Improvements in the Electrowinning of Chromium[1,2]

R. R. Lloyd, J. B. Rosenbaum, V. E. Homme, L. P. Davis, and C. C. Merrill

Minerals Division, Bureau of Mines, U. S. Department of the Interior, Boulder City, Nevada

ABSTRACT

Improvements in the electrowinning of chromium from trivalent or "chrome alum" solutions, made since publication of a previous paper, are disclosed. Elimination of sodium sulfate from the electrolyte and changes in cell design have decreased the cost of electrowinning chromium metal. Details of the new cell design and data obtained with a 120-pound-per-day cell are discussed.

The sensitivity of laboratory-size cells to certain critical impurities and other variables tends to obscure the possibilities of this type of electrolyte. Research in pilot-plant cells has shown that proper cell design and operation on a sufficiently large scale can largely overcome the sensitivity of chromium sulfate electrolytes to impurities and, to a lesser extent, to pH and other variables.

Introduction

Since publication of previous reports (1) on the electrowinning of chromium from trivalent solutions, extensive work has been done on simplifying the electrolyte and the electrolytic cell. The purpose of this work has been to decrease the cost of producing electrolytic chromium by decreasing both plant construction and operating costs.

Preparation of cell feed has been simplified by dispensing with sodium sulfate from the electrolyte, which not only eliminates the problem of recovering the sodium salt but also results in easier cell control. Cell feed consists solely of a concentrated solution of chromium ammonium alum.

The early pilot-plant cell (2) met the complex requirements for successful deposition of metal, but it was expensive to construct and proved to be relatively difficult to operate because of the necessity for continuously operating several pumps. Experiments with a series of cells of more conventional design resulted in the development of a simplified cell with better operating characteristics. The improved cell design and new electrolyte, plus a further study of operating variables, have substantially increased the tolerance of the cell to critical impurities and have made production of heavier deposits a practical operation.

Production of electrolytic chromium is one phase of the Bureau of Mines study on the economic utilization of substandard domestic chromium ores.

Cell Construction

Design Requirements

The successful electrodeposition of chromium at a high current efficiency from chromium sulfate solutions requires control of the pH between relatively narrow limits and conservation of the divalent chromium formed at the cathode. Diaphragms are essential, not only to prevent the sulfuric acid formed at the anode from mixing with the catholyte but also to prevent the chromic acid formed at the anode from oxidizing the divalent chromium. In addition to preventing the anolyte from mixing with the catholyte, the diaphragm must control the quantity of catholyte that flows into the anolyte. The ideal diaphragm, therefore, is one with a limited and uniform porosity.

The quantity of catholyte flowing into the anolyte controls the pH by controlling the ammonium ion concentration of the anolyte. If the highly acid anolyte does not also contain ammonium ion, the transference rate of hydrogen ion into the catholyte is greater than the evolution of hydrogen at the cathode and the pH of the catholyte drops. In other words, if the ammonium ion concentration of the anolyte is increased, the pH of the catholyte will increase and vice versa.

A further requisite for deposition of metal is a rapid but nonturbulent flow of electrolyte over the cathode surface.

Anode Compartments

The anode compartment of the new cell, shown in Fig. 1, meets the essential requirements of an anode holder or frame, anolyte chamber, diaphragm, and diaphragm support in one self-supported unit. It consists of a frame fabricated from strips of 1-inch (2.54 cm) and $\frac{3}{8}$-inch (0.95 cm) Lucite or Plexiglas sheet with a No. 17 Vinyon cloth diaphragm cemented to each side. Two outlets are provided for circulating anolyte to a common header. The compartment was designed to minimize machining of Lucite, an important cost item. Lucite strips are cut from polished sheets with a circular power saw and cemented together on the polished surfaces. The

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$\frac{3}{8}$-inch (0.95 cm) strip is left out of the top side, except for a small piece in the center, and is lapped with the 1-inch (2.54 cm) strips at the corners to make a tongue-and-groove joint. The only machining required is drilling of the circulation outlets and, occasionally, sanding of a projecting corner joint to give a relatively flat surface for the diaphragm. The outlets are extended by cementing short lengths of Lucite tubing to the frame.[3]

[3] Labor averages 1.25 man-hours per frame for assembly and 0.75 man-hour for cementing the diaphragm in place. Specialized equipment could decrease these costs. Cost of Lucite, cement, and Vinyon diaphragms averages $24.13 per anode compartment.

