



(*Liquid analysis*)

Effective, long term operation of hydrocarbon processing plants is dependent on critical analytical measurements. Gas analysis, for example, may monitor potential sources of hazardous combustibles from process heaters, catalytic crackers and power boilers. Liquid analysers such as pH and conductivity, on the other hand, tend to have a lower profile in refinery operation. However, liquid analysis comes centre stage when the refinery is attempting to prevent downtime. After all, water causes corrosion, a costly, long term issue in refineries, and the careful control of the pH, conductivity and other water parameters can prevent deterioration of vital metal surfaces. Liquid analysis also plays an important role in optimising a number of steps in hydrocarbon processing and in meeting wastewater regulations. This article presents a tutorial on the application of liquid analytical measurements in the refinery and a guide to selecting appropriate instrumentation.

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analysis is a critical factor
in refinery operation.

one or two weeks, thereby causing a maintenance headache and significant expense. The problem is preventable by seeking out pH sensors with high area references designed specifically to prevent clogging and coating in heavy solids applications.

Crude unit overhead

The upper third of the refinery's crude tower produces light oil with substantial amounts of water that must be allowed to drop out of a separator vessel. Salt impurities found in most crude oils are more soluble in water than in oil and tend to accumulate in the distillate (or overhead) product. These impurities cause the separated water to become quite acidic. The corrosive acidic water will attack metal process equipment, particularly the upper portion of the crude tower, overhead piping, condensers and accumulators (Figure 2). To avoid this, a sample is drawn from the bottom of the accumulator and, after another separation step, is measured for pH. A proportional controller regulates the feed of a neutralising chemical into the overhead product. The flow system creates a time lag of 15 - 45 mins between injection of the neutraliser and pH measurement at the sensor, which can cause slow response to large changes and oscillations for periodic changes. In order to minimise these problems, the pH is neutralised in two stages. Firstly, a film forming corrosion inhibitor (an organic amine), which also has neutralising properties, is manually fed into the overhead to neutralise 70 - 80% of the stream acidity. If flowrates vary, flow paced control can be used. This coarse pH adjustment forms a protective coating on the metal surfaces. Secondly, a proportional control system is used to 'trim' the pH to within two pH units of the setpoint (usually between 5.5 and 6.5). This is achieved by separately injecting ammonia or other amines to correct only the final 20 - 30% of the acidity. The proportional pH control signal can be generated by the pH analyser, or from a separate controller or DCS.

Cooling towers

Cooling towers produce their effect through the evaporation of a small fraction of the water and heat exchange with the air passing through the tower. The evaporation causes a concentration of dissolved solids, which can cause scale and corrosion in the heat exchange equipment. These effects are controlled with the aid of continuous conductivity and pH measurements. The concentration of the impurities in the water is measured by a contacting conductivity sensor. A conductivity controller opens the blowdown valve when the conductivity becomes too high and causes a demand for makeup water, which reduces the concentration of impurities. As most of the impurities in the cooling water are alkaline, they

The key to corrosion prevention

Virtually every area of the refinery in which corrosion is an issue requires pH measurement and control. A number of these are outlined below.

Tail gas cleanup

Operation of tail gas in a tail gas cleanup unit (TGCU) involves heating the tail gas in a reactor to maximise conversion of sulfide to hydrogen sulfide. The hot product gas is cooled in a heat exchanger to produce steam, quenched with water and then contacted with a selective amine that removes the hydrogen sulfide. Maximum removal efficiency occurs at lower temperatures. The hot gas enters near the bottom of the tower while a recirculating water quench is sprayed from above (Figure 1). Some of the quench water is removed for treatment and fresh makeup water is added as replacement. The sulfide compounds tend to accumulate in the quench water, increasing the suspended solids and causing the pH of the quench water to drop. To prevent corrosion, the quench water must be kept between pH 8 and 9 through the addition of amines (or caustic). This balance is maintained by continuous, online pH measurement placed in the quench tower, as shown in Figure 1. Refinery engineers must be cautious in the selection of pH sensors for this application because the dissolved sulfides and other ions in the quench water can poison a silver based reference electrode and cause premature sensor failure. Even more significant is the fact that the combination of hard water and sulfur salts in the quench water produce insoluble coatings that require daily cleaning, while conventional pH reference junctions can become permanently plugged, requiring replacement in only

are less soluble at high pH values. Usually, a small quantity of sulfuric acid, controlled by a general purpose pH sensor, is added to the circulating water to lower the pH and prevent the formation of scale. Chlorine sensors are also employed in the cooling tower to monitor chlorine levels used to inhibit the growth of algae and slime.

