the **conduit**

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Cation Conductivity + Sodium = Good Steam Monitoring

By David Daniels

Operators of a supercritical unit noticed that sodium monitors went into alarm and showed extremely high sodium levels in the feedwater and steam. Checking the cation conductivity monitors, they found no significant increase on these and therefore concluded that the sodium analyzers must be malfunctioning and continued to operate the unit. Hours later the unit was finally shut down, because of other indications of massive contamination. Later it was discovered that all the caustic from an anion regeneration had contaminated feedwater, gone through the supercritical boiler and precipitated onto the turbine and steam piping. The cost to the plant for a full chemical cleaning of the boiler, turbine cleaning and soaking, and associated maintenance was in the millions.

To understand what went wrong here, we need to discuss cation conductivity and sodium monitoring.

**Cation Conductivity -
A quick review**

Cation conductivity is a conductivity measurement taken after the sample has passed through a hydrogen-form cation resin. This cation resin replaces cations such as sodium, calcium, and ammonium, with hydrogen; turning dissolved salts, such as sodium chloride into its acid form, in this case, hydrochloric acid. As such, cation conductivity, strictly speaking, is a measure of the anions in solution (as all the cations have been replaced with hydrogen).

In the acid form, the conductivity measurement of a pure water or condensate sample decreases and becomes far more sensitive to slight increases in the concentration of the remaining anions. Studies have shown that ppb levels of chloride and sulfate contamination can be detected. Utilities have shown that changes in cation conductivity can be used to find very small condenser tube leaks.

The cation conductivity of the sample is a composite of all the anions in the sample. The contribution of each anion is a function of its concentration and activity coefficient of the ion. Cation conductivity is not a direct measure of any specific property of the sample, nor its corrosivity. It is also not possible to determine how much of the cation conductivity is due to a specific contaminant. Assuming no anionic impurities, the minimum value for cation

conductivity is the same as for specific conductivity, approximately 0.06µS/cm at 25°C (77°F).

However, in spite of it being so general, cation conductivity has proven to be a relatively inexpensive and very reliable indication of contamination in ultrapure water. For this reason, all steam turbine OEMs have a strict cation conductivity limit and exceeding this limit during operation will void the turbine warranty. Although chloride and sulfate are the actual "bad actors" on the turbine, the manufactures regard cation conductivity as so trustworthy, that only GE specifies separate chloride and sulfate limits in addition to cation conductivity.

Cation conductivity will also respond to bicarbonate and organic acids, such as formic or acetic acid. Organic acids and dissolved carbon dioxide in steam can be the result of organic contamination in the

boiler feedwater or the breakdown of carbon-based treatment chemicals, such as neutralizing amines or oxygen scavengers.

The sensitivity of cation conductivity is one of its great advantages. Even low part per billion levels of contamination can be detected allowing operators to detect very small condenser tube leaks, for example. **Table 1** shows the equivalent cation conductivity that would be produced by different concentrations of chloride, sulfate, and carbonate. All concentrations are expressed in parts per billion. For example, a cation conductivity of 0.2 mS/cm can be produced by 16.5 ppb chloride or 22 ppb sulfate or 46 ppb carbonate. Obviously in the real world, solutions contain a combination of these and other anions.

Sodium Monitoring

Sodium is the only accurate way to infer the hydroxide concentration in steam. Contamination of steam typically occurs via carryover from the drum or through contaminated feedwater entering the steam path through the attemperation sprays. Since non-volatile boiler treatments are typically sodium based, the measurement of sodium is an excellent indication of the mechanical carryover from the drum into the steam. In standard demineralizers, caustic solutions are used to regenerate the anion resins. Therefore the potential for sodium hydroxide contamination of steam is always present in plants with demineralizers.

Sodium monitors use a specialized specific ion electrode technique and can detect sub ppb levels of sodium. Sample temperature and flow are critical for accurate measurements as is the proper sampling nozzle. Sodium analyzers are more complex and much more expensive than cation conductivity monitors. If there is only one sodium monitor at the plant, it should be on the critical main steam sample. A second sodium monitor is often placed at the condensate pump discharge (or polisher effluent) to detect contamination from the condenser or demineralizer.

