Questioning The Relevance Of Cation Conductivity Monitoring In Modern Combined Cycle Power Plants.

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ABSTRACT

Cation (or acid) conductivity is the main control parameter in the cycle chemistry of many combined-cycle power plants today. However, hundreds of these systems consistently fail to achieve cation conductivity values that are required to meet the strict steam turbine OEM specifications.

This paper describes the cycle history of a combined cycle cogeneration plant in the U.S. Southwest and relates it to plant asset integrity. Commissioned in the late 1980s, this 120 MWe (1x1x1, combined cycle, GE 7EA x Zurn HRSG x GE steam turbine) plant was designed for and operated in base loaded mode for 15 years before converting to two-shift cycling approximately two years ago. Plant records show that during its entire operating life, cation conductivity readings throughout the cycle (condensate, feedwater, steam) ranged between 2-5 microSiemens/cm. This is more than an order of magnitude higher than the maximum allowable values in recent turbine OEM specifications. Organic matter and other contaminants also consistently exceeded recommended industry guidelines. However, several major turbine inspections reveal a turbine in excellent condition. In more than 17 years of plant operating life, past problems have been limited to a few expansion-related failures in the feedwater economizer and high-pressure superheater drain during the first year of operation. The paper describes other key cycle chemistry data, including internal treatment and condensate treatment regimes, and proposes alternative monitoring techniques to cation conductivity.

PLANT AND SYSTEM DESCRIPTION

The PowerSmith Cogeneration facility is a 120 MW combined cycle, cogeneration plant located near Oklahoma City, OK. The plant was commissioned into commercial operation in September 1989. It is configured around a GE Frame 7EA1 gas turbine (natural gas fired) exhausting into a Zurn heat recovery steam generator (HRSG) train that produces steam at three pressure levels. Steam from the HRSG is used to run a GE 44.4 MW auto-extraction, condensing steam turbine generator set. Duct burner firing occurs on average 12% of total operating time. The plant also uses a steam injection system for NO_x control.

Most intermediate pressure steam (IP steam) is exported for process and heating to a host plant nearby – the Dayton Bridgestone Firestone facility.   Low-pressure steam is used for boiler feedwater deaeration. Turbine exhaust steam is condensed in a Yuba condenser, tied to a 4-cell Hammond cooling tower.

**FIGURE 1 – PowerSmith Cogeneration plant**

The HRSG is rated as follows:

HP   345,300 lb/h @ 1,330 psig and 945°F
IP   39,100 lb/h @   325 psig and 475°F
LP   36,800 lb/h @   14 psig, saturated

The plant ran on base load mode for 15 years with less than 8 annual starts (1989-2004). In late 2004, a new contract was signed that requires daily cycling operation. Normally, the plant runs in part load if ambient temperature is less than 90°F. The internal boiler chemical treatment regime is based on congruent pH/PO_4 control and utilized mostly monosodium phosphate (MSP) since the commissioning date until very recently. The use of MSP was due to significant sodium leakage from the demineralizing plant. Boiler feedwater and condensate pH are controlled with a morpholine/cyclohexylamine blend. Oxygen concentration is controlled with diethylhydroxylamine (DEHA). The boiler feedwater preparation plant receives municipal water that is upgraded by PowerSmith Cogeneration according to Figure 2 below. Process condensate from the host plant flows through a mixed-bed condensate polisher prior to entering the cycle at the deaerator storage tank.

FIGURE 2. – Basic Flow Schematic Of Boiler Feedwater Preparation Plant
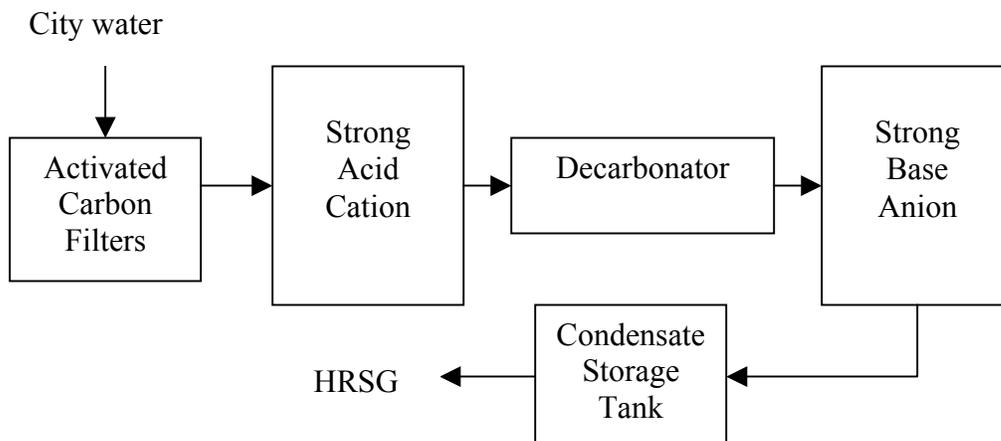
BACKGROUND

Much has been written about cation conductivity and its use as one of the main control parameters in the cycle chemistry of high-purity boiler systems. Turbine manufacturers and other organizations purport that cation conductivity (CC) is a superior diagnostic tool and that out-of-range CC target values will lead to increased corrosion in cycle components.

