

Application of Fuel Additives to Reduce Corrosion and Stack Emissions in Saline Water Conversion Corporation's Boilers

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ABSTRACT

This paper deals with the burning of heavy residual fuel oil containing ~ 3.5 % sulfur and low vanadium (~ 40 ppm) under conditions prevalent in heating boilers to assess the use of fuel chemical additives on the formation of noxious and corrosive products of combustion.

Saline Water Conversion Corporation's (SWCC's) boilers that are attached to the dual-purpose desalination/power plants in the Western Province of Saudi Arabia using heavy residual fuel oil are reported to have chronic corrosion problems causing unscheduled shutdown and frequent replacement of equipment resulting in high maintenance costs and loss of production besides creating environmental problems. The effectiveness of fuel chemical additives in controlling boiler internal corrosion and reducing the emission of hazardous gases was tested. Three magnesium-based compounds (A, B & E), one organic-based compound (C), and another hydrocarbon-based non-metallic (D) additive were selected based on the literature provided by the companies. Evaluation was carried out by online monitoring of flue gas parameters such as SO₂, SO₃, CO₂ and NO_x, acid dew point, rates of acid build-up and quantitative determination of boiler soots. The effects of the additives on the boiler performance were also monitored by evaluating boiler load, efficiency, flue gas outlet temperature, opacity, fuel and steam flows. The boiler's internals were inspected before and after the testing of each additive.

The results of the three MgO-based slurries tested were quite comparable. The organically based Mg-compound and the non-metallic additive showed lower efficiency in the cold end of the boiler. Though there was a slight decrease in the performance of the additives as the dose rates decreased, the optimum dose rates determined were 150–160 mg · kg⁻¹ for chemical A, 200–250 mg · kg⁻¹ for chemical B, 180–190 mg · kg⁻¹ for chemical C, 500 mg · kg⁻¹ for chemical D and 250 mg · kg⁻¹ for chemical E to be effective. Based on the studies, chemical A was found to be the most effective and economical among the five chemicals tested.

INTRODUCTION

The majority of Saline Water Conversion Corporation's (SWCC) desalination plants are dual purpose, producing both water and power. The installed freshwater capacity is 3 · 10⁶ m³ per day, with more than 5 000 MW electricity [1]. Although most of the power plants in the Eastern Province were designed to use both liquid and gaseous fuels, they have been burning gaseous fuels. However, the power plants in the Western Province use residual oil, Bunker "C," as fuel. Oil fuels emit enormous amounts of noxious and toxic pollutants to the environment during combustion, apart from creating extensive corrosion problems for the plant parts and equipment. While emission problems lead to public outcry, corrosion will result in a loss of metals and a decline in the structural integrity in the air heaters, ducts, stacks, etc. The oxides produced during combustion have a deleterious effect on biological sys-

tems and contribute greatly to general atmospheric pollution. For example, carbon monoxide causes headaches, nausea, dizziness, muscular depression and death due to chemical anoxemia. Formaldehyde, a carcinogen, causes irritation to the eyes and upper respiratory tract and gastrointestinal upsets with kidney damage. Nitrogen oxides cause bronchial irritation, dizziness and headaches. Sulfur oxides cause irritation to mucous membranes of the eyes and throat and severe irritation to the lungs [2]. In addition to contributing to air pollution, combustion byproducts, especially sulfur (S), sodium (Na) and vanadium (V), are responsible for most of the corrosion which is encountered in continuous combustion systems [3–7]. The need to reduce the amount of harmful pollutants formed in the combustion process is of great importance.

Various methods have been used with varying degrees of success to reduce hazardous stack emissions and prevent plant corrosion, such as (i) use of high quality fuel [8,9], (ii) flue gas desulfurization [10–12], and (iii) use of chemical additives.

Additives are used in oil-fired boilers mainly for the following purposes [13]:

- (a) to reduce emissions of SO_3 and acid smut;
- (b) to minimize corrosion in air heaters, economizers, furnaces and superheaters;
- (c) to reduce tube fouling;
- (d) to reduce flue gas opacity;
- (e) to prevent slagging and deposits;
- (f) to improve soot quality and reduce soot quantity.

The most effective among the many fuel additives used are based on MgO or $\text{Mg}(\text{OH})_2$, which are generally available in oil-dispersed forms. Magnesium additives are the best choice for three reasons: (i) they combine with the vanadium oxides and hence increase the melting point of the ash components to a level above the system temperatures so they are no longer sticky; (ii) they modify the ash that forms to a soft, powdery and extremely friable form [9,14,15]; and (iii) they effectively neutralize the acid that condenses on the cooler parts of the air heating system forming neutral MgSO_4 .

In 1989 some preliminary tests were carried out for a short period using a $\text{Mg}(\text{OH})_2$ -based additive in boiler #10 of Jeddah Phase IV (SWCC) [16,17]. These tests yielded promising results such as reduced SO_3 content and acid dew point, reduced quantity and improved quality of ash, etc. But since the duration of the test was very short, an extensive test program was carried out in a boiler unit in Jeddah Phase III [18–20]. Three additives were tested:

- (a) MGOH, a slurry of $\text{Mg}(\text{OH})_2$ dispersed in organic solvent
- (b) MGOA, a thick slurry of MgO -based additive, and
- (c) MGOB, a special grade MgO powder dispersed in demineralized water.

The results from all three additives were quite comparable, with MGOH reported to be the best among the three. Improved flue gas and soot characteristics, significant reductions in SO_3 content and acid dew points, reduced soot quantities, etc. have been observed with the use of these additives.

Many of the fuel additives available on the market contain metals or metallic compounds. The results of a study have shown that the use of metallic additives causes a high

concentration of metal compounds in the flue gas, and the possible toxicity of these new emissions makes the use of these additives questionable [21]. Recently some companies have come up with new and improved chemical additives. ChemAdd Company of London has come up with their unique non-metallic additive. It is a complex mixture of hydrocarbons. The company claims that the chemical:

- (a) improves combustion;
- (b) reduces the amount of pollutants;
- (c) reduces the amount of corrosion by reduction in the formation of SO_3 and higher oxides of sodium and vanadium;
- (d) has detergent properties (cleaning effect);
- (e) has dispersancy properties (for better fuel atomization).

