

Research Article

Fire-Side Corrosion: A Case Study of Failed Tubes of a Fossil Fuel Boiler

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The failures of superheater and reheater boiler tubes operating in a power plant utilizing natural gas or mazut as a fuel have been analysed and the fire-side corrosion has been suggested as the main reason for the failure in boiler tubes. The tubes have been provided by a fossil fuel power plant in Iran and optical and electron microscopy investigations have been performed on the tubes as well as the corrosion products on their surfaces. The results showed that the thickness of the failed tubes is not uniform which suggests that fire-side corrosion has happened on the tubes. Fire-side corrosion is caused by the reaction of combustion products with oxide layers on the tube surface resulting in metal loss and consequently tubes fracture. However, the tubes corrosion behaviour did not follow the conventional models of the fire-side corrosion. Given that, using the corrosion monitoring techniques for these boiler tubes seems essential. As a result, the thickness of the boiler tubes in different parts of the boiler has been recorded and critical points are selected accordingly. Such critical points are selected for installation of corrosion monitoring probes.

1. Introduction

Fossil fuels are still one of the major sources of energy in our society because of their capacity to generate huge amounts of electricity. However, unforeseen failures in boilers cause them to shut down and stop electricity generation. Main failures in boilers stem from severe damage in boiler tubes which can be affected by the tube material, boiler service temperature, and chemical composition of the fossil fuel [1]. Moreover, tube position, temperature, and pressure can also promote the boiler collapse. Understanding the failure mechanism of boiler tubes and determining critical points which are undergoing the most damage are appropriate approaches to prevent boilers shut-downs [2].

The corrosion of boiler tubes is one of the remaining challenges in fossil fuel power plants. Tubes failure leading to the plant shut-down and tubes repair and replacement and welding and required welding inspections cause tremendous costs. On the other hand, due to depletion of high-grade fuels and also for economic reasons, residual fuel oil along with

coal is extensively used in the energy generation systems, which contains sodium, vanadium, and sulphur as impurities. These impurities can encourage some sorts of corrosion in boiler tubes. For instance, high-temperature corrosion in coal fired boilers is mainly caused as a result of the presence of impurities like sulphur, alkali metals, and chlorine in the coal. During boilers operation, low melting point deposits such as $\text{Na}_2\text{O}\cdot\text{V}_2\text{O}_4\cdot 11\text{V}_2\text{O}_5$ ($T_m = 535^\circ\text{C}$) are formed on the surface of superheater and reheater tubes. On the fire side of a tube, the metal protective oxide layer will be dissolved in these molten deposits and accelerates the corrosion. This phenomenon is known as fire-side corrosion which can happen either uniformly or in a localized manner and its rate is between 50 and 300 nanometers per hour. However, under a severe condition, it can be even faster which decreases the lifetime of tubes to less than two years.

In the combustion system, sodium sulphate and oxide are formed from the reaction of Na, O, and S. Vanadium reacts with oxygen to form V_2O_5 and other complex vanadates. These compounds, commonly known as ash, deposit on the

TABLE 1: Chemical composition of low-alloy steel: ASTM A213 T12 and A213 T22.

Wt.%	Carbon	Manganese	Phosphorus	Sulphur	Silicon	Chromium	Molybdenum
A213 T12	0.05–0.15	0.30–0.61	0.025	0.025	0.50	0.8–1.25	0.44–0.65
A213 T22	0.05–0.15	0.30–0.60	0.025	0.025	0.50	1.90–2.60	0.87–1.13

