Fuel Processing Technology 141 (2016) 276–284

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Down-time corrosion in boilers

Frida Jones *, Daniel Ryde, Anders Hjörnhede

SP Technical Research Institute of Sweden, Energy and Bioeconomy, Box 857, SE-501 15 Borås, Sweden

ARTICLE INFO

Article history:
Received 22 March 2015
Received in revised form 24 September 2015
Accepted 3 October 2015
Available online 23 October 2015

Keywords:
Down-time corrosion,
Online-corrosion probe,
Deposits

ABSTRACT

Down-time corrosion can occur on boiler surfaces, e.g. furnace walls, superheaters, or economizers that are covered with hygroscopic deposits, when the temperature drops under 100 °C. This scenario takes place when a boiler is shut-down for cleaning, maintenance, or other reasons, such as unplanned shut-downs. Initially, the dry deposits will absorb moisture from the surrounding air, potentially creating a corrosive environment. After this, corrosive acids can form in the deposits.

In this study modified online-corrosion probes were used in combination with deposits taken from 6 different boilers at various locations (for example, from the furnace, the superheater, and the economizer), where the fuels have been waste, demolition wood or biomass. The deposits were ground and dried in an oven at 160 °C for several hours before exposed to a moist environment (RH 65%) during online measuring of the corrosion rate and the pitting activity. Four types of alloys were tested: low-alloy ST45.8-steel, 9% Cr ferritic P91-steel, austenitic stainless steel 304L, and Ni-based super Alloy 625.

The results for ST45.8 show that in biomass boilers a corrosion rate from negligible values up to 0.7 mm/year can be reached within a week, while waste-fired boilers can have rates as high as 1.8 mm/year. Furthermore, for some samples from waste-fired boilers show a high pitting activity already after 24 h. The tests with the P91-steel show values up to 0.16 mm/year, for samples from different locations in the boiler. For 304L and Alloy 625 the down-time corrosion was negligible even after a two-week exposure.

The ability to follow the down-time corrosion online has provided data that show that even though thought to be negligible, the risk of down-time corrosion is of significance, especially if the fuel is waste. Also, even if the initial corrosion rate is low, it increases during the first 24 h due to the exposure to moist environment, motivating immediate cleaning of the boilers after shut-down, especially on surfaces of lower steel quality.

1. Introduction

Down-time corrosion can occur on boiler surfaces, e.g. furnace walls, superheaters, or economizers that are covered with hygroscopic deposits when the temperature drops under 100 °C. This scenario takes place when a boiler is shut down for cleaning, maintenance, or other reasons, such as unplanned shut downs. Initially, the dry deposits will absorb moisture from the surrounding air, creating a potentially corrosive environment. Furthermore, depending on the chemical composition of the deposits, it is possible that corrosive substances are formed in the deposits when in contact with moisture. Down-time corrosion can also occur if improper procedures are used during boiler shut-down; this is especially true for down-time corrosion on the economizer.

To reduce the effects of down-time corrosion it is common to clean the boilers as soon as possible after shut down, either by blasting, brushing, washing or scraping the surfaces. Sometimes the flue gas is diluted during the shut-down procedure, or soot blowing takes place simultaneously, to minimize the effects. Generally, down-time corrosion is considered negligible compared to the corrosion taking place during the boiler process. However, the field of down-time corrosion still needs investigation and the process need to be further studied as several observations suggest that the corrosion rate could be substantial. If this type of corrosion can be minimized or avoided by simple measures, material investment costs could be decreased and boiler lifetime improved.

This study focuses on uniform corrosion by measuring the corrosion rate, and pitting by measuring a parameter denoted pitting corrosion index. These two corrosion mechanisms are thought to be the most important when it comes to down-time corrosion. When the protective oxide layer of steel is broken down and corrosion appears more or less over a whole surface it is considered uniform corrosion. When the corrosion is limited to smaller areas it is local corrosion, also called pitting. The formed pits are often very small but the corrosion rate can be high (several mm/year is not unusual) and results in a small but detrimental puncture of the material. This kind of corrosion is common in acidic environments with access to chloride ions.

Although there is a general consent that boilers operating on chloride-rich fuel, such as straw, have problems with down-time

---

* Corresponding author.
E-mail address: frida.jones@sp.se (F. Jones).

http://dx.doi.org/10.1016/j.fuproc.2015.10.009
0378-3820/

corrosion there are only a few available studies. This is mostly due to the difficulties performing measurements on this type of corrosion.

Some observations of down-time corrosion include a study of a coal power plant where the corrosion rate was measured with real-time corrosion probes during a three month period. During shut-down, as the temperature decreased, the corrosion went from immeasurable levels to as high as 0.4 mm/year. The corrosion occurred when moisture from the air was absorbed into the deposits forming acids. The corrosion subsided and after twelve weeks it had stopped. The study concluded that the acids were consumed and/or neutralized after this time [1,2]. Another study shows that coatings of austenitic stainless steel can be sensitive to down-time corrosion. If the coating has tension due to residues and is exposed to acid environment it can crack owing to stress corrosion [3]. In a study of a boiler in Haag, The Netherlands a high corrosion rate was measured (7–8 mm/year) on the primary superheater. It was concluded that the corrosion was mainly caused by an adjustment of the primary and secondary air but also by down-time corrosion [4,5].

