

Final Verdict on Vapor Ingress of Chlorinated Compounds via Weak Tube/Tubesheet Joints

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ABSTRACT

This paper concludes a series of publications on investigations at Shand Power Station (SaskPower) to understand selective chloride cycling in this plant. With naval brass tubesheet, dezincification was implicated as the corrosion mechanism at naval brass tube-to-tubesheet joints, which created vapor pathways for recirculating cooling water (RCW) chlorine compounds into the water/steam circuit, eventually forming chlorides. Replacing the tubesheet with Duplex 2507 SS, the expectation was that the chloride cycling would end. Yet it persisted. The paper provides evidence that even with new metallurgies, vapor ingress via weak tube-to-tubesheet joints has mainly been responsible for the persisting chloride cycling. Organochlorine compounds leaching from the tubesheet/shell interface gasket have also been shown to potentially contribute to the chloride cycling, to a major extent earlier on, but becoming less significant over time. Plugging of the leaking tubes at tube-to-tubesheet joints reduced the average daily increases in boiler chloride from $28.4 \mu\text{g} \cdot \text{L}^{-1}$ to $2.7 \mu\text{g} \cdot \text{L}^{-1}$, supporting the notion that the RCW was the principal source of the chloride contamination.

INTRODUCTION AND BACKGROUND

Chloride is a well-known corrosive inorganic ion which can potentially cause or contribute to equipment breakdown, e.g. boiler tube failures from acid chloride attacks and steam turbine failures from chloride stress and crevice corrosion of turbine blades [1–5]. It has been specifically noted to contribute to corrosion fatigue, stress corrosion cracking (SCC), and pitting in low-pressure (LP) turbines and to corrosion, hydrogen damage, and pitting in boilers, as well as to have a synergistic effect on drum boiler waterwall corrosion in the presence of oxygen and copper oxide [6].

There are various known sources of chloride ingress into the water/steam cycle including the following: make-up water contamination [6,7], feedwater contamination from sources such as condenser tube leaks [6,8] and/or bearing cooling water for the condensate return pumps [9], leakage from condensate polishers [4,7], or contaminants entering the system via chemical injections [8]. In January 2009, SaskPower's Shand Power Station Unit 1 started experiencing boiler chloride cycling of such a nature and magnitude that these well-known causative factors could not individually or cumulatively account for it [10].

This current paper is the final in a series of publications about understanding the root cause(s) of the boiler chloride cycling to ensure proper redress of the issue. In the first paper, we provided evidence that the chloride cycling being experienced could not be explained by current popularly known or reported routes of chloride ingress, including the popular condenser tube water leak [10]. In the subsequent five publications [11–15], we illustrated that the boiler contamination which could be observed in selective chloride cycling was emanating from the recirculating cooling water (RCW), but from pathway(s) completely different from the classic condenser tube water leaks. We proposed that residual chlorine compounds and/or chlorides could ingress both in vapor and aqueous forms into the steam side of the condenser through weak seals of tube-to-tubesheet joints, the latter route (water-borne pathway) being minor (only ~ 4.3% [14]) and likely based on solubility differences as the mechanistic reason for the selective chloride (over sulfate) ingress from RCW sources into the steam side of the condenser.

Dezincification was implicated as the main corrosion mechanism, occurring from attacks of oxidizing chlorinated compounds at weak naval brass tube-to-tubesheet joints, thus creating vapor pathways for chlorinated compounds with significant vapor pressures (e.g. free chlorine

species – HOCl and Cl_2 , chloramines – NH_2Cl , NHCl_2 and NCl_3 , trihalomethanes (THMs), haloacetic acids, HCl, etc.) to enter into the steam side of the condenser via weak seals and/or porous de-alloyed brass at the joints. Under typical conditions of operation in this plant, an estimated cumulative chloride concentration of up to $4.5\mu\text{g}\cdot\text{L}^{-1}$ in the boiler feedwater is possible from these sources, with CHCl_3 , NH_2Cl , and CBrCl_2 as the three most expected dominant contributors [12]. Though the potential contributions from HOCl and NHCl_2 are modest under normal operations, they are expected to be higher under low RCW pH excursion conditions.

Prior to the initiation of the selective chloride cycling, the original condenser tubes of 70/30 and 90/10Cu/Ni had been identified as experiencing some form of de-alloying (denickelification [11]), as shown by condenser leakage, and were therefore earmarked to be replaced. In the spring of 2012, the condenser tubes were replaced with SEA-CURE® tubing, but not the tubesheets, which is not an uncommon practice within the electric power industry. However, during the re-tubing process, several examples of damage to the tubesheets were detected. De-alloying of tubesheet holes was observed in numerous locations, which were repaired with titanium epoxy and plastic epoxy applied on all tubesheet faces [13]. Yet failures linked with chlorine species attacks became obvious soon after such repairs, showing variations in the boiler chloride-to-sodium ratio (BCSR) and restoring the chloride cycling to levels comparable to those before the project, barely two years after the condenser re-tubing. Shell and waterbox inspection of the condenser in the spring of 2014 confirmed deterioration of the epoxy cladding and several leak paths at tube-to-tubesheet joints [14,15]. Maintenance efforts were made to fix the leakage associated with the weak tube-to-tubesheet joints, i.e. the contamination pathway. This did not solve the problem. The need to replace the tubesheets became more pressing and in the fall of 2016 new condenser tubes (SEA-CURE®) and tubesheets (2507 Duplex SS) were installed.

With the replacement of both the condenser tubes and the tubesheets, the expectation was that the chloride cycling would be terminated. However, it persisted, even to levels higher than the occasions leading to the condenser replacement project. This raised the following legitimate questions:

- a) Was the experienced chloride cycling indeed related to the condenser as postulated?

- b) Was it the same source of chloride contamination as in the past (perhaps attributed erroneously to the condenser) which had still persisted? If so, why was recent cycling even worse than before the condenser tube and tubesheet replacement in 2016?
- c) Were there some activities during the condenser replacement outage which could be responsible for a renewed chloride cycling?

The current paper is an investigatory report on the search for answers to the queries above and provides final evidence in support of the hypothesis that the selective chloride cycling in the boiler experienced at this plant is indeed primarily due to vapor ingress of chlorinated compounds of high vapor pressure from the RCW into the condensate water (hotwell) via weak seals at tube-to-tubesheet joints. Irrespective of the metallurgies of the condenser tubes and tubesheets, the phenomenon would occur once the joint seals are weak enough to allow vapor (and not necessarily or barely any liquid) passage.

MATERIALS AND METHODS

Plant Design, and Operating and Maintenance Conditions

Shand Power Station (SaskPower), a 305MW coal (lignite)-fired single unit power plant, has followed zero liquid discharge (ZLD) requirements since commission in 1992. An induced draft counter flow cooling tower (CT) and an open recirculating system are used for heat rejection. Make-up to the CT is a blend of constructed wetland treated secondary effluent and surface water of varying proportions throughout the year [16–18]. Sodium hypochlorite is used as an oxidizing biocide to pre-treat and treat the RCW and the consumption is high ($\sim 439000 \pm 53000\text{L}$ of 15% solution annually in recent times (i.e. since 2014) to maintain CT residual chlorine at $\sim 0.28 \pm 0.16\text{mg}\cdot\text{L}^{-1}$ during warmer periods from May to October and at $\sim 0.33 \pm 0.26\text{mg}\cdot\text{L}^{-1}$ during colder periods from April to November). Further details of the chemistry, design, and operating conditions of the cooling tower/condenser systems and the water/steam circuit, as well as the monitoring protocols for the water/steam cycle chemistry, have been outlined previously [10–14,16–18].

Time Period	Start Date	End Date	Work Done	Inspection: Dates & Activities
Outage 1	April 17, 2014	May 16, 2014	Repairs to breached epoxies on the condenser	
Phase 1	May 16, 2014	August 26, 2016		August 16, 2014 (Observed Coating Defects); March 2–3, 2015/ March 18–20, 2015
Outage 2	August 26, 2016	October 22, 2016	Condenser tubes and tubesheets replaced	
Phase 2	October 22, 2016	May 11, 2018		February 28–March 3, 2017: Solid deposits taken from condenser steam side and CEP strainers for EOCl and XRF analyses
Outage 3	May 11, 2018	June 10, 2018	Leaking tube-to-tubesheet joints were fixed	May 11–June 8, 2018: Gasket materials taken from con- denser for EOCl and XRF analyses
Phase 3	June 10, 2018	September 6, 2018		No condenser inspection

Table 1:
Inspection, outage dates, and work activities for the various phases during the investigation period.

Condenser Inspections and Outage Activities

The period of the current investigation is divided into three phases as shown in Table 1. For these phases, the condenser (waterboxes and shell side) was inspected during the maintenance/inspection outages as indicated in Table 1. During inspections, pictures were taken as well as available samples collected for analysis as described below.

