APPLICATION NOTE

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Reduction Monitoring in the Chromium Wastewater Treatment Process

Industry: Electrical and Electronics
Product: pH/ORP Analyzer

Introduction

Wastewater from electroplating facilities and certain types of chemical plants contains toxic forms of hexavalent chromium such as chromate and dichromate. The hexavalent chromium in this wastewater must be reduced before the water can be discharged. This requires a two-step process: hexavalent chromium (CR^6) is reduced to trivalent chromium (CR^3); and CR^3 is precipitated as chromium hydroxide. As the oxidation-reduction potential (ORP) and the speed of the reduction reaction are closely tied to the pH value, ORP and pH analyzers are used to ensure proper control of the reduction process through such means as the injection of reducing agents.

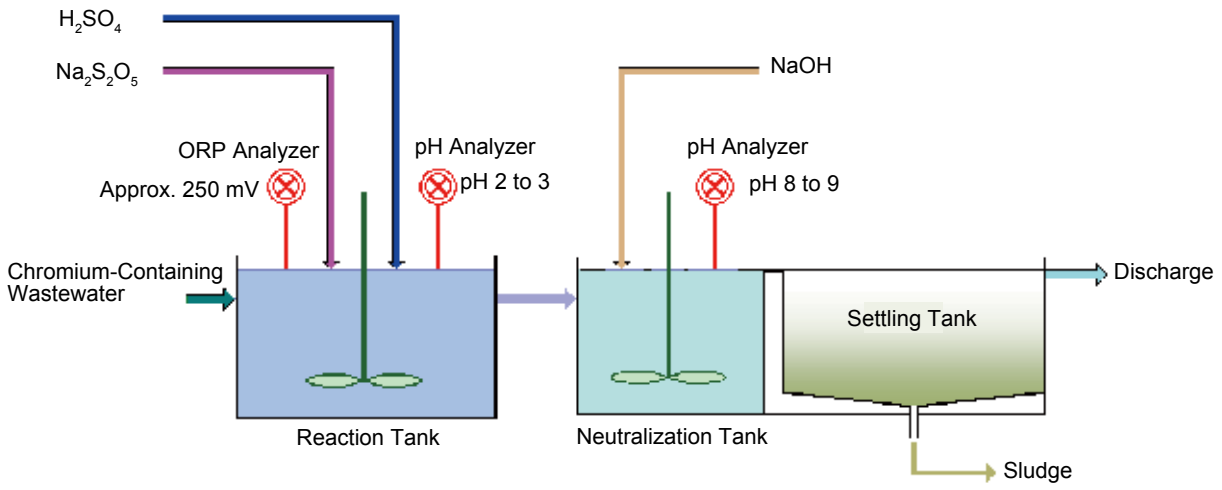
pH and ORP measurements in these reaction tanks are complicated by the presence of chrome and sulfur dioxide, which can poison the sensor reference under certain circumstances. pH and ORP control in these applications may be conducted using alarm relays and a simple on/off control scheme such as available in the PH450G Analyzer. Alternatively, the 4-20mA current output can be used directly for proportional control, or sent to a distributed control system as needed. The PH202G/PH450G can measure both ORP and pH. Both 2-wire and 4-wire analyzers are suitable for this measurement system. A gold electrode should be used for ORP measurement of chromium wastewater.

Expected Benefits

- Measures pH/ORP of chromate wastewater continuously
- Reduces operating costs

Process Overview

First, hexavalent chromium, either in the form of chromate or dichromate, is reduced to trivalent chromium. Wastewater flows into the first reaction tank, where the pH is measured and sulfuric acid is automatically brought into the process until a pH set point value in the acidic range is achieved. The reaction time is just a few minutes, and a lower pH for an even faster reaction would require considerably more acid. At the same time, the oxidation reduction potential (ORP) of the solution is measured, and sulfur dioxide (SO_2), sodium sulfite, or sodium metabisulfite is automatically injected until an ORP value of approximately 280 mV is achieved.
Then in the second tank, the pH is raised to 8.5 by the addition of an alkaline solution such as ammonia or caustic (NaOH), where it is converted to chromium hydroxide. The precipitate, although heavier than the water, does not drop to the bottom due to agitation in the tank. The mixed slurry flows to a settling tank, where the trivalent (Cr^{3+}) chrome settles to the bottom and the clear chromium-free water flows over the tank for further treatment. Chemicals known as coagulants are sometimes added to the second reaction tank to help form larger particles and aid in sludge removal. The reducing agent may be a substance such as ferrous sulfate, sodium metabisulfite, or sulfur dioxide. Chemicals known as coagulants are sometimes added to the second reaction tank to help form larger particles and aid in sludge removal.



