

Application Note

Oxidation Monitoring in the Cyanide Wastewater Treatment Process

Industry: Chemical, Electrical and Electronics
Product: pH/ORP Process Liquid Analyzers

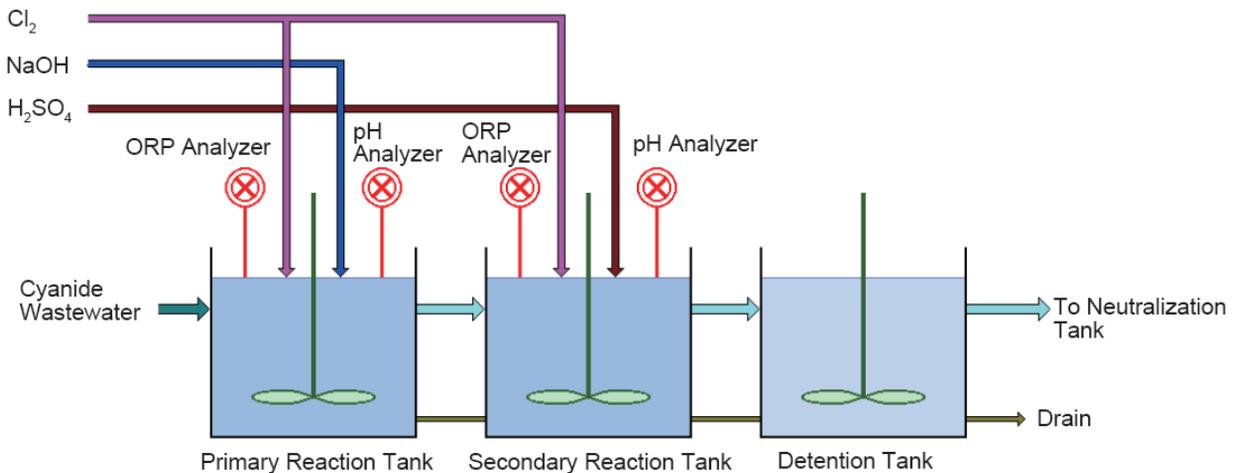
Introduction

Cyanide-bearing wastewater from mining and electroplating facilities and certain types of chemical plants is toxic and must be treated by oxidation with chlorine or chloride to bring the cyanide concentration within regulatory limits. The waste materials contain alkaline, rare earth metals, and other heavy metals such as iron, nickel, zinc, cadmium, copper, silver and gold. As well as sometimes can contain the deadly poison, cyanide.

Currently Federal and State regulatory agencies require that cyanide discharge should be below 0.5 ppm, but with the changing community tightening of this parameter may occur. Therefore it is best to totally destroy the cyanide before discharging waste into the environment. This can be accomplished by controlling the pH and ORP values of the wastewater.

As the speed of the oxidation reaction is closely tied to the pH value, a pH meter is used together with an ORP (oxidation-reduction potential) meter to monitor the completion of the reaction. The use of these meters also ensures that excessive amounts of chemicals (e.g., chlorine) are not used to produce the reaction. Both 2-wire and 4-wire meters are suitable for this measurement system.

The 2-wire PH202G transmitter can measure both ORP and pH. (Two transmitters are required if pH and ORP must be measured simultaneously.) A gold electrode should be used for ORP measurement of cyanide-containing solutions.



	Primary reaction	Secondary reaction
Chemical reaction	$\text{NaCN} + \text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCNO} + 2\text{NaCl} + \text{H}_2\text{O}$	$2\text{NaCNO} + 4\text{NaOH} + 3\text{Cl}_2 \rightarrow 2\text{CO}_2 + 6\text{NaCl} + \text{N}_2 + 2\text{H}_2\text{O}$
pH value	$10 < \text{pH} < 11$	$7.5 < \text{pH} < 8.5$
ORP value	Approx. 300 to 350 mV	Approx. 600 to 650 mV

Figure 1.

Application

Cyanide decomposition takes place in two stages. In the primary reaction, cyanide is oxidized to cyanate under high alkaline conditions (high pH and ORP). In the first reaction tank, the pH of the waste is measured and caustic (NaOH at 50% strength) is injected to raise the pH to 10 or higher. The oxidation reduction potential (ORP) of the waste is measured, and chlorine gas (Cl₂) is automatically injected to raise the ORP to 400 mV or higher. The reaction normally occurs within 5 to 10 minutes.

