

A Case Study on Causes of Scale Formation- Induced Damage in Boiler Tubes

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Abstract

Boiler tubes are exposed to several damaging factors because of their specific utilization conditions. The most important damaging factor in boiler tubes is corrosion. The causes of damage in boiler tubes in petrochemical industries are investigated in this study. These investigations include visual observations, scanning electron microscopy (SEM) images, composition and XRD analysis of scales, measurements of surface density of scales and elemental analysis of feed water and wastewater of boilers. In order to prevent damaging and corrosion in boilers it is proposed to enhance the quality of DM feed water, so that intense variations of pH and chlorine content in feed water is minimized. Meanwhile, boiler feed water treatment based on application of both mineral and organics additives is recommended to change to application of only organic additives.

Keywords: Corrosion, Scale, Boiler, pH Variations

Introduction

Degradation of boiler tubes is one of the important causes of unwanted shutdowns of boilers and petrochemical plants [1-4]. Therefore, the evaluation and assessment of damaged tubes in order to determine degradation cause (s) and consequently, applying required modifications to prevent subsequent degradations are of importance role [5-8].

There are several degradation mechanisms regarding to material, location and conditions of utilization. In this work, damaged parts of boiler tubes were compared with the undamaged ones in order to analyze the cause(s) of deterioration [9-12]. According to specific mechanism of each type of degradation, the steps of degradation analysis are varying [13-15]. The substantial steps of degradation are listed as following:

- Assessment of design parameters and utilization history of boiler
- Visual inspection of damaged part
- Chemical analysis
- Dimension measurement

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- Macroscopic investigation
- Optical and electronic microscopy investigation

Corrosion issues are considerably reduced using appropriate design (wear reduction), periodical chemical washing, oxygen control and scavenging, pH control, enhancement of feed water quality [16-20].

Experimental

Samples were taken from damaged tubes of studied boiler. Visual and microstructure of samples inspected with the aid of optical and scanning electron microscopy (SEM). Elemental analysis conducted using EDAX method. Composition of scales characterized with the aid of XRD method. Chemical composition of feed water and weight of surface area of scales determined according standard method ASTM D3843-05.

Results and Discussion

Inspection of boiler showed that one of boiler tubes has been damaged approximately 30 cm upper than its bottom, caused by corrosion of inner surface (Figure 1).

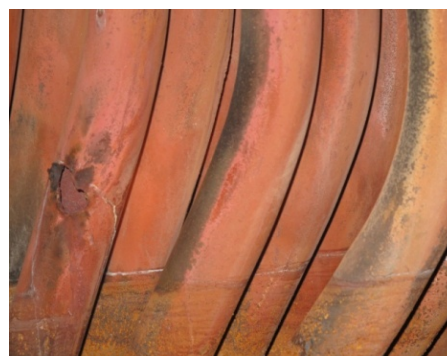


Figure 1: Tube damage

Inner surface corrosion induced deterioration and thinning of this tube is shown in figure 2. It is clear that the corrosion reduced the tube thickness. Then this tube eventually ruptured because of lack in pressure strength.



Figure 2: Tube damage at higher resolution

As it is seen in figure 3, gradual and zonal scale formation and corrosion is observed in tube side, which is exposed to fire. These are hard, sticky and dark brown colored scales. The amount of these scales is considerably high in area of 30-50 cm over mud drum, which is exposed to hot gases. The occurrence of corrosion is obvious under these scales.



Figure 3: Unholed tubes

A 6 cm piece from two tubes was selected as blank and its weight and inner surface area was measured. These blanks are immersed in standard acid solution at 70 °C. After necessary time for detachment of scales, the tubes weighed and (weight difference: inner surface area) ratio were determined as a measure of need to inspection and acid washing. These results are given in table 1.

Table 1: Results of weight of surface area of scales

Precipitation Density (mg/cm ²)	Sample Internal Area (cm ²)	Precipitation Weight (g)	Sample Weight After Acid Washing(g)	Sample Weight Before Cleaning (g)	
44.25	37.49	1.659	113.437	115.096	Bank tube Boiler (Back Gas flow side) (Top)
49.95	37.04	1.850	110.786	112.636	Bank tube Boiler (Back Gas flow side) (Bottom)

Considering the results of table 1 and according to ASTM D 3843 standard, weight of surface area in both samples is much greater

than maximum standard value (<40 mg/cm²). So, both samples belong to (highly fouled) ranking of above mentioned standard.

In order to investigate the morphology of scales and changes in microstructure of tube surface in corroded area, sample with hard sticky scale was selected and subjected to optical and scanning electron microscopy after appropriate preparation. SEM study presents that the outer surface of tube has no protective oxide coating, but the inner surface possesses a thin oxide layer and a porous scale (Fig. 4). As is depicted in fig.4, several cracks are present in oxide layer, which may lead to lack of adhesion of this layer to tube surface and hence, the lack of protection against corrosion. Because of porosity of scales and cracked character of oxide layer, corrosives diffuse into these layers and facilitate the surface corrosion of tube surface.

