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Effect of temperature gradient on composition and morphology of synthetic chlorine-containing biomass boiler deposits

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ABSTRACT

A novel laboratory method has been developed to study the chemical and physical behavior of ash deposits in a temperature gradient. Experiments with synthetic alkali salt mixtures similar to biomass boiler deposits show that alkali chlorides evaporate from hotter particles in the deposit and condense on colder particles closer to the cooled metal surface or even condense on the metal surface. Formation of a partially or completely molten layer in the outer hotter region closer to the flue gas is also observed in the experiments.

The effect of time is shown to be significant for the enrichment of chlorides as longer experiment time leads to higher amounts of vaporization, transport and condensation within the deposits.

These effects are quantitatively verified using Computational Fluid Dynamics modeling.

The transport of alkali chloride vapors becomes negligible if the deposit and metal temperature is cold enough. An enrichment of alkali chlorides towards the cooled metal surface occurs and can increase chlorine-induced corrosion of superheaters as the deposits mature over time.

The experimental observations are similar to superheater deposit morphologies observed in biomass boilers, such as straw-fired grate boilers.

1. Introduction

Fireside corrosion is an important reason for costly unscheduled shutdowns of biomass-fired boilers [1]. Corrosion of superheater materials is often connected to the presence of corrosive deposits and especially the presence of a molten phase at the alloy/deposit interface can lead to severe corrosion [2,3]. Steam temperatures in superheaters are often kept below the first melting temperature of the deposits to minimize the risk of severe corrosion [4–6]. However, it has been shown that corrosion of superheater materials may also occur even if a molten phase is not in contact with the superheater material surface, for example if the deposit contains chlorides [1,7–9]. Skrifvars et al. [7,8] showed in laboratory corrosion tests that high nickel alloys had good corrosion resistance to chloride-containing deposits at temperatures below the first melting temperature of the deposit, whereas low-alloyed and austenitic steels were corroded if the deposit contained small amounts of chlorine, even at subsolidus conditions.

Typically, the main ash-forming elements in various biomass fuels are Ca, K, Si, and Mg [10–12] but fast growing energy crops or different agricultural residues, such as wheat straw, can contain high levels of Cl, S, and P. The presence of chlorine in the ash deposits is problematic due to the formation of low-melting mixtures containing metal chlorides.

Straw-fired grate boilers often exhibit heat exchanger deposits containing high amounts of KCl and K_2SO_4 with minor amounts of Ca- and Si-compounds, such as K-silicates and Ca-silicates [13,14]. The first-melting temperature for KCl + K_2SO_4 mixtures is 690 °C [4] but the addition of Na-compounds, such as NaCl or Na_2SO_4, or corrosion products, such as K_2CrO_4 or $FeCl_2$, may lower the first-melting temperature of the deposit by several hundred degrees [1].

Superheater deposits in black liquor recovery boilers consist mainly of Na_2SO_4, Na_2CO_3, and NaCl with minor amounts of corresponding K-compounds [15]. Na and S originate from the cooking chemicals in the pulping process, whereas K and Cl are non-process elements mainly originating from the wood raw material. The deposits typically have first melting temperatures between 500 and 600 °C.

Biomass boilers firing woody biomass fuels tend to have less problematic superheater deposits compared to the straw-fired boilers, due to lower ash contents and lower levels of Cl. However, fuel mixtures containing waste fractions, such as waste wood or municipal solid waste, are highly problematic due to the presence of heavy metals, such as Zn and Pb. Deposits containing $PbCl_2$ or $ZnCl_2$ can melt at temperatures as low as 300 °C [16,17].

Hansen et al. [13] and Jensen et al. [18] have studied the detailed composition and morphology of superheater deposits from straw-fired grate boilers. Hansen et al. [13] studied both deposits from air-cooled probes and mature deposits sampled directly from the boiler. The mature deposits showed a characteristic layered structure parallel with the metal surface of the superheater. Six layers were observed and were

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as follows starting with the innermost layer next to the metal surface: a) Fe/Cr oxide layer; b) dense K_2SO_4 with small inclusions of Fe-oxide; c) porous layer of KCl; d) dense layer of KCl; e) dense layer of KCl with inclusions of ash particles; f) porous layer consisting of sintered fly ash particles containing Ca and Si. The two innermost layers were up to 100 μm thick, whereas the four outer layers were several millimeters thick. The probe deposits consisted of an inner layer of KCl and an outer layer of sintered fly ash. Jensen et al. [18] observed a similar structure of the superheater deposits with three main layers. The inner layer consisted of several sublayers with a Fe-oxide scale next to the superheater covered by a dense layer mainly consisting of K_2SO_4, followed by a porous layer of KCl flakes and then a dense layer of mainly KCl. The intermediate layer consisted of dense KCl with inclusions of silicate and Ca-rich particles. The outermost layer was very porous, consisting mainly of Si- and Ca-rich particles glued together by molten KCl and K_2SO_4. The reported steam temperatures were 400–500 °C and the flue gas temperatures were around 900–1000 °C. Based on the SEM images, some of the inner layers in the deposit had not experienced temperatures above the melting temperature of KCl (771 °C) or the solidus temperature of KCl + K_2SO_4 mixtures (690 °C), whereas the outer layers showed evidence of being molten at some point in time.

The temperature gradient from the superheater material through the deposit to the flue gas can be several hundred degrees Celsius. A schematic picture of the temperature profile of a heat exchanger/deposit cross-section is shown in Fig. 1 [19].

