

CORROSION IN LOW NO_x FIRING CONDITIONS

W.M.M. Huijbregts *, J.B. Janssen **, O.C.J. Rens **

Power-Gen '98, Milan, June 9-11, 1998

* KEMA Nederland B.V. , The Netherlands

** UNA Amsterdam, The Netherlands

Summary

Rather severe corrosion was observed in the 680 MWe coal fired power unit of Hemweg 8, installed with Low NO_x burners. Microscopic examinations of the tube sections showed that corrosion over approx. 30% of the side walls occurred because of:

- sulphidation
- chloride enrichment on the metal-oxide interface
- thermal fatigue cracks in combination with sulphidation and chloride enrichment on the crack tips (Alligator Skin Cracking).

To stop the corrosion, various countermeasures were taken:

- installation of gas sniffle points in the waterwalls, the following gases were measured: CO, CO₂, O₂ and occasionally H₂S
- application of curtain air and adjustments of the burners, curtain air and the burners were adjusted so that the gas environment at the water wall contained less than 2% CO
- installation of corrosion probes, the probes can be removed and new ones can be mounted during operation
- microscopic examination of the layers formed on the probes from regular examination of the probes the quality of the layer could be derived judging from the amount of sulphides and porosity
- laboratory corrosion tests in sulphidizing gases the corrosion rate constants in dependence of temperature and reducing gas composition were determined and by means of these corrosion rate constants the material loss of the waterwall tubes was calculated.

Introduction

It is well known that severe corrosion of low-alloyed steels will take place in sulphidising gas environments, such as in coal gasification and waste incineration plants. Properly protective oxide layers cannot be formed in sulphidising conditions. In such situations corrosion is controlled by selecting high alloyed materials and by regular replacement of the heat exchangers, respectively.

When the low NO_x corrosion failures from the Hemweg 8 power plant were examined, the scales were very familiar because of the extensive studies of the samples exposed under coal gasification conditions in pilot plants as well as in laboratory tests conducted at KEMA in the past (1, 2). Corrosion scales on mild and low-alloyed steels formed under oxidising firing conditions generally consist of well-adhered magnetite layers. The scales formed under reducing conditions however, are porous with many sulphide inclusions and cracks. These layers have very poor resistance to further corrosion.

Operating conditions

The supercritical coal-fired boiler at Hemweg 8 has 18 burners on 3 rows each in the front and the rear wall. The boiler has a capacity of 680 MWe. The pulverised coal blend had a maximum of 1% S and 0.1% Cl. This is the generally used coal blend for all Dutch power stations.

For a short while a small amount of sewage sludge was co-fired as a demonstration project. The amount and the composition of the sludge was such that the coal-sludge blend did not differ from the composition of the usually applied coal-blend regarding sulphur, chlorine and heavy metals.

The boiler came into operation firing coal in October 1993 and the first corrosion was noticed in December 1996, because of a leakage near a soot blower. This tube had failed because of a combination of sulphidation and the erosive action of the soot blower. Microscopic examination of the corrosion scales in detail also showed that the scale was typical of reducing atmospheres.

Tube wall thicknesses were measured over the whole water wall and several areas with severe corrosion were found. The zones most attacked in the side walls (with wall thickness smaller than 4 mm) were provisionally repaired by surface welding in January. The boiler was taken into operation again in February 1997.

In May 1997 the boiler underwent massive repairs of the water walls and by means of 36 air nozzles, curtain air was introduced. Gas snaffle points were mounted at 40 locations in the water wall. Besides, corrosion probes were mounted for regular examination of the corrosion scales formed.

In August 1997 the boiler came into operation again. The wing burners were adjusted during operation to influence flame shape and air ratio, which had the most significant result in optimising the gas atmosphere at the side walls.

Examinations

Boiler tubes

The boiler tubes were examined by means of various techniques:

- Advanced optical microscopy
- Scanning Electron Microscopy
- Radiograph Micro Analysis.

Various corrosion phenomena were found:

1. In the area of the soot blowers erosion-corrosion of the tube occurred (Figure 1). Because of the poor quality of the oxide layer and the high pressure of the soot blowers, the scale was blown away regularly.

