Film-forming amine product as an alternative to carbohydrazide oxygen scavenger in high pressure boilers

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A B S T R A C T

Hydrazine has been largely replaced by carbohydrazide (CHZ) as an oxygen scavenger due to safety and health concerns and CHZ is now used in Saline Water Conversion Corporation (SWCC) high pressure boilers. However, the operational problem of phosphate hide-out has become a continuous challenge for the plant operators. Advances in boiler water treatment have shown that effective corrosion control and prevention of scaling can be achieved by using a mixture of film-forming and alkalizing amines and polycarboxylates [Film Forming Amine Product (FFAP)]. With the use of FFAP, carbohydrazide/ammonia treatment of make-up water and phosphate treatment in the drum will not be required. A uniform FFAP formulation was used throughout the test.

The evaluation study was carried out at a boiler of the Yanbu Phase 1 Desalination and Power Plant (Mitsubishi) generating 60 MWh, with make-up water of 15 t h^{-1} producing 330 t h^{-1} steam at a pressure of 67 barg and temperature of 480 °C.

The trial provided evidence that FFAP was a good alternative to use of an oxygen scavenger. Changeover from CHZ to FFAP without phosphate addition in the drum was done initially by dosing FFAP from both hydrazine tank and phosphate tank so that pH was maintained to the required values in both feed water and drum water. With the optimal dose rate (0.6 ppm) maintaining FFAP in the range of 0.3–1.0 ppm in feed water, all the key parameters (pH, ammonia and specific conductivity) were within the specified boiler design limits. The average corrosion rates on the water side were low for both CHZ and FFAP treatment (0.009 ± 0.001 mm y^{-1}), however FFAP treated coupons showed much lower corrosion rates compared to CHZ in the steam side (0.0006 ± 0.0003 mm y^{-1} cf. 0.0075 ± 0.0006 mm y^{-1}).

1. Introduction

The Saline Water Conversion Corporation (SWCC) produces electrical power and drinking water for the Kingdom of Saudi Arabia through its dual-purpose plants located in Al-Jubail, Al-Khobar, Al-Khafji, Shoaibah, Yanbu, Al-Shoqaiq and Ras Al-Khair. The total power generated from these plants is approximately 5000 MW. The core of the power generation process are the boilers (60 throughout the SWCC system), which produce high-pressure steam that drives the blades of the turbines for generating electricity. In all these

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boilers, oxygen scavengers are used to control oxygen and maintain a passive magnetite layer inside the boiler tubes. The feed water used in boilers is usually the make-up water produced from demineralization plant and the returned condensate from turbines and brine heaters. There is a high chance of contamination of the feed water with dissolved solids, dissolved gases and suspended matter. The common gases that have a strong impact on boiler chemistry are oxygen and carbon dioxide dissolved in feed water.

Dissolved oxygen is a constant threat to steam generator tube integrity and acts as a catalyst for many types of corrosion [1]. Small quantities of dissolved oxygen can cause severe pitting corrosion in boilers and assist in the ammonia corrosion on copper alloy [2]. Air leakage into the system is another source of oxygen. Incomplete removal of oxygen from the feed water allows it to reach the boiler where it will flash off with the steam and, together with ingressed oxygen, can cause condensate corrosion problems [3]. Generally, deaerators are employed in power plants to control and mechanically eliminate oxygen from feed water. However, deaerators cannot totally eliminate dissolved oxygen from feed water. The most popular technique to achieve almost complete elimination of dissolved oxygen in boiler feed water is through the use of chemical oxygen scavengers [4,5].

Among the many oxygen scavengers available are hydrazine, carbohydrazide, N-diethyl hydroxylamine, hydroxyquinone and erythorbic acid [6–12]. Hydrazine has been extensively used as an effective oxygen scavenger [12] and was previously utilized in many of the high-pressure boilers of SWCC. At low temperatures the scavenging effect of hydrazine is quite slow [13,14]. In addition, health concerns have been raised over the use of hydrazine [15]. Carbohydrazide is a less hazardous compound that presents fewer health and safety concerns and has the same limits to its effectiveness as hydrazine, since it decomposes to hydrazine in the boiler. Though carbohydrazide was able to resolve the issue of safety and health concerns, congruent phosphate treatment (CPT) led to significant problems in phosphate hideout [16–18]. CPT is maintenance of the Na/PO_4 ratio at around 2.6 while also maintaining the alkalinity high enough to minimize corrosion [19,20]. Boiler water in a high heat flux zone is likely to concentrate due to evaporation. Local conditions may prevent adequate mixing with bulk liquid phase and over time, a concentration gradient will develop between the bulk boiler water and the localized solution in contact with the magnetite surface. Localized concentrations for some species may thus be two or more orders of magnitude higher than in the bulk boiler [21]. Under these conditions, salts with limited solubility, such as those incorporating phosphate species, may exceed their solubility limits and undergo precipitation or hideout. Hideout can be at its worst in a cycling unit. Shutdowns and startups, and even load changes, cause precipitation and dissolution of phosphates. This in turn causes wide fluctuations in boiler water chemistry. Phosphate hideout appears to be further influenced by the cleanliness of the boiler tubes, and becomes more severe with increased deposit loading, particularly iron oxides. The evidence indicates that sodium phosphates form a sodium-iron-phosphate complex with the magnetite layer. Severe hideout and the reverse dissolution process have been known to force boiler water pH below 7 in cycling units [21].

