Intelligent TOC Sensor Provides Continuous Analysis

One of China’s largest power generation companies required real-time TOC monitoring in their makeup water and cycle chemistry samples. To ensure measurement reliability they chose METTLER TOLEDO Thornton’s 5000TOCi Sensor.

Plant background
Jiaxing Power Plant is a large thermal power enterprise in Zhejiang Province, China with eight operating units and installed capacity of 5,000 MW. It is operated by the Zheneng Group and is their largest power generation plant. The Jiaxing plant has a record of leadership among similar large coal-fired power plants including high achievements in production safety, efficient operation, and technology.

TOC monitoring is critical for guideline compliance
Controlling organic content in the water/steam cycle for the safety and efficient operation of power generation units is critical. Around the world, thermal power units with high capacity, high temperature/pressure generator sets have strict steam quality specifications regarding the total organic carbon (TOC) content in cycle chemistry. China promulgated the Quality Criterion of Water and Steam for Generating Unit and Steam Power GB/T 12145-2008 and also tightened the TOC content requirements for make-up water (see table next page).

Accurate measurements are needed to confirm compliance with guidelines and regulatory requirements of the industry. These TOC limits are benchmarks for feedwater and steam in actual plant operation to preserve the safety of turbines. Organics enter the boiler under elevated temperature and pressure conditions from the feedwater and makeup water. Organic matter decomposition at high temperatures produces organic acids and results
in a mix of carbon dioxide and organic acids that lower the water’s pH, leading to increased corrosion or additional chemical consumption to neutralize the acids. The anions of these compounds will also lead to increased cation conductivity readings and can mask more corrosive materials as well as making it difficult to comply with cation conductivity limits.

Removing organic contamination can lower operating costs

Normally, the largest source of organics is the makeup water supply. If the treatment system does not remove them, they can enter the steam/water cycle. In some cases, damaged ion exchange resin itself may contribute organics to the makeup water stream. Although anion resin in good condition will remove organics, the organics will eventually foul the resin making it less efficient. The resin will ultimately require cleaning or replacement. The detection and correction of organic contamination can lower the operating costs of makeup water treatment systems.

Incomparable 5000TOCi Sensor

After investigating the benefits of on-line, real-time, continuous TOC analysis the Jiaxing Power Plant installed the METTLER TOLEDO Thornton 5000TOCi Total Organic Carbon Sensor and M800 Transmitter. A Jiaxing Power Plant instrumentation engineer noted: “The METTLER TOLEDO TOC sensor cannot be compared with similar instruments. Measurement with the 5000TOCi is accurate, stable, convenient, and low maintenance, and it is indeed a very good industrial analyzer ideal for power plant water/steam measurements.”

<table>
<thead>
<tr>
<th>Standard specification</th>
<th>Feedwater TOC (ppbC)</th>
<th>Makeup water TOC (ppbC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL/T 912-2005</td>
<td>≤ 200</td>
<td>≤ 200</td>
</tr>
<tr>
<td>GB/T 12145-2008</td>
<td>≤ 100</td>
<td></td>
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<tr>
<td>VGB-S-010-T-00 (VGB-R450L)</td>
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Requirements for make-up water
Flexible transmitter
The associated M800 readout transmitter provides a color touchscreen display of all measurement parameters: conductivity and temperature as well as TOC. It also offers trending displays plus time averaged and peak values for more efficient data evaluation. The M800 multi-channel, multi-parameter capability allows up to four analytical sensors in any combination of conductivity, pH, ORP, dissolved oxygen, as well as TOC to be displayed and provides output signals for all of them.

Benefits of 5000TOCi and M800 system:
- Continuous, real time, on-line detection provides a true picture of TOC content in feedwater, make up water and steam.
- Semi-automatic calibration process ensures accurate results, thereby improving instrument reliability.
- Automatic flow control eliminates the effects of changes in system pressure, improving the reliability of TOC analysis.
- iMonitor on M800 transmitter provides at-a-glance sensor diagnostics and status for maintenance planning.
- Multi-parameter, multi-channel versatility for analysis of TOC and other critical processes parameters.

Intelligent Sensor Management
The 5000TOCi Sensor provides continuous, rapid, and reliable monitoring of power plant makeup water and steam TOC content. It uses Intelligent Sensor Management (ISM®) technology which boosts sensor performance, simplifies installation and operation, and enables predictive maintenance. ISM features include the storing of all calibration and identification data directly in the sensor to simplify documentation and startup. Predictive maintenance service reminders enable better maintenance planning, which saves time and expense. The 5000TOCi sends a robust digital signal to the transmitter with no degradation of measurement accuracy. The continuous on-line analysis ensures a rapid indication of any changes in TOC, with response time of only one minute.

