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# CEP

## CHEMICAL ENGINEERING PROGRESS

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### THE ELECTROLYTIC PROCESS FOR CHROMATE REMOVAL IN COOLING TOWERS

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## POLLUTION CONTROL PRACTICES:

# The Electrolytic Process For Chromate Removal In Cooling Towers

**This process is the least expensive and the most efficient way of removing chromate to meet the regulations of federal, state, and local pollution control agencies.**

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Water is wasted from cooling tower systems to prevent deposition and fouling. This blowdown water contains all the constituents that are in the cooling tower water itself such as, suspended solids, metals oxides, concentrated salts, dispersants, and corrosion inhibitors. Processing the blowdown water before discharging is necessary in order to meet environmental discharge regulations.

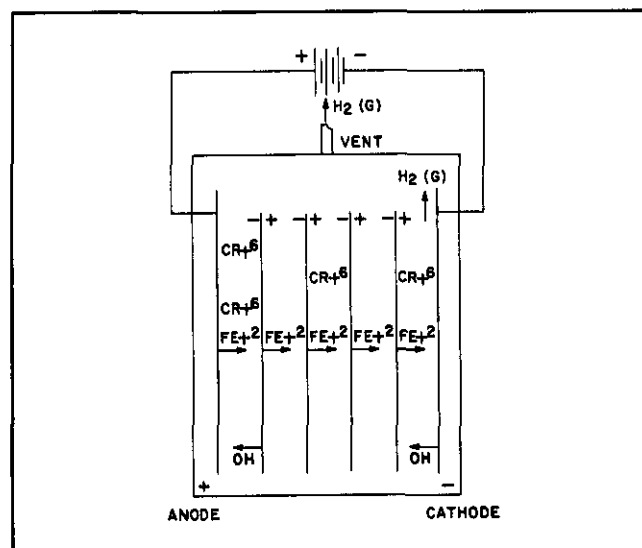
Chromates are widely used as a corrosion inhibitor in cooling water. The results of chromate usage are excellent,

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but in recent years chromates have been considered a very toxic water pollutant. Environmental regulations limit chromate discharge to a maximum level of 0.05 ppm as hexavalent chromium in drinking water. The National Pollution Discharge Elimination System has imposed a 1.0 mg/L total chromium limit on the plant effluent of First Chemical Corp.

The process to be engaged for removal of chromates must be economical, efficient, easy to operate and easy to control. The electrolytic process can satisfy these requirements.

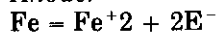
Recent estimates have indicated that over \$70 billion is spent in the United States annually as a result of corrosion (1). The main problem that corrosion causes is the destruction of equipment and the subsequent cost of equipment replacement and plant operating downtime. Therefore, it behooves industry to find the most effective and economical corrosion inhibitor to prevent this avoidable expense.



**Figure 1. Electrolytic process.**

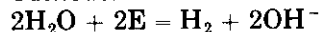
**Table 1. Electrochemical process reactions.**

### Anode:



Iron = Ferrous Ions + Electrons

### Cathode:

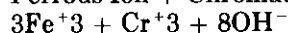


Water + Electrons = Hydrogen + Hydroxyl Ion

### Fluid:

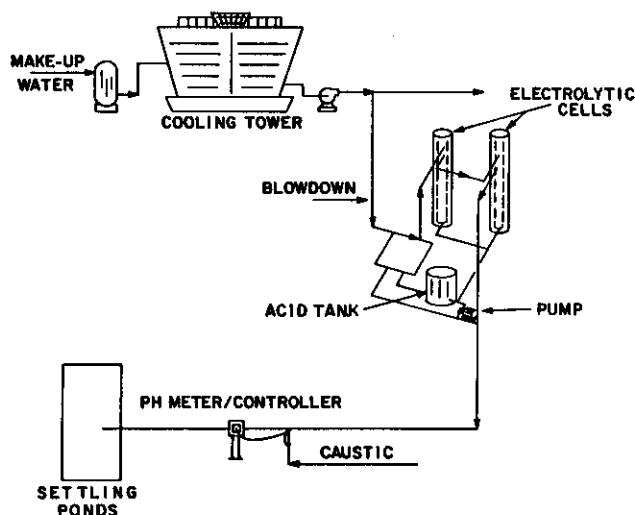


Ferrous Ion + Chromate Ion + Water =



Ferric Ion + Chromic Ion + Hydroxyl Ion

**Figure 2.**  
Cooling water  
blowdown.



Chromate, the most effective and economical corrosion inhibitor, is employed by First Chemical Corp. We are consistently achieving less than 1 mil per year corrosion rates from the application of chromates.

