Seeing is believing

Optical sensors clear air for flare stack, combustion airflow
Sensing pH, controlling pH

Liquid analysis systems and sensors are cost effective tools against corrosion.

Water plus metal equals corrosion. This reality attacks the bottom line of every steam driven power generation plant in the world. In a steam power plant, high purity water is heated and boiled to make steam, which energizes and powers a turbine to produce electricity. Water and steam are in constant contact with metal surfaces threatening the integrity of plant equipment like condensers, heaters, pumps, piping, boilers, and turbines.

Fortunately, water purification and chemical treatment greatly reduce and control the corrosion in the plant. Ensuring good cycle chemistry to prevent corrosion, however, requires accurate and continuous analytical measurements in the demineralization train, cooling water, condensate, and boiler feed-water and steam systems.

While the guidelines given below address the needs of a steam driven power generation facility, they can also be useful in other manufacturing facilities where water plays an important role.

By Brian LaBelle
Rust reaction

Chemical reaction:

\[ 2e^- + O_2 + H_2O \rightarrow 2OH^- \]

Deposition of iron hydroxide (Fe(OH)_2)

Corrosion occurs when metal ions transfer from a base metal to water and combine with oxygen to become hydroxides and solid metal hydroxides. Resultant particles often travel to other parts of the system and are deposited.

**Deposit is a poor conductor**

Once a deposit forms, it attracts more suspended solids and the deposit grows. Deposits frequently accumulate on heat exchange surfaces, boiler tubes, and heaters.

The deposit is a poorer conductor of heat than metal and therefore interferes with heat transfer across the tube. This lowers the overall cycle efficiency and can cause local tube overheating failures. Deposits can also significantly lower the efficiency of the turbines and, in turn, become corrosion sites when dissolved solids trapped in the deposit concentrate as the liquid boils away. Eventually, the concentration reaches highly corrosive levels and severe under-deposit corrosion occurs.

A tough oxide film that protects the base metal is the best way to defend iron and copper from corrosion. For iron and carbon steel, the protective film is magnetite.

For copper and copper alloys, the protective film is cuprous oxide. This film works only in the presence of properly controlled water chemistry.

Proper water chemistry also ensures that the film won't wear away and, if a break occurs, the film quickly repairs itself.

Controlling water chemistry requires maintaining high purity water, controlling pH, monitoring for trace quantities of dissolved oxygen, and, if necessary, controlling the feed of a scavenging agent like hydrazine.

**Demineralization train**

The first line of defense against corrosion in a steam power plant is the use of high purity water. Producing that water is the function of the demineralization train, which converts raw water containing between 100 and 1,500 ppm dissolved solids into water that contains no more than 10 to 20 ppb dissolved solids. Treatment steps may include filtration, softening, chlorine removal, reverse osmosis, degasification, and ion exchange.

Efficient reverse osmosis (RO), in which water forces through a semi-permeable membrane, can remove approximately 98% of the dissolved salts and silica in raw water and nearly all large organic molecules. Contacting conductivity sensors placed in the feed water and the permeate of the RO let plant operators monitor the water quality and overall efficiency of the RO system.

Conductivity measurements in RO permeate and high purity water are not simple, however. The composition of the feed water changes and the membrane affects the conductivity of the permeate. Calibrating sensors against a National Institute of Standards and Technology (NIST) traceable calibrated cell of a known cell constant or by calibrating the sensor in a certified solution. However, upon exposure to the atmosphere, high purity conductivity standards and water foul through the absorption of carbon dioxide from the surrounding air and any residue in the sample container. To prevent contamination, it may be desirable to use sensors pre-calibrated to NIST standards. Conductivity validation instruments are available that connect to the process via tubing, eliminating the effects of the atmosphere on the measurement.

Typically, feedwater to an RO sys-
these systems become exhausted and must be regenerated using sulfuric or hydrochloric acid for cation resin and sodium hydroxide for anion. The monitoring of the concentration of both of these substances must happen continuously with conductivity sensors measuring the regenerant as it enters the tank. During rinse, toroidal conductivity measurement made on the bed effluent determines how well rinsed the regenerants are.

**Variations in cooling tower design**

In the condenser, recirculating cooling water converts turbine exhaust steam into condensate. Cooling water usually contains high levels of dissolved solids, and leakage of cooling water into the steam cycle is a major source of contamination.

Leaks introduce ions that raise the conductivity and increase the corrosiveness of the feed-water, boiler-water, and steam. To give early indication of leakage and to monitor the overall condenser performance, the cation conductivity of the condensate pump discharge registers on a flow-through conductivity sensor.

In addition, monitoring condensate and feed-water purity requires measuring cation conductivity. After the condensate passes through the cation column, the conductance of the contaminating salt increases as it converts to a significantly more conductive acid.