In the secondary reaction, the cyanate is further oxidized under near-neutral conditions and converted to harmless carbon dioxide and nitrogen gases. In the second reaction tank, the pH of the waste is measured, and acid is injected to lower pH to 7-8. This process takes 2 to 5 minutes. In the third reaction tank, the ORP of the waste is measured and chlorine gas (Cl₂) is automatically injected to raise the ORP to 600 mV or higher (Meanwhile the pH controller maintains the set-point at 7-8, correcting for any acidity created by the addition of the chlorine gas). This reaction occurs, taking 10 to 15 minutes, then the cyanide is eventually converted to harmless materials by the above reaction and the waste can be discharged.

-Measures pH/ORP of cyanide wastewater continuously reduces operating costs.

Solution

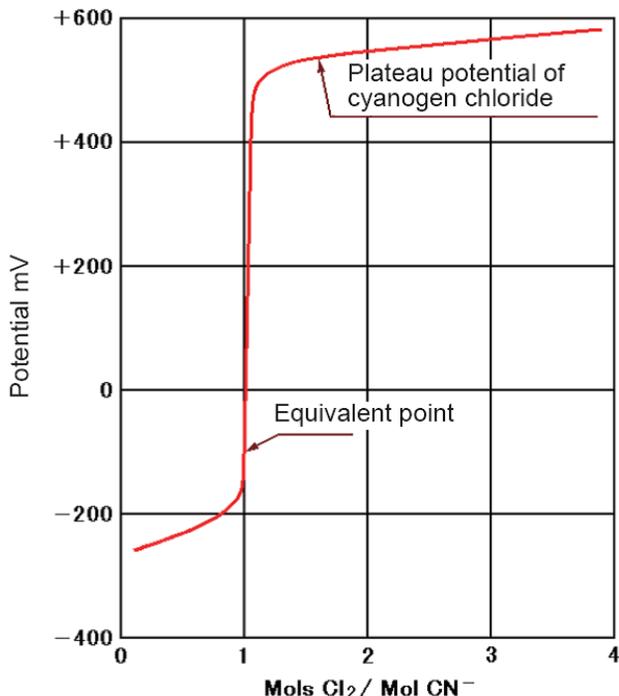


Figure 2.

Measurement Conditions

A gold electrode should be used to ensure accurate measurement of ORP in cyanide solutions. When the potential is near or under 200 mV during the cyanide oxidation process, a platinum electrode produces a catalytic reaction that causes hydrogen to form on the electrode surface. This generates potential and affects measured values.

pH and ORP levels in this area can be simultaneously monitored with the PH450 pH/ORP Analyzer. The model PH450 pH/ORP Analyzer performs continuous sensor diagnostics to notify the user when the sensor is coated or the glass electrode has broken.

The PH20 "Tempress" sensor with has a 3/4" NPT threads is convenient to install and use in the reaction tanks. Adapters enable it to be converted into a 1" MNPT thread, as well as a flow thru assembly or direct insertion assembly with a cleaning system. This sensor features four separate elements (pH, reference, temperature, ORP) in a rugged PVDF body. The integral number-coded cable and integral NPT threads allow for easy and convenient installation. When used with PH4050 or PH202 pH/ORP Analyzers, it can give simultaneous measurements of pH and ORP is possible with one sensor.

Product Recommendation

Measurement System

Process Liquid Analyzer:

- 2-wire FLEXA pH/ORP Analyzer
- 4-wire PH450G pH/ORP Analyzer

Sensor Selection:

Option #1: FU20 pH/ORP Combination electrode
Alternatively, SENCOM sensor can be used. (FU20F).

Option #2: PH20 All-in-one PH/ORP Electrode

Option #3: FF20 Flow-thru assembly with individual measure, reference and temperature electrodes with the automatic cleaning assembly, K1547PJ

Option #4: PH8HS Submersion holder with KCl refillable ORP sensor, Model OR8EFG, and KCl Refillable pH Sensor, Model PH8EFP

Note: For additional information on this application contact the local Yokogawa Process Liquid Analyzer Department