Since there are many fuel additives available on the market, five were selected for evaluation in this project. The additives were chosen according to the different formulations available and can be categorized as follows:

1. Slurries (MgO in light oil)
2. Aqueous products (MgO in water)
3. Emulsions (oil-soluble Mg compounds)
4. Organo-metallic compounds of Mg (oil-soluble nanoparticles)
5. Non-metallic (hydrocarbons)

This paper summarizes the results of the trial tests carried out for the performance evaluation of fuel chemical additives at one of the boilers of the SWCC Shoaiba Plant complex.

Research Objectives

1. To evaluate the performance of different fuel chemical additives in reducing stack emissions and increasing combustion efficiency;
2. To determine the effect of additives on SO_3 , SO_2 and NO_x generation and acid dew point;
3. To evaluate the quality and quantity of soot/dust production;
4. To determine the optimum dose rate;
5. To evaluate hot and cold side corrosion rates with and without additive;
6. To investigate any adverse effects of the additives on the boiler performance such as fouling of burner and boiler tubes, plugging of the air heaters, etc.

EXPERIMENTAL

The fuel oil used in the boilers is high sulfur, low vanadium residual oil supplied by ARAMCO. Boiler #1 from Phase I (at Shoaiba Plant) and Boiler #7 from Phase III (Jeddah Plant) were selected for the trial tests as the test units. The boilers were almost the same, with a maximum generation capacity of 65 MW, steam flow of $335 \text{ t} \cdot \text{h}^{-1}$, and fuel flow of $24 \text{ t} \cdot \text{h}^{-1}$. They have 9 steam-assisted burners on 3 levels.

The additive dosing system consisted of a feed tank with a motorized stirrer to keep the chemical continuously homogenized. The chemical was transferred into the feed tank using a transfer pump. The chemical was dosed into the fuel oil line through a dosing pump controlled by the computer. The dose rates were controlled by adjusting the pump stroke and were monitored periodically by checking the levels manually as well as in the computer. A separate dosing system supplied by the company was used during the tests for Chemical C as shown in Figure 1. In this case the chemical was mixed with water before injection.

After high-pressure water washing, the test unit was put in operation and after achieving a stable condition, operational and chemical parameters were monitored without dosing any chemical additive for one week. Then the chemical was dosed at the high rate of $10 \text{ L} \cdot \text{h}^{-1}$ ($\approx 800 \text{ mg} \cdot \text{kg}^{-1}$ as MgO) for 24 hours to achieve stabilization (pH at 5 min ≈ 4.0). The chemical was pumped into the fuel oil and tests were carried out while maintaining the dose rate of $350 \text{ mg} \cdot \text{L}^{-1}$ for one week, $250 \text{ mg} \cdot \text{kg}^{-1}$ for 5 weeks and $150 \text{ mg} \cdot \text{kg}^{-1}$ for one week while monitoring all parameters. Then the unit was shut down for internal inspection at the end of the testing.

Chemical Characteristics of the Additives

Of the five additives tested, four were magnesium-based and one was a hydrocarbon containing small particles of magnesium dispersed in it. Chemical A is a slurry based on micronized MgO (60 %) in light oil containing cerium and manganese as catalysts, claimed by the company to be combustion enhancers. Chemical B is also a slurry, combining a stable dispersion of fine-sized MgO (60 %) and a powerful organic combustion catalyst containing iron and cerium. Chemical C is an organically based Mg-compound containing 12 % Mg as MgO. This chemical was mixed with water before injection into the fuel line. A separate dosing system was used for dosing the chemical which was provided by the company. Chemical D as claimed by the company is non-metallic, a hydrocarbon containing a small quantity of fine Mg particles dispersed into it. Chemical E is a Mg-based additive supplied as a thick slurry in light oil containing 63 % Mg as MgO. The specialty of this chemical as claimed by the company is that MgO present in the chemical is specially produced as 0–2.5 μm porous MgO with a very high internal surface area.

Analytical Parameters and Procedures

Flue Gas Analysis The following parameters were determined in the boiler flue gases after the air heater (at the stack) as per the methods indicated:

- SO_2 , NO_x , CO, CO_2 , O_2 , hydrocarbons and flue gas temperature were monitored using a portable flue gas analyzer (TESTO-350 XL).
- Acid dew point and rate of build-up (RBU) were determined using a portable Land Instrument Model-200.

