Question 12: What are your Best Practices for maintaining good reliability of pH analyzers in sulfuric acid alkylation service?

FRY (Delek Refining Ltd)

First, I should offer the caveat that we have struggled with this as well. So, if anyone else will volunteer their experience after I am done, I would be very grateful.

At our Lion Oil facility, they feel as if they have relatively good reliability on their analyzer. They emphasize that they use a Lummus ABB analyzer, and they make sure that it is always wet. Our technician in Tyler also agrees that you want to make sure that it is wet at all times to avoid damaging the components. You also want to avoid it getting too hot, which could damage the instrument. Check your practices. Make sure that when the operators clear out whatever associated equipment is nearby that they are not accidentally steaming out the pH probe, which will damage it. At this time, we are actually considering putting a pH sampling conditioning system in place because we are still not happy with our performance.

So, some of the Best Practices we have learned but which we have yet to verify personally are that you want to filter and cool the sample and control the velocity across the probe. Part of the reason that you want to control the temperature is not just to prevent damaging of the probe, but also because there is a difference between the pH at a high temperature and at room temperature, which your lab will be testing. So, cooling the sample will avoid any discrepancies between your online results and your lab results. Also, by filtering and controlling the velocity, you can avoid a lot of the noise that can get in there from operational changes.

And then, I have also heard it suggested to use a high pH buffer solution when calibrating, but I have noticed that some suppliers do not seem to offer a high pH.

Post-Conference Update: Since the conference ended, we have doubled the alkaline waterwash circulation rate, which seems to have eliminated many of the low pH excursions that used to be frequent on the online analyzer.

BURTON (Motiva Enterprises LLC)

We have struggled with pH analyzers as well, and the only action we have found to be effective is to frequently calibrate them and do spot check and routine preventative maintenance. When you start seeing deviations between your offline and online measurements, then additional maintenance is required. So again, I concur with Emerson. If anyone has a Best Practice out there, I am more than welcome to hear it.

ADRIAN SKIPPER (Phillips 66)

When I worked at DuPont for about five years, I saw what I thought were good Best Practices compared to what I have seen in the oil industry. DuPont did not have as much hydrocarbon to manage, but they went above and beyond what I have seen in the oil industry where I worked the daily calibrations, that you mentioned with the buffers, using multiple instruments. On the same stream, I saw that work well at Alliance and Philips 66, and having the ability to either automatically or manually switch between the analyzer works best as a cross-check on a daily shift basis. Removing the oil and keeping it from getting onto the probe will really help as well, if you happen to have the analyzer in an oily system.

LIZA PACHECO (DuPont Clean Technologies)

In sulfuric acid alkylation plants, alkaline water is used to neutralize acidic components that are present in the hydrocarbon effluent. To achieve the neutralization, the alkaline water pH is typically maintained between 11 and 12, and the temperature controlled between 120°F and 160°F. The pH meter performance and life are negatively impacted by the high temperature, high pressure, high alkalinity, and particles that may be present in the alkaline water stream. In many cases, customers have reported that the average life of the pH meter in this service is between one and three months. Some of the Best Practices to maximize the life and reliability of the pH sensor are the following:

- Determine the right location to install the pH sensor. The location should be based on the principles of maximizing sensor response while minimizing how often the sensor must be removed for maintenance. Typically, in the alkaline waterwash service, a representative sample is taken through a slip stream for analysis. It is recommended to maintain a velocity greater than 5 fps but less than 10 fps to reduce the accumulation of fouling material while minimizing sensor wear. A filter is also recommended to remove any undissolved particles that can cause abrasion on the sensor.

- Select the right pH sensor to meet the process conditions. This step is imperative because high temperatures and pressures accelerate the aging of the pH sensor which causes unstable readings and slow response. Also, the pH sensor glass should be designed with special formulation for a high alkalinity environment.

- Develop a maintenance program. The frequency at which a sensor should be inspected, cleaned, and calibrated can be determined only by experience. Although the required frequency is application-dependent, it is recommended to clean/inspect the sensor once per week and perform a calibration twice per month. Today, sensors and transmitters have the ability to record diagnostic data. The trending data will allow the user to evaluate the state of the sensor and develop a maintenance schedule. Two main sensor diagnostics are the glass impedance and reference impedance. A sudden drop in glass impedance identifies a cracked or broken glass. High glass impedance implies that the sensor is nearing the end of its life and should be replaced as soon as possible. An increase in reference impedance can indicate that the liquid junction is plugged or coated or that the reference electrode is not in the process solution.

- Beware of variations in laboratory samples when comparing to the process. The actual pH of the

process changes with temperature due to variations in the dissociation constant of water. A change in the amount of dissociation can cause a change in the apparent pH measurement. For example, if an alkaline water sample is taken at 120°F (49°C), the pH meter will indicate a value of 11.6 pH. If the pH measurement is taken again at 77°F (25°C), the pH meter will show an increase in pH (12 pH) even though the sample contains the same amount of caustic.

- Condition the sample. To extend the life of the pH sensor, the alkaline water sample can be conditioned to achieve a less severe environment. Through a slip stream, a representative sample is filtered, cooled, depressured, and degassed before the pH sensor.

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2015