The presentation gives an overview on the chemical and mineralogical processes during the deposition of gaseous, liquid or solid species from the flue gas to the boiler tubes and on the later following processes in the deposited salts and ashes, which are relevant for corrosion mechanisms. Using this information it can be shown that specific chemical environments with a potential for corrosion can be found in waste- and biomass-to-energy plants as well as in coal- and RDF-fired boilers too.

The presented data was collected from field studies with probes collecting disposable species from the flue gas, from observations made on samples and from failure case studies in waste- and biomass-to-energy plants in Germany.

1 Formation of Deposits

For on-line monitoring of the deposition processes from the flue gas to the boiler tubes special probes can be used. Table 1 shows the results of a sampling campaign in a waste-to-energy boiler performed at flue gas temperatures of 850°, 600°, 350° and 200°C. The results were originally published in German language under ‘Systematisierung und Bewertung von verfügbaren Maßnahmen zur Korrosionsminderung in der betrieblichen Praxis von MVA mittels partikelförmiger Rauchgasbestandteile’ (final report EU 22 promoted by Bayerisches Staatsministerium für Umwelt, Gesundheit und Verbraucherschutz in 2005, available as PDF download on www.chemin.de). The pictures show the surface of the deposition probe which is a fine-meshed sieve. By sampling at different flue gas temperatures, the physical and chemical properties of the flue gas load (salts and ashes) are monitored and the chemical composition and phases can be analysed.

The monitored physical and chemical properties are:
- 850°C-Position (1. pass): The mesh of the sieve piles ash particles, the former single components can not be distinguished. The formed clusters have a sheet-like coating. A second type of particles are spheres of different size. They presumably are melt drops which were frozen before deposition. The spheres have no coating. A third type of particles is visible as a very thin coating extending on the whole surface of the fine wires
(marked by arrows). To form an extensive, fine coating the deposited particles must be very fine-grained, in terms of physics they are aerosols.

- 600°C-Position (bottom of 2. pass): The magnified detail shows that bigger spheres form impact structures in the thin coating on the sieve (‘like a stone was thrown into mud’). The viscosity of the coating and the chemical analysis identifies it as molten chlorides and sulphates (salts).

  In contrast to the 850°C-position more fine grained particles pile in the mesh, they sinter together. The aerosol coating on the spheres and the mesh is thicker. This indicates that the proportion of aerosols increases in the cooling flue gas.

  In close-up details a regular growth of very fine salt crystals is visible (crystal size max. 1 μm), indicating that gaseous species turn to solid state = desublimation. Therefore desublimation considerably forms salt deposits.

- 350°C-Position (3. pass, behind the superheater):

  The significance of aerosols between the 850° and 600°C-position is further increased at the 350°C-position. Dense, sintered and very fine-grained piles lie in the mesh and the sieve and spheres are coated thick. The picture documents the dominance of aerosols in the particle sizes and a pronounced desublimation of gaseous species.

- 200°C-Position (end of boiler): Here the picture changes fundamentally. Mayor part are piles of very fine-grained spheres that form clusters. In contrast to the former and hotter positions no extensive, molten textures are visible. The sieve bears no coating, indicating the stop of desublimation.

The method of the deposition probe allows a monitoring of the load of salts in the flue gas, which forms coatings on the boiler materials by deposition of aerosols and by desublimation (transformation from gaseous state to solid state) during burning a given fuel, during a preset or varied firing control system etc. The important role of salts as trigger of corrosion is shown in the next chapter.

2 Components in Deposits, Salts are relevant for Corrosion

The deposits consist of ashes and salts.

The ash component can not react with the steel of a boiler under the normal conditions (flue gas and material temperatures) of a conventional firing of waste and biomass. And they can not indirectly trigger corrosion, e.g. by vaporization of corrosive species. Metallic aluminium could cause exothermal reactions in the deposits. Therefore around aluminium particles molten salts frequently are visible. They decompose and only relicts can be found after some thousand hours.

The salt component causes corrosion. Two ways of interaction can be distinguished:

- On the one hand a direct contact of solid or liquid salts to the steel surface. Most relevant for corrosion are saltmelts, frequently chloride and chloride-sulphate melts (e.g. binary and ternary mixtures of alkaline- and heavy metal-chlorides and combinations of chlorides and sulphates, e.g. lead-potassium-chloride-sulphate).