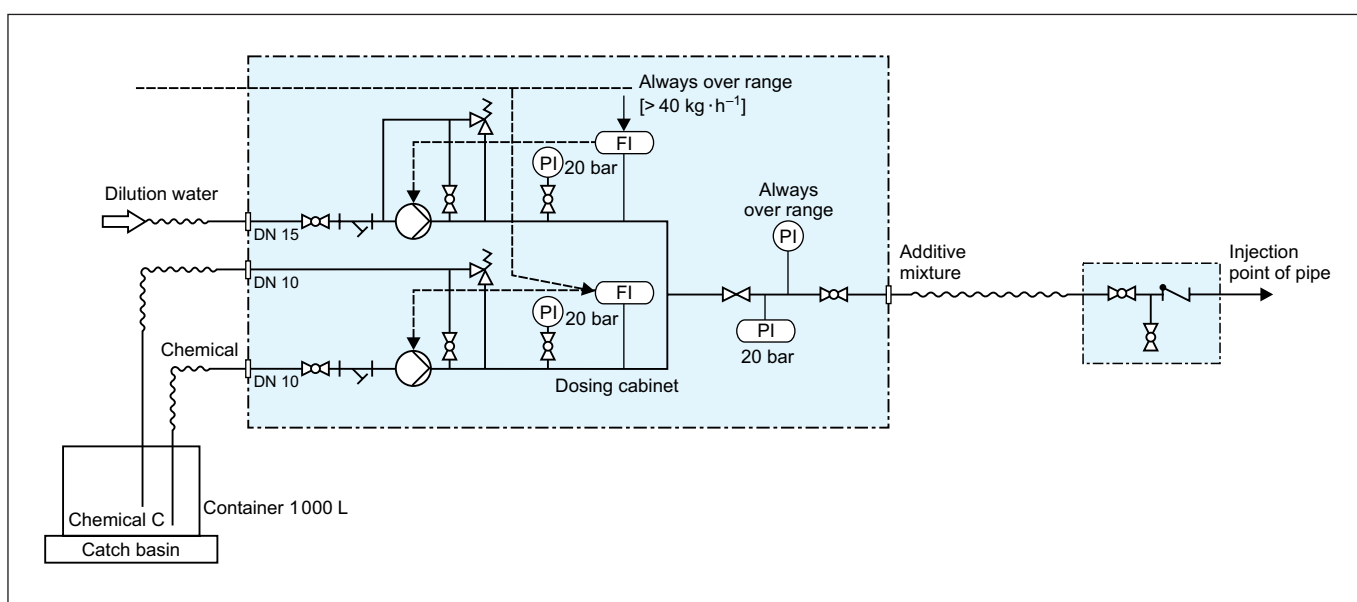


Figure 1:
Chemical fuel additive dosing system for Chemical C.

Ash (Soot) Analysis Regular soot samples were collected and analyzed for the following parameters:

- pH (at 5 minutes and 60 minutes) and conductivity of 1 % slurry were analyzed by pH and conductivity meters;
- Acid content of 1 % slurry as H_2SO_4 by titrimetry;
- Unburned carbon [22];
- Magnesium (soluble and total), vanadium, nickel, aluminum, sodium and moisture content [23].

Fuel Oil Analysis Fuel oil used during the study was withdrawn from the storage tanks and given for analysis to external agencies (Table 1). The following parameters were analyzed:

- Physical parameters: gravity, viscosity at 50 °C and gross calorific value.
- Chemical parameters: carbon, nitrogen, hydrogen, sulfur, vanadium and sodium.

Corrosion Monitoring Corrosion coupons were installed during the additive testing with the help of the plant personnel in the following two locations:

- Upstream (hot end) of the air heater: three coupons were installed before the commencement of the tests.
- Downstream (cold end) of the air heater: three coupons as above.

The coupons were removed during the boiler shutdown inspection and evaluated for corrosion rate by the weight loss method [33].

Boiler Operation Parameters Fuel and steam flows, boiler efficiency, temperature of the flue gases at the inlet and outlet to the air heater, air heater pressure differential (Δp), and the flue gas density were monitored.

Boiler Shutdown Inspection Internal inspection of the boiler was carried out at the end of additive testing. Besides visual checks and photographic documentation, chemical analyses of several deposit samples were carried out.

RESULTS AND DISCUSSION

Flue Gas Parameters

Typical measurements of SO_3 , acid dew point and rate of acid build-up (RBU) are shown in Table 2. Concentration levels determined for SO_3 clearly show that by the use of all five additives a substantial reduction in SO_3 was achievable. The effect of dose rates on SO_3 reduction was not very dramatic. Average reductions of SO_3 in the flue gases independent of the dose rates for all five chemicals were found to be in the range of 80–90 % at 2.2 % excess of oxygen.

During one week of initial measurements, before additive dosing, the SO_2 content varied from 4 249–4 454 $mg \cdot m^{-3}$ with an average concentration of 4 380 $mg \cdot m^{-3}$ (Table 2). The average SO_2 contents at an optimum dosing rate with chemicals A, B, C, D and E were found to be 4 249 $mg \cdot m^{-3}$, 4 908 $mg \cdot m^{-3}$, 4 465 $mg \cdot m^{-3}$, 4 451 $mg \cdot m^{-3}$ and 4 407 $mg \cdot m^{-3}$, respectively. Except in the case of chemical B it was observed that the additive dosing did not have a significant effect on the SO_2 content in the flue gas.

Parameters	Unit	Method	Range
Ash	%	[24]	0.013–0.04
Asphaltenes		[25]	4.06–4.2
Carbon residue		[26]	10.87–16.69
Sulfur		[27]	3.32–3.69
Nitrogen		[28]	0.21
Vanadium	$mg \cdot kg^{-1}$	[29]	32–36
Nickel			9–11
Sodium			6–11
Calcium			2
Aluminum			< 5
Specific gravity at 25.5 °C	—	[30]	0.96
Viscosity at 50 °C	$m^2 \cdot s^{-1}$	[31]	$(312–364) \cdot 10^{-6}$
Calorific value	$MJ \cdot kg^{-1}$	[32]	41.91–42.71

Table 1:
Major constituents in the fuel oil.
Data in % are mass portions
The analyses were done at
Al-Hoty Stanger, Al-Khobar;
Intertek Caleb Brett, Yanbu;
Gamlen Industries, France;
and HALAB, GmbH.

Parameters	Dose Rate [mg · kg ⁻¹]	SO ₂ [mg · m ⁻³]	NO _x [mg · m ⁻³]	SO ₃ [mg · m ⁻³]	Acid Dew Point Temperature [°C]
No Additive	0	4 380	406	3.6–16	120–130
Chemical A	350	4 146	327	NA	NA
	250	4 202	415	0.5–0.7	99–104
	150	4 313	451	1.8–3.2	110–115
Chemical B	350	NA	NA	NA	NA
	250	4 908	419	0.7–1.8	104–110
	150	4 779	400	1.8–3.2	110–115
Chemical C	600	4 547	327	0.7	104
	500	4 465	389	0.7–1.8	104–110
	400	4 659	352	0.7–1.8	104–110
Chemical D	350	4 703	329	0.4–0.5	93–99
	250	4 451	333	0.4–0.5	93–99
	125	4 873	320	0.5	99–104
Chemical E	200	4 427	344	NA	NA
	180	4 407	353	0.5–0.7	99–104
	120	4 424	359	NA	NA

Table 2:

Average SO₃, acid dew point, RBU, NO_x and SO₂ values in flue gases for the five chemical fuel additives tested.