Chromate is an anodic corrosion inhibitor that form a passive film of ferric and chromic oxide. When the film is formed, there is no difference in electrical potential between the anodes and cathode areas, and corrosion stops.

Although chromate corrosion inhibitors are very effective in the cooling systems, they are considered very toxic water pollutants. In order to use chromates for corrosion control, we had to apply the electrolytic metal removal process to allow the continued use of chromate without violating discharge regulations.

A small current (amps) is passed through cold rolled steel plates (electrodes) anodes and cathodes to produce ferrous hydroxide, Figure 1. Chromate is reduced from the hexavalent form to the insoluble trivalent chromium by the ferrous hydroxide, Table 1. Theoretically, 3.22 lb (1.46 kg) of iron would be used to reduce 1 lb (0.45 kg) of hexavalent chromium to the trivalent state.

The ferrous, ferric and chromium hydroxide, which forms, are colloidal and gelatinous. These precipitates and other solids tend to collect on the plates and interferes with the flow of water between them. They also can cause an insulating film that can prevent the generation of ferrous

ions to make the electrolytic process possible. To alleviate the problem, the plates are washed daily with 8–10%  $H_2SO_4$  to remove the insulating film. This particular acid is used, since it is the least expensive and easy to obtain. It is a by-product of the nitration process which we operate.

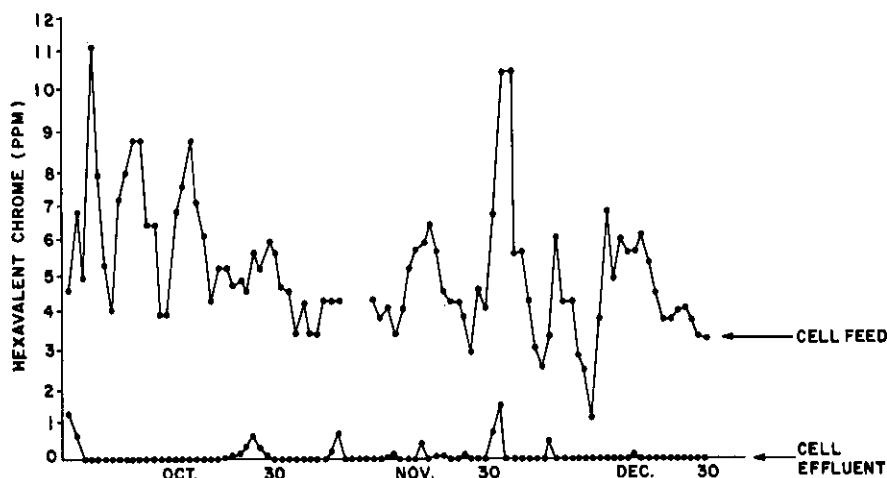
### Performance and operation

Cooling water blowdown at the rate of 50 gpm (3.2 L/s) is taken from the cooling tower exit line. This is the feed for the electrolytic process. The feedwater has a 6.3–6.5 pH, conductivity of 300–500 mohm and chromate residual of 10–15 ppm (chromium 4.4–6.7 ppm), Figure 2.

The amperage, which indicates the strength of the current applied to the anodes and cathodes of the plates, depends on the amount of chromate and the flow rate of the feedwater. If the flow rate or chromate level are not uniform or synchronized with the amperage, complete reduction of chromate will not be obtained. The amperage of the unit should be adjusted regularly depending upon the flow rate, chromate in the feed, and the amount of hexavalent chromium in the effluent.

The electrodes (plates) are bipolar; so in order to have uniform dissolution of iron, the current is reversed once a day. The current reversal prevents the possibility of buckling of the electrodes which could cause shorting between

**Figure 3.**  
Amount of  
chromium on  
settling pond.



adjacent electrodes and mechanical difficulties in removing a worn electrode from the cell (2).

Due to the precipitates, the formation of insulating iron oxides and other solids that tend to cling to the plates, it is necessary to wash the plates with 8–10%  $\text{H}_2\text{SO}_4$ . Acid washing once a day keeps the plates in good condition and free of any matter that might build up and decrease the efficiency of the unit.

Numerous phenomena occur that will indicate the need of a plate change as follows:

1) *Voltage*. An increase in voltage shows that the plates are spent.

2) *Unit Effluent*. If the hexavalent chromium in the effluent increases, but no change was made in flow rate and chromate residual, it is time to change.

3) *Amperage*. There is no change in flow rate or chromate residual, but the amperage has to be increased to try to complete the reduction of chromate.

4) *Amperage Hours*. A log of the amperage hours will give an indication of the life of the plates at a given time and at uniform conditions.