In order to make a preliminary choice for evaluation of a suitable alternative to oxygen scavenger in SWCC commercial boilers, available literature of the products was reviewed including technical datasheets, reports of practical applications on commercial running boilers, and toxicity certificates of the products. A commercial film-forming amine product (Helamin, FFAP) consisting of film-forming polyamines, steam-volatile amines, and polycarboxylates of varying volatility (which allows control of the pH at the beginning, middle and end section of the condensate system, as well as the boiler feed water tanks) was selected as the most suitable alternative to oxygen scavenger for evaluation. This formulation contains a film-forming amine which is adsorbed by the boiler or pipe surface to form a hydrophobic membrane protecting the metal against corrosion and encouraging formation of a smooth and compact magnetite layer which inhibits corrosion [22]. At high temperatures it has been found to improve the structure of magnetite layer and increase the protective effect [23–30]. Thermal and oxidative decomposition show formation of organic anions (formate, acetate and propionate) in very low concentration with negligible effect on the pH of the condensate. The main criterion for selection of FFAP was to avoid the phosphate hideout problem, as with use of film-forming additives no phosphate treatment is required. A solution to this problem had been requested by the operations and maintenance team at Yanbu dual-purpose plant.

1.1. Research objectives

The main objective of this study was to study the use of a film-forming amine (polyamine), alkalizing amine and polycarboxylate formulation (Film Forming Amine Product, FFAP) as an alternative to oxygen scavenger without the phosphate treatment in the high
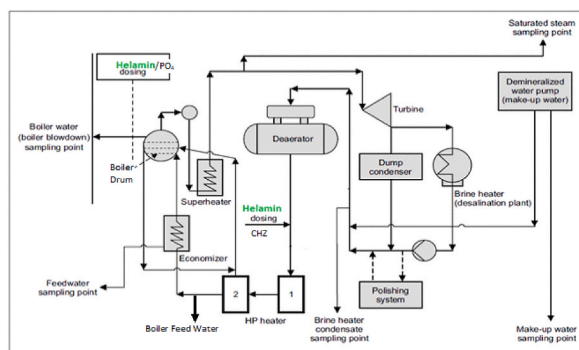

Fig. 1. Schematic drawing of Boiler feed water system.

pressure boiler of the SWCC Plant at Yanbu. Further objectives were to optimize dose rate and determine corrosion rate.

2. Experimental

Boiler # 2 of Phase 1 at the Yanbu SWCC integrated water and power plants, which produces high pressure steam that drives the blades of turbines each generating 60 MWh, was selected for the trial tests. The boiler is a pressurized box type water tube boiler of Mitsubishi make with makeup water of 15 t h^{-1} (Fig. 1). The maximum continuous rating of steam is 330 t h^{-1}. The feed comprising condensed steam plus make-up water is first passed through the deaerator at a pressure of 2 bar and temperature of 132 °C. After the deaerator the feed water is dosed with a chemical scavenger and then is heated at HP heater, at a temperature of 320 °C. Coordinated phosphate treatment is done in boiler drum for pH adjustment. From the boiler drum it is passed into the super heater. The superheated steam at a temperature of 480 °C and 67 barg goes to the turbine. The steam leaving the turbine is sent to heat the recycled brine of desalination plants (Fig. 1). The material of brine heater is made of copper alloys.

Baseline data using the original treatment, comprising dosing with ammonia (make-up water), carbohydrazide (feed water) and phosphate (boiler drum) was developed over a period of three months. This data consisted of operation as well as chemical parameters, such as iron and copper concentrations in the feed water sample and other control parameters (pH, ammonia, chloride, specific conductivity and dissolved oxygen). Carbohydrazide was injected in feed water at the deaerator outlet at a dose rate of 0.5 ppm with residual of 20–40 ppb.

All boiler chemistry limits and test conditions were maintained in the boiler (Tables 1 and 2). Original dosage requirements of the commercial FFAP (Helamin) were specified by the supplier as 5 ppm with respect to the feed water flow, with a residual of 1.0–2.0 ppm in boiler feed water.

2.1. Start-up procedure with FFAP

Before filling of the boiler, both dosing tanks (hydrazine and phosphate) were thoroughly cleaned by flushing the tanks with demineralized water. 25% FFAP solution was then prepared in both the dosing tanks by transferring 125 L of FFAP and diluting to 500 L, then mixing for 5 min with the mixer.

At the hydrazine dosing point, FFAP dosing commenced with 100% pump stroke (new pump), equivalent to 6 L h^{-1}, until the boiler filling was completed. At the phosphate tank, FFAP dosing commenced with 100% pump stroke equivalent to 4.5 L h^{-1} until the boiler filling was completed. Initially, the FFAP dosing pump (hydrazine and phosphate) was maintained at 100% stroke. If all the parameters are satisfactory (boiler water pH in the range of 9.5–10 and feed water and condensate in the range of 8.8–9.5), the FFAP dosing was stopped at Phosphate tank and boiler blow down was opened (if required) and adjusted according to Yanbu power plant design values (Table 2).