Sampling, Experimental Methods, and Testing

On-line continuous monitoring and daily grab water sampling at different water/steam cycle locations for various parameters were in accordance with EPRI's guidelines [6,19]. For this power plant, the most critical parameter for early detection of condenser leakage is sodium at the condensate extraction pump (CEP) outlet, which other parameters are used to confirm [10]. In keeping with EPRI's guidelines [6,19], apart from some start-up conditions when silica is an issue, most of the requirement for blow-down from the boiler/steam drum at this plant is based on sulfate or chloride. As discussed previously [10], the facility has two Dionex-IC instruments: IC-DX-2000 for measuring these ions from grab sampling and IC-DX-800 as an on-line instrumentation. During the period of investigation however, the on-line IC was not always available and therefore the chloride and sulfate data reported in this current paper are mostly based on daily analysis by the IC-DX-2000 instrument.

In addition to the routine sampling and testing, water samples from the CEP outlet and the boiler were taken on January 24, February 13, and March 7, 2017 (i.e. during the second phase (Table 1)), for extractable organochlorine (EOCl) analysis. On February 13, 2017, other sampling locations including product from the mixed beds, condenser make-up supply tanks (known in the plant as low-level and high-level tanks), and the deaerator outlet were also sampled for EOCl analysis.

Some solid samples were also obtained during the second phase from the condenser steam side, the CEP suction strainers, and the magnetic strainers from the boiler feed pumps. Apart from a planned inspection outage on February 28 to March 3, 2017 (Table 1), some swab samples from the CEP suction strainers were taken earlier during a short outage on January 26, 2017, for both EOCl and X-ray fluorescence (XRF) spectroscopic analysis (see details below). As a qualitative measure, a methanol/water mixture and water (1L in each case) were also used to extract unquantified deposits from boiler feed pump magnetic strainers for EOCl analysis during preventative maintenance (PM) work done on February 13, 2017. The water extract, together with an acetone/methanol extract of the sample, was also analyzed by inductively coupled mass spectrometry (ICP-MS) to provide relative proportions of the elemental composition of the solids trapped by the strainers. Similarly, cotton swab samples of unquantified dark film observed on the tubes and tubesheet surfaces at

the steam side during the February 28 to March 3, 2017, inspection were also analyzed for EOCl, as a qualitative measure.

During the May 11 to June 10, 2018, maintenance outage, a cut piece of gasket material extending about 3 cm into the condensate side of the condenser from the tubesheet/shell interface was analyzed by XRF and for EOCl. For comparison, a protruding gasket piece at the condenser exterior of the tubesheet/shell interface was also cut for the same analysis. Attempts were also made to simulate chlorine extraction from the gasket material under the high pH conditions inside the condensate side of the condenser by placing a piece of each of the two gasket materials (one previously exposed and the other not at all exposed to the condenser steam side condition) into a 200 mL beaker containing 100 mL of $0.01 \text{ mol} \cdot \text{L}^{-1}$ ammonia solution (pH ~ 10). To also simulate the potential for oxidizing chlorine species (ingressing into the steam side) to leach chlorine from the gasket materials, two drops of household bleach solution were added to the material previously exposed to the condenser condensate side conditions.

Inside the condensate side of the condenser, specifically inside the gland steam hotwell drain, crushed and folded rubber chunks were found. These samples were also analyzed for EOCl.

Extractable organochlorine analysis The EOCl analyses were performed by the Environmental Analytical Laboratories of the Saskatchewan Research Council (SRC) by neutron activation analysis (NAA) after extracting the organic chlorine content with toluene.

X-ray fluorescence (XRF) spectroscopy Elemental analysis (expressed commonly as oxides in % wt/wt) for the gasket samples and the solids obtained from the CEP strainers were performed by Bruker S8Tiger XRF using the Quant Express Method. To provide an indication of the accuracy of the analysis, standard reference materials were also analyzed and the results compared with theoretical values. Generally, apart from SO_3 , the measured standard values deviated only by less than 10% from the standard theoretical values; for Cl, which is of focal interest in this discussion, the measured value deviated by $-0.02 \pm 10.3\%$ from the theoretical value. The XRF measurements were all performed by the Chemical Services Group of SaskPower, in Regina.

Inductively coupled mass spectrometer (ICP-MS)

A 1 g aliquot of sample was combined with 0.5 mL of trace metal grade nitric acid (HNO_3) and placed in a 65°C water bath for one hour. The samples were then brought up to 10 mL with a 2% HNO_3 and 3% hydrochloric acid (HCl) matrix solution. A further 1/5 dilution was made using the matrix solution, and analysis performed using an Agilent 8800 Triple Quadrupole ICP-MS. To provide an indication of the accuracy of the analysis, a quality control standard was also analyzed (in triplicate) and the average results compared with the theoretical values. Generally, the measured standard values deviated by less than 10% from the theoretical check standard. The ICP-MS measurements were also performed by the Chemical Services Group of SaskPower, in Regina.

RESULTS AND DISCUSSION

As mentioned earlier (Table 1), the period of the current investigation is divided into three phases: the first began upon returning from an outage when repairs to breached epoxies on the condenser were made and continued until an outage for condenser tube and tubesheet replacements; the second started upon returning from that outage and continued until the next biennial maintenance outage on May 11, 2018; and the last went from June 10, 2018 (returning from that outage), until September 6, 2018. These three phases are discussed separately below.

Pre Condenser Tube/Tubesheet Replacement Period [PHASE 1]

Though repairs to damaged tubesheet holes and replacement of the Cu-Ni condenser tubes with SEA-CURE[®] tubes to ensure good barriers were performed in spring 2012 to eliminate tube-to-tubesheet joint leaks and block this likely path for volatile chlorinated species, the benefits of these efforts were short lived. Barely two years after the repairs the chloride ingress had returned to levels comparable to before the repairs, leading to suspicions that the epoxy coating which served as the only barrier against this potential ingress had started to fail [14,15]. Inspection of the condenser waterboxes and the steam side during the spring (April/May) 2014 outage confirmed deterioration of the epoxy cladding and tube-to-tubesheet joints [14].

Repairs to failed/failing sections of the epoxy cladding, particularly at tube-to-tubesheet joints, were made during the outage. Inspection on August 16, 2014, showed that defects of the coating at the tube-ends were still evident, some even

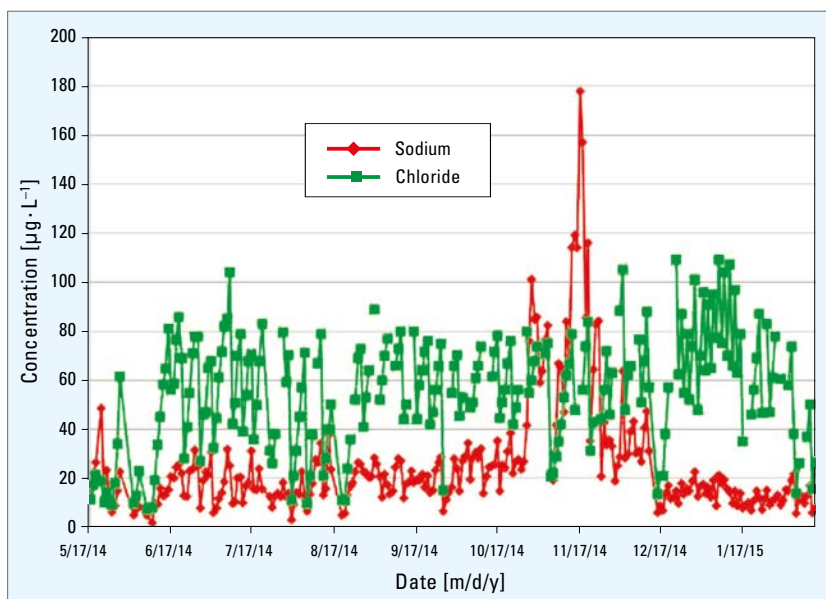


Figure 1:
Daily concentrations of boiler sodium and chloride from May 17, 2014, to February 12, 2015. For clarity some data points, especially during start-ups, have been removed.

from recent repairs. As shown in Figure 1, the chloride cycling continued, leading to frequent blow-down of the boiler water. In fact, with the high rate of cycling, concerns about chloride-induced damage by operating consistently at high chloride concentrations led to a decision to tighten the boiler chloride limit proposed by EPRI [6,19] from $\sim 110 \mu\text{g}\cdot\text{L}^{-1}$ (according to the operating pressure of this unit) to $80 \mu\text{g}\cdot\text{L}^{-1}$. Generally, a fair correlation (correlation strength, R^2) was

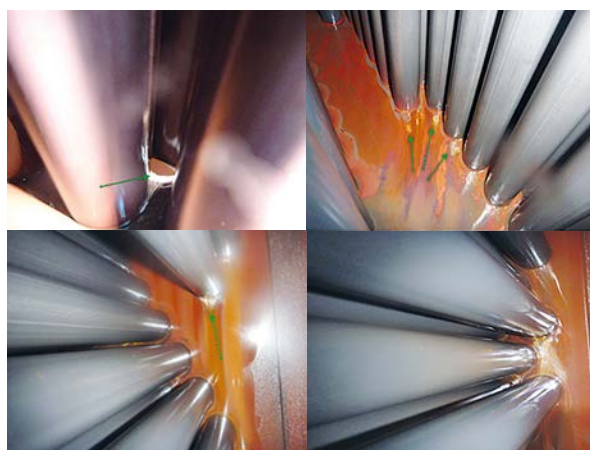


Figure 2:
Photographs taken on March 18–20, 2015, of leaking tube-to-tubesheet joints. The leakages were plugged by inserting pin-and-collar metal plugs into both ends of the affected tubes to ensure tight seals for the tube-to-tubesheet joints. Although tube removal to plug tubesheet holes is effective in addressing tube-to-tubesheet joint leaks, it is a risky venture should the plug fail. A rubber plug inserted into a tubesheet hole (after removing an affected tube with a leaking joint) earlier on March 3, 2015, was short-lived and already fractured on March 9, 2015.

evident between the boiler sodium and chloride from May 17 to October 24, 2014 ($R^2 = 0.34$; $n = 129$ or $R^2 = 0.54$, excluding 5 obviously discordant data points), suggesting some common source of these ions, with the condenser as a likely culprit. However, Figure 1 points to some activity from October 25 to December 17, 2014, that compromised this relation ($R^2 = 0.17$). Following that activity, the correlation between sodium and chloride was somewhat restored ($R^2 = 0.48$; $n = 46$) and the chloride cycling generally worsened.