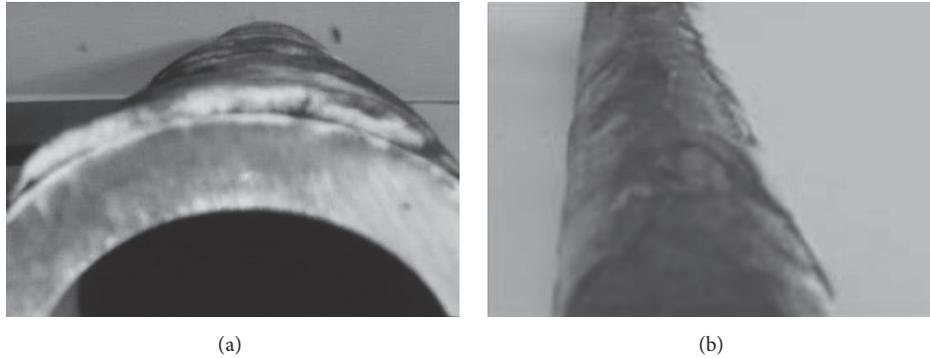


FIGURE 1: (a) Cross section of a boiler tube with deposits on the surface and (b) surface of a boiler tube after two years in the service condition.

surface of materials and induce corrosion. During combustion, these elements combine to form various types of vapours and condensed phases [3]. The chemistry of reactions taking place during combustion is complex and highly variable. Degradation of materials occurs when these molten compounds destroy the natural protective oxide layer of the materials surface during boiler operation [4]. The complex environment (thermal, chemical, and mechanical) on the boiler service condition makes it extremely difficult for a material to endure all the tough situations imposed on it [1]. Therefore, to prevent catastrophic failures, it is important to understand and predict corrosion behaviour on the tubes surfaces in advance. It should also be noted that temperature and internal pressure are different in different parts of a boiler. Thus, thickness measurements of the boiler tubes and determination of critical points are appropriate approaches.

In this work, the in situ thickness measurement of tubes at different parts of a fossil fuel power plant in Iran has been performed and the damaged tubes were collected for more root cause analysis. Optical microscopy (OM), scanning electron microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS), and X-ray diffraction (XRD) have been used to study morphology, chemical composition, and structure of failed tubes and corrosion products on top of the tubes. Thickness measurement data has been used to determine the critical points in the boiler.

2. Experimental

Failed tubes of the boiler were transferred directly from boiler unit to the laboratory. After visual inspection, the tubes have been cut for cross section studies. The samples were ground using successive finer grades of SiC papers, up to 2000, and then polished to a mirror finish by 0.3 and 0.05 μm alumina slurry. OM, SEM, EDS, and XRD have been utilized to characterize the samples and corrosion products. In situ

thickness measurement was performed by ultrasonic testing (UT) in the power plant site. The thickness values reported in this paper are the average value of at least 3 measurements with six-month intervals. Superheater and reheater tubes were made of a low-alloy steel, ASTM A213 T22 and A213 T12, respectively, with a chemical composition presented in Table 1 [5].

3. Results

Figure 1 depicts a superheater tube with the corrosion products and deposits on its surface. The surface of the tube which was exposed to fire is covered by a layer of thick, coarse, and adhesive deposit. Its yellow colour suggests the presence of sulphur in the layer.

The thickness measurements indicate that thickness in failed tubes is dramatically decreased to values lower than the critical value for boiler tubes. According to Figure 2, this phenomenon is more apparent in the fire side of tubes.

Figures 3–6 demonstrate the microstructures of boiler failed superheater and reheater tubes. Based on Figure 3, the structure of superheater in the surface vicinity is slightly different from the bulk material, with more spherical carbide in grain boundaries compared to the ferritic microstructure of the bulk material. Such difference in microstructure has previously been reported in the literature [6]. In Figure 4 a porous and nonuniform deposit layer on the tube is shown.

The microstructure of reheater tube is the same as the superheater; however, the deposit layers on the reheaters are uniform, suggesting a general corrosion on the reheater tube surfaces (see Figures 5 and 6).

The morphology of deposit layers on the external surface of the reheater and superheater has further been studied by SEM and the images are shown in Figure 7.