All steam turbine manufacturers impose onerous steam purity specifications and guidelines that require turbine users to operate below 0.2 microSiemens/cm cation conductivity in their final steam. This requirement is often very difficult, if not impossible, to meet during the various modes of plant operation, even in base load, steady-state conditions.

However, many plants have neither the configuration and operating conditions nor the expertise to achieve and maintain a high-purity water environment commensurate with the 0.2 microSiemens/cm target value. Many plants, including but not limited to cogeneration units, utilize beneficial (often essential) chemical treatment practices that require the use of reducing agents (oxygen scavengers and/or metal passivators) as well as neutralizing amines for pH control.

In high-pressure boilers, these substances may generate decomposition products that may increase cation conductivity. When this happens, the higher cation conductivity fingerprint may add an undesirable masking effect to the monitoring effort. Of special concern is the potential presence of acidic anions such as Cl^- that may go undetected. An ubiquitous cycle contaminant, carbon dioxide, that enters the cycle through air in-leakage or chemical decomposition, also adds significantly to CC and poses the same masking risk.

Past surveys such as the one conducted by one of the authors of this paper in 2001 (1) suggest that cation conductivity monitoring is a poor predictor of cycle corrosion in power plants, and an unreliable monitoring method for many combined cycle power plant operators. Discreet data from 31 turbines in 20 Canadian boiler plants in the power and other industries showed that despite grossly elevated cation conductivity and high levels of volatile organics in the cycle, no significant metallurgical failures occurred over an extensive time period of operation. Although similar results can easily be seen in many power plants today, the authors were surprised with PowerSmith Cogeneration's stellar performance over the past 17 years.

So, in light of the above background, the following questions are pertinent:

- How well or poorly does cation conductivity correlate to the incidence of metallurgical failure in the cycle?
- How can plants benefit from long-tested and proven chemical regimens whilst maintaining monitoring alertness to far more deleterious contaminants such as chlorides, sulfates and nitrates?
- How reliable is cation conductivity monitoring today in predicting cycle corrosion?

DISCUSSION

In 17 years of operation, PowerSmith Cogeneration has had very little negative to report with regards to its steam cycle. Two major steam turbine outages performed since the beginning of commercial operation as well as annual borescope inspections of steam turbine and HRSG components show no metallurgical concerns. A turbine inspection in 1999 showed moderate sodium phosphate deposition on several bucket dovetails, wheelfaces and diaphragm partitions. The leading edge of the 17th stage bucket was lightly eroded (etching). A subsequent investigation determined that poor operational practices (mainly poor drum level control and high sodium leakage from water

treatment plant) and water droplet impingement were, respectively, the root causes of the two problems. Other components in the cycle (HRSG, condenser, hotwell, gas turbine NO_x steam injection system, etc) have also been mostly trouble-free since commissioning and start-up. During the first year of operation, there were a few expansion related failures in the feedwater economizer and high-pressure superheater drain.

Cycle chemistry at PowerSmith Cogeneration has historically been kept simple. The sodium salt of metaphosphoric acid (MSP) is added separately to the HRSG IP and HP drums at a rate required to achieve the control ranges for pH and PO_4 (see Table 1 below). The amine blend and a reducing agent for oxygen control are added to the feewater.

Table 1 – Control Chart For HRSG Drum Chemistry

	LP drum	IP drum	HP drum
PH	9.4-10.6	9.4-10.6	9.3-10.1
PO₄ (mg/L)	N/A	20-30	10-15
Conductivity (μS/cm)	< 20	< 250	< 150
Silica (mg/L)	-	< 35	< 2

N/A = not applicable

Table 2 summarizes the range of values seen during the total operating life of the plant. Of particular interest are the high cation conductivity values experienced over the life of the plant. The average cation conductivity at this facility has consistently exceeded the maximum steam turbine guideline by more than an order of magnitude. The concentration of low molecular weight aliphatic acids (e.g. formic, acetic) were also sporadically tested and shown to be relatively high, with values typically in the 0.4-2.5 mg/L range (it is important to note that this volatile TOC is present in a neutralized (non-acidic) form during normal operating conditions). However, random ultra-low threshold level analyses of acidic anions (chloride, sulfate), consistently show these species to be below turbine manufacture guidelines (< 3-5 μg/L).

