Corrosion in Recycled Wood Combustion – Theory and Solutions

Hanna Kinnunen, Sonja Enestam and Patrik Yrjas

1. Recycled wood as a fuel ................................................................. 562
2. Presence and form of heavy metals in the furnace ....................... 562
3. Behaviour and presence of chlorides in the deposits .................... 564
   3.1. Short-term deposits .............................................................. 564
   3.2. Long-term deposits ............................................................. 566
   3.3. Laboratory-scale deposits ...................................................... 567
4. Corrosivity of lead-including deposits ........................................... 567
5. Corrosion mechanism of lead-including deposits ......................... 568
6. Conclusions and solutions ............................................................. 570
7. Literature .................................................................................... 572

The use of waste-derived fuels, such as recycled wood, is a good and sustainable way to produce heat and electricity, minimize the use of fossil fuels and increase the use of renewable energy. Besides, waste-based fuels are relatively cheap and widely available. However, this trend is not totally trouble-free because of alkali metals, heavy metals and chlorine, which waste-based fuels typically contain in higher shares than coal and oil. These-ash forming elements increase the tendency of high-temperature corrosion and fouling of heat transfer surfaces. In recycled wood firing, alkali chlorides are present in combination with heavy metals, and the corrosion starting temperature may be considerably lower than with virgin wood combustion. In practice, this means that corrosion issues might be present in furnace walls, low-temperature superheaters and economisers.

In boiler design, the key parameter is the composition of the fuel or fuel mixture. This specifies the final steam temperature, layout of the boiler and material solutions. Understanding the corrosion phenomena enables the most cost-effective boiler design and material selection. Several studies have been made and a more detailed understanding has been gained during the recent years when combating high-temperature corrosion issues related to recycled wood combustion and heavy metal induced corrosion. The main findings are summarized in this article and some solutions to minimize unscheduled boiler shutdowns and to maximize boiler capacity are presented.
1. Recycled wood as a fuel

Recycled wood has become an attractive replacement for fossil fuels and virgin wood, due to its low price and ready availability. Many countries are trying to decrease landfelling by increasing recycling; at the same time, energy recovery from wastes is increasing. Recycled wood derives from several different waste-based sources, such as manufacturing industries, construction and demolition contractors and municipal recycling centres. It may contain leftover pieces from furniture manufacturing, packaging material and wood pallets [9]. In addition, plastics, metals, glass, stones, concrete and soil may be present, which increase the ash content of the fuel [9]. Due to these impurities, recycled wood may contain elevated concentrations of heavy metals, such as lead (Pb) and zinc (Zn), chlorine (Cl), sodium (Na) and potassium (K). All these elements contribute to corrosion, fouling and slagging during combustion, each of which reduces the boiler efficiency.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>28.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.3</td>
</tr>
<tr>
<td>Ash (815 °C)</td>
<td>3.3</td>
<td>48.7</td>
<td>5.9</td>
<td>2.1</td>
<td>39.6</td>
<td>0.08</td>
<td>0.35</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1,400</td>
<td>6,200</td>
<td>1,600</td>
<td>1,100</td>
<td>900</td>
<td>4,500</td>
<td>210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (calculated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LHV dry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: An example of the chemical composition of recycled wood

2. Presence and form of heavy metals in the furnace

Several of the ash-forming elements are present in the gas phase as vapours in the conditions prevailing in a boiler furnace [12]. These gases form fine particles when they condense on colder surfaces or nucleate when cooled in the convection pass. To study the presence and form of heavy metals in the boiler furnace, fine particle measurements were carried out in a 63 MWth bubbling fluidised bed (BFB) boiler firing recycled wood. The method (DLPI = Dekati Ltd. -type low-pressure mass impactor, ELPI = electrical low-pressure impactor) forces gaseous, condensable elements to form aerosols which are aerodynamically size-fractionated and sampled on different impactor plates. These impactor plates are then analysed to determine both mass and composition. Particles smaller than 1 µm are known to be in gaseous form and hence the impactor stages containing these particles are of particular interest. The fine-mode cut size used in this work was 1.6 µm. Two parallel samples were collected from each measurement location for further treatment by a water- and acid leaching method. K, Na, calcium (Ca), Pb and Zn as well as Cl, sulphate (SO\textsubscript{4}^{2-}) and bromine (Br) were found in the water-leached fraction. Others, 31 distinct elements in total, were found in the acid-leached fraction. K, Na, Ca, Zn and Pb concentrations were determined.
with an inductively coupled plasma mass spectrometer (ICP-MS) while $\text{SO}_4^{2-}$ and Cl were determined with ion chromatography (IC) from the water-leached samples. The same method was used for the acid-leached samples.

