Cyanide Waste Treatment

**Introduction**
There are three typical plating processes that produce wastes: stripping, cleaning, and plating. Stripping baths contain solutions of acids, including sulfuric, nitric, hydrochloric or hydrofluoric. These acids are used to remove dirt and oxide deposits from metal surfaces to ensure proper conditions for plating. Cleaning baths contain organic solvents (for removing oil and grease,) and wetting agents. The plating baths contain the solutions of the metal to be plated. These are usually metal salts such as chromic acid, cadmium oxide or copper cyanide. The wastes from these three processes are mainly composed of cyanides, chromates, acids and alkalies. In this application we will focus on the cyanide wastes only.

**Application**
The main source of cyanide wastes originates from “drag-out” of plating solutions into rinse tanks. These cyanide-containing wastes are extremely toxic and must be removed (require complete destruction) before discharge into a sewer system.

**Treatment**
Cyanide waste treatment is usually a two-stage process. Stage 1 oxidizes cyanide to cyanate using oxidizing agents such as chlorine or sodium hypochlorite in the presence of an alkali (high pH). The second stage oxidizes the cyanate (which is much less toxic than cyanide) to carbon dioxide and nitrogen through the use of additional chlorine or sodium hypochlorite, but at a lower pH level than used in the first treatment stage.

**First Stage**
The following equation illustrates the chemical breakdown of cyanide to cyanate:

\[
\text{NaCN + 2NaOH + Cl}_2 \rightarrow \text{NaCNO} + \text{H}_2\text{O}
\]

First, the pH is adjusted and controlled to a pH of 10 or higher by adding caustic.

*NOTE: pH10 or higher must be maintained because dangerous cyanogen chloride (CNCI) or hydrogen cyanide (HCN) gas could be instantaneously released if the cyanide containing waste was allowed to come in contact with acid.*

After increasing the pH, the ORP (oxidation reduction potential) is then increased to approximately (+) 250 mV by addition of an oxidizing agent (example: hypochlorite). ORP is monitored to track the sharp change that occurs (typically 50 mV) when all the cyanide is oxidized to cyanate. This reaction takes place in 15 to 30 minutes with continuous mixing.

*Fig. 1*
NOTE: The absolute ORP value will vary from process to process and with pH changes. Therefore, pH control is necessary during the process. Also, the actual ORP setpoint must be specifically determined in each case.

**Second Stage**
The following equation illustrates the oxidation of cyanate:

$$2NaCN0 + 4NaOH + 3Cl2 \rightarrow 6NaCl + 2CO2 + N2 + 2H2O$$

The second stage reaction is carried out at a slightly lower pH (8.5 to 9 pH). This lower pH is due to the consumption of the alkali in the first stage. Acid is not typically added at this point to reduce pH, instead NaOH is added to maintain pH control. Also, additional oxidant is added until the ORP increases to approximately (+) 300 mV. Remember that this value may vary depending on the makeup of the process.

**Instrumentation**
For a typical two-stage cyanide destruct system as shown in Figure 1, two pH and two ORP controlling systems are suggested. The use of flat-surface, self-cleaning pH & ORP electrodes are recommended. Cleaning frequency is reduced and much time can be saved. All controllers should be on/off type that have a control relay with adjustable deadband. It is recommended that the controllers also have alarm relays to alert the operator of conditions outside the normal range. Instrument choice is yours. Transmitter for pH and ORP with control via a PLC is also a good choice.

For a cyanide destruct system, it is specifically recommended that the ORP sensors have gold (rather than platinum) electrode surface. Two important reasons for this are: they produce a larger millivolt differential, and the gold electrode cannot be poisoned by wastes containing cadmium or zinc.

- Four pH/ORP Controllers (your choice)
- Two pH Sensors (Model 970211)
- Two ORP Sensors w/Gold Electrode (Model 970466)

**Conclusion**
Since each waste stream is unique, it is recommended that the effluent be analyzed to ensure proper destruction of extremely toxic cyanide waste. Many other reactions can occur with other organics or metals in the waste stream, which may require more oxidant, larger retention times or other process changes.