Interactions of PbCl$_2$ with Alkali Salts in Ash Deposits and Effects on Boiler Corrosion

Jonne Niemi,*‡ Hanna Kinnunen,†,‡ Daniel Lindberg,† and Sonja Enestam‡

†Johan Gadolin Process Chemistry Centre, Laboratory of Inorganic Chemistry, Åbo Akademi University, Piispankatu 8, FI-20500 Turku, Finland
‡Valmet Technologies Oy, Lentokentänkatu 11, P.O. Box 109, FI-33101 Tampere, Finland

ABSTRACT: A novel temperature gradient laboratory-scale corrosion test method was used to study PbCl$_2$ migration, interactions with SiO$_2$, NaCl, Na$_2$SO$_4$, KCl, K$_2$SO$_4$, or NaCl−KCl (50:50 wt %) and corrosion of carbon steel in waste-fired boilers. Two different steel temperatures (200 and 400 °C) were tested. The temperature in the furnace above the deposits was 700−800 °C. Exposure times of 4 and 24 h were used. The deposit cross sections were analyzed using SEM/EDXA. The results show that PbCl$_2$ vaporized and condensed in the adjacent deposits. PbCl$_2$ did not interact with SiO$_2$ but caused severe corrosion. Deposits containing Na$_2$SO$_4$, K$_2$SO$_4$, and/or KCl reacted with the PbCl$_2$, forming various new compounds (Na$_3$Pb$_2$(SO$_4$)$_3$Cl, K$_3$Pb$_2$(SO$_4$)$_3$Cl, and/or K$_2$PbCl$_4$). In addition, melt formation was observed with all alkali salt deposits. Visibly more Pb was found in deposits where reactions between PbCl$_2$ and alkali salts were possible, i.e., Pb was observed to be bound to the reaction products. No measurable corrosion was observed with steel temperature at 200 °C, while steel temperature of 400 °C resulted in catastrophic corrosion. PbCl$_2$ in contact with the steel surface lead to faster corrosion than K$_2$PbCl$_4$.

1. INTRODUCTION

Combustion of recovered waste wood (or recycled wood) is known to cause severe corrosion problems on furnace walls.1−5 Waste wood’s tendency to increase corrosivity is caused by elevated concentrations of heavy metals, chlorine, and alkali metals (potassium and sodium) together with relatively low sulfur content.6−8 Especially heavy metals are known to be very corrosive, because they decrease the first melting temperatures of pure alkali salt deposits and increase the risk of molten phase induced corrosion.9,10

Several studies have focused on fireside corrosion in waste-fired boilers.1−3,5,10−17 According to the latest results, Pb forms lead−potassium chlorides in the deposits and these compounds are suggested to cause the corrosion on furnace walls.11,15−17 There are two known solid Pb−K−Cl compounds: K$_2$PbCl$_4$ and K$_3$Pb$_2$Cl$_6$. The first one was observed in laboratory testing and the latter one has been found from boiler heat transfer surfaces.16−18 However, the detailed formation mechanism of Pb−K−Cl species in boiler environments is still unknown. In laboratory corrosion experiments, interaction of K$_2$SO$_4$ and PbCl$_2$ and the formation of a caracolite-type compound K$_3$Pb$_2$(SO$_4$)$_3$Cl has been observed.16 In the same publication, a novel gradient corrosion furnace method was used for the first time for Pb-containing salts. The novel testing method has been used earlier for alkali chloride-alkali sulfate mixtures, increasing the understanding of alkali chloride migration within boiler tube deposits and clarifying the importance of understanding the effects of temperature gradients on corrosion reactions.16,20 Temperature gradients may play a vital role in PbCl$_2$ induced corrosion by the means of local melt formation and proximity of a molten phase to the tube surface.17

Waste wood is composed of different types of wood fractions and can also include high amounts of Zn. Based on laboratory studies, ZnCl$_2$ has been proven to be corrosive at similar temperatures as PbCl$_2$.13,21,22 However, Zn oxidizes easily in the areas where corrosion has been found to be the most severe.5,19 ZnO is also shown to be corrosive but at higher temperatures than usual furnace wall material temperatures.13 Thus, it is assumed that the main corrosion issues when firing recovered waste wood are caused mainly by Pb associated with Cl.

Despite the fact that S is a good corrosion prevention agent against alkali chloride induced corrosion, its effectiveness against PbCl$_2$ induced corrosion is still not fully understood.14−30 Sewage sludge was reported to decrease the amounts of K, Na, and Cl on the furnace wall deposits leading to reduced corrosion of Ni-based 625 alloy.28 However, carbon steel was not included in the test matrix. Folkeson et al.26 reported the effect of S addition on fireside corrosion of stainless and low alloyed steels. They reported a positive effect with stainless steel but low alloyed steel corroded regardless of the S feed. In addition, laboratory measurements have shown K$_2$SO$_4$ to react with PbCl$_2$ and to form a caracolite-type mixture, K$_3$Pb$_2$(SO$_4$)$_3$Cl, which also induces increased corrosion with carbon steel material.16

The purpose of this study is to investigate the interaction of gaseous PbCl$_2$ with K and Na salts that are found in boiler deposits, with special focus on the formation of corrosive alkali lead compounds. The laboratory tests were performed using two different synthetic deposit materials that were applied on an air-cooled probe on adjacent alloy samples separated by a heat-resistant barrier. The first deposit component was always PbCl$_2$ and the other was either NaCl, Na$_2$SO$_4$, KCl, K$_2$SO$_4$, KCl−NaCl mixture, or inert SiO$_2$. Although in a boiler
environment, other ash forming elements are also likely to affects the behavior of PbCl₂, this paper concentrates on a simplified system in order to gain a better understanding of the detailed phenomena. The focus was set to study the vaporization, condensation, and reactivity of PbCl₂, within the other deposit. Two different material temperatures (200 and 400 °C) were selected to examine the effect of the temperature and temperature gradient for the gas-phase migration of chlorides and reaction with the other component for formation of a possible melt. The higher steel temperature (400 °C) was chosen to represent a typical superheater temperature used in waste-fired boiler units, while the lower temperature (200 °C) was chosen as a comparison temperature.

2. EXPERIMENTAL SECTION

The reactivity and migration of PbCl₂ was tested in SiO₂, NaCl, Na₂SO₄, KCl, K₂SO₄, and KCl–NaCl (50:50 wt %). The principal experimental equipment was the same as used by Lindberg et al.¹⁹ and Niemi et al.²⁰, an air-cooled probe with interchangeable steel rings covered with salt deposits (Figure 1). The probe is inserted into a tube furnace where it is heated up. Once the probe reaches its target temperature (200 or 400 °C), cooling is initiated and the probe temperature is kept at the target temperature throughout the experiment. The furnace is heated to its target temperature of 980 °C (steel temperature at 200 °C) or ∼800 °C (steel temperature at 400 °C) above the deposits. The difference in the probe and furnace temperature leads to a steep temperature gradient over the deposit material, simulating a temperature profile of a boiler deposit. Deposit thickness of approximately 10 mm was used throughout. This resulted in a temperature gradient of ∼50 °C/mm over the deposit. At the end of the experiment, the probe is removed from the furnace and rapidly cooled down to room temperature.

