	0.1	0.1	5.6		
#11	9-20-89							464	#3
Feed			500.0	450.0	-	-	4.3		
eff #1		286.1	-	-			5.6		

TABLE A1
ADSORPTION REMOVAL DATA (page 2)

RUN #	Date	Volume Liters	TOT CR	HEX CR	Copper	Iron	pH	Flowrate ml/min	Column #
#12	9-20-89							340	#1
Feed			500.0	450.0	-	-	4.2		
eff #1		308.8	8.5	5.1	-	-	5.0		
#13	9-28-89							510	#2
Feed			470.0	460.0	6.0	0.6	4.2		
eff #1			7.5	0.02	0.2	0.1	3.1		
eff #2		407.9	7.5	5.6	0.1	0.1	3.6		
#14	10-2-89							420	#1
Feed (1)			480.0	360.0	6.5	7.2	4.3		
Feed (2)			480.0	470.0	5.3	0.6	4.2		
eff #1			9.4	0.01	0.3	0.2	3.3		
eff #2			3.1	0.01	0.1	0.1	3.5		
eff #3		640	11.0	10.7	0.1	0.1	3.7		
#15	10-10-89							460	#2
Feed (1)			501.0	480.0	5.1	0.9	4.2		
Feed (2)			622.0	600.0	7.7	2.2	4.4		
eff #1		189.6	17.0	2.0	1.2	0.2	3.6		
#16	10-12-89							502	#1
Feed (1)			950.0	920.0	12.0	3.0	4.2		
Feed (2)			1026.0	1000.0	13.0	2.4	4.2		
eff #1		135.9	17.0	1.4	1.5	0.3	3.4		

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*Estimated Values

TABLE A2
JERSEY CHROME RINSE WATER CHARACTERIZATION*

Test	Result Mg/L
pH	1.6
Suspended Solids	6
TOC	23
COD	455
Hexavalent Chromium	2700
Trivalent Chromium	-
Total Chromium	2700
Sulfates	140
Chlorides	Nil
Iron	57
Copper	25
Lead	0.6
Sodium	30
Hardness as $CaCO_3$	Nil

*Pittsburgh Applied Research Corporation report of June 20, 1989

TABLE A3
WATER RINSE DATA

		Results in mg/l					
RUN #	Date	Total Cr	Hex Cr	Tri Cr	pH	Copper	Iron
Run #11	9-28-89						
column #3							
rinse #1		770	.1	769.9	2		
rinse #2		550	.01	549.99	2		
rinse #3	10-2-89	700	.03	699.97	2.2 (overnight soak)		
Run #12							
column #1							
rinse #1	9-28-89	640	.01	639.99	2		
rinse #2		390	.01	389.99	2.1		
rinse #3	10-2-89	900	.33	899.67	1.9 (overnight soak)		
Run #13							
column #2							
rinse #1	10-5-89	720	2.88	717.12	2.2		
rinse #2		350	4.22	345.78	2.1		
Run #16							
column #1							
rinse #1	10-18-89	560	1.6	558.4	2.3	36	29
rinse #2		390	1.26	388.74	2.2	40	30

Each rinse used one bed volume of clean water. The first and second rinses were gravity drain with about 15-30 minutes holding time.

Table A4

SUMMARY OF ELECTROLYTIC METAL RECOVERY ANALYSES

EMR RUN #	A	B	C	D	E	F	G	H	I
Variable									
Feed Concentration Cr_{TOT} (mg/l)	661	740	--	--	--	2050	1650*	--	3000**
Copper (mg/l)	--	8.6	--	--	--	65	61	--	98
Iron (mg/l)	--	7.6	--	--	--	43	24	--	100
Effluent Concentration Cr+6, (mg/l)	259	--	--	--	--	640	870	--	626
Cr+3, (mg/l)	364	--	--	--	--	1010	730	--	1024
Cr_{TOT}, (mg/l)	623	--	--	--	--	1650	1600	--	1650
Copper (mg/l)	--	--	--	--	--	61	78	--	113
Iron (mg/l)	--	--	--	--	--	24	24	--	48
System Volume	139.9	--	--	--	--	121	121	--	92.6
Run Time (hrs)	6.5	5.4	4.0	3.7	4.0	3.6	1.9	2.5	2.6
Average amp-hrs	29.9	29.5	30.7	101.7	124.1	120.35	76.3	109.0	77.9
Average Voltage	8.6	10.3	10.3	7.5	6.7	7.0	6.0	6.9	7.7
Power (kWh)	1.66	1.64	1.27	2.78	3.27	2.97	0.80	1.95	1.69
Product Recovered (grams)	12.0	20.6	7.2	38.5	34.4	78.7	11.9	18.9	51.9

*Feed: Cr + 6 = 640 mg/l, Cr + 3 = 1010 mg/l

**Feed: Cr +3 2995.1 mg/l, Cr + 6 = 4.9 mg/l