A previous study has shown that online-corrosion probes are useful when studying down-time corrosion [6]. Since this study a new generation of probes is available, with improved technique and up to fifty times faster measurement cycle. They also have a very high accuracy; at a corrosion rate of 0.5 mm/year the deviation is only 0.1%, although the accuracy is lower at very low corrosion rates.

By performing online studies of corrosion rates more qualified information about the corrosion process is gained. The corrosion rate is seldom constant and it is plausible that the most damaging corrosion takes place during 10% of the time causing 90% of the material loss. By measuring online the most unfavorable corrosion conditions can be identified. This cannot be done when assuming that the material loss is divided by the exposure time, which is the conventional way of estimate corrosion rates. This type of online measurements can also be used to characterize different deposits owing to how corrosive they are, or study corrosion rates on different alloys to choose the most suitable for the wanted application. Some examples of techniques [7,8] to measure the corrosion rate online:

Electrical Resistance (ER)

Zero Resistance Amperemetry (ZRA) or Galvanic Current (GC)

Linear Polarization Resistance (LPR)/Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Noise (EN)

Out of these techniques only Electrochemical Noise can measure pitting, while the others only measure uniform corrosion.

The aim of this study is to characterize the down-time corrosion rate for different alloys with different fuels, and see if it is necessary to take action to minimize the down-time corrosion. Traditionally down-time corrosion is thought to be negligible compared to the corrosion occurring during operation. In addition, boiler shut-down time is limited; from that the material temperature reaches 100 °C during the shut-down to cleaning it is normally not more than a few days, maximum a few weeks. However, the corrosion rate could be high during this time period and cannot be considered completely negligible. Furthermore, different fuels and alloys might show different corrosion rates, hence different material losses (if any) during boiler shut-down.

It is also of interest to study how the corrosion rate changes with time. It can be assumed that moisture can be absorbed from the surrounding air when the deposit temperature reaches 100 °C, which will then increase the corrosion rate. By the absorption of moisture it is also possible that acids form in the deposits and depending on the deposit composition different acids with different strength might form at different times. It is therefore of interest to see when the maximum corrosion rate is reached, when it decreases and when it can be considered negligible. If the results would show a significant contribution to the total corrosion at some positions in the boiler, it is easy to prioritize cleaning of these surfaces at boiler shut-down.

Since deposits have different composition at different positions in the boiler, such as boiler wall, superheater, and economizer, deposits from all these positions are used in this study. Deposits will also have different compositions owing to the fuel; therefore the study includes several different boilers operating on different fuels.

2. Materials and methods

2.1. Deposit samples

To be able to perform a test that resembles the true conditions as much as possible, the deposit samples were taken from various positions in six different boilers as soon as possible after boiler shut-down. They were directly taken to the laboratory and placed in desiccators. The sample positions varied between the different boilers depending on the availability to certain positions. Table 1 shows from which boiler and position the samples were taken.

The sample preparation started with grinding of the deposits, either by hand in a mortar or in an electrical grinder depending on the hardness of the deposit. After this de-ionized water was added to the

Table 1
Plant, sample position, fuel and alloy used for the tests.

Plant	Sample position	Fuel	ST45.8	P91	304L	Alloy 625
1	Primary superheater	Waste	X	X		
1	Furnace top	Waste	X	X		X
1	Economizer	Waste	X	X		
2a	Inside center tube	Waste	X			
2a	Secondary superheater	Waste	X	X	X	
2a	Economizer	Waste	X	X		
2b	Furnace	Demolition wood	X			
3	Fly ash (superheater)	Demolition wood	X	X		
4	Furnace	Biomass	X	X	X	
5a	Loop seal	Demolition wood	X			
5b	Furnace	Waste	X	X		
6	Superheater (1)	Demolition wood	X	X		
6	Superheater (2)	Demolition wood	X	X		
6	Superheater (3)	Demolition wood	X	X		

Table 2
XRF-analysis results for chosen elements in the deposit samples.

Plant, position, fuel		Element (%)	Cl	S	K	Pb	Zn	Ca
1	Primary superheater	Waste	2.2	4.6	1.0	0.3	1.2	22
1	Furnace top	Waste	2.9	2.8	1.6	0.4	0.7	20
1	Economizer	Waste	4.8	3.5	1.1	0.2	0.8	21
2a	Inside center tube	Waste	0.2	2.4	0.7	< 0.1	2.6	3.0
2a	Secondary superheater	Waste	2.8	2.3	1.0	0.2	1.0	2.5
2a	Economizer	Waste	2.6	2.7	1.7	1.2	1.0	4.3
2b	Furnace	Demolition wood	0.4	8.0	9.0	1.4	9.2	17
3	Fly ash (superheater)	Demolition wood	3.4	3.7	2.0	0.9	2.0	16
4	Furnace	Biomass	2.1	3.5	8.7	0.1	2.3	11
5a	Loop seal	Demolition wood	0.2	4.6	3.1	9.0	1.7	13
5b	Furnace	Waste	0.1	<0.1	0.2	0.1	0.5	21
6	Superheater (1)	Demolition wood	<0.1	10	8.1	3.9	6.2	7.4
6	Superheater (2)	Demolition wood	< 0.1	9.5	8.1	3.4	3.7	8.3
6	Superheater (3)	Demolition wood	0.1	10	11	1.3	2.4	8.5