After cooling, the deposit material is glued to the sample ring with a few drops of epoxy resin. Once the epoxy is set, the probe is disassembled and the deposit samples are cast in epoxy resin, cut to reveal a cross-section, and the cross-section is analyzed and characterized using scanning electron microscopy and energy dispersive X-ray analysis (SEM/EDXA).

Differing from the experiments of Lindberg et al.¹⁹ and Niemi et al.²⁰, where two test rings were covered with the same deposit material, in this study the two steel rings housed in the probe contained different deposit materials. The ring no. 1 contained PbCl₂ and the ring no. 2 contained either SiO₂, NaCl, Na₂SO₄, KCl, K₂SO₄ or KCl–NaCl (50:50 wt %) (Figure 1). The deposit materials were separated by a wall formed out of fire-sealant paste consisting of sodium silicates and kaolin.

The KCl–NaCl (50:50 wt %) mixture was premelted at 800 °C to form a homogeneous mixture, ground, and sieved to a size fraction of 53–250 μm. The same size fraction was also used for the other alkali salts.

The different deposit materials were tested with different steel temperatures (200 and 400 °C) and exposure times (4 and 24 h). The same furnace set-temperature (980 °C) was used throughout. As the temperature profiles are expected to be similar between samples with the same temperatures but with different target deposit materials, also similar vaporization and diffusion behavior for the PbCl₂ was expected to occur in experiments with different target deposit materials. The condensation of PbCl₂ in the target deposit might differ between different compositions due to reactions and interactions (e.g., melt formation). The experimental matrix is summarized in Table 1. The steel material used in the experiments was carbon steel EN 10216-2 P235GH (composition shown in Table 2).

3. RESULTS AND DISCUSSION

3.1. Deposit Chemistry. 3.1.1. SiO₂ and PbCl₂. The experiments with SiO₂ were conducted in order to study the gas-phase migration of PbCl₂ to, and within, a chemically inert deposit. SiO₂ was chosen as the deposit material because it does not react or form melt with PbCl₂. The inertness offered a way to focus only on the migration of PbCl₂ without considering the reactions or interactions with the deposit material.

In the 24 h/200 °C experiment, there were no signs of PbCl₂ in the SiO₂ deposit. In addition, no significant corrosion of the steel was observed. Gas-phase migration was confirmed as the migration mechanism in the SiO₂ deposits with steel temperature at 400 °C. In the 4 h/400 °C experiment, high amounts of PbCl₂ were found within the SiO₂ deposit and even on the oxide layer/steel surface (Figure 2). In addition, significant corrosion was observed already after 4 h exposure.

In the 24 h/400 °C experiment, a thick oxide layer was observed in the SiO₂ covered sample. Pure PbCl₂ was observed within the oxide layer but not in the deposit layer itself. Although the deposit layer did not contain PbCl₂, it is likely the PbCl₂ migrated to the oxide layer via gas-phase.
In the 4 h/400 °C experiment, the PbCl₂ source deposit was observed to be almost depleted at the end of the experiment. In the 24 h/400 °C experiment, the PbCl₂ source was observed completely depleted. This indicates that in the 24 h experiment, with steel temperature at 400 °C, there had not been any significant PbCl₂ feed into the gas-phase after 4 h from the experiment start. The lack of continuous PbCl₂ feed results in a case where the PbCl₂ that had already migrated into the SiO₂ deposit would revaporize into the gas-phase once the partial pressure of PbCl₂ in the furnace air drops. This explains the lack of PbCl₂ in the SiO₂ deposit in the 24 h/400 °C experiment and possibly also in the 24 h/200 °C experiment.

3.1.2. NaCl and PbCl₂. The experiments with NaCl showed that PbCl₂ migrates to, and within, the deposit via gas-phase. In the 4 h/400 °C experiment, clear signs of sintering of particles indicate melt formation within the deposit during the experiment. Pure NaCl has a melting point of 801 °C, whereas the solidus temperature of NaCl–PbCl₂ is 409 °C. In addition, PbCl₂ was observed entrapped within NaCl particles indicating eutectic melt formation. The solidus temperature corresponds well with the fact that PbCl₂ inclusions in the NaCl particles were observed also in particles just above the steel surface, i.e., close to 400 °C.

Similar to the 4 h/400 °C SiO₂ experiment, the corrosion layer was observed to include PbCl₂. However, the amount of PbCl₂ was observed to be lower and the oxide layer was thinner. This can be explained by the eutectic melting of the NaCl–PbCl₂ system. In a case where there is a surplus of NaCl when compared to PbCl₂, all of the PbCl₂ will be included in the liquid-phase, lowering its partial pressure in the gas-phase and inhibiting the gas-phase migration to the steel.

In the 24 h/400 °C experiment with NaCl, only minor amounts of PbCl₂ were observed within the deposit. However, signs of melting were observed throughout the deposit, indicating a presence of PbCl₂ during the experiment. In addition, the oxide layer was observed to be rich in PbCl₂.

3.1.3. Na₂SO₄ and PbCl₂. In the 24 h/200 °C experiment with Na₂SO₄, relatively high amounts of Pb and Cl were observed within the deposits. The Pb species were found within a certain distance from the steel and also in an enriched area (see Figure 3). The deposit particles close to the hot furnace air had clearly experienced melting during the experiment, indicating PbCl₂ presence as pure Na₂SO₄ has a melting point of 884 °C. In addition to melting, Na₂SO₄ and PbCl₂ were observed to react with each other and form Na₃Pb₂(SO₄)₃Cl, a known mineral caracolite (melting point 701 °C), which has also been observed in waste fired boilers. Formation of Na₃Pb₂(SO₄)₃Cl from a reaction between Na₂SO₄ and PbCl₂ would also yield NaCl according to reaction 1. NaCl was also observed within the deposit, supporting the proposed overall reaction.

\[
3\text{Na}_2\text{SO}_4(s) + 2\text{PbCl}_2(g/\text{l/s}) \rightleftharpoons \text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}(s) + 3\text{NaCl}(g/\text{s})
\]
The formation of NaCl within the deposit further affects the melting behavior of the deposit. Binary mixtures of Na₂SO₄–NaCl and NaCl–PbCl₂ have solidus temperatures of 626 and 409 °C, respectively. To our knowledge, the thermodynamic properties of the Na₂SO₄–NaCl–PbSO₄–PbCl₂ have not been evaluated in the literature. However, if the trend is similar as with the K₂SO₄–KCl–PbSO₄–PbCl₂ system, the solidus temperature of the Na₂SO₄–NaCl–PbSO₄–PbCl₂ system should not be significantly lower than the solidus temperature of the NaCl–PbCl₂ system. Approximately in the middle of the deposit, a threshold between a sintered and nonsintered layer was observed, indicating the location of melt within the deposit (Figure 3). The region was estimated to be found in the temperature region of ~400 °C.