Such difference in corrosion products and oxide layers on the superheater and reheater tubes stems from the position of

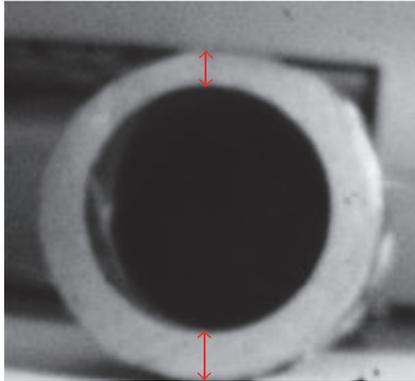


FIGURE 2: Cross section of a failed boiler tube. Metal loss in fire side of the tube is clear.

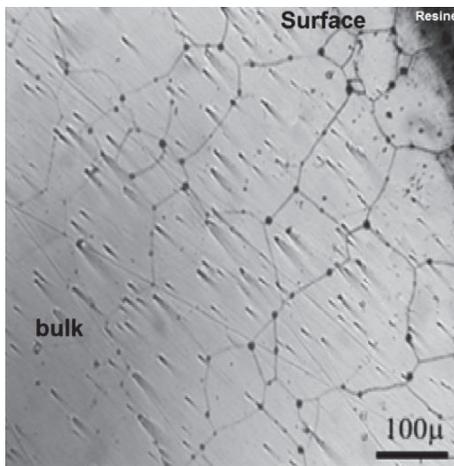


FIGURE 3: Optical microscopy image of superheater microstructure.

TABLE 2: XRD results of deposits on the reheater and superheater tube surfaces.

Main components	Minor components
Na_2SO_4	$\text{NaV}_6\text{O}_{15}$
$\text{CrFe}(\text{VO}_4)_2$	Fe_2O_3

superheater tubes which are exposed to higher temperatures and also more fuel impurities, particularly alkali metal chlorides. The chemical composition and structure of corrosion products were investigated with XRD (Figure 8) and the results were summarized in Table 2 in which Na_2SO_4 and $\text{CrFe}(\text{VO}_4)_2$ are the major components. These results are consistent with Energy-Dispersive X-ray Spectroscopy (EDS) data which showed Fe, Cr, V, Na, O, and S in corrosion products.

To understand the source of Na, S, and V, the chemical composition of the fuel that is being used in the boiler has also been explored and shown in Table 3.

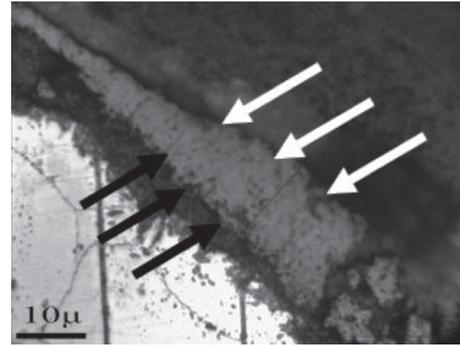


FIGURE 4: Optical microscopy image of corrosion products on the surfaces of superheater tubes.

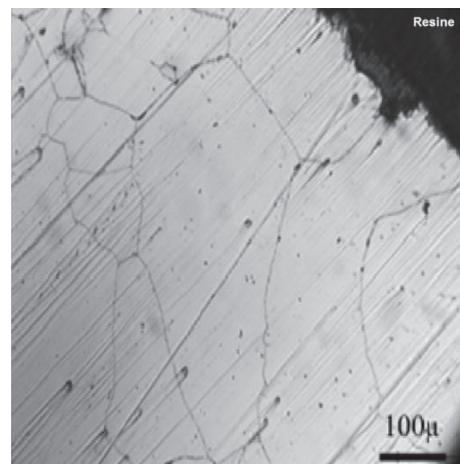


FIGURE 5: Optical microscopy image of reheater microstructure.

TABLE 3: Ca, K, and Na content in fuel of the power plant.