2.2. Analytical parameters and procedures

2.2.1. Boiler water chemistry

The following parameters for boiler water chemistry were determined: pH, ammonia, copper, dissolved oxygen, conductivity, residual chemical (carbohydrazide/FFAP), iron and phosphate at the following sampling points:

(a) Make-up water (MU)
(b) Feed Water (FW).
(c) Boiler Drum (Drum water) (DW).
(d) Saturated Steam (SS)

Table 1
Chemical parameter limits for normal operation.

Parameters/Samples	Condensate		Feed Water	Boiler Drum (Drum Water)	Saturated Steam	Live Steam
	BHC	TC				
pH	8.8 – 9.5	8.8 –9.5	8.8 – 9.5	9.5 – 10	8.7 – 9.2	8.8 – 9.5
Specific Conductivity (µS cm^{-1})	1.5 – 7.5	1.5 – 7.5	1.5 – 7.5	15 – 100	<3	1.5 – 6.5
Copper (ppb)	0 – 20	0 – 20	0 – 20	0 – 20		0 – 20
Ammonia (ppm)	0.3 – 1.0	0.3 – 1.0	0.3 – 1.0	0.3 – 1.0		0 – 1.0
Iron (ppb)	0 – 30	0 – 30	0 – 30	0 – 30		0 – 30
Dissolved O$_2$ (ppb)			Nil or <7			
Hydrazine (ppb)			10 – 25			
Silica (ppb)		0 – 20		0 – 3	<20	0 – 20
Sodium (ppb)					<10	
Chloride (ppm)				0 – 0.5	<0.05	
Phosphate (ppm)				3 – 10		
P-Alkalinity(ppm)				1 – 3.5		
Total Alkalinity (ppm)				3 – 12		

Table 2
Test conditions (Design values).

Equipment	Capacity (liter)	Water/Steam		
		p (barg)	T ($^\circ$C)	Flow (t h^{-1})
Condenser		−0.9	50	165
Deaerator		2	132	345
Boiler feed Pump		95	130	205
HP Heater			320	320
Boiler drum		76 - 78	292 - 293	330
Super heater		67	480	330
Hydrazine tank pump	500	9		
Phosphate tank pump	500	80		

(e) Live Steam (LS)
(f) Brine heater condensate (BHC)
(g) Turbine condensate (TC)

Copper and iron were analyzed using ICP/OES (PerkinElmer, Optima 2100 DV), pH using pH meter (TOA-DKK, model HM-20J), dissolved oxygen by online oxygen meter, conductivity by conductometer (TOA-DKK, model CM-30R), and ammonia, phosphate and carbohydrazide using Hach spectrometer DR 6000 and Hach standard methods.

2.2.2. Corrosion monitoring
The typical grade of carbon steel used in boiler tubes in SWCC desalination plants has the following specifications: C = 0.27% max., Si = 0.10 min, Mn = 0.93 max., S = 0.035 max., P = 0.035 max. Corrosion coupons of steel grade SA 210 Gr. A1 (C = 0.083%, Si = 0.196%, Mn = 0.599%, S = 0.002%, P = 0.008%) and cupronickel (Cu = 66%, Fe = 0.736%, Mn = 0,942%, Ni = 32%) were installed with the help of plant personnel in the following locations:
Boiler Drum: Two coupons of carbon steel were placed in the water side and two coupons on the steam side.
Steam Condensate: Two coupons of carbon steel (FFAP test); two coupons of cupronickel (CHZ test).
The coupons were withdrawn during the boiler shutdown for physical examination and evaluated for corrosion potential by weight loss. Photographs were taken of the coupons before and after exposure.

2.2.3. Boiler shutdown inspection
Internal inspection of the boiler was carried out at the end of testing. Besides visual checks and photographic documentation, chemical analysis of several deposit samples was carried out by SEM/EDX (JEOL model JSM-640 LV; Oxford INCA model 7573 EDX detector). Data was collected and analyzed with INCA software.

2.2.4. Photometric determination of FFAP
The FFAP contains a mixture of alkylamines which react with 4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein (Rose Bengal) compound [31] to form a colored complex of alkanolamines, which dissolves in acetic acid. This was measured using a Hach DR5000 UV-Vis Spectrometer (565 nm). This method can be calibrated with standard solutions to measure between 0.05 and 30.0 ppm of FFAP.

2.2.5. Thermal efficiency
Thermal efficiency was calculated as a percentage based on the amount of steam generated (Q) and the amount of fuel consumed (q) using standard values for the enthalpy of steam (H$_{vap}$), enthalpy of liquid water (H$_w$), and gross calorific value of the fuel (GCV),
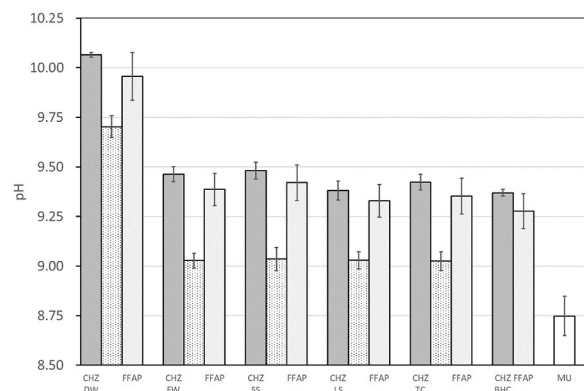

Fig. 2. Average pH values for CHZ (2016, solid; 2015 dotted) and FFAP in different streams of the boiler.

according to the expression:

Thermal efficiency = Q/q × (H$_{vap}$ − H$_w$)/GCV

3. Results & Discussion

3.1. Boiler chemistry

Average values for the pH determined in FW, DW, SS and LS with FFAP (n = 86) and with carbohydrazide determined in the same month (2016, n = 4) and one year previously (2015, n = 92) are shown in Fig. 2.

