UNDERAPPRECIATED RISKS AND DANGERS OF ORGANIC / TOC CONTAMINATION IN POWER PLANT CYCLE CHEMISTRY

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WATER CHEMISTRY MANAGEMENT

This paper/presentation will review the often underappreciated risks that Organic / TOC contamination represents in power plant today. Updates will be provided on industry standards based on boiler pressure, new and emerging technology that makes it easier than ever before to continuously monitor TOC in the SWAS panel, the laboratory and even in a portable configuration for rapid trouble shooting and diagnostics of organic contamination.

The underlying technology will be briefly discussed and how it has been specifically designed for ultrapure water and rapid measurements.

Introduction

While most efforts at producing pure water are aimed at removing minerals, these purifying processes do not necessarily remove organic compounds. There is an increasing awareness of the operational risks and damage that organics can cause in power generation equipment and this is driving changes in water treatment methods as well as increasing the need to continuously monitor TOC (total organic carbon). Controlling organics is especially critical in Supercritical plants, cogeneration power/steam cycles, where the purified condensate water returning from production processes is subject to organic contamination or any plant that pulls raw water from highly organic sources. Key to confirming and troubleshooting organics removal or lack of removal, is reliable on-line total organic carbon (TOC) measurement.

Effects Of Organics

Organic contamination of pure power plant waters can cause a number of costly problems, including fouling of resins in make-up and condensate deionizers that requires frequent resin cleaning and replacement; break down of organics to acids that lower the pH of condensate and cause boiler and turbine corrosion; deposition onto heat exchange surfaces leading to significantly reduced efficiency; and foaming in the boiler that can increase carryover of other contaminants into the steam. The occurrence of any of these problems can be a major concern in plants.

Sources Cogeneration

In the power/steam cogeneration cycle, steam is generated to drive turbines to produce electricity. In cogeneration plants it is then diverted to production processes to provide heat/steam before being condensed and circulated back to the boilers to be reused in power generation. It is the purified condensate water returning from the production processes that is most likely to be subject to organic contamination from leaks while the steam is being used for heat or other parts of the production process. Depending on the production process, organic contamination may exceed acceptable limits and disrupt the cogeneration cycle. The treatment system to remove such contamination needs to be carefully designed to ensure it can withstand any organics spikes caused by plant disturbances or in-leakage events.

Sources All Plants

In plants of all types, the primary/significant source of organics is make-up water. Surface waters have higher levels of naturally occurring organics than ground waters. But ground water sources are being depleted or not available in many areas. As a result, there is greater reliance on surface water, reclaimed water and even municipal wastewater as the raw source for high purity make-up water for the water/steam cycle. A further complication is that surface water sources typically have substantial seasonal variations in concentration and types of organics. A treatment system that uses source water with low organics during one season may be seriously challenged in another season. Even greater changes in source water composition can strain a treatment system if it must alternate between surface water high in organics during wet seasons and ground water high in minerals in dry periods. Another source of organics is ion exchange resins in the treatment system as the beads themselves are composed of organic polymers. Resin fines from physical breakdown of the beads can find their way into the steam cycle if they are not fully trapped. Chemical breakdown of resins produces trace contaminants: sulfonic acids from cation resins and amines from anion resins. In addition, traces of processing solvents may also be released. These contaminants may include inorganic constituents in their structure such as chloride and sulfate that are released in the steam cycle through thermal degradation and become even more corrosive.

Additional sources of organic contamination are present directly in the steam cycle, including pump lubricants, condenser leaks and condensate polishing resins. Organic cycle chemistry additives like pH buffering or Film forming amines, where used, represent a further potential source that must be compatible with the overall cycle and closely monitored to prevent unintended negative consequences.

Industry Guidelines

Due to the increasing acknowledgement of the risks of organics to plant health, especially with boiler pressures ever increasing to supercritical and ultra-supercritical levels trying to achieve greater efficiency, it is important to revisit established guidelines for TOC/organics safety limits. As you see in the table below, as boiler pressure increases, TOC/organics limits decrease to very low acceptable levels :

| Drum Operation	Pressure	TOC & Oily Matter Limits
Psig 0-300	MPa 0-2.07	Less than 1000ppb
Psig 301-450	MPa 2.08-3.10	Less than 1000ppb
Psig 451-600	MPa 3.11-4.14	Less than 500ppb
Psig 601-900	MPa 4.15-6.21	Less than 500ppb
Psig 901-1500	MPa 6.22-10.34	Less than 200ppb
Psig 1501-2000	MPa 10.35-13.79	Less than 200ppb
Psig 2001 and above	MPa 13.8 and above	Less than 100ppb

TOC Measurement Technology

Testing for organics for both cogeneration and tradition plants is often done at the condensate return. Condensate purity is normally monitored by conductivity measurements, with resistivity measurements becoming effective early-warning systems [1]. The effectiveness of resistivity measurements is due in part to its sensitivity at ppb levels [2]. However, as discussed, organic compounds from production processes for a cogeneration plant or failures in the water treatment process may contaminate the condensate.

