pH/ORP measurement
Refinery wastewater

Measurement made easy

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**Oil and gas
refinery wastewater**

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Introduction

In April of 2008 Conoco Phillips paid $1.2 million dollars in fines to the United States Environmental Protection Agency. These infractions were for one refinery located in Borger, Texas. Findings included more than 2000 violations of the refinery's clean water effluent limits over a seven year period leading up to 2006.

It is not uncommon for a large oil refinery to produce 8 to 10 MGD of wastewater. This water contains a multitude of challenging contaminants that the refinery must deal with:

- Residual hydrocarbons from various parts of the refinery
- Salts (mainly sulfur and chloride compounds) from sour crude refining
- Ammonia compounds from nitrogen extracted from the crude
- Cyanides from the fluid catalytic cracker and coker
- Hydrofluoric acid from alkalization processes
- Volatile Organic Compounds (VOCs) such as benzene and toluene

The major use for water in a refinery is steam generation. Steam requires not only removal of the contaminants, but that the water is brought back to near ultra-pure quality. If residual contaminants are left in the steam, the refinery faces the possibility of corrosive condensate that can damage piping and processing equipment. Also, frequent blowdown caused by contamination reduces the efficiency of steam generation.

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Treatment

Most refineries have a centralized wastewater treatment facility to handle the volume of water generated by the processing end of the plant. Smaller operations also occur at various stages of the refining process. These smaller pre-treatment facilities remove the initial contaminants generated at that particular stage in the refining process.

It is nearly impossible to cover all refinery wastewater pH applications here. The following sections highlight the majority of measurement points.

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API separators

These units are used in the pretreatment of insoluble hydrocarbons within the water. The separator relies on the different densities of water and hydrocarbons to allow the varying liquids to 'separate' as they flow through a tank. The refinery skims the lighter hydrocarbons from the surface of the water and pumps the heavier liquids from the bottom of the tank. Baffles within the tank help further to partition the oil from the water. Plants typically measure the pH of the water effluent at the outlet of the separator. Changes in pH can alert the downstream treatment processes of potential problems.

All pH sensors specified for this process should include the Wood Next Step Reference junction and the coat-resistant 'J' Glass electrode. PTFE is not recommended.

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Coagulation

This process involves adding polymers or aluminum salts to the water. These coagulation chemicals have an opposite electrolytic charge than the contaminants in the wastewater. The coagulant causes the contaminants to bond together. The resulting 'floc' then drops out of solution as sludge. The effectiveness of the coagulation chemical often depends on the water's pH. The pH measurement usually takes place either downstream of chemical mixers or in the clarifier where coagulation occurs.

Bioreactors

Fixed film bioreactors can remove volatile organic compounds (VOCs) from the wastewater. These reactors rely on bacteria that convert the VOCs to non-hazardous sludge. The pH of the bioreactor must be controlled between 6.5 to 7.0 to keep the bacteria from harm. The point of pH measurement is often on the inlet to the bioreactor to warn of any non-compliant water.

Drain and return lines

The inlet drains and condensate return feed the water treatment facility from various parts of the refinery. Both pH and conductivity are used to safeguard the water treatment plant from strongly contaminated water.

The ABB solution – TB(X)5 sensors

The nature of refinery wastewater makes pH measurement difficult. Refineries use dip-style and retractable-style sensors, depending on the mounting requirements of the application. ABB recommends the TB(X)551 sensors (see Figure 1) in dip applications while the TB(X)557 (see Figure 2) and TB(X)587 cover the majority of in-line retractable installations.

In all these applications the reference must be a type A or type D, wood, next step style. Glass should be the chemically resistant type 'J' glass unless particulates are present, which favor a type 1, flat glass. Regular cleaning is always required. High-pressure water cleans all these sensors. For manual cleaning, crews can simply use a small spray can filled with a mixture of water and a small amount of glass cleaner and pressurized with compressed air. For online measurements, refineries can bring a water line into a flow cell or, for in-line pressurized services, a TB18 Safe-T-Clean valve can be used.

Figure 1   TB(X)551 sensor – can be used in submersible applications or in sample lines

Figure 2   Retractable TB(X)557 sensor for in-line wastewater pH measurement

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