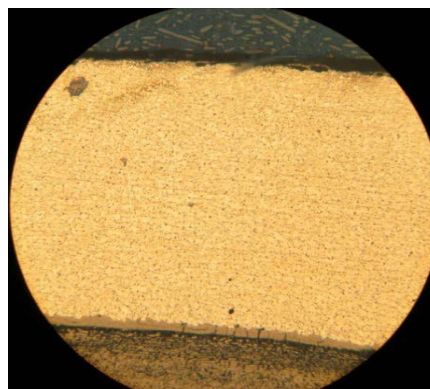


Figure 4: Cracked porous oxide layer of scale on inner tube surface

The presence of a protecting layer of scales in the inner surface of tube is shown in figure 5, which has been taken from zone located approximately 10 cm away from damaged zone. This layer possesses several cracks. Corrosives in association with water diffuse into layer of scales through these cracks. This phenomenon promotes the zonal corrosion.

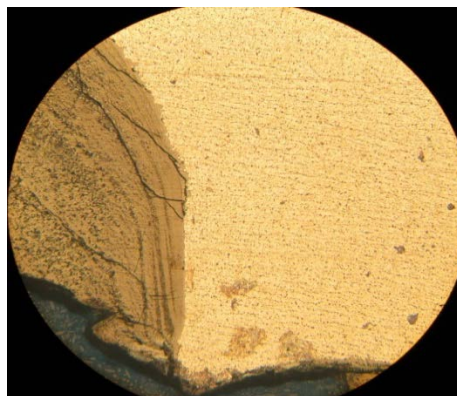


Figure 5: Numerous cracks and diffusion of corrosives into the protective layer of scale on inner tube surface

Fig 6 shows the tube cross section in damaged area. It is observed that oxide layer is cracked in several zones. As it was mentioned

earlier, the presence of these cracks facilitates the diffusion of corrosives into the surface of tube surface.

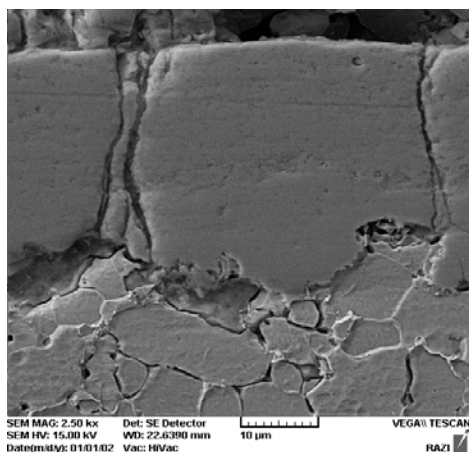


Figure 6: Corrosion initiation at the interface of protective layer and tube surface at the end of protective layer

The onset of corrosion at the interface of protecting layer and surface of tube surface is shown with higher magnification in figure 7. It is clear that the corrosion initiates at the crack tips of protective layer, which act as directing channels for corrosives to the tube surfaces. As it is shown in figures 6 and 7, diffusion of

corrosives from inner surface of tubes through these cracks to interface of oxide layer and tube surface causes corrosion.

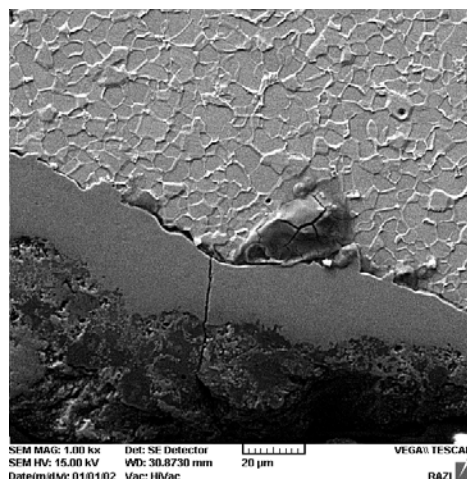


Figure 7: Tube cross section of the tube and crack in damaged zone

Chlorine map and corrosion germination under protecting layer is depicted in figure 8. This map clearly suggests chlorine ions aggregation in crack tips and interface between metal and oxide layer which causes corrosion germination in this zone.