Each compartment holds one anode, which consists of a split sheet of lead-1 per cent silver alloy burned to a lead-covered copper header bar, as shown in Fig. 1. The alloy sheet is split vertically so as to pass by the brace at the center of the top Lucite strips, and is suspended freely in the compartment except for the bottom edge which is centered between the diaphragms by a bottom groove.

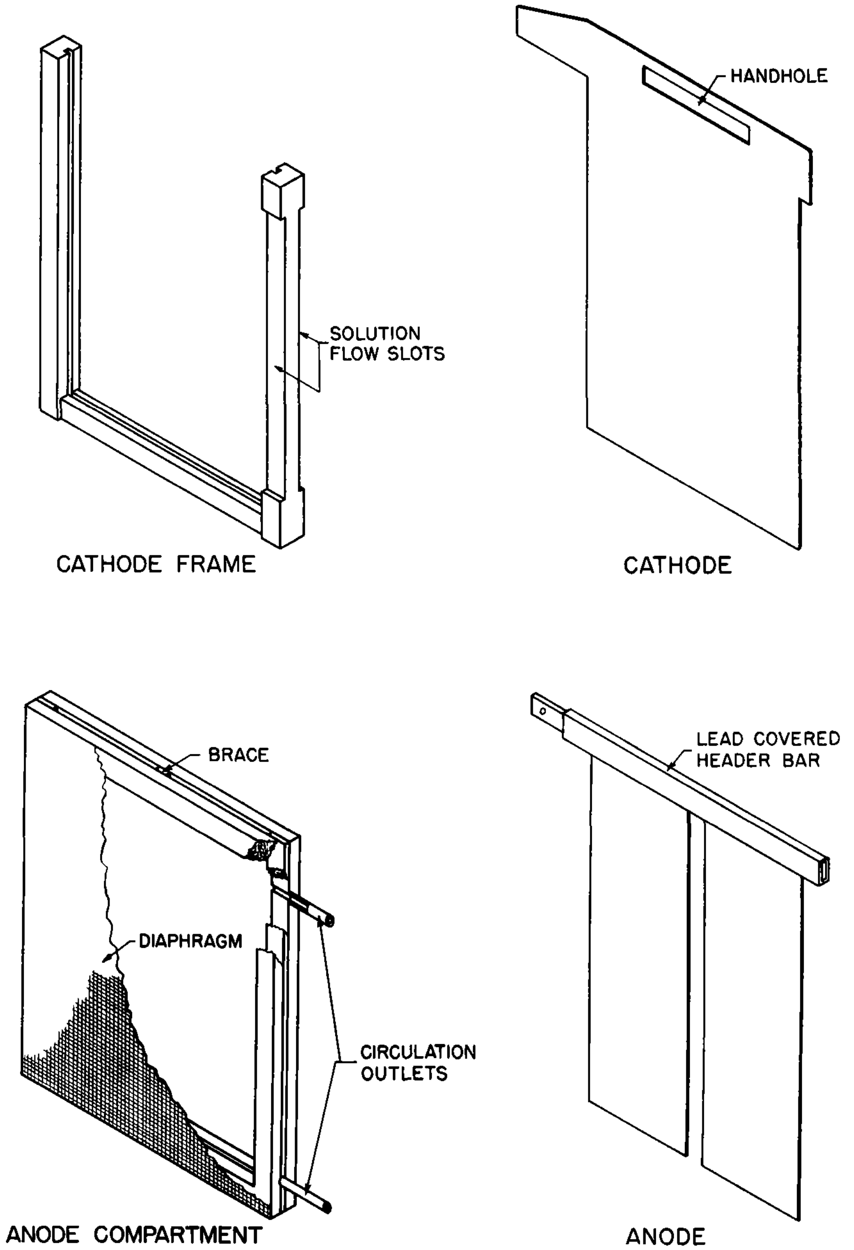

Fig. 1. Details of cathode frame, cathode, anode compartment, and anode.