Cation Conductivity AND Sodium

There are three entities that can cause stress corrosion cracking in turbine steels; namely chloride, sulfate, and hydroxide. Chloride and sulfate can cause pitting and stress corrosion cracking in blades. Excessive hydroxide concentrations in the steam can result in caustic stress corrosion cracking particularly of rotor steels.

The use of cation conductivity effectively detects low levels of chloride and sulfate, but consider what cation conductivity would do in the case of sodium hydroxide contamination. Sodium hydroxide would enter the cation exchanger column where the sodium ion would promptly be exchanged for a hydrogen ion. The hydrogen ion would combine with the hydroxide from the contamination to produce water and so will go undetected. This is the mistake made by the operators in the experience cited at the beginning of this article. They assumed that if there was no cation conductivity increase there could be no contamination.

A combination of sodium and cation conductivity monitoring in the same location will detect all three corrosive species. As of this writing, the conductivity probe and a cation resin and associated piping costs between $1,000-1,500. Maintenance consists of changing the cation cartridge when it is about 75% exhausted (the resin changes colors as it becomes exhausted) and a very rare changing of a conductivity probe. By comparison, a low-level sodium analyzer is $7,000-8,000 and requires regular maintenance, refilling of reagents, and calibration by a trained technician.

In comparison with the alternative, both cation conductivity and sodium monitoring are cheap insurance.

Table 1 Concentration of chloride, sulfate, and carbonate required to generate various levels of cation conductivity [1]

Species	Cation Conductivity at 25°C in μS/cm			
	0.2	0.3	0.5	1.0
Chloride, ppb (as HCl)	16.5	25	43	85
Sulfate, ppb (as H_2SO_4)	22	33	57	112
Carbonate, ppb (as carbon dioxide)	46	90	225	780

[1] Bursik, A "Cation Conductivity—What are We Talking About" PowerPlant Chemistry 2002, 4(10) pg 598-603

Sampling Points for Cation Conductivity

Cation conductivity is typically measured at three points in the steam cycle: the condensate pump discharge, economizer inlet, and on the main steam line if the plant is using a solid alkali boiler treatment such as phosphate or caustic. Units using AVT also need to monitor cation conductivity of the boiler water. If the plant has a condensate polisher, cation conductivity will also be monitored on the polisher outlet. Below is a brief description of why these sampling points are important.

Condensate Pump Discharge

Contamination entering the boiler feedwater typically comes from one of two sources—condenser tube leaks or demineralizer or other makeup system problems. Feedwater makeup is usually added to the condenser. Therefore, if anything goes wrong, the first indication of the problem will be on analyzers at the condensate pump discharge. This value is so important that it has been reported that some plants have two cation conductivity sampling points at the condensate pump discharge and trip the unit if both show a high reading.

If there is a condensate polisher, cation conductivity monitors before and after the polisher are important to judge the effectiveness of the polishers.

Economizer Inlet

If condensate return from plant processes or heat exchangers are fed directly to the deaerator, the difference between the cation conductivity at the economizer inlet and the condensate pump discharge would be the contribution of these hot returns.

If there are no process returns going to the deaerator, the cation conductivity measurement at the economizer inlet serves as a back-up for the critical analysis at the condensate pump. If only one of the units were reading high, it might be an indication of a problem with the meter, but if both are out of limits, it is very likely that there is a real contamination issue.

Boiler

If the boiler water chemistry regime is all volatile treatment or AVT, cation conductivity must be monitored on the boiler water. Typical operation of a boiler on AVT is with the boiler blowdown closed, which allows the concentration of even small amounts of contamination. Even ppb levels of chloride and sulfate can significantly decrease the boiler pH at temperature[2] and result in corrosion of the boiler. The operator may not be aware of the problem since the pH at 25°C may not be similarly affected. Ammonia, fed to adjust the pH of the feedwater is not significantly hydrolyzed at boiler water temperatures, but will be once the sample is cooled.

Main Steam

Measurement of the purity of main steam close to the turbine inlet is critical as it is the best indication of what actually is going to the turbine. Therefore, it is critical to measure cation conductivity at this point. This is why turbine manufacturers require monitoring of the main steam.