Component	Calcium	Potassium	Sodium
Amount ($\mu\text{g}/\text{m}^3$)	28.77	0.58	0.91

4. Discussion

It is well known in fire-side corrosion that some corrosive species such as S, V, Na, and K in fossil fuels lead to deposits formation on the tube surfaces and consequently severe corrosion. Corrosion mechanism does strongly depend on the fuel chemical composition, boiler working temperature, amount of excess air, and the tube materials. Fuels impurities form low melting point deposits which are ionic conductive and are able to transfer the electrons. Vanadium has different oxidation states and can be easily oxidized to VO, VO_2 , and V_2O_5 . Sulphur also is oxidized to SO_2 and SO_3 depending on the temperature and amount of oxygen content in the boiler and according to (1) reacts with fuel impurities:



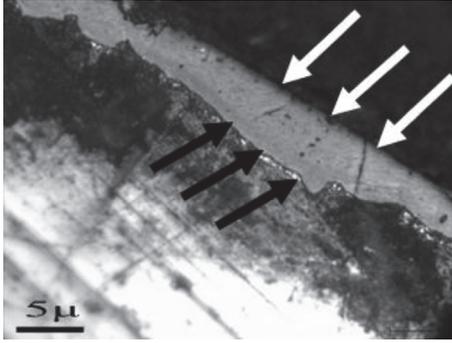
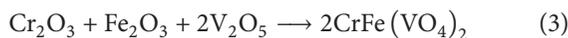
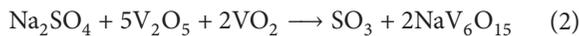


FIGURE 6: Optical microscopy image of corrosion products on the surfaces of reheater tubes.

where Na_2SO_4 was detected by XRD (Table 2). In the boiler condition, in initial stages, an oxide film forms on the tube surface. Sodium sulphate then deposits on the oxide layer. Afterward, the outer surface of Na_2SO_4 layer begins to become sticky and absorb fly ash particles which results in dissolving the oxide layer of metal and increasing the deposit thickness. By increasing the deposit thickness and temperature gradient in it, the deposits and oxide layers start moving and to be washed away from the surface and hence further oxidation of the metal will happen [7]. Although NaCl does not have any direct effect on the corrosion, it causes the oxide layers of metals to peel off and exposes the bare metal to the corrosive condition. In this situation, chromium diffuses from the bulk material to the surface to form a new passive layer and, in consequence, Cr depletion has occurred (Table 1). In other words, in the presence of NaCl (Figure 9), Cr is lost from the surface as volatile chromic chloride and the oxidation rate to replace the normal chromic oxide film will increase [8]. Nonetheless, the serious metal loss does not stem from gas-phase oxidation if the metal is not exposed to temperatures above its intended working range (610°C for A213 T22, e.g.). High rate corrosions happen in the presence of liquid phase on the surface of metals. There are two main reasons for high rate of liquid corrosion; first chemical reactions in liquids are generally faster than solid-solid reactions and also a liquid phase can act as an electrolyte for electrons transfer [7].

Our studies revealed that $\text{NaV}_6\text{O}_{15}$ and $\text{CrFe}(\text{VO}_4)_2$ are also formed according to following:



These compounds melt at low temperature, about 625°C , and destroy the oxide layer. Ability to form protective oxide scales has a significant effect on corrosion resistance at high temperatures. In chlorine-containing environments chlorine disturbs the formation of protective oxides and poorly protective metal oxides may form. In the present study, detailed microscopy images showed that chlorine broke the protective oxide layers in superheater tubes surfaces.

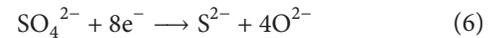
Alloying with sufficient amount of chromium to form a chromium-rich oxide may thus increase the resistance to chlorination [9]. However, corrosion under deposits is highly complex, with a number of competing reactions taking place, and the stability of metal oxides contra metal chlorides is not sufficient to accurately predict alloy performance.

Vanadium salts also attack the metal surface in various ways; they can act as an oxygen carrier or distort a metal oxide layer. Moreover, such salts are able to dissolve the protective oxide layers.

