Government regulations are making it more difficult to treat the rinse waters from plating operations. Because of its toxicity, hexavalent chromium has a lower effluent limit than most other metals. The standard treatment method involves reduction of the hexavalent chromium to trivalent chromium with SO₂ or NaHSO₃, then precipitation of the chromium as chromium hydroxide with lime or sodium hydroxide. While this method can bring the effluent within EPA specifications, it produces a metal hydroxide sludge that must be disposed of in a landfill. It is better from the platers' point of view to recover and reuse the hexavalent chromium, thus eliminating the disposal cost and the future liability.

Platers have been recovering chromic acid from plating rinse waters for many years, using evaporation and ion exchange. Electrolytic recovery systems are also available, with electrodialysis allowing purification and recovery. This paper will describe another electrolytic system and will present both laboratory and field data. The objectives were to recover the chromic acid for reuse, to reduce or eliminate the water flow to the rinse system, to reduce the waste treatment and to reduce the volume of hazardous sludge.

Laboratory studies have evaluated the effect of a number of variables on the recovery of hexavalent chromium and the data are presented. Data are also presented for field tests in two commercial plating facilities. In these tests, the system has allowed us to reduce or eliminate the water feed to the rinse system and has reduced the need for waste treatment.

Experimental

The lab studies were conducted in a two compartment cell (Figure 1) consisting of anode and cathode compartments separated by a porous polymeric separator, Elramix™, (Elramix™ is a trademark of ELTECH Research Corporation) produced by
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ELTECH. A dilute chromic acid solution was pumped through the cathode compartment of the cell and the anionic chromate ions were transported through the separator into the anolyte chamber where a concentrated chromic acid solution was formed. The anode was a DSA® anode (DSA® is a Registered Trademark of Electrode Corporation), consisting of titanium mesh coated with a precious metal oxide coating. The cathode was a nickel, copper or titanium mesh. The separator area was 4 in.² and the catholyte and anolyte volumes were 125 mls. Flow rates up to 100 mls per minute were used.

A multi-compartment test cell was designed for commercial testing. The anodes were installed in PVC anode frames which had Elramix™ separators on two sides. Each frame fitted in a groove on one side of the cell and there was a half-inch gap at the other side. The gaps alternated between the right and left sides so that the rinse water flowed in a serpentine fashion from side to side as it flowed through the cell, as shown in Figure 2. Both DSA® and lead anodes were evaluated. The standard cathode material was copper mesh, but other metals and shapes have been used. The electrical connections for the anodes and cathodes were in parallel. Chromic acid solution collected in the anode chambers and exited through a manifold on the bottom of the cell and collected in an anolyte tank.

The rectifiers used for both the lab and field studies were controlled at 40 or 45 volts. The cell current was then a function of the solution conductivity, which was determined by the concentration of the hexavalent chromium. The current increased as the concentration increased.

For the lab studies, the catholyte, or waste solution, was prepared by dissolving chromic acid in DI water. The concentration was measured by titration with thiosulfate and by ICP. In the field test studies, actual rinse waters were used. For some tests, the concentration was adjusted by adding drag-out solution to the rinse.

Results and Discussion

Laboratory studies have been carried out with a two-compartment cell in which the anode and cathode are separated by an Elramix separator. Anolyte and catholyte solutions were prepared by dissolving chromic acid in deionized water to obtain the required concentration. Figure 3 shows the effect of the anolyte and the catholyte concentrations on the recovery of the chromium under the standard operating conditions of 100 mls/min, flow and 45v. Anolyte concentrations of 1 to 300 gpl CrO₃, and catholyte concentrations of 25 to 500 ppm Cr(VI) were used in the study. The anolyte was recirculated through a 1 liter reservoir to maintain the concentration during the test.
The Single Pass Recovery (%SPR) is calculated as shown below;

\[
%\text{SPR} = \frac{(\text{inlet conc.} - \text{outlet conc.})}{\text{inlet conc.}} \times 100
\]

This is the recovery under the operating conditions of the cell and varies with changes in the cell voltage and flow rate. The slide shows that the SPR decreases as the anolyte concentration increases and as the catholyte concentration decreases. However, at low anolyte concentrations, the SPR is almost independent of the catholyte concentration. It is possible to produce an anolyte at the plating bath concentration, but only for high catholyte, or rinse water, concentrations. Tests were terminated before the anolyte concentration changed significantly.