In the 24 h/400 °C experiment with Na₂SO₄, no Pb was observed within the deposit but high amounts were observed in the oxide layer, similar to the corresponding SiO₂ and NaCl experiments. However, Cl was observed in minor amounts within the deposit, in the form of NaCl, indicating a similar Na₃Pb₂(SO₄)₃Cl formation, as in the 24 h/200 °C experiment, had taken place. In addition, Na₃Pb₂(SO₄)₃Cl was observed on the oxide scale. The NaCl was exclusively observed on the furnace-facing side of particles, indicating gas-phase migration toward the steel surface via vaporization-condensation of NaCl, or that the furnace-facing side was the reaction site. Signs of melting were observed at constant distance from the steel surface, roughly in the middle of the deposit. With steel temperature at 400 °C and the outer layer of the deposit at a maximum temperature of ~800 °C, the middle of the deposit would have experienced temperatures of ~600 °C. This is close to the Na₂SO₄–NaCl solidus temperature (626 °C).

3.1.4. KCl and PbCl₂. In the 24 h/200 °C experiment with KCl, clear sintering of the deposit was observed. The uppermost particles of the deposit had not sintered, but closer to the steel clear signs of sintering were observed. This implies that sufficiently low local temperature was needed for the condensation of the PbCl₂. The temperature in the area, where the Pb-species were observed, was estimated to be ~400–500 °C during the experiment.

The majority of the Pb-containing species observed in the deposit were found just above the region where the sintering started, in the form of K₂PbCl₄. This suggests that the PbCl₂ reacted with the KCl of the deposit, forming K₂PbCl₄ (reaction 2). There is also a possibility of forming KPB₅Cl₄ (reaction 3), but no KPB₅Cl₄ was observed in the experiments. A possible formation route for K₂PbCl₄ is via gas-phase KPB₅Cl₄ (reactions 4 and 5). According to the SEM/EDXA results, the main reaction product was K₂PbCl₄, which is logical as PbCl₂ is the limiting reactant and there is a surplus of KCl. The lowest temperature, where melt can be formed in the PbCl₂–KCl system, is 409 °C with PbCl₂ present in the deposit. The peritectic temperature of K₂PbCl₄ is 488 °C, which is in the range where the Pb-species were observed within the deposit. A zoomed in image (right) showing the K₂PbCl₄ within the deposit. Figure 4. SEM backscatter image of the 24 h/400 °C KCl deposit and a zoomed in image (right) showing the K₂PbCl₄ within the deposit.

The Pb-containing species were observed in higher quantities (Figure 4). The Pb-containing species found within the deposit layer were either observed on the furnace-facing side of particles or entrapped within a KCl particle or matrix. The presence of Pb-species on the furnace-facing side of KCl particles implies gas-phase migration to be responsible for the Pb presence in the deposit. The mechanism is similar as described by others.19,20 The higher amount of Pb-species found in the 400 °C experiment than in the 200 °C experiment also supports gas-phase migration. The higher temperature at the PbCl₂ source deposit results in higher concentration of PbCl₂ in the gas-phase, which increases the condensation of PbCl₂ at the target deposit. The entrapped Pb-species in and between KCl particles indicate that melting has occurred. Similar to the 200 °C experiment, the Pb-species found in the deposit were mainly K₂PbCl₄.

Compared to the SiO₂, NaCl, and Na₂SO₄ experiments with steel temperatures at 200 and 400 °C and exposure time of 24 h, more Pb was found in the corresponding KCl deposits, with the exception of the 24 h/200 °C experiment with Na₂SO₄. The formation of K₂PbCl₄ can explain the difference. K₂PbCl₄ does not occur in the gas-phase, which means that for K₂PbCl₄ to reevaporize from the KCl deposit, it would need to react back to KCl and PbCl₂ (reaction 2), or to KPbCl₃(g) and KCl (reaction 5). The need for reactions to form components that are able to vaporize could function as a limiting step for the revaporization back to the furnace.

3.1.5. K₂SO₄ and PbCl₂. In the 24 h/200 °C experiment with K₂SO₄ only minor amounts of Pb and Cl were found in the deposit layer. The Pb and Cl that were observed, were found in between K₂SO₄ particles. In addition, there were signs of sintering at the outer edge of the deposit. K₂SO₄ has a melting point of 1069 °C and has a low vapor pressure at the experiment conditions, which indicates that at some point during the experiment there had been Pb and Cl containing species present within the deposit to induce sintering.

With steel temperature at 400 °C, high amount of both Pb and Cl were found within the deposit. In addition, the whole deposit displayed a sintered structure. Close to the steel surface, there was a compact region (Figure 5) that was enriched in Pb and Cl. Pb and Cl were also observed both above and below the compact region, mainly on the furnace-facing side of the particles. Similar behavior was reported by Kinnunen et al.16 in synthetic premixed deposits consisting of PbCl₂ and K₂SO₄.

The layers above the compact region had a composition corresponding approximately to K₂Pb₃(SO₄)₃Cl, which was first observed by Kinnunen et al.16 with a composition similar to that of caracolite (Na₃Pb₂(SO₄)₃Cl). The compact region itself consisted of the same K₂Pb₃(SO₄)₃Cl and of K₂PbCl₄ that surrounded the K₂SO₄ particles. The K₂SO₄ particles...
above the compact region had clearly experienced a presence of a molten phase during the experiment. Below the compact region, the main Pb-containing specie observed was K₂PbCl₄ with minor amounts of K₃Pb₂(SO₄)₃Cl close to the compact region. In addition, minor amounts of KCl were found within the deposit, which supports the formation of K₃Pb₂(SO₄)₃Cl, according to reaction 6.

\[
2\text{PbCl}_2(\text{g/l/s}) + 3\text{K}_2\text{SO}_4(\text{s}) \xrightarrow{\text{reaction 6}} K_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}(s) + 3\text{KCl}(g/s)
\]

The formation of KCl can act as a trigger to a number of effects within the K₂SO₄ deposit. With KCl present in the deposit, reactions 2–5 are also plausible to occur in the K₂SO₄ deposit. In addition, KCl and K₂SO₄ form a eutectic melt (solidus temperature 690 °C), which could partly be responsible for the sintering of the upper deposit, as shown by others.²⁰⁻²¹ What strikes us as interesting is the fact that the Pb-species are enriched into a compact region within the deposit structure. The region is found near the steel surface, which means that the temperature in the area is somewhere around 420–450 °C. Kinnunen et al.¹⁶ estimated that their Pb-enriched region was 403 °C. Unfortunately, the proposed K₃Pb₂(SO₄)₃Cl phase has not been fully identified and corroborated to exist. Therefore, there is no thermodynamic data available for K₃Pb₂(SO₄)₃Cl to estimate its melting properties. Due to the fact that KCl is formed in the deposit, melt formation is plausible at similar temperature as with the KCl deposit (409 °C). In addition, the K₂SO₄–KCl–PbSO₄–PbCl₂ system has a reported lowest melting temperature of 403 °C.⁶⁶ However, the compact region was observed at a higher temperature, indicating that solidification of a molten phase occurred at a higher temperature for the mixture in question.

Similar to the KCl and Na₂SO₄ deposits, the PbCl₂ had reacted with the deposit material, which is likely to inhibit the revaporization of PbCl₂ into the furnace. Therefore, the amount of Pb and Cl found in the deposit is significantly higher than in the corresponding experiments with SiO₂ and NaCl deposits.