> www.mt.com/toc
Protecting Turbines with Low Maintenance Sodium and Silica Analyzers

To shield turbines from corrosion and scaling, sodium and silica in the power cycle must be maintained at negligible levels. Determining contamination at low ppb levels requires highly capable equipment. METTLER TOLEDO’s sodium and silica analyzers combine accuracy and reliability with low maintenance.

Brazilian co-generation company
Economic development in Brazil is resulting in an ever-increasing requirement for energy and fuel. Some of this demand is being met by a major sugar company who uses part of their crop to produce 2 billion liters of ethanol annually, and through co-generation supplies the country’s electricity grid with 1.5 million MWh.

Minimizing downtime to repair corrosion and clean deposition from turbines and piping is vital to co-generation efficiency, so the company maintains tight control of water and steam condensate quality. In a mill near the state of São Paulo, sodium and silica are closely monitored to indicate the level of water purity.

Consequences of sodium and silica contamination
Any sodium present in the steam cycle becomes highly concentrated in the condensate that accumulates on low pressure turbine blades or in crevices of other components. Caustic gouging in boiler tubes is another area of concern. In cooling water, sodium contributes to condenser leaks.

Silica volatilizes with steam and deposits on high pressure turbine blades. Even a modest thickness of silicate reduces capacity, lowers efficiency, and can cause imbalance. Silica also contributes to deposits on heat exchange surfaces and reduces thermal efficiency in other parts of the plant.

2800Si Silica Analyzer
2300Na Sodium Analyzer
Sodium is detectable via conductivity, but not at the sensitivity required to monitor small condenser leaks (a rise in sodium of 0.2 ppb would increase conductivity by only 0.001 μS/cm). Silica has negligible conductivity and cannot be reliably detected using conductivity measurements. Dependable sodium and silica measurement at low ppb levels requires highly specialized analyzers.

**Advanced sodium and silica analyzers**

METTLER TOLEDO’s 2300Na Sodium and 2800Si Silica Analyzers combine industry-proven technology with innovative design to provide assurance of water purity in power cycle chemistry applications.

The 2300Na Analyzer determines sodium levels by first conditioning the sample to prevent hydrogen ion interference by controlling the input flow and the pH, then uses a sodium ion-selective sensor to precisely determine sodium levels.

The analyzer possesses a very wide measurement range of 0.001 to 100,000 ppb and has a rapid refresh rate of one measurement per second. Fully automatic calibration ensures reliable operation and saves time.

**2300Na Sodium Analyzer**

- Fully automatic, unattended calibration ensures reliable operation and saves time
- Reagent addition confirmation by pH Check to safeguard consistent measurement results
- Four analog outputs for sodium, adjusted pH and temperature with choice of scaling to enable full integration into data acquisition or control system

**2800Si Silica Analyzer**

- Fully automatic, unattended calibration – provides excellent repeatability and saves operator time
- Automatic zeroing with every measurement – ensures measurement stability
- Large reagent containers enable a long service interval – reducing maintenance

Similar to the 2300Na, the 2800Si also allows measurements directly from the process or samples collected at other points.

**On-line analyzers match lab measurements**

Impressed with the features of the analyzers, the plant installed one of each in their laboratory and for a period compared the results from the units with those of laboratory equipment. Both analyzers showed excellent correlation with lab results.

After an additional 60 days of testing the analyzers in real plant conditions plant technicians had the highest confidence in their results and stopped obtaining secondary sodium and silica lab measurements.

**Accurate and reliable**

Our customer is very impressed by the analyzers’ measurement accuracy and they are more than satisfied with their low maintenance requirement which frees technicians from routine maintenance. The sensitivity and reliability of the 2300Na and 2800Si are providing the plant with assurance that their turbines are thoroughly protected.

If you want to protect you turbines, visit:

- [www.mt.com/Thornton-silica](http://www.mt.com/Thornton-silica)
Ensuring Water Purity in Demineralization and RO Processes

To confirm impurities have been removed from make-up water requires highly sensitive, fast responding on-line sensors. Reliable measurements and unequalled ease of use convinced a US power plant to select METTLER TOLEDO Thornton solutions.

Water impurity removal
To optimize steam turbine efficiency and the quality of steam and boiler feedwater, make-up water needs to be as high quality as possible. As there is a constant loss of cycle water for power generation, it is always necessary to have a continual source of incoming water.

All water supplies contain impurities which are present as dissolved solids (cations and anions), colloids, suspended solids or organic materials. These impurities must be removed to prevent them from endangering power plant cycle components and processes. Makeup water treatment almost always includes demineralization to remove dissolved impurities.

Demineralization and reverse osmosis
In the demineralization of water by ion exchange, strong acid cation resin in the hydrogen form converts dissolved salts into their corresponding acids, and strong base anion resin in the hydroxide form removes these acids. Demineralization produces water similar in quality to distillation, but at a lower cost for most fresh waters.

