

CHROME REDUCTION AND REMOVAL OF HEAVY METALS
IN THE PRESENCE OF CHELATING AGENTS

In the electroplating industry the use of electroless solutions has increased tremendously over the past years. These electroless solutions use complex chemicals commonly called chelating agents. The reaction occurring between the chelating agents and the metal ions is frequently called chelation.

Chelation is an equilibrium reaction between a metal ion and a complexing agent. The reaction is characterized by the formation of more than one bond between the complexing agent and the metal. Molecules called ligands form covalent bonds with the metal ions creating a ring around the metal, thus restricting any reaction between the metal and other ions in the solution.

Chelating agents such as phosphates, ammonia, and EDTA are commonly used in cleaning and electroplating solutions. Some of the various functions of these chelates are:

1. To hold a large reserve of metal ions in the soluble form.
2. To increase the current density of the plating solution.
3. To control the deposition of the metal, improving the physical characteristics of the deposit.
4. To keep impurities in solution so they do not plate out with the desired metal.

In some cases, particularly in the presence of strong chelating agents, special treatment is necessary in order to remove the bound metals. Chelated metals such as nickel and copper can only be replaced by some material capable of forming an even stronger bond. The effectiveness of these complexing agents to hold metals in solution inhibits the ability to efficiently treat wastewater.

As we move through 1985, electroplaters are faced with the responsibility of cleaning up wastewater. In the years to come, the effluent point source limitations for effluent discharge will only become more stringent. The time is upon us, platers are forced to look at new technologies for the removal of heavy metals, specifically in the presence of chelating agents. Wastewater treatment by the addition of lime or caustic soda to adjust the pH in the range of low metal solubility is not effective when chelating agents are present. Waste streams containing strong chelating agents must be segregated from other waste streams to prevent chelation with free metals in solution. The use of ferrous sulfate treatment will effectively break the ligand-metal bond to allow precipitation of heavy metals. In the process, the ferrous ions successfully break the chelating ring. However, excess ferrous sulfate must be present in order to drive the precipitation reaction to completion and the cost of ferrous sulfate is high in comparison with the other hydroxide precipitating agents. The disposal of the metallic sulfide sludge may also pose a problem. This type of treatment is not practical in parts of the country where the amount of sulfates in wastewater are restricted.

The actual reaction occurring between the ferrous sulfate and the complexing agent is not entirely understood but it is known that the ferrous ion is the active agent in the reaction. A few of the theories regarding the reaction between ferrous ions and the chelating compound are as follows:

1. A replacement reaction occurs between the ferrous ions and the chelated metal ion. In this process, a ferrous ion physically replaces the metal ion allowing precipitation of the metal as a hydroxide.
2. The ferrous ion acts as a reducing agent, reducing the chelated compound to its unstable state allowing the metal to be precipitated from the solution.

Although the mechanism of the reaction taking place in the above theories is unknown, it can be concluded that the introduction of the ferrous ion during treatment will achieve metal concentrations well below the limits of wastewater discharge.

One method of wastewater treatment that is commercially available today is the GT Column that generates activated ferrous ions into the wastewater stream. This unique technology was developed 8 years ago specifically for the use of chrome reduction to get away from the use of toxic SO₂ gas or bisulfite metering. The destruction of chelated compounds was not then considered, however, experimental data showed that the activated ferrous ions generated in the GT Column did effectively and economically eliminate heavy metals in the presence of chelating agents.

CHROME REDUCTION

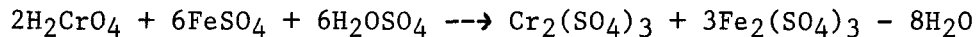
SYSTEM CONCEPT

The GT Column is a chrome reduction system that eliminates the need for SO₂ gas or the metering of sodium bisulfite into chrome streams to reduce hexavalent chrome (Cr⁺⁶) to its less toxic trivalent (Cr⁺³) state. Chrome waste effluent is acidified in a chrome collection tank before entering the column. After exposure to the GT Element activated ferrous ions are produced which in turn reduces hexavalent chrome to its trivalent state with the following reaction:



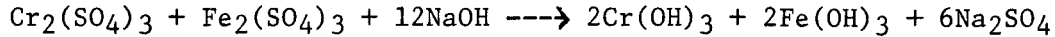
This reaction differs from ferrous sulfate and generates far less sludge.

