



Research article

High-temperature corrosion due to lead chloride mixtures simulating fireside deposits in boilers firing recycled wood



Hanna Kinnunen^{a,b,*}, Daniel Lindberg^b, Tor Laurén^b, Mikko Uusitalo^a, Dorota Bankiewicz^b, Sonja Enestam^a, Patrik Yrjas^b

^a Valmet Technologies, Lentokentänkatu 11, PO Box 109, FI-33101 Tampere, Finland

^b Johan Gadolin Process Chemistry Centre, c/o Laboratory of Inorganic Chemistry, Åbo Akademi University, Piispankatu 8, 20500 Turku, Finland

ARTICLE INFO

Article history:

Received 30 May 2017

Received in revised form 12 July 2017

Accepted 12 July 2017

Available online 18 July 2017

Keywords:

High temperature corrosion

Lead potassium chloride

Waste wood combustion

Superheater

Furnace wall

ABSTRACT

One of the biggest operational concerns in recycled wood combustion, is the risk for formation of low melting, corrosive deposits. The deposits present on low-temperature heat transfer surfaces (material temperature < 400 °C) are composed of alkali metals, chlorine, sulphur, heavy metals or, as is often the case, a mixture of these. K₂SO₄ is commonly regarded as non-corrosive, but there have been indications that K₂SO₄ may worsen the PbCl₂ induced corrosion. Consequently, a more detailed study with these compounds was of very high interest. This paper reports the results obtained from 24-hour isothermal laboratory corrosion tests with PbCl₂ mixed with either K₂SO₄ or SiO₂. The tests were carried out at 350 °C using low alloy steel (16Mo3). The interaction between PbCl₂ and K₂SO₄ was investigated in a furnace with a temperature gradient.

As a result, a mixture of PbCl₂ and K₂SO₄ is more corrosive than PbCl₂ mixed with SiO₂. Corrosion was noticed below the deposit's first melting temperature. However, for a mixture of FeCl₂, KCl and PbCl₂, the first melting temperature is below 350 °C which could explain the high oxidation rate observed below the first melting temperature of the deposit. A solid phase or a mixture of phases with the composition of K₃Pb₂(SO₄)₃Cl was observed in the tests with SEM/EDX for the first time.

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1. Introduction

Corrosion problems in heat transfer surfaces are limiting the rise of the steam temperatures in power boilers. Alkali chlorides are usually the main reason for corrosion of the hottest superheaters and they have been shown to be corrosive at material temperatures above 450 °C [1,2]. Alkali chloride induced corrosion has been a widely-investigated topic over the years and different corrosion mechanisms, as well as remedies, have been suggested [1–9]. One of the suggested corrosion mechanisms is so-called active oxidation, where gaseous chlorine diffuses through the oxide layer and reacts with the steel, forming metal chlorides. The formed volatile metal chlorides diffuse outwards through the oxide layer; when the O₂ partial pressure is high enough, the metal chlorides are oxidised releasing chlorine gas, which in turn partly diffuses back to the steel-oxide interface [3,4]. Another suggested mechanism is that chloride salts form eutectic melts which dissolve iron from the steel [2,5]. The third theory proposes that hydrogen chloride and oxygen are absorbed to the steel surface followed by further dissociation into H⁺, Cl⁻ and O²⁻ ions. In this process water vapour evaporates

and at the same time Cl⁻ ions migrate to the oxide grain boundaries forming metal chlorides [6].

The increased use of recycled wood containing fuels has resulted in corrosion related challenges on low-temperature heat transfer surfaces, such as furnace walls and primary superheaters. Corrosion on these cooler surfaces is caused by heavy metal chlorides or by a combination of heavy metal and alkali chlorides [5,9–12]. Typical deposits on heat transfer surfaces with a material temperature below 400 °C are composed of a mixture of alkali metals (sodium and potassium), chlorine, sulphur and heavy metals. The first melting temperature of these types of deposits can drop below 350 °C.