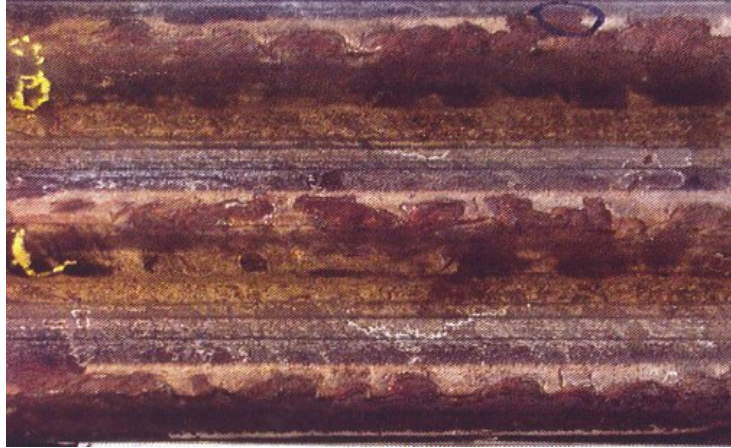


Figure 1 Tubes damaged by erosion-corrosion because of the erosive action of the soot blowers

2. The scale on the most corroded tubes in the side walls consists of various layers:
 - a topotactically grown oxide layer with many sulphides in it (Figure 2). The topotactically grown oxide layer should normally provide the protection from severe corrosion. Because of the porous structure and the large amount of sulphides, the protection effectiveness of this layer is very low.

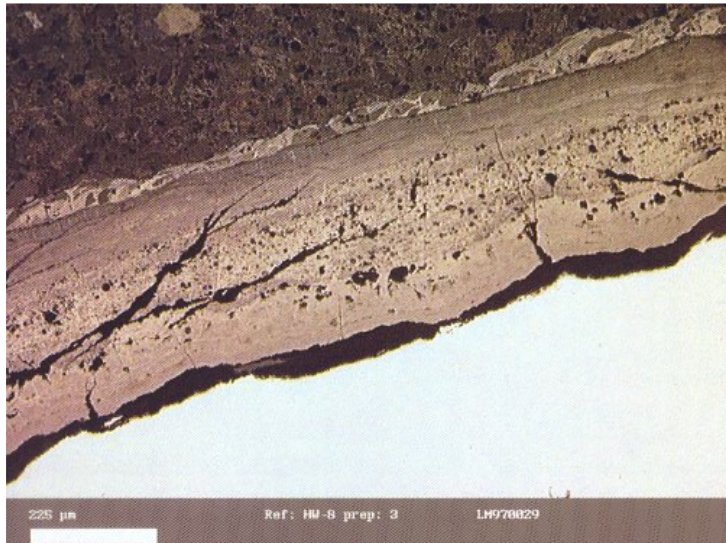


Figure 2 The topotactically grown corrosion scale. In the oxide layer many sulphides are found. The sulphides have also grown in the cracks of the oxide

- Besides, at the oxide-metal interface the element Cl was found and sometimes also intergranular corrosion (Figure 3).

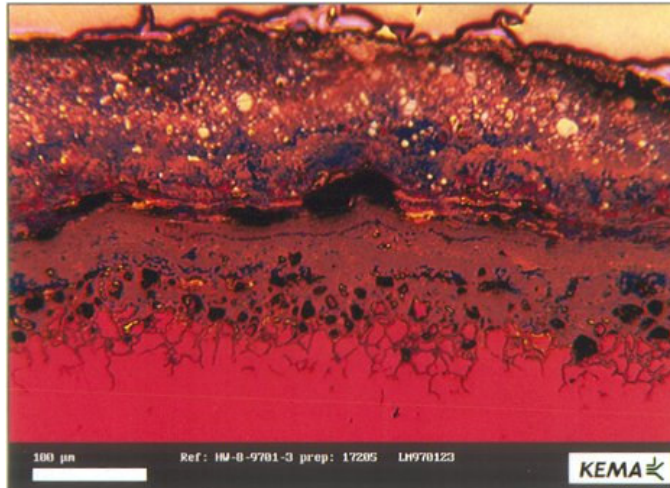


Figure 3 At the metal-oxide interface the element Cl is sometimes found. In a few cases this resulted in severe intergranular corrosion

- an epitaxial layer with many coarse crystalline sulphides and oxides and in between fly-ash particles the sulphides were present as FeS and as FeS₂, the latter species indicating a relatively severe sulphidising atmosphere
- a deposit layer of fly-ash particles; in this layer an enrichment of heavy metal compounds was found (Figure 4) The metals found were: Pb, Zn, Sb, Sn, Ni, Cu, Ge, Se and As. It was typical that the heavy metals were mainly present in the outside deposit layer. A very sharp border was often present under which the heavy metals were not noticed.

