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Simultaneous melt and vapor induced ash deposit aging mechanisms – Mathematical model and experimental observations

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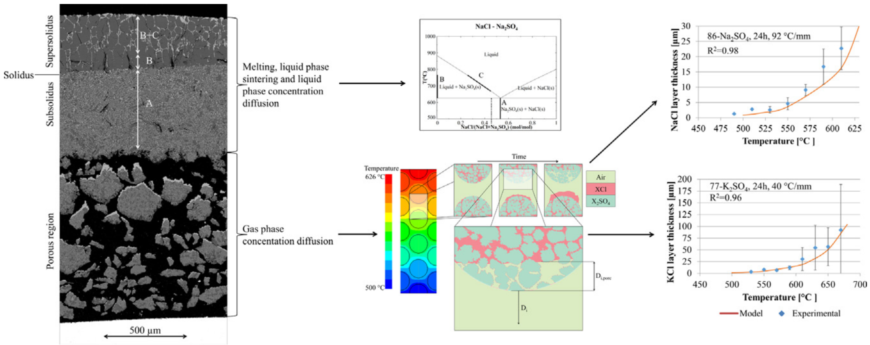
HIGHLIGHTS

- Temperature gradient observed to affect microstructure and composition.
- Liquid-phase sintering recognized as responsible for deposit densification.
- Liquid-phase migration due to temperature gradient zone melting observed.
- Gas-phase alkali chloride migration towards colder temperatures observed and modeled.

GRAPHICAL ABSTRACT



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ABSTRACT

A laboratory method was used to study the effects of temperature gradients on synthetic ash deposits consisting of KCl-K_2SO_4 or NaCl-Na_2SO_4. The cross-sections of the deposits were analyzed using SEM/EDX. The deposits were observed to form multilayered morphologies, with porous inner layers and dense outer layers. In addition, the outer layer composition was homogenized. The densification and chemical homogenization occurred by liquid-phase sintering and by temperature gradient induced liquid-phase migration. Alkali chlorides were observed to migrate in the gas-phase towards the colder temperatures. The phenomenon was modeled and recognized to be temperature gradient induced Fickian gas-phase concentration diffusion. The migration rate is directly proportional to the temperature gradient and increases exponentially as a function of the absolute temperature. The microstructure of the particle of origin for the gaseous species was observed to function as a crucial limiting factor for the migration rate. The results show that temperature gradients affect the morphology and chemistry of ash deposits and induce alkali chloride migration towards the steel surface.

1. Introduction

Steam temperature is a key parameter for increasing the electrical efficiency of boilers. Increasing the steam temperature from 400 °C to 500 °C in a condensing turbine leads to approximately 20% more power generated from the same amount fuel (Brossard et al., 2009). The steam temperatures in biomass and waste-fired boilers are in general lower than the steam temperatures in coal-fired boilers, due to the greater risk of corrosion (Hupa et al., 2017; Nielsen et al., 2000). The two important factors increasing the corrosion rate of heat exchanger steel are the presence of melt in contact with the steel surface and the content of Cl in the deposit (Skrifvars et al., 2008; Skrifvars et al., 2010).

Biomass ash compositions vary from the relatively low Cl contents with wood (Werkelin et al., 2005) to the high Cl-containing

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ash, for example with wheat straw (Baxter et al., 1998; Miles et al., 1996). K compounds are common in heat exchanger ash deposits in biomass firing (Baxter et al., 1998), while Na compounds are more typical in ash deposits in municipal waste firing (Enestam et al., 2013). NaCl, Na_2SO_4, Na_2CO_3 and their K counterparts are commonly found in black liquor recovery boiler heat exchanger deposits (Fujikawa et al., 1999; Hupa et al., 2001; Tran, 1997). In waste fired units, $ZnCl_2$ and $PbCl_2$ compound have been observed and studied to be highly corrosive (Bankiewicz et al., 2013). Kinnunen et al. (2017) showed that low melting alkali-lead-chloride mixtures are found in waste fired units and that they are highly corrosive, even with low steam temperatures. In addition to Cl species, also other halide (Br and F) species have been observed to be corrosive (Wu et al., 2015).

Volatile species, such as alkali chlorides, are known to deposit on heat exchanger surfaces from the flue gas (Broström et al., 2013). In addition to condensation build-up, alkali chlorides in general lead to an increased molten-phase or lowered viscosity of the fly ash, for example by forming low melting eutectic mixtures with alkali sulfates (Lindberg et al., 2007). The increased molten-phase in return leads to increased fouling of the heat exchangers. Although deposit build-up mechanisms are relatively well known (Baxter, 1993), less is known about the deposit aging mechanisms.

