



Mettler-Toledo
Process Analytics

pH
Conductivity
Dissolved O₂
Sodium
Silica

In-line Analytical Measurements

for Corrosion Prevention in Chemical Plants and Refineries

METTLER TOLEDO

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Prevent Corrosion with the Help of In-line Analytics

Prevention is better than cure. A statement that is particularly true when dealing with corrosion and its effects. It is not just the repair or replacement of damaged equipment that is expensive: Significant amounts of money are lost on subsequent production downtime, environmental damage, and health and safety hazards. Taken together, annual costs of corrosion have been estimated at 3 trillion USD globally, of which approximately 25 % can be attributed to process industries and power utilities.

External measures such as painting, coating, and cathodic protection may offer satisfactory measures in sustaining integrity of engineering structures, but protecting the inside of process equipment requires a different approach. Constructing an entire plant from corrosion resistant, exotic materials usually involves an exorbitant initial cost. Therefore, corrosion protection programs are usually based on chemical treatment. The effectiveness of specialty chemicals very much depends on process conditions, and as these may vary, so will the quality of the treatment. To err on the safe side by expensive overdosing of corrosion inhibitors has therefore become the rule rather than exception.

This guide shows you the role in-line analytics play in keeping corrosion under control and avoiding unnecessary chemicals consumption in (petro)chemical plants and refineries as well as in power and cogen facilities.

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Fighting Corrosion, Scaling, and Fouling in China's Largest Petrochemical Plant

Case Study

It is estimated that the global cost of oil and petrochemical refinery corrosion and deposition exceeds US\$ 15 billion annually. In cooling water systems a lot can be done to minimize it, with the help of dependable, intelligent measurement systems.

Massive petrochemical refinery

The China Petroleum & Chemical Corporation, more commonly known as Sinopec, is the world's second biggest chemical company by revenue. Saudi Basic Industries Corporation (Sabic) is the fifth. In 2009, these two giants established a joint venture to create the Sinopec Sabic Tianjin Petrochemical Plant, a world-scale petrochemical facility located near Tianjin, China.

Built at a cost of US \$ 2.7 billion, the vast facility's ethylene cracker and eight downstream units came on stream in 2010. The site has an annual output of 3.2 million tons of chemical products including ethylene, polypropylene, butadiene, and phenol.

Controlling recirculated water quality

Significant investment went into the plant's cooling water system, and to keep it in optimal condition corrosion, scaling, and fouling in the recirculated water has to be minimized. Plant technicians must tightly control water quality through treatment with caustic, acid, and biocides to achieve this. Controlling reagent dosing is realized via pH and ORP measurement, with the goal being to maintain the recirculation water within a pH range of 6.5–7.5 with a set-point for ORP of 550 mV.

Regardless of how well the water quality regime is maintained, the level of total dissolved solids will gradually increase until blowdown becomes necessary. Recognizing when to initiate blowdown is most often achieved through conductivity measurements. There are costs associated with conducting blowdown either too soon (more frequent treatment of feedwater) or too late (deposition in piping), so conductivity sensor accuracy is essential.

High performance sensors are key

The in-line pH, ORP, and conductivity sensors that were installed during plant commissioning proved problematic. Replacement parts were difficult to obtain, time spent on maintenance was excessive, and lab analyses of grab samples showed that measurements from the sensors were often incorrect. The low cost



of these systems was quickly proven to be a false economy, and more dependable solutions were sought. METTLER TOLEDO was approached to supply in-line systems that would offer measurement accuracy, long sensor operating life, and low maintenance.

Combined pH/ORP sensor reduces number of measurement points

For pH measurement we put forward our InPro 3250 i probe as being the most suitable. The InPro 3250 i is a pre-pressurized, liquid electrolyte sensor that delivers fast, accurate measurements. It features an auxiliary platinum electrode that offers a major benefit to Sinopec Sabic, the sensor can also measure ORP. Therefore, the number of measurement points in the recirculated water system could be reduced.

ISM® brings major gains

The InPro 3250 i is one of METTLER TOLEDO's Intelligent Sensor Management (ISM) family of sensors. ISM technology increases measurement

uptime, simplifies sensor handling, and lowers operating costs. These benefits are possible due to the specially developed microchip embedded in ISM sensors. For the InPro 3250 i this circuitry allows pH calculation within the sensor itself. The pH value is then transferred to the connected transmitter via a highly stable digital signal. The microprocessor also contains advanced diagnostic algorithms that provide continuous data on sensor "health", so operators know when sensor calibration or replacement will be required.

The features of ISM likewise offer significant benefits for Sinopec Sabic in the measurement of conductivity.

One sensor type for many applications

METTLER TOLEDO Thornton specializes in water analytics. Typically, conductivity measurement for pure water, cooling system water, and chemical processes requires three different sensors due to the extreme differences in conductivity. To combat this, Thornton developed UniCond®, a digital conductivity sensor that can measure from pure water to wastewater to industrial process fluids.

UniCond is capable of this exceptional rangeability because, like ISM pH sensors, conductivity measurement and analog to digital conversion takes place in the sensor itself. This approach bypasses the

problems of cable capacitance and resistance which are the reasons why analog sensors have a narrow measurement range. This restriction means many analog conductivity sensor types are required across a petrochemical facility. With UniCond only one sensor type is required for all these applications, resulting in reduced inventory and operator training.

Powerful and flexible transmitter

For use with the InPro 3250 i and UniCond sensors, Sinopec Sabic selected the multichannel version of our M800 ISM transmitter series. This is a multi-parameter unit designed to offer the highest installation flexibility and, with its color touchscreen, excellent ease of use. The M800's iMonitor diagnostics utility predicts sensor maintenance and details corrective actions before process measurements are affected.

Reliable solution and competent local service

Plant technicians are very satisfied, not just with the reliability and performance of the METTLER TOLEDO ISM solutions, but also the local support available from our service department. Sinopec Sabic is now running its cooling water treatment regime with confidence.