It is possible to reduce the Cr(VI) concentration to very low levels by recycling the catholyte through the cell. Data in Figure 4 show that it is possible to meet the EPA specifications for effluents, but only with low anolyte concentrations and with multiple passes through the cell. A 300 mg/l Cr(VI) solution was passed through the cathode compartment and collected. It was then passed through again, the concentration being determined at each pass. The effluent concentration was 0.04 mg/l after nine passes with the 1 gpl anolyte. At the higher anolyte concentrations, the effluent concentration stabilized at 2.5 and 4.5 mg/l. The %SPR was 60 to 70% for each pass through the cell, but because of the low concentration, the overall recovery rate was very low. Very low effluent concentrations are only practical when adequate time is available to recycle the effluent.

The recovery rate is affected by the flow rate through the cell. An increase in the flow rate will cause the SPR to decrease (Figure 5). The starting catholyte concentration was again 300 mg/l Cr(VI) and a 1 gpl anolyte concentration was used. When the flow is doubled, the SPR decreases by about 50% for the two-compartment cell and the total recovery appears to be independent of the flow rate.

A series of tests with controlled current showed that the recovery was directly dependent on the cell current (Figure 6). The anolyte concentration was controlled at 1 gpl by recirculating through a 1 liter reservoir, and the catholyte was maintained at 460 mg/l. The current was controlled by varying the cell voltage. As the current increased, the SPR increased. To maximize the recovery, the cell should be run at the maximum voltage. At high rinse water concentrations, this will result in the maximum cell current and a reduced voltage. But, over the normal rinse water concentration range, the cell voltage will be the maximum and the current will be dependent on the concentration.

Two field tests were set up at Advance Plating and Woodhill Plating in Cleveland, Ohio. Initially, a RETEC 07 test cell was used. This cell has seven anode
chambers with a separator area of 4 ft\(^2\). The cells have been operated at flow rates of 0.5 to 0.6 gal/min., at 45v with a maximum current of 60 amps. This system used both DSA\(^\circ\) and lead anodes, but the lead was not stable. Both copper and titanium cathodes have been used.

During cell operation, the efficiency for electrodeposition is very low and the predominant reaction at the cathode is the reduction of water with the formation of hydrogen gas and hydroxide ion. Because the cell is separated, the hydroxide causes an increase in the catholyte pH. Trivalent chromium, and other metal impurities which are dragged out of the plating bath, precipitate as metal hydroxides in the cell. While the hydroxide sludge can be filtered, we have found it to be more convenient to settle it out. For the small 07 cell, we have used a 30-gallon settling tank and have collected about 0.5 lbs. of sludge per week at Advance Plating. This material is the sludge that would have been formed from the trivalent chromium and other tramp metals during waste treatment. The sludge that would have been produced from the hexavalent chromium has been eliminated. The preferred arrangement is to place the cell higher than the rinse tank, pump to the cell, then flow by gravity from the cell to the settling tank, then by gravity back to the rinse tank. Figure 7 shows a typical composition for the sludge collected from the Woodhill test.

Woodhill used three rinse tanks with counter-current flow at 2 gal/min. The recovery cell was fed from the first rinse tank and recycled to the third rinse at 0.5 gal/min. The water addition to the rinse system was terminated. The rinse tank and test cell arrangement is shown in Figure 8.

The second test was run on a replate line at Advance Plating which has two rinse tanks, not counter-current, with 2 gal/min. water flow to each (Figure 9). The cell was installed on the first tank, recycled at 0.6 gal/min., and the water flow to the rinse tank was stopped.

When the cell was run overnight, the concentration of chromium in the rinse water decreased and reached its lowest level at the start of the plating shift. It then increased throughout the day and was dependent on the work load. As the concentration increased, the cell current also increased. Figure 10 shows the cell current vs the concentration in the first rinse. At high concentration, the current reaches 35 amps with a cell voltage of 45v.