The measurement locations were situated before and after the secondary air inlets and before and after the tertiary air inlets, Figure 1. The concentrations of the water-soluble elements in the collected fine particle samples are presented for each of the measurement locations in Figure 1.

Figure 1: Concentrations of water-soluble elements in fine particle samples collected from the measurement locations; the thickness of each ribbon describes the element concentration
When considering the fractions < 1.6 µm, Na, K and Cl are the main elements present in the lower furnace. In fact, they are the prevailing elements throughout all measurement locations. The concentration of sulphate increases as the Cl concentration decreases after the tertiary air, indicating that some sulphation of the chlorides in the fine fraction has taken place after the final air inlet. Thus, alkalis have been present as chlorides until the tertiary air. Pb is present in all the measurement locations, and the concentration is at its highest between the secondary and tertiary air inlets. This particular location has earlier been reported as one of the problematic areas in boilers from the corrosion perspective [2]. Most of the Pb is bound to Cl since sulphates were not present until the tertiary air. When considering the leaching results, it can be calculated that more than 70 % of the Pb is present as chlorides.

The amount of Pb was clearly higher as compared to Zn. The amount of Zn was quite small before the tertiary air inlets. Zn was found to be at water-soluble form before the tertiary airs as well, but the amount was clearly lower than that of Pb. The presence of Zn as water-soluble form was more emphasised after the tertiary air inlets where the combustion is already complete.

3. Behaviour and presence of chlorides in the deposits

3.1. Short-term deposits

Deposit samples with a temperature-controlled probe can be used to study the condensing behavior of some of the ash-forming compounds during combustion. Full-scale short-term (2 h) deposit probe samples were collected from a 120 MWth recycled wood firing circulating fluidised bed (CFB) boiler and from the BFB boiler described in the previous chapter, Figure 2. A detailed characterisation of the collected deposits was carried out with Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX) and with X-ray diffraction (XRD).

Figure 2: Long-term corrosion and short-term deposit probe measurement locations and test material temperatures in the CFB (left) and BFB (right) boilers
The deposit compositions from the wind-side (= towards flue gas flow) of the probe are plotted in Figure 3. It should be kept in mind that the samples differed by measurement locations as well as by the probe temperature. Despite the differences in the measurement environments, the compounds found were similar.

<table>
<thead>
<tr>
<th>CFB</th>
<th>BFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g \sim 800 , ^\circ C$</td>
<td>$T_g \sim 490 , ^\circ C$</td>
</tr>
<tr>
<td>$T_{mat} \sim 360 , ^\circ C$</td>
<td>$T_{mat} \sim 360 , ^\circ C$</td>
</tr>
<tr>
<td>NaCl</td>
<td>NaCl</td>
</tr>
<tr>
<td>KCl</td>
<td>KCl</td>
</tr>
<tr>
<td>$\text{KPb}_2\text{Cl}_5$</td>
<td>$\text{KPb}_2\text{Cl}_5$</td>
</tr>
<tr>
<td>$(\text{KPb}\text{Cl}_3)_3\cdot\text{H}_2\text{O}$</td>
<td>$(\text{KPb}\text{Cl}_3)_3\cdot\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Na$_2$ZnCl$_4$·3H$_2$O</td>
<td>Na$_2$ZnCl$_4$·3H$_2$O</td>
</tr>
</tbody>
</table>

Figure 3: Elements characterised with SEM/EDX in deposits from the wind side of the short-term probe and compounds as characterised with XRD; the deposit sampling time was 2 h.