FeSO₄ reduction & reaction:



The solution then discharges into a neutralization tank for proper pH adjustment by sodium hydroxide or calcium hydroxide:

GT Column Precipitation



FeSO₄ Precipitation



Flocculant can be added before the stream enters the clarifier, where the hydroxide sludges rapidly separate. Metals that are difficult to precipitate alone, such as cadmium, zinc, and copper are more easily co-precipitated with the active ferrous ions produced by the GT Column. It has also been found that the activated ferrous ions generated in the column have broken chelates from printed circuit board shops and aided in precipitating the copper ions.

Typical Application for Chrome Concentrations up to 500 ppm

When a system is set up to process a chrome stream with concentrations up to 500 ppm (figure 1), the stream should pass through the GT Column.

A chrome collection and acidification tank collects the chrome stream. An acidification system with pH probe, monitor, and acid feed meter pump (H₂SO₄ or HCL) is used to continuously monitor and lower the pH before the stream reaches the column. The incoming stream is mixed mechanically to lower the pH to a satisfactory level (see table 1). When the solution in the tank fills to a high enough level, it activates a level switch, which turns on a column pump that takes suction through a fine filter. The pump sends the solution through a flow control valve and a check valve to the column. (The check valve prevents backsiphoning from the column when the column pump shuts off. The solution must cover the GT Element at all times to prevent oxidizing).

GT Column

Table 1. Collection and Acidification Tank pH Levels

| Cr+6 PPM | pH |
|----------|-----|
| 10..... | 2.4 |
| 25..... | 2.2 |
| 50..... | 2.0 |
| 100..... | 1.8 |
| 250..... | 1.6 |
| 500..... | 1.4 |

The GT Column pump sends the stream into the column inlet and down through a central pipe to the bottom chamber below the perforated plate. This influent then rises through the filter mat and GT Element where the chromium reduction takes place. The column level rises until it reaches the outlet pipe where it discharges by gravity to a reaction or neutralization tank for proper pH adjustment.