► www.mt.com/ISM-chem

► www.mt.com/UniCond



Beating Corrosion pH Control in Overhead Condensers

Corrosion in distillation tower and condenser tubing is a common and costly problem. Maintaining an optimal pH level in the process water significantly reduces corrosion, but the process conditions require extremely robust pH measurement systems. For a refinery in Alaska, the accuracy and long lifetime of the InPro 4800i electrode has led to major improvements in corrosion control.

Tough environment

In distillation tower process water, low pH and high pH both lead to corrosion of condenser tubing. Correct feeding of corrosion inhibitors is a classic application for pH control, but it is also notoriously problematic. High temperatures and pressures, the presence of sulfides and coating from hydrocarbons means pH electrodes can fail in a matter of days. A major refinery in Alaska was struggling to maintain pH measurements in a sample line off an overhead condenser. They had tried electrodes from a number of suppliers, but despite cleaning and calibrating on a daily basis the probes were surviving for no more than a week or two. Excessive costs for sensor maintenance and replacement, plus concerns that corrosion inhibitors were at times being under or over fed, made refinery engineers determined to find a reliable solution. METTLER TOLEDO was happy to install a trial measurement system comprising an InPro 4800i pH electrode, InFit 761e sensor housing and M420 transmitter.

pH electrode for extreme conditions

The Ex-approved InPro 4800i series has a number of features that make it suitable for refinery processes:

- It operates comfortably in temperatures up to 130 °C (266 °F) and pressures of 13 barg (188 psig).
- Its very long diffusion path means it has a strong resistance to contamination from sulfides, salts, and organic and mineral acids.
- The sensor features an annular junction made from PTFE to prevent scale build-up.



Detail of InPro 4800i pH electrode showing long diffusion path



In short, the electrode is a low maintenance sensor which is highly tolerant of the conditions found in distillation towers. The "i" in the sensor's name indicates that it features METTLER TOLEDO's Intelligent Sensor Management (ISM) technology. ISM provides a number of unique features that further reduce maintenance requirements and simplify handling.

Predictive diagnostics

ISM sensors monitor themselves for wear and tear as well as their need for calibration. This information is displayed on the M420 transmitter as the Dynamic Lifetime Indicator and Adaptive Calibration Timer. These two tools keep technicians informed on the status and performance of the electrode, thereby allowing maintenance to be conducted before pH measurement is compromised.

Plug and measure

Calibrating sensors in the field is often cumbersome, and during winter for technicians at our customer's

refinery in Alaska, is also very cold! ISM sensors eliminate this problem as they can be calibrated in the comfort of a workshop. Using a laptop or PC, a simple USB connection and METTLER TOLEDO's iSense Asset Suite software, an InPro 4800i can be pre-calibrated then stored until it is needed. When sensor exchange is required, the pre-calibrated electrode is simply swapped with the current electrode and the system is ready to measure again in a few moments.

InFit 761e sensor housing

This is one of the most versatile housings on the market due to the wide variety of body materials, O-rings, process connections and insertion lengths that are available. The InFit 761e is highly durable and protects sensors from harsh external conditions.



M400 2-Wire transmitter

The M400 2-Wire transmitter accepts both ISM and conventional sensors. Its easy operation and large backlit display combine to provide intuitive straightforward operation. The M400 2-Wire also provides HART communication capability, two configurable output signals and PID control.

Significant cost savings

A six-month trial of METTLER TOLEDO's system was extremely successful and the equipment was permanently installed. Refinery technicians are impressed with the InPro 4800i's resilience to the process conditions, and infrequent need for maintenance. Now, instead of exchanging the pH electrode every two weeks or less, replacement is only required every two months. Technicians also appreciate ISM's diagnostics providing forewarning of sensor maintenance or exchange. Perhaps most significantly, the reliable continuous pH data has resulted in a drop of 10% in the use of corrosion inhibitors. If you need durable pH measurement systems at your refinery, go to:

► www.mt.com/InPro4800

► www.mt.com/ISM



TNK-BP Improves Its Desalting with In-line pH Analysis

Inadequate desalting was causing significant problems for TNK-BP. Thanks to the robust, reliable pH system provided by METTLER TOLEDO not only has desalting greatly improved, the quality of the final products has benefitted too.

Major producer

TNK-BP is a leading Russian oil company and is among the top ten privately-owned oil companies in the world in terms of crude oil production. The company was formed in 2003 as a result of the merger of BP's Russian oil and gas assets and the oil and gas assets of the Alfa, Access/Renova group (AAR).

TNK-BP employs approximately 50,000 people, mostly located in eight major areas of Russia and Ukraine. In 2009 the company produced on average 1.69 mboed.

At one of TNK-BP's refining subsidiaries in western Russia, they produce a wide range of high-quality oil products including motor gasoline, diesel fuel, jet fuel and lubricants.

Importance of pH

In the desalter operation at the refinery they use a pH measurement to monitor the water effluent as it allows the control of pH in the desalter itself. However, they were unhappy with the performance and lifespan of the pH electrodes they were using which, because of incorrect measurement, was leading to corrosion and fouling problems downstream. They asked METTLER TOLEDO Process Analytics if we could provide a more dependable system that would be easy to maintain.



InPro 4260 pH electrode showing the open junction of the Xerolyt Extra solid polymer electrode



Complete system

We recommended our InPro 4260 electrode combined with the InTrac 777 retractable housing and pH 2100 transmitter.

InPro 4260

This electrode features Xerolyt Extra solid polymer electrolyte for precise pH measurement and longer lifetime, even in the most difficult high particle concentration and hydrocarbon environments. This diaphragm-less probe features an open junction, allowing direct contact between process media and electrolyte. As there is no diaphragm, the possibility of clogging is greatly reduced, as is the need for frequent cleaning.

InTrac 777

This retractable housing includes an integral flushing chamber in which the electrode can be cleaned without process interruption.

M400 2-Wire

The loop-powered transmitter is designed for continuous, accurate, reliable measurement of demanding



process applications, making it ideal for refinery environments. The M400 2-Wire features HART communication and offers full ISM functionality.

Satisfied customer

The complete system provides exactly what TNK-BP required: longer electrode life, accurate measurements and simple maintenance. But even more importantly, the more efficient desalting has improved the quality of the refinery's final products. Such is TNK-BP's satisfaction that they are planning to install six further METTLER TOLEDO systems.