NA – not analyzed

NO_x concentrations were found not to be affected by the additive dosing. NO_x levels are reported to be influenced significantly by the excess combustion air and the nitrogen content in fuel oil. The fluctuations observed may be due either to the variations in excess combustion air or to the nitrogen content in the fuel oil.

As shown in Figure 2 acid dew points and RBU also indicated substantial reductions in the flue gas for all five chemicals. The average acid dew points for Chemical A, Chemical D and Chemical E were quite similar in the range of 99–104 °C. This indicated a decrease of 16–21 °C in acid dew points due to additive dosing. For Chemical B and Chemical C the acid dew points were in the range of 104–110 °C, indicating a decrease of 10–16 °C. Several studies have shown the rate of acid build-up to be a good indicator of the corrosiveness of flue gases and an RBU value close to or less than 100 μA · min⁻¹ is indicative of non-corrosive flue gases [34]. The present study showed the RBU determined at an optimum dose rate at various concentrations of excess oxygen for each additive to decrease quite significantly from the baseline value (120 μA · min⁻¹ without additive). As the excess oxygen level decreases, the RBU value also decreases since it is a formation of SO₃ content in the flue gases and the latter is

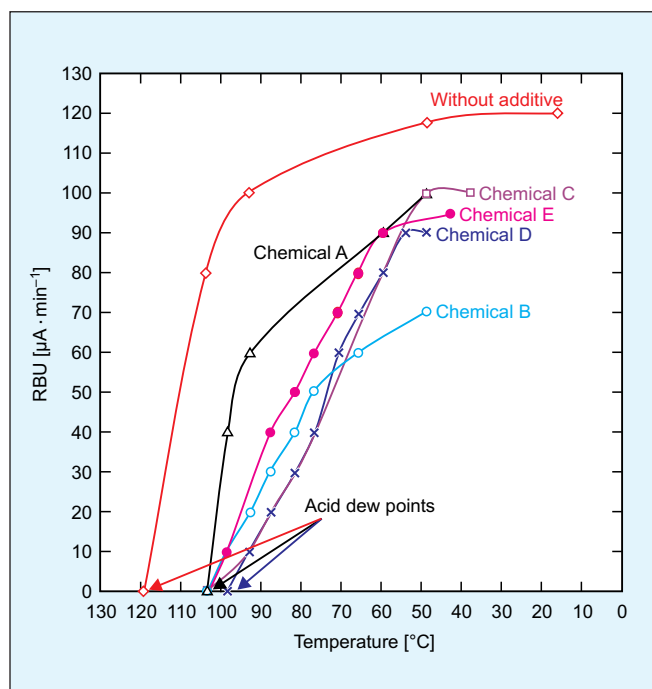


Figure 2:
Effect of additive dosing on acid dew points and RBU.

Parameters	Dose Rate mg · L ⁻¹	pH		Free Acidity [% H ₂ SO ₄]	Total Acidity [% H ₂ SO ₄]	Unburned C [%]	Soluble Mg [mg · kg ⁻¹]	Vanadium [mg · kg ⁻¹]
		5 min	60 min					
No Additive	0	2.48	2.59	7.11	12.46	86	0.07	0.17
Chemical A	350	3.95	4.46	nil	~1	79	1.2	0.48
	250	3.75	4.59	nil	~1	82	1.26	0.47
	150	3.59	4.02	0.29	~2	81	1.15	0.83
Chemical B	350	4.83	6.37	nil	~1	79	2.20	0.4
	250	3.56	4.27	0.38	~3	75	1.23	0.74
	150	3.52	4.45	0.2	~2	57	2.22	0.5
Chemical C	600	2.37	2.47	5.83	9.8	85	2.0	0.27
	500	2.48	2.73	5	14	51	1.67	0.31
	400	2.37	2.46	4.9	14	65	0.77	0.51
Chemical D	350	2.65	2.75	2.06	3.5	82	0.1	0.26
	250	2.65	2.75	1.2	1.9	82	0.24	0.34
	125	2.65	2.75	1.4	2.2	83	0.07	0.23
Chemical E	200	2.92	3.19	1.65	5.37	88	0.85	0.19
	180	3.39	4.12	0.15	0.99	86	0.55	0.25
	120	2.88	3.32	0.67	1.38	87	0.68	0.12

Table 3:

Average pH, acidity, unburned carbon, soluble magnesium and vanadium values in the fly ash for the five chemical fuel additives tested.

low at low excess oxygen. Chemical A exhibited better performance than the other four additives with an RBU value of 60 $\mu\text{A} \cdot \text{min}^{-1}$ with 1.5 % excess oxygen. The results in general indicate effective neutralization of the flue gas by the additives (Table 2).

Boiler Soot Characteristics

Reduction in the moisture content showed the drying out of the soot and colour change to grayish as a result of additive dosing. The magnesium will help to dry out the soot and ash particles by increasing the melting temperature of the deposits formed in the high temperature zone. The pH of 1 % slurry of the ash samples treated with Chemical A and Chemical B increased above 3.5 whereas for Chemical C and Chemical E it was below 3.5 (Table 3). With Chemical D treatment pH determined at 5 minutes and 60 minutes remained almost constant at 2.65 and 2.75 respectively. pH between 3.5–4.0 is considered to be adequate for corrosion protection. Free acidity, determined as % H₂SO₄ for Chemical A was found to be nil, whereas Chemical B, Chemical D and Chemical E showed 0.2 %, 1.2 % and 0.15 % respectively. Chemical C exceptionally showed a higher value (5.0 %) of acidity, indicating

a corrosive nature of the soot. In general, the pH of 1 % slurry of soot samples treated with Chemical A showed the samples to be non-corrosive and free of acid, which was confirmed from the SO₃ content, RBU values and acid dew point. The soot samples for Chemical B, Chemical D and Chemical E showed a little acidity, though significant reductions in the SO₃ content, acid dew point and RBU values were observed, indicating that the additive dose rate is insufficient for the total neutralization of the acid formed at the cold end of the boiler. The above data shows that the soot samples treated with Chemical A produced the greatest neutralization efficiency among the five chemicals tested.