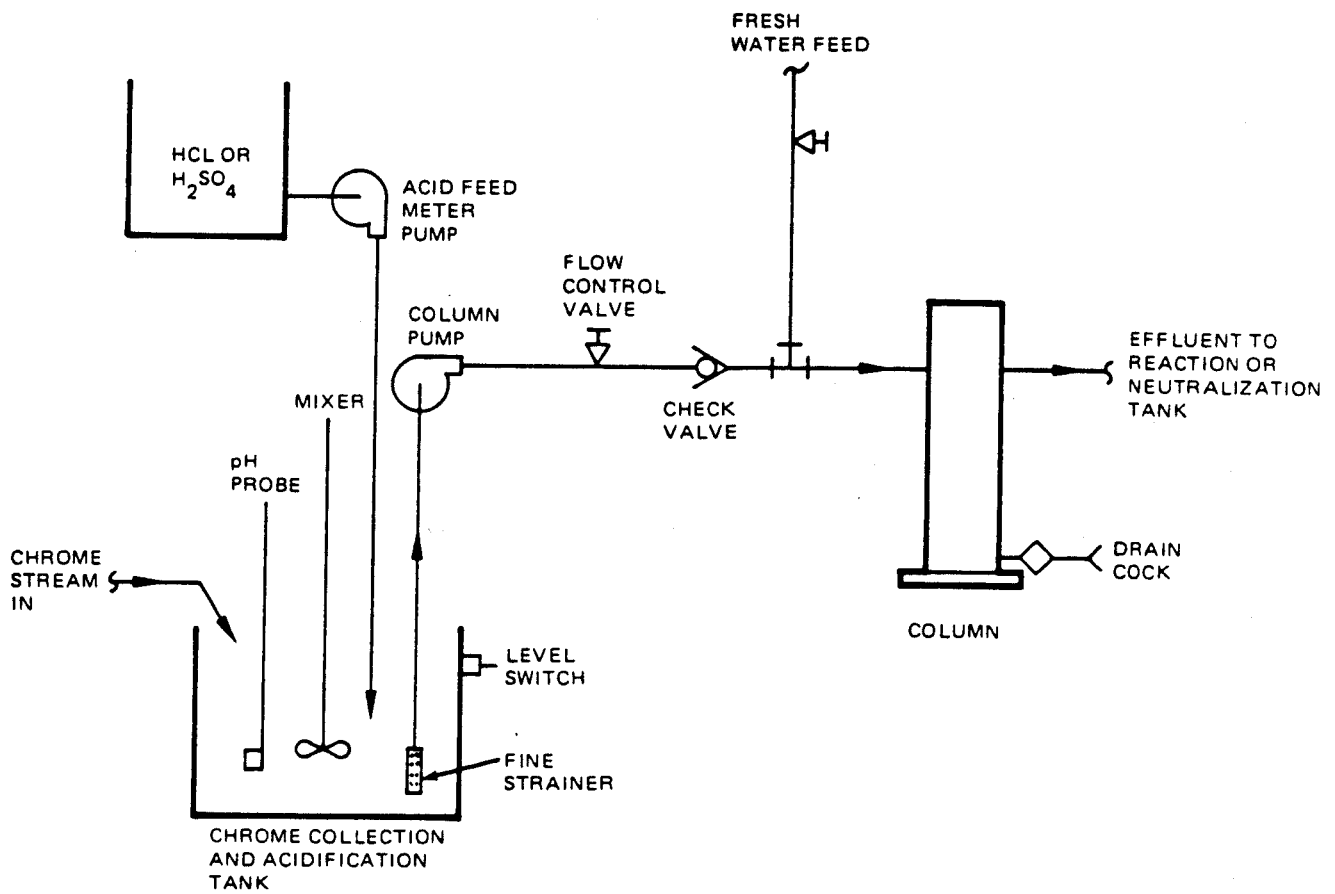


Figure 1 - Flow Diagram for Chrome Concentrations up to 500 ppm

Typical Slip Stream Application

When chrome stream concentrations are below 20 ppm, it is advisable to use a slip stream method, saving considerably on acid and alkaline cost.

In this method, 15% of the stream is acidified and diverted to the GT Column as shown in figure 2. Excess ferrous ions are liberated and exit with the CR^{+3} . The main stream and column effluent are then mixed in a reaction tank, where excess ferrous ions from the column react with the CR^{+6} and are reduced to CR^{+3} . As the reaction tank fills, it eventually overflows into the neutralization tank by gravity.

The reaction tank should have all the rinse streams passing into it before neutralization. This will allow any CR^{+6} that may come from floor spills or occasional rinses to react and be reduced. Mixing column effluent with other metals, such as zinc, cad, lead, copper, etc., prior to neutralization, helps in co-precipitating to low limits.