There is an increased emphasis in the industry on the re-use of cooling water using cooling towers. The cooling effect comes by the evaporation of a small fraction of water and heat exchange with the air passing through the cooling tower. As the water evaporates, however, the dissolved solids concentrate, ultimately causing scale and corrosion in the heat exchange equipment. While there are many variations in cooling tower design, a common feature is the control of water quality with the use of continuous pH and conductivity measurements to maintain a given set of conditions. A contacting conductivity sensor measures the relative concentration of the impurities in the water. The analyzer for that sensor initiates the opening of a blowdown valve when the conductivity becomes too high. Higher purity make-up water is then introduced which lowers the conductivity.

Since most impurities in cooling water are alkaline, a small quantity of sulfuric acid added in to the circulating water to lower the pH and thus prevent the formation of scale. Measuring this sulfuric acid concentration and keeping the pH below seven, where scaling is less likely to occur (as indicated by the Langelier Index), is best accomplished by a general-purpose pH sensor. Cooling water that contains a high level of suspended solids, however, requires the use of more specialized pH sensors more resistant to fouling.

**Condensate feed-water**

The cooling tower turns steam into water after leaving the turbine. Make-up water from the demineralization train adds to this water to become feed-water, which pumps through a series of heaters to the boiler. Controlling corrosion in the condensate and feed-water system is usually accomplished in one of two ways—all volatile treatment (AVT) and oxygenated treatment (OT). AVT uses ammonia to control pH and hydrazine to provide a reducing environment for protection of copper alloys. AVT requires measurement of ammonia, dissolved oxygen, and hydrazine. Ammonia measurement can happen either directly or indirectly from pH and conductivity. The indirect method is useful because ammonia reacts in water to produce hydroxide ion. Both conductivity, which is a measurement of ions in solutions, and pH, which is an indirect measurement of hydroxide ion, can combine to yield the ammonia concentration. OT uses ammonia to control pH and trace oxygen to provide a slightly oxidizing environment that promotes formation of a tough modified oxide film. Water quality for OT is more stringent than for AVT, requiring cation conductivity of less than 0.15 micro Siemens/centimeter. It is necessary to measure dissolved oxygen, pH, and cation conductivity in feed-water systems using the OT method. pH measurement can be difficult in low conductivity water and requires the use of flowing reference technology. A pH measurement requires electrical continuity between the reference and glass electrodes and a path to the solution ground. High purity water does not provide enough conductivity to reliably complete these paths and causes junction potential that registers as erratic drift and offset in the pH measurement. A flowing reference eliminates this effect by stabilizing the junction potential. This measurement takes place in a bypass line in order to preserve the quality of the feed-water and preferably in a stainless steel measurement chamber to dissipate the electrostatic current generated by the high purity water. Since high purity pH is flow sensitive, flow rates should be very low and constant.
Boiler water steam treatment

The boiler is the final collection point for all the corrosive and scale-producing contaminants generated upstream. Solid corrosion scales on the boiler tube surfaces and grows by collecting more suspended matter. Eventually, overheating and tube failure occur. Maintenance of a protective oxide film is the optimum way to limit water corrosion, and this more readily happens when maintaining a low concentration of dissolved solids in a slightly alkaline pH environment. To accomplish this, continuous measurement of both pH and conductivity needs to happen. Conductivity measures the concentration of dissolved solids and a long-life conductivity sensor is required. To maintain the alkaline environment required, power plants commonly buffer the boiler water with sodium hydrosulfite and sodium phosphate salts. Overfeeding or underfeeding of these chemicals can be damaging, however, and therefore accurate pH and phosphate measurements are critical.

Boiler water also undergoes treatment in order to produce high-purity steam. Impurities enter this boiler water from the boiler drum and from vaporous carryover, which deposits on the turbine and causes erosion damage. Silica is the most notorious contaminant, and it is necessary to measure it in the boiler water and steam. Salts such as sodium hydrosulfite and ammonia salts also vaporize in the steam and flow into the turbine where they precipitate, concentrate, and become highly corrosive. To control contamination in the steam, the conductivity measurement of the boiler water must happen, which indirectly measures the dissolved solids. Then, blowdown controls the amount of contamination.

So, to avoid the uncontrolled corrosion that costs the power industry billions of dollars every year, monitor water quality rigorously and control that quality continuously.

Liquid analysis systems and sensors are hard working, easy-to-use, cost-effective tools when measured against the impact of corrosion on plant costs and operations.

While every plant is different, generally an array of pH and conductivity sensing instruments is required for virtually every step of the steam-power generation process.

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Grab samples and other periodic measurement techniques are inadequate to the task. Only continuous, real-time analysis offers the assurance of water quality that corrosion control requires.

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Behind the byline

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