According to laboratory measurements, lead chloride (PbCl₂) has been found to be corrosive as a pure PbCl₂ salt and when mixed with potassium sulphate (K₂SO₄) or potassium chloride (KCl) [13,14]. A couple of possible corrosion mechanisms of such deposits are presented in the literature [5,10–12,15]. Laboratory investigations with synthetic salts on a low alloy steel have shown that corrosion caused by heavy metal chlorides initiated formation of metal chlorides and that the corrosion could be enhanced by the presence of a melt [5,10–12,15]. In a full-scale boiler, a combination of potassium and lead was shown to be corrosive at water wall temperatures (<400 °C) when using an Inconel 625 type alloy. In the same study, a low alloy steel was suggested to have been attacked by hydrogen chloride [11]. Talus et al. [16] proposed that

* Corresponding author at: Valmet Technologies, Lentokentänkatu 11, PO Box 109, FI-33101 Tampere, Finland.

E-mail address: hanna.kinnunen@valmet.com (H. Kinnunen).

lead and lead oxide (PbO) react with iron chloride (FeCl₂), forming PbCl₂, which was then combined with alkali chlorides. It has also been shown that PbCl₂ causes accelerated corrosion by forming chromates with stainless steel [17].

The role of zinc in the corrosion process is still unclear. Zinc is often present in waste based fuels [18] and zinc chloride (ZnCl₂) has been shown to be corrosive and also to lower the first melting temperature of a deposit [14,19,20]. However, in the bottom part of the furnace where the gas composition is more reducing than oxidising, zinc is most likely to condense as metallic zinc. When moving upwards in the furnace, to the secondary and tertiary air levels, the atmosphere becomes more oxidising. In an oxidising atmosphere, zinc is oxidised to zinc oxide (ZnO) at temperatures above 300 °C [10]. ZnO has been found to be significantly less corrosive than ZnCl₂ [14]. Thus, this study focuses on PbCl₂.

Sulphur is a well-known remedy against alkali chloride induced high-temperature corrosion. It has been shown that co-combustion with a sulphur-rich fuel or using sulphur containing additives, will convert harmful alkali chlorides to less harmful alkali sulphates [1,3,7–9]. Pure alkali sulphates do not cause corrosion below 500 °C [21]. The influence of sulphur on heavy metal chloride induced corrosion is, however, not yet fully understood. Combustion studies of sewage sludge together with waste wood suggested that sewage sludge reduces the amount of chlorides in the superheater deposits, and also observed a reduction of corrosion in furnace walls [22].

The purpose of this study was to identify the corrosivity of PbCl₂ mixed with K₂SO₄ in greater detail. PbCl₂ was also mixed with silicon dioxide (SiO₂) in order to pinpoint the effect of K₂SO₄.

2. Experimental

2.1. Corrosion tests

Isothermal corrosion furnace tests were carried out to study and compare the different corrosivities between two PbCl₂ containing synthetic salt mixtures. The experiments were performed using a commercial low alloy ferritic steel: EN10216-2 16Mo3. The selected steel is widely used as wall panel and low-temperature superheater material in industrial boilers. Table 1 presents the standard elemental composition of the steel in weight-%.

The test specimens were approximately 20 × 20 mm coupons with a thickness of 5 mm. The steel samples were ground with ethanol using SiC paper with a final grit of 1000 and then cleaned in an ultrasonic bath. Before the tests, the coupons were pre-oxidised in a furnace for 24 h at 200 °C. Afterwards, each coupon was covered with a salt mixture (0.25 g/specimen) consisting of either pure K₂SO₄ or 50 wt-% PbCl₂ mixed with either 50 wt-% K₂SO₄ or 50 wt-% SiO₂. SiO₂ was selected as the other salt component due to its low reactivity and to have equal amounts of PbCl₂ as weight-% in both salts. The chemical compositions of the salt mixtures are presented in Table 2. The PbCl₂-K₂SO₄ salt mixture was pre-melted at 500 °C for 30 min and ground afterwards to ensure adequate mixing of the salts.