No. 17 Vinyon is sufficiently heavy and resistant to stretching so that no diaphragm bracing is required; bracing is necessary with lighter fabrics. Untreated No. 17 Vinyon also has a lower and more uniform electrical resistance than the coated or preshrunk diaphragms previously used.

Oxygen generated in the compartment escapes through the narrow slit between the anode and the top Lucite strips. Acid spray carried by the escaping gas impinges on the overhanging lead-covered anode bar and any not removed is deflected toward the ventilating system.

Cathode Frames and Cathodes

The cathode frame, also shown in Fig. 1, is fabricated from Douglas fir. The fir strips are cut $2\frac{1}{4}$ inches (5.71 cm) wide from standard 2-inch (5.08 cm) timber and are fastened together with monel screws. The bottom strip and one upright strip are cut on the sides to provide flow slots for free circulation of catholyte from the cell tank, when the cathode frames are assembled with the anode compartments. Evolution of hydrogen at the cathode causes a rapid, but controlled, circulation of catholyte in at the bottom and out the side of the frame. The importance of rapid, uniform circulation cannot be overemphasized. The effect of rapid movement of the catholyte is to maintain the pH at the cathode surfaces more nearly uniform and closer to the pH of the body of the solution. The result is a wider pH range for efficient plating and a greatly increased tolerance to impurities. The concentrations of some critical impurities, such as aluminum and lead, in the standard pilot-plant electrolyte, are five to ten times as great as those which can be tolerated in laboratory cells.

Average cathode-to-diaphragm distance has been increased from 0.7 to 1.1 inches (1.78 to 2.79 cm). The result is an increase in cell potential of 0.33 volt, but the increased power cost is more than offset by decreased labor costs. The wider spacing means better circulation of catholyte, less straightening of cathodes, and heavier deposits. In addition to the advantage of removing the cathodes for stripping less often, the heavier deposits are easier to strip and are more attractive to the prospective consumer.

Cathode plates are ordinarily type 316 stainless steel, and each plate has 7.5 ft^2 (70 dm^2) of submerged area. The area was reduced from 10 ft^2 (93 dm^2) because the larger plate with deposited chromium was too heavy to handle by hand. The cathodes measure $20\frac{1}{2}$ by 34 in. (52.1 by 86.4 cm) overall, including the hand-hole at the top. They should have been made 20 by 36 in. (50.8 by 91.4 cm) to obtain maximum utilization of standard stainless steel sheet. Aluminum cathodes with integral header bars or connector lugs are being tried on an experimental basis. The cathode shown in Fig. 1 is of this type. The integral cathode was designed to avoid the problem of protecting copper header bars from cell spray, but it is also cheaper, lighter, and easier to handle than a conventional-type cathode. Chromium deposited on aluminum has a darkened surface next to the plate, and the aluminum plates are more difficult to maintain than stainless steel, but the lower cost and lighter weight may outbalance the disadvantages. Sodium-free electrolyte does not attack the cathode plates at the solution line.

Cell Assembly

The cell is assembled by starting with an anode compartment in one corner of the cell tank and alternately placing cathode frames and anode compartments until all the frames are in place. The assembly requires one more anode compartment than cathode frame, and the two unused outside diaphragms are made impervious to solution flow. Fig. 2 is a photograph of a 10-cathode, 120-pound-per-day cell being assembled. Two anode compartments and two cathode frames are in place. The numbers are placed on the following parts: (1) top edge of anode, (2) cathode, (3) anode bus, (4) cathode bus, (5) anolyte header, (6) ventilation hood, (7) heat exchanger, and (8) flexible connection to anolyte header. The bottom supports for the frames are made of fir and are slotted to maintain the proper positions of the anode compartments and cathode frames. The slots are $2\frac{1}{2}$ inches wide (6.35 cm), and spaces between the slots are $2\frac{1}{4}$ inches (5.72 cm). This arrangement spaces the cathodes on $4\frac{3}{4}$-inch (12.1 cm) centers and leaves a $\frac{1}{8}$-inch (0.32 cm) space for each set of frames to allow for uneven frame strips. After all of the frames are in place, a top spacer bar is placed in position. This bar may be seen in Fig. 3, a photograph of the completed cell in operation. Also visible in Fig. 3 are (9) anolyte overflow, (10) catholyte overflow, and (11) immersion pH assembly. This assembly is a standard unit for indicating pH continuously and is equipped with high-temperature glass and calomel electrodes and a resistance thermometer. The cathodes shown in Fig. 3 are stainless steel, with copper header bars. The copper bars and rivets are covered with various experimental protective coatings, as follows: 1 thermoplastic resin, 5 aluminum metal spray, 2 lead spray, and 2 stainless steel spray.