If you want to improve the desalting operation at your refinery, go to:

► www.mt.com/PRO-pH



Stay Ahead of Fouling

pH Control in Ethylene Quenching

In the production of olefins, naphtha or natural gas feedstock is steam cracked at high temperatures in a cracking furnace. This sets off a variety of reactions which are brought to a halt by quenching the produced gas mixture with water. The mixture, containing approximately 38% ethylene, is then separated in several compression and fractionation steps. Emulsification problems after quenching can lead to severe fouling, or loss of efficiency and manufacturing capacity.

Background

Ethylene and propylene are arguably the most important basic organic chemicals. The global output of ethylene is currently around 130 million metric tons annually, and is growing substantially. More than half of the total production of ethylene is used for the production of polyethylene. The biggest growth in ethylene production comes from the Middle East and Asia.

Process

Although various processes and feedstocks for the production of olefins exist, thermal cracking of saturated hydrocarbons is nowadays the predominant technology. The process can be divided into four steps:

1. Steam cracking

Together with superheated steam, feedstock such as naphtha is fed into a tube furnace. Here the saturated hydrocarbons crack under temperatures between 750 and 1,000 °C.

2. Quenching

To avoid any undesired secondary reactions the cracked gas mixture is rapidly cooled by direct quenching with water. Heat is recovered through steam production in heat exchangers.

3. Purification

Process water and pyrolysis gasoline are separated and the gaseous hydrocarbons are compressed, condensed and washed with caustic to remove acid gases such as hydrogen sulfide and carbon dioxide.

4. Drying and cryogenic distillation

Before the mixture is passed through a series of low temperature fractional distillation columns, it needs to be dried in order to avoid the formation of ice.

Quench tower

In the quenching step (2), heavy gasolines condense in water that circulates through the quench tower and



gaseous products leave the tower from the top. The condensed gasolines and water separate in the sump of the tower or in an oil/water separator connected to the bottom of the tower. Many of the hydrocarbons in the sump have similar densities to that of water, which can lead to emulsion forming in the sump. Breaking the emulsion can be very complicated, and together with the quench water, hydrocarbons can circulate back into the tower. This leads to greater fouling of the packed tower, reduced heat transfer and an increase in downtime.

The separation process can be controlled effectively, and emulsion forming largely avoided, by maintaining



InPro 4800 i pH electrode

proper quench water pH values through injection of neutralizers such as caustic soda or organic amines.

Instrumentation

Depending on the feedstock, especially with natural gas feeds, the quench water can be highly contaminated. This makes pH measurement and control a complicated issue.

The InPro 4800 i pH electrode, with annular PTFE reference diaphragm and extra long diffusion path, is designed for service in tough environments. It resists fouling due to hydrocarbon contaminants and sulfides, guaranteeing high accuracy and fast response throughout its long life.

Featuring Intelligent Sensor Management (ISM) technology, the sensor provides full diagnostics that advise the operator when maintenance is due.

The corresponding transmitter for the electrode is the M400 2-Wire, a two-wire pH analyzer that is fully certified for hazardous area use and offers HART® communication and ISM diagnostic functionality.

In cases of extreme fouling, the EasyClean 400 automatic, electrode cleaning and calibration system guarantees continuous availability and maximum reliability of the measurement.

► www.mt.com/PRO-petrochem



Improved Optical DO Technology

Minimizes Power and Cogeneration Plant Corrosion

In power plant cycle chemistry, control of dissolved oxygen (DO) is essential to minimize corrosion and the subsequent deposition of metal oxide corrosion products in critical components. Therefore, measuring DO in power plants is a fundamental process management parameter. However, many plants still use membrane-based polarographic sensors for DO determination, and although this technology is reliable in ideal conditions, in reality it can be problematic. Issues with DO measurement using polarographic probes have been eliminated by sensors that utilize optical technology. The high performance and reliability of optical sensors is the reason for their increasing use in power plants.

Dissolved oxygen application overview

DO limits and their rationale are clearly delineated in the many industry cycle chemistry guidelines established by EPRI, ASME, VGB and other organizations.^[1,2,3] These limits have been carefully established based on water chemistry treatment, boiler type, and operating pressures and component alloys.

There are two basic feedwater chemistry strategies used to manage DO: reducing and oxidizing. Reducing conditions must be maintained where copper alloys are used in feedwater components and/or where high feedwater quality cannot be maintained. Under these conditions DO must be kept at very low ppb levels to prevent corrosion. The second strategy is to use an appropriate level of oxidation. This can only be used when feedwater quality is high and feedwater components are composed of all-ferrous alloys that can be passivated with controlled oxidation. To support low DO levels in the cycle, makeup water treatment includes deaeration to prevent introduction of oxygen to the condenser hotwell at the start of the feedwater train.

In addition to cycle chemistry applications, some power plants measure and control DO in generator stator cooling water to minimize copper corrosion in that loop.

Cycle chemistry

All volatile treatment - reducing, or AVT(R), is needed when there are copper alloys in the feedwater train and/or where feedwater quality is low. AVT(R) uses deaeration and a reducing agent (hydrazine or other reducing amine) to decrease the DO content to low single digit ppb concentrations in order to create a protective, reduced, cuprous oxide layer on the copper alloy. At these low DO levels, accuracy, sensitivity,



stability, and reliability become critical for management of the reducing agent feed rate. If the DO measurement is inaccurate, it can lead to excessive reducing agent feed which is a financial waste and, potentially trigger unwanted side effects. More importantly, it can contribute to conditions that lead to single-phase flow accelerated corrosion and catastrophic failure. For this reason, oxidation reduction potential measurement is also recommended for this application to detect excessively reducing conditions.

For plants with all-ferrous feedwater trains, all volatile treatment - oxidizing, or AVT(O), has significant advantages. No reducing agent is used and the mildly oxidizing conditions promote the development of red ferric oxide hydrate (FeOOH) over blue steel's magnetite (Fe₃O₄) layer. This combination creates the most durable surface and results in the least corrosion product transport. To accomplish this, the DO concentration is controlled by deaeration and adjustment of feedwater heater vents.