- On the other hand a gaseous mobilization causes a common gas system between salts and steels - an indirect gaseous attack:

  Here gaseous species can be guided by concentration gradients, e.g. by consumption of chlorine gas on the steel surface (= corrosion). The formed iron chloride vaporizes in direction of the deposits.
Two simple, but important ideas: 1) The less the chlorine concentration is (the 'partial pressure of chlorine'), the lower is the amount of chlorine that can be mobilized in direction to the steel and the lower is the dynamic of corrosion. 2) A big distance between chloride salts and the steel reduces the possibility of a common gas exchange system - therefore the texture and the chemical and mineralogical developments in the deposits are very important to corrosion.

3 Development of Deposits

The deposited salts and ashes can be studied in samples collected during an outage. In contrast to the irregular and statistical textures visible on the deposition probe (Table 1), the deposits developed over several thousand hours yield highly organized structures, e.g. Table 2:

- Round caverns indicate the vaporization of some species.
- Big, solid crystals grow from the solid matrix (sub-solidus-state, not molten)
- The matrix segregates into two components (sub-solvus-segregation)

Some further frequently seen processes are:

- Sulphatation of chlorides by $\text{SO}_2$ and $\text{SO}_3$.
- Increasing of the density of the textures by sintering, melting and crystal growth.
- Mechanical influences of rappers, water guns etc.
- Influence of internal stress by the formation of corrosion products and by resulting chemical reactions (e.g. oxidation of iron chloride).

Table 3 to Table 5 show that similar corrosion phenomena and mechanisms can occur in boilers fired with different fuels, as the formation and development of the deposits are similar. This gives evidence that specific chemical environments can occur in different constructed boilers. Here the role of lead salts is emphasized, which are easily visible by their white colour in Table 4.

In all six examples the macroscopic and microscopic indications are typical for high temperature chlorine corrosion (gaseous attack of chlorine). The texture of the steel is degenerated along the grain boundaries. Wall thickness measurements show a material loss of up to 1.9 mm per 1,000 hours.

Basic information on samples, fuels and firing:

A) Superheater tube of a waste-to-energy plant, moving grate, centre-flow firing, steam temperature ca. 400°C, flue gas temperature ca. 430-510°C;

B) Boiler tube of a coal fired plant, boiling temperature ca. 340°C, the tube was situated in side wall at the height level of a burner (burner situated in the front wall), the flue gas temperature can not be sense fully declared, due to the radiation;

C) Superheater tube of a plant for refuse derived fuels, bubbling fluidized bed, steam temperature ca. 380°C, flue gas temperatures ca. 450-480°C;

D) Boiler tube of a plant for refuse derived fuels, spreader feeder above vibration grate, boiling temperature ca. 260°C, flue gas temperature ca. >800°C;
E und F) Boiler tubes from same built boilers at two different locations, biomass-to-energy plants, waste wood, spreader feeder over travelling stoker, boiling temperature ca. 280°C, the tubes come from the side walls next to the grate, therefore the flue gas temperature can not be sense fully declared, due to the radiation;

Example A, superheater from waste-to-energy plant:
The wall thickness is degenerated by extensive flat pits of several centimetres width. From the shown sample the loose ashes of light brown colour were removed during sampling. Some remnants of the ashes are visible in form of spheres.
On the tube surface lays a thin magnetite scale. Above it follows a complex textured layer of different sulphate salts (Na, K, Ca, Fe and Zn). The outer white layer (see bse-mode picture in Table 4) respectively the light yellow colour in the element maps (Table 5) indicate that lead salts formed a solid sintered mantle approximately 0.2 to 0.3 mm above the tube surface all around the tube. The lead salts have chlorine and sulphur (sulphate). They penetrate into the inner salt layer in a molten state (salt melts).
During operation conditions both outer salt layers keep elastic (no cracks are visible), in contrast to the magnetite scale (several cracks). The elastic condition and the completely dense texture of the outer salt layers give evidence for sintering and melting.

Example B, boiler wall of a pulverized coal fired boiler:
At the height level of the burners the tubes are extensively degenerated. The circumference of the tubes is still circle shaped and does not show typical morphological patterns which would visually indicate the severe material loss.
The approx. 0.05 mm thick layer on the tube surface (dark grey colour in bse-mode picture of Table 4) consists of iron chloride. Then follow iron sulphates and oxides, with local spots of iron sulphide next to the iron chloride. The adjacent layer is formed by lead salts (white layer in Table 4). This layer shows crystals and dense, sheet like textures. Above it follows a few millimetres thick sulphate layer and then, next to the flue gas, a few millimetres thick, porous cover with spheres (slag, mostly oxides).
All layers yield brittle cracks, except the lead salt layer. This gives evidence for an elastic, molten state of the lead salts during boiler operation.

