Process Controls SalesNet
pH and ORP Applications

Chrome Waste Treatment

Measuring and Controlling pH and ORP Levels

Background
Measuring and controlling pH/ORP levels in chrome waste treatment process is necessary for control and destruction of toxic chemicals as well as ensuring conformance to regulatory requirement for effluent monitoring. However, a significant reduction in chemical usage, resulting in cost savings can also be realized by measuring and controlling pH and ORP levels in chrome waste treatment.

Chromates are used as corrosion inhibitors in cooling towers and in various metal-finishing applications, including bright dip, conversion coating, and chrome plating. The resulting wastewaters from rinse tanks, dumps, and cooling tower blowdown contain soluble chromium ion, Cr^{6+}. This toxic ion must be removed before discharging the water into the environment, typically to a level less than 0.05 ppm.

The most frequently used technique for chrome removal is a two-stage chemical treatment process. The first stage lowers the pH and adds reducing agents to convert the chrome from soluble Cr^{6+} to Cr^{3+}. The second stage neutralizes the wastewater, forming insoluble chromium hydroxide, which can be removed. For consistent treatment and stable control in this type of process, well-mixed reaction tanks with volume for adequate retention time are required, as shown in Figure 1. Retention time is calculated as the filled or usable tank volume divided by the waste flow rate and should typically be 10 minutes or more.

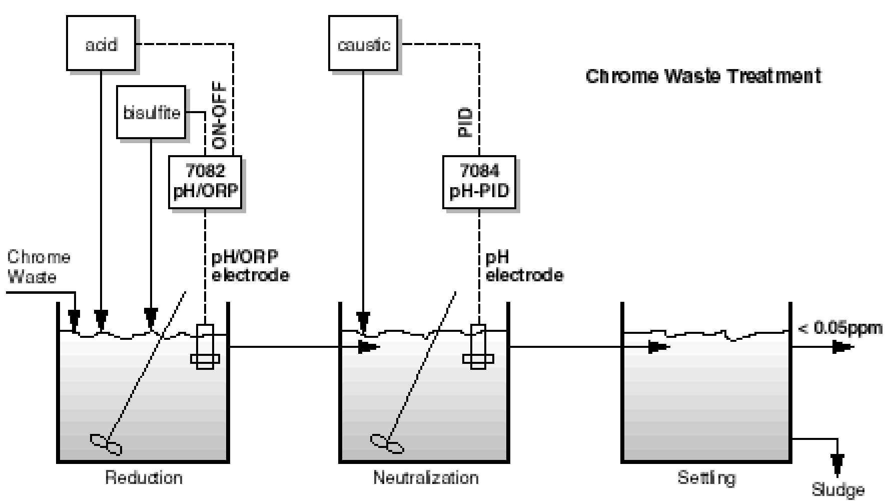

figure 1

First Stage

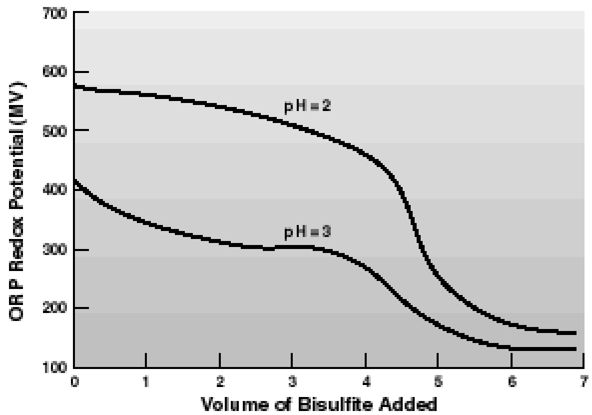

figure 2 - chrome reduction typical titration curves

Sulfuric acid is used to lower the pH to approximately 2.5 to promote the reduction reaction and ensure complete treatment. The reducing agent may be sulfur dioxide, sodium sulfite, sodium bisulfite, sodium metabisulfite, sodium hydrosulfite, or ferrous sulfate. The reaction is shown below with the chromate expressed as chromic acid, CrO_3, with a +6 charge on the chromium. The reducing agent is expressed as sulfurous acid, H_2SO_3, which is generated by sulfites at low pH. The result is chromium sulfate, $Cr_2(SO_4)_3$, with a +3 charge on the chromium.

$$\mathbf{2CrO_3 + 3H_2SO_3 \;--->\; Cr_2(SO_4)_3 + 3H_2O}$$

The first-stage reaction is monitored and controlled by two independent control loops: acid addition by pH control and reducing agent addition by ORP or oxidation-reduction potential control. These loops can often be handled with On-Off control using solenoid valves or metering pumps. The pH controller simply calls for additional acid whenever the pH rises above 2.5. The ORP controller calls for additional reducing agent whenever the redox potential rises above about +250 mV. (The + polarity is of the metal ORP electrode with respect to the reference electrode.)