In both boilers, sodium chloride (NaCl) and potassium chloride (KCl) were identified in all deposit samples. The share of Cl was remarkably high in each of the analysed deposits. The higher the difference between the flue gas and material temperatures, the more Cl-containing compounds condensed. Pb was determined to be bound together with K and Cl as $\text{KPb}_2\text{Cl}_5$ and $(\text{KPb}\text{Cl}_3)_3\cdot\text{H}_2\text{O}$. A higher intensity was clearly detected for $\text{KPb}_2\text{Cl}_5$. $(\text{KPb}\text{Cl}_3)_3\cdot\text{H}_2\text{O}$ was not detected in the BFB sample. Instead, small amounts of lead chloride (PbCl$_2$) as well as lead oxide (PbO$_2$) were detected after the secondary air. In the superheater pass, the only Pb-including compound was $\text{KPb}_2\text{Cl}_5$. The share of Pb decreased when moving from the cooler material temperatures to the warmer surfaces. The share of Pb decreases along with decreasing flue gas temperature.

Zn was found together with Na or K, as Na$_2$ZnCl$_4$·3H$_2$O in the CFB probe sample and as K$_2$ZnCl$_4$ in the BFB sample. The share of Zn was clearly emphasised in the sample with lower material temperature. The share of Zn in the deposit sample with a material temperature of 262 °C was over 20 wt-%.
3.2. Long-term deposits

Two five-month corrosion probe tests were carried out in the CFB boiler to study the effects of the flue gas temperature on the deposit composition and on the corrosivity of the deposits, Figure 2. The set material temperature was in both cases the same, 360 °C, and the flue gas temperatures were 800 °C and 490 °C. The material rings at both test locations suffered from severe corrosion. The average measured corrosion rate in the hot flue gas area was ~0.8 mm/year and in the cooler flue gas zone ~0.4 mm/year.

<table>
<thead>
<tr>
<th>O</th>
<th>Cl</th>
<th>K</th>
<th>Pb</th>
<th>Fe</th>
<th>Na</th>
<th>Ca</th>
<th>S</th>
<th>O</th>
<th>Cl</th>
<th>K</th>
<th>Pb</th>
<th>Fe</th>
<th>Na</th>
<th>Ca</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.1</td>
<td>3.3</td>
<td>1.5</td>
<td>1.2</td>
<td>1.2</td>
<td>9.7</td>
<td>11.4</td>
<td>1</td>
<td>62.0</td>
<td>5.2</td>
<td>6.7</td>
<td>5.7</td>
<td>0.3</td>
<td>5.7</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>54.1</td>
<td>12.1</td>
<td>4.0</td>
<td>2.5</td>
<td>17.6</td>
<td>4.1</td>
<td>2.9</td>
<td>2.6</td>
<td>2</td>
<td>65.2</td>
<td>1.3</td>
<td>0.7</td>
<td>0.5</td>
<td>30.3</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>60.5</td>
<td>22.3</td>
<td>12.4</td>
<td>4.7</td>
<td>3</td>
<td>61.1</td>
<td>21.5</td>
<td>11.2</td>
<td>4</td>
<td>62.6</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
<td>36.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>36.1</td>
<td>63.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: Cross-sections and analyses points of the hot and cooler flue gas corrosion probe, wind side

The cross-sections of the deposits could be divided into different layers, Figure 4. All the layers were analysed using area analysis with SEM/EDX. High amounts of Pb were found in the both probe samples but no Zn was detected. Layer 1, closest to the flue gas, consisted mostly of Ca, Cl, K, Na, iron (Fe) and oxygen. In the cooler flue gas sample, Pb was also present. When moving closer to the steel surface (layer 2), the amount of Fe was more prevalent and the amount of sulphur (S) decreased. The Cl content increased in the hot flue gas sample, and Pb was also detected. This layer included elements from both the deposit and corrosion product layers and could be a mixture of these in both cases. Layer 3 consisted of K, Na, Pb and Cl. The composition of layer 3 was almost identical in both the hot and cooler flue gas samples. K was the most predominant alkali metal. Based on the XRD analyses from the short-term deposit samples, the composition could be a mixture of NaCl, KCl and K₂PbCl₅. Layer 4 contained Fe oxide and residues of Cl. In the cooler flue gas sample, residues from K and Pb were also detected. Clear signs of iron chloride (FeCl₂) (point 5) were observed in the hot flue gas sample. FeCl₂ was detected just above the steel surface before the oxide layer,
which is a sign that corrosion proceeds via FeCl$_2$ formation. The thickness of the Fe oxide layer underneath the K-Na-Pb-Cl mixture was about 400 µm in the hot flue gas area and roughly 260 µm in the cooler flue gas area.