AVT(O) treatment may not provide adequate oxygen to passivate the entire feedwater train. To extend oxidizing

conditions, oxygenated treatment (OT) - the practice of feeding oxygen ahead of feedwater heaters - ensures that mildly oxidizing conditions are maintained and that FeOOH passivation covers the entire feedwater system. A reliable DO measurement is vital to confirm correct operation (in the 30–150 ppb range).

Stator cooling

Consistent and efficient power generation with water-cooled generator stators depends on stator integrity. Proper cooling water monitoring and treatment can minimize copper corrosion and fouling from corrosion products. If not controlled, deposits of copper oxides can restrict and even the narrow flow channels of stator bars. Consequences of deposition can range from a mild increase in stator pressure drop, to significant efficiency loss, and ultimately to hot spots that permanently damage stator bars.

As shown in Figure 1, the corrosion rate of copper is strongly influenced by DO concentration, pH and temperature also significantly influence the corrosion rate of copper. These relationships have been thoroughly studied and there is now an increasing appreciation for the need to monitor these three critical parameters. In addition, to prevent electrical flash over as well as to minimize corrosion, conductivity must be maintained at very low levels, usually in the area of $<3\mu\text{S}/\text{cm}$.

As shown in Figure 1, DO influence is unusual in that either very low or very high concentrations will minimize corrosion, whereas mid-range concentrations are most detrimental. This leads to two strategies for handling DO: it must be controlled to either <20 ppb or $>2,000$ ppb. Concentrations between these levels promote rapid copper attack and it is important that any excursions into this “no-man’s-land” be severely limited. Slightly elevated pH, between 8 and 9, also has great benefit on reducing corrosion and has led to a growing number of plants monitoring and adjusting this parameter.

Continuous, reliable DO measurements are the key to ensuring the right conditions are maintained. For generators using the low DO strategy, DO measurement can confirm that air is not leaking into the system at the deionizer or other components of the circulating system and causing the DO level to rise into the high corrosion region. From the other direction, for generators using the high DO strategy, a DO measurement can ascertain that the hydrogen atmosphere within the generator core is not displacing

oxygen in the coolant and lowering it into the corrosive mid-range.

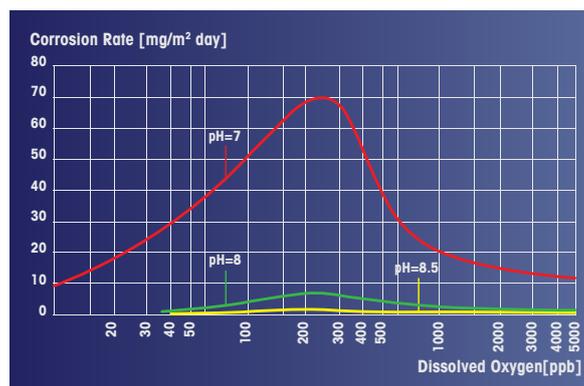


Fig. 1: Copper corrosion rate as influenced by dissolved oxygen and pH (graphic enhancement courtesy Power Plant Chemistry)

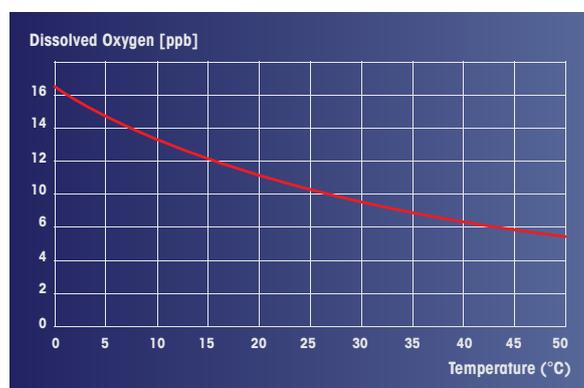


Fig. 2: Solubility of dissolved oxygen

When following the low DO strategy, it is a requirement of the measuring instrumentation that it must not be subject to interference from dissolved hydrogen. This interference is a common problem among polarographic sensors. Hydrogen produces a negative response from such sensors, resulting in misleading low DO readings and a false sense of security.

Makeup water treatment

DO is a concern in final makeup water before it goes into the storage tank and the condenser hotwell where DO levels are generally kept as low as possible. Deaeration is a critical stage in makeup water treatment to meet this requirement. To monitor the performance of the deaerator, DO measurement is essential. A fast responding sensor can immediately alert the operator to any upset in deaerator operation before significant amounts of air are allowed to reach the hotwell.

Oxygen solubility

The critical applications mentioned above, all require accurate and reliable DO measurement across a range of concentrations, but particularly at low levels of detection. Since there is a wide and evolving

variety of analytical instrumentation available for this purpose, such equipment must be selected carefully to optimize the balance of accuracy, stability, and low maintenance. A review of the available technology can start with a basic understanding of oxygen solubility.

Oxygen has a temperature-dependent solubility in water at atmospheric pressure, as shown in Figure 2. If the graph curve was extrapolated, the solubility at 100 °C would be zero as water vapor pressure reaches one atmosphere at boiling. The entire curve would be shifted upwards if the pressure over the water were increased. Working in the opposite direction, deaerators depend on partial vacuum and/or elevated temperatures to remove all dissolved gases.

Traditional dissolved oxygen sensor operation

Traditional DO sensors are electrochemical devices that take advantage of the gas permeability of polymer membranes to isolate the electrolyte of the sensor from the sample. This separation enables a sensor to provide a controlled environment for the electrodes and electrolyte while allowing oxygen to enter from the sample and react. Such a design keeps the electrochemistry well-controlled and uncontaminated. Figure 3 is a simplified illustration of the tip of an electrochemical DO sensor showing the sample at the bottom; the layered PTFE, silicone, and stainless steel mesh membrane; and the cathode and electrolyte inside the probe.

The diffusion rate of oxygen through the membrane is proportional to the partial pressure of oxygen in the sample. The membrane material and thickness also affect the diffusion rate, but they are fixed and those properties are accounted for in calibration and temperature compensation.