3.1.6. KCl–NaCl and PbCl₂. With the mixture of KCl–NaCl (50:50 wt %), the results showed that even when mixed with another component the KCl reacts with PbCl₂ forming K₃PbCl₄. In the 24 h/200 °C experiment, K₃PbCl₄ was observed locally on the furnace-facing side and within the original salt particles. The layers of K₃PbCl₄ on the furnace-facing side of the original salt particles included also some Na, in the cation ratio of 1:8:4 Na–K–Pb. The ratio corresponds well to the SEM/EDXA point analysis results by Kinnunen et al.¹⁷ from a deposit collected from a recycled wood firing CFB boiler. Within the original particles it seemed that the KCl of the particle had reacted with the PbCl₂ and the original (K,Na)Cl–(Na,K)Cl matrix was substituted with a K₃PbCl₄–(Na,K)Cl matrix (Figure 6). Formation of the K₃PbCl₄–(Na,K)Cl matrix results in a K depletion from the original salt particle.

Figure 5. SEM backscatter image and EDXA elemental maps of the 24 h/400 °C K₂SO₄ deposit. The figure shows (1) K₃Pb₂(SO₄)₃Cl on top of K₂SO₄ particles, (2) the Pb and Cl enriched region, (3) K₃PbCl₄ and K₃Pb₂(SO₄)₃Cl on top of K₂SO₄ particles, and (4) the oxide layer.

Figure 6. SEM backscatter image and EDXA maps of a salt particle in the outer part of the KCl–NaCl deposit in the 24 h/200 °C experiment. The image shows how the Pb species are enriched on the furnace-facing side of the salt particles and even penetrate into the original salt particles, resulting in K depleted areas.

Similar results were also observed in the 24 h/400 °C experiment. K₃PbCl₄ was observed on and within the original salt particles close to the steel surface and on the oxide layer. In addition, the deposit was observed to have sintered throughout. The outer part of the deposit was observed to have melted during the experiment, which is understandable as the solidus temperature of the KCl–NaCl mixture in question is 657 °C. Closer to the steel, the particles were bridging, implying that small amounts of melt had been present during the experiment, which indicates that Pb species had been distributed throughout. In the 24 h/400 °C experiment, the salt particles were observed to have a different microstructure as a function of temperature within the deposit. The particles in colder temperatures had a fairly homogeneous conglomerate microstructure. In higher temperatures, the conglomerate microstructure became more heterogeneous and at the same time the furnace-facing sides of the particles were observed to be enriched in NaCl. The NaCl enrichment is likely a result of the K₃PbCl₄ formation (see Figure 6) and subsequent reaction back to volatile species (reactions 2 and 5) and vaporization of KCl, KPbCl₄, and PbCl₂, which results in the depletion of K at the top of the salt particles.

3.2. Corrosion. This section will concentrate on the 400 °C experiments due to no significant corrosion observed in the
200 °C experiments. The measured corrosion layer thicknesses are summarized in Table 3. The corrosion layer thicknesses were measured from the SEM backscatter images. The thicknesses were measured in 10 separate points per sample along the oxide layer. Any gaps between oxide layers were not included into the thickness measurements.

The corrosion layer under the SiO2 deposit was observed to be the thickest compared to other deposits with the same exposure time. Interestingly the smallest amount of Pb and Cl was found within the SiO2 deposit after 24 h exposure. With the 4 h/400 °C experiment, the corrosion layer was observed to be compact and consist of three distinct layers (Figure 7).

Table 3. Corrosion Layer Average Thickness and Largest Deviation from the Average

| deposit material | corrosion layer thickness [μm] | Pb-containing species on the oxide layer | within the oxide layer |
|------------------|--------------------------------|----------------------------------------|-----------------------|
| SiO2             | 630 ± 15                       | PbCl2, Pb2OCl2                         | Na2Pb2(SO4)2Cl |
| NaCl             | 260 ± 20                       | PbCl2                                 | Na2Pb2(SO4)2Cl |
| Na2SO4           | 360 ± 57                       | PbCl2, Pb2PbCl2                         | Na2Pb2(SO4)2Cl |
| KCl              | 110 ± 30                       | K2PbCl4                                | K2PbCl4 |
| K2SO4            | 70 ± 45                        | K2PbCl4                                | K2PbCl4 |
| KCI-Cl           | 50 ± 13                        | K2PbCl4                                | K2PbCl4 |

The table also shows the observed Pb-containing species, on and within the oxide layer, with different deposit materials.

Figure 7. SEM backscatter image of the corrosion layer from the 4 h/400 °C experiment with SiO2. The image shows an FeCl2 layer on the steel surface, minor amounts of PbCl2 on the FeCl2 layer, followed by a dense Fe2O3 layer, and a mixed layer of Fe2O3 + PbCl2.

The layer closest to the steel consisted mainly of Fe and Cl, indicating the presence of FeCl2. The second layer from the steel consisted mainly of Fe and O in an atomic ratio of ~2:3. In addition, minor amounts of Pb and Cl were observed within the layer. The third layer from the steel was a mixture of Fe, Pb, O, Cl, and some Si. The layer was mixed but the bulk composition indicates that the layer consisted of Fe2O3, PbCl2, PbO, and SiO2.

The compact and intertwined morphology with PbCl2 and Fe2O3 implies that melt had been present at some point. Pure PbCl2 has a melting point of 500 °C, which is significantly higher than the steel temperature during the experiment. However, if FeCl3 is formed as a corrosion product at the steel surface, it forms a mixture with PbCl2, which forms a melt at ~410–420 °C, and could explain the compact structure.

With 24 h/400 °C SiO2 experiment, the oxide layer was thick and porous. The corrosion products were observed in layers consisting of Fe and O. The Fe2O3 layer were mixed with minor amounts of Pb and Cl. The amount of Pb and Cl was observed to be higher close to the steel surface than in the outer part of the oxide layer (Figure 8).

In the 4 h/400 °C experiment with NaCl, the corrosion layer was similar as in the corresponding SiO2 experiment. Closest to the steel there was a layer consisting mainly of Fe and Cl, followed by layers with intertwined Pb, Fe, and Cl. Na was not observed within the corrosion layer. In the 24 h/400 °C experiment, the oxide layer was similar but thicker. In addition, there were several Fe2O3 layers mixed with PbCl2. The bulk of the PbCl2 was found in the middle of the oxide layer, in droplet-like shapes (Figure 9).

The Na2SO4 deposit in the 24 h/400 °C experiment produced a layered oxide scale. Similar to the experiments with SiO2 and NaCl, there were signs of FeCl2 formation close to the steel surface. Otherwise the oxide layer consisted of Fe, Pb, Cl, and O. The Fe2O3 layers were porous and PbCl2 was observed on the furnace-facing side of those layers. Interestingly no Na was observed within the oxide layer, although there was Na on top of the oxide layer in the form of Na2Pb2(SO4)2Cl (Figure 10).