3.3. Laboratory-scale deposits

In this work Pb was found together with K and Cl in the full-scale boiler measurements and previously thermodynamic modelling studies have predicted the formation of condensed K$_2$PbCl$_4$ and KPB$_2$Cl$_5$ [6]. The formation routes of K$_2$PbCl$_4$ (s) and KPB$_2$Cl$_5$ (s) compounds are assumed to proceed either via PbCl$_2$ (g/l/s) and KCl (g/s) or via KPBCl$_3$ (g) and KCl (g/s). The formation, vaporisation and condensation of these compounds inside artificial deposits were further studied with a novel gradient oven test method. Two different synthetic salts were applied simultaneously on two different rings. Ring 1 held PbCl$_2$ and Ring 2 held either quartz (SiO$_2$), NaCl, sodium sulphate (Na$_2$SO$_4$), KCl, potassium sulphate (K$_2$SO$_4$) or a KCl- NaCl (50:50 wt-%) mixture. The ring temperatures were set to 200 °C and 400 °C and the exposure times were 4 h and 24 h. The furnace set temperature was 980 °C. The material used in the tests was carbon steel P235GH.

Vaporized PbCl$_2$ that was originally placed on Ring 1, was observed to react with Na$_2$SO$_4$, KCl and K$_2$SO$_4$ on Ring 2. In contrast, no interactions with NaCl or with SiO$_2$ were observed. PbCl$_2$’s interaction with alkali sulphates resulted in the formation of caracolite, Na$_3$Pb$_2$(SO$_4$)$_3$Cl, and a caracolite-type compound, K$_3$Pb$_2$(SO$_4$)$_3$Cl. In addition, K$_2$PbCl$_4$ was formed in the deposits in the presence of K$_2$SO$_4$. In the test with PbCl$_2$ on Ring 1 and KCl on Ring 2, K$_2$PbCl$_4$ was detected. No PbCl$_2$ was observed on Ring 2. In the test with Na$_2$SO$_4$, Na$_3$Pb$_2$(SO$_4$)$_3$Cl was observed, but in this case also some PbCl$_2$ was found in the sample cross-section. A summary of the observed interactions and compounds is described below:

- PbCl$_2$ + NaCl → no interaction
- PbCl$_2$ + SiO$_2$ → no interaction
- PbCl$_2$ + Na$_2$SO$_4$ → Na$_3$Pb$_2$(SO$_4$)$_3$Cl + NaCl
- PbCl$_2$ + KCl → K$_2$PbCl$_4$
- PbCl$_2$ + K$_2$SO$_4$ → K$_3$Pb$_2$(SO$_4$)$_3$Cl + KCl + K$_2$PbCl$_4$
- PbCl$_2$ + KCl + NaCl → NaCl + K$_2$PbCl$_4$

4. Corrosivity of lead-including deposits

High amounts of Pb were found in the full-scale long-term deposits but no Zn was observed. In addition, Pb has been found to form a mixture with K and Cl. Further, the laboratory tests showed that PbCl$_2$ also reacts with alkali sulphates, forming K$_2$Pb$_2$(SO$_4$)$_3$Cl or Na$_3$Pb$_2$(SO$_4$)$_3$Cl. The threshold temperature for PbCl$_2$-induced corrosion was determined for a mixture with a small amount of PbCl$_2$ (5 wt-%)
together with K$_2$SO$_4$ (95 wt-%). K$_2$SO$_4$ was of interest because it is generally considered as non-corrosive in boiler conditions and corrosion tests showed no increased oxidation at 500 °C [5]. Tests were carried out at different test temperatures with two low-alloy steels (16Mo3 and 10CrMo9-10) and with a nickel (Ni)-based steel (Alloy 625) Figure 5. In the corrosion test method used, the corrosion is usually assumed to be severe when the oxide layer thickness exceeds 20 µm [4].