Oxygen molecules that permeate the membrane react at the cathode, producing a current in direct proportion to the quantity of oxygen in the sample. The current is the measurement signal which matches the oxygen partial pressure and therefore the concentration of DO, at least at constant temperature.

To derive a concentration measurement from partial pressure with varying temperature, the signal must be compensated for based on the relationship shown in Figure 2. That is, the DO concentration in water that a partial pressure represents, depends on temperature. The sensor's resistance temperature detector (RTD)

signal is used by the instrument to temperature compensate the measurement. Further background on the use of these types of DO sensors is described in an ASTM standard.^[4]

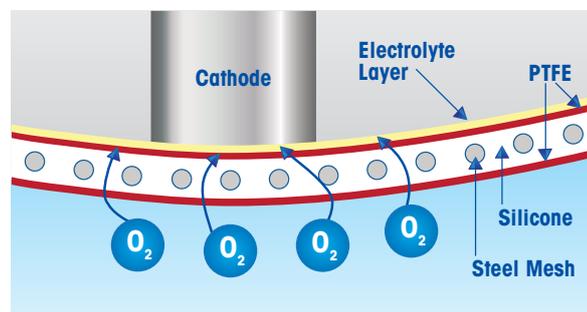


Fig. 3: Schematic view of a polarographic DO sensor

Polarographic sensor limitations

Although widely used, electrochemical measurement technology has a number of shortcomings. Reviewing these limitations provides a greater appreciation for the advances of newer technology.

Membrane-based DO sensors typically have a slow downscale response. This is because any oxygen which accumulates in the electrolyte during air calibration, startup, or high DO excursions takes a long time to diffuse back out of the membrane, or be consumed at the cathode or at a guard electrode. Therefore, high DO readings will persist after the probe is returned to a low DO sample. This issue is particularly frustrating after an air calibration cycle when the operator has to control DO in some applications while waiting for the sensor to recover to normal measurement levels. It can also be costly during plant startups when feedwater must be deaerated to acceptable levels before proceeding to full pressure. If slow DO sensor response delays a plant startup, massive amounts of fuel are wasted and power sales opportunities are forfeited until the DO measurement response finally meets the startup requirement.

At low flow rates conventional probe designs allow a relatively large amount of oxygen to pass through the membrane and more readily deplete the oxygen from the sample layer next to the membrane. This results in readings that are lower than the true value. The same effect applies to membrane fouling: conventional probes have a significant sensitivity to coatings because of their consumption of oxygen from the sample, and they will produce increasingly greater negative errors as coating builds up. It is due to these

issues that these older sensors are sensitive to low flow rates and poor flow housing design. Dissolved hydrogen interferes with most membrane-based, polarographic DO sensors. Hydrogen is often present in power plant stator cooling and nuclear power plant water samples, and it can suppress the measurement of DO or even result in negative readings.

However, the most frequently voiced problem with polarographic technology centers around the frequency and costs of maintaining and calibrating the sensors. Power plant operators have reported that such sensors can require membrane replacements and calibration as frequently as monthly. This is driven by performance degradation, causing a loss in measurement confidence. Depending on the sensor type, maintenance can involve disassembly involving specialized tools, cleaning with hazardous chemicals, polishing electrode surfaces, and careful reassembly where membrane placement is critical. Even quarterly maintenance cycles mean unnecessary measurement downtime, additional costs, and a heavy labor investment at a time when most power plants are looking to reduce maintenance workload.

Optical sensor technology

About a decade ago, the first generation of optical-based DO sensors were introduced for ppb level measurements in power plants. These sensors use a technology known as fluorescence quenching to determine DO levels. Fluorescence is a phenomenon where a material absorbs light of a specific wavelength (color) and after a short time emits some of the light at a different wavelength.

Fluorescence quenching describes the rate of reduction of fluorescence caused by another substance (the quencher), in this case, oxygen. The degree of quenching depends on the amount of oxygen present in the sample. The quenching is quantified by measuring the phase shift between light absorbance and emittance.

The observed phase shift is directly related to the concentration of oxygen, as shown in Figure 4. However, the shape of the curve is not linear as with membrane-based polarographic sensors, but instead follows the Stern-Volmer equation. By very carefully measuring the intensity and lifetime of the fluorescence, optical DO sensors can precisely calculate the concentration of oxygen in the sample.

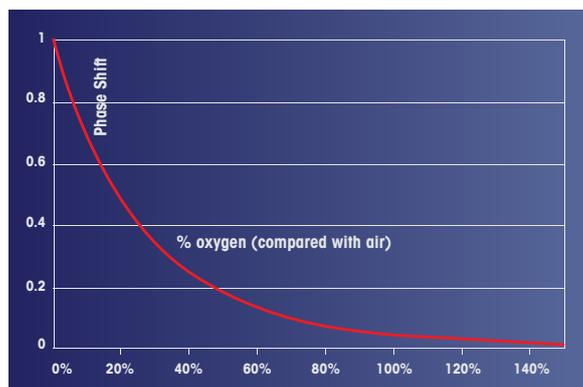


Fig. 4: Optical DO sensor response

First generation optical sensors had limitations in the areas of the lifetime of the light sensitive material (chromophore), low-end sensitivity, and reliability. After successive extensive development work, the second generation sensors are showing excellent performance in all of these areas.

METTLER TOLEDO's Pure Water Optical DO Sensor incorporates the latest developments in this technology, including the use of an easily replaceable unit, the OptoCap, which houses the chromophore.

As can be seen in Figure 5, blue-green light is generated by an LED and is transferred to the chromophore within the OptoCap via fiber-optic cable. The return red fluorescence also passes through the fiber-optic to the detector. Based on the timing and intensity (phase shift) between the two light signals, a precise dissolved oxygen value is obtained.

Response time is on the order of four to five times faster than that of polarographic sensors. Maintenance is simplified and its frequency greatly reduced. Rather than the complicated and time-consuming maintenance several times per year for polarographic sensors, the Pure Water Optical DO sensor only requires annual replacement of the OptoCap.

The significantly faster response of the Pure Water Optical DO Sensor means air calibration is simple and far less time consuming. Additionally, process calibrations allow performance optimization of the sensor without interfering with plant operation.