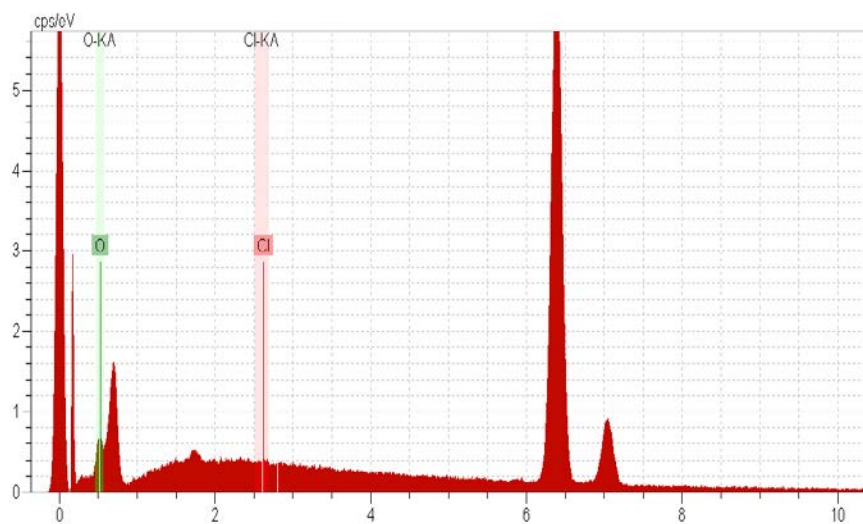


Figure 8: Map of elemental chlorine and oxygen

Analysis of 3 samples of boiler water including DM feed water, polymer plant condensed water and mud drum water is given in table 2.

Table 2: Analysis of boiler feed water

Test Method	Mud Drum water Sample	polymer plant condensed water	DM feed water	
ASTM D1293	6.66	5.22	4.80	pH(at 25°C)

St.Method 2540C	16.1	3.30	2.19	TDS(mg/lit)(at 25°C)
St.Method 2510B	30.5	6.48	4.32	Conductivity (µs/cm) (at 25°C)
St.Method 2340C	<0.1	0.3	0.1	Ca (mg/lit)
St.Method 2340C	<0.05	<0.05	<0.05	Mg (mg/lit)
St.Method 2320B	5	3	2	CaCO ₃ (mg/lit)
St.Method 4500Cl-E	4	2	2	Cl ⁻ (mg/lit)
ASTM D515	5.3	----	----	PO ₄ ³⁻ (mg/lit)

St.Method 3111 B	3.2	<0.05	<0.05	Na (mg/lit)
St.Method 3111 B	<0.05	<0.05	<0.05	Zn (mg/lit)

Data in table 2, including pH and chlorine ion concentration shows a great difference with the ones proposed in boiler maintenance manual. In other word, lack of control on feed water and wastewater quality was confirmed as main cause of corrosion in this case. Scales of steam drum were collected and subjected to analysis too. Results of qualitative analysis and XRD micrograph of these scales are given in table 3 and fig 9, respectively

Table 3: Qualitative analysis of steam drum scales

Number	Name	Chemical Composition
1	Magnetite	Fe_3O_4
2	Hematite	Fe_2O_3
3	Iron	Fe
4	Calcite	CaCO_3
5	Hydroxylfluoroxypatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
6	Wollastonite	CaSiO_3

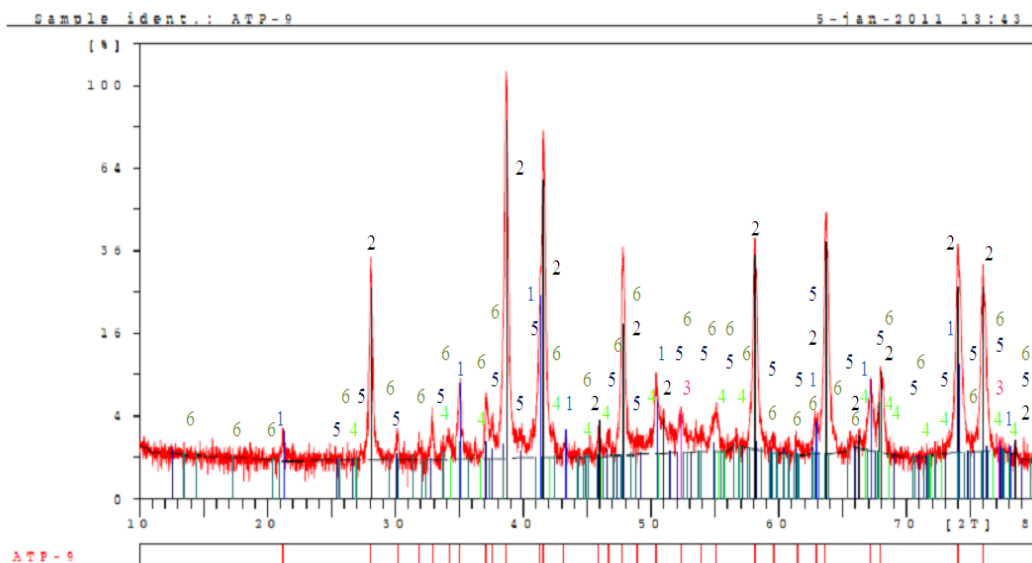


Figure 9: XRD graph of steam drum scales

Conclusions

- Scale formation in the inner surface of tubes is the main cause of corrosion and thickness reduction and damage in this study.
- Weight of surface area in scale samples is much greater than 40 mg/cm². Samples belong to (highly fooled) ranking.
- Corrosion initiates at the crack tips of scale layer, which act as directing channels for corrosives to the tube surfaces. Diffusion of corrosives from inner surface of tubes through these cracks to interface of oxide layer and tube surface causes corrosion.
- Chlorine ion aggregation in crack tips and interface between metal and oxide layer causes corrosion germination.

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