During inspection and a condenser leak check early in March of 2015, 122 tubes were painstakingly identified as showing tube-to-tubesheet leakage (see Figure 2) and were plugged with pin-and-collar metal plugs to ensure tight seals for the tube-to-tubesheet

joints. These repairs proved to be successful in addressing the main tube-to-tubesheet leakages, as the selective chloride cycling decreased significantly. As exemplified in Figure 3, prior to the outage in fall 2016 to replace both the condenser tubes and the tubesheets, the boiler chloride concentrations were generally low and could barely be responsible for any boiler "continuous blow-downs" (CBDs). CBDs were largely due to high sulfate concentrations and not chloride, as was the case before the tube-to-tubesheet joint seal repairs in March 2015 (see Figure 1). Success in addressing the chloride cycling by sealing leaking tube-to-tubesheet joints had also been observed earlier, when the leaking tubes were removed and the tubesheet holes plugged [11,12]. Thus, tight seals at tube-to-tubesheet joints would ensure the elimination of such selective chloride cycling, which emanates from the RCW side of the condenser via ingress of gaseous chlorinated compounds. Note that despite this success in removing affected tubes to plug tubesheet holes to fix leaking tube-to-tubesheet joints, our experience does point to this approach as risky, should the plugs fail, hence it is not recommended.

Post Condenser Tube/Tubesheet Replacement till Biennial Outage in 2018 [PHASE 2]

With both the condenser tubes and the tubesheets replaced, the obvious expectation was to see termination of the chloride cycling. However, the chloride cycling persisted, at levels

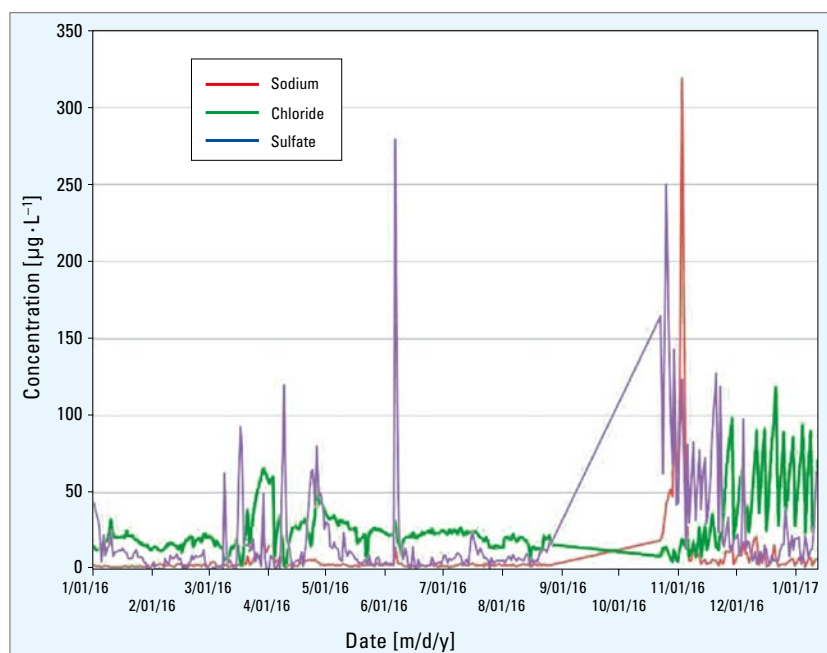


Figure 3:
Daily concentrations of boiler sodium, chloride, and sulfate in 2016.

even higher than during the period just prior to the condenser replacement project. See Figure 3 for the initial stages upon returning from the overhaul (October 22, 2016, to January 12, 2017) as compared to the pre-overhaul period (January 1, 2016, to August 26, 2016).

Could the condenser still be the culprit source despite installation of new tubes/tubesheets?

Assessing relations with RCW residual chlorine levels: In the early stages (about the first week) upon returning from the condenser replacement project (Table 2, entry 1), the condenser involvement in the condensate contamination was evident in the form of convective flux of liquid (aqueous RCW) into the condensate water carrying higher concentrations of sodium over chloride (Figure 3). This is displayed by moderate boiler chloride cycling, an inverse relation between the BCSR and total chloramine (TCA), a strong relation between boiler chloride and sodium suggesting a common source, a strong relation between the RCW chlorination level (free chlorine (FC) or TCA) and boiler sodium, and finally, a fair relation between the RCW chlorination levels and boiler chloride. It should be noted that the typical RCW sodium-to-chloride ratio for this plant is about 2.3 to 3.0 [14,15] and chlorination level variations would be reflected in RCW sodium (and chloride) concentrations, since the chlorination product (sodium hypochlorite) is a major direct source of sodium and

an indirect source of chloride via redox reactions. As shown in Table 2 (entry 2), the negative correlation between BCSR and TCA was maintained up to the 3rd to 4th week in operation, but the big drop in correlation strength (R^2) between boiler chloride and sodium from entry 1 to 2 (Table 2) suggests inclusion of a different significant source of chloride, which may be unrelated to the RCW. Further evidence for a different chloride source than the RCW is shown by the lack of a relation between TCA and the boiler chloride, although a relation to boiler sodium was somehow retained. (See below for discussions on a potential involvement of organic chlorine compounds leaching from gaskets employed between the

tubesheet/condenser shell interfaces.) It is worthy of note that during these early 3 to 4 weeks of operation, the generating unit was operating on partial loads of 179 ± 4 MW.

Unlike early stages of operation, although involvement of the newly installed condenser in the condensate contamination was still evident, it showed in a different form from the 4th to 15th week in operation, when the typical generating load was 286 ± 27 MW. Instead of convective (water) flow from the RCW into the condensate water, vapor diffusive flux of chlorinated compounds, as reported earlier [14,15], was more apparent, as could be seen in: a) high boiler chloride cycling (see Figure 4 from January 28 to February 5, 2017, for instance), and b) an increasing strength of correlation between the BCSR and RCW chlorine levels (TCA or FC) (see entries 3 to 5 in Table 2). The strong correlation between boiler chloride and sodium supports a common source of these two parameters, i.e. the RCW. Initially, potentially large gaps at tube-to-tubesheet joints from possibly improperly rolled tubes could lead to convective (water) flow from the RCW, which would transport both sodium and chloride ions. After further cycling of the generating unit, involvement of the condenser in selective boiler water chloride cycling would become more eminent, characterized not only by the positive correlation of TCA with the BCSR, but also with boiler chloride (Table 2, entry 5). Over several cycles, any potential gaps at the joints were likely to tighten due to metal ex-