The cation conductivity of the main steam contains contributions from saturated steam from the drum and the attemperation or desuperheating water. Depending on the amount of attemperation spray and the quality of the feedwater, this can be a significant source of cation conductivity in the steam.

Main steam cation conductivity is also directly related to the purity of the saturated steam exiting the drum. Boiler water has much higher concentrations of contaminants such as chloride and sulfate. Steam drums are designed remove water droplets with physical separators such that there is less than 0.2% mechanical carryover of water in the steam. If the steam separation devices are not working properly or if operational changes such as a sudden change in drum level reduce the effectiveness of these devices, significant amounts of boiler water can be carried over into the steam, into the superheater and eventually onto the turbine. Main steam cation conductivity will detect the problem and alert operators to the contamination.

Main Steam vs Saturated Steam

Often both the main steam and saturated steam sample lines are typically plumbed into the sample panel. The saturated steam line is used when the level gauge on the drum is calibrated. Since the sample contains no superheat, it puts less of a load on the primary sample chillers than does the main steam sample. However, saturated steam samples are troublesome. Often the sample comes off one steam riser out of eight that exit the drum. Problems with separators, belly plates, or the steam chest (CE boilers) may not be noticed unless the problem and riser with the

[2] Bursik, A. "AVT Guidelines for Drum Boilers and the pH at Temperature", PowerPlant Chemistry 2003, 5(4) pg 225-232

sample point happen to coincide. The saturated steam sample also does not include contribution of the attemperation water, which may be significant, particularly during startup. Finally, saturated steam, because it is a two-phase sample, is more difficult to sample representatively than a single phase superheated steam sample.

Detecting Leaks and Mechanical Carryover— Sodium or Cation Conductivity

Cooling waters vary widely in the amount of dissolved salts and also in the amount of sodium they contain. Almost all naturally occurring waters, including salt water, contain significant percentage of calcium and magnesium ions. The electrical charges in every solution must balance. For every cation in solution, there must be a charge equivalent of anion.

The advantage that cation conductivity has over sodium for detecting condenser tube leaks is that it is a property of the sum total of all the anionic constituents in the sample, not just a single cation, as is the sodium analyzer. The real

rationale for putting a sodium analyzer at the condensate pump discharge is to monitor for sodium hydroxide contamination. Since this contamination is likely to come from the demineralizer, many utilities feel it is sufficient to monitor the specific conductivity of the demineralizer effluent or the condensate storage tank, instead of investing in another sodium analyzer. In certain cases, sodium is monitored on the demineralizer.

To monitor for mechanical carryover from the steam drum, cation conductivity and sodium are on a more equal footing. In a boiler that operates on a phosphate-based treatment, sodium is inherent in the boiler water. Assuming a molar sodium to phosphate ratio of 3:1, the boiler will contain 0.73 ppm of sodium for every 1 ppm of phosphate.

Most utility boilers only use the boiler blowdown during startup to remove silica, excess phosphate, and any other contamination that may have entered the boiler due to maintenance activity during the outage. The closed blowdown allows even trace amounts of contaminants such as chloride and sulfate to concentrate.

It is possible for an operating utility boiler on a low phosphate regime to have as much chloride and sulfate as sodium in the boiler water. The newest versions of sodium analyzers are trustworthy down to 1ppb. Cation conductivity cannot accurately detect such low levels of single anions. So sodium analyzer would seem to be a better bet. However, mechanical carryover will contain everything in the boiler water, and therefore it is possible for cation conductivity to be as sensitive as sodium analyzer to carryover. It certainly has the potential to be more reliable.

For boilers using AVT or OT, only low ppb levels of sodium hydroxide leakage can be expected from polishers. In these cases, cation conductivity would be the preferred method for detecting carryover.

In the end, it pays to have both sodium and cation conductivity to provide a complete picture of contamination in the steam cycle.

Calendar of Events

May 11-13

Electric Utility Chemistry Workshop
Champaign, Illinois
eucworkshop@ad.uiuc.edu

October 17-21

International Water Conference
Pittsburgh, PA
www.eswp.com

November 2-5

EPRI Conference on Boiler Tube and HRSG Tube Failures and Inspections
San Diego, CA
www.epri.com

Risk-Based Materials Selection for 21ˢᵗ Century FGD Systems

By Peter Ellis

US utilities are again turning toward coal-fired generation for assured base-load capacity without the uncertainty and volatility of natural gas and fuel oil prices and supply.