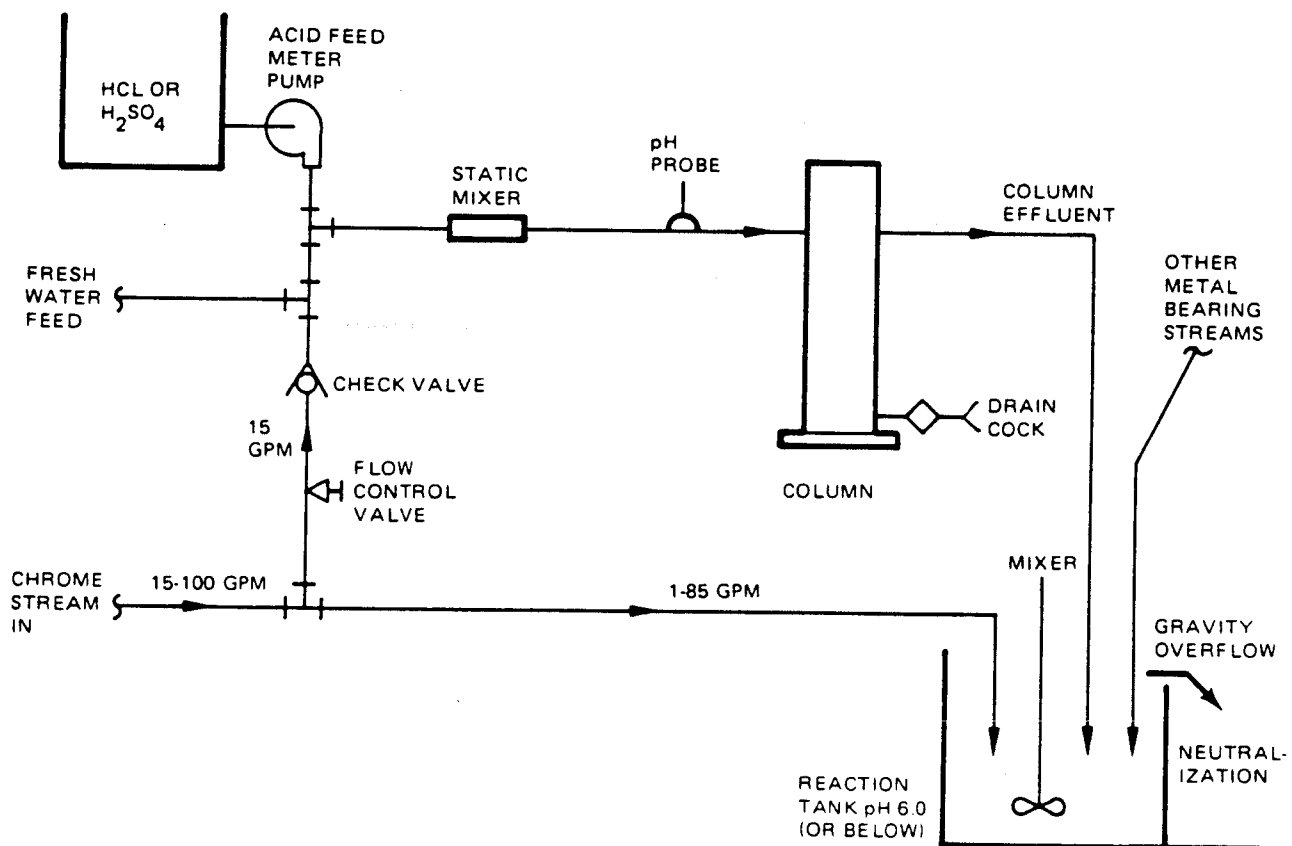


Figure 2. Flow Diagram for Slip Stream Method

Alternative Bypass Application for PCB Manufacturing

Copper is very difficult to precipitate in waste streams from printed circuit board (PCB) manufacturing due to chelating from ammoniated etches and electroless copper baths, heavy concentrations can be cut to a lesser degree. Maintaining a good squeegee system on the etcher also helps reduce its dragout. These methods will reduce chelate concentrations to levels that can be handled by the column effluent also helps to co-precipitate other metals, such as lead and tin.

By placing a reaction tank in the main stream before neutralization (as shown in Figure 3), the column will discharge it into the reaction tank at 15% of stream volume. Secondly, if chrome is used to desmut, the column can be set to pull the chrome rinse through the column and discharge it to the reaction tank. This would reduce the CR^{+6} and create ferrous ions at the same time, which in turn will break chelates so copper will precipitate in clarifier.