The areas on the tube surfaces which are covered by molten sulphates are generally anode. We expect to see such behaviour on the side of tubes which are exposed to fire. Therefore, as Figure 8 illustrates, the areas with thick deposits are locally cathode while the areas with thinner and molten deposit layers are locally anodes and expose highest corrosion rate by molten salts. In other words, there are 4 sites in a tube cross section: a safe area on the opposite side of the fire, a cathodic area with thick deposits, and two anodic sites with molten corrosion products as shown in Figures 10 and 11. From the electrochemistry points of view, (4) occurs at anodic part leading to metal loss:



At the cathodic sites, a variety of reactions can take place and use the generated electrons. Two most probable reactions are [7]



However, Figure 2 shows a different behaviour from the aforementioned model and the most material loss was observed in the fire-side part. It means that the area is experiencing the highest level of corrosion and cannot be a cathode. Some tubes in this study were not following the normal fire-side corrosion mechanism and behave differently. It can be because of the low thickness of deposit layer and locally high temperature (800°C) of the material surface which is leading to uniformly melting the whole deposits on the fire side of tubes. As there is no comprehensive corrosion model to predict high-temperature corrosion of all tubes, thickness measurements and corrosion monitoring of boiler tubes seem necessary since the proposed mechanisms are not able to predict the metals corrosion in harsh condition. The present corrosion models are taking the temperature of system, metallurgical parameters, and to some extent the composition of fuel to the account, while system aerodynamic parameters and the temperature of metal surfaces are not considered.

In this part, thickness measurement results are discussed. The measurement has been carried out in platen superheater, final superheater, medium reheater, and final reheater tubes of the boiler where they are prone to the high rate of damage and failure according to the power plant engineers and technical personnel. All measurements have been done three times at three different positions of the tube. Figure 12 shows the drawing of platen superheater. The nominal thickness of tubes in this part of the boiler is 4 mm and, as can be seen in

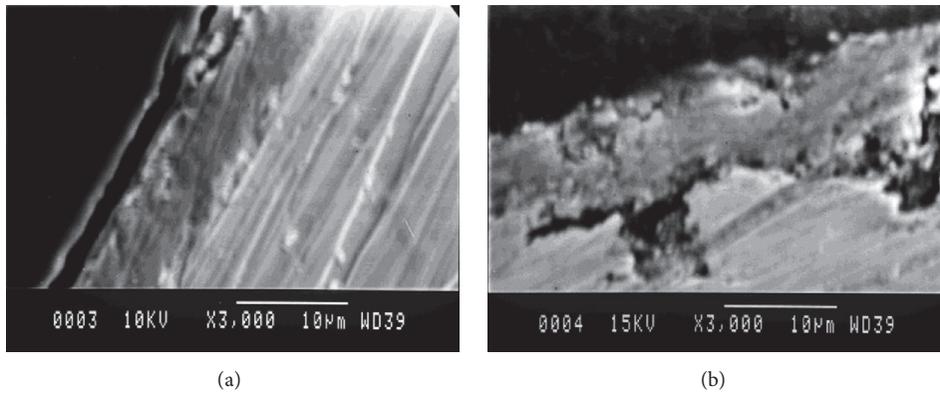


FIGURE 7: SEM images of corrosion products and deposit on the surface of (a) reheater and (b) superheater tubes.