The heat exchanger is fabricated of Karbate pipe and is mounted on the side of the anolyte header where the flow of catholyte is maximum. The cathode frames are elevated from the bottom of the cell tank to allow for free circulation of catholyte and to provide a space for accumulation of insoluble residue. At rare intervals large pieces of metal will separate from a cathode while still in the cell, and if a space is not provided for the metal to fall free of the frame it is necessary to shut the cell down to remove the metal before another cathode can be inserted in the frame. The space at the end of the cell is useful in assembling the cell, while both the bottom and end spaces increase the volume of the catholyte. A large catholyte volume helps to stabilize the pH, the chromium concentration, and the specific gravity.

The anolyte overflow pipe is connected to the anolyte header inside the cell, and the level of the anolyte can be changed readily by a slight turn of a pipe cap on the overflow. Correct flow of catholyte into the anolyte is obtained, ordinarily, when the level difference is about 0.3 inch (0.76 cm). Excess catholyte flows out of the catholyte overflow. Water is added to the anolyte head tank to keep the specific gravity lower than that of the catholyte.

Operating Data

The cell feed contains chromic sulfate and ammonium sulfate in the proportions existing in the alum, $(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$; the catholyte solution contains chromous sulfate, chromic sulfate, and ammonium sulfate; and the anolyte contains chromic sulfate, chromic acid, ammonium sulfate, and sulfuric acid. Typical analyses of the three solutions are shown in Table I.

