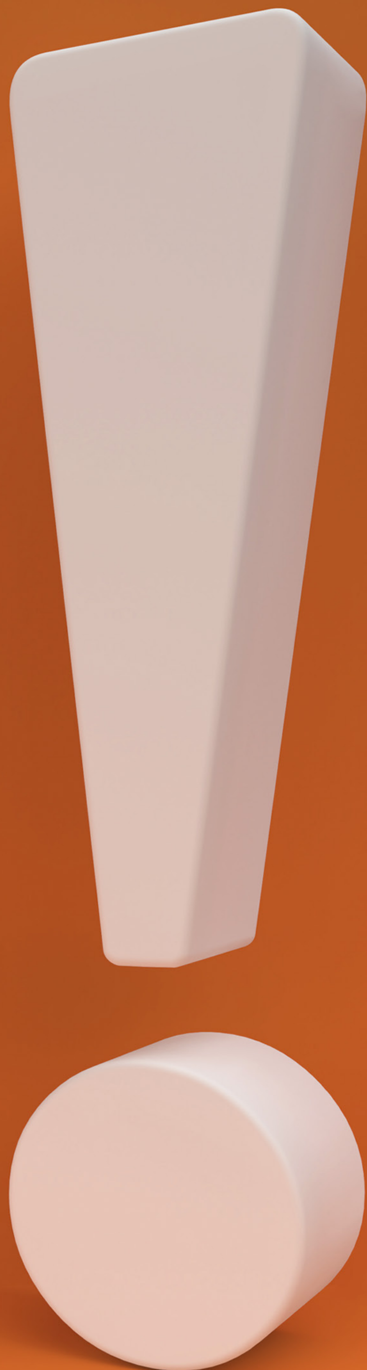
THE IMPORTANCE OF INSTRUMENTATION

Andrew Smith, Emerson, USA, demonstrates why effective treatment of wastewater in refineries and chemical plants depends on the right liquid analytical instrumentation.



The production of oil and heavy chemicals creates effluents, due to the nature of the processes and feedstocks, which are dispersed primarily in two streams: air and water. Air pollution tends to get more attention due to its visibility, but water pollutants can also become a serious issue because of their effect on drinking water supplies. In the US, the Environmental Protection Agency (EPA) regulates petroleum refining effluents under 40 CFR Part 419, which dates back to 1974 and has been updated many times. Other similar bodies exist throughout the world covering their respective geographical areas.

As a result, refineries and chemical plants have sections of their facilities dedicated to water treatment (Figure 1), just as they have scrubbers and baghouses for air pollutants. These are critical processes because regulatory bodies can fine producers for violating water standards.

As a case in point, the EPA launched an environmental compliance investigation into one US refinery in relation to spill prevention and wastewater discharge. The refinery was assessed civil penalties totalling more than US$225 000 and was required to install new monitoring equipment, update its cleaning and inspection programmes, and prevent future unauthorised discharges.

This was a significant fine, levied to convince management of the importance of compliance. In the worst case, a facility can lose its licence to operate for a period of time, further underscoring the importance of effective treatment and monitoring.

Figure 1. Refineries and large chemical processing plants invariably have a wastewater treatment plant for the facility.

Figure 2. Different production units each create their unique range of effluents.

Sources of water pollution

The EPA has compiled lists of pollutants based on data collected and observations of working refineries: "The EPA used 2013 discharge monitoring report (DMR) data and knowledge of the process to identify 26 pollutants likely to be present in petroleum refining wastewater, including metals, nutrients, organics, and other priority pollutants. This listing includes pollutants with high toxicity (high toxic weight factors (TWF)), pollutants identified in the existing Petroleum Refining Effluent Guidelines or Refinery National Pollutant Discharge Elimination System permits, and pollutants that may be present in wet scrubber purge."[1]

A condensed list of water pollution sources includes:

- Desalter water – water produced from washing raw crude prior to topping operations.
- Sour water – wastewater from steam stripping and fractionating operations that comes into contact with the crude being processed.
- Other process water – wastewater from product washing, catalyst regeneration, and dehydrogenation reactions.
- Spent caustic – formed in extraction of acidic compounds from product streams.
- Tank bottoms – bottom sediment and water settles to the bottom of tanks used to store raw crude. The bottoms are periodically removed.
- Cooling tower – once-through cooling tower water and cooling tower blowdown to prevent build-up of dissolved solids in closed-loop cooling systems.
- Condensate blowdown – blowdown from boilers and steam generators to control build-up of dissolved solids.
- Source water treatment system – source water must be treated prior to use in the refinery. Waste streams may include water from sludge dewatering (if lime softening is used), ion exchange regeneration water, or reverse osmosis wastewater.
- Storm water – process area and non-process area runoff from storm events.
- Ballast water – ballast water from product tankers.
- Scrubber water – wastewater taken from scrubbers once it is saturated with solids or captured effluent.

Sensors to identify critical pollutants

Once critical pollutants are identified, it is necessary to determine which are actually present and in what quantities. In a high-school chemistry class, this could be approached through a mix of distillation and boiling off of the water to see what residues are left. However, in a working refinery (Figure 2), at least some of the most critical measurements – particularly those that can fluctuate day-to-day – must be continuous and made in real-time so adjustments can be made to processes via automation systems. Others, such as specific heavy metals, may only call for taking periodic samples and performing laboratory analysis.