Entry #s	Period [d/m/y]		BCSR/TCA <i>R</i> ² { <i>m</i> }	BCSR/FC <i>R</i> ² { <i>m</i> }	Cl ⁻ /Na ⁺ <i>R</i> ² { <i>m</i> } [<i>n</i>]	Correlation Coefficient (<i>R</i> ²)			
	Start	End				Cl ⁻ /TCA	Cl ⁻ /FC	Na ⁺ /TCA	Na ⁺ /FC
Post Condenser Tube/Tubesheet Period until 2018 Spring Overhaul (Phase 2)									
1	23/10/16	02/11/16	0.45 {−0.12}	0.25 {−0.6}	0.81 {0.05} [7]	0.44	0.50	0.71	0.84
2	04/11/16	16/11/16	0.55 {−2.8}	0.00 {2.0}	0.02 {0.1} [13]	−0.03	0.01	0.38	0.00
3	17/11/16	04/01/17	0.41 {8.3}	0.14 {14.8}	0.30 {2.8} [46]	0.18	0.01	−0.12	−0.07
4	05/01/17	25/01/17	0.53 {11.0}	0.40 {37.0}	0.89 {7.9} [21]	−0.05	−0.04	−0.07	−0.13
5	28/01/17 ^c	05/02/17 ^c	0.69 {16.3}	0.44 {9.4}	0.92 {9.4} [8]	0.93	0.42	0.54	0.34
6	06/02/17	28/02/17	− ^a	0.20 {−5.5}	0.80 {9.1} [23]	− ^a	0.06	− ^a	0.24
7	03/03/17 ^d	26/03/17 ^d	− ^a	0.26 {−1.7}	0.74 {4.1} [24]	− ^a	−0.14	− ^a	−0.04
8	30/03/17 ^c	29/05/17 ^c	0.27 {−3.3} ^b	0.29 {−16.0}	0.65 {6.9} [60]	0.01 ^b	0.01	0.10 ^b	0.10
9	30/05/17 ^d	13/07/17 ^d	0.00 {0.3} ^b	0.04 {−4.1}	0.59 {5.4} [39]	0.03 ^b	−0.02	0.03 ^b	0.01
10	14/07/17 ^c	10/08/17 ^c	0.37 {6.4} ^b	0.04 {−9.6}	0.64 {9.0} [28]	−0.03 ^e	0.01	−0.25	0.02
11	11/08/17 ^d	27/09/17 ^d	0.01 {−1.0} ^b	0.05 {−5.7}	0.61 {8.3} [47]	0.01	−0.03	0.01	0.00
12	28/09/17 ^c	24/10/17 ^c	0.14 {−1.5} ^b	0.13 {−3.5}	0.64 {7.3} [27]	−0.07	−0.02	0.00	0.01
13	01/11/17 ^c	23/12/17 ^c	0.24 {4.9} ^b	0.05 {3.1}	0.64 {6.6} [53]	0.39 ^b	−0.02	0.37 ^b	−0.05
14	24/12/17	05/01/18	− ^a	0.04 {−4.9}	0.67 {18.3} [13]	− ^a	−0.28	− ^a	−0.29
15	09/01/18 ^d	22/01/18 ^d	− ^a	0.01 {0.9}	0.70 {4.3} [14]	− ^a	−0.15	− ^a	−0.02
16	23/01/18 ^c	15/02/18 ^c	− ^a	0.13 {−7.7}	0.52 {9.4} [24]	− ^a	−0.08	− ^a	−0.01
17	16/02/18	15/03/18	− ^a	0.01 {2.1}	0.52 {11.5} [26]	− ^a	−0.05	− ^a	−0.17
18	15/03/18 ^d	09/04/18 ^d	0.28 {−1.0} ^f	0.01 {1.2}	0.62 {15.1} [25]	−0.03 ^f	−0.05	0.00 ^f	−0.03
19	09/04/18 ^c	11/05/18 ^c	0.38 {−1.4} ^f	0.08 {−7.2}	0.51 {9.1} [31]	−0.01 ^f	0.00	0.15 ^f	0.05
Post Biennial Maintenance Outage in Spring 2018 (Phase 3)									
20	10/06/18	06/09/18	0.02 {0.1}	0.01 {0.1}	0.91 {1.8} [89]	0.01 ^f	0.20	0.01 ^f	0.18

Table 2:

Correlation coefficient (R^2) and slopes (m) for relations between boiler chloride (Cl⁻), boiler sodium (Na⁺) or boiler chloride-to-sodium ratio (BCSR) and various chlorine forms in RCW: free chlorine (FC) and total chloramine (TCA); the difference between total chlorine (TC) and FC, for n number of samples, as well as for boiler chloride correlation to boiler sodium (where (–) connotes an inverse relation) for phases 2 and 3.

^a During the period, TCs exceeded the high end (2.2 mg · L⁻¹) of the typical selected range for chlorine measurements and hence no reliable data was available for the correlation analysis;

^b Data involving TC ≥ 2.2 mg · L⁻¹ were eliminated in the correlation analysis;

^c Period when the daily rise in boiler chloride generally followed an increasing trend;

^d Period when the daily rise in boiler chloride generally followed a decreasing trend;

^e By excluding data from July 15 and 16 and August 8 in addition to those with TC ≥ 2.2 mg · L⁻¹, a R^2 of 0.27 was obtained Cl⁻/TCA;

^f Data used includes the actual measured data of TC ≥ 2.2 mg · L⁻¹.

pansion, thus reducing the convective flow and allowing molecular diffusive transfer of volatile chlorinated compounds through these still weak joints, resulting in concomitant selective boiler chloride cycling [11–15].

Also, unlike early stages when a drop in the correlation (R^2) for boiler chloride/sodium was observed (Table 2, entry 1 and 2), an increasing trend is observed over time from entry 2 to 5 (Table 2), suggesting a minimization of the effect from other chloride source(s) (see above). As noted above, the reduced effect from any other sources of chloride (or rather an accentuated RCW chloride source contamination) on the boiler chemistry is further evidenced by a good to fair correlation of TCA with boiler chloride (Table 1, entry 5). Such a correlation was however

lacking during the 10th to 13th weeks in operation (Table 2, entry 4) and is likely related to the loss of RCW chlorination for that period, which resulted in low FC (0.04 ± 0.03 mg · L⁻¹) and TCA (0.07 ± 0.04 mg · L⁻¹). It has to be noted however that this condition did not prevent the selective chloride cycling or BCSR variation in an obvious way (see Figure 5). With a strong correlation (R^2 = 0.89) between boiler chloride and sodium (Table 2, entry 4) to suggest the RCW as a more exclusive source of these parameters in the condensate water, the lacking correlation between TCA and boiler chloride may be explained by the low spread of the chlorine levels in the RCW during the period. Furthermore, it also has to be noted that apart from oxidizing chlorine forms (i.e. FC and TCA), there are other chlorine compounds in

the RCW that are even more volatile and can ingress in volatile forms into the condensate water. Thus, the poor correlation of the BCSR with oxidizing forms of chlorine in the RCW does not necessarily preclude the condenser's involvement in the chloride cycling. Previously [12], we had shown CHCl_3 and CBrCl_2 to be amongst the three most dominant expected contributors of chloride under the normal operating conditions of this plant.

As shown in Figure 4, a decreasing trend in the daily chloride rise began on February 19, 2017. Returning from a February 28 outage, a significant reduction in chloride cycling was realized (see Figure 4), decreasing the average daily rise of $38.5 \pm 14.0 \mu\text{g} \cdot \text{L}^{-1}$ (during the period covering the guillotine gate and boiler relieve valve repair outages) to $9.5 \pm 3.8 \mu\text{g} \cdot \text{L}^{-1}$ (during the period covering the boiler relieve valve and A-RCW pump repair outages, March 26, 2017). This is despite maintaining high RCW chlorination ($\text{FC} = 0.48 \pm 0.37 \text{mg} \cdot \text{L}^{-1}$; $\text{TCA} \geq 1.70 \pm 0.36 \text{mg} \cdot \text{L}^{-1}$). Thus, the high chloride cycling observed upon returning from the guillotine gate related outage (Figure 4) and ascribed to high RCW chlorination was not maintained. Such sporadic influences on boiler chloride cycling due to vapor diffusion flux of chloramines have been noted in an earlier paper [15].

After returning a repaired RCW pump to service on March 30, 2017, a general increasing trend in the chloride cycling was restored (see Stage IA in Figure 4), but paradoxically an inverse relation was observed between the BCSR and TCA ($R^2 = 0.27$) until May 29, 2017 (see Table 2, entry 8). A similar increasing trend in chloride cycling occurred between July 14 and August 10, 2017 (see Stage IB in Figure 4), except a fair correlation between the BCSR and TCA was positive this time ($R^2 = 0.37$; Table 2, entry 10), thus still suggesting the RCW as a likely source of vapor diffusion flux of chlorinated compound ingress into the condensate system.

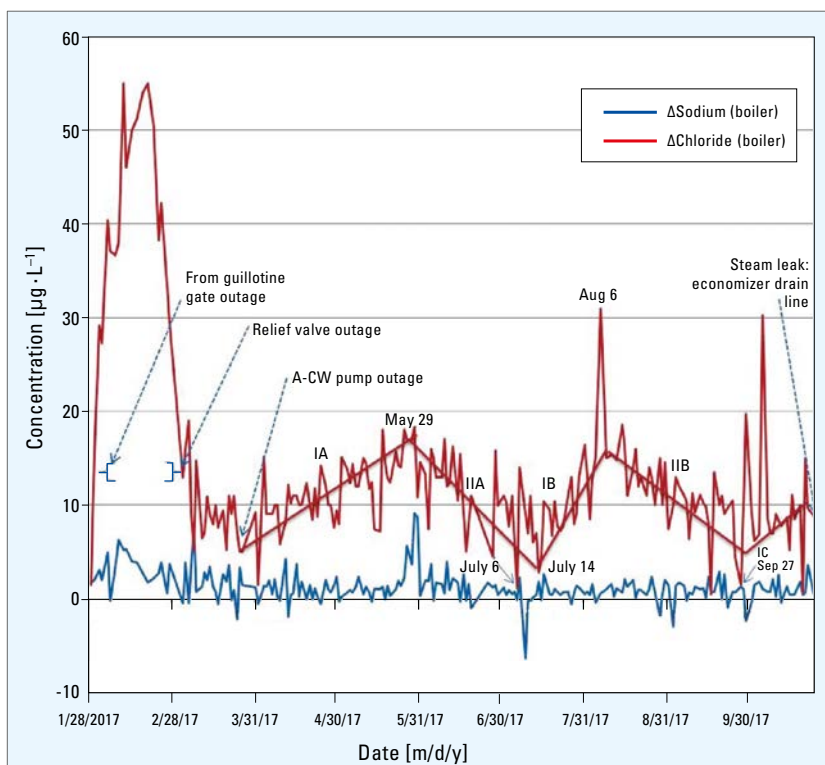


Figure 4:

Daily changes in sodium and chloride concentrations (positive for increases and negative for decreases) in the boiler drum from January 28 to October 24, 2017. Data for days of upset boiler conditions and/or when the boiler had been blown down are omitted.