Reaction
Sodium metabisulfite

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3$$
$$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O$$
$$Na_2Cr_2O_7 + 3NaHSO_3 + 5H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 5NaHSO_4 + 4H_2O$$
$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4$$

AN 10B01N01-03E http://www.yokogawa.com/an/index.htm

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Solution Details

Measurement system

2-wire/4-wire pH/ORP measurement system

Sensor

KCl refillable ORP sensor

OR8EFG-AU-❑❑-TT1-❑*A

KCl refillable pH sensor

PH8EFP-❑❑-TN-TT1-N-❑*A

Submersion type holder

PH8HS-PP-❑❑-T-NN-NN*A

Terminal box (when needed)

WTB10-PH1 (for 2-wire system)

WTB10-PH3 (for 4-wire system)

Converter/transmitter

2-wire transmitter (pH/ORP)

PH202G-E-E

4-wire pH/ORP converter

PH450G-A-❑

Distributor (for 2-wire system)

PH201G- A❑*B

Measurement Conditions

1. Check solutions for ORP analyzer

Oxidation-reduction potential of check solutions (quinhydrone/iron solutions)

A check solution is used to determine whether the ORP sensor is operating correctly. There are two types of check solutions: quinhydrone and iron.

Quinhydrone solution: approx. 200 to 300 mV

Iron solution: approx. 420 to 520 mV

Unlike a pH standard solution, an ORP check solution does not always indicate a constant reference value. Whether the sensor is operating normally can be determined by seeing whether its readings are within the acceptable range.

Preparation of a check solution (250 mL)

Quinhydrone solution: Dissolve the following reagent in pure water and dilute to 250 mL.

Quinhydrone salts: P/N K9024EC

Ferrous & ferric: dissolve the following reagent in a 2-mol/L sulfuric acid solution and dilute to 250 mL.

Ferrous & ferric salts: P/N K9024ED

2. Use of a gold electrode for ORP measurement

For ORP measurement of chromate wastewater, the use of a gold electrode is recommended.

Utilities

PH202G

Power supply: 17 to 40 V DC (from distributor)

PH450G

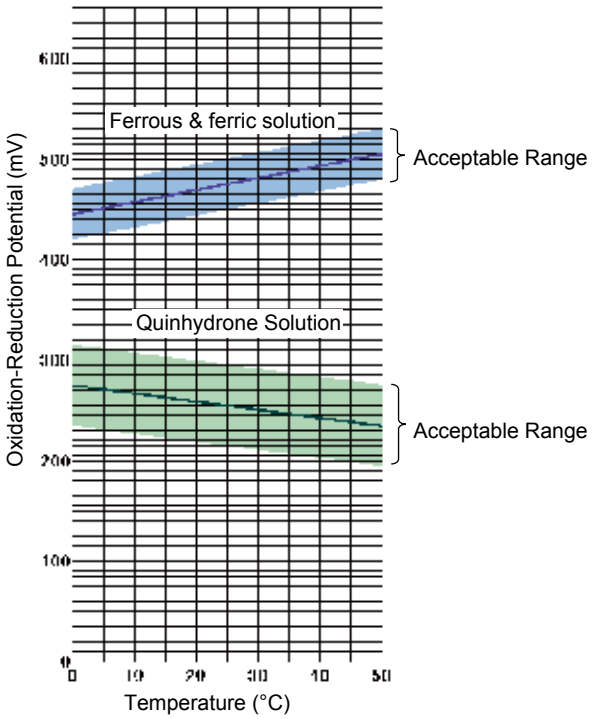
Power supply: 96 to 264 V AC, 50/60 Hz

Power consumption: approx. 15 VA

PH201G distributor

Power supply: 100 V: 20 to130 V DC/80 to 138 V AC, 47 to 63 Hz
220 V: 120 to 340 V DC/138 to 264 V AC, 47 to 63 Hz

Power consumption: 24 V DC: approx. 200 mA
100 V AC: approx. 7 VA
220 V AC: approx. 11 VA



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