Laboratory scale high-temperature corrosion studies have mainly been conducted in isothermal conditions with a real or synthetic ash deposit on the steel surface. However, during boiler operation, there is a temperature gradient over the heat exchanger deposits. Some corrosion studies have considered the temperature gradient. Brossard et al. (2009, 2011) carried out corrosion experiments in a simulated municipal solid waste incineration. Their set-up produces temperature gradients by having a fluid–cooled metal tube placed in a combustion chamber, heated by a gas burner. The flue gas temperatures were 450–850 °C and the metal tube temperature was 400 °C. They reported that the corrosion rate of steel was affected by the flue gas temperature and the presence of melt on the steel surface. Similar results were reported by Liu et al. (2017). Their work with a laboratory-scale temperature gradient set-up shows that high-chlorine containing coal ash induces higher corrosion rates than low-chlorine containing coal ash. Kawahara (2006) conducted temperature gradient corrosion tests with synthetic corrosion deposits, applied on top of a metal surface. The tests were conducted with fluctuating metal (270–550 °C) and furnace (550–750 °C) temperatures. The study focused on corrosion and the effects of temperature gradient on corrosion mechanisms. Kawahara's results show that thermal cycles can affect the tube material, e.g. break up or deteriorate the protective oxide scale. In addition, Kawahara noted that there is a connection between temperature gradient and the penetration of corrosive species to the metal surface. Covino et al. (2003) studied the effect of temperature gradients on corrosion of metallic cobalt and carbon steel. Their results show temperature gradient induced diffusion effects within the cobalt oxide layer. Lagerbom et al. (2001) conducted laboratory-scale corrosion tests with steel samples exposed to salt deposits. They applied steel temperatures of 470–560 °C and gas temperatures of 700–800 °C. They reported distinct segregated salt layer formation and diffusion effects within the deposit due to the Soret effect (Griffiths and Phillips, 1991). Regardless of these reports, the role of temperature gradients in the high-temperature corrosion and ash deposit aging mechanisms is still unclear.

A laboratory method to study the effects of industrially relevant temperature gradients on ash deposits and corrosion of steel has been developed recently (Lindberg et al., 2016). Lindberg et al. (2016) reported temperature gradient induced species segregation in synthetic ash deposits. Similar multilayered deposit morphologies have been observed in straw-fired boilers (Hansen et al., 2000; Jensen et al., 2004; Michelsen et al., 1998). In addition to the layer segregation, Lindberg et al. (2016) found out that alkali chlorides migrate, in gas-phase, within the deposits due to temperature gradients. They presented a procedure to quantitatively determine the alkali chloride gas-phase transport in porous synthetic ash deposits and compared the results to CFD-model predictions. A similar transport phenomenon has been earlier reported by others (Carter et al., 1969; Carter et al., 1971; Lemaire and Bowen, 1982a; Lemaire and Bowen, 1982b; Nadeau et al., 1971; Nichols, 1969) as a pore motion in monolith crystals of KCl and NaCl due to a temperature gradient applied over a salt monolith.

The objective of this study is to investigate the effects of temperature gradient on heat exchanger deposit morphology and chemical composition. This paper concentrates on mechanisms involving a liquid-phase and on the gas-phase effects taking place in temperature ranges below the first melting temperature (solidus temperature) of deposits. The aim is to gain a more comprehensive understanding of the fundamental phenomena taking place in boiler ash deposits and to gain a better understanding of the alkali chloride migration within ash deposits and the factors affecting the migration rate.

2. Material and methods

The laboratory set-up used for the temperature gradient exposure consists of an air-cooled probe, on which the ash deposit was placed upon, a tube furnace, and a PID regulator. The set-up is the same as used by Lindberg et al. (2016). The probe consists of three concentric steel tubes. The outermost tube is a protective insulating tube, the middle tube holds the two sample rings and the innermost tube feeds the cooling air into the space between the middle and innermost tubes. The insulating tube prevents direct contact between the hot furnace air and the middle tube, stabilizing the experiment conditions. There is an opening in the insulating tube in order to allow direct contact between the sample rings and the hot furnace environment. The PID regulator gets its in-signal from a thermocouple that is inserted in one of the sample rings. An additional thermocouple was inserted in the other sample ring, to record the steel temperature during experiments. The ring, in which the recording thermocouple was located, was generally ~10 °C hotter than the control ring. In addition, a thermocouple was placed above the sample rings to record the air temperature during experiments, which was measured to be ~800 °C in the experiments. The furnace and probe cross-section are schematically depicted in Fig. 1.

Mixtures of KCl-K_2SO_4 or NaCl-Na_2SO_4 were used to produce synthetic ash deposits. The melting properties of the synthetic ashes were determined using thermodynamic calculations, conducted with Factsage, version 6.4 (Bale et al., 2016). The FTsalt database was used as the thermodynamic source data. The melting behavior of the synthetic ashes was studied with DTA (Differential Thermal Analysis). The DTA tests were conducted with a TA Instruments SDT Q600. Approximately 10 mg of the ash was analyzed by heating the sample to a temperature approximately 20 °C above the liquidus temperature of the ash, with the exception of four deposit compositions (see Table 1) that were not heated above the liquidus temperature to avoid loss of alkali chlorides due to volatilization. The sample was subsequently cooled to 500 °C, followed by additional heating and cooling cycles. The heating and cooling rates were 20 °C/min. Values for the solidus and liquidus temperatures were extracted from the raw data and the results are presented in Table 1 together with the chemical compositions and calculated melting properties.

The synthetic ashes were pre-treated, to achieve homogeneity, in a way that is consistent with a procedure used in isothermal cor-