The 24 h/400 °C experiment with KCI resulted in a thinner oxide layer when compared to the SiO2, NaCl, and Na2SO4 experiments. No pure PbCl2 was observed within the KCl deposit or within the oxide layer, contrary to the SiO2, NaCl, and Na2SO4 experiments. Instead, Pb and Cl within the oxide layer associated with K, in the form of K2PbCl4. The Pb-containing species were observed on and within the oxide layer. This is similar to results reported by others. Moreover, the oxide layer was denser than in the corresponding SiO2, NaCl, and Na2SO4 deposits and contained visibly less Pb-containing species (Figure 11). In addition, some signs of FeCl3 formation at the steel surface were observed.

The K2SO4 deposit with the 24 h/400 °C experiment resulted in an oxide layer, which had an uneven thickness and was compact. Contrary to the other experiments, FeCl3 was not clearly observed at the steel surface. Even so, its presence cannot be completely ruled out. K, Pb, and Cl were observed within the oxide layer similar to the KCl deposits, and they were associated in ratios corresponding to the composition of K2PbCl4. In addition, analysis showed KCl present on the oxide layer. The proposed K2Pb2(SO4)2Cl was not observed within the oxide layer.

The KCI—NaCl mixture with 24 h/400 °C resulted, surprisingly, in the thinnest oxide layer. Pb was observed as K2PbCl4 on top of the oxide layer. Within the oxide layer, some K2PbCl4 was observed. In addition, within the deposit, Pb was observed in roughly a 1:1 ratio with Cl and some K present. The composition corresponds roughly to a mixture of K2PbCl4 and Pb2OCl2. Some signs of FeCl3 formation at the steel surface were observed. The salt particles (K2PbCl4—KCI—NaCl) close to the steel surface have a composition, which according to the prediction of Kinnunen et al. has a solidus temperature 398 °C. The predicted solidus temperature is below the steel temperature (400 °C), which would result in a molten phase on the steel surface. However, molten salts often lead to rapid corrosion rates, which can be argued to...
not be the case in the KCl–NaCl 24 h/400 °C experiment. Kinnunen et al.17 note that their predicted solidus temperature for the K₂PbCl₄–KCl–NaCl system is ~15 °C lower than the reported measured values by others.32,40 If the same trend is true for the K₂PbCl₄–KCl–NaCl system, it would mean that the solidus temperature of the system is above the steel temperature and the molten phase is not as likely to come into contact with the steel surface. It is also possible that it takes a long time for PbCl₂ to reach the steel surface when it can be bound in molten phase with NaCl. The formation of a PbCl₂–NaCl melt lowers the partial pressure of PbCl₂ in the gas phase, which slows down the migration to the steel surface. This is supported by the similar corrosion behavior, neglecting the thickness, between the deposits. With both deposit materials, the oxide layer was similar in nature and composition, suggesting that only the initiation was slower with the NaCl.

With Na₂SO₄, the corrosion layer was thinner than with NaCl although the oxide layer was qualitatively similar. The formation of Na₂Pb₃(SO₄)₂Cl further binds the Pb into a less corrosive compound, which inhibits the corrosion. Even with Na₂SO₄, some PbCl₂ was observed within the oxide layer, which implies that either all of the PbCl₂ did not react or that Na₂Pb₃(SO₄)₂Cl can decompose and form PbCl₂ at the oxide layer.

In experiments with the K-salts, the reactions of PbCl₂ with the deposit material seemed to further inhibit the corrosion. Especially the formation of K₂PbCl₄ seems to bind the Pb and Cl in a form in which they are not as corrosive as pure PbCl₂. In the presence of K₂SO₄, the formation of the K₂Pb₃(SO₄)₂Cl binds Pb and yields KCl, which can further react with PbCl₂.

The KCl–NaCl mixture resulted in the lowest amount of corrosion. The formation of K₂PbCl₄ inhibits the transport of Pb-containing species to the steel. In addition, the KCl is bound into a matrix together with NaCl, which means that even some of the resulting K₂PbCl₄ is bound to a matrix, which inhibits the revaporization.

The corrosion layer thickness results imply that pure PbCl₂ is more corrosive than Na₂Pb₃(SO₄)₂Cl, K₂PbCl₄, or K₂Pb₃(SO₄)₂Cl. The higher corrosivity of PbCl₂ is possibly connected to the active oxidation mechanism induced by Cl₂ (or HCl).41 According to active oxidation, gaseous Cl₂ (or HCl) penetrates the oxide scale and reacts with the steel, forming volatile metal chlorides, which diffuse outward and subsequently oxidize in higher O₂ partial pressures. The oxidization of metal chlorides yields metal oxides and Cl₂. The regenerated Cl₂ is again available for penetration of the newly formed oxide scale and to continue the attack on the steel surface. In addition, the penetration of Cl₂ has been speculated to be enhanced by temperature gradients.42

An alternative Cl induced corrosion mechanism has been proposed for steel exposed to KCl.43 According to the mechanism, KCl dissociates at the oxide scale surface in the presence of oxygen and water vapor, forming KOH and Cl⁻. In addition, a simultaneous oxidation of Fe takes place at the steel surface resulting in Fe²⁺ ions. The Cl⁻ ions diffuse rapidly to the steel surface and react with the Fe²⁺ ions to form FeCl₂.
Similar mechanism could occur with PbCl₂, where PbCl₂ reacts at the oxide scale to form PbO and Cl⁻.

Both of the fore described corrosion mechanisms lead to the formation of metal chlorides at the steel-oxide interface. The presence of FeCl₂ can further result in the formation of melt together with other corrosion layer or deposit components, resulting in rapid molten phase induced corrosion. In addition, in the both proposed mechanisms Cl⁻ is the key component, which induces rapid corrosion. Therefore, the differences between the corrosivity of PbCl₂, Na₃Pb₂(SO₄)₃Cl, K₂PbCl₄, and K₃Pb₂(SO₄)₃Cl is likely connected to the stability of the species, i.e., how easily the component yields free Cl⁻ either in the form of Cl⁻ ions or gaseous Cl₂. It seems that Cl⁻ is released more easily from PbCl₂, either as Cl⁻ or Cl₂, than from Na₃Pb₂(SO₄)₃Cl, K₂PbCl₄, or K₃Pb₂(SO₄)₃Cl in the temperature of 400 °C, resulting in the fastest corrosion rates. NaCl and KCl also include Cl⁻ but they are considered less corrosive than PbCl₂. This behavior is often connected to the melting behavior, i.e., mixtures containing PbCl₂ often have lower melting temperatures. In addition, alkali chlorides are

Figure 11. SEM backscatter image and elemental maps of the corrosion layer from the 24 h/400 °C experiment with KCl.