Example C, superheater, RDF fired bubbling fluidized bed:
The full wall thickness was degenerated by extensive flat pits of several centimetres width in less than one year of operation.
On the tube surface an irregular textured layer of iron oxides and chlorides is situated (dark grey colour in Table 4). On it follow iron oxides (lighter grey colour). In both constituents some iron sulphates are present. All is mantled by a very dense layer of lead chlorides and sulphates (white colour). While the inner layers show brittle cracks, the lead salts were elastic during operation (molten).
In that specific case, at several positions the lead salts were replaced by copper salts, but the corrosion mechanisms and the degradation rate was the same.

Example D, boiler, RDF fired, spreader feeder and vibration grate:
Like in example B, the extent and the areas of the degradation were not easily visible by eye-view.
The bse-mode picture (Table 4) shows a complex, dotted distribution of several phases (called eutectic texture):

a) Lead salts (white colour);

b) Chlorides, sulphates and chloride-sulphate-salts of zinc and iron (medium greyscale), near to the tube;

c) Other mixed salts and oxides (dark greyscale), near to the flue gas;

The eutectic texture is the evidence for a frozen salt melt. No cracks occurred during boiler operation. The distance between the melt and the tube is almost zero (here in the pictures a gap is visible; the reason is, that the frozen salt layer is very brittle and chipped off during sampling). But hence the presence of a salt melt, no pits which are typical for salt melt corrosion are visible in the tube surface, but only the intercrystalline attack of chlorine gas.

Examples E and F, same built boilers of a biomass-to-energy plants at two different locations, spreader feeder over travelling stoker:

Both damaged boilers showed no significant corrosion phenomena. The degradation regularly occurred over the tubes circumference.

The lead salts in example E (white colour in bse-mode picture of Table 4) form a palisade like eutectic texture (frozen melt).

The lead salts in example F have formed a solid layer within the corrosion scales (iron oxide). To reach that position, they must have penetrated the scales as molten salts. The top side of the layer is shaped irregular and there is a gap to the next layer of the scale. The irregular shape and the gap are evidence for the vaporization of the lead salts (release of chlorine gas).

4 Discussion

The examples show that similar processes of formation and development of deposits can occur regardless the given fuels or firing technologies. The corrosion mechanisms resulting underneath the deposits are caused by the development in the deposits - they are similar in all shown examples. Therefore the knowledge of the chemical environment in boilers puts light on the corrosion processes and helps to initiate measures to reduce corrosion.

The formation and development of deposits is driven by chemical and mineralogical processes depending on the parameters of matter [X] and temperature [T]. The following list explains the chain of processes by using the example of chlorides:

- The release of chlorides from the fuel into the flue gas depends on the properties of the chlorine-/ chloride bearing components and of the firing conditions.

  Therefore the components and their chemical composition of the fuel are of importance (household waste or industrial waste). It is important to find suitable firing conditions for (short- and longterm changing) fuels. That means to find a preset for the existing parameters of a firing system, which focuses on corrosion minimization.

  The potential for corrosion of fuel- and firing-conditions can be evaluated by analysing the proportion of ashes to salts (Ash-Salt-Proportion, the ‘ASP’-concept).

- Chlorides and especially lead chlorides have a high vapour pressure and therefore escape from hot flue gas by desublimation (changing from gas to solid state) on cooler surfaces, which are available on the tubes (cooling trap).
These processes can be monitored by a deposit probe, which samples the desublimating and condensating salts on-line during operation at specific fuel-firing-conditions (e.g. Table 1).

- Depending on the saturation of gaseous salts in the flue gas the deposition of salts (chlorides, sulphates, chloride-sulphates etc.) starts by condensation (from gas to liquid) and desublimation anyhow.
- Depending on the heat flux a temperature gradient is generated in the deposits. The growth of the deposits increases the temperature and that forces the deposited to release corrosive chlorine gas.