The pH values for both CHZ and FFAP were found to be maintained within the required limits of 8.8 and 9.5 for BHC, FW, SS, LS and TC whereas for DW pH was at the extreme upper end of the required limits of 9.5 and 10. The pH values determined for make-up water during the trial tests fell on average below the required limits of 8.8 and 9.2.

The average values for ammonia determined with FFAP showed a slight increase compared to CHZ 2015 but were found to be within the limits in the range of 0.3–1.0 ppm for FW, BHC and TC respectively. For LS and DW average values for ammonia were in the range of 0–1.0 ppm (Fig. 3).

Specific conductivity values were higher with FFAP than with carbohydrazide (2015 measurements), consistent with the higher pH values observed, but the average values determined were found to be within the limits in the range of 0–7.5 μS cm^{-1} for FW, SS, TC and BHC for LS in the range of 0–6.5 μS cm^{-1} and DW was 15–100 μS cm^{-1} (Fig. 4). The slightly higher values may be attributed to ammonia contamination from other boilers that were treated with ammonia and due to common condenser header and mixing of condensate [32].

With FFAP dosing the average concentrations for iron and copper in FW, DW, BHC, SS, LS and TC were found to be at trace levels. However, BHC, FW, and TC showed elevated levels of Cu early in the operation of the system, suggesting that FFAP was having a cleaning effect on the Cu–Ni tubes of the brine heater.

Average dissolved oxygen with both carbohydrazide and FFAP in the feed water was found to be < 5 ppb. Chloride determined for both carbohydrazide and FFAP in DW was also found to be in the limit range of 0–0.5 ppm (Fig. 5). Silica in DW and LS treated with FFAP was found to be in trace levels.

Cation conductivity is one of the best ways to monitor for contaminants within a steam or water sample. It is also referred to as Conductivity after Ion Exchange (CACE), Acid Conductivity and After Exchange Conductivity. However, many operators find it difficult to interpret cation conductivity readings, particularly at plants whose steam generators use water containing either naturally occurring or purposefully added organic compounds. The major turbine manufacturers demand conductivity of steam ≤0.2 μS cm^{-1}. A slight increase in cation conductivity in the steam generation system with use of PPF. The cation conductivity may go up to 0.5 μS cm^{-1}. Industry experience proves that even at increased cation conductivity, operation of the cycle in the presence of FFAP is possible without failure or damage [33]. Unfortunately, CACE could not be determined in the present study due to the non-functioning of the cation conductivity system.

The boiler operation parameters were maintained within the normally experienced range and the average thermal efficiency for CHZ treatment was found to be 96.3 ± 0.9% and for FFAP treatment 96.5 ± 0.5%.

3.2. Optimization of FFAP dose rate

With optimized dose rates for CHZ, residual hydrazine should be maintained around 20 ppb in feed water according to plant specifications, but the values determined were not consistent and most frequently zero within the limits of detection. This suggests that the dosage of CHZ used was not sufficient to maintain the necessary residual in the feed water and thus in the system. Changeover from
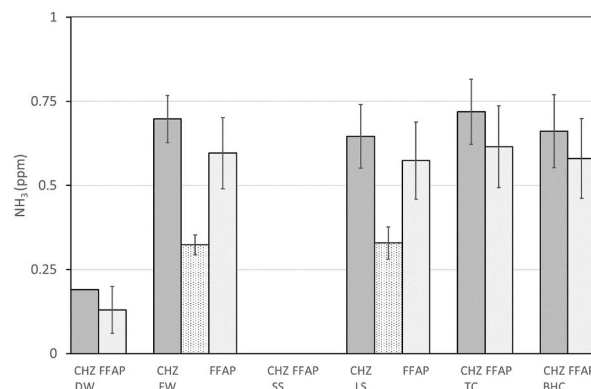