An appreciable reduction in the carbon content from 76 % without additive to an average of 50 % with 500 mg · kg⁻¹ of additive was observed for the soot samples treated with Chemical C, indicating that the additive has appreciable effects on combustion, while for the other four additives no appreciable change in the carbon content was noticed.

Chemical analyses of soot were undertaken to determine the concentration of soluble magnesium and other corrosive constituents present (Table 3). Chemical A and Chemical B treated soot samples showed an increase in soluble

magnesium content from 0.07 % to greater than 1.5 %, confirming the effective neutralization forming soluble magnesium sulfate. Though Chemical C also showed a high value of 1.55 % for soluble magnesium, total neutralization of the soot was not attained as indicated from the pH and acid content. In the case of Chemical D and Chemical E the value was less as was observed earlier, indicating that total neutralization was not achieved.

Vanadium content in the soot samples treated with all the five additives showed a similar increasing trend with dosing. These results show that vanadium is being effectively converted to high melting species by reaction with magnesium which can be easily blown out of the boiler under normal gas velocities. In the absence of magnesium, vanadium forms low melting deposits on the boiler surfaces in high temperature zones causing corrosion and also helping as a catalyst in conversion of SO_2 to SO_3 which condenses on the cooler surfaces resulting in acid corrosion. The results as shown in Table 3 show that these additives were quite effective in reducing corrosion in both high-temperature and low-temperature zones. Chemical A and Chemical B showed better performance as indicated by the vanadium content.

A steady decrease in the iron content in the soot samples was noticed from 3.67 % (before additive dosing) to 0.4 % as the dosing continued, indicating a reduction in the corrosion of the boiler and thereby indicating the effectiveness of the chemical fuel additives Chemical A, Chemical D and Chemical E. Chemical B and Chemical C showed a decrease to 1.23 % and 0.85 %, respectively.

Initial dosing did not have any effect on the sodium content of the soot, but as the dosing continued there was an appreciable increase, indicating the formation of high-melting Na-Mg-V compounds in the soot with all the chemicals except Chemical D, which showed a decrease.

Nickel concentrations in the soot sample initially showed a high value but as the additive dosing continued it was found to decrease, indicating the formation of nickel compounds that get deposited as soft scales on the boiler tubes.

The effect of the additives on a reduction in the quantity of soot could not be studied.

Boiler Performance

No appreciable change in the efficiency of the boiler was noticed and it almost remained constant when treated with Chemical A, Chemical C and Chemical E, while a small reduction of 0.6 % with Chemical B and 0.3 % with Chemical D was observed. Internal inspection of the boiler after each additive testing showed that most of the tube surfaces in the tertiary superheaters were covered with

thick deposits with Chemical B. The decrease in efficiency with Chemical B can be attributed to these thick deposits. An increase in the flue gas exit temperature of 30–40 °C was observed with Chemical A and Chemical B, while Chemical D, Chemical C and Chemical E showed an increase of 20–25 °C. This was attributed to the coating of heat exchanger surfaces by MgO from the additive. This coating is expected to have a lower heat transfer capacity and is thermally reflective in nature, resulting in higher temperatures of the exit flue gases. However this did not result in any appreciable decrease in the boiler efficiency. The Δp across the air heaters was monitored continuously in order to check fouling of the air heaters due to the additive dosing. It was found to remain steady, indicating no fouling due to additive dosing.

Internal Condition of the Boiler

Internal inspection of the boiler after each additive testing showed that the condition of the furnace was generally good with soft scales (in the form of flakes which can be easily removed by hand) on the tubes and some loose hard deposits in-between the tubes as shown in Figure 3. The deposits on the surface of the tubes and in-between the tubes contained Fe, V, Mg, S, Na and Ni. The brown color of the deposits appears to be due to the presence of a significant amount of iron oxide as corrosion products. In the case of Chemical B, a huge collection of the deposits was observed at the corners in the furnace. This may be due to the agglomeration of the unreacted additive in combination with other impurities. The larger particle size of the additive is known to enhance agglomeration of the deposits and once they become too heavy to be removed from the boiler by normal gas velocities, they will accumulate inside the boiler. It is quite probable that the presence of deposits in larger volumes is due to the bigger particle size of the additive. The Ni concentration is comparatively less in these samples. In the case of Chemical D, black powdery deposits were found which indicated carbon deposits from the hydrocarbon additive.

Primary superheater tubes were found to have a uniform 2–3 mm thickness of thin scales (Figure 4). The scales were yellowish-white and of soft powdery material. The chemical analysis showed that the scales were rich in Mg and V with a significant amount of Ni and Fe. The secondary superheater tubes, in contrast, had hard scales (2–3 mm). The scales were yellowish-green in color. The greenish yellow or off-white color of MgO/MgSO_4 was perhaps due to the presence of Ni-salts as inclusions. Samples analyzed were found to contain significant amounts of MgO/MgSO_4 , and appreciable quantities of vanadium, iron, nickel and other complex compounds. They normally form a thin reflective coating on the heat transfer surfaces and prevent corrosion by acting as a barrier between the flue gases and the metal surfaces.