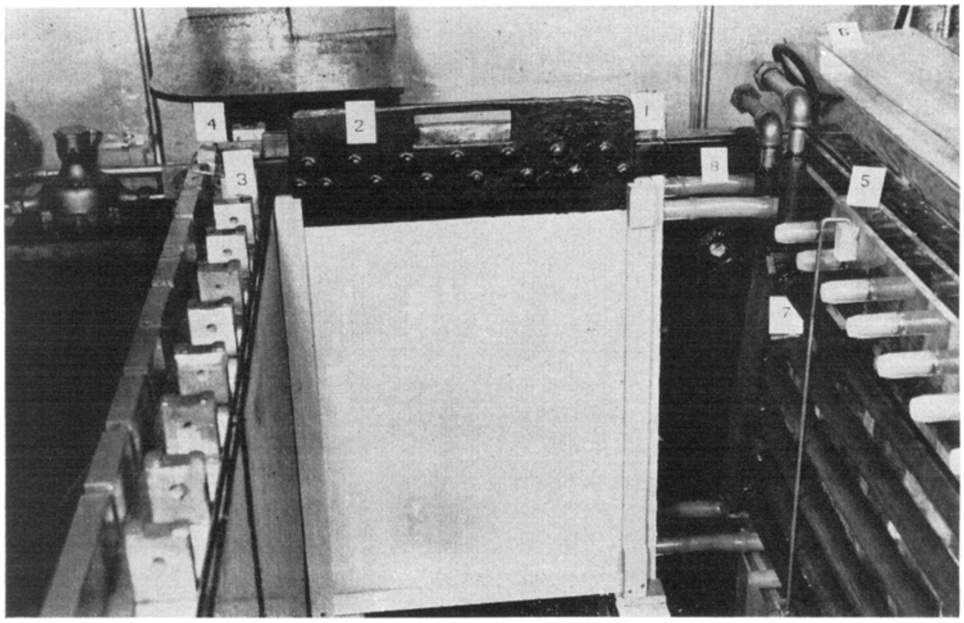

Fig. 2. Ten-cathode cell being assembled

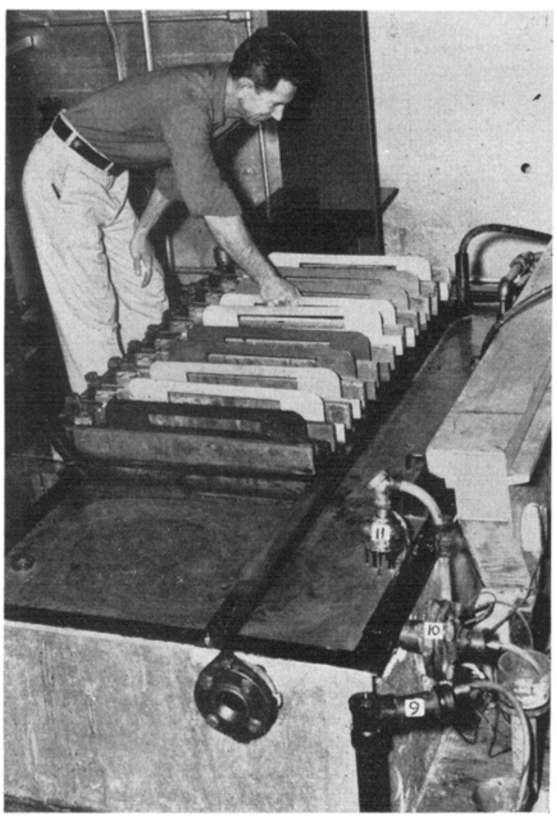

Fig. 3. Chromium electrowinning cell in operation

In addition to the essential constituents shown, the cell feed normally contains the following impurities in g/l: iron, 0.3 to 0.5; aluminum, 0.05 to 0.5; lead, 0.02 to 0.03; calcium, 0.03; magnesium, 0.01; titanium, 0.008; vanadium, 0.05; manganese, 0.01; copper, 0.001; nickel, 0.003; molybdenum, 0.0003; and silica, 0.03. Analyses of the deposited metal show 0.1 to 0.4 per cent iron and may show spectrographic traces of calcium, magnesium, aluminum, silicon, lead, and copper. A 60-pound-per-day cell has been operated for extended periods, using alum crystals and water for cell feed, but the previously prepared solution is more convenient.

A previous paper (1) described the catholyte then in use as a chromium sulfate-ammonium sulfate-sodium sulfate electrolyte, and discussed the necessity for periodically adding a soluble sulfite to obtain an adherent deposit at a reasonable current efficiency. This electrolyte produced good deposits and was used for all original development work on the process. However, the necessity for adding sodium sulfate to cell feed prepared from chromium ammonium alum proved to be an important cost item and every effort was made to eliminate sodium as an essential catholyte constituent. It was successfully eliminated partially by increasing the ammonium sulfate concentration and partially by a better understanding of the effect of such variables as catholyte temperature and rate of circulation. The mechanism whereby sulfite additions modified the character of the deposited metal in the original process has not been definitely determined but, in the quantities previously used, sulfite appears to be entirely without effect in the present process.

It is essential that the ammonium sulfate concentration of the catholyte be maintained at more than 80 g/l NH_3 for the best results. This control is accomplished by regulating the concentration of the cell feed. One advantage of the two-component electrolyte is that the ammonium sulfate concentration can be approximated when the chromium analysis and specific gravity are known. The large differential in the NH_3 concentration of the cell feed and the

TABLE I. *Typical analyses of cell feed, catholyte, and anolyte solutions, grams per liter*

	Cr				NH_3	H_2SO_4
	Total	+6	+3	+2		
Cell feed	132	Nil	132	Nil	43.2	—
Catholyte	40	Nil	17	23	90.0	—
Anolyte	22	20	2	Nil	18.0	290

catholyte is a measure of the ammonium-ion transference from the anolyte, although about 5 g/l is the result of concentration by evaporation of the catholyte. The total chromium concentration of the catholyte can vary considerably, but it is normally held at 40 g/l, plus or minus 3 g/l, to facilitate maintaining the proper specific-gravity differential between the anolyte and catholyte. An increase in chromium concentration of the catholyte increases the adherence of the metal to a minor extent, while a decrease below 35 g/l may cause a drop in current efficiency. If the chromium concentration of the catholyte is held at 40 g/l, the distribution of chromium entering the cell in the feed is 72.7 per cent plated on the cathodes, 20 per cent in the anolyte overflow, and 7.3 per cent in the catholyte overflow.

