pH/ORP measurement
Refinery quench tower

Introduction

One major challenge facing oil refiners is removal of sulfur compounds from crude oil during the refining process. The term ‘sweet’ crude refers to crude oil that is low in sulfur and carbon dioxide compounds. It’s the preferred feedstock for most oil producers as it easier to refine into gasoline and other derivatives.

‘Sour’ crude denotes crude oil that contains 0.5 % or greater sulfides. Since impurities are higher in sour crude, more steps must be taken in processing to create the required product. Sour crude refining involves removal of the sulfur compounds by liberating them as hydrogen sulfide (H₂S) gas. This reduced form of sulfur is carcinogenic. When combined with crude oil or water it is also highly corrosive.

Once the H₂S gas separates from the oil it must be processed. Most refineries have a Sulfur Recovery Unit (SRU) that reclaims the H₂S by oxidizing it with sulfur dioxide (SO₂). The resultant elemental sulfur drops out of the gas and serves as a by-product to make sulfuric acid and other resalable products. SRUs are typically 95 to 99 % effective in removing sulfur compounds. Any residual gas is referred to as ‘tail gas’ and undergoes further processing in a Tail Gas Cleanup Unit (TGCU).
Tail gas and the quench tower

To comply with environmental and health & safety regulations, the refinery must reduce sulfur compounds in the tail gas from approximately 10000 to 10 ppm. The tail gas may contain a mixture of sulfur compounds in the form of hydrogen sulfide, sulfur dioxide, carbonyl sulfide, carbon disulfide and even some elemental sulfur in vapor form.

The first stage of the TGCU heats the gas in a reactor to reduce the various sulfur compounds to H\textsubscript{2}S gas. The gas flows from the reactor to the quench tower. Water sprays down from above as the H\textsubscript{2}S gas flows up through the quench tower.

The water reacts with the H\textsubscript{2}S gas and creates sour (acidic sulfur-containing) water. Depending on its pH, some sour water is directed to a stripper while the remainder re-circulates.

To control the acidic effects of the sour water, the plant keeps the quench water at 7 pH or above through the addition of caustic, ammonia or amines. Amines raise the pH and have a secondary effect of reacting further with the H\textsubscript{2}S gas. Make-up water is also added to the quench tower if too much sour water is being drawn off to the stripper.

The ABB solution – TB(X)5 sensors

High sulfide concentrations in the sour quench water are the biggest challenge for this pH measurement. Sulfides are extremely mobile ions with a reputation for passing through the porous reference junction in pH sensors. Once inside the pH sensor, the sulfides migrate to the AgCl reference element and convert it to AgS.

This makes the reference voltage unstable and the pH probe unreliable. Furthermore, the high temperature of the tail gas can elevate the quench water temperature coming from the bottom of the tower. Water pressures are usually near 100 psig (6.9 bar).
Commonly, the pH measurement in these applications is made in a sample line that refineries refer to as ‘fast loops’. A fast loop takes a sample of the pressurized process liquid off the main pipeline and boosts the pressure with a pump to enable the sample to flow past the pH sensor and back into the process. Isolation valves are mounted upstream and downstream of the sensor to close the sample line for cleaning and for electrode calibration. The TB(X)551 sensor is ideal for these applications as its twist-lock design allows for easy installation and removal. For new installations, the TB(X)587 is a 1 inch retractable sensor that can be supplied equipped with an integral isolation valve to negate the need for separate valves upstream and downstream of the measurement.

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.