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Modelling of thermal behaviour of iron oxide layers on boiler tubes

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Abstract. Slender boiler tubes are subject to localised swelling when they are exposed to excessive heat. The latter is due to the formation of an oxide layer, which acts as an insulation barrier. This excessive heat can lead to microstructural changes in the material that would reduce the mechanical strength and would eventually lead to critical and catastrophic failure. Detecting such creep damage remains a formidable challenge for boiler operators. It involves a costly process of shutting down the plant, performing electromagnetic and ultrasonic non-destructive inspection, repairing or replacing damaged tubes and finally restarting the plant to resume its service.

This research explores through a model developed using a finite element computer simulation platform the thermal behaviour of slender tubes under constant temperature exceeding 723 °K. Our simulation results demonstrate that hematite layers up to 15µm thickness inside the tubes do not act as insulation. They clearly show the process of long term overheating on the outside of boiler tubes which in turn leads to initiation of flaws.

1. Introduction

Boilers and other heavy industrial equipment operating at high temperatures and pressure are designed for a finite life [1]. The lifetime of boilers and steam generators are between 20 to 30 years [2]. In recent years, heavy industrial structures have aged beyond their design lifetime. Indeed, most boiler tubes have been operating for more than 30 years. Therefore, frequent inspections are required to ensure that the boilers are still safe to use and it is cost effective to keep them running for longer periods. **Figure 1** shows the areas of one aqua tube wall subject to overheating.

The temperature inside the water wall tubes can reach 943 °K. However, super heaters and reheaters can operate at temperatures of nearly 1163 °K. At these temperatures, microstructural changes occur in ferritic steel structures but they do not pose a substantial risk of failure [2]. One study conducted by Graham and Waleed [3] at Saudi Aramco on 101 cases of boiler tubes concluded that 24% of tubes such as furnaces fail due to long term overheating and 6% of tubes such as super heaters fail due to short term overheating. The distribution of damage mechanisms is depicted in **Figure 2**.



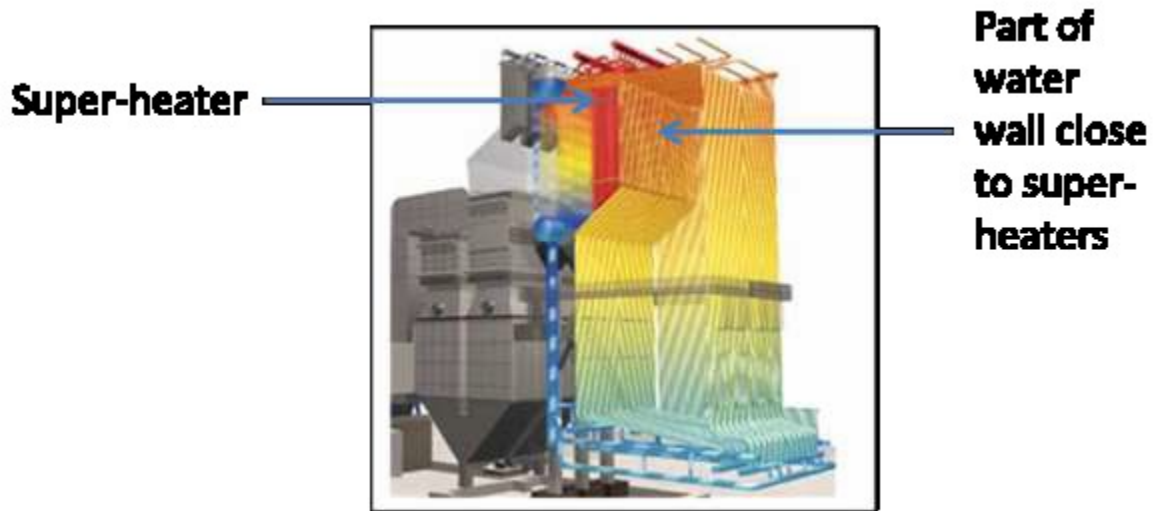


Figure 1: Hot areas shown in red are subject to overheating in a boiler [4].