According to the test results, the threshold temperature for 16Mo3 was observed to be around 325 °C under the test conditions. This is clearly below the first melting temperature of the salt mixture (the lowest T0 for a PbCl$_2$-K$_2$SO$_4$ system is 403 °C). The threshold temperature for the low-alloy 10CrMo9-10 steel was a bit higher, 350 °C, probably due to the minimal chromium (Cr)-alloying. No corrosion was observed with Alloy 625, which was tested only at the two highest temperatures, 350 and 375 °C. 16Mo3 was not tested at 375 °C due to the high corrosion rate already observed at 325 °C.

5. Corrosion mechanism of lead-including deposits

Based on the studies presented in the previous chapters, it seems evident that Pb may be closely associated with K, Cl (and S) in deposits when firing recycled wood. Zn was present only occasionally and in smaller shares than Pb. These findings show that corrosion can occur below the first melting temperature of the deposit; this has also been addressed in the literature [11]. One reason for this could be the formation of a common melt between the deposit and corrosion products. The first melting temperature for a KCl-FeCl$_2$ mixture is 355 °C [7]. For the PbCl$_2$-KCl-FeCl$_2$ system the first melting temperature vary between 312 °C and 334 °C depending on the composition [8]. This might explain why an increased oxidation is already seen below the deposit’s first melting temperature. The presence of FeCl$_2$ was observed in the full-scale
and laboratory-scale measurements just above the steel material. The results indicate that corrosion follows the already-known Cl-induced corrosion mechanism by the formation of FeCl₂ with Fe-based steels [10].

The possible melt formation in the presence of FeCl₂ was studied in laboratory-scale corrosion oven tests. A test salt composed of equal amounts of FeCl₂, PbCl₂ and KCl was used. FeCl₂, an intermediate corrosion product according to the Cl-induced corrosion mechanism, was added to the salt mixture to verify possible reactions with the other salt components. The tests were carried out at 300 °C and 340 °C, the first temperature being below and the second above the first melting temperature of a FeCl₂-PbCl₂-KCl mixture. The exposure time was 8 hours and the tests were carried out in ambient air.

<table>
<thead>
<tr>
<th>Point</th>
<th>O at-%</th>
<th>Fe at-%</th>
<th>K at-%</th>
<th>Pb at-%</th>
<th>Cl at-%</th>
<th>Possible compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.9</td>
<td>29.7</td>
<td>11.1</td>
<td>53.3</td>
<td></td>
<td>K₂PbCl₄+K-Fe-Cl</td>
</tr>
<tr>
<td>2</td>
<td>61.5</td>
<td>37.2</td>
<td>0.3</td>
<td>1.0</td>
<td></td>
<td>Iron oxide</td>
</tr>
<tr>
<td>3</td>
<td>34.5</td>
<td>15.5</td>
<td>6.9</td>
<td>12.0</td>
<td>31.1</td>
<td>Not identified</td>
</tr>
<tr>
<td>4</td>
<td>59.5</td>
<td>38.3</td>
<td>0.4</td>
<td>1.8</td>
<td></td>
<td>Iron oxide</td>
</tr>
<tr>
<td>5</td>
<td>40.4</td>
<td>27.1</td>
<td></td>
<td></td>
<td>32.5</td>
<td>Iron oxide/chloride</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Point</th>
<th>O at-%</th>
<th>Fe at-%</th>
<th>K at-%</th>
<th>Pb at-%</th>
<th>Cl at-%</th>
<th>Possible compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49.5</td>
<td>50.5</td>
<td></td>
<td></td>
<td></td>
<td>KCl</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>31.6</td>
<td>10.9</td>
<td>57.3</td>
<td></td>
<td>K₂PbCl₄+KCl</td>
</tr>
<tr>
<td>3</td>
<td>61.5</td>
<td>36.1</td>
<td>0.4</td>
<td>0.6</td>
<td>1.4</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>4</td>
<td>57.0</td>
<td>41.1</td>
<td>0.6</td>
<td></td>
<td>1.4</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>5</td>
<td>57.5</td>
<td>35.1</td>
<td>1.6</td>
<td></td>
<td>5.8</td>
<td>Iron oxide/chloride+KCl</td>
</tr>
</tbody>
</table>