Table 4. Summary of the Salts and Salt Systems within the Deposits, As Well As in the Corrosion Layer, And Their Lowest Melting Temperatures

| deposit material | detected salt | lowest melting temperature [°C] | composition | lowest melting temperature, [°C] |
|------------------|---------------|---------------------------------|-------------|---------------------------------|
| SiO₂             | PbCl₂         | 501⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
| NaCl             | NaCl          | 801⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | PbCl₂         | 501⁴⁴                          |             | NaCl–FeCl₂: 378¹⁵             |
|                  | NaCl–PbCl₂    | 409³²                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
| Na₂SO₄           | Na₂SO₄        | 884⁴⁴                          |             | NaCl–FeCl₂: 378¹⁵             |
|                  | PbCl₂         | 501⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | Na₂Pb(SO₄)₃Cl| 701⁵³                          |             | NaCl–FeCl₂: 378¹⁵             |
|                  | NaCl–Na₂SO₄  | 626⁶⁶                         |             | NaCl–FeCl₂: 378¹⁵             |
|                  | NaCl–PbCl₂   | 409³²                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | NaCl–Na₂SO₄–PbCl₂–PbSO₄ | n.a. (<409) |             |                                |
| KCl              | KCl           | 771⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | PbCl₂         | 501⁴⁴                          | KCl–FeCl₂: 350⁶⁵ | PbCl₂–FeCl₂–KCl: 312¹⁶     |
|                  | K₂PbCl₄       | 488⁷²                          | KCl–FeCl₂: 350⁶⁵ | PbCl₂–FeCl₂–KCl: 312¹⁶     |
|                  | KCl–PbCl₂     | 409³²                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
| K₂SO₄            | K₂SO₄         | 1069⁶⁴                         | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | PbCl₂         | 501⁴⁴                          | Fe₃O₄, FeCl₂ | KCl–FeCl₂: 350⁶⁵             |
|                  | K₂PbCl₄       | 488⁷²                          | Fe₃O₄, FeCl₂ | KCl–FeCl₂: 350⁶⁵             |
|                  | KCl–K₂SO₄    | 690⁶⁶                          | Fe₃O₄, FeCl₂ | KCl–FeCl₂: 350⁶⁵             |
|                  | KCl–PbCl₂     | 409³²                          | Fe₃O₄, FeCl₂ | KCl–FeCl₂: 350⁶⁵             |
|                  | KCl–K₂SO₄–PbCl₂–PbSO₄ | 403⁶⁶   | Fe₃O₄, FeCl₂ | KCl–FeCl₂: 350⁶⁵             |
| NaCl–KCl         | NaCl          | 801⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | KCl           | 771⁴⁴                          | Fe₃O₄, FeCl₂ | PbCl₂–FeCl₂: 410–420¹⁶,¹⁸     |
|                  | PbCl₂         | 501⁴⁴                          | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
|                  | K₂PbCl₄       | 488⁷²                          | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
|                  | NaCl–KCl     | 657⁵⁵                          | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
|                  | NaCl–PbCl₂   | 409³²                          | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
|                  | KCl–PbCl₂    | 409³²                          | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
|                  | K₂PbCl₄–KCl–NaCl | 398¹⁷   | Fe₃O₄, FeCl₂ | NaCl–FeCl₂: 378¹⁵             |
also more stable than PbCl₂, meaning they do not release Cl for the corrosion reaction as easily.

The liquid phase is in contact with the steel surface can also enhance the corrosion rate of the steel. Table 4 shows that melt has potentially been in contact with the steel surface in all of the experiments with steel temperature at 400 °C. Although the solidus temperature of the PbCl₂–FeCl₂ is estimated to be 410−420 °C,16,38 it is likely that the melt has come into contact with the steel at 400 °C. The temperature gradient across both the deposit and the oxide layer enables melt formation in the higher temperatures. The formed melt can trickle down to the steel surface and get in contact with the steel before it solidifies. In addition, there are slight temperature fluctuations that can cause an occasional rise in the steel temperature.

Signs of PbCl₂–FeCl₂ melt formation can be seen, for example, in Figure 7. When a binary melt of PbCl₂–FeCl₂ is formed, the components are mixed. When O₂ concentration increases and FeCl₂ is oxidized to iron oxide, the mixture solidifies, resulting in a solid matrix of iron oxide and PbCl₂ observed in Figure 7.

Due to the temperature gradient, the solid PbCl₂ is exposed to a driving force toward the colder temperature, i.e., the steel surface. Vaporization from the iron oxide matrix and condensation at the colder surface is likely responsible for the PbCl₂ rich areas within the oxide layers as well as the porous iron oxide matrixes observed in Figures 8−10.

4. COMPARISON TO COLLECTED BOILER DEPOSIT

The structure and chemical composition of the synthetic deposits were compared to a superheater deposit collected from recycled wood fired CFB-boiler. A cross-section and SEM/EDXA analyses of this deposit are presented in Figure 12. Superheater material temperature at the deposit sampling place is ∼400–420 °C and flue gas temperature is ∼850 °C. The lower part (tube side) of the superheater deposit has a dense and layered structure whereas the upper part (flue gas side) is coarser. Two different alternating layers were recognized in the lower part: FeₓOᵧ (point 4, Figure 12) and K₂PbCl₄ (point 3, Figure 12).
Above these alternating layers, a KCl–NaCl mixture was detected (point 2, Figure 12). The uppermost part of the deposit is composed of several mixed elements: Na, S, Cl, K, Ca, Fe, Pb, Al, and Si (point 1 and area, Figure 12). The structure and the chemical composition of the boiler deposit correlate well with the synthetic deposits used and formed in the gradient furnace. As observed within the gradient furnace experiments and confirmed with the superheater deposit, K reacts with Pb and Cl and forms a K–Pb–Cl mixture even if Na would be available. In this study, K–Pb–Cl was noticed to be highly corrosive, even though PbCl₂ seemed to be the most corrosive salt. However, PbCl₂ was not found in deposits where either K₃Pb₂(SO₄)₃Cl or K₂PbCl₄ was formed in deposits where either K₃Pb₂(SO₄)₃Cl or KCl seemed to bind Pb in the deposit by inhibiting not reacting with PbCl₂ (i.e., SiO₂ and NaCl). KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed that the mechanisms observed in the laboratory experiments environments, the collected boiler deposit shows how K from the analyzed boiler deposit nor from the gradient furnace deposits when K-salts were present. The major Pb-containing mixture in both cases was K₂PbCl₄.

Although other ash forming elements (e.g., Ca, Al) could also affect the migration and interactions of Pb and Cl in boiler environments, the collected boiler deposit shows how K–Pb–Cl mixtures are still formed in the oxide layer. This indicates that the mechanisms observed in the laboratory experiments are also relevant in more complicated industrial systems.

5. CONCLUSIONS AND IMPLICATIONS
PbCl₂ was observed to react with Na₂SO₄, KCl, and K₂SO₄. In contrary, no reaction with NaCl was noticed. PbCl₂ interaction with alkali sulfates resulted in the formation of caracolite, Na₃Pb₂(SO₄)₃Cl, and caracolite-type compound, K₃Pb₂(SO₄)₃Cl. K₂PbCl₄ was formed in deposits where either KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed K₃Pb₂(SO₄)₃Cl seemed to bind Pb in the deposit by inhibiting revaporization back to the furnace. This resulted in more Pb found in deposits but also in a slower corrosion rate. The caracolite, Na₃Pb₂(SO₄)₃Cl bound also some Pb, but PbCl₂ was still found in the sample cross-section, which resulted in an enhanced corrosion rate. The deposit reactions and corrosion results are summarized in Figure 13.

The results showed no increased corrosion with material temperature at 200 °C, whereas all the deposit materials were found to be extremely corrosive at 400 °C, when using carbon steel material. The most corrosive agent was pure PbCl₂ salt. Thus, the highest corrosion rates were detected with deposits not reacting with PbCl₂ (i.e., SO₂ and NaCl).