Reverse osmosis (RO) units typically precede demineralization units as they provide feedwater of a higher quality, which increases the efficiency of the ion exchangers. On both demineralization and RO, monitoring of pH and conductivity is vital for process control.

US energy company
A large US electric and natural gas company located in the Midwest provides a comprehensive portfolio of energy-related products and services to over 3 million electricity customers and 1 million natural gas customers. For installation of new RO and water demineralization systems at the plant, a well-respected Canada-based supplier was selected.

The water system supplier and the power company initially agreed to install another provider’s pH and conductivity monitoring systems on the new equipment. However, the supplier was interested in METTLER TOLEDO’s Intelligent Sensor Management (ISM®) technology and arranged for a demonstration for them and power plant representatives to determine its benefits.

On-line sensors that are easier to use and calibrate
Ease of sensor installation, configuration, and calibration were all benefits appreciated by the decision-making team. The water system supplier and the power company representatives were also impressed by the innovation of the ISM concept and the many features designed to improve water monitoring processes while reducing the amount of maintenance required. In particular, the power company felt that the ISM solutions were much easier to use and calibrate than competitive systems, which resulted in a decision to choose the METTLER TOLEDO Thornton systems for the new demineralization and RO units.

Keeping processes on target
The newly installed systems are now providing user-friendly operation and the measurement accuracy and continuous measurements from the sensors is ensuring both demineralization and RO processes remain on track at all times.

Find out more at:
www.mt.com/pro_power
M800 multi-parameter, multi-channel transmitter
- Multi-channel functionality reduces cost per measurement point
- Color touchscreen and intuitive menu structure simplify operation
- iMonitor sensor diagnostics utility
- Traffic light color-coded sensor function status

Find out more about the M800
➤ www.mt.com/M800

UniCond conductivity sensor
- Extremely wide rangeability
- 33 % greater accuracy over analog sensors
- Can be calibrated while still in the process
- No signal degradation over long cables

Watch the video on UniCond Sensor set up
➤ www.mt.com/UniCond-video

pHure pH sensor
- Pressurized gel electrolyte for extended life
- Low volume flow housing encourages corrosion particles to flush-through control system
- Can be calibrated in any convenient location away from the process
- Plug and Measure means commissioning and start-up are fast and error-free

Watch the video on pHure Sensor installation
➤ www.mt.com/pHure-video
In-line Analysis
Frequently Asked Questions

Successful in-line measurements depend on good installation and operating techniques as well as optimized instrumentation. Here are some common questions and recommendations to optimize these measurements.

Should cycle chemistry samples be filtered upstream of sensors? Yes. Sample filtration upstream of sensors can prevent accumulation of corrosion products in the sensors and reduce cleaning requirements. However, the filter must be replaced frequently or the build up of particulate surface area on the filter will greatly slow down response time as pure water samples flow through the accumulation.

METTLER TOLEDO Thornton sensors and flow housings are designed to produce high flow velocities that carry any particles through the system without accumulating. This avoids most of the need for cleaning even without filters. An exception is the 2300Na series Sodium Analyzers which have an internal sample filter to prevent possible plugging of small solenoid valves. During initial startup when large quantities of corrosion products and debris come through the sample lines, it is good practice to bypass the sample panel altogether.

For high purity water, what sample flowrate is required for pH and conductivity sensors? The measurements of these parameters are not inherently flow dependent. However, flowrate may affect sample contamination and therefore the measurement may change. In very high purity samples, any air in-leakage will add carbon dioxide to the sample which forms carbonic acid, raising conductivity and lowering pH. Polymer sample tubing may allow air to permeate the tubing and produce the same effect. Higher sample flowrates will dilute any air leaks and provide more representative results. Low flowrates may also allow the sample to dissolve trace contaminants from piping walls and yield a higher conductivity reading.

pH measurement of low conductivity samples can be vulnerable to static charges built up around the sample from too high flowrates. To prevent this, pH sensor flowrate specifications must be observed.

Does pH calculated from conductivity really work? The pH of ammonia, amine or caustic treated cycle chemistry samples can be calculated very accurately from specific and cation conductivity measurements. The specific conductivity is dominated by the highly conductive hydroxide ion associated with caustic, ammonia and/or amines. The cation conductivity accounts for any trace contaminants in the sample. Since conductivity is very nearly linear with concentration, it has a very high resolution of measurement. pH on the other hand is logarithmic with concentration which gives reduced resolution. In addition, the reference diaphragm or junction potential of a pH electrode has at least ± 0.1 pH uncertainty when measuring low conductivity samples. Therefore, the calculated pH is typically more accurate on cycle chemistry samples, as long as the pH is greater than 7.5 and the specific conductivity is at least 4 times the cation conductivity. As a backup in case of upset if the pH goes below 7.5, an electrode pH measurement is still highly recommended.