These organics are generally non-conductive and therefore cannot be detected via conductivity measurement. For detection of these organics, they must be converted to a form that produces conductive species in pure water. In TOC measurements, organics are oxidized and produce carbonic acid (a conductive species). The conductivity of the carbonic acid generated is then measured and correlated to the amount of organic contamination present in the water.

Oxidation

The primary means of oxidation is the use of ultraviolet (UV) radiation at 185 nm and 254 nm. It is impossible to describe the detailed photo-oxidation mechanism of every conceivable organic oxidation reaction and, in many cases, it is not clearly known at the molecular level. Regardless of the organics involved, the end
result is normally a reaction which can be summarized in the following equation :

$$C_X H_Y O_Z + [O] + UV \rightarrow xCO_2 + H_2O \qquad eq (1)$$
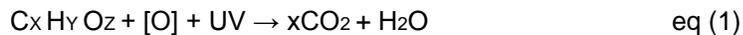
where $C_X H_Y O_Z$ is the organic contaminant and [O] is an oxidation source, usually oxygen or persulfate. The oxidation of the organic carbon to carbon dioxide (CO_2) results in the formation of dissolved CO_2 in water. This leads to the formation of an unstable intermediate, carbonic acid (H_2CO_3), which is a weak acid and partially dissociates to ionic species.

$$CO_2 + H_2O \rightarrow (H_2CO_3) \rightarrow H_+ + HCO_3^- \qquad eq (2)$$
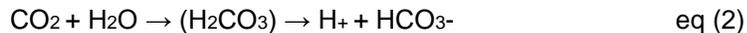
The extent of the formation of ionic species is controlled by physical chemical equilibria [3] and is described according to eq (3).

$$K1 = ([H_+] [HCO_3^-])/[CO_2]aq = 4.45 \times 10_{-7} \text{ at } 25o \text{ C} \qquad eq (3)$$

Detection

The strategic reason to form CO_2 is based not just on the relative ease of oxidizing organic contaminants, but on its detectability and quantification by various analytical methods, including conductivity. When ionic species are present in pure water, conductivity represents the most sensitive real-time means of detection. The reaction products described in eq (2) are not only detectable by conductivity, they are also optimized for detection due to the formation of highly conductive H_+. Figure 1 shows the relationship between conductivity and concentration of carbon (as CO_2) at 25°C. Based on eq (3), known chemical equations for conductivity and the chemical equilibria for this system, the amount of carbon can be determined. This is usually expressed in "ppb" (µg/L).

Figure 1
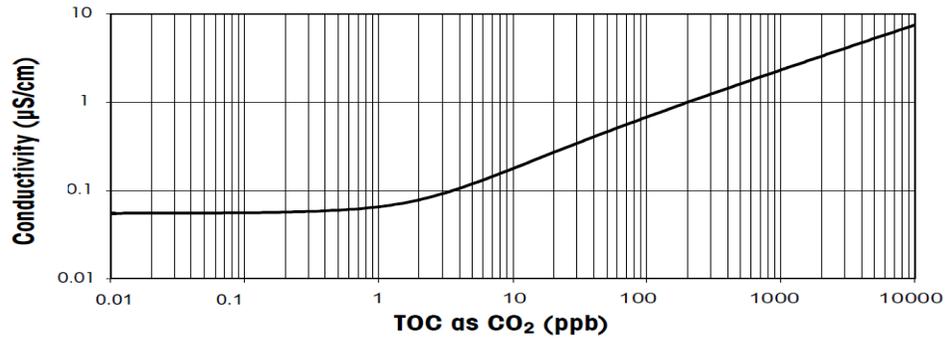
## Typical TOC / Organic Contamination Issues

Starting with the boiler, the organics can be deposited onto heat exchange surfaces, which significantly reduces their efficiency. Plants with deposits of this type, typical report declines in steam output/pressure overtime. However, the more serious risk is when the organics are exposed to elevated temperatures in the boilers, partial thermal degradation and oxidation of the organic contaminants occurs. This process produces organic acids which can lower pH, sometimes quite rapidly and lead to additional corrosion, boiler tube failures and even greater inefficiencies in power generation. Organics can also cause foaming and carryover of other contaminants into the steam which can corrode expensive turbines. When measured at the condensate return, other measurements of key parameters such as, pH, specific/cation conductivity, and DO are used with Total Organic Carbon (TOC), for a more complete view to the risks of contamination, subsequent deposits and corrosion. It is important to note that plants that measure TOC with these other parameters have found that organic and inorganic contamination do not always coincide. It is possible for the water to be contaminated with organic compounds without being contaminated with conductive substances. Therefore, on-line TOC measurement is a key monitoring parameter to protect power generation equipment.