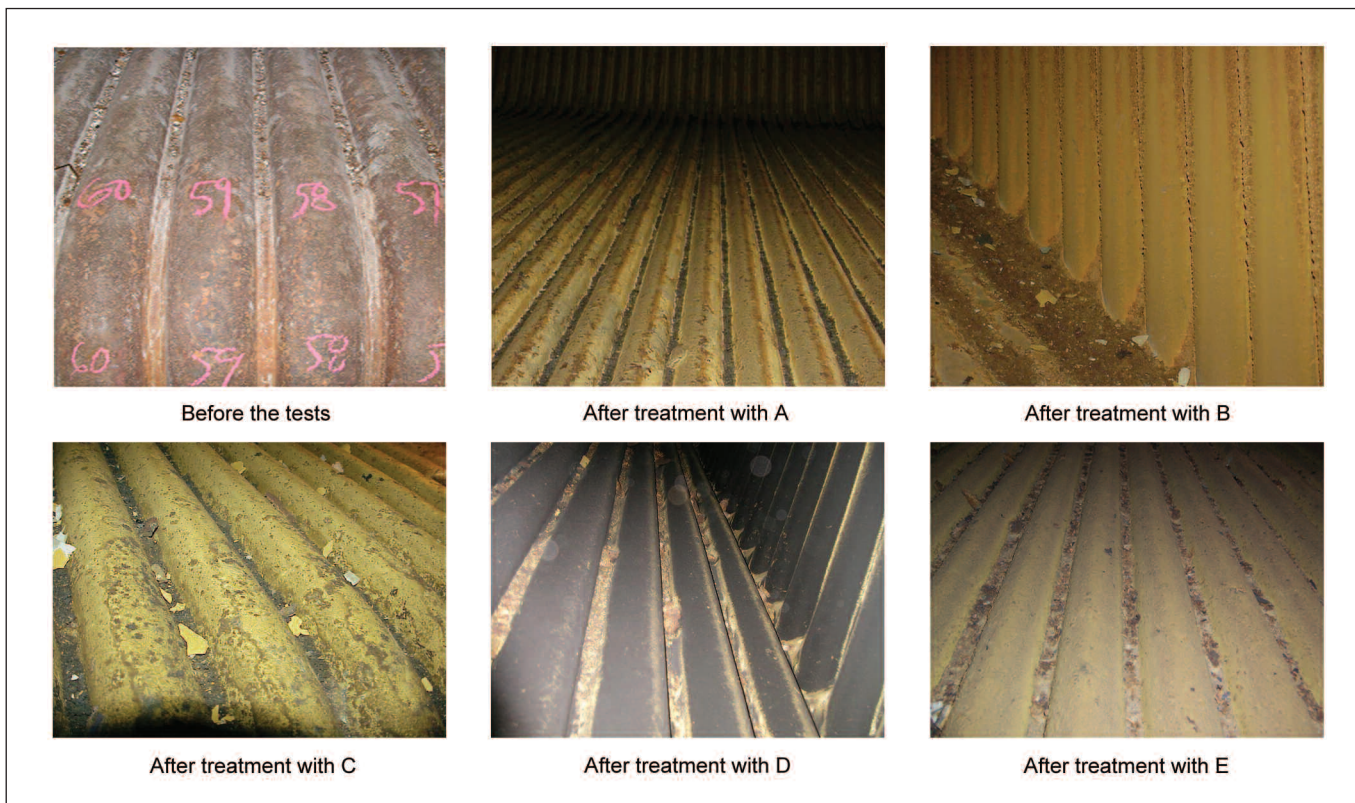


Figure 3: Furnace tubes before and after the tests.



Figure 4: Superheater tubes before and after the tests.

Tertiary superheater tubes treated with Chemical B showed huge slagging deposits with a thickness of 8–10 mm. Chemical analysis showed the deposits to be rich in vanadium and magnesium with small quantities of sodium and iron. It is quite probable that the presence of thick deposits resulting in slagging may be due to the bigger particle size of the additive.

Economizer tubes were found to have a very thin layer of soft, brown deposits in the form of flakes (Figure 5). Secondary economizer deposits were found to contain both Mg and Ni in significant concentrations with vanadium as a major constituent. Vanadium is presumably in the form of V_2O_5 or magnesium vanadate. These brown deposits have inclusions of a yellowish or white product, which is MgO.

Flue ducts upstream and downstream of the air heater had uniform grayish deposits resulting in the formation of a buffer layer providing good corrosion protection to the air heaters. Air heater elements were found to be generally satisfactory upstream (hot end) but the downstream (cold end) air heater elements were found to be dirty with large amounts of a grayish-yellow pasty material (Figure 6).

In summary, of the three slurries used in this trial, Chemical A and Chemical B caused the boiler surfaces to be

covered with soft deposits in the form of flakes which were easily blown or removed by hand while Chemical E showed very thin hard deposits. The organic compound of magnesium, Chemical C, also showed the boiler surfaces to be covered with good soft deposits. In the case of the non-metallic hydrocarbon, Chemical D, the deposits were fine and powdery with black carbon deposition over them.

Corrosion Studies

Corrosion studies carried out separately for each chemical by the weight loss method indicated a low corrosion rate. Hot end corrosion was highest at $0.0594 \text{ mm} \cdot \text{a}^{-1}$ (2.34 mpy) in the case of Chemical D and lowest at $0.0411 \text{ mm} \cdot \text{a}^{-1}$ (1.62 mpy) in the case of Chemical A. For the other additives the corrosion rates were found to be within this range. The cold end corrosion rate was also found to be highest ($0.0406 \text{ mm} \cdot \text{a}^{-1}$ or 1.60 mpy) with Chemical D. However, the overall corrosion rates were relatively low irrespective of the hot or cold zones. The presence of the magnesium sulfate and magnesium vanadate in the deposits indicated a chemical reaction between sulfur and vanadium (present in the fuel) and MgO (present in the additive). The low corrosion rate at the air heater could be attributed to the reactions of sulfur and vanadium from the oil with magnesium-based additives.