Figure 6: A SEM/EDX image of the cross-section of the exposed steel and its corrosion layer with five-point analyses (300 °C on the left and 340 °C on the right)

A narrow FeCl₂ ribbon was found just above the steel surface at both temperatures, Figure 6 (point 5). Above the FeCl₂ was an Fe-oxide layer, which was much thicker at the higher test temperature (30 µm vs. 140 µm). However, part of the FeCl₂ salt may have oxidised during the tests, partially contributing to the increased oxide layer. Pb-including compounds were observed within and above the Fe oxide layer at the lower test temperature (point 3). The white areas seem to include all elements from the original salt mixture (Fe, K, Pb and Cl), indicating that these elements will interact and form a melt or sintered particles. The absence of oxygen in this area shows that no oxides were present. The shape of the particles supports the assumption of a melt formation, as they are round-shaped. If this is the case, it is already occurring below the calculated T₀ for a FeCl₂-KCl-PbCl₂ system. At the higher test temperature, no particles including
Pb could be found within the Fe oxide layer (point 4). Instead, Pb-including particles were located above the Fe oxide layer and only small residues of Fe could be detected from those particles (point 2).

The results argue that corrosion proceeds via FeCl₂ formation with Fe-based steels as the Pb including deposits get into contact with the steel. PbCl₂ and K-Pb-Cl-including compounds are all able to initiate the corrosion reaction. Corrosion probably proceeds following an active oxidation mechanism, in which Cl gas is formed and reacts with the steel, producing FeCl₂. To initiate the corrosion, no molten phase is initially needed. Initiation and formation of FeCl₂ already occurs at relatively low temperatures (300 °C). In the second stage as the corrosion proceeds, FeCl₂ could form a local melt together with Pb-including particles. Melt formation increases the oxide layer thickness and destroys the steel, which increases towards higher material temperatures.

6. Conclusions and solutions

Understanding the path from fuel to stack is important in order to find cost-effective solutions related to boiler design and material selection. Fine particle measurements when firing recycled wood showed that the major part of Pb is in form of chlorides in the furnace area. The concentration was as its highest between the secondary and tertiary air levels, which is also reported to be one of the most problematic areas in the boiler from the standpoint of corrosion. The amount of Pb was clearly higher than the amount of Zn.

Pb was found to be present in short- and long-term deposits collected during recycled wood firing in fluidised bed boilers. The Pb was found together with K and Cl; pure PbCl₂ was rarely present. Zn was not found at all in the long-term deposits. Based on the probe measurements, the shares of Pb showed a high temperature dependence, as it seemed to be higher in the samples with lower material temperatures, and the share decreased while moving from hot to cooler flue gas temperatures. Although, the share of Pb decreased with cooler flue gas temperatures, a similar K-Pb-Cl compound was found in the deposits. However, clear differences in the corrosion rates were observed (0.4 mm/year vs. 0.8 mm/year). During the short-term deposit probe measurements, the share of Zn was clearly higher in the samples with lower material temperatures. The highest share was found at temperatures below the usual furnace wall temperatures, indicating that Zn tends to condense at lower surface temperatures than Pb. All these findings indicate that corrosion problems in recycled wood firing are mainly caused by Pb including compounds, rather than Zn.

Corrosion tests with a FeCl₂-PbCl₂-KCl mixture below (300 °C) and above (340 °C) the first melting temperature showed that Fe, K, Pb and Cl interact and form a melt or sinter particles together. The shape of the particles supported melt formation. As expected a thicker oxide layer was observed at higher temperatures. However, this possible melt formation was already observed at the lower test temperature, which was 12 °C below the predicted lowest first melting temperature (312 °C).
Knowledge of the formation of corrosive species and their condensation behaviour can be used in boiler design to provide novel solutions regarding the design and placement of superheaters to avoid the condensation of corrosive chlorides on heat exchanger surfaces. One example is the loop seal superheater, Figure 7. In the case of a CFB boiler, the hottest superheater can be placed in the loop seal, where the amount of corrosive chlorides is lower compared to the furnace or convective pass after the cyclone. By placing the hottest superheater into the loop seal, major corrosion failures can be avoided, and higher steam temperatures can be achieved.