Liquid measurement for process improvement

In addition to corrosion control, some liquid measurements are required to ensure optimised operations in strippers and separators.

Sour water stripper

Any refinery processing crude that contains sulfur will produce both sour gas and sour water, meaning that they contain hydrogen sulfide. The reuse and disposal of this water require removing these sulfides through stripping. While air stripping is possible, steam stripping is typically used because it liberates more hydrogen sulfide due to the higher heat applied. The process is complicated by the presence of other chemicals such as ammonia, phenol and cyanide. The stripping process uses a gas stream to force both the hydrogen sulfide and ammonia out of the solution and into the gas phase for further treatment. This presents a problem in that the ideal pH for stripping hydrogen sulfide is below five (above five, sulfide is primarily found in the form of ions). Conversely, efficient ammonia stripping requires a pH above 10 to prevent the formation of ammonium ion that cannot be stripped. Although the optimum strategy would be to use two separate strippers, economics usually dictate a compromise.

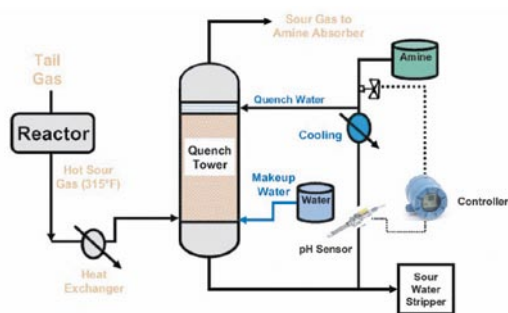


FIGURE 1

Figure 1. Continuous online pH measurement keeps the quench water between pH 8 and 9.

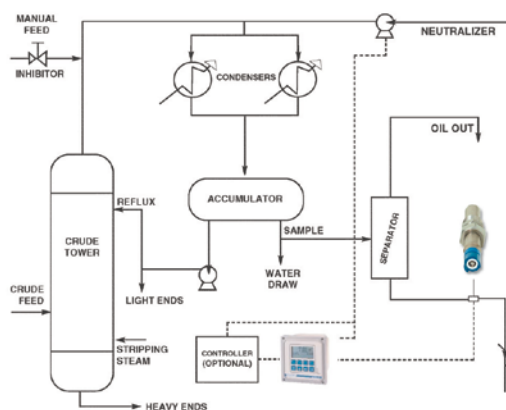


FIGURE 2

Figure 2. To avoid corrosion, a sample drawn from the accumulator is measured for pH.

Using a pH value around 8 allows an adequate removal of both gases. Injecting caustic near the bottom of the tower improves the ammonia stripping while still allowing sulfide stripping at the top. Measuring the pH of sour water, however, is a significant challenge for the equipment. Temperatures are very high to facilitate the removal of gases. Hydrogen sulfide can poison and plug the reference by precipitation with silver ion. Ammonia and cyanide can poison the reference by forming a complex with silver ion. The problems are so severe in sour water that some pH sensors can become unstable within one day. Details of how to avoid these problems are explained in the sensor guidelines below.

Separators

Separators are frequently used in the treatment of refinery wastewater, allowing heavier liquids to settle below lighter liquids, which are then skimmed off. The wastewater may contain insoluble oil, sludge and some soluble components, the latter requiring further treatment. A number of measurement technologies are able to distinguish between the oil and water phases in the separator, but the most cost effective method is electrical conductivity. Conductivity is based on the simple principle that aqueous solutions are good conductors of electricity while non-aqueous solutions are not. As water accumulates in a separator, a conductivity sensor mounted above the vessel outlet can sense the presence of the aqueous phase due to the increase in conductivity. Typically, the conductivity of the 'rag' water layer, directly adjacent to the organic layer, is quite high because impurities tend to collect there. This makes detection of the interface quite easy as the organic layer will not conduct. A conductivity transmitter will indicate the increased conductivity of the water using the 4-20 mA current output or digitally for Hart® or FOUNDATION fieldbus® devices. A discharge valve can be opened on a signal from the DCS or PLC and closed once the conductivity drops back to zero.

pH measurement is also used in the treatment of refinery wastewater. At the discharge from the API Separator, pH control enhances the efficiency of secondary waste treatment processes such as flocculation. Even at the wastewater stage, sensors must be carefully selected and cleaning programs instituted to maintain cost effective operation.