Fig. 3. Average Ammonia values for CHZ (2016, solid; 2015 dotted) and FFAP in different streams of the boiler.
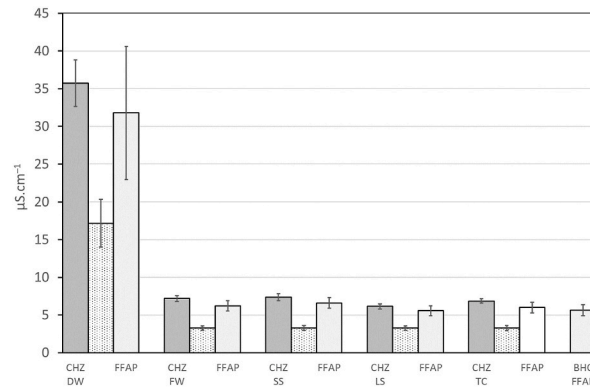
Fig. 4. Average Specific conductivity values for CHZ (2016, solid; 2015 dotted) and FFAP in different streams of the boiler.
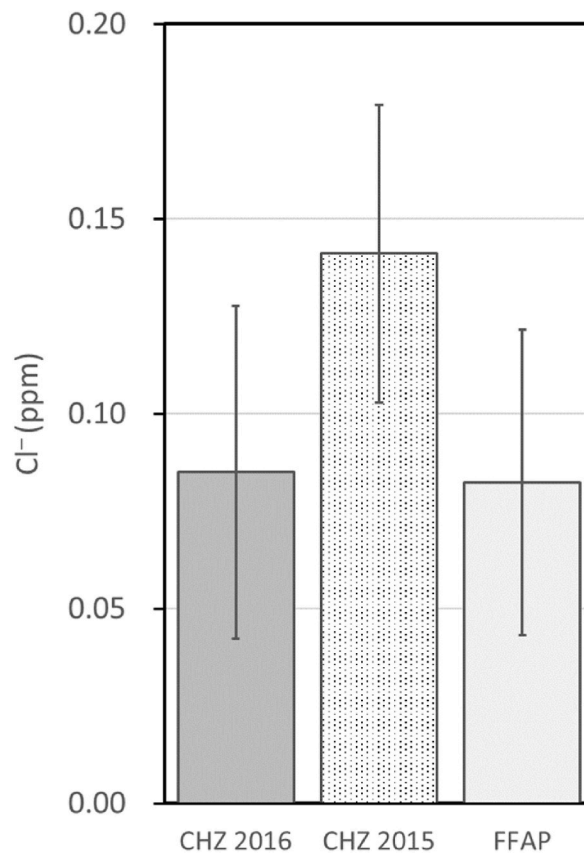

Fig. 5. Average Chloride values for CHZ and FFAP in drum water of the boiler.

CHZ to FFAP without phosphate addition in the drum was done initially by dosing FFAP from both Hydrazine tank and phosphate tank so that pH was maintained to the required values in both feed water and drum water. Initially 25% concentration of FFAP was prepared in both tanks. At both the dosing pumps (hydrazine and phosphate) 100% pump stroke was maintained till all the parameters were satisfactory (boiler water pH in the range of 9.5–10 and feed water and condensate in the range of 8.8–9.5), boiler blow down was opened (if required) and adjusted according to Yanbu power plant design values (Table 2).

When all the parameters were stabilized and the boiler operation was as per normal, FFAP injection at the phosphate tank was stopped and dose rate optimized by controlling the FFAP concentration in the hydrazine tank and pump stroke till the FFAP residual in feed water was consistent in the range of 0.3–1 ppm (Fig. 6).

The dose rate was optimized to 1.8 L h^{-1} (30% pump stroke) equivalent to 0.6 ppm (with FFAP concentration of 10% in the hydrazine tank) by monitoring FFAP residual as equivalent to 0.3–1 ppm in feed water. All the key parameters (pH, ammonia and

specific conductivity) were found to be within the baseline limits (Figs. 2–4). FFAP was also monitored in DW, SS, LS, TC and BHC, in all the locations the residual FFAP was found to be well maintained (Fig. 6).

3.3. Corrosion studies

The exposed coupons with CHZ treatment were visually examined. A uniform and non-porous oxide film was found to be adhered on the coupons indicating the protective nature of the films (Plate 1). Coupons exposed with FFAP treatment were found to have uniform and non-porous black coating type film adhered on the coupons indicating the protective polyamine film was formed (Plate 2). Efforts to remove the film from the coupons for investigation were unsuccessful.

The average corrosion rates determined with CHZ dosing for carbon steel coupons fixed in the boiler drum at water side and steam side were 0.0097 mm y^{-1} and 0.0075 mm y^{-1} respectively (Table 3), whereas that determined with FFAP treatment were 0.0094 mm y^{-1} and 0.0006 mm y^{-1} respectively (Table 4). Though the corrosion rate for water side was comparable for both CHZ and FFAP, steam side corrosion rates with FFAP treatment showed remarkable reduction. This indicated the FFAP gave better protection from corrosion at the steam side, consistent with previous reports of its effectiveness [34].

Although the steam condenser material is copper/nickel, carbon steel coupons were installed in both environments due to the unavailability of Cu/Ni coupons at the time of the FFAP tests. This provides an indicative corrosion rate for comparison of the two treatments. In the steam condenser the average corrosion rates with CHZ treatment were found to be higher (0.0189 ± 0.0010 mm y^{-1}) on cupronickel, than with the FFAP (0.0049 ± 0.0002 mm y^{-1}) on carbon steel.

Thickness of the coupons measured after the treatment (Fig. 7) showed that the coupons treated with CHZ were thicker than those treated with FFAP indicating that a very thin protecting layer of FFAP polymer was adherent on the coupons [34].

3.4. Physical examination of coupons

Physical examination of the carbon steel coupons treated with carbohydrazide retrieved from the drum (water and steam side, Plate #1) showed dark grey oxide scales and these scales appeared to be protective.