Other cell operating data are shown in Table II. The current efficiency is based on deposition from the trivalent state since the cell feed contains only trivalent chromium. The addition agent, Goulac, is a lignin sulfonate and is added to maintain a protective froth over the catholyte. Froth holds down spray and inhibits atmospheric oxidation of the divalent chromium. At the current density and current efficiency shown, a 73-hour plate will weigh 5 lb/ft² (0.25 kg/dm²) and vary in thickness from 0.15 to 0.20 inch (0.38 to 0.51 cm). If the current density is cut to 67 amp/ft² (7.2 amp/dm²), the time of deposition can be extended to 96 hours for a deposit which averages 5.5 lb/ft² (0.27 kg/dm²). The principal disadvantage of the lower current density is lower production per cell, but this may be offset by lower cell voltage and lower power costs. At 67 amp/ft² (7.2 amp/dm²) the power consumption is about 5.0 kwhr/lb of metal.

The temperature of the catholyte must be 46°C or higher for optimum current efficiency, and operation at still higher temperatures has some advantages. Tolerance of the catholyte to heavy-metal impurities, such as lead, increases, and the sulfur and iron analyses of the finished metal decrease with increasing temperature. A solution containing 30 mg/l of lead gives a current efficiency of 60 per cent at 60°C, but only 52 to 53 per cent at 50°C. The permissible pH range for optimum deposition in-

TABLE II. *Cell-operating data*

Current density	80 amp/ft² (8.6 amp/dm²)
Cell potential	4.8 volts
Current efficiency (Based on $C^{+3} \rightarrow Cr^0$)	60%
Kwhr/lb metal	5.6
pH	2.45 to 2.65
Temperature	59 ± 1°C
Time of deposition	72 to 80 hours
Addition agent	0.03 g Goulac/liter of cell feed

creases with increasing temperature and the decrease in sulfur and iron is a result of a higher operating pH. Chromium deposited at 60°C is not as bright as metal deposited at 50°C, but the deposit is more uniform.

At 60°C, a pH range of 2.3 to 2.35 results in a sulfide sulfur content averaging 0.03 per cent, while a pH range of 2.5 to 2.6 results in a sulfur content averaging 0.01 per cent. A previous paper showed that a pH averaging 1.86, at 32.3°C, resulted in a sulfur content of 0.07 per cent. Since a decrease in current density results in a decreased pH at the plating surface, any thin spots on a cathode caused by an excessively bent cathode plate results in metal which contains higher sulfur and iron than the average. The high-current-density metal on the opposite side of the plate contains less sulfur and iron than the average.

At 60°C the lower limit for pH is about 2.3. Below this limit, the current efficiency drops and deposition may completely stop and then restart at intervals, causing a striated metal. This phenomenon is caused by the fact that the instant deposition

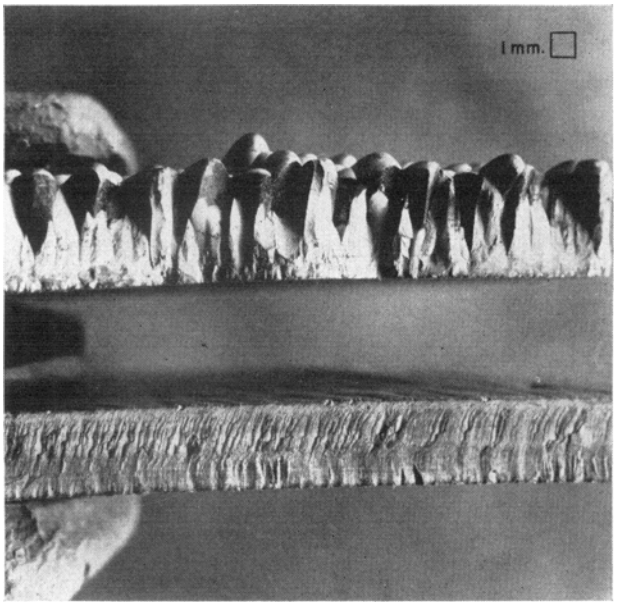

FIG. 4. Macrocamera photograph of two representative chromium deposits.