Sensor selection for refineries

pH sensors can be subject to several different damaging conditions in a refinery. The reference electrode can be poisoned by sulfide compounds or heavy metals. The reference junction can be coated or fouled by hydrocarbons or solids. The sensor's internals can be subjected to thermal expansion stress or chemical attack. Engineers and technicians should seek out sensors designed specifically for the rigours of hydrocarbon processing. The savings in maintenance cost will far outweigh any increased cost of a higher performance sensor, with the added benefit of increased measurement availability.

Thermal stress

In areas of the refinery such as the sour water stripper, sensors are exposed to varying temperatures. Many general purpose pH sensors are not designed for temperature changes and may fail due to thermal stresses, especially in the area near the tip of the glass electrode. Today, however, a few sensor models are designed for operation at temperatures over 140 °C (under pressure) and continue to provide rapid

response and stable readings after months of service. With improved glass technology and improved mechanical design, these sensors are continuously measuring in processes that were thought to be unfeasible.

Coating and fouling

New sensor designs for demanding applications use a variety of improvements to resist the effects of coating and poisoning. Engineers should look for reference electrolytes that resist viscosity breakdown with temperature to prevent the process liquid from getting into the sensor. Composite reference junctions with larger surface areas for process contact and coating resistant pore structures should be selected to resist coating and plugging from suspended solids. A multiple junction design is useful to protect the silver reference electrode from sulfide in the process stream by preventing direct contact between the silver and sulfide ions.

New high performance sensors extend the life of the sensor, and reduce the time and money needed for maintenance. At the same time, their longevity and accuracy can be greatly enhanced by an intelligent maintenance plan based on feedback from sensor diagnostics. Not only are new sensors designed for easy replacement of the reference junction and electrolyte, but together with new analyser software, they can both determine that these changes are necessary and predict when they may be needed in the future. Interestingly, this has led the industry to come full circle and again offer the option of rebuildable/refillable references, with the potential to significantly reduce costs (Figure 3).

Selection criteria for liquid analysers

The principal selection criteria for analysers is based on available power, the installation environment and network connectivity requirements. Analysers are divided into four wire and two wire instruments; four wire generally being AC powered (although sometimes available in DC), and two wire being DC-loop powered. Some areas of the refinery may require analysers that are certified as intrinsically safe. Analysers that are to be mounted outside should be rated IP65 (Figure 4) and can be located close to the sensor even in the harshest environments.



Figure 4. Analysers can be mounted outside to withstand even the harshest environments.

Four wire instruments can be located in a control room away from the process, and may be chosen for safe areas such as wastewater processing. Four wire instruments have become extremely sophisticated with multi-parameter instruments available with dual inputs (Figure 5).

Many instruments have large, easy to read screens and are simple to operate, requiring very little instruction. They also have quickstart screens that appear when the unit is initially powered. The instrument auto-recognises each measurement board and the display prompts the user to configure each sensor in a few quick steps for immediate deployment.

The optimum solution for the process starts with selecting the right sensor to match the process needs. In most cases, the instrument is selected for the available power and communication requirements, such as HART and FOUNDATION fieldbus, as well as preventative diagnostics. Some plants will need a combination of surface mount, panel mount and pipe mount enclosures, with either keypad access or handheld infrared remote for local calibration and configuration of the instruments.

For the refinery environment, some instruments offer built-in diagnostic capabilities that can signal the condition of a sensor, the instrument, the overall loop and the process. This ability to anticipate trouble and perform timely maintenance can reduce downtime and operational costs.

Conclusion

With these guidelines on the selection and application of liquid analysis in the refinery, petroleum plants can make significant steps toward reducing downtime and improving operations.



Figure 3. Refinery applications demand long life pH sensors in poisoning and coating conditions.



Figure 5. Sophisticated four wire instruments with advanced diagnostics can be located in control rooms and other safe areas.