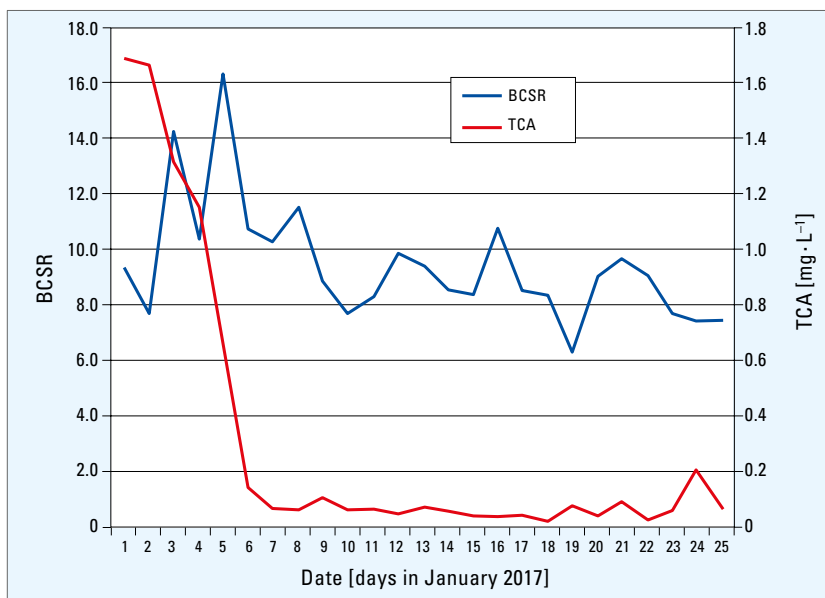


Figure 5:

Plots of the boiler chloride-to-sodium ratio (BCSR) and total chloramine (TCA) in January 2017, showing periods with no RCW chlorination, but of no significant influence on the BCSR.

Contrary to the increasing (daily chloride rise) trends observed for Stages IA and IB, a decreasing trend in daily chloride rise was generally observed from May 29 to July 14, 2017 (Stage IIA), and from Aug. 11 to Sept. 27, 2017 (Stage IIB), and essentially no correlation was observed between the BCSR and TCA, nor was there any appreciable correlation between the daily boiler chloride rise (or chloride concentration) and TCA (Table 2, entries 9 and 11). The moderate correlation strength between boiler chloride and sodium for this period ($R^2 \approx 0.62$) coupled with essentially no correlation between TCA and boiler chloride may suggest a temporary cessation of the RCW source of chloride contamination and/or may merely reflect a decreasing influence of an RCW-independent source of chloride with a more moderate impact than was observed earlier in operation.

Leading up to another outage on October 24, 2017 (forced outage due to a steam leak on the economizer drain line), the chloride cycling continued but the daily increases were more variable ($9.87 \pm 5.91 \mu\text{g} \cdot \text{L}^{-1}$) and the correlation between TCA and the BCSR was negative and only fair (Table 2, entry 12). The reader should note the somewhat similar phenomenon, i.e. an increasing chloride cycling with a paradoxical inverse relation between the BCSR and TCA, as discussed above for early operational periods after the condenser replacement and later from March 30 to May 29, 2017 (Stage IA Figure 4 and

Table 2, entry 8), suggesting a possible domination of convective flux of both liquid (aqueous RCW) and vapors of chlorinated compound (over diffusive vapor flux) from the RCW via weak tube-to-tubesheet joints transporting sodium as a dominant dissolved ion (over chloride). The condenser's involvement as a contamination source is therefore still possible, with the effect being less obvious due to two possible scenarios: a) minimization of vapor diffusion flux of chlorinated compounds, and/or b) a significant contribution of chloride from other source(s) independent of RCW chlorination. A positive TCA correlation with the BCSR would occur when the diffusion flux of volatile chlorinated compounds dominates convective fluxes of RCW. With RCW as the main source of the condensate contamination or BCSR variations, whether convective (liquid and vapor) flow or exclusively diffusion (vapor) flux dominates, a strong boiler chloride versus sodium correlation is expected, as they are from a common source. A significant presence of chloride (or sodium) sources independent of the RCW would mask such a correlation.

Unique daily increases occurred in late December 2017, which escalated even more about a week later, resulting in an average $53.0 \pm 16.9 \mu\text{g} \cdot \text{L}^{-1}$ chloride rise per day for the period (Table 2, entry 14). In fact, the daily rises in chloride were reminiscent of an earlier trend (i.e. Table 2, entry 5), although the slope was uniquely steeper here, suggesting a stronger diffusive flux of chlorinated vapor compound contribution from the RCW source. The phenomenon where an increasing daily rise in boiler chloride concentration (I-Stages) is followed by a decreasing daily rise (II-Stages) (see Figure 4) repeated as the episode was followed by a decreasing daily chloride rise from January 9–22, 2018 (Stage II; Table 2, entry 15), and then by an increasing daily chloride rise till February 15, 2018 (Stage I; Table 2, entry 16) (see Figure 6). The phenomenon seemed to even be present afterwards, although it had become less obvious leading up to the plant biennial overhaul outage in May (Figure 6), i.e. after over a year and 7 months in operation following the installation of the new condenser tubes/tubesheets.

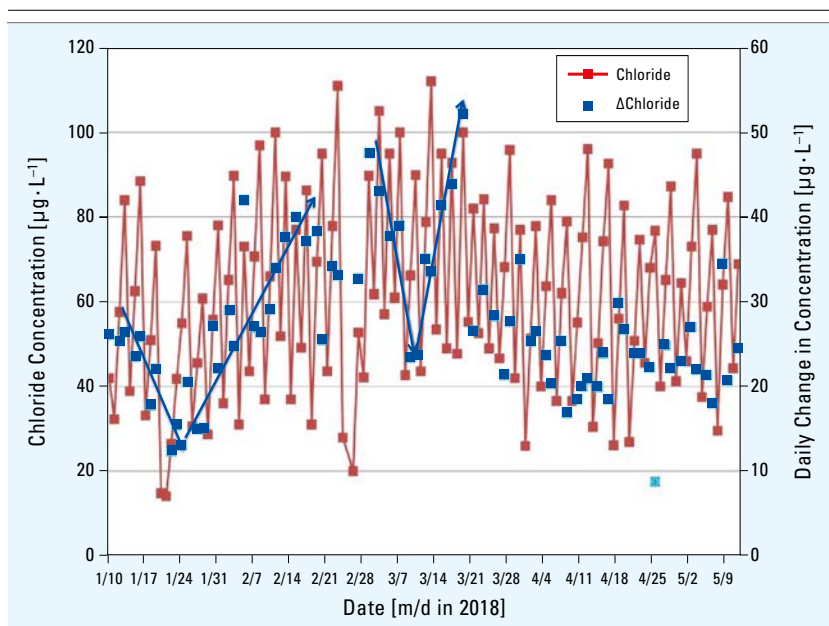


Figure 6:
Daily boiler chloride concentrations and daily changes in chloride from January 10 to October 24, 2017. Data for days of upset boiler conditions and/or when the boiler had been blown down are omitted.

Leading into the overhaul, the daily increase in boiler chloride concentration was $22.5 \pm 4.9 \mu\text{g} \cdot \text{L}^{-1}$ and the correlation results (Table 2, entry 19) were reminiscent of a blend of diffusive vapor flux and viscous water flow contribution from the RCW source, as well as from an RCW-unrelated source. The R^2 for boiler chloride versus boiler sodium was only moderate (0.51), suggesting that the boiler contamination was not from an exclusive source, but from multiple sources. The relatively high BCSR average of 9.1 is reminiscent of a significant contribution from the RCW diffusion flux of vapor chlorinated compounds, e.g. chloramines [15], and the moderate negative correlation between TCA and the BCSR ($R^2 = 0.38$) suggests a significant contribution of sodium into the condensate water from the RCW convective flow.

To revisit the question asked earlier in this section: *Could the condenser still be the culprit despite the new tube/tubesheet installation?* Yes, based on correlations between TCA and the BCSR, boiler chloride or daily changes in boiler chloride concentrations (Table 2 and Figures 3 to 6), the involvement of the condenser is implicated, but due to the interference of yet another influencing factor (and perhaps an absence of porous metals in promoting diffusive vapor flux), the observed relations are weak in comparison to the periods before the replacement of both the copper-bearing condenser tubes and the tubesheets [14, 15]. In the next sections we provide further evidence in support of the condenser's involvement as a major source of the chloride cycling.

Assessing relations between condenser backpressure and feedwater parameters: There is other evidence indicating the condenser as a major source of the chloride cycling even after the installation of new tubes and tubesheets, and it is as follows:

■ Reduced condenser backpressure (stronger vacuum) seemed to cause an increase in CEP sodium (see Figures 7 and 8A).

■ Evidence exists to support an occasional inverse relation between dissolved oxygen (DO), oxidation reduction potential (ORP) (CEP and deaerator outlets), and condenser backpressure (see Figures 8A and B).