Multi-parameter, multi-channel instruments

In addition to the improvements offered with optical DO technology, instrumentation has also improved. Meters can also couple a DO measurement with additional channels of specific and cation conductivity, pH, and ORP in the same instrument.

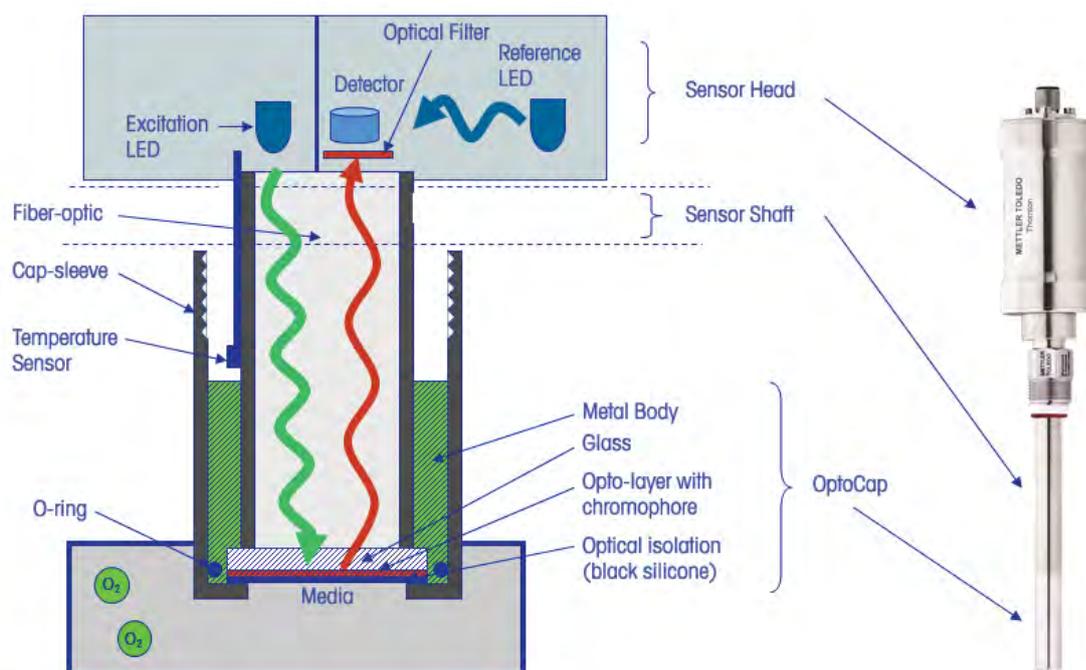


Fig. 5: Design and measurement principle of the Pure Water Optical DO Sensor

This can be especially convenient when multiple measurements are crucial to the success of a particular water chemistry treatment scheme, such as oxygenated treatment, where DO limits depend on cation conductivity levels. Combined measurements are also critical in maximizing the number of measurements in a given panel space and in reducing instrumentation costs.

Conclusion

Controlling dissolved oxygen levels can be critical in power plant chemistry applications. The development of highly reliable optical DO measurement provides benefits including less downtime, and less risk of corrosion of expensive equipment. Reduced frequency and complexity of maintenance saves labor and keeps water systems up and running for longer periods, resulting in lower operating costs. Significantly faster response time enables faster start-up since the operator is not waiting for DO levels to stabilize in the electrolyte as is the case with electrochemical sensors.

Further, the increased reliability of the DO measurement creates more confidence among operating personnel in reacting to cycle chemistry and ultrapure water system upsets.

References

1. "Comprehensive Cycle Chemistry Guidelines for Fossil Plants," 1021767, Electric Power Research Institute, Palo Alto, CA (2011).
2. "Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers," (1994).
"Consensus on Operating Practices for Control of Water and Steam Chemistry in Combined Cycle and Cogeneration," (2012).
"Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (2006).
American Society of Mechanical Engineers, New York.
3. "VGB-Standard, Feedwater, Boiler Water and Steam Quality for Power Plants/Industrial Plants," VGB-S-010-T-00;2011-12.EN.
4. Standard Test Method for On-Line Measurement of Low-Level Dissolved Oxygen in Water, ASTM International D5462-13, W. Conshohocken, PA.

► www.mt.com/thornton-do

Power Plant Conductivity Measurement in Water Treatment and Cycle Chemistry

Conductivity measurement throughout a power plant treatment system from raw water to ultrapure water has typically required a variety of sensors to span the range. With new sensor technology this is no longer necessary and, at the same time, higher accuracy can be achieved.

Makeup water measurements

Monitoring and controlling makeup water treatment systems using reverse osmosis requires multiple conductivity measurements of feed and product water. With seawater feed, the conductivity can run especially high, near 50 mS/cm, which normally necessitates high cell constant, 4-electrode or inductive conductivity sensors.

As water moves through the RO system, dissolved mineral concentration and conductivity are sequentially reduced, requiring many more measurement points, usually with progressively lower cell constant sensors. Finally, deionized product water can be produced at $<0.06 \mu\text{S}/\text{cm}$ where conductivity provides the final quality indication. This measurement often needs a very low cell constant. From the RO system input to the output there is a reduction in conductivity of nearly six orders of magnitude! Confirmed high measurement accuracy of the final product water is essential to prove compliance with guidelines and standards for water purity. Where water treatment is outsourced, dependable continuous measurement of product water is necessary to verify fulfillment of contract specifications.

Sensor simplification

With the appropriate choice of sensor technology, all of the above measurements can be made using a single model of conductivity sensor. Conductivity measurement using Intelligent Sensor Management (ISM) technology opens up a whole new range of capabilities. UniCond® conductivity sensors with ISM have their measuring circuit, calibration memory and analog-to-digital conversion built in. The on-board measuring circuit enables optimized measuring techniques. There are no limitations imposed by long leadwire resistance and capacitance. The circuit includes internal auto-ranging that is able to achieve unprecedented rangeability. Only a digital signal is output by the sensor and neither the



conductivity nor the temperature measurement are affected by long cable runs.