For high purity water conductivity measurements, what is the optimum cell constant? The conductivity cell constant is determined by the mechanical design of the electrodes. It is the distance between electrodes divided by the effective cross-sectional area of the fluid between them, with units of cm⁻¹.

Low cell constants (closely spaced electrodes) are generally needed to make measurements in low conductivity samples and this must be compatible with the measuring circuit design. However, if the spacing is too close, the sensor will tend to accumulate particles such as ion exchange resin fines or corrosion products. These can short out the sensor, cause erroneously high conductivity readings and require frequent sensor cleaning or replacement.
METTLER TOLEDO Thornton conductivity measuring circuits are designed to provide high accuracy measurements using a 0.1 cm⁻¹ cell constant which has relatively wide electrode spacing and does not accumulate particles. Some other instrumentation requires a 0.01 cm⁻¹ constant sensor which has very close electrode spacing and will tend to accumulate particles between them.

**Where is ORP or redox potential measurement appropriate?**

Oxidation-reduction or redox potential is a non-specific measure of all oxidizing and reducing materials in a sample. Oxidizing agents include chlorine, oxygen, peroxide, etc. Reducing agents include bisulfite, hydrazine and other reducing amines. ORP is used in makeup water dechlorination stages to monitor the presence of a slight excess of bisulfite and the absence of chlorine. It can provide a sensitive alarm for the breakthrough of traces of chlorine which would damage reverse osmosis membranes or ion exchange resin. ORP is also used in cycle chemistry monitoring with all-volatile treatment using a reducing agent. It can monitor the reducing conditions where hydrazine or other reducing amines are used to minimize dissolved oxygen concentrations. It can warn of excessively reducing conditions that could lead to dangerous flow-accelerated corrosion.

**What causes high, flow-sensitive dissolved oxygen measurements?**

Dissolved oxygen samples at ppb levels are very vulnerable to trace leaks into the sample line. Although the line may be under pressure, a slightly loose compression fitting, rotameter gasket or valve packing can actually allow some air to diffuse through a thin water film and raise the dissolved oxygen content of the sample at ppb levels. The reading then also becomes flow-sensitive since a higher flow-rate will dilute the leak and result in a lower reading. Care must be taken to assure that all fittings are air tight.

**Is temperature compensation of cycle chemistry measurements critical if good sample cooling is provided?**

A good sample cooling system can bring the sample temperature very close to the standard 25 °C. However, the tubing, valves, flowmeter, and possibly a cation exchange column downstream of the cooler will allow the sample to be significantly influenced by the ambient temperature around the panel. Therefore, accurate temperature compensation is still a very important consideration. METTLER TOLEDO Thornton has especially accurate temperature compensation for cation conductivity compared with other instrumentation.

Find out how Thornton systems can improve your in-line analysis, at:

➤ [www.mt.com/pro_power](http://www.mt.com/pro_power)
Confidence in Ultrapure Water Systems with a Pure Water Optical DO Sensor

Minimizing corrosion is vitally important in power plant cycle chemistry monitoring and generator stator cooling. The Pure Water Optical Dissolved Oxygen Sensor with Intelligent Sensor Management (ISM®) technology provides fast response, high accuracy, and increased stability in demanding, low ppb-level ultrapure water applications.

Traditionally, dissolved oxygen (DO) measurement has been achieved using amperometric sensors. Although these measure accurately they often respond slowly to changes in DO and require frequent, time consuming maintenance.

The Pure Water Optical DO Sensor provides outstanding measurement performance with low detection limit, the fastest response available and minimal drift, and therefore significantly improves oxygen monitoring. METTLER TOLEDO’s proprietary OptoCap sensing element provides very accurate oxygen determination and easy maintenance without electrolyte handling. Additionally, the OptoCap eliminates the need for polarization, making the measurement system quickly available and reducing downtime.

ISM simplifies sensor handling and provides diagnostic tools that predict the need for sensor maintenance before measurements are affected.

Find out more at: www.mt.com/opticalDO

Your benefits

Fastest response
METTLER TOLEDO’s proprietary Optical DO technology delivers the fastest response available providing confidence in the integrity of your ultrapure water system and equipment.

Reduced maintenance
No electrolyte or polarization eliminates the need for frequent, time consuming service.

Intelligent Sensor Management
ISM provides simple sensor handling, and predictive diagnostics for proactive maintenance.
Keep Up to Date
Power Generation Competence Center

METTLER TOLEDO Thornton is dedicated to continuous improvement in producing instruments for the detection of impurities in power plant water systems. Our online resource keeps you informed as to our latest developments in monitoring and measuring pure water and steam in power generating facilities.

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