stops the increased evolution of hydrogen causes the pH to rise sharply, and deposition starts again in 10 to 30 minutes. Sharp depolarization and, later, repolarization of the cathode may be readily seen on the chart of a current-potential recorder. The upper pH limit is less sharp and operation at a pH up to 2.8 or possibly higher is not deleterious unless prolonged.

Oxygen content of the metal varies ordinarily from 0.13 to 0.32 per cent, corresponding to 0.4 to 1.0 per cent Cr_2O_3, and may run considerably higher under certain conditions. Careful control of the cell produces metal averaging about 0.15 per cent oxygen, but efforts to eliminate the oxide have not been successful. One disadvantage of Cr_2O_3 in the chromium deposit is the fact that trees or other metal which fall off the cathodes do not dissolve completely in the catholyte. At least part of the resulting residue is fine enough to remain suspended in the bath, where it may cause pits in the deposited metal. The exact mechanism of pitting has not been de-

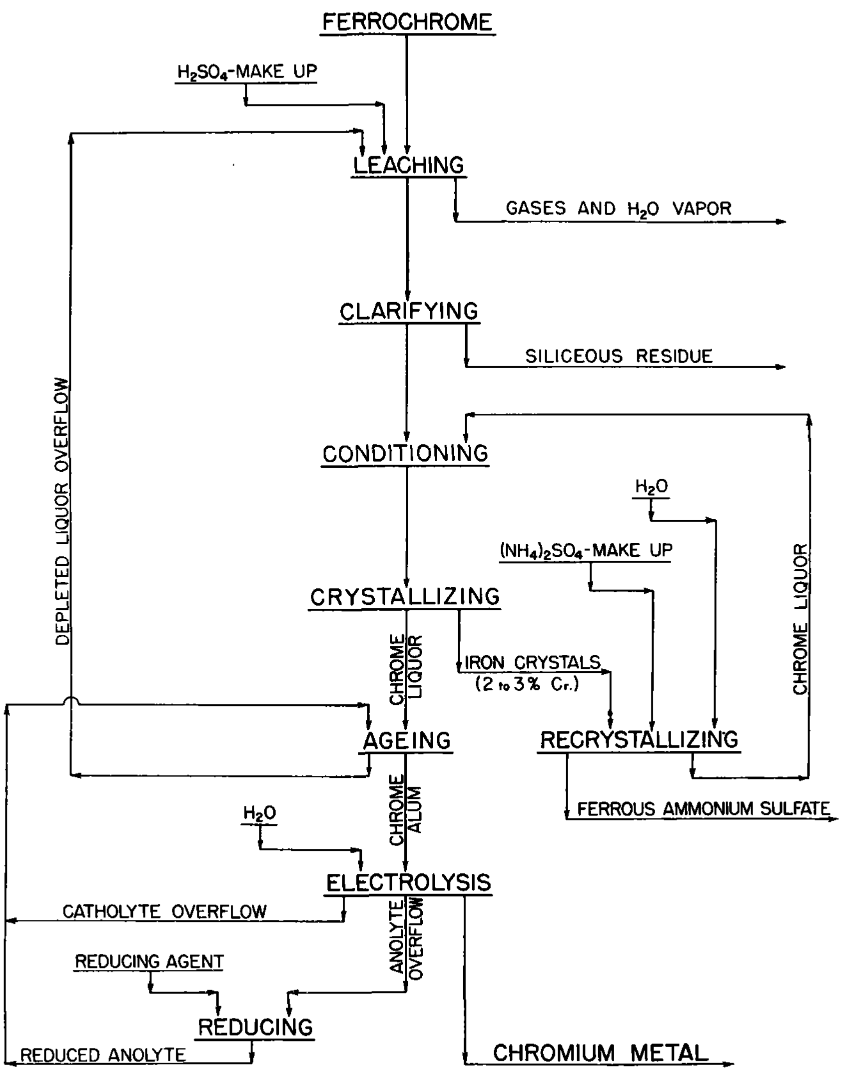

FIG. 5. Flow sheet of chromium-from-ferrochrome process.