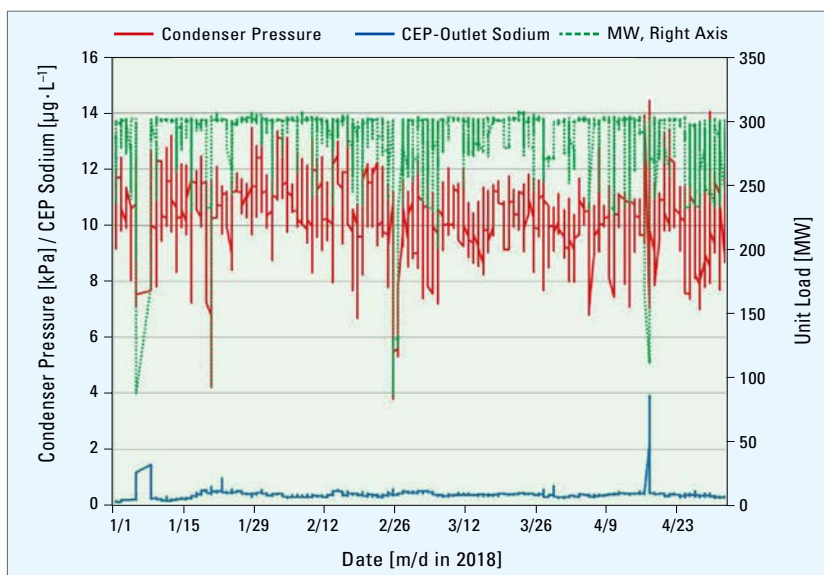


Figure 7:

Unit load and condenser backpressure versus sodium concentration in the feedwater at the condenser extraction pump (CEP) outlet for about a 4- to 5-month period leading up to the biennial maintenance overhaul on May 11, 2018. Unit outage, trips, and start-up conditions of generating loads less than 80 MW have been excluded.

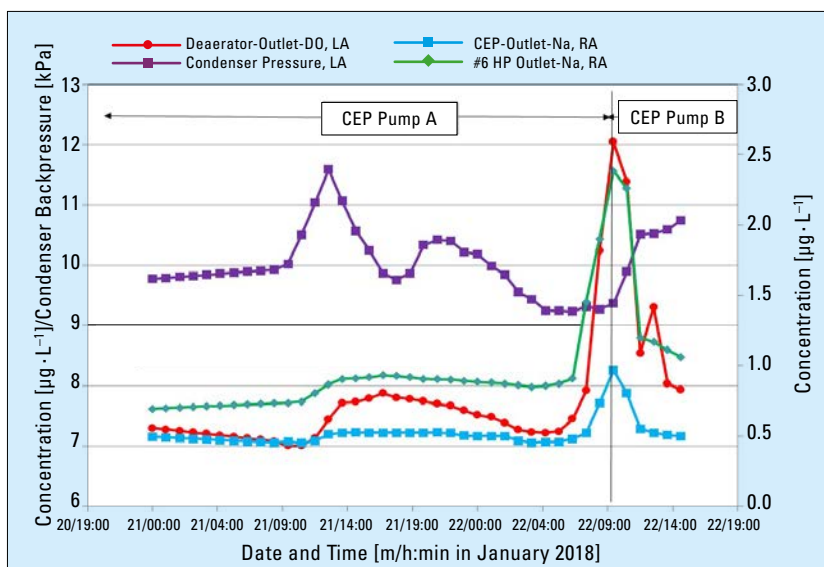


Figure 8A:

Condenser backpressure versus sodium concentration in the feedwater at the condenser extraction pump (CEP) and #6 high-pressure (HP) outlets and dissolved oxygen (DO) concentration after the deaerator from January 21 (00:00) to January 22 (15:00), 2018, which involved switching of the CEP Pump from one (A) to the other (B). Variations in condenser backpressure were not due to variations in generating load, which was fairly constant at a full load of 301.8 ± 1.5 MW throughout the period.

LA left axis

RA right axis

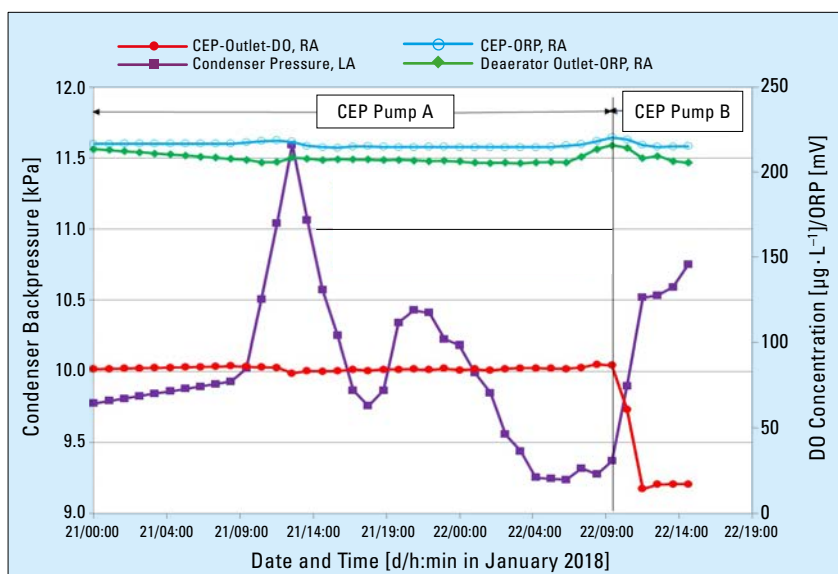


Figure 8B:

Condenser backpressure versus oxidation reduction potential (ORP) after the CEP pump and the deaerator and dissolved oxygen (DO) concentration after the CEP pump from January 21 (00:00) to January 22 (15:00), 2018, which involved switching of the CEP Pump from one (A) to the other (B). Variations in condenser backpressure were not due to variations in generating load, which was fairly constant at a full load of 301.8 ± 1.5 MW throughout the period.

- Evidence exists to support an occasional positive relation between DO, ORP (CEP and deaerator), and the CEP and the last high-pressure (HP) heater (i.e. #6 HP heater) sodium (as associated with condenser backpressure) (see Figure 8A and B).

Clear evidence exists for an inverse relation between CEP DO and condenser backpressure on switching CEP pumps, and there is further evidence that the strength of such an inverse relation (R^2) depends on the particular CEP pump in operation.

As shown in Figures 8A and B, a reduction in condenser backpressure at 13:00 on January 21, 2018 (when unit load was essentially invariant (303.2 ± 2.1 MW)), led to increases in the feedwater (CEP and #6 HP) sodium, as well as increases in DO at the deaerator and CEP outlets. Furthermore, in response to a sustained reduced condenser backpressure of about 9.2 kPa (i.e. from January 22, 05:00 to 10:00), the increase in CEP and deaerator DO as well as CEP and #6 HP sodium concentrations became more apparent. The sustained low condenser backpressure also resulted in a moderate increase in ORP at the CEP outlets and a higher increase at the deaerator outlets. By switching CEP pumps (from Pump-A (south) to Pump-B (north)) to address a high CEP DO concern, the surges occurring initially

for various parameters reversed back to original levels, except for CEP DO, where the reduction extended below the background level (with Pump-A in operation and experiencing DO ingress) to typical operating levels (when there is less concern with DO ingress).

It is noteworthy that from an earlier outage (March 27, 2017) to repair one RCW pump (A) and also when the suction strainer of CEP Pump-A was removed for cleaning and inspection, chloride cycling reminiscent of the dominant convective flux of the aqueous form of RCW into the water/steam cycle (as realized during early stages of operation with the newly installed condenser tubes/tubesheet) re-emerged (see Table 2, entry 8 and Figure 4). It was concluded that some leak paths (likely at tube-to-tubesheet joints) had re-emerged or enlarged. At the same time, CEP DO escalated during the running of the CEP Pump-A (and not the CEP Pump-B).

The source of the oxygen contamination was however unclear, whether from the cooling water side via the leak paths or from atmospheric air at the suction sides of the CEP pumps (i.e. outside the condenser). The fact that the high DO was associated only with the CEP Pump-A prompted the latter as the initial target. Various external efforts to potentially seal all suspicious associated flanges did not improve the problem. Numerous attempts to identify any potential leaks also proved negative.

The possibility that the oxygen source was from the condenser cooling water side could therefore not be discounted. The CEP Pump-A had often been noted by the operating staff to be a "stronger" pump with better output, although identical to the CEP Pump-B; hence, it is conceivable that the former pump would pull adequate suction and draw more air from the RCW side into the water/steam cycle than would the latter pump. This notion may explain how the CEP Pump-A-related DO problem later diminished after sealing identified tube-to-tubesheet joint leaks.

The various observations discussed above jointly point to potential leak paths at the condenser steam side/RCW interfaces (e.g. tube-to-tubesheet joints or porous welds in condenser tubes as identified in some tubes during the re-tubing project) allowing liquid (from RCW

carrying soluble parameters such as sodium and other ions) and gaseous (e.g. oxygen and vapor of volatile chlorinated compounds) transfer into the condenser steam side. To identify the potential leak paths and plug them, a condenser leak check was planned for the biennial maintenance overhaul in May 2018.