Comparison of synthetic deposits with real superheater deposit showed that corrosion results from the gradient furnace experiments are qualitatively similar to observations from boilers. The corrosion front and corrosion products were surprisingly similar between the real and synthetic deposits. The gradient furnace testing method proved to be a practical tool for further corrosion studies in laboratory-scale testing of superheater materials and deposit chemistry.

5. CONCLUSIONS AND IMPLICATIONS

PbCl₂ was observed to react with Na₂SO₄, KCl, and K₂SO₄. In contrary, no reaction with NaCl was noticed. PbCl₂ interaction with alkali sulfates resulted in the formation of caracolite, Na₃Pb₂(SO₄)₃Cl, and caracolite-type compound, K₃Pb₂(SO₄)₃Cl. K₂PbCl₄ was formed in deposits where either KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed K₃Pb₂(SO₄)₃Cl seemed to bind Pb in the deposit by inhibiting revaporization back to the furnace. This resulted in more Pb found in deposits but also in a slower corrosion rate. The caracolite, Na₃Pb₂(SO₄)₃Cl bound also some Pb, but PbCl₂ was still found in the sample cross-section, which resulted in an enhanced corrosion rate. The deposit reactions and corrosion results are summarized in Figure 13.

The results showed no increased corrosion with material temperature at 200 °C, whereas all the deposit materials were found to be extremely corrosive at 400 °C, when using carbon steel material. The most corrosive agent was pure PbCl₂ salt. Thus, the highest corrosion rates were detected with deposits not reacting with PbCl₂ (i.e., SO₂ and NaCl).

Comparison of synthetic deposits with real superheater deposit showed that corrosion results from the gradient furnace experiments are qualitatively similar to observations from boilers. The corrosion front and corrosion products were surprisingly similar between the real and synthetic deposits. The gradient furnace testing method proved to be a practical tool for further corrosion studies in laboratory-scale testing of superheater materials and deposit chemistry.

5. CONCLUSIONS AND IMPLICATIONS

PbCl₂ was observed to react with Na₂SO₄, KCl, and K₂SO₄. In contrary, no reaction with NaCl was noticed. PbCl₂ interaction with alkali sulfates resulted in the formation of caracolite, Na₃Pb₂(SO₄)₃Cl, and caracolite-type compound, K₃Pb₂(SO₄)₃Cl. K₂PbCl₄ was formed in deposits where either KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed K₃Pb₂(SO₄)₃Cl seemed to bind Pb in the deposit by inhibiting revaporization back to the furnace. This resulted in more Pb found in deposits but also in a slower corrosion rate. The caracolite, Na₃Pb₂(SO₄)₃Cl bound also some Pb, but PbCl₂ was still found in the sample cross-section, which resulted in an enhanced corrosion rate. The deposit reactions and corrosion results are summarized in Figure 13.

The results showed no increased corrosion with material temperature at 200 °C, whereas all the deposit materials were found to be extremely corrosive at 400 °C, when using carbon steel material. The most corrosive agent was pure PbCl₂ salt. Thus, the highest corrosion rates were detected with deposits not reacting with PbCl₂ (i.e., SO₂ and NaCl).

Comparison of synthetic deposits with real superheater deposit showed that corrosion results from the gradient furnace experiments are qualitatively similar to observations from boilers. The corrosion front and corrosion products were surprisingly similar between the real and synthetic deposits. The gradient furnace testing method proved to be a practical tool for further corrosion studies in laboratory-scale testing of superheater materials and deposit chemistry.

5. CONCLUSIONS AND IMPLICATIONS

PbCl₂ was observed to react with Na₂SO₄, KCl, and K₂SO₄. In contrary, no reaction with NaCl was noticed. PbCl₂ interaction with alkali sulfates resulted in the formation of caracolite, Na₃Pb₂(SO₄)₃Cl, and caracolite-type compound, K₃Pb₂(SO₄)₃Cl. K₂PbCl₄ was formed in deposits where either KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed K₃Pb₂(SO₄)₃Cl seemed to bind Pb in the deposit by inhibiting revaporization back to the furnace. This resulted in more Pb found in deposits but also in a slower corrosion rate. The caracolite, Na₃Pb₂(SO₄)₃Cl bound also some Pb, but PbCl₂ was still found in the sample cross-section, which resulted in an enhanced corrosion rate. The deposit reactions and corrosion results are summarized in Figure 13.

The results showed no increased corrosion with material temperature at 200 °C, whereas all the deposit materials were found to be extremely corrosive at 400 °C, when using carbon steel material. The most corrosive agent was pure PbCl₂ salt. Thus, the highest corrosion rates were detected with deposits not reacting with PbCl₂ (i.e., SO₂ and NaCl).

Comparison of synthetic deposits with real superheater deposit showed that corrosion results from the gradient furnace experiments are qualitatively similar to observations from boilers. The corrosion front and corrosion products were surprisingly similar between the real and synthetic deposits. The gradient furnace testing method proved to be a practical tool for further corrosion studies in laboratory-scale testing of superheater materials and deposit chemistry.

5. CONCLUSIONS AND IMPLICATIONS

PbCl₂ was observed to react with Na₂SO₄, KCl, and K₂SO₄. In contrary, no reaction with NaCl was noticed. PbCl₂ interaction with alkali sulfates resulted in the formation of caracolite, Na₃Pb₂(SO₄)₃Cl, and caracolite-type compound, K₃Pb₂(SO₄)₃Cl. K₂PbCl₄ was formed in deposits where either KCl or K₂SO₄ was present. Both K₂PbCl₄ and the proposed K₃Pb₂(SO₄)₃Cl seemed to bind Pb in the deposit by inhibiting revaporization back to the furnace. This resulted in more Pb found in deposits but also in a slower corrosion rate. The caracolite, Na₃Pb₂(SO₄)₃Cl bound also some Pb, but PbCl₂ was still found in the sample cross-section, which resulted in an enhanced corrosion rate. The deposit reactions and corrosion results are summarized in Figure 13.

The results showed no increased corrosion with material temperature at 200 °C, whereas all the deposit materials were found to be extremely corrosive at 400 °C, when using carbon steel material. The most corrosive agent was pure PbCl₂ salt. Thus, the highest corrosion rates were detected with deposits not reacting with PbCl₂ (i.e., SO₂ and NaCl).

Comparison of synthetic deposits with real superheater deposit showed that corrosion results from the gradient furnace experiments are qualitatively similar to observations from boilers. The corrosion front and corrosion products were surprisingly similar between the real and synthetic deposits. The gradient furnace testing method proved to be a practical tool for further corrosion studies in laboratory-scale testing of superheater materials and deposit chemistry.
morphism of synthetic chlorine-containing biomass boiler deposits. *Fuel Process. Technol.* **2016**, *141*, 285–298.

(20) Niemi, J.; Lindberg, D.; Engblom, M.; Hupa, M. Simultaneous melt and vapor induced ash deposit aging mechanisms – Mathematical model and experimental observations. *Chem. Eng. Sci.* **2017**, *173*, 196–207.