termined, but it is believed that a suspended particle may become charged and plate out on the cathode; a funnel-shaped hole then forms with the apex on the deposited particle. This problem has been met by circulating the catholyte though a filter press, either continuously or periodically, to remove the residue. The cell may be operated for as long as ten days without filtering, and without the deposited chromium becoming noticeably pitted, but excessive pitting may start at any time. Pits tend to cause trees, which in turn fall off and cause more pits.

Oxygen in Electrolytic Chromium

All electrodeposited chromium contains oxygen (3), and the subject of the form and distribution of oxygen in chromium from the chromic acid bath has received attention by several workers. Snavely (4) gives a good review of the pertinent literature. In view of the manifest interest in the oxide occurrence, it is believed that the findings concerning oxide in chromium produced from chromium sulfate solutions would be of interest. Fig. 4, taken with a macrocamera, shows an enlarged view of two thick rough-broken, but unpolished, chromium deposits. These two samples represent opposite ends of the practical pH range; the sample on the top was deposited at the upper end of the range, and the sample on the bottom at the lower end. The high pH metal plainly shows stress cracking with dark inclusions, identified by x-ray studies as amorphous chromic oxide. Nevertheless, metal analyses consistently show less oxide in deposits of this type than in the bright, fine-textured deposits obtained at the low end of the pH range. Oxygen analyses of the samples shown were 0.15 per cent for the top sample and 0.40 per cent for the bottom sample. It will be noted that the low pH sample shows one or two striations, caused by flashing. As the number of these striations increase, the oxygen content increases. It may be concluded from the above discussion that the oxygen present in the cracks represents only part of the total oxygen.

If oxygen is attributed to the deposition of basic compounds, the upper end of the pH range would be expected to give the greatest oxide content, but the opposite is true. A precipitate caused by a high pH at the cathode surface would also be expected to contain ammonium and sulfate radicals, but no definite relationship has been noted between oxygen and either sulfate or sulfide sulfur. If the pH of the electrolyte is allowed to remain above the accepted deposition range for an extended period, basic compounds will precipitate in the solution and eventually cover the surface of the deposited metal, but this action does not appear to be the cause of the normal oxygen content of electrodeposited chromium.

Alum Preparation

Chromium ammonium alum for cell feed may be prepared directly from the ore (1), or from sodium dichromate by conventional methods, or from ferrochrome. Alum for current operations is being produced from high-carbon ferrochrome by the process flow sheet shown in Fig. 5. Detailed pilot-plant data concerning this process and the production of ferrochrome from low-grade ores will be the subject of a future publication.

Alum prepared from ferrochrome or by acid dissolution of the ore normally contains a small quantity of iron, which is deposited with the chromium, while iron-free alum is produced from sodium dichromate.

Summary

Development of a more conventional type electrolytic cell and elimination of sodium sulfate from the electrolyte has substantially decreased the cost of electrowinning chromium from chrome alum solutions. The most important economies may be listed as follows: elimination of a sodium sulfate recovery step from the cell-feed preparation flow sheet; elimination of a final aluminum-removal step from the cell-feed preparation flow sheet; a decrease in the cost of constructing the tank house by decreasing the cost per cell and increasing the production rate per cell; and a decrease in the operating labor for cell control and metal stripping. In addition to decreasing the cost of producing metal, the appearance and average purity of the chromium have been improved. Efforts to eliminate oxygen from the deposited chromium have not been successful, but some of the factors affecting oxygen content have been determined and metal containing only 0.15 per cent oxygen can be produced for extended periods.

Chromium ammonium alum suitable for cell feed has been prepared from high-carbon ferrochrome on a continuous basis.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the JOURNAL.

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