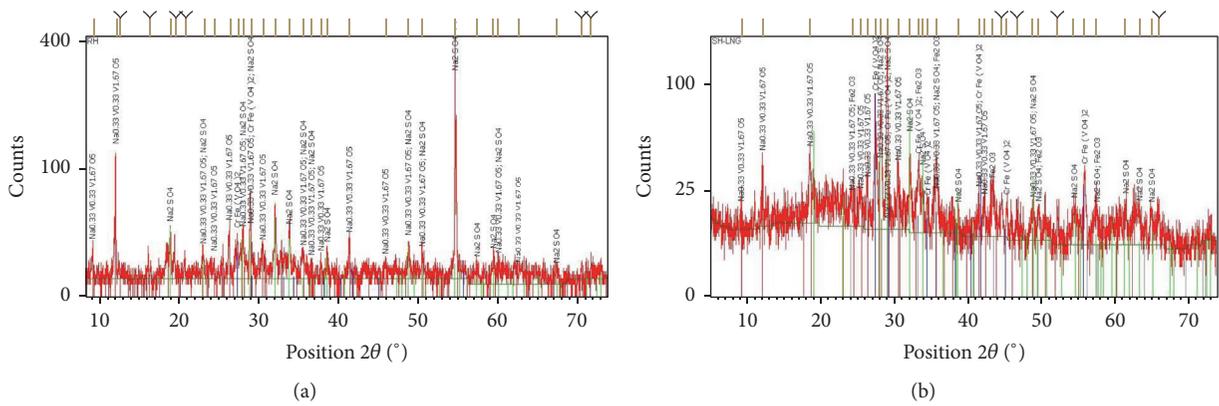


FIGURE 8: XRD patterns of corrosion products and deposits on the surface of (a) reheater and (b) superheater tubes.

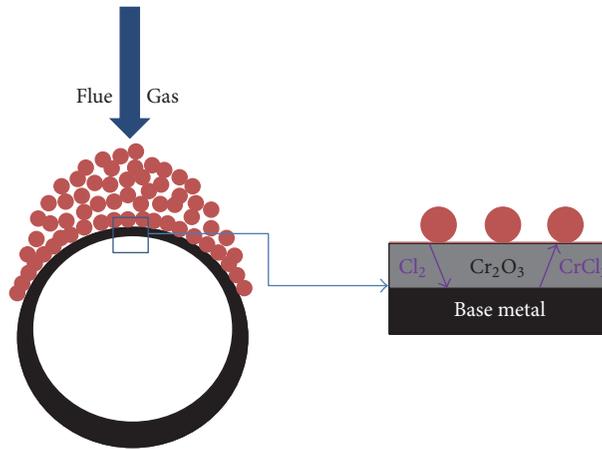


FIGURE 9: Schematic of the fire-side corrosion in the presence of chlorine.

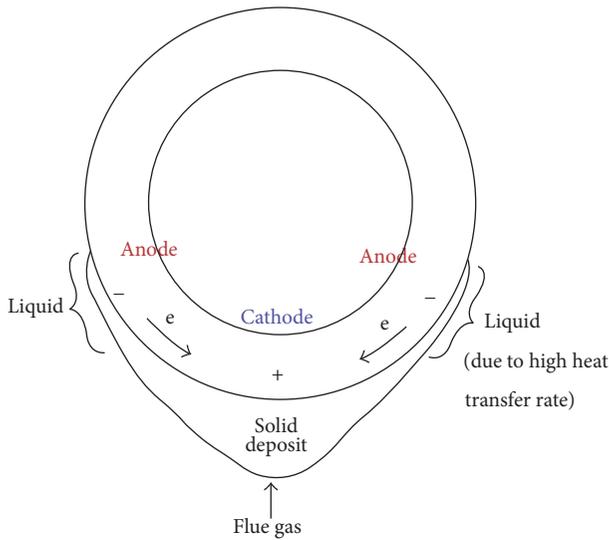


FIGURE 10: Schematic of corrosion under deposits on the tubes [7].



FIGURE 11: Cross section image of a boiler tube [10]; anodic zones with high metal loss rate are indicated.

Figure 13, the tube thickness of the fire side in some areas (position 2) is less than critical thickness value. Critical thickness is a minimum required thickness of tubes to service with no damage and failure risk in the boiler temperature and pressure. These areas are shown with red points in Figure 12.

Similarly, some areas with a thickness lower than the critical thickness in final superheater with a nominal thickness of 5.3 mm were determined (Figure 14).

The nominal thickness in medium and final reheater tubes was 3.5 and 3.4 mm, respectively. The reheaters schematics with the critical points are indicated in Figure 15.

