

# Process Controls SalesNet

## pH and ORP Applications

### Cyanide Waste Treatment

#### Measuring and Controlling pH and ORP Levels

##### Background

Cyanide solutions are used in plating baths for zinc, cadmium, copper, brass, silver, and gold. The toxic rinse waters and dumps from these operations require destruction of the cyanide before discharge, typically to a level below 0.1 ppm.

The most frequently used technique for cyanide destruction is a one- or two-stage chemical treatment process. The first stage raises the pH of the solution and oxidizes cyanide to less toxic cyanate. When required, the second stage neutralizes and further oxidizes cyanate to harmless carbonate and nitrogen. The neutralization also allows the metals to be precipitated and separated from the effluent.

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.

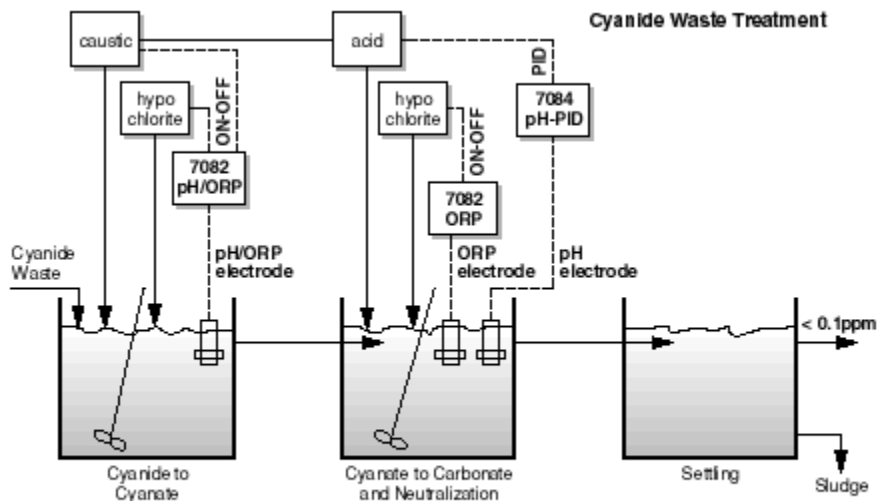


figure 1

##### First Stage

Sodium hydroxide, a caustic, is used to raise the pH to approximately 11 to promote the oxidation reaction and ensure complete treatment. The oxidizing agent is generally chlorine or sodium hypochlorite, NaOCl. The overall reaction for the first stage is shown below, with cyanide expressed in ionic form,  $CN^-$ , and the result as sodium cyanate,  $NaCNO$ , and chloride ion,  $Cl^-$ .

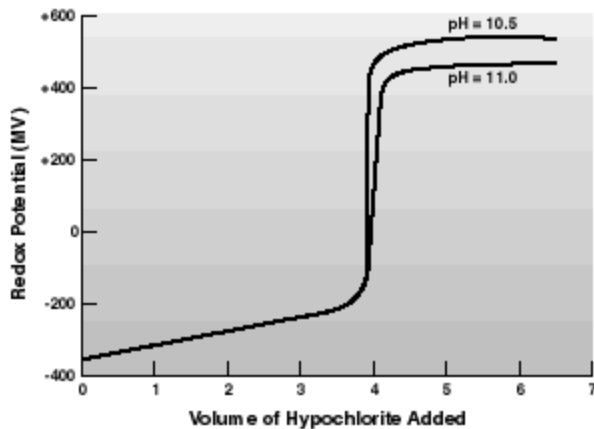
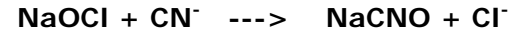


figure 2 - First-stage cyanide oxidation typical titration curve



The first-stage reaction is monitored and controlled by independent control loops: caustic addition by pH control and oxidizing agent addition by oxidation-reduction potential (ORP or redox potential) control. These loops can often be handled with On-Off control using solenoid valves or metering pumps. The pH controller calls for additional caustic whenever the pH falls below 11. The ORP controller calls for additional chlorine whenever the ORP falls below about +450 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 cyanide is treated as a batch. With continuous treatment, operation is maintained in the oxidized, positive region of the curve near the nominal +450 mV setpoint. The ORP setpoint can vary from installation to installation, depending on pH, oxidizing agent, presence of various metals in solution, and type of reference electrode. The exact setpoint for a given installation should be determined empirically at the potential where all the cyanide has been oxidized but without excess chlorine feed. This point can be verified with a sensitive colorimetric test kit or similar check for cyanide.