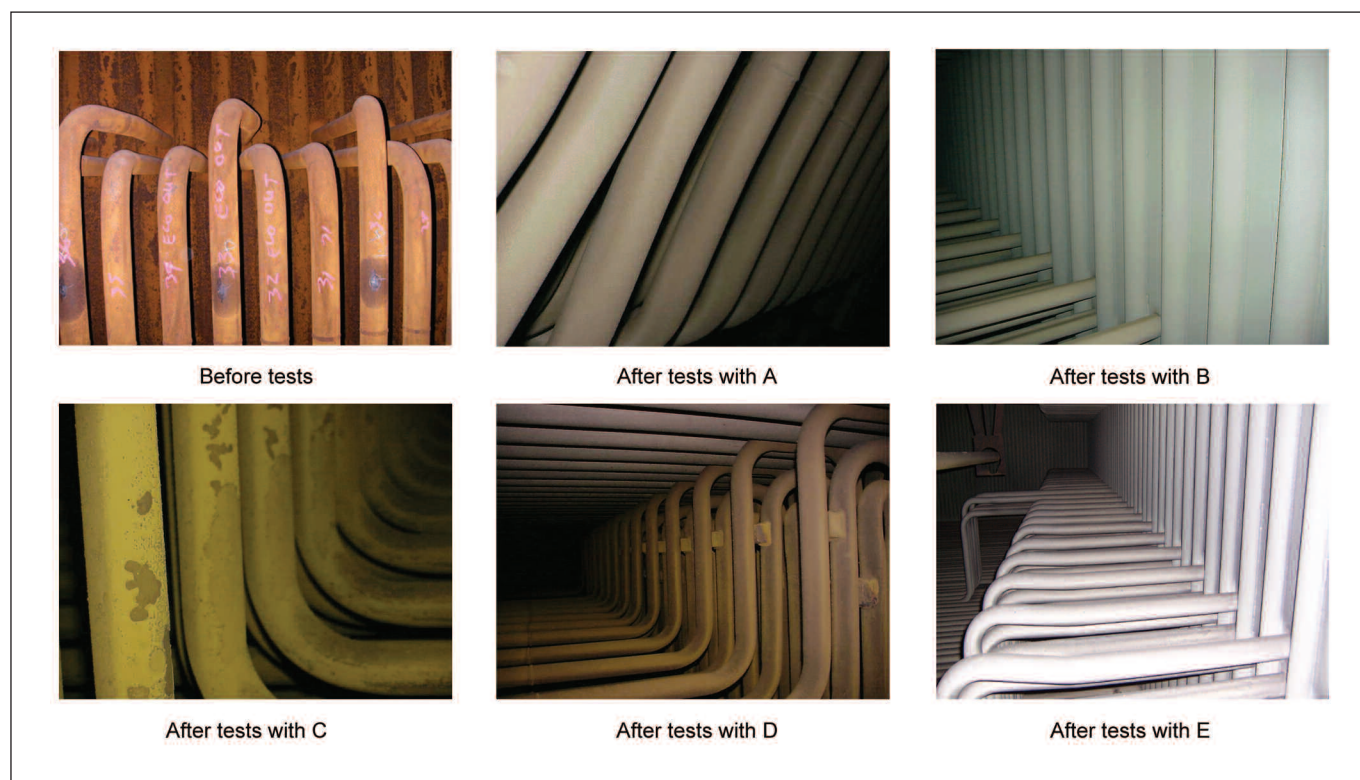


Figure 5: Economizer tubes before and after the tests.

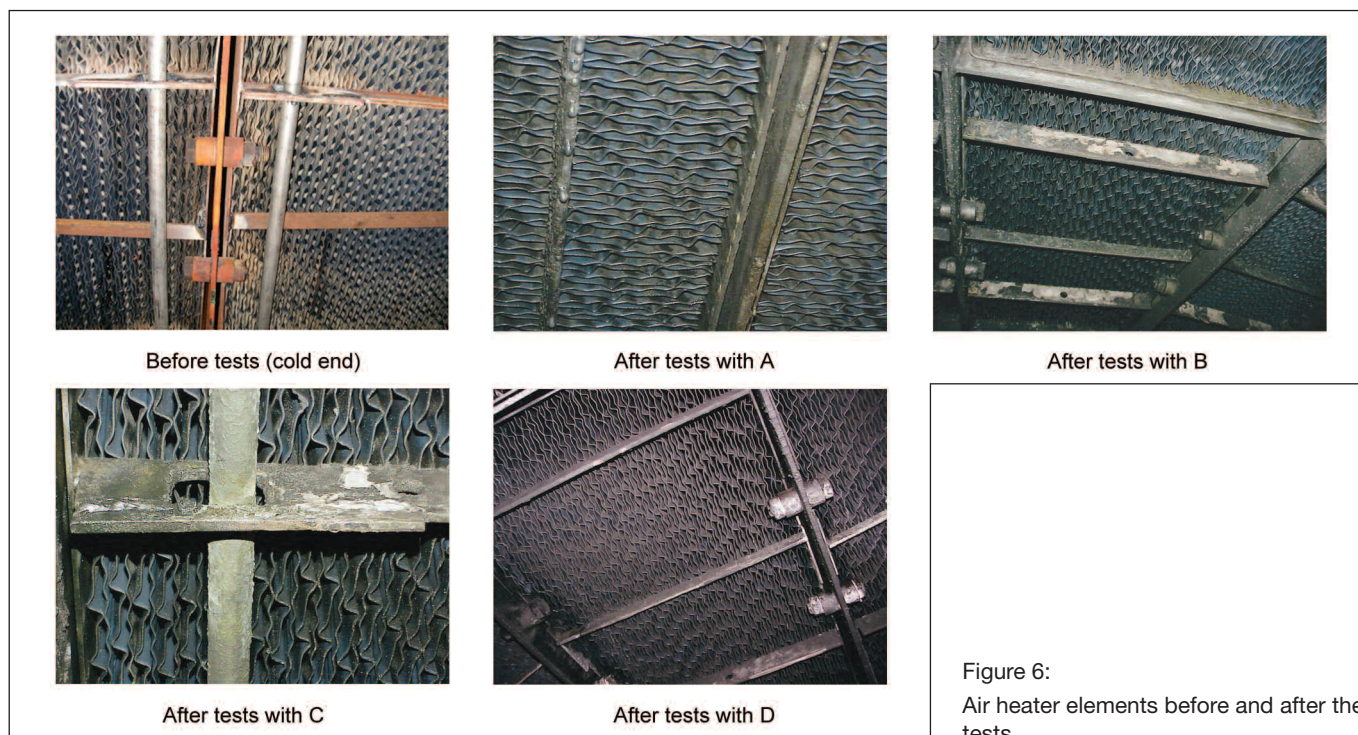


Figure 6:
Air heater elements before and after the tests.