5. Conclusion

In conclusion, we found that different anodic and cathodic regions are formed under deposits on tube surfaces. Thus,

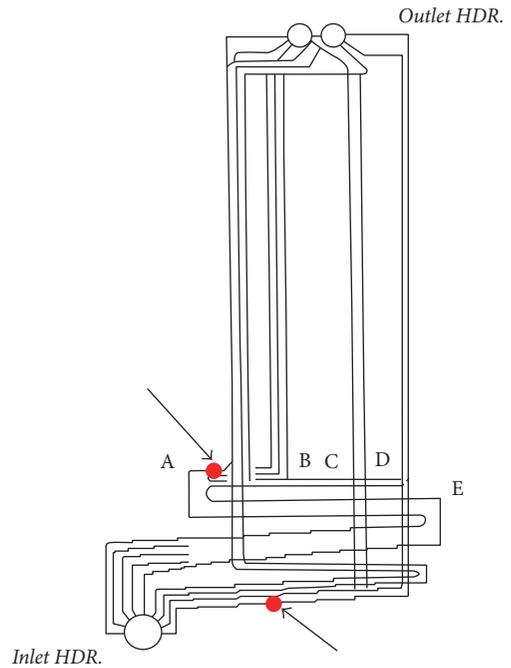


FIGURE 12: Schematic of the platen superheater with determined critical points.

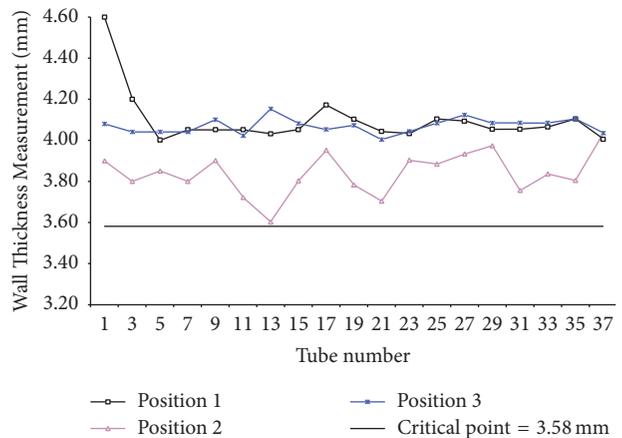


FIGURE 13: Thickness measurements of the platen superheater at zone A.

materials corrosion behaviour in harsh condition cannot be anticipated by available corrosion models since the fuels contain impurities and the tubes work in high pressure and temperature service condition. To estimate the corrosion rate and prevent unforeseen failures, frequent inspections are requested, yet the inspections are offline. Online corrosion monitoring is an appropriate approach to monitor tubes corrosion in service. Thus, monitoring probe should be placed in critical points with the highest corrosion rates. In this work, critical points in the fossil fuel boiler have been determined by UT thickness measurements. The most damage, corrosion, and metal loss were diagnosed in final superheater tubes.