With FFAP treatment coupons retrieved from both water and steam side of the drum were found to have uniform non-porous, dark-grey polyamine film adhered and appeared to be protective (Plate #2). The presence of a film on the surface as deduced from the observation that water droplets did not wet the surface. SEM/EDX of exposed coupons (water side) with carbohydrazide treatment showed predominantly iron and traces of manganese and phosphate (Fig. 8a). The phosphate deposits are expected because of the phosphate treatment. The coupons exposed with FFAP treatment also showed predominantly iron with substantial amounts of copper and nickel (Fig. 8b). The presence of copper and nickel can be attributed to corrosion products from the Cu–Ni tubes in the top brine heater which are deposited on the coupons in the water side of the boiler after the initial cleaning effect of the FFAP, becoming occluded in the protective layer.

3.5. Boiler inspection and deposits analysis

The inside of the boiler drum treated with carbohydrazide was covered with an adherent dark-grey uniform layer of oxide scale. Analysis of the deposits treated with carbohydrazide showed that iron was predominant along with significant amounts of copper (11.23%) and nickel (3.15%). The presence of high concentration of copper and nickel was attributed to carryover of corrosion products from the copper alloy heat exchanger tubes of the top brine heater which became occluded in the oxide layer.

With FFAP treatment, the inside of the drum was covered with a uniform thin black powdery layer of polyamine that could not be removed in good quantity for analysis. The corresponding deposits on the corrosion coupons were analyzed and found to be mainly composed of iron with substantial amounts of copper and nickel indicating carryover of corrosion products (Fig. 8).
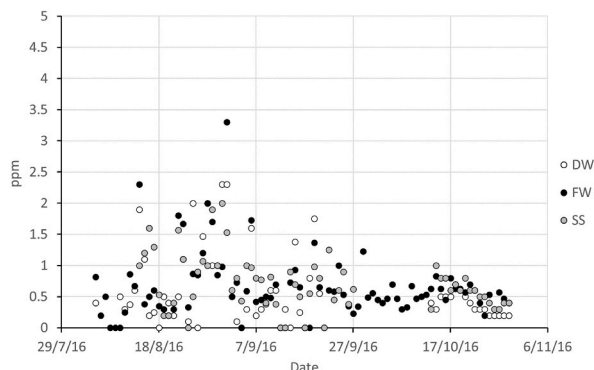

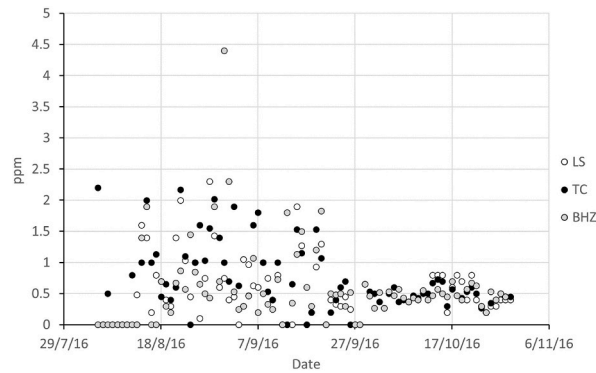**Fig. 6a.** Average values for FFAP in Drum water, Feed water and Saturated steam of the boiler.

Fig. 6b. Average values for FFAP in (a) Live steam (b) Turbine condensate and (c) Brine heater condensate of the boiler.
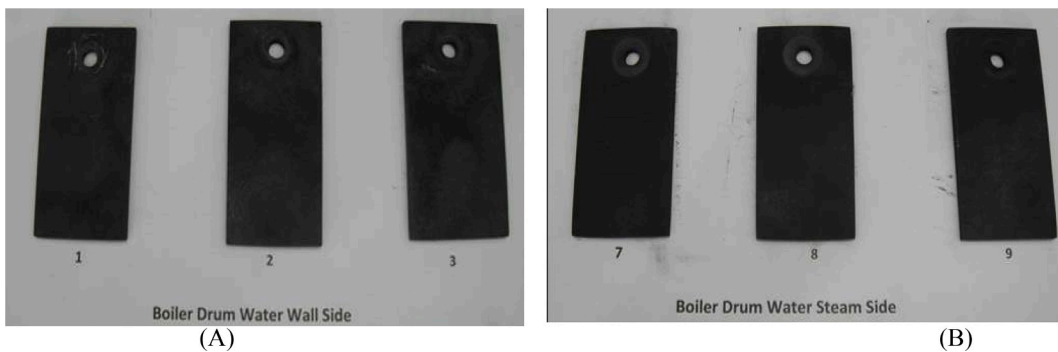