pH has a direct effect on ORP, as shown in Figure 2. Thus, pH must be closely controlled to achieve consistent ORP control, especially if hypochlorite is used as the oxidizing agent. Hypochlorite addition raises pH; if unchecked, this results in lowered ORP, calling for additional hypochlorite—a runaway situation. Careful pH control and location of the ORP electrode some distance away from the hypochlorite addition point eliminates this difficulty.

Gold ORP electrodes give more reliable measurement than platinum for this application. Platinum may catalyze some additional reactions at its surface and is more subject to coating than gold. The solubility of gold in cyanide solutions does not present a problem, since it is in contact primarily with cyanate. Any slight loss of gold actually serves to keep the electrode clean.

### Second Stage

The wastewater is neutralized to promote additional oxidation as well as to meet discharge pH limits. Sulfuric acid is typically used to lower the pH to about 8.5, allowing the second oxidation to occur more rapidly. Acid addition must have fail-safe design, since pH levels below 7 can generate highly toxic hydrogen cyanide if the first-stage oxidation was not complete.

Additional chlorine is added, either in proportion to that added in the first stage or by separate ORP control, to complete the oxidation to sodium bicarbonate,  $\text{NaHCO}_3$ , in the following reaction:



ORP control in the second tank is very similar to that in the first, except that the control point is near +600 mV. pH control in the second stage is more difficult than the first because the control point is closer to the sensitive neutral area. Proportional pH control is usually used here.

A subsequent settling tank and/or filter can remove suspended metal hydroxides, although further treatment may be required to lower some metal concentrations below their hydroxide solubilities.

### **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 in this situation. The steps are sequenced, changing the pH and ORP setpoints to obtain the same treatment result. Caustic is added to raise pH to 11. Chlorine is added to raise the ORP to about +450 mV, simultaneously adding more caustic, as required to maintain a pH of 11. An interlock must be provided to prevent acid addition before positive oxidation of all cyanide. Then acid can be added to neutralize the batch, and further chlorine oxidation completes the cyanate-to-carbonate conversion. A settling period can then remove solids, or the batch can be pumped directly to another settling tank or pond.

### **ORP Measurement**

An oxidation-reduction reaction involves the transfer of electrons from the ion being oxidized to the oxidizing agent. In this application, chlorine accepts electrons from the cyanide to oxidize it, while simultaneously the chlorine is being reduced to chloride.

ORP is a measure of the status of an oxidation-reduction reaction. The gold electrode detects the solution's ability to accept or donate electrons. An oxidizing ion (hypochlorite) accepts electrons and tends to make the electrode more positive. A reducing ion (cyanide) provides electrons and tends to make the electrode more negative. The resulting 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, the electrode potential cannot be related to a definite concentration of cyanide or cyanate and therefore cannot be used as a final monitor of effluent 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 electrode response.

### **Recommended Honeywell Equipment:**

For Cyanide to Cyanate, First Stage:

- 7777 Durafet® or Meredian® II pH electrode assembly
- 7082 pH Analyzer
- 7777 Meredian II ORP electrode assembly
- 7082 ORP Analyzer

Alternate for Cyanide to Cyanate:

- 7773 pH and ORP electrode assembly
- ORP gold electrode

- Terminal (p/n 31316441)
- 7082 Simultaneous pH/ORP Analyzer

For Cyanate to Bicarbonate, Second Stage:

- 7777 Meredian II ORP electrode assembly
- 7082 ORP Analyzer
- 7777 Durafet® or Meredian® II pH electrode assembly
- 7084 pH PID controller

Alternate for Cyanate to Bicarbonate, Second Stage:

- 7773 pH and ORP electrode assembly
- 7082 ORP Analyzer
- 7084 pH PID controller

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