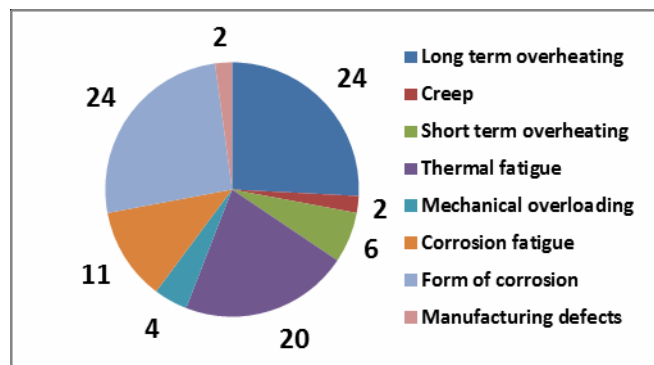


Figure 2: Boiler tubes common damage mechanisms.

Overheating is associated with the formation of different oxide layers with different thicknesses over the internal surface of the tubes where less than 3% Cr is present. At temperatures below 833 °K and high partial pressure of O₂ this film is made of two layers: 1) a magnetite (Fe₂O₃) layer and 2) a hematite (Fe₂O₄) layer. At temperatures higher than 873 °C an additional layer of iron monoxide (FeO) also appears.

The effects of the oxidation layers on the mechanical behaviour of materials manifest themselves in a reduction of the tube cross section, which increases the localised stress. The film growth causes an insulation of this section leading to a temperature increase within the cross section and acceleration of material degradation. Also, spalling of oxide scales can be beneficial to reduce the aforementioned effects, but can conversely result in tube overheating if it becomes entrapped in the system, thus reducing the flow rate in this section [5].

The presence of two or more layers of dissimilar materials, which present a mismatch between the coefficients of thermal expansion, induces stress. As consequence, a delamination or more likely a crack would occur. In this paper, we study the effects of long term overheating due to the formation of oxide layers inside boiler tubes. We use finite element method in order to model the thermal behaviour of the tube under long term overheating. The study is conduct under stationary conditions to reflect real boiler conditions.

2. Methodology

The data of operating pressure, design pressure, design temperature and feed water temperature used in our study is sourced from a VU-60 boiler [6] (see Table 1). The structure is made of seamless carbon steel and is 6000 mm long with approximately 60 mm outside diameter and 50 mm inside diameter. It is subject to heating in excess of 450 °C in one longitudinal half. In reality, the tube length, diameter and thickness depend on the work pressure and the quantity of steam height generated.

Table 1: Boiler operational parameters [6]

Model	VU-60
Operating pressure	6.423 [MPa]
Design pressure	6.816 [MPa]
Design temperature	728.15 [°K]
Feed water temperature	463.15 [°K]

One-half of the tube is expose to ambient temperature while the other half is expose to a combustion chamber. After a certain height, steam starts to evaporate from boiled water inside the tube. It is in this part of the tube where the oxide layer is likely to form and grow causing long term overheating due to the reduction in heat transfer between tube wall and steam. As the diffusion rate of these oxide layers raises exponentially with the temperature new alloys are develop slowing the growth rate. The heat transfer through a steel tube wall with iron oxide layer can be considered unidirectional as shown in **Figure 3**.

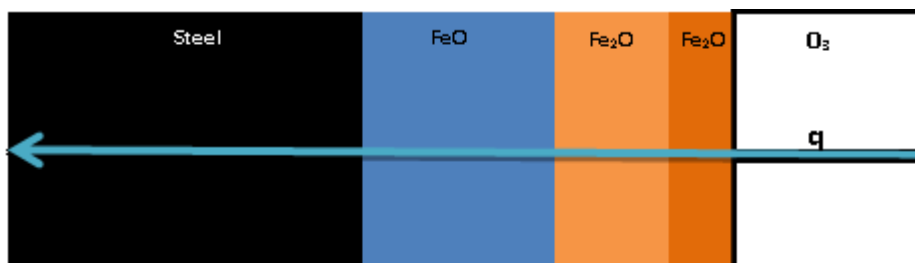


Figure 3: Heat transfer through iron oxide layer [7].