The plate change requires approximately two hours with two employees. If the spent plates are torn, it is possible that stray pieces of metal may still be in the cells. If the stray metal is allowed to stay in the cell after the plate replacement, the voltage will remain low. A magnet can be used to get the stray metal out of the cells to alleviate the problem of low voltage. Before the unit is put back in service after plate replacement, the plates are acid washed to remove any oil film that can decrease the efficiency of the unit.

The unit effluent contains suspended iron and chromium hydroxide, zinc hydroxide, phosphate and silt, the settleability and precipitation of these materials can be enhanced by the addition of  $\text{NaOH}$ . A pH controller is installed in the discharge line to insure that the effluent pH is adjusted to 11 pH and high-pH boiler blowdown is added to the settling pond. The settling pond effluent is pumped to the plant final effluent tank to help maintain the 6–9 pH.

Data have proven that the total chromium of the pond will change as the pH decreases or increases in the pond. The settleability of the trivalent chromium is decreased as the pH of the pond water drops below 10 which in turn causes the total chromium to increase in the pond.

Once per day, the effluent from the unit is tested as part of a regular control routine to make sure the effluent is maintained at a less than 1.0 ppm chromium level. A sample of the effluent is taken and processed using a spectrophotometer. A proportional pink coloration develops, if hexavalent chromium is present when 1,5 diphenylcarbonhydrazide is added. High absorption of 540 nm wavelength is proportional to color intensity. Also, total chromium is determined daily on the settling pond, Figure 3.

## Economic and environmental factors

After operating round-the-clock for years, the unit has performed efficiently and very economically. The electrolytic process has provided a substantially lower investment and operating cost as compared to using other processes to remove chromate such as ion exchange or chemical reduction. It is estimated our unit uses 5 kWh/lb (40 MJ/kg) of chromium removed. Electrode usage is approximately 3.22 lb (1.46 kg) of iron per lb (0.45 kg) of chromium. The operating cost is approximately 85% plate (electrode) replacement and 15% power. Total cost of reducing the chromate is \$0.50/1,000 gal (\$0.13/m<sup>3</sup>) of cooling tower blowdown treated.

We feel that the electrolytic unit is the most feasible means of achieving a low treatment cost and still meet the requirement of the NPDES permit.

The chromic and ferric hydroxide mixture appears as suspended solids in the electrolytic chromate removal process. These solids must be removed from the unit effluent.

A lagoon or pond is the least expensive means of clarification, since the solids settle quite well if given ample retention time and the pH of the lagoon water is high enough to keep these solids settleable.

The ultimate sludge disposal is dependent on local conditions and regulations. The new EPA regulations for the disposal of hazardous waste as stated by the Resource Conservation and Recovery Act has established guidelines to determine if a solid waste is hazardous.

"In the case of sludge generated by the Andco process in treating cooling tower blowdown, the sludge has only to pass the EPA toxicity test to be considered non-hazardous." The EPA toxicity test is an extraction procedure at pH 5 using acetic acid. The sludge is considered non-hazardous if the leachate contains less than 5-ppm chromium (3).

Andco asked EPA how this will affect sludge disposal. EPA stated: "Since our sludge is not considered hazardous, disposal in non-secure landfills, municipal garbage dump or even on-site would be permissible. Such disposal is, of course, subject to local and state regulations in force." (3)

## In summary

Faced with a demanding NPDES permit, we chose to use the electrolytic metal removal process for the treatment of chromate in cooling tower blowdown. The blowdown contains 10–15 ppm chromate or 4.4–6.7 ppm chromium which cannot be discharged untreated from the First Chemical Corp.

The electrolytic process consists of sacrificial iron electrodes that have direct current applied to the electrode's anodes and cathodes to produce ferrous hydroxide. Chromate is then reduced from the hexavalent form to the insoluble trivalent state by the ferrous hydroxide.

The electrolytic process has consistently removed chromate to less than 0.05-ppm chromium. It operates at an estimated cost of \$0.50/1000 gal (\$0.13/m<sup>3</sup>) of cooling tower blowdown treated.

The electrolytic process is the least expensive and the most efficient in removing chromate in order to meet the regulations of federal, state and local pollution control agencies. #

## Acknowledgment

The author wishes to express his appreciation to First Chemical Corp. for allowing this technical information to be presented at the AIChE meeting. Special thanks is extended to John Heil and Bob Barker for the corporate emphasis given to achieving compliance with all environmental standards. Additionally, Earl Adams and Johnny Smith have assisted greatly in the preparation of data and schematics presented in this article.

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T. Taylor, a utility and wastewater treatment supervisor for First Chemical Corp., earned an associate degree in environmental technology at the State Technical Institute at Memphis. He is experienced in the treatment of boilerwater and cooling water as well as the treatment of organic waste.