



## Cyanide Waste Treatment

This application note provides basic information about the treatment of extremely toxic cyanide wastes commonly found in the plating industry. Basic system guidelines are described along with typical operating parameters for reference.

There are three basic plating room processes that produce wastes: stripping, cleaning, and plating. Stripping baths contain solutions of acids, mainly sulfuric, nitric, hydrochloric or hydrofluoric. These

acidic solutions are used to remove dirt and oxide deposits from metal surfaces to insure proper conditions for plating. Cleaning baths contain organic solvents for removing oil and grease, or organic emulsions containing wetting agents. Plating baths are solutions of the metal to be plated. Examples include chromic acid, cadmium oxide or copper cyanide. The wastes from these three processes are mainly composed of cyanides, chromates, acids, and alkalis.

### Application

The main source of cyanide wastes originates from "drag-out" of plating solutions into rinse tanks. These cyanide-bearing wastes are extremely toxic and require

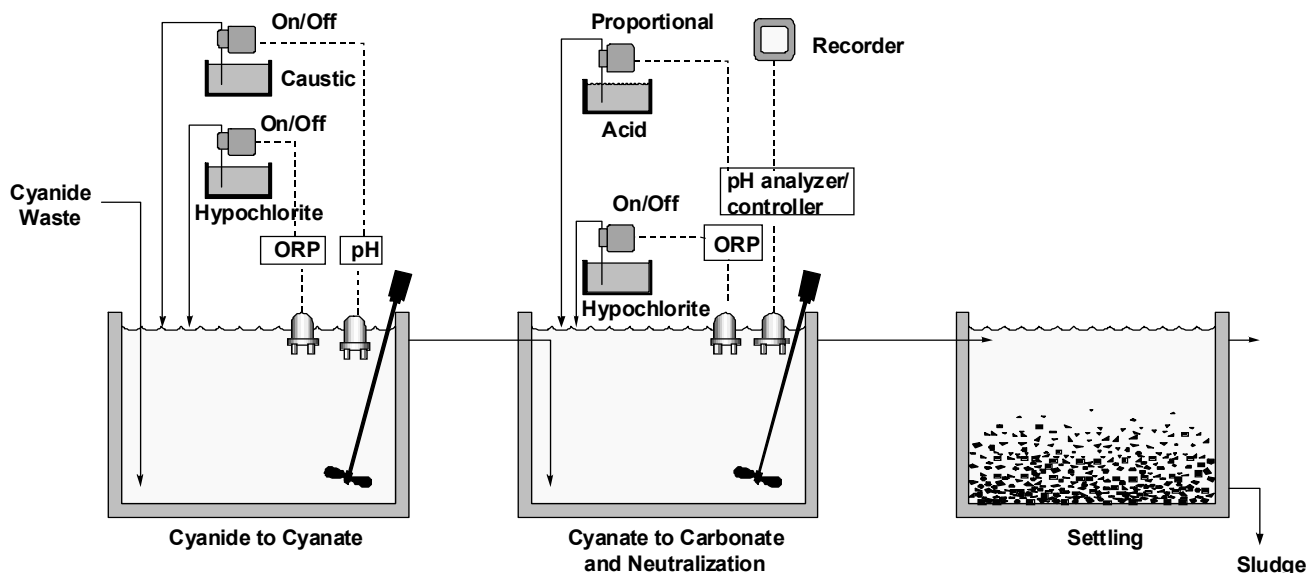
complete destruction before discharge into a sewer system.

### Treatment

Cyanide wastes are usually treated with a two-stage process. The first stage 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 more chlorine or sodium hypochlorite, but at a lower pH level than used in the first treatment stage.

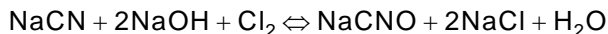
Figure 1 Typical Two-stage Cyanide Destruct System



# Application Note AN-PR1

## First Stage

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



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

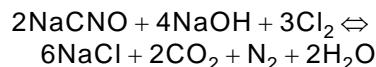
**NOTE:** This is a very important step because dangerous cyanogen chloride (CNCl) or hydrogen cyanide (HCN) gas could be instantaneously released if the cyanide containing waste was allowed to come in contact with an acidic solution.

After increasing the pH, the ORP (oxidation reduction potential) is then increased to approximately (+) 250 mV through addition of an oxidizing agent such as hypochlorite. The reason for measuring the ORP is that a sharp change occurs (typically 50 mV) when all the cyanide is oxidized to cyanate. This reaction occurs typically in 15 to 30 minutes of continuous mixing.

**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:



The second stage reaction is normally carried out at a slightly lower pH (8.5 to 9 pH). The lower pH is a normal response to the consumption of the alkali in the first stage. It is not typical to add acid to lower the pH at this point, just NaOH to maintain pH control. Additional oxidant is added until the ORP increases to approximately (+) 300 mV. 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 required. All four controllers should be the 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.

For a cyanide destruct system, it is specifically recommended that the ORP sensors have the more expensive gold (rather than platinum) electrode. There are two important reasons for this: they produce a

larger millivolt differential, and the gold electrode cannot be poisoned by wastes containing cadmium or zinc.

A typical control system supplied by GLI International consists of:

- Four pH/ORP Controllers
- Two pH Sensors
- Two ORP Sensors w/Gold Electrode
- Four Sensor Mounting Hardware Assemblies

## Conclusion

Since each waste stream is unique, it is highly recommended that the effluent be carefully analyzed to insure 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.

## References

Cushnie. *Electroplating Wastewater Pollution Control Technology*, Noyes Publications.

Hach Company, *pH Measurement*, Technical Bulletin No. TB-P1.

Hach Company, *Oxidation Reduction Potential (ORP) Measurement*, Technical Bulletin No. TB-R1.



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