Physical evidence in support of the condenser as a major source of RCW ingress: Finding potential leaks at tube-to-tubesheet joints or from porous welds in the condenser tubes using the hydro-dye leak check technique was expected to be a challenging task and to require special attention to find the expected multiple minor leaks. Thus, double the typical dose of fluorescein was employed when flooding the condenser steam side with the dye solution whilst the condenser was still hot or warm to keep the metals in expanded states and allow for detection of small leaks that would permit gaseous transfer and not necessarily liquid transfer.

Inspecting for leaks inside the condenser waterboxes with ultra-violet (UV) light after allowing flooding for over 24 hours revealed (dry) yellowish-green glowing specks (presumably of the dye) within cavities at tube-to-tubesheet joints and occasionally multiple occurrences of such specks around the circumference of some tubes (see the top pictures in Figure 9). Seventy-nine (79) tubes were identified with such characteristics, of which about 84% were from the condenser outlet waterboxes: 46 from the north and 20 from the south condenser. (This was unlike the case for the naval brass condenser, where the majority of tube-to-tubesheet joint leaks were found at the return bonnet of the condenser [13].) The leaking tubes were randomly distributed. It is however interesting to note that one of the identified leaking tubes had been found with a tube-to-tubesheet joint weeper leak during the original hydrotest after installation of the new tube/tubesheet and had been re-rolled in an attempt to seal the joint.

Although upon initial external consultation, the glowing specks around the tubes were suggested to be due to dye-stained white fibers from cotton rags used to wipe the leakage-dye off the tubesheet faces to clean off larger tube leaks, there was no reason to believe this was the case here as no obvious liquid leak was found anywhere inside the waterboxes. The circumferential locations of the specks around the tubes, coupled with the fact that there were no signs of these specks outside the tubesheet faces, provide some basis to suggest that the observed

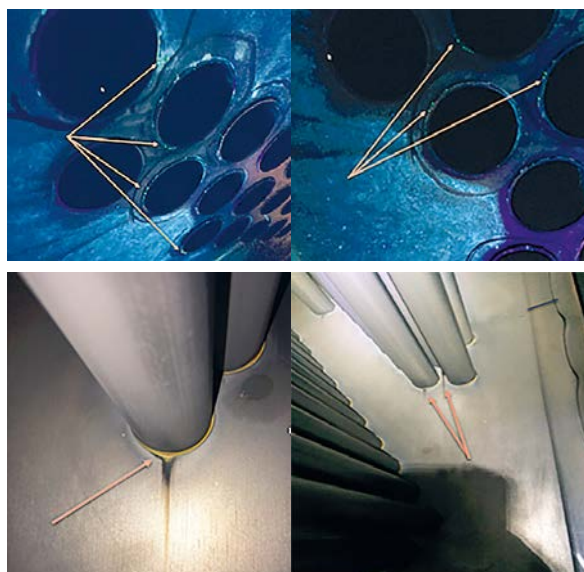


Figure 9: Photos taken in May 2018 of waterboxes showing potential leaks at the circumferential section of some condenser tubes (top pictures) and of the steam side showing some emerging leaks at some tube-to-tubesheet joints (bottom pictures).

"dry" glowing spots were indeed due to vapor of the hot dye solution used for the leak check. This would lend support to the hypothesis that there were tube-to-tubesheet joint leak paths that allowed vapor transfer and not necessarily liquid passage. All tube holes associated with the identified potential leaking joints were therefore plugged with metal pin-and-collar plugs to seal the leaks.

Inspection of the steam side of the condenser (after draining the dye solution) revealed nine (9) other tube-to-tubesheet joint leaks, which appeared as streaks underneath the leaking tubes (see the bottom pictures in Figure 9). These leaks were found at peripheral tubes. None of these tubes however coincided with those found in the waterboxes (see above). Eight of the affected tube-to-tubesheet joints were also from the north condenser outlet waterbox. These affected tubes were likewise plugged with metal pin-and-collar plugs to seal the joint leaks.

What are the other possible sources for the renewed chloride cycling?

Foreign chlorine-containing (solid) materials within the water/steam cycle: The evidence provided thus far does not point to the condenser as an exclusive source, but also suggests the possible involvement of a leaching source of organochlorine material left in the water/steam circuit during the 2016 overhaul. Initially, lubricants used in aiding the insertion of condenser tubes

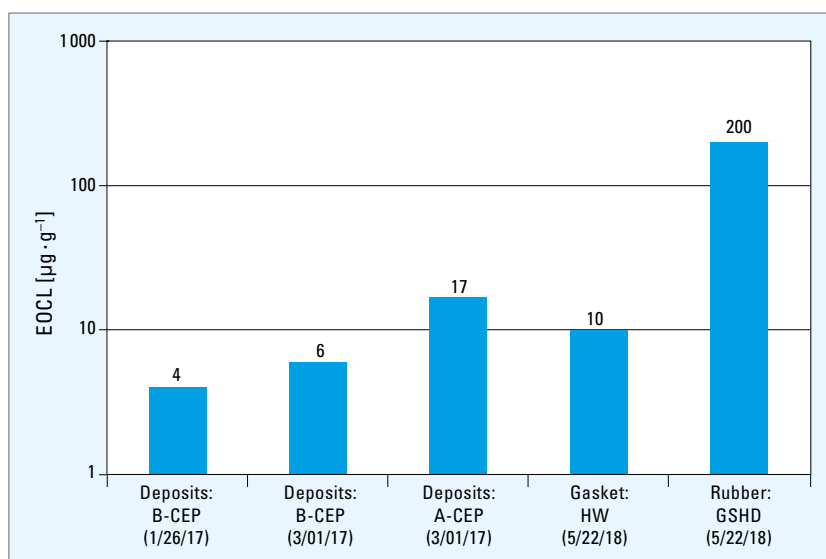


Figure 10:

Extractable organochlorine (EOCl) content of various samples collected within the condensate/feedwater system: Deposits:B- and A-CEP, for heterogeneous solids trapped in the CEP strainers; Gasket:HW, for gasket material protruding from the tubesheet/waterbox interface into the hotwell side of the condenser; and Rubber:GSHD for rubber material located inside the gland steam hotwell drain. The sampling dates are given in parentheses.

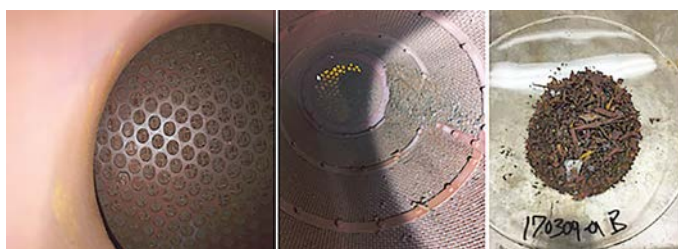


Figure 11:

Photos taken on January 26, 2017, of the exterior section of a CEP strainer (left), and on March 1, 2017, of the interior section of a CEP strainer (middle) and of the solid materials removed from the strainer (right).

through baffle plate and tubesheet holes were suspected, but there was no indication they contained chlorinated compounds. Furthermore, EOCl analysis of the dark film (presumably some form of lubricants) observed on tubesheet and tube surfaces inside the condenser steam side during the second phase (February 28 to March 3, 2017) showed an absence of extractable organochlorine compounds.

In fact, considering the persistent nature of the potential source, it was unlikely to be a liquid material, but rather solid material(s) which seemed to have significantly leached out into the water/steam circuit early in operation, following installation of the new tubes and tubesheets. Possible materials include organochlorine treated wood (in scaffolds) and neoprene and other organochlorine (e.g. hypalon and chlorinated polyethylene (CPE)) gaskets, O-rings, hoses, expansion joints, adhesives (including duct tapes), etc. Some safety equipment such as face masks, gloves, boots, and goggles or goggle straps may also contain neoprene and could inadvertently have been left inside feedwater units (hotwell, LP and HP heaters, deaerator etc.) or the boiler drum during inspection or maintenance work.

The following are some direct pieces of evidence in support of potential solid organochlorine materials within the water/steam circuit:

- CEP and boiler water samples taken on January 24, 2017, contained organochlorides ($50\mu\text{g}\cdot\text{L}^{-1}\text{Cl}$) although CEP and boiler water samples taken later on February 13, 2017, for organochlorides were below the detection limit.
- Swab samples taken on January 26, 2017, from the strainer of CEP Pump-B (left picture in Figure 11) showed the presence of organochlorides ($4\mu\text{g}\cdot\text{g}^{-1}\text{Cl}$) (see Figure 10).
- Methanol/water extract from the boiler feed pump magnetic filter sample taken on February 13, 2017, contained organochlorine compounds ($100\mu\text{g}\cdot\text{L}^{-1}\text{Cl}$).
- During the February 28 to March 3, 2017, condenser inspection outage:
 - Debris observed inside both CEP strainers (including wooden chips from scaffolds inside the hotwell during the condenser work – see the middle and right pictures in Figure 11) showed the presence of organochlorides ($17\mu\text{g}\cdot\text{g}^{-1}\text{Cl}$ for the CEP Pump-A and $6\mu\text{g}\cdot\text{g}^{-1}\text{Cl}$ for the CEP Pump-B) (see Figure 10).
 - XRF analysis of the debris from the CEP strainers showed an appreciable presence of chlorine as an element (0.3%); elemental oxide composition in the debris included Fe_2O_3 (73.8%), SiO_2 (5.2%), CuO (1.2%), PbO (1.2%), and MgO (1%).