Plate 1. Photographs showing carbon steel coupons after exposure in drum (A) water side and (B) steam side under CHZ treatment.
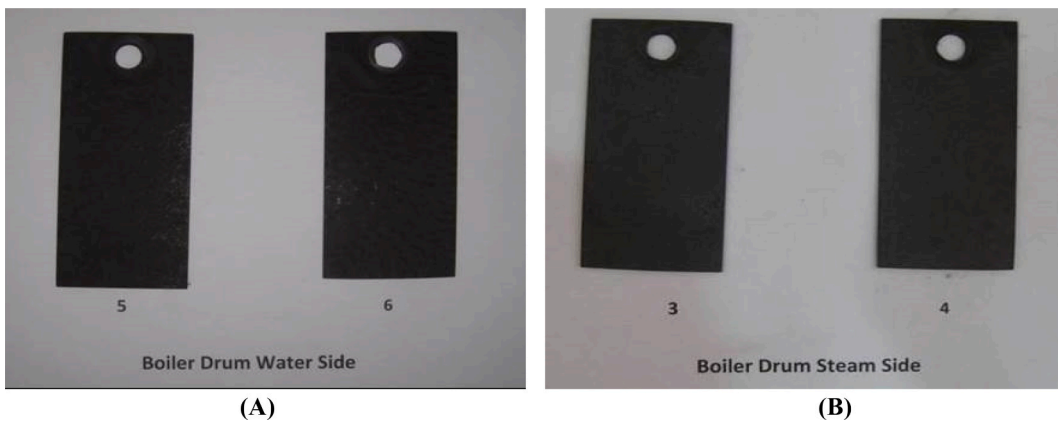

Plate 2. Photographs showing carbon steel coupons after exposure in drum (A) water side and (B) steam side under FFAP treatment.

3.6. Boiler restart with FFAP after trial test completion

After FFAP treatment the boiler was restarted to confirm that no negative effects were caused by the test. Since phosphate treatment was used in the boiler drum for the base line data collected with CHZ treatment, residual phosphate was still present in the boiler water. This was flushed by opening the boiler blow down till the phosphate value was zero. After restarting the boiler, phosphate values were checked and no phosphate was detected.

Under FFAP treatment an increase in the boiler feed water pump pressure (0.09 bar maximum) was observed and the strainer was found to have deposits. The deposits collected and analyzed were found to be corrosion products, predominantly iron oxides. The iron oxides found in the feed water pump strainer were attributed to a long boiler shutdown and restart (10–12 months) after the CHZ treatment and previous to the FFAP test. In the beginning of boiler start-up, the iron level in both feed water and boiler water was in the

Table 3

Corrosion rate determination with CHZ.

Holder No.	Location	Coupon No.	Grade	Surface area (mm^2)	Initial weight (g)	Final weight (g)	weight loss (mg)	mm y^{-1}	Average mm y^{-1}
1	Boiler Drum (Water side)	**2**	C–S	426.72	155.1493	154.8858	263.5	0.010058	0.0097 ±
		3	C–S	441.96	161.9825	161.729	253.5	0.009347	0.0004
2	Boiler Drum (Steam side)	**8**	C–S	421.64	154.0329	153.8251	207.8	0.008026	0.0075 ±
		9	C–S	429.26	155.9536	155.7728	180.8	0.006883	0.0006
3	Steam Condenser	**5**	Cu/Ni	448.56	166.3167	165.821	495.7	0.017983	0.0189 ± 0.0010
		6	Cu/Ni	441.96	163.9621	163.4265	535.6	0.019710	

* These coupons were prepared, cleaned and corrosion rate were calculated as per ASTM standard G1-90.
Exposure started on: 01.06.2015; Exposure ended on: 02.08.16.

Table 4

Corrosion rate determination with FFAP.

Holder No.	Location	Coupon No.	Grade	Surface area (mm^2)	Initial weight (g)	Final weight (g)	weight loss (mg)	mm y^{-1}	Average mm y^{-1}
1	Boiler Drum (Water side)	**5**	C–S	444.5	132.8208	132.5896	231.2	0.010617	0.0094 ±
		6	C–S	421.64	69.7466	69.579	167.6	0.008128	0.0013
2	Boiler Drum (Steam side)	**3**	C–S	419.1	70.2173	70.1984	18.9	0.000919	0.0006 ±
		4	C–S	411.48	68.1273	68.1199	7.4	0.000355	0.0003
3	Steam Condenser	**1**	C–S	444.5	132.6726	132.5625	110.1	0.005054	0.0049 ±
		2	C–S	416.56	110.672	110.5762	95.8	0.004699	0.0002

* These coupons were prepared, cleaned and corrosion rate were calculated as per ASTM standard G1-90.
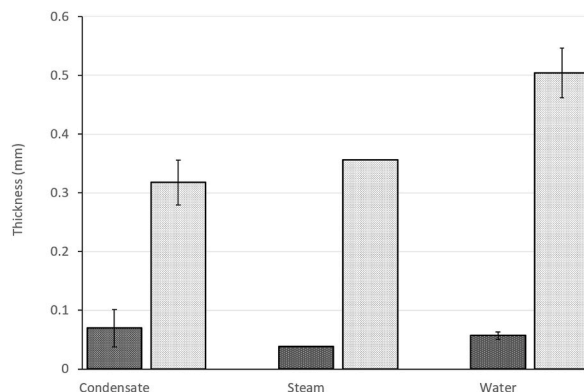Exposure started on: 01.08.2016; Exposure ended on: 30.10.16.

Fig. 7a. Average thickness of surface layer on the corrosion coupons with CHZ (lighter) and FFAP (darker) in different locations of the Boiler.

range of 20 ppb, but this fell to the limits of detection within one month. Restarting the boiler after the trial test shutdown and after more than one month of operation, no increase in the boiler feed water pump pressure was observed and the feed water pump strainer was found to be clean. Four months data was recorded after the restart of the boiler. The boiler water chemistry and the boiler operation parameters were found to be maintained within the design values. Residual FFAP was also found to be maintained at an average of ~1 ppm.