The ORP titration curve, Figure 2, shows the entire millivolt range if Cr^{6+} chrome is treated as a batch. With continuous treatment, operation is maintained in the completely reduced portion of the curve near the +250 mV setpoint. The ORP setpoint can vary from installation to installation, depending on pH, reducing agent, presence of additional contaminants and dissolved oxygen, and the type of reference electrode. The exact setpoint for a given installation should be determined empirically at a potential where all the Cr^{6+} has been reduced, but without excess sulfite consumption, which can release sulfur dioxide gas. This point can be verified with a sensitive colorimetric test kit or similar check.

Chrome reduction is slow; 10 to 15 minutes may be required for a complete reaction. This time increases if the pH is controlled at higher levels. Variation of pH also has a direct effect on the ORP, as shown in Figure 2. Thus pH must be closely controlled to achieve consistent ORP control.

Second Stage

The wastewater is neutralized to precipitate the Cr^{3+} as insoluble chromium hydroxide, $Cr(OH)_3$, as well as to meet discharge pH limits. Sodium hydroxide, NaOH, or lime are used to raise the pH to 7.5 to 8.5 in the following reaction:

$$\mathbf{Cr_2(SO_4)_3 + 6\ NaOH \;--->\; 3\ Na_2SO_4 + 2\ Cr(OH)_3}$$

pH control in the second stage is more difficult than in the first, since the control point is closer to the sensitive neutral area. Although this reaction is fast, retention time of at least 10 minutes is usually needed for continuous treatment to achieve stability. Proportional pH control is often required in this stage.

A subsequent settling tank and/or filter removes the suspended chromium hydroxide. Flocculating agents have been found helpful in this separation.

Batch Treatment

While Figure 1 shows the arrangement for continuous treatment, all steps can be accomplished with semiautomatic batch control. Only a single tank with one pH controller and one ORP controller are required. The steps of the treatment are sequenced, changing the pH setpoint to give the same results: Acid is added to lower pH to 2.5, then reducing agent is added to lower redox potential to +250 mV. After a few minutes to ensure complete reaction and possibly a test for Cr^{6+}, sodium hydroxide is added to raise the pH to 8. A settling period then follows, or the batch is pumped out to a separate settling tank or pond.

ORP Measurement

An oxidation-reduction reaction involves the transfer of electrons from the reducing agent to the ion being reduced. In this application, sulfur in the sulfite ion donates electrons to reduce chromium, while simultaneously the chromium oxidizes the sulfur.

ORP is a measurement of the status of an oxidation-reduction reaction. The platinum or gold electrode detects the solution's ability to accept or donate electrons. A reducing ion (sulfite) provides electrons and tends to make the electrode more negative. An oxidizing ion (Cr^{6+}) accepts electrons and tends to make the electrode more positive. The net electrode potential is related to the ratio of concentrations of the reducing and oxidizing ions in the solution. It is extremely sensitive in measuring the degree of treatment in the reaction tank. However, it cannot be related to a definite concentration of chrome and therefore cannot be used as a final effluent monitor of chrome concentration.

Reliable ORP measurement requires a very clean metal electrode surface. Routine cleaning of electrodes with a soft cloth, dilute acids, and/or cleaning agents is recommended to promote fast response. Control at low pH levels in the first stage of treatment has also been found to help maintain clean ORP electrodes.

Recommended Honeywell Equipment

For Reduction:

7777 Durafet or Meredian pH Electrode Assembly
7082 pH Analyzer
7777 Meredian ORP Electrode Assembly
7082 ORP Analyzer

Alternative for Reduction:

7773 pH and ORP Electrode Assembly
Glass pH Electrode
ORP Electrode (platinum)
Terminal (p/n 31316441)
7082 Simultaneous pH/ORP Analyzer

For Neutralization:

7777 Durafet or Meredian pH Electrode Assembly

7084 pH PID Controller

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