Figure 7: Sideview of a CFB boiler designed for waste fuels; the hottest superheater is located in the loop seal and other superheaters after the empty pass to avoid chloride-induced corrosion

Another solution is to place superheaters after the empty pass, Figure 7. The empty pass can be designed for boilers firing fuels with an elevated risk of fouling and corrosion. The idea of the empty pass is to cool down the flue gas temperature in order to reduce the amount of corrosive chlorides in the gas phase and place the superheaters after the empty pass. The flue gas temperature before the empty pass is typically ~850 °C and after the empty pass about 650 °C.

Another solution which has been developed based on an understanding of corrosion phenomena is the double sleeve/tube superheater. The surface temperature of the superheater is increased above the condensation temperature of the corrosive chlorides by a double tube arrangement. This innovative design has increased the operating lifetime of the tertiary superheater in a waste-fired boiler (from few months up to several years).
The operating lifetime of boiler components can also be increased by using more corrosion resistant materials. However, a selection of material is always a question of price versus life time, efficiency and profitability. In furnace walls and superheaters, nickel-based overlay weld materials, such as Inconel 625, can be used to reduce corrosion potential and corrosion rate. The use of high chromium austenitic stainless steels is favoured in the hottest superheaters. Another option is to use tube shields in the most corrosive locations. Tube shields are also widely used against erosion.

Sulphur-based additives are known to be effective against alkali chloride induced superheater corrosion, but their effect on heavy metal chloride induced corrosion is not yet fully understood. Sewage sludge was reported to decrease the amount of K, Cl and Na in furnace wall deposits, leading to reduced corrosion of a Ni-based 625 alloy and FeCrAl-alloys [1]. However, low-alloy steels were not included in the test matrix. The addition of peat ash to demolition wood seemed to decrease chloride concentration in aerosols, but on the other hand it lead to an increase of the levels of Zn and Pb [3]. Additives injected into the bottom part of the furnace or mixed with the fuel might not have enough time to react before they reach the furnace walls, and are thus ineffective against furnace wall corrosion.

Despite of the numerous achievements and solutions mentioned above, efforts and co-operational studies between boiler manufacturers, energy companies and different research parties are still needed. Increasing the fuel range for existing markets, development of new technologies and moving existing technologies to new markets and geographical areas involve challenges requiring further research and development.

7. Literature


Contact Person

MSc. (Tech.) Hanna Kinnunen
Valmet Technologies Oy
Specialist, Combustibility & Corrosion Research and Development
Lentokentänkatu 11
33101 Tampere
FINLAND
+358 443579412
hanna.kinnunen@valmet.com

Other institution involved
Åbo Akademi University
We dedicate ourselves to current process and plant engineering as well as political, legal and economic issues, as far as they relate to waste and recycling industries, energy and raw materials industries or immission control. Our mission is to enable communication between politics, administration, industry, science and technology.

We organize conferences and congresses and publish reference books on the prevailing issues of our target group. Continuously, we are looking for interesting speakers, current topics and exciting projects to develop our offer. We are happy to be inspired by new ideas and discuss their feasibility.

Since more than thirty years the TK Verlag publishes reference books about various themes of technical environment protection:

- thermal waste treatment and energetic recovery,
- technical documentation on waste-to-energy plants,
- mechanical-biological treatment and solid recovered fuels,
- recycling and raw materials,
- mineral by-products and waste,
- strategies & environmental legislation,
- immission control,
- biological waste treatment.

Overall, we have published around two thousand technical contributions, which represent as a whole the technical, economic, legal and political development of the last decades. More recently, we started to provide a big part of these contributions for free download on our homepage.

Our conferences at a glance:

- Berliner Abfallwirtschafts- und Energiekonferenz
- Berliner Recycling- und Rohstoffkonferenz
- Berliner Konferenz Mineralische Nebenprodukte und Abfälle
- IRRC – Waste-to-Energy
- Berliner Klärschlammkonferenz