All UniCond sensor calibration data is stored in integral memory so it can never be lost or mixed up if sensors and transmitters are interchanged. The combination of both integral measuring circuit and memory means that the factory calibration accuracy and the installed accuracy are identical. There is no degradation of performance regardless of cable length or routing. Use of correct calibration data is assured.

Cycle chemistry measurements

Many cycle chemistry samples include suspended corrosion product particles released during plant startups and load changes. These particles can become trapped between the electrodes of conventional conductivity sensors used to measure pure waters. This results in a partially shorted sensor and erroneously high conductivity readings. UniCond sensors have considerably wider electrode spacing than other conductivity sensors for pure water ranges. This enables UniCond sensors to operate in the presence of corrosion products with no loss of performance.



Conductivity sensors—left, conventional closely spaced electrodes; right, wider spacing available with UniCond sensors

UniCond sensors can provide particularly accurate measurements on cycle chemistry samples. Their certified ASTM- and NIST-traceable calibration of cell constant and temperature measurement provide assurance of highest accuracy factory and operating calibration. Industry-leading accuracy is achieved because calibration includes both the sensing elements and the measuring circuit and there are no changes caused by installation. UniCond conductivity sensor technology with ISM, provides the highest performance available for makeup water and cycle chemistry measurements.

► www.mt.com/UniCond



pH Measurement in Low Conductivity Samples

Power plant cycle chemistry guidelines and standards specify narrow ranges of pH to minimize corrosion of highly valuable components. In addition, makeup water treatment systems using two-pass reverse osmosis optimize performance by careful control of pH between passes. In both of these applications, pH must be measured accurately under the difficult conditions of low conductivity.

Background

pH measurements in high purity water must be made on side-stream samples in conductive flow-through housings with discharge to open drain at atmospheric pressure. This ensures a sample uncontaminated by contact with air and minimal, constant sample pressure at the reference electrode diaphragm or junction — the primary source of instability in this measurement.

A stainless steel housing is typically used to shield the measurement from electrical noise. The side-stream sample line should be of very small diameter to minimize sample delays at the low flows needed for the measurement and to minimize waste of costly high purity water. Measurement becomes more difficult as sample water purity increases (particularly when conductivity falls below $50 \mu\text{S}/\text{cm}$). Under these conditions the electrical resistance between the glass measuring membrane and the reference electrode intensifies and the potential at the reference junction/diaphragm can become more variable. Streaming potentials or static charges generated at the surfaces of flow housings, electrodes, etc. increase. In general, the measurement becomes noisier. In addition, a significant offset may occur between buffer calibration and high purity measurements due to the large differences of ionic strength at the reference junction/diaphragm between these two solutions.

A further consideration is the sample flowrate vs. flow housing volume. With a relatively large volume housing (as needed to hold separate measuring, reference and temperature compensator elements), any corrosion product or ion exchange resin particles in the sample tend to settle and accumulate in the flow housing where they can absorb and desorb ionic materials. The resulting delayed response can be detrimental to performance and accuracy.



Alternatively, an electrode system that has measuring, reference and temperature compensator elements built into a single probe can be used with a very low volume housing that prevents particles from accumulating because they are carried out with the sample flow. As a result, a much faster response is obtained.

Options

In addition to the basics of a sealed, low volume, conductive flow housing and single probe electrode, there are a variety of reference electrode systems available. These include gel filled, pressurized gel filled and liquid electrolyte filled.

Gel-filled electrodes are not suitable for high purity water because the diaphragm/junction potential is so strongly influenced by the type of sample, resulting in an offset of 0.5 pH or more between calibration and measurement in high purity water.

Pressurized gel-filled electrodes provide more stability of the reference diaphragm/junction potential by forcing a small amount of potassium chloride gel through it. The METTLER TOLEDO Thornton pHure Sensor™ system offers this type of electrode. It requires no maintenance other than occasional calibration throughout its one-year life.



pHure Sensor with pressurized gel-filled reference system

Liquid electrolyte electrodes provide the highest accuracy of measurement by maintaining a steady flow of liquid electrolyte through the junction/ diaphragm. It requires refilling the liquid electrolyte periodically and can have a life of several years. The METTLER TOLEDO Thornton pHure Sensor LE has this capability, plus it includes convenient buffer calibration containers built-in.



pHure Sensor LE with liquid electrolyte reference system

Intelligent Sensor Management

METTLER TOLEDO Thornton pHure Sensor electrodes are available with Intelligent Sensor Management (ISM). This technology offers a number of valuable features including; fast error-free startup with Plug and Measure, embedded measurement circuitry for greater signal integrity, on-board storing of factory and user calibration data, plus real-time predictive diagnostics.

These sensors conform with STM Standard D5128, Test Method for On-Line pH Measurement of Water of Low Conductivity.

► www.mt.com/PRO_power



Reliable Silica Measurement for Pure Water Treatment and Turbine Protection

The presence of silica in boiler feedwater can very quickly lead to deposit formation in turbines. As it can only be removed during out-of-service cleaning, preventing silica from entering the water cycle is the best course of action.

Background

Silica is in all water supplies and requires membrane separation and/or ion exchange for its removal. With ion exchange, it is the most loosely held anionic contaminant and therefore the first to break through an anion or mixed bed ion exchanger.

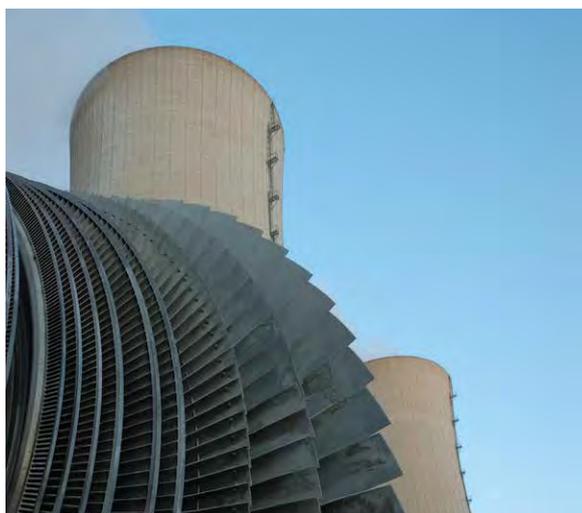
Monitoring silica in makeup water treatment immediately after anion exchange provides the key parameter for initiating regeneration. Sensing the first silica break-through and stopping the run reduces the operating cost of mixed bed ion exchangers downstream by lowering the frequency of their more expensive and more time-consuming regenerations compared with single bed ion exchangers.