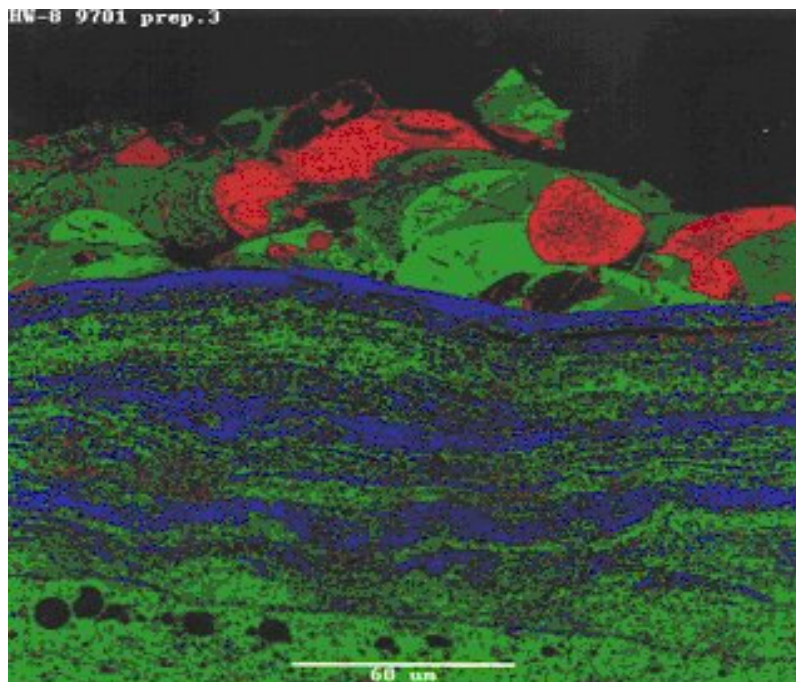


Figure 4 A Scanning Electron Microscope image, the places of presence of heavy metals are blue (detail of Figure 1).

- in some tubes on the outside of the deposit layer, round particles with dendritical structures were found. This indicates fast solidification of molten ash and pyrite particles. The composition of these particles varied from iron sulphides to CaAlKFesilicates (fly-ash)
 - many tubes had deposits of black carbon, originating from the flame impingement process.
3. Some of the tubes at the rear wall in the neighbourhood of the burners showed first indications of Alligator Skin Cracking (ASC, Figure 5) When a sulphidising atmosphere is present under moderate thermal fatigue conditions the oxide scale is less protective and the cracks are deeper and filled with sulphide containing oxide. In this situation the phenomenon is called ASC. Even with the moderate amount of chlorine content in the coal, volatile Cl compounds, like HCl and FeCl₂, will condense in reducing atmospheres at the coolest places in the oxide layers, the oxide-metal interface. The element Cl is also often found at the crack tip of the ASC cracks.



Figure 5 Typical Alligator Skin Cracks in one of the tubes at the rear water wall

Gas measurements

The composition of the gas at the sniffle points was measured, as soon as the boiler came into operation in August 1997. Over early the entire side walls the gas had a rather reducing composition. As long as the CO amount was more than 3 v% the gas was considered as too reductive, a properly protective oxide layer cannot be formed.

This was concluded from practical experiences (DOE) and from theoretical thermodynamic calculations of the sulphur, chlorine and oxygen partial pressure and the corrosion products that could be considered as the thermodynamically stable ones. If sulphides and chlorides are the thermodynamically stable ones, then the chance of formation of properly protective oxide layers is very low. So the burner settings were regulated in such a way that the gas composition was optimal for the formation of a properly protective magnetite layer.

Corrosion probes

The first probes were already removed as soon as 5 weeks after the restart of the boiler. The burners were not yet adjusted properly. The corrosion scales of the probes were examined by means of

microscopic techniques. The scale still contained many sulphides and a thick deposit layer of fly-ash and even heavy metal compounds were noticed (Figure 6).