For example, choosing from the list of pollution sources above, how is it possible to monitor spent caustic wastewater? What pollutants might be contained in the stream, and what is the best sensor for the task?

To begin with, there is no reason to look for things that are not there. There is a short list of potential pollutants from a given source within a facility. The caustic hydrogen sulfide and mercaptan removal section of a unit is not likely to produce ammonia, so there is no need to look for it. So, the question becomes: how does the relevant effluent at this point in the process change water characteristics in a measurable way that can also indicate the amount of harmful pollutants?

For wastewater evaluation, there are four characteristics able to provide useful information for monitoring because most effluents change at least one, if not more, of these characteristics in predictable ways:

- pH (acid-alkaline scale).
- Oxidation-reduction potential (ORP).
- Conductivity.
- Dissolved oxygen (DO).

Fortunately, all four of these can be quantified accurately and reliably by making measurements in real-time.

Matching sensor and effluent

The sensor selection process in each application should hinge on determining which water characteristic will change in the most measurable and quantifiable way. Remaining with the spent caustic example, such a stream will likely contain sulfides and carbonates, both of which can change the pH and conductivity. The questions will be:

which in this case has the greater effect? Can one of those sensors provide an accurate picture, or are both necessary?

Answering these types of questions and making correct sensor selections calls for cooperation between the plant's internal engineering staff and trusted instrumentation partners. Questions of range, repeatability, accuracy, reliability, maintainability, and other performance characteristics need to be examined in specific situations. For example, in a given application, conductivity or pH could both be highly useful measurements, but conductivity might be less maintenance-intensive. In another situation, the opposite might be the case. The following typical sensor characteristics can help provide an initial sorting for a new application.

pH/ORP

Sensors for these two variables are very similar and some do double duty. An internal reference electrode provides a stable reference signal in changing process environments. These sensors can be maintenance-intensive, so selection must be made carefully to specify a unit able to function reliably for weeks or months at a time. Some sensors can be rebuilt easily, replacing the reference electrolyte to extend service life and maintain high accuracy. Poor-quality sensors can be damaged by electrolyte leakage or poisoning.

When supported by an advanced transmitter, high-quality pH/ORP sensors can reliably provide condition diagnostic information about the sensor itself and the process for long periods of time without any required maintenance.

Conductivity

Contacting sensors can typically handle specific ranges of electrolytic conductivity up to a maximum of 20 000 microsiemens per cm (µS/cm). They can determine the presence of acids and bases by raising conductivity, as well as the presence of hydrocarbons in water by reducing it. Contacting sensors can be damaged by corrosive liquid attack and are best applied where there are not high levels of particulates. Some models can be inserted into the stream to take a reading and withdrawn when not needed.

DO

These sensors are usually installed in the wastewater treatment area to monitor aeration, indicating DO at the ppm level, so they monitor the process rather than identifying a specific effluent. There are two technologies: membrane-based amperometric sensors and optical DO sensors. The former contain an internal electrolyte to complete the circuit between the cathode exposed to the process media and the internal anode, along with a temperature sensor to compensate the reading for changes in the permeability of the membrane with temperature.

Optical DO sensors do not have the internal electrolyte, so they are less maintenance-intensive. They can calibrate themselves automatically in water-saturated air.

Aeration basins are often frothy and dirty environments, so DO sensors may end up being coated with sticky froth, which can impair effective measurements. This is especially problematic with amperometric designs. Some plants install an automated spray nozzle connected to a freshwater supply with a timer to clean the sensor periodically. Another option is to purchase membrane-based amperometric DO sensors with a jet spray cleaner option.

While all wastewater might ultimately end up in the plant's wastewater treatment plant, it will have come from many sources and some, such as spent caustic, will have already passed through a specialised pre-treatment process.

Monitoring from specific processes should be as close to the individual source as possible, since once the streams are mixed it will be far more difficult to attribute an effluent to a single source. Some measurements of the final mix and treated wastewater leaving the plant will undoubtedly be necessary, but these provide little indication as to the source.

Process control in addition to monitoring

While the discussion so far has been about wastewater treatment, these same techniques can support process control. As a case in point, a refinery in Asia had a problem with tank bottom water accumulating in naphtha and pyrolysis gasoline tanks. Draining this water periodically was a manual process, where an operator had to watch a sight glass as the water was being pumped out, often for hours at a time. The operator's job was to concentrate on the sight glass, and call the control room on a radio for a shutdown as soon as the liquid changed colour.

The plant automated this process by installing a retractable conductivity sensor. Now, when it is time to drain the tanks, the operator inserts the probe and opens the valve. Tank bottom water has normal conductivity of 650 to 1000 µS/cm. Once naphtha reaches the sensor, conductivity drops almost immediately, triggering the valve to shut down automatically.

The importance of instrumentation

Refining and heavy chemical manufacturing depends on well-functioning instrumentation and analysers. Monitoring and controlling production processes are a priority, but effluent monitoring is also critical. Avoiding fines is an obvious incentive, but more positive aspects – such as safety, environmental stewardship, and good corporate citizenship – should also drive decisions. Making effective analyser selections depends on a partnership with a provider able to help in the application of all aspects of a successful solution. HE

Reference

1. US EPA, 'Petroleum Refining Effluent Guidelines Studies and Guidance', https://www.epa.gov/eg/petroleum-refining-effluent-guidelines-studies-and-guidance