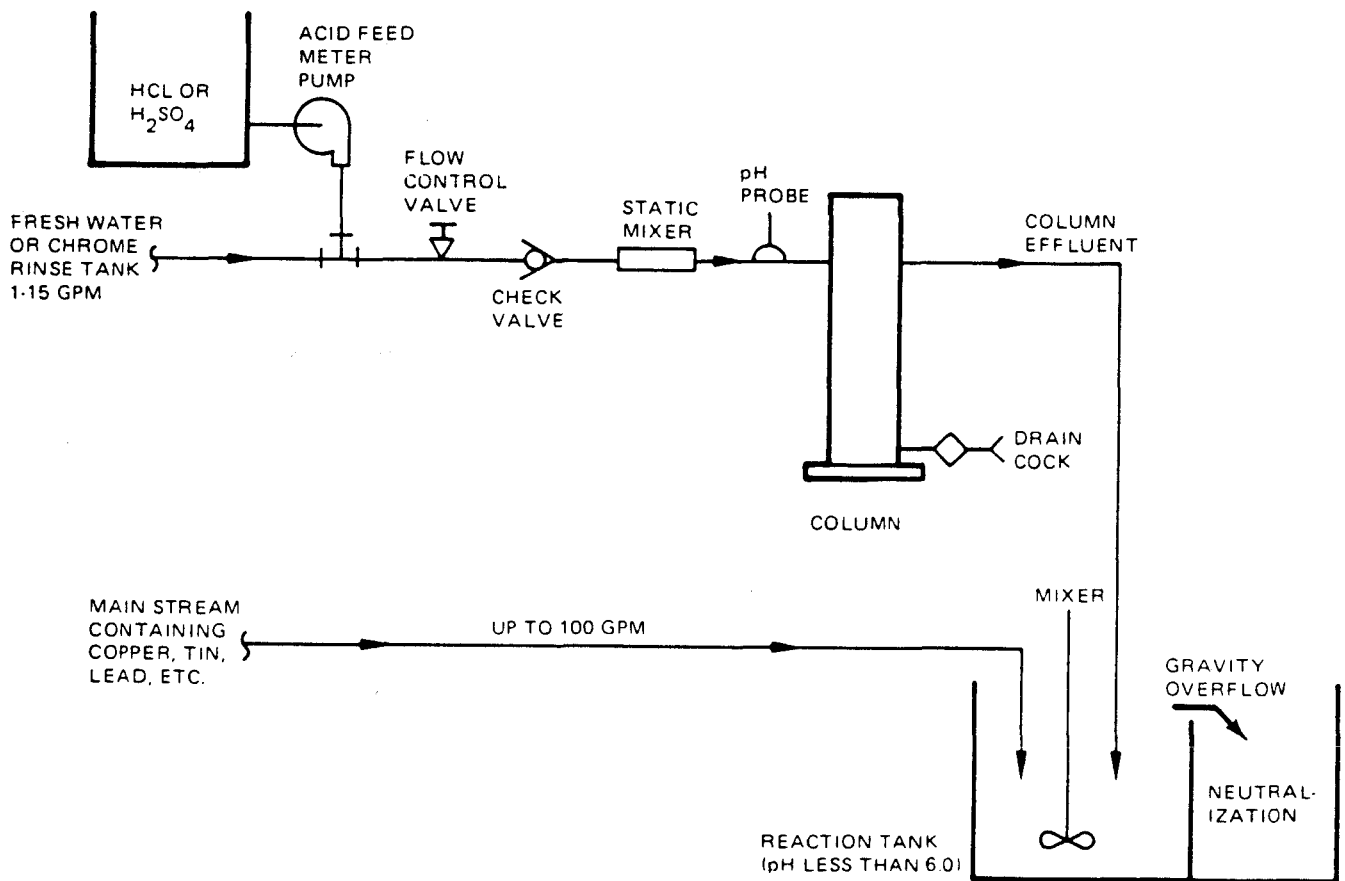


Figure 3. Flow Diagram for Alternate Bypass Method.