(21) Bankiewicz, D.; Alonso-Herranz, E.; Yrjas, P.; Laurén, T.; Splutter, H.; Hupa, M. Role of ZnCl2 in High-Temperature Corrosion in a Bench-Scale Fluidized Bed Firing Simulated Waste Wood Pellets. *Energy Fuels* **2011**, *25* (8), 3476–3483.

(22) Larsson, E. The Corrosive Effects of Chloride Salts on Water Walls and Superheater Materials in Waste and Biomass-Fired Power Plants. Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden, 2014.

(23) Jones, F.; Tran, H.; Lindberg, D.; Zhao, L.; Hupa, M. Thermal Stability of Zinc Compounds. *Energy Fuels* **2013**, *27* (10), 5663–5669.

(24) Viklund, P.; Pettersson, R.; Hjörnæs, A.; Henderson, P.; Sjövall, P. Effect of sulphur containing additive on initial corrosion of superheater tubes in waste fired boiler. *Corros. Eng., Sci. Technol.* **2009**, *44* (3), 234–240.

(25) Aho, M.; Yrjas, P.; Taipale, R.; Hupa, M.; Silvennoinen, J. Reduction of superheater corrosion by co-firing risky biomass with sewage sludge. *Fuel* **2010**, *89* (9), 2376–2386.

(26) Folkeson, N.; Pettersson, J.; Pettersson, C.; Johansson, L. G.; Skog, E.; Andersson, B.Å.; Enestam, S.; Tuiramo, J.; Jonasson, A.; Heikne, B.; Svensson, J. E. Fireside corrosion of stainless and low alloyed steels in a waste-fired CFB boiler; The effect of adding sulphur to the fuel. *Mater. Sci. Forum* **2008**, *595–598*, 289–297.

(27) Karlsson, S. Reducing Alkali Chloride-Induced High Temperature Corrosion by Sulphur Containing Additives – A Combined Laboratory and Field Study. Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden, 2015.

(28) Alipour, Y.; Talus, A.; Henderson, P.; Norling, R. The effect of co-firing sewage sludge with used wood on the corrosion of an FeCrAl alloy and a nickel-based alloy in the furnace region. *Fuel Process. Technol.* **2015**, *138*, 805–813.

(29) Karlsson, S.; Åmand, L.-E.; Liske, J. Reducing high-temperature corrosion on high-alloyed stainless steel superheaters by co-combustion of municipal sewage sludge in a fluidised bed boiler. *Fuel* **2015**, *139*, 482–493.

(30) Yrjas, P.; Aho, M.; Zevenhoven, M.; Taipale, R.; Silvennoinen, J.; Hupa, M. Co-firing of sewage sludge with bark in a bench-scale bubbling fluidised bed - a study of deposits and emissions. In *Proceedings of the 20th International Conference on Fluidized Bed Combustion*, Yue, G., Zhang, H., Zhao, C., Luo, Z., Eds.; Springer: Berlin, Heidelberg, 2009; pp 922–929.

(31) National Center for Biotechnology Information. PubChem Substance Database, SID = 24856289, https://pubchem.ncbi.nlm.nih.gov/substance/24856289 (accessed February 19, 2018).

(32) Gabriel, A.; Pelton, A. D. Phase-Diagram Measurements and Thermodynamic Analysis of the PbCl2-NaCl, PbCl2-KCl, PbCl2-KCl-NaCl Systems. *Can. J. Chem.* **1985**, *63* (11), 3276–3282.

(33) Knazyev, A. V.; Bulanov, E. N.; Smirnova, N. N.; Korokin, V. Z.; Shushunov, A. N.; Blokhina, A. G. Low-temperature heat capacity and thermal expansion of synthetic caracolite Na3Pb2(SO4)3(3)Cl. *Thermochim. Acta* **2014**, *596*, 1–5.

(34) Verbinnen, B.; De Greef, J.; Van Caneghem, J. Theory and practice of corrosion related to ashes and deposits in a WtE boiler. *Waste Manage.* **2018**, *73*, 307–312.

(35) Enestam, S.; Roman, C.; Niemi, J.; Boström, D.; Backman, R.; Mäkelä, K.; Hupa, M. Occurrence of zinc and lead in aerosols and deposits in the fluidized-bed combustion of recovered waste wood. *Poljehvoff* **2011**, *25* (4), 1396–1404.

(36) Dombrovskaya, N. S. Double decomposition in the absence of a solvent XXXIV. Reversible reciprocal system of potassium and lead chlorides and sulfates. *Izvestiya Sektora Fiziko-Khimicheskogo Analiza, Institut Obozhevi i Neorganicheskoi Khimi*, Akademiya Nauk SSSR **1938**, *11*, 135–150.

(37) Hagemark, K.; Hengstenberg, D.; Blander, M. Association in vapors of iodine salts. The vapor mixtures potassium chloride-lead chloride and rubidium chloride-lead chloride. *J. Phys. Chem.* **1967**, *71* (6), 1819–23.

(38) Seo, W. G.; Matsuura, H.; Tsukihashi, F. Calculation of phase diagrams for the FeCl2, PbCl2, and ZnCl2 binary systems by using molecular dynamics simulation. *Metall. Mater. Trans. B* **2006**, *37* (2), 239–251.

(39) Yang, J.; Wen, J.; Liu, Q.; Wu, G.; Liu, L.; Lan, Y. Distribution of heavy metals in the flue gas from municipal solid waste incineration fly ash melt process. *Asian J. Chem.* **2013**, *25* (1), 157–160.

(40) Teis, K. Crystallographic and thermal investigation of systems formed by lead chloride with the chlorides of univalent metals. *Jahrb. Min. Bel.-Bd.* **1914**, *37*, 766–818.

(41) Grabke, H. J.; Reese, E.; Spiegel, M. The Effects of Chlorides, Hydrogen-Chloride, and Sulfur-Dioxide in the Oxidation of Steels Below Deposits. *Corros. Sci.* **1995**, *37* (7), 1023–1043.

(42) Kawahara, Y. Evaluation of high-temperature corrosion life using temperature gradient corrosion test with thermal cycle component in waste combustion environments. *Mater. Corros.* **2006**, *57* (1), 60–72.

(43) Folkeson, N.; Jonsson, T.; Halvarsson, M.; Johansson, L. G.; Svensson, J. E. The influence of small amounts of KCl(s) on the high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 and 500 degrees C. *Mater. Corros.* **2011**, *62* (7), 606–615.

(44) Bale, C. W.; Belisle, E.; Chartrand, P.; Decterov, S. A.; Eriksson, G.; Gherbi, A. E.; Hack, K.; Jung, J. H.; Kang, Y. B.; Melancon, J.; Pelton, A. D.; Petersen, S.; Robelin, C.; Sangster, J.; Spencer, P.; Van Ende, M. A. FactSage thermochemical software and databases, 2010–2016. CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2016**, 54, 35–53.

(45) Chase, M. W. NIST-JANAF Thermochemical Tables, 4th ed.; American Institute of Physics: 1998.

(46) Lindberg, D.; Backman, R.; Chartrand, P. Thermodynamic evaluation and optimization of the (NaCl+Na2SO4+Na2CO3+KCl +K2SO4+K2CO3) system. *J. Chem. Thermodyn.* **2007**, *39* (7), 1001–1021.