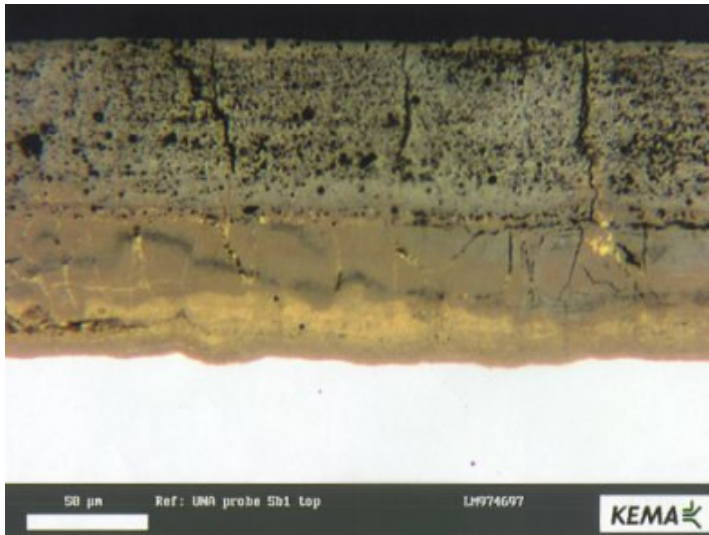


Figure 6 The high-sulphide layer on the corrosion probe, after 4 weeks of operation

After a period of approximately 4 weeks under conditions with adjusted burners, the oxide layer improved. Fewer sulphides and deposits were present on the probes (Figure 7).

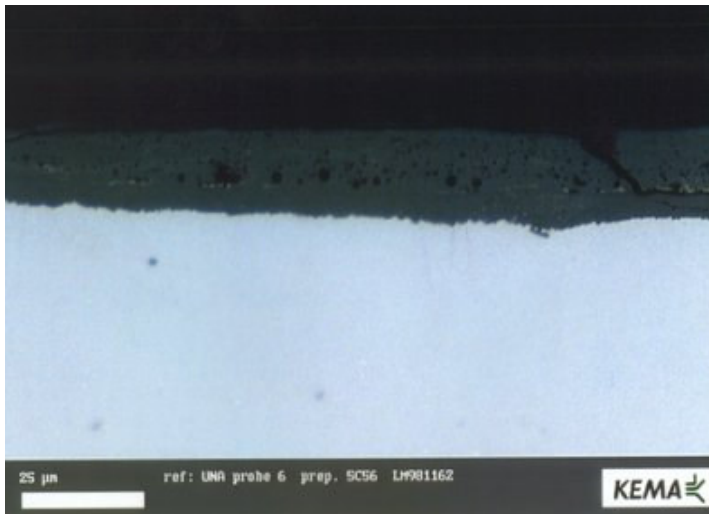


Figure 7 The oxide layer after adjustment of the burners and air curtain introduction. The layer is more protective now

Laboratory tests

Corrosion exposure tests on the 13CrMo4.4 steel were conducted in a gas mixture with the same sulphidising grade as that in the Hemweg 8 boiler. The temperature was chosen in the range of 350 to 450 °C and the exposure times were only ca. 40 hours.

Nevertheless, relatively thick oxide and sulphide layers were formed. From the thickness of the topotactical corrosion scale the corrosion rate constant was calculated, assuming a parabolic corrosion rate.

Despite the poor protective oxide layer in sulphidising atmospheres, the corrosion will decrease at longer times according to a parabolic law. This was concluded by R. John (3) and later also in our

own examinations on samples exposed in coal gasifier pilot plants and in laboratory exposures (2). The corrosion rate can be coupled to the gas mixture by introducing a gas factor (G) in the corrosion rate equation.

$$X = Kt^{0.5}$$

$$\log K = a_0 + a_1 G + a_2 1000/T$$

We define the gas factor G as being:

$$G = \text{gas factor} = \log(pS_2) + 0.5\log(pCl_2) - 0.75\log(pO_2)$$

The pS_2 , pCl_2 and pO_2 pressures are dependent on temperature and for each gas composition these pressures can be calculated thermodynamically. So for each temperature the gas factor was calculated too.

The first series of experiments were conducted in a temperature range of 400 to 450 °C and at a gas factor range from -6.5 up to 9. By means of regression analysis the constants a_0 , a_1 and a_2 could be determined for the corrosion rate constant K being 3.09, - 3.77 and 0.03, respectively.. (These values and the Figures 8 and 9 differ from the original figures because of a mistake in the original text.)

In Figure 8 the measured and calculated K values are presented. In more recent publications such regression data were also published (4,5).