The next figure (Figure 11) shows the SPR and the total chromium recovery vs the rinse concentration for the Woodhill test. The SPR decreases with increasing concentration, but the total recovery increases with increasing concentration. The recovery reached a maximum of over 11 gms/hr. in this test.
Over a 24-hour period, with one shift operation at Woodhill, the concentration in the first rinse increased to 97 ppm Cr, but overnight it was reduced to 20 ppm, ready for the start of the next shift (Figure 12). The graph also shows the concentration over a 24-hour period for single-shift operation at Advance Plating. The peak concentration is acceptable for a one shift operation, but a second shift would increase it to an unacceptable level for good rinsing. The small 07 cell is acceptable for a one shift operation in this size plant, but is probably not acceptable for a two shift operation.

Following the encouraging field-test results, a Model 6 cell was designed to handle larger rinse systems. This cell has six anode compartments with 20 ft.\(^2\) of separator, a flow rate of 2 to 4 gal/min., and a maximum current of 250 amps at 40v. It has been tested in the same two plating facilities. The next two graphs (Figures 13 and 14) show the SPR, cell current and chromium recovery vs. the rinse concentration for two flow rates. At the low flow rate, 2 gal/min., the cell current increased with increasing concentration, but at about 100 ppm it reached the rectifier limit of 225 amps and remained steady. The SPR was stable until the cell current reached a maximum and then declined slowly. The total recovery continued to increase, but at a low rate after the current stabilized. At the higher flow of 4 gal/min., the cell current reached its maximum at about 200 ppm Cr. The SPR was reasonably constant over the complete range and the total recovery increased in step with the current. The higher cell current for the 2 gal/min. flow was a result of the higher cell temperature, and higher conductivity, which resulted from the lower flow. In a recycle system where total recovery is important, the flow should be as high as possible for maximum recovery. However, when the outlet concentration is important, a low flow rate will be better.

The 24-hour concentration profile for the RETEC 6 shows that the rinse concentration stabilizes in a narrow range and is independent of time (Figure 15). It would maintain the same range over a two or three shift day and is therefore more effective than the smaller cell.

The higher flow rate in the Model 6 cell makes it impractical to use a settling tank. A packed bed clarifier was developed which has given satisfactory results and kept the precipitated hydroxides out of the rinse system.

The cost for recovery of chromic acid has been calculated using the data depicted in Figure 14. This covers a concentration range of 65 to 210 ppm Cr(VI) at a flow rate of 4 gal/min. and a cell voltage of 40v. The power required was approximately 38 KWH per lb. of chromic acid over the whole concentration range and the cost was about $3.00 per lb. at an electricity cost of $0.08 per KWH. This does not include a factor for the inefficiency of the rectifier. To offset the cost of recovery, we have to consider the replacement cost of the chromic acid, the cost of rinse
water (600 gal. per lb. at a concentration of 100 ppm Cr(VI)), treatment chemicals and solid waste disposal.

Conclusion

In conclusion, an electrolytic cell has been developed for the recovery of hexavalent chromium from plating rinse waters. Chromic acid has been recovered and reused in the plating bath. Fresh water addition to the rinse tanks has been eliminated. Chemical treatment is no longer required for the dragout from the plating system, and the volume of hazardous waste has been significantly reduced.
Figure 1. Chromium Recovery Laboratory Cell
Figure 2. Commercial Chrome Recovery Cell
Figure 3. Recovery Rate vs. Concentration
Figure 4. Reduction to EPA Limit
Figure 5. Effect of Flow Rate on Recovery
Figure 6. Effect of Current Density

Anolyte Conc. 1 gpl; Catholyte Conc. 460 ppm
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Figure 7. Composition of Woodhill Sludge.
Figure 8. Woodhill Rinse System
Figure 9. Advance Rinse System
Figure 10. Effect of Concentration on Current.
Figure 11. Effect of Concentration on Recovery.
Figure 12. Rinse Water Concentration, 40 Hours.
Figure 13. Effect of Concentration, 2 Gal/Min.
Figure 14. Effect of Concentration, 4 Gal/Min.
Figure 15. Rinse Water Concentration, 40 Hours.