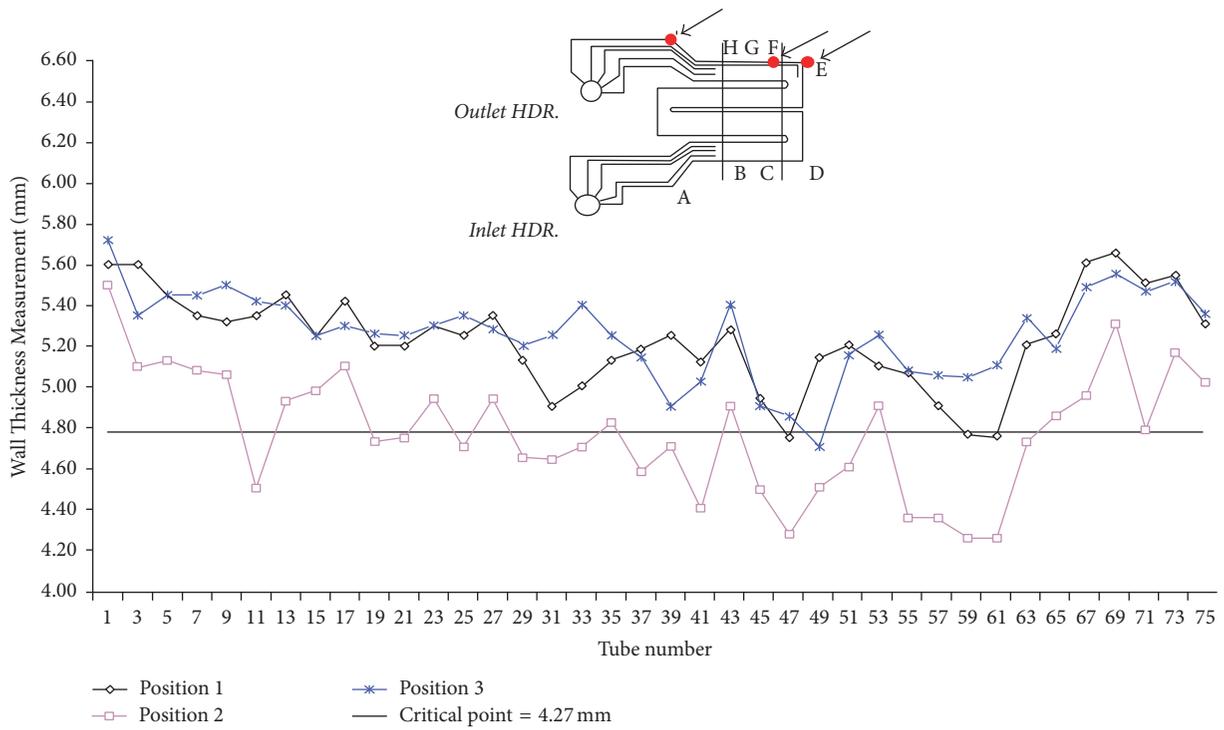


FIGURE 14: Schematic of the final superheater with determined critical points and thickness values of the tubes in zone E.

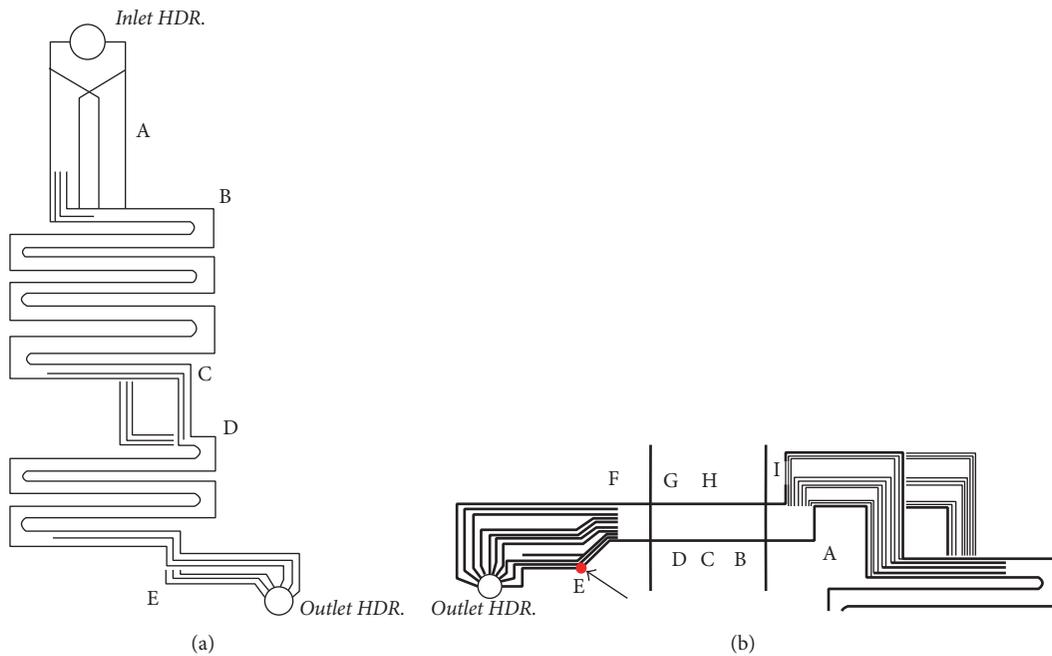


FIGURE 15: Schematic of (a) medium reheat and (b) final reheat with determined critical points.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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