These processes can only be monitored by using the deposits which were built up during the service time (e.g. Table 2). It e.g. allows to compare different corrosion conditions (favourable/ not favourable), which puts light on different local conditions in a boiler (e.g. cooling traps).
Table 1

On-line monitoring of the deposition of salts and ashes from the flue gas at different flue gas temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ca. 600°C</td>
<td>Before sampling, „clean sieve“</td>
</tr>
<tr>
<td>ca. 350°C</td>
<td>Sample, T ca. 600°C</td>
</tr>
<tr>
<td>ca. 850°C</td>
<td>Sample, T ca. 600°C</td>
</tr>
<tr>
<td>ca. 200°C</td>
<td>Sample, T ca. 600°C</td>
</tr>
</tbody>
</table>

- **Impacts, craters in molten aerosol coating (chlorides and sulfates)**
- **Delamination** indicates a thin coating = desublimated aerosols
- **Thick coating of aerosols on the sieve**
- **Piles of particles, no aerosols on the sieve**
Table 2

Chemical and Mineralogical Processes in the Salt-Ash-Deposits
develop Highly Organized Textures

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**Development**

- deposition probe, deposit formed after some seconds
- time, temperature, substance
- deposit after ca. 7400 h
Table 3

Similar development of deposits and resulting corrosion mechanisms under different fuel- and firing conditions; continues on next page

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>WTE, moving grate, centre-flow firing, superheater</td>
<td>400-510°C</td>
</tr>
<tr>
<td>B</td>
<td>Pulverized coal firing, boiler</td>
<td>340°C up to flame temp.</td>
</tr>
<tr>
<td>C</td>
<td>RDF-firing, bubbling fluidized bed, superheater</td>
<td>380-480°C</td>
</tr>
<tr>
<td>D</td>
<td>EBS, vibration grate, spreader feeder, boiler</td>
<td>260°C up to &gt;800°C</td>
</tr>
<tr>
<td>E</td>
<td>Waste wood, travelling stoker, spreader feeder, boiler at location 1</td>
<td>280°C up to flame temp.</td>
</tr>
<tr>
<td>F</td>
<td>Waste wood, travelling stoker, spreader feeder, boiler at location 2</td>
<td>280°C up to flame temp.</td>
</tr>
</tbody>
</table>
Table 4

Similar development of deposits and resulting corrosion mechanisms under different fuel- and firing conditions; continues on next page

The red frames mark positions of element maps, which are shown in the next table.

<table>
<thead>
<tr>
<th>Fuel Firing Conditions</th>
<th>T-window Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>WTE, moving grate, centre-flow firing, superheater</td>
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<tr>
<td>Waste wood, travelling stoker, spreader feeder, boiler at location 2</td>
<td>280°C up to flame temp.</td>
</tr>
</tbody>
</table>
Table 5

Similar development of deposits and resulting corrosion mechanisms under different fuel-and firing conditions

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
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<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>S</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>Fe</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
<tr>
<td>Cl</td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Table 6

Schematic application of the ash-salt-proportion

Photograph (SEM-picture): View on dust collected from the flue gas, showing the flue gas components ash (blue arrow) and salt (orange arrow).

The chemical analysis and calculation allows defining variations between the both components, which is expressed in the diagram below. While high ash contents are a good state for a boiler (ashes do not cause corrosion), high salt contents are 'bad' (as the salts trigger the corrosion, e.g. by chlorides).
Table 7

Degradation and ash-salt-proportion - optimization of firing conditions

Degradation, front wall above the refractory lining

Deviation of the ash content from the reference point [%]

ASP-Proportions in:
- boiler 1 (less good)
- and boiler 2 (good)
corresponding to the shown degradation rates

ASP-Proportions in:
- the boilers after an optimization campaign

Formation and Development of Salt-Ash-Deposits (Fouling) regarding the Chemical Environment
Table 8

Effect of industrial waste (shredder) on the ash-salt-proportion

<table>
<thead>
<tr>
<th>Deviation of the salt content from the reference point [%]</th>
<th>Deviation of the ash content from the reference point [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL1 vor E-Filter, ohne Shredder</td>
<td>OL1 vor E-Filter, mit 30% Shredder</td>
</tr>
<tr>
<td>OL1 vor E-Filter, Shredder</td>
<td>OL1 vor E-Filter, 'undefined shredder'</td>
</tr>
<tr>
<td>Var_Salz</td>
<td>Var_A sche</td>
</tr>
<tr>
<td>'Good' standard waste</td>
<td>'Bad' standard waste</td>
</tr>
</tbody>
</table>

- 'undefined shredder'

Note: The graph shows the deviation of the ash and salt content from the reference point for different waste compositions.