The capital cost of the Equipment Associates GT Column is equivalent or less than that of conventional bisulfite reduction. With the GT Column, ORP monitor and probe, bisulfite mixing tank, mixer, and metering pump need not be purchased or maintained. No SO₂ fuming will have to be dealt with in mixing metabisulfite powder with water.

Operation costs are equivalent to that of bisulfite reduction of chrome with less maintenance costs due to no chemical mixing, ORP standardizing, or metering pump maintenance.

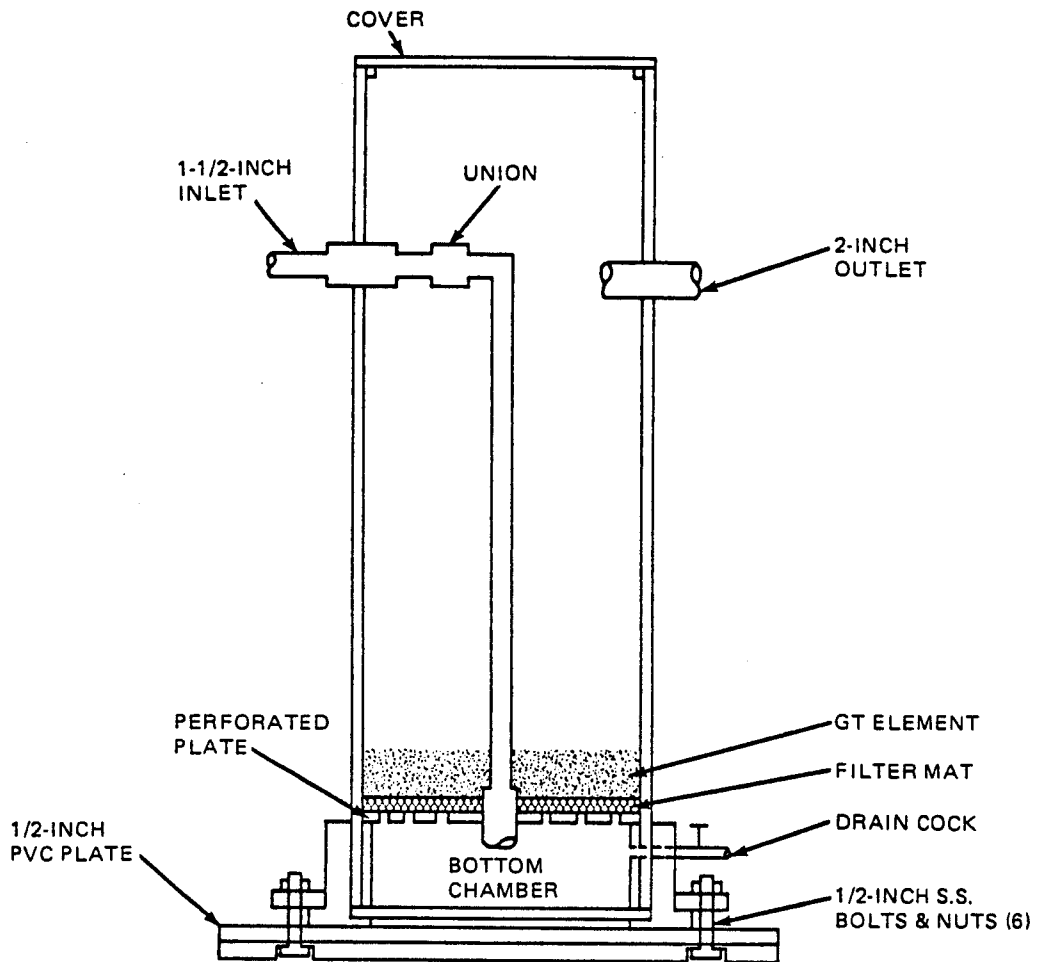


Figure 4. GT Column Cross Section View

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