The maximum steam temperature in the superheater of a biomass boiler is typically around 500 °C. At the steel/deposit interface, the temperature is slightly higher. In an ideal case, the first melting temperature, also called T_0, of the deposit is higher than the temperature at the steel/deposit interface in order to reduce corrosion risks. Assuming a chemically homogenous deposit and steady-state conditions, the T_0 isotherm will be at a fixed distance from the steel/deposit surface. The melt fraction will increase towards the flue gas side of the cross-section. In case the deposit is situated on a vertical surface, the partially molten deposit will tend to flow downwards when the melt fraction is high enough or viscosity of the molten phase is low enough. A melt fraction of 70% on mass basis is a commonly used criterion for alkali salt deposits, and the corresponding temperature is called the flow temperature or T_{70} [19–21].

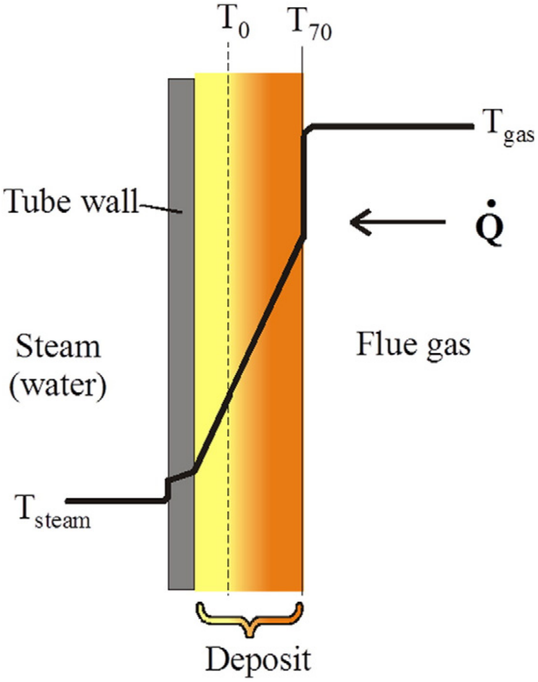

Fig. 1. Schematic picture of a cross-section of a superheater tube and deposit. The schematic temperature profile is shown with the black line, where the temperature is qualitatively depicted on the vertical axis. The T_0-line depicts the isotherm within the deposit corresponding to the first melting temperature and T_{70} depicts the isotherm corresponding to the flow temperature of the deposit. The figure is based on Backman et al. [18].

Many laboratory test setups for studying ash-related high-temperature corrosion in combustion environments have been developed for isothermal conditions [7,8,22,23]. Real or synthetic ash deposits are either applied on a steel or alloy sample, or the steel is inserted in a salt sample and subsequently inserted in a furnace at a fixed temperature and standard time. However, in boiler environments, the superheater material and the deposit are exposed to a temperature gradient that can be several hundred degrees Celsius going from the steam in the superheater, through the steel and the deposit to the hot flue gas.

Only a few experimental setups have been reported for ash-related corrosion with a thermal gradient over the superheater material and deposit. Lagerbom et al. [24], Kawahara [25] and Brossard et al. [26] have developed laboratory test setups for studying the corrosion of superheater materials in temperature gradients. Only Lagerbom et al. [24] reported details of the deposit properties. The alloy samples were carbon steel (13CrMo4–5) and a nickel based super alloy (Alloy 625), and the deposits were mixtures of Na_2SO_4, K_2SO_4, NaCl, and KCl. The sample temperature was between 470 and 560 °C, and the gas temperature in the furnace was between 700 and 800 °C. They observed that the deposits were segregated in to two or three distinct layers during the experiments. If the sample temperature was low, the deposit layer closest to the metal was similar to the original salt mixture. The upper layer had the composition of a predicted molten phase of the partly molten bulk composition and the intermediate layer had the composition of the predicted solid phase. The lowest layer was not present if the sample temperature was above the first-melting temperature of bulk composition.

It is clear from the study of Lagerbom et al. [24] that the physical and chemical properties of the deposit change over time in a thermal gradient. Some of the changes may be related to sintering dependent on local temperature [27], vaporization/condensation of volatile species, phase separation connected to the formation of a melt, and the thermal diffusion process called the Soret effect [28], where an initially homogenous system evolves a composition gradient under the thermal gradient. However, this effect occurs mainly in homogenous phases, such as aqueous solutions or melts.

Lindberg et al. [29] developed a novel laboratory method to study the effect of temperature gradients on deposit chemistry and morphology, as well as superheater steel corrosion. Different alkali salt mixtures were studied. The temperature of the deposit/steel interface was set to 400 °C or 500 °C and a deposit layer with an initial thickness of about 5 mm was applied on steel rings. The furnace temperature was set to 980 °C but the measured temperature just above the deposit surface was about 800 °C. A eutectic mixture of NaCl + Na_2SO_4 with a first melting temperature of 626 °C, showed the formation of a eutectic layer towards the hot region of the furnace, whereas the colder part remained as a porous layer. Migration of NaCl was observed in the porous layer, with alkali chloride transport from the hot region towards colder regions within the porous layer. Condensation of pure chloride on deposit particles was observed and the condensation layer thickness decreased towards the metal surface. Experiments were also made for synthetic black liquor recovery boiler deposits, which are rich in Na_2SO_4 with minor amounts of NaCl, KCl, and K_2SO_4. Enrichment of chloride close to the deposit/steel interface was also observed. The chloride enrichment was probably due to enrichment of a chloride-rich molten phase as the whole deposit was completely sintered due to the low first melting temperature (around 520–530 °C). The corrosion of the steels in the experiments was similar to experiments performed at isothermal conditions.

The objective of the present study was to investigate the effect of the melting properties on the morphology of synthetic deposits with compositions similar to black liquor recovery boiler deposits (NaCl + Na_2SO_4