4. Conclusions

The suitability and efficiency of a commercial film-forming amine polyamine/polycarboxylate/alkalizing amines formulation (FFAP, Helamin) as an alternative to oxygen scavenger in SWCC high pressure boiler was confirmed, omitting phosphate and ammonia treatment at the optimized dose rate of 0.6 ppm while maintaining the boiler chemistry within design limits. It is important to continue with continuous boiler blow down and regular intermittent blow down and not to overdose FFAP during the cleaning process.

The dose rate was optimized to maintain FFAP residual between 0.3 and 1.0 ppm in feed water by adjustment to 1.8 L h^{-1} (30% pump stroke) equivalent to 0.6 ppm (with FFAP concentration of 10%).

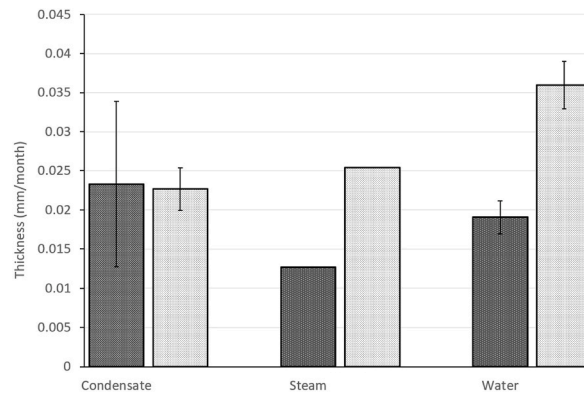Iron and copper levels measured at boiler feed water and drum water were reduced to trace levels.

Fig. 7b. Normalized thickness of surface layer on the corrosion coupons with CHZ (lighter) and FFAP (darker) in different locations of the Boiler.
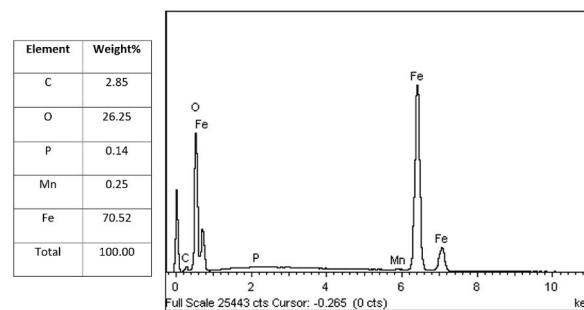

Element	Weight%
C	2.85
O	26.25
P	0.14
Mn	0.25
Fe	70.52
Total	100.00

Fig. 8a. SEM-EDX of carbon steel coupon (Water Side) treated with CHZ.

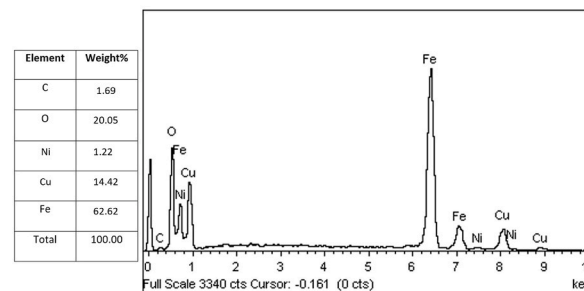| Element	Weight%
C	1.69
O	20.05
Ni	1.22
Cu	14.42
Fe	62.62
Total	100.00

Fig. 8b. SEM-EDX of carbon steel coupon (Water Side) treated with FFAP.

The average corrosion rates indicated similar corrosion in the presence of either CHZ (0.0097 ± 0.0004 mm y^{-1}) or FFAP (0.0094 ± 0.0013 mm y^{-1}) on the water side, however FFAP (0.0006 ± 0.0003 mm y^{-1}) showed much lower rates compared to CHZ (0.0075 ± 0.0006 mm y^{-1}) on the steam side. In the condenser the average corrosion rates with CHZ treatment were found to be higher (0.0189 ± 0.0010 mm y^{-1}), than FFAP (0.0049 ± 0.0002 mm y^{-1}).

Thickness of the coupons measured after the treatment before cleaning showed that the coupons treated with CHZ had higher thickness than that treated with FFAP indicating that a very thin protecting layer of FFAP polymer was adhered on the coupons.

Physical examination of the CHZ exposed coupons revealed the development of uniform, non-porous iron oxide film adhered on the metal indicating the protective nature of the film. Whereas FFAP exposed coupons were found to have uniform non-porous, dark-grey polyamine film adhered which appeared to be protective. Overall, FFAP was found to be a suitable additive for corrosion control in the boilers of the SWCC high pressure boilers.

Carbohydrazide has now been phased out in favor of FFAP across the SWCC system of integrated water and power plants.

Author statement

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Supervision, Conceptualization, Methodology, Project Administration, Writing – Review & Editing; Ali Al-Sahary: Methodology, Investigation; Christopher M. Fellows: Writing – Review & Editing; Visualization; Ibrahim M Alfarsani: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wri.2023.100212.

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