The oxide layers growing are due to the partial pressure of oxygen over the tube wall. If not all oxygen formed over the tube wall is consumed the oxygen bubble tries scape from the oxide layer. The movement of bubbles trying scape from the oxide layer creates porosity inside the oxide layer. Each oxide layer has a different energy of formation. This difference of energy of formation causes some discontinuity from one layer to another layer. In this model, we assume a unidirectional heat flux, there is a perfect adherence between the oxide layers and tube wall, and there is no porosity inside the oxides [7]. With this assumption, the heat quantity that flows through the oxide layers and tube wall is given by the equation:

$$q = k \frac{dT}{dx} \quad (1)$$

Where:

- q=heat transfer rate,
- k=material thermal conductivity,
- A=material cross section,

T=temperature in degrees Kelvin, and,
x=material thickness.

In a stationary study, equation (1) reduces to:

$$\mathbf{q} = \mathbf{k} \quad (2)$$

A

Assuming also that the oxide layer is composed of 90% wustite, 8% magnetite and 2% hematite [3], we impose a maximum oxide layer thickness of 1000 μm . Therefore, the wustite layer will have a thickness of 900 μm , the magnetite layer will be 80 μm and the hematite layer will be 20 μm .

We also consider the design temperature (728 $^{\circ}\text{K}$) as the upper limit and the inlet water temperature (463 $^{\circ}\text{K}$) as the steam temperature limit. We start our study by considering a new tube without any oxide layer and then we gradually add hematite layers of 10 μm , 15 μm and 20 μm to explore the effects on heat distribution on the tube wall. The material properties used in this study are show in **Table 2**.

Table 2: Thermo-mechanical properties.

Material	k (W/mK)	ρ (kg/m ³)	C_p (J/kgK)
Carbon steel	44.5	7850	475
FeO	3.2	7750	725
Fe ₃ O ₄	1.5	5600	800
Fe ₂ O ₃	1.2	4900	980

COMSOL Multiphysics®^[1] ver. 4.4 is used with heat transfer in solids for modelling these phenomena.

3. Results

The results obtained by isothermal contour analysis shows that the oxide layers growing act as insulation, making the tube wall facing the combustion chamber hotter than the tube wall inside the refractory wall. We also observe that as the oxide layers grow the internal surface of the tubes facing the combustion chamber becomes colder than the outside surface in the combustion chamber.

The isothermal contour of carbon steel tubes without oxide layers show that the temperature varies from 813 $^{\circ}\text{K}$ on the tube surface in contact with combustion chamber to 693 $^{\circ}\text{K}$ on the steam in contact with tube.

When a hematite layer grows over the internal surface of tube, the temperature profile varies from 783 $^{\circ}\text{K}$ to 503 $^{\circ}\text{K}$ for a 10 μm hematite oxide layer. For a 15 μm hematite oxide layer the temperature varies from 783 $^{\circ}\text{K}$ to 635 $^{\circ}\text{K}$ and for a 20 μm hematite oxide layer the temperature varies from 783 $^{\circ}\text{K}$ to 582 $^{\circ}\text{K}$.

When a magnetite oxide layer is added to a hematite oxide layer the temperature profile varies from 783 $^{\circ}\text{K}$ to 529 $^{\circ}\text{K}$ for 60 μm and 80 μm of magnetite. This indicates, as observed in the field, that at a certain magnetite thickness this oxide acts as a protective layer.

When we added a wustite oxide layer to the magnetite oxide layer the temperature profile varies from 783 $^{\circ}\text{K}$ to 476 $^{\circ}\text{K}$ for 450 μm and 675 μm wustite and from 783 $^{\circ}\text{K}$ to 529 $^{\circ}\text{K}$ for a 900 μm wustite.

Our results, using isothermal contours from COMSOL Multiphysics®, show that there is a critical thickness of oxide layer where the temperature profile changes. These changes in the temperature profile could be associated with coarsening pores and crack growth inside the oxide layer, as shown in **Figure 4** [7].

¹ Comsol Multiphysics is a trademark from COMSOL Inc.