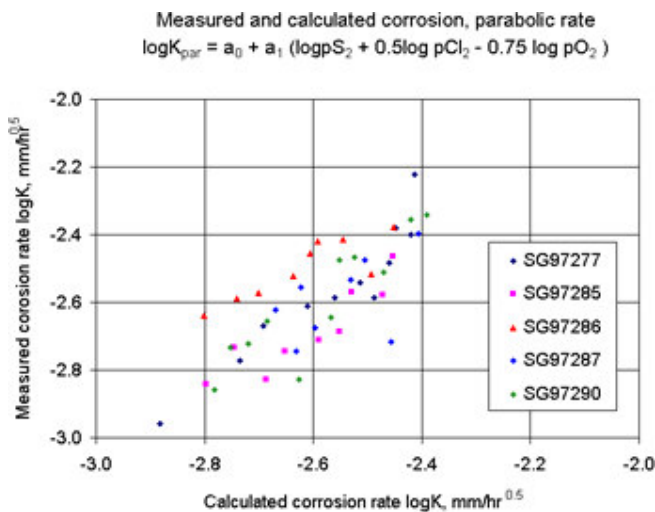


Figure 8 The calculated and measured corrosion rate constants in a sulphidising gas

Knowing these constants and the gas compositions on the water wall, the corrosion rate of the tubes can be calculated. In Figure 9 an example has been given of the thickness of the corrosion scale for the Hemweg 8 unit, assuming various gas factors for a metal temperature of 375 °C.

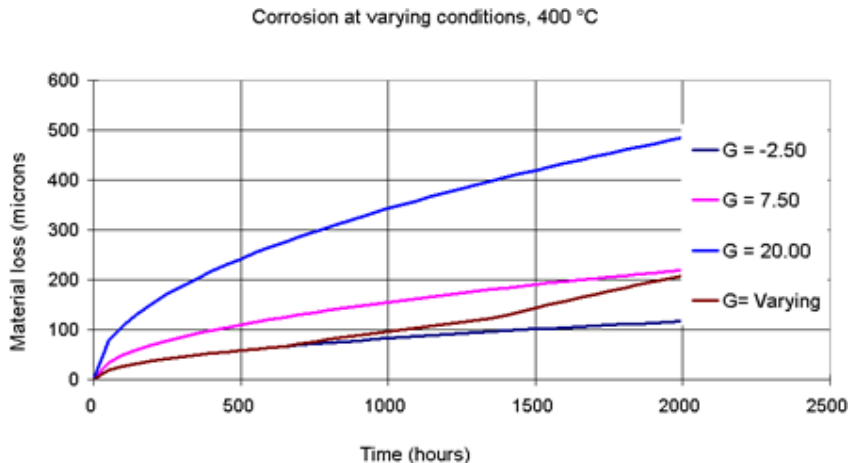


Figure 9 An example of calculating the corrosion at 375 °C of the tube wall based on the data of the gas measurements. A parabolic corrosion rate has been assumed

Conclusions

- Corrosion in the Hemweg 8 boiler was a result of low NO_x corrosion. Reducing atmospheres were present at the water wall, so that a properly protective oxide layer could not be formed.
- Such a reducing atmosphere was a result of misadjustment of the burners and lack of an air curtain.
- It appeared that the shape of the flame plays an important role in creating the optimal atmosphere at the walls for prevention of low NO_x corrosion.
- No clear indications were found that co-firing of sewage sludge has influenced the corrosion process.
- The amount of sulphides in the topotactically grown oxide layer is a measure for the protection effectiveness of the scale.
- The corrosion on the water wall tubes can be followed very easily by installing corrosion probes and determining the quality of the oxide layer at regular times.
- Measurements of the gas composition by means of sniffle points in the water wall help to control the burner adjustment. The CO-content should be at least less than 2 v%.
- By means of the corrosion rate constants, determined in laboratory experiments for various gas compositions, the corrosion rates of the water wall tubes can be calculated.
- The gas measurements and the corrosion probes are considered to be good tools to follow possible corrosion and fouling of the water walls, in particular when various coal blends and co-firing are applied.

Acknowledgement

The authors thank the board of UNA for their permission to publish the results of the examinations. During the period of examination of the boiler tubes, an inquiry was sent to many institutes and power companies for their corrosion experiences with low NO_x firing. Thanks to all those who replied and gave us the information and support in our research. Thanks to all coworkers of UNA for the discussions and their efforts put into this publication.

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