- XRF analysis of the woody part of the debris did not show a detectable or reportable level of chlorine (i.e. < 0.1 %).
- XRF analysis of the magnetic and non-magnetic fraction (after picking out most of the wood) showed a significant amount of chlorine in the non-magnetic fraction (2.7%) and a non-detectable level in the magnetic fraction (i.e. < 0.1 %).

It is inferable from the above results that there existed some solid material(s) upstream of the CEP pumps (likely in the hotwell, if not within the steam turbine unit) that may have disintegrated into finer material and become trapped on strainers within the feedwater system. Therefore, going into the 2018 overhaul, a thorough inspection of the condenser steam side was also planned to identify likely source(s) of the solid organochlorine compounds.

Tubesheet/shell interface gaskets as a potential chloride contamination source: As shown in the picture at the bottom right of Figure 9, gasket material extending ~ 3cm into the condenser steam side from tubesheet/shell interfaces at all edges was exposed to warm ammoniated condensate water. NAA analysis of the gasket sample showed an EOCI concentration of $10 \mu\text{g} \cdot \text{g}^{-1}$ Cl (Figure 10). The gasket sample was also analyzed by XRF and showed the presence of 5.2% Cl. In comparison, a sample of the protruding gasket from the tubesheet/shell interface from the condenser exterior showed the presence of a higher chloride amount (i.e. 7.6% Cl). These results would together suggest possible leaching of chlorinated compounds from the gasket into the water/steam circuit.

To confirm that such leaching occurred at the condenser steam side during operation, the gasket material not previously exposed to the condenser steam side conditions was soaked in ammonia solution (pH 10), but the Cl content stayed essentially the same as before. Similarly, soaking the gasket material previously exposed to the condenser steam side conditions in ammonia solution (pH 10) with added drops of household sodium hypochlorite solution (to simulate chloramine contact) did not affect the Cl content of the gasket appreciably. Even leaving the samples to soak for a month with occasional agitation did not change the outcome. It has to be noted however that despite our inability to demonstrate leaching of chlorine from the gasket material with ammonia solution under the limited laboratory conditions, the occurrence of this phenomenon under actual operating conditions

cannot be excluded. The differential XRF Cl data for the gasket materials exposed or not exposed to the steam side conditions is in itself strong evidence for the potential leaching of chlorinated compounds from the gasket material.

Also, NAA analysis of some crushed and folded rubber chunk samples found inside the gland steam hotwell drain showed a substantially high EOCI concentration of $200 \mu\text{g} \cdot \text{g}^{-1}$ Cl (Figure 10). The source of this rubber material is uncertain, but considering the small quantity present, it is unlikely this would be an exclusive major source of the chloride cycling. The possibility of gasket pieces that may have fallen into the hotwell during the tube/tubesheet replacement project and may have found their way during operation via the feedwater or attemperation system into the gland steam condenser is conceivable, although we do not have any evidence at this point to support that.

Post Biennial Maintenance Outage in Spring 2018 [PHASE 3]

For about three months leading up to the biennial maintenance overhaul, the average daily increase in boiler chloride was $28.4 \pm 8.7 \mu\text{g} \cdot \text{L}^{-1}$, but this decreased substantially to only $2.7 \pm 2.0 \mu\text{g} \cdot \text{L}^{-1}$ for three months after the 88 identified leaking tubes around the tube-to-tubesheet joints were plugged with metal pin-and-collar plugs to seal the joint leaks (see Figure 12). The positive outcome of addressing the condenser leaks provides an unequivocal justification for the condenser as the major source of the water/steam circuit chloride contamination after installation of the new condenser tubes and tubesheets. However, it would be naïve to expect a complete nullification of this source of chloride contamination as any such potential tube-to-tubesheet joint leaks within the tube bundle are difficult to locate merely by one visual inspection from the steam side. As shown in Figure 12, despite the lower daily increases in the boiler chloride concentration, a reasonable variability is evident. Most daily increases over $4 \mu\text{g} \cdot \text{L}^{-1}$ happened at points when significant variation in generated load occurred, which also matched significant variation in the condenser backpressure and/or condenser outlet temperature, still suggesting the involvement of the condenser even after plugging of the identified leaking tubes. Future inspections may reveal other leaks to address in eliminating the RCW chloride source contamination to the water/steam cycle.

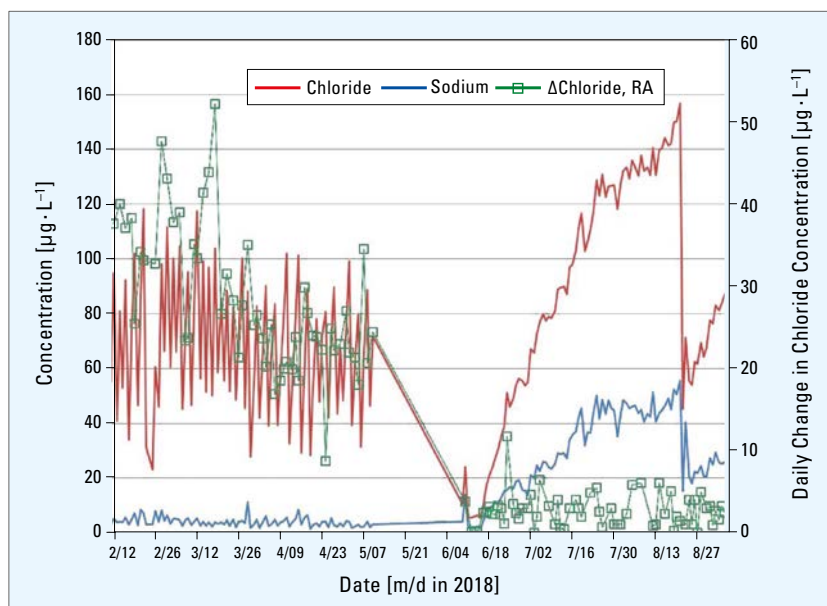


Figure 12: Daily concentrations of sodium and chloride and daily increases in chloride concentration from February 12 to September 6, 2018. Data for days of upset boiler conditions and/or when the boiler had been blown down are omitted.

As shown in Table 2 (entry 20) and also from Figure 12, a strong correlation was present between the boiler chloride and sodium concentrations, suggesting some common source for the two parameters; this is still likely to be the RCW source, as discussed above. However, the relatively low BCSR during this period (1.9 ± 0.3) coupled with the poor correlation between TCA and BCSR or the boiler chloride and sodium would suggest a minimal contribution from diffusive vapor flux of volatile chlorinated compounds, but potentially a significant contribution from a blend of convective vapor flux of volatile chlorinated compounds and gasket leaching of organochlorine compounds into the water/steam cycle. Prior to plugging the affected leaking tubes, the BCSR, which can be gauged by the slopes (m) of the boiler chloride versus sodium linear equation, was (apart from the early weeks of operation) generally greater than 4, even for periods when the daily chloride increase showed a decreasing trend (II-Stages). Traditional through-wall condenser tube leaks cannot explain the chloride cycling marked by a high BCSR as the RCW sodium concentration is a factor of about 2–3 times larger than the RCW chloride concentration.

CONCLUSIONS

To identify the source(s) of chloride contamination into the water/steam circuit of the Shand Power Station generation unit after installation of new condenser tubes and tubesheets, an investigation was pursued, the outcome of which has been reported here. The results point to the RCW as the main source of the chloride contamination via weak tube-to-tube-sheet joints. This could be observed at the early stages of operation after the condenser replacement project as convective flux of liquid (water) transfer, which is evidenced by a good inverse correlation between the RCW chlorine levels (FC and TCA) and the BCSR as well as a positive correlation with boiler sodium and to a lesser extent the boiler chloride. After the fourth week of operation (i.e. after several cycles of the unit, when metal expansion expectedly may have somehow closed

potential gaps at the joints), the nature of the observed chloride cycling was reminiscent of diffusive (vapor) flux of chlorinated compounds into the steam side of the condenser as previously reported. This was also reflected ultimately in the good correlation between TCA and the BCSR, but the period was uniquely marked by high BCSRs. Thereafter, the chloride contribution from the RCW source into the water/steam cycle was intermittent, as shown in the increasing trend of daily surges interspersed with decreasing trends of the surges.

There is also evidence to suggest there was leaching of organochlorine gasket material into the water/steam cycle starting the 3rd to 4th week of operation. The effect of this source seemed to have decreased over time, but was significant enough to obscure an obvious characterization of the RCW effect on the chloride cycling. However, leaving the gasket materials in place but sealing identified tube-to-tubesheet leaks reduced the daily increase in boiler chloride from $28.4 \pm 8.7 \mu\text{g} \cdot \text{L}^{-1}$ to only $2.7 \pm 2.0 \mu\text{g} \cdot \text{L}^{-1}$, supporting the idea that the principal source of the chloride contamination was the RCW.

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