Table 2 – Range of results since commissioning/start-up

	Boiler Feedwater	Condensate	HP Steam
PH (< 2004)	8.3 – 9.6	8.8 – 9.2	8.8 – 9.2
PH (present)	9.3 – 10.1	8.8 – 9.2	8.8 – 9.2
Conductivity (μS/cm)	< 7	5- 60	< 10
Cation conductivity (μS/cm)	N/M	N/M	0.5 – 5
SiO₂ (μg/L)	< 20	< 20	< 20
Na (μg/L)	20-100	<10	5-45
Cl (μg/L)	3-14	-	< 5
DEHA (reducing agent) (μg/L): <2004	150-250	150-250	N/M
DEHA (reducing agent) (μg/L): Present	50-150	50-150	N/M
Fe (μg/L)	< 20	< 20	< 10
Oxygen (μg/L)	< 5	N/M	N/A

N/M = not measured ; N/A = not applicable

Due to more frequent and irregular cycling in recent months, the plant has struggled to maintain target pH values in the HRSG drums, especially in the high-pressure evaporator. The plant design lacks the flexibility to control feedwater recirculation flow to the economizers. Drum level control is often challenging, requiring increased drum water purging during cycling operation to suppress economizer steaming. This excessive bleed-off leads to lower residence times and depressed pH values that recently resulted in a change to a higher sodium-to-phosphate ratio product to maintain optimum pH.

FIGURE 3 – Last detailed outage in March 2006 revealed neither metallurgical failures nor deposition in the steam path (plant is in operation since 1989)

Table 3 – Design versus actual operating HRSG drum pressures

(psig)	HP	IP	LP
Design Pressure	1,330	325	14
Typical Operating Pressure	1300	360	27

CONCLUSIONS AND RECOMMENDATIONS

The following comments are provided:

- There is a remarkable absence of any metallurgical failures related to cycle chemistry during the 17-year plant life.
- Notwithstanding the high reducing conditions in the HRSG feewater ($[O_2]< 7\mu/L$) throughout 17 years of continous operation, there have been no incidents of flow-assisted corrosion (FAC) in the cycle.
- There is negligible iron tranport phenomena occurring throughout the cycle including the host condensate, despite high reducing conditions in the HRSG feedwater throughout 17-year plant life.
- No reported metallurgical failures at host plant associated with steam or condensate purity
- Have "within design" plant operating conditions since commercial commissioning contributed to the above-described successes at this facility? For example:

        o Steam loads were kept below the HRSG's maximum rated capacity.
        o Appropriate drum pressure control was maintained that avoided the formation of so-called "fat steam" that results in high fluid flow velocities in HRSG tubing (of special concern here are LP and IP evaporator tubes). This phenomenon was a contributing factor in severe FAC at several combined cycle facilities, including a well-documented case history in Mississauga, Ontario (3).

- Has base-loaded operation for 15 years (as per intended design) helped avoid metallurgical failures in the boiler system?
- How much of a role have materials of construction and HRSG design played in this success story?
- Authors recommend that higher importance be given to the monitoring of acid anions such as chloride and sulfate (highly aggressive to the plant metallurgy).   They also concur with the current industry guidelines for these ions – most specify < 5 μg/L for individual anions.
- It is recommended that cation conductivity only be used as an indicator of "gross contamination".
- Authors recommend that ion chromatography be considered for monitoring acid anions in boiler feedwater, boiler water and steam.

This case history shows a clear lack of correlation at this plant between high cation conductivity plant readings and the actual rate of metallurgical failure in the water/steam cycle. Comparable results are experienced today at many similar facilities. An alternative, more reliable technology exists today capable of monitoring ionic contamination in steam. Smaller, more affordable ion chromatography systems such as those manufactured by Dionex are well suited for frequent monitoring of deleterious ions such as chloride in boiler feedwater, boiler water and steam.

New designs have made this technology more reliable, and easier to use and maintain. The current steam purity guideline for cation conductivity places an onerous burden on end users without intrinsically guaranteeing any results.

Table 4 – ASTM specification for key HRSG heat-tranfer components at PowerSmith Cogeneration plant

	Primary & Seconday Superheaters A213 – T22	Feedwater Heater A213 - 304	HP/IP/LP Evaporators & Economizers A178 Gr. A
Cr	1.9-2.6	18.0-20.0	-
Mo	0.87-1.05	-	-
Ni	-	8.0-11.0	-
C	0.05-0.15	< 0.08	0.06-0.18
Mn	0.3-0.6	<2.0	0.27-0.63

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