The samples were exposed in a horizontal tube furnace for 24 h at 350 °C in ambient air. After the corrosion tests, the samples were placed in a mould, cast in epoxy and cut through the middle to reveal the cross-section. The cross-sectional surfaces were polished in kerosene using SiC paper with a final grit of 2500 and were then cleaned in petroleum

Table 1

The composition of the test steel in weight-%. The composition is informed according to the EN 10216-2 standard.

	C [wt-%]	Si	Mn	Cr	Mo	Ni	Others
16Mo3	0.12–0.20	≤0.35	0.40–0.90	≤0.30	0.25–0.35	≤0.30	Al, P, S

Table 2

The chemical compositions of the salt mixtures in weight- and mol-%.

	Salt mixtures [weight-%]			Salt mixtures [mol-%]		
	PbCl ₂	K ₂ SO ₄	SiO ₂	PbCl ₂	K ₂ SO ₄	SiO ₂
Salt 1	–	100	–	–	100	–
Salt 2	50	50	–	38.5	61.5	–
Salt 3	50	–	50	17.8	82.2	–

ether and an ultrasonic bath. The prepared samples were analysed with Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX) to measure the thickness of the oxide layer and to identify various chemical elements in the layer.

Corrosion products were identified using X-ray images, and the oxide layer thickness was determined using scanning electron microscope (SEM) backscatter images. Several SEM images were combined to form a panoramic picture of the whole cross-section. The resulting images were digitally enhanced based on differences in the contrast. An example of the treatment stages of a typical SEM panoramic picture is presented in Fig. 1.

After the panoramic images were coloured, the thickness of the oxide layer was determined for each vertical line of pixels and was recalculated to µm. The method has also been described by Westén-Karlsson [23]. The corrosion layer was determined by the thickness of the oxide layer for each line, and the corrosion attack is expressed as the mean thickness of the oxide layer.

A gradient furnace test was carried out to study the interaction between PbCl₂ and K₂SO₄ particles. A ring-shaped carbon steel sample was covered with a salt mixture containing 10 wt-% (6.5 mol-%) of PbCl₂ and 90 wt-% (93.5 mol-%) of K₂SO₄. No pre-melting of the salt components was performed. The particle diameter was 100–500 µm for K₂SO₄ and 10–30 µm for PbCl₂. The salts were exposed in the gradient furnace for 24 h using a steel temperature of 310 °C and a gas temperature of approximately 800 °C. The method has been described by Lindberg et al. [24]. The main equipment used in the temperature gradient corrosion experiments was a corrosion probe placed into a tube furnace. The corrosion probe consists of a probe and a protective tube. The protective tube surrounds the probe except for a window exposing part of the steel sample rings to the furnace environment. The outer protective tube was mounted on the air-cooled probe in order to reduce the cooling effect from the probe, and thereby to decrease the need for heating the tube furnace, resulting in more stable temperatures. The inner probe has two removable sample rings, which are equipped with thermocouples. The temperature of one of the test rings on the probe is regulated with a proportional-integral-derivative controller (PID controller) adjusting the flow of the cooling air. The temperature of the other test ring is monitored and logged during the test run. Typically, a difference of 5–10 °C is formed between the rings. The typical furnace set temperature is 980 °C, which gives a gas temperature of around 800 °C about 1 cm above the deposit, when the probe temperature is around 300–500 °C. Typical temperature gradients across the salt deposits are around 50–100 °C/mm in the radial direction. Additional thermocouples can be installed on the outside of the protective tube to measure the temperature between the sample probe and the alumina tube in the furnace. The inner probe is the same as used by Bankiewicz et al. [25].

Roughly 0.5 g of the salt mixture is applied on top of each ring on an area of about 10 mm × 20 mm. It corresponds to a thickness of about 5 mm of salt prior to the experiment. The edges of the application area on the rings are surrounded by a protective paste to hold the salt in place in case of melting of the salts. For the experiments, the probe is inserted into a cold tube furnace and both the probe and the furnace are heated to their set temperatures. As stable temperatures were reached, the experiment was run for 24 h, and

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