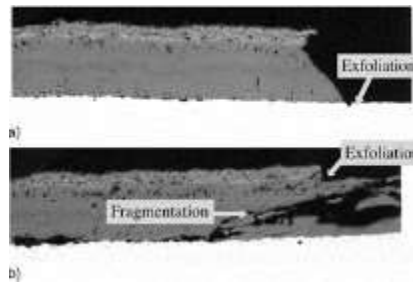
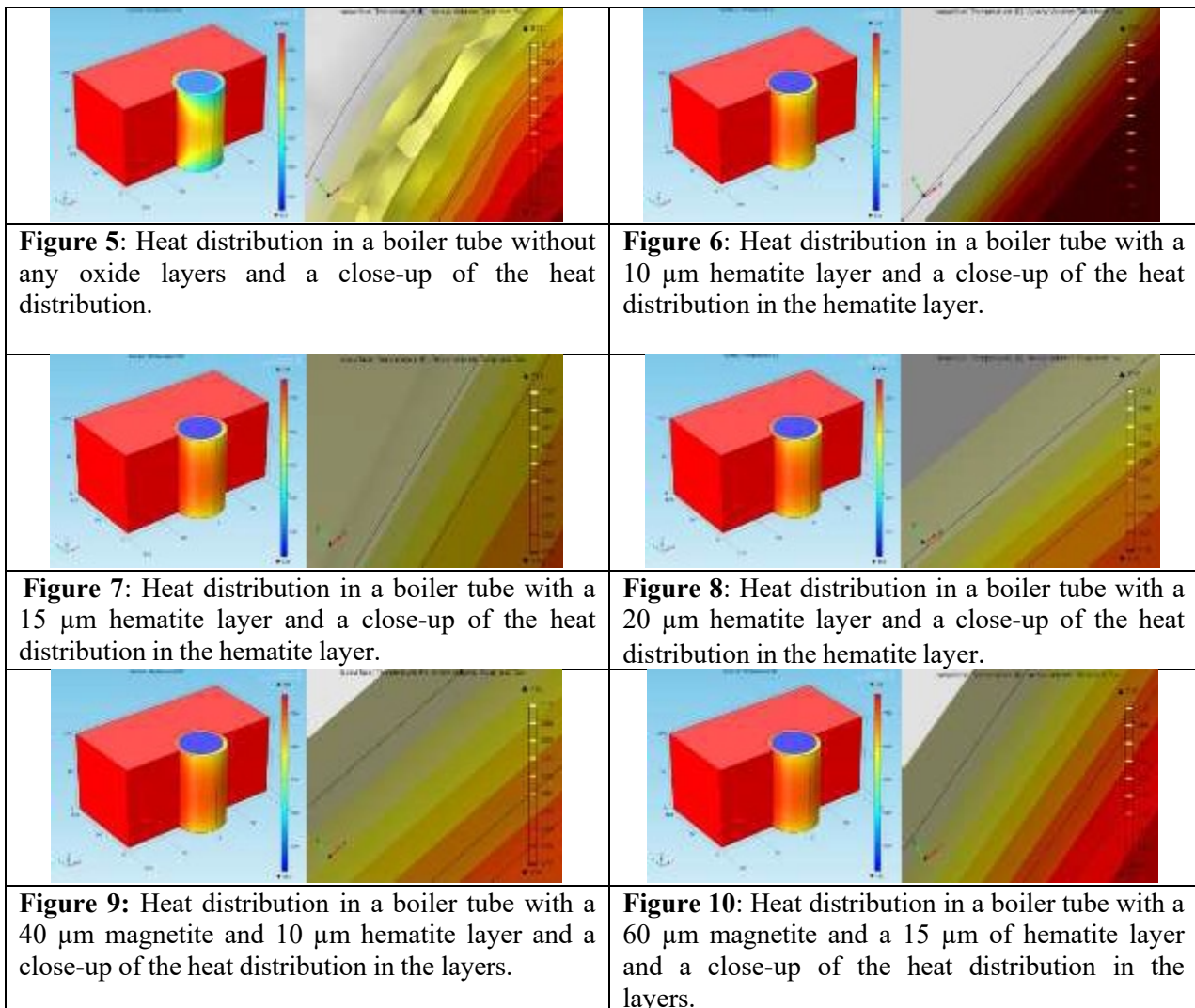