TOC Sensor Design

To ensure that TOC contamination is quickly detected and measures are taken to control it, it is highly beneficial to have a TOC sensor that continually monitors and rapidly responds to changing levels of contamination. It should also offer features that constantly provide diagnostics of the sensor's performance, to ensure that the measurement is reliable and accurate while also providing notice to the user regarding the need for maintenance.

Figure 3 shows a simplified layout of a typical TOC sensor, with oxidation and detection processes outlined. The fastest responding instruments using this technique have a high-intensity UV lamp with a continuously flowing sample through the sensor. Such designs operate without any moving parts, membranes or chemicals, which increases reliability and reduces running costs.

Figure 3 - Flow path of a direct conductivity TOC sensor
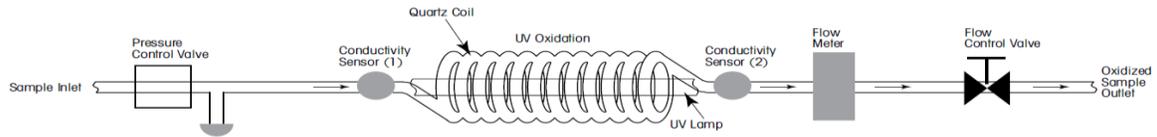
The conductivity measured at Sensor 1 is background conductivity due to dissolved carbon dioxide and any minerals already present in the water. The change in conductivity measured by Sensor 2 is due to any organics that were oxidized by the UV lamp and converted into carbonic acid. If the temperature of the condensate is too high, a sample conditioning coil may be placed at the sensor inlet to reduce the temperature to near ambient conditions. Where particulates are present, sample filtration may also be required. This technology does have application limitations. It is used only on pure water samples with the background conductivity less than 2 µS/cm and TOC of 0.05 - 2000 ppb. However, conductivity can easily be kept within range with the use of a cation resin column: the same type and in many cases the same column that is commonly used in water sample panels to measure cation conductivity in the same sample location.

Advanced Measurement Solution

METTLER TOLEDO Thornton's on-line 5000TOCi and portable 450TOC both use the UV oxidation technique to provide continuous and reliable monitoring of TOC levels in any water sampling location. Response time is particularly fast for both units, taking approximately 60 seconds for the sample to pass from the inlet, to be fully oxidized and move to the second conductivity sensor.

Recent advances in sensor/transmitter technology include the development of systems with sensor diagnostics. METTLER TOLEDO's Intelligent Sensor Management (ISMR) is one such solution. Pairing the 5000TOCi Sensor with the multi-parameter M800 Transmitter, provides a complete system to not only monitor the TOC contamination in the boiler steam cycle, but also ensure the measurement is always dependable. With the system's Plug and Measure feature, calibration and diagnostic data storage in the

sensor, calibration warnings, and hardware failure notifications, the 5000TOCi Sensor /M800 Transmitter solution provides measurement reliability as well as immediate notification of any sensor upsets. The system also provides trend, peak and average data reporting for a more complete picture of water quality over time.

Moreover, use of the multi-parameter, multi-channel M800 Transmitter allows the measurement of three additional parameters. Such a configuration provides the ability to monitor all critical parameters such as pH, dissolved oxygen and conductivity along with TOC, to provide a complete picture of the water quality at a measurement point. With features such as trend graphs for each parameter and computed measurements such as calculated pH, calculated CO_2 and calculated ammonia, the M800 provides an additional level of monitoring to ensure water quality is always within acceptable limits for all parameters.

Conclusion

Considering that organic contamination is capable of causing process disruptions as well as damage to expensive capital equipment, it is essential to continuously measure TOC in the cogeneration cycle. TOC monitoring and control will not only ensure effective operation of the cycle, but also avoid any unplanned shutdown of production processes due to disruption in steam/heat. To effectively implement such monitoring, on-line measurement of TOC is critical in obtaining a real-time assessment of water/steam quality. Moreover, with on-line measurements being increasingly used for decision making, instrument capabilities and performance must be commensurate with this responsibility. METTLER TOLEDO Thornton provides a complete multi-channel, multi-parameter solution for TOC and related high purity water measurements. The 5000TOCi Sensor with M800 Transmitter delivers fast, real-time, continuous measurements. The additional benefits of Intelligent Sensor Management (ISMR) technology include predictive maintenance for assurance of system performance at all times. The 450TOC is a portable solution for quick profiling of TOC at any point in the water/steam cycle.

References

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2. "Ultrapure Water - The Standard for Resistivity Measurements of Ultrapure Water", A.C. Bevilacqua, 17th Annual Semiconductor Pure Water and Chemicals Conference, Santa Clara, California, March 2-5, 1998.

3. T.S. Light, B. Kingman, A.C. Bevilacqua, "The Conductivity of Low Concentrations of CO2 Dissolved in Ultrapure Water from 0-100°C", 209th American Chemical Society National Meeting, Anaheim, CA, April 2-6, 1995.