Makeup water quality after mixed bed deionization can be very sensitively monitored at low ppb silica concentrations. Silica has negligible conductivity and therefore cannot be detected using conductivity measurements.

Silica volatilizes with steam and deposits on high pressure turbine blades in a silicate form that is extremely difficult to remove. In the turbine, even a modest thickness of silicate reduces capacity, lowers efficiency and can cause imbalance. In the worst case it can result in thrown blades. Silica also contributes to deposits on heat exchange surfaces and reduces thermal efficiency in other parts of the plant.

Silica is always present in cooling water so ppb-level silica measurement is extremely sensitive in detecting small condenser leaks and for identifying exhaustion of condensate polishers. As mentioned previously, this sensitivity is needed because conductivity cannot detect silica.

Direct, continuous silica measurement is the best means to protect against contamination from spent anion resin and from steam carryover.



Silica measurement

Accurate silica measurement requires care in order to achieve consistent results. The measurement uses a molybdate reagent that produces a color change with silica that is detected photometrically. To achieve low level sensitivity, the color change is enhanced using an additional reducing reagent. Some reaction time must be allowed to achieve the full color change. Phosphate also reacts with molybdates. In boiler drum samples where phosphate is used, the phosphate must be sequestered by a third reagent to prevent interference. Silica measurement also must accommodate changes in sample and optics clarity without drifting.

Solution

The design of the METTLER TOLEDO Thornton 2800Si Silica Analyzer is optimized to handle these measurement challenges. With each measurement cycle, it re-zeroes itself on the sample to correct for any changes in optics or sample clarity. The 2800Si then meters in the appropriate amounts of reagents, allows completion of the color change reactions and takes the measurement. After thorough automatic rinsing, it repeats the measurement cycle based on user-configured timing. This timing can be used to optimize the compromise between response time and reagent consumption.



METTLER TOLEDO Thornton 2800Si Silica Analyzer

The 2800Si Analyzer enables unattended automatic span calibration at a user-configured interval. It uses a relatively high concentration standard solution that is easy to prepare and handle. The standard is automatically and consistently diluted to low concentrations for calibration near the range of measurement.

The METTLER TOLEDO Thornton 2800Si analyzer is contained in a fully enclosed cabinet to protect reagent containers and other components from the plant environment.

► www.mt.com/thornton-silica



Safeguard Water and Steam Purity with a Sodium Analyzer

Reliable, automatic, on-line analysis of sodium in water and steam samples helps prevent damaging corrosion and deposits in power plant pure water systems and steam turbines.

Background

Sodium is one of the most common cations in water supplies and requires membrane separation, distillation or ion exchange for its removal. Even with ion exchange, it is the most loosely held cation and therefore the first to break through a cation exchange resin bed.

Monitoring sodium in makeup water treatment immediately after cation exchange provides the key parameter for initiating regeneration. Sensing the first sodium break-through and stopping the run reduces the load on mixed bed ion exchangers downstream by lowering the frequency of their more expensive and more time-consuming mixed bed regenerations compared with single bed ion exchangers.

Makeup water quality after mixed bed deionization can be very sensitively monitored at sub-ppb sodium concentrations. Sodium is representative of ionic contamination in general so its confirmation at such low levels along with very low conductivity provides confidence in the pure water quality entering the steam/water cycle. Sodium is responsible for various types of corrosion.

Sodium hydroxide is more volatile than other sodium salts and can be assumed to be the dominant sodium species carried over in steam.

Corrosion mechanisms include caustic embrittlement and stress corrosion which are aggravated as caustic concentrates tremendously in the first condensate contacting low pressure turbine blades or in crevices of other components. Great effort is expended in monitoring proper boiler operation to assure minimal carryover of contaminants in the steam. Caustic gouging in boiler tubes is another area of concern.

Sodium is always present in cooling water so ppb-level sodium measurement is extremely sensitive in detecting small condenser leaks. This sensitivity exceeds that of cation conductivity by a significant



margin. For example, 0.2 ppb of sodium (0.5 ppb as NaCl) would increase conductivity by only 0.001 $\mu\text{S}/\text{cm}$. Early detection of contamination allows time for planning corrective action before the condenser leaks enlarge and serious damage occurs.

Sodium measurement challenges

Accurate trace level sodium measurement requires a number of precautions in order to achieve consistent results. The measurement uses an ion-selective sodium electrode, reference electrode and sample conditioning to assure response only to sodium. Conditioning consists of raising the pH of the sample to prevent interference from hydrogen ion. The design must also keep the reference electrode downstream of the sodium electrode to prevent reference electrolyte from contaminating the sample before it is measured. A further challenge is that calibration at very low concentrations can be difficult because standards at that low level are quite vulnerable to contamination.

Solution

The design of the METTLER TOLEDO Thornton 2300Na Sodium Analyzer is based on extensive instrumentation experience and is optimized to handle these measurement challenges. The electrode is formulated for high selectivity to sodium ion and is complemented by the use of diisopropylamine reagent which has properties to support that selectivity. The 2300Na includes a pH measurement to ensure that proper reagent addition is actually achieved and alarms on low pH. For efficiency, the reference

electrode serves both the sodium and the pH measurements.

For calibration, the 2300Na provides unattended automatic calibration. It uses a relatively high concentration standard solution that is easy to prepare and handle. The standard is automatically and consistently diluted to low concentrations for calibration near the range of measurement. Multiple

additions of the standard accomplish the known-addition method that fully calibrates the analyzer.

The METTLER TOLEDO Thornton 2300Na is available in a fully enclosed cabinet for installations on the plant floor or in a more accessible enclosure for cleaner environments.

► www.mt.com/thornton-sodium



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Intelligent Sensor Management for Chemical Processes

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Greater process reliability **Easy sensor handling** **Reduced maintenance**

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- Head Mount Transmitter- M100

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