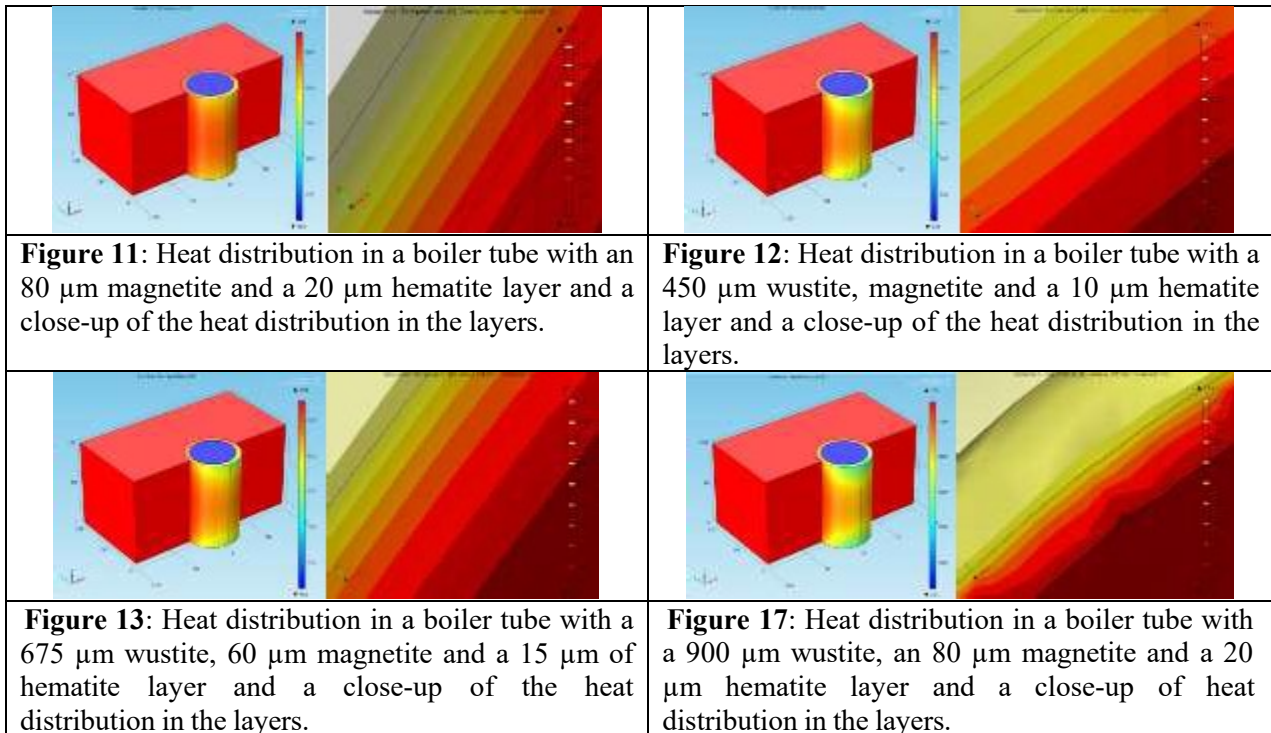