The 21ˢᵗ-Century pollution abatement technology that will make these coal-fired environmentally and economically successful is a far cry indeed from the 20ᵗʰ-Century FGD systems as shown in the sidebar.

Unlike 20ᵗʰ-Century FGD systems—so highly redundant that virtually any component except the ductwork could be "spared" for major maintenance while the system remained on line—the 21ˢᵗ-century FGD systems will have zero redundancy of critical components.

The crux of economic success for these systems is selection of materials that can operate with only touch-up repairs during bi-annual or tri-annual outages.

The Materials Designer's Dilemma

The challenge to the designer is significant. Materials reliability for these systems must be extremely high since materials unreliability in any critical area will force the entire plant off-line, resulting in large financial losses.

The materials selected must be durable enough to withstand the FGD process environment for at least 20 years with only the kind of spot touch-up that can be performed during the brief scheduled maintenance outages. The lowest cost materials capable of meeting the challenge must be selected.

Formally or informally, the designer must make a complex series of risk-benefit trade-offs in which the benefit of avoided up-front cost achieved by selecting a less resistant material is weighed against the potential losses if the less costly material lacks adequate corrosion resistance.

Risk = probability x consequences

The Missing Component

Calculating the erected costs using different materials of construction, as well as the financial losses that could occur if the FGD system is forced into a significant outage due to selection of inadequate materials, are straightforward.

Up until now, the missing component required for risk-based alloy selection has been reliable estimates of the probabilities of failure (maintenance resulting in forced outages or excessive extension of scheduled outages).

The FGD Materials Performance Estimator© calculates the odds against obtaining at least 20 years of minimum maintenance service from engineered tile construction and 24 candidate alloy materials, including a

20ᵗʰ Century FGD Technology	21ˢᵗ Century FGD Technology
Attributes: • One-of-a-kind designs • At least five different sorbants (scrubbing agents to remove sulfur oxides from the flue gas) • Multiple configurations • Highly redundant systems • Experimentation with various lining materials such as rubber, ceramics, stainless steel alloys, and titanium. **Results:** • Wealth of corrosion and failure experience	**Attributes:** • Single sorbant—limestone slurry • Three gas-liquid contact technologies • Low-NOx combustion upstream of the FGD • To achieve "zero discharge" with respect to wastewater • Zero redundancy and two to three year outage intervals

number of potentially lower cost alternatives to the high chromium-molybdenum-nickel alloys traditionally used to combat high chlorides.

This tool is the culmination of more than 22 years of independent investigation of FGD materials failures by M&M Engineering personnel, including first-hand experience with the performance of organic resin coatings, rubber linings, engineered tile systems, an a wide range of alloys at more than 25 separate FGD systems.

Out of this accumulated data, M&M Engineering established quantitative correlations between 20-year FGD performance, the specific composition of the alloy, and the chloride content and pH of the FGD process stream.

M&M Engineering incorporated these proprietary correlations into stochastic algorithms considering historic lot-to-lot composition variability of any given alloy and reasonably assumed uncertainty distributions of the chloride and pH of the slurry based on the user-input values.

Results may be printed in tabular form including the input conditions or incorporated into a more in-depth report.

For more information, please contact Peter Ellis at 512-407-3751.

2004 HRSG Users Group Meeting

The HRSG User Group met at the Saddlebrook Resort near Tampa, Florida March 4-5. This is the first meeting the Users Group has had in a number of years not associated with the Electric Power conference and it was tremendously successful. The Users Group registration had to be closed at 300 participants. The attendees were primarily owner/operators of HRSG units with a good smattering of representatives from HRSG manufacturers, and major component suppliers.

As usual, the majority of the conference consisted of question and answer sessions moderated by Bob Anderson, Chairman of the Users Group. This type of user participation is the hallmark of the Group, where formal presentations are limited and used primarily to stimulate discussion. Participants know that they will hear about problems that other operators are having and get ample opportunity to have their questions answered.

The group also puts on a Fall Maintenance Workshop. We will let you know on the dates and locations of further HRSG Users Group activities as they become available or check out their website at www.hrsgusers.org.

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