Parameters	No Additive	Chemical A			Chemical B			Chemical C			Chemical D			Chemical E		
		350*	250*	150*	350*	250*	150*	600*	500*	400*	350*	250*	125*	200*	180*	120*
pH (5 min)	2.48	3.95	3.75	3.59	4.83	3.56	3.52	2.37	2.48	2.37	2.65	2.65	2.65	2.92	3.39	2.88
pH (60 min)	2.59	4.46	4.59	4.02	6.37	4.27	4.45	2.47	2.73	2.46	2.75	2.75	2.75	3.19	4.12	3.32
Free acidity [% H ₂ SO ₄]	7.11	nil	nil	0.29	nil	0.38	0.2	5.83	5.0	4.9	2.06	1.2	1.4	1.65	0.15	0.67
Total acidity [% HH ₂ SO ₄]	12.46	~1	~1	~2	~1	~3	~2	9.8	14	14	3.5	1.9	2.2	5.37	0.99	1.38
Unburned carbon [%]	86	79	82	81	79	75	57	85	51	65	82	82	83	88	86	87
SO ₃ [mg · m ⁻³]	3.6–16		0.5–0.7	1.8–3.2		0.7–1.8	1.8–3.2	0.7	0.7–1.8	0.7–1.8	0.4–0.5	0.4–0.5	0.5–0.7		0.5–0.7	
Acid dew point temp. [°C]	120–130		99–104	110–115		104–110	110–115	104	104–110	104–110	93–99	93–99	99–104		99–104	
Corrosion rate [mm · a ⁻¹]		0.041 1 (hot end)			0.043 2 (hot end)			0.043 2 (hot end)			0.059 4 (hot end)			0.049 5 (hot end)		
		0.034 5 (cold end)			0.033 0 (cold end)			0.035 6 (cold end)			0.040 6 (cold end)			NA (cold end)		
Optimum dose rate [mg · kg ⁻¹]		150–160			200–250			500			250–300			180–190		
Boiler internal deposits		green yellowish-white, 2–3 mm thick, in the form of flakes and easily detachable on the superheater tubes			Brown, 8–10 mm thick on tertiary superheater tubes, easily detachable and a large collection in the furnace			Yellowish-grey, soft powdery material, 1–2 mm thick on superheater tubes			black powdery material 1–2 mm thick on top of brown and yellowish-white deposits on superheater tubes, furnace tubes and air heater elements			thin deposits difficult to remove on the superheater and economizer tubes		
Efficiency		remained almost constant			0.6 % reduction was noticed			remained almost constant			0.3 % reduction was noticed			remained almost constant		

Table 4:
Summary of the test results.

* additive dose rate [mg · kg⁻¹]

Optimum Dose Rate

On the basis of the results obtained with varying dose rates as given in Table 4, the optimum dose rates required were 150–160 mg · kg⁻¹ for Chemical A, 200–250 mg · kg⁻¹ for Chemical B, 500 mg · L⁻¹ for Chemical C, 250 mg · L⁻¹ for

Chemical D, and 180–190 mg · kg⁻¹ for Chemical E. Compared to Chemical A, Chemical B will require a 45 % higher dose rate, Chemical C will require about a 300 % higher dose rate, Chemical D will require a 77 % higher dose rate and Chemical E will require a 22 % higher dose rate.

CONCLUSIONS

- (a) A significantly greater neutralization efficiency of ash pH (3.5 to 4.0) was observed for the samples treated with Chemical A, Chemical B and Chemical E whereas the pH was lower than 3.0, showing inefficient neutralization, for Chemical C and Chemical D. This indicated that Chemical A, Chemical B and Chemical E are more suitable than the other two at the given optimum dose rates.
- (b) Soot samples for Chemical A were found to be dry and friable with nil free acidity. Chemical B, Chemical E, Chemical C and Chemical D showed 0.2 %, 0.15 %, 5.0 % and 1.2 % free acidity, respectively. This indicated that Chemical A was best suited due to the non-corrosive and neutral character of the soot generated during the additive dosing.
- (c) All five chemicals showed comparatively similar results in terms of improved flue gas characteristics. Significant reductions in SO₃ content and acid dew points were observed during the additive dosing. These results indicated that magnesium-based additives were effective in reducing SO₃ content and acid dew points in the flue gases.
- (d) The presence of appreciable amounts of neutral magnesium sulfate and vanadium compounds in the boiler soot samples indicated that MgO in the additive was quite effective in converting catalytically active V₂O₅ and low-melting compounds into high-melting compounds, which do not get adhered on the metal surface and can be easily blown. These high-melting compounds also help in preventing the destruction of the protective oxide layer on the heat exchanger in hot zones of the boiler, thus reducing hot end corrosion.
- (e) The pressure differential (Δp) across the air heaters remained steady indicating that no fouling occurred due to additive dosing. Air heater ducts were found to be covered with neutral magnesium compounds, which are quite effective in protecting metallic parts where the temperatures are below the acid dew point.
- (f) Reduction in RBU ($< 100 \mu\text{A} \cdot \text{min}^{-1}$) and corrosion studies using coupons installed in the air heater ducts (cold and hot ends) showed that the corrosion rates were very low, except in the case of Chemical D, which showed $0.0594 \text{ mm} \cdot \text{a}^{-1}$ (2.34 mpy) at the hot end.
- (g) No adverse effects such as plugging of burner tips, fouling of air heaters, etc. were noticed due to additive dosing. The thickness of deposits observed on the heat exchangers was highest in the case of Chemical B (8–10 mm), resulting in a reduction in the efficiency of 0.6 %.
- (h) Optimum dose rates determined indicated a dose rate of $150\text{--}160 \text{ mg} \cdot \text{kg}^{-1}$ for Chemical A, $200\text{--}250 \text{ mg} \cdot \text{kg}^{-1}$ for Chemical B, $500 \text{ mg} \cdot \text{kg}^{-1}$ for Chemical C, $250 \text{ mg} \cdot \text{kg}^{-1}$ for Chemical D, and $180\text{--}190 \text{ mg} \cdot \text{kg}^{-1}$ for Chemical E.
- (i) Compared to Chemical A, Chemical B will require a 45 % higher dose rate, Chemical C will require about a 300 % higher dose rate, Chemical D will require a 77 % higher dose rate and Chemical E will require a 22 % higher dose rate.
- (j) Based on the studies, Chemical A was found to be the most effective of the five chemicals tested.

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