Figure 4: Picture showing coarse pores and exfoliation in hematite oxide layer [7].





Figures 17 to 20 show the refractory effects of each iron oxide layer as it grows

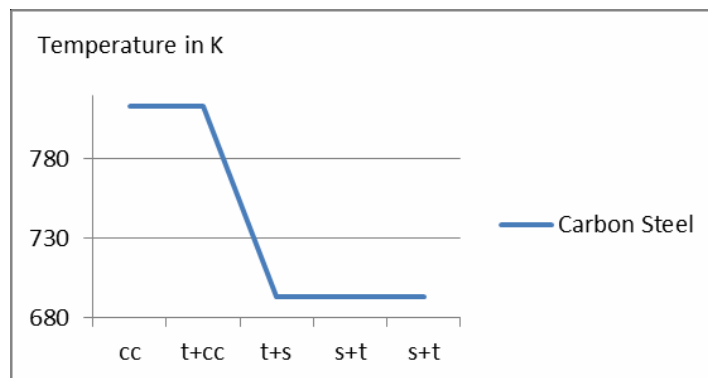


Figure 17: Graph showing a carbon steel without oxides.

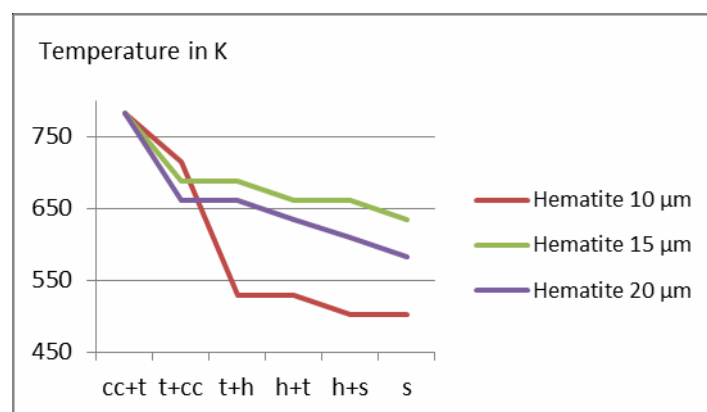


Figure 18: Graph showing the refractory effect of a hematite layer growing.

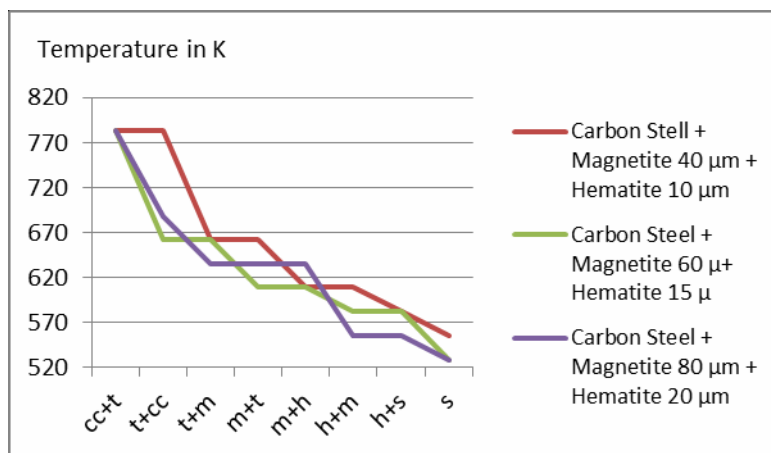


Figure 19: Graph showing the refractory effect of a hematite and magnetite layer growing.

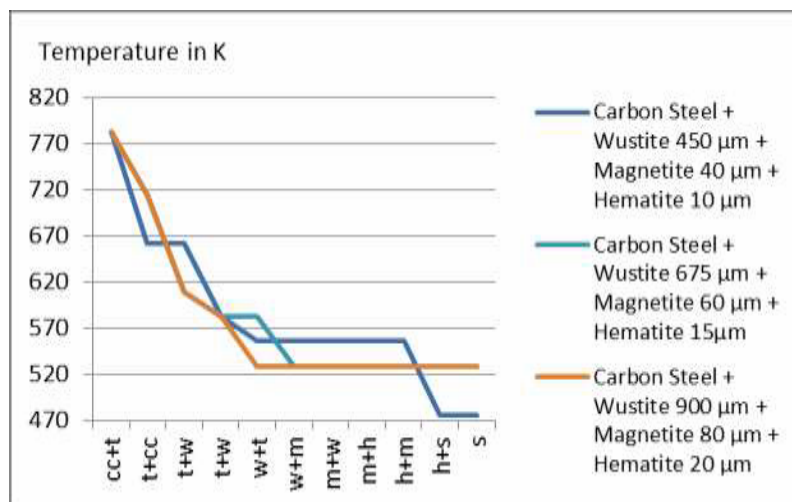


Figure 20: Graph showing the refractory effect of a wustite, magnetite and hematite layer growing.

3. Conclusion.

The simulation of oxides growing indicates that:

- 1 – A thinner layer of hematite up to 10 μm is less refractory than a thicker hematite layer over 10 μm. It seems to be due to thinner layers of hematite being more compact than thicker layers which permits oxygen to penetrate through hematite oxide to form magnetite.
- 2 – Magnetite and hematite layers are less refractory than hematite.
- 3 – Having a wustite, magnetite and hematite layer is the worst composition of oxides layers and the most refractory. This composition affects the heat distribution causing microstructural changes that leads tube failure. The refractory behaviour of this composition of oxide layers could be associated with the fact that wustite is an iron and chromium oxide. This composition, due to the chromium content, is more refractory.
- 4 – An effective control of oxygen content in the feed water, the operating temperature and the use of NDT techniques which is able to measure hematite thickness could prevent tubes failure.

Acknowledgments

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