Corrosion in fire tube boilers of biomass combustion plants

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Introduction

The main biomass fuels used in Austria are bark, wood chips and sawdust, to a minor extent also straw. Despite the fact that these fuels (except straw) contain low concentrations of chlorine and sulphur (in comparison to coal) severe corrosion occurred in several wood chips and bark combustion plants equipped with hot water fire-tube boilers and lead to leakage of several heat exchangers tubes after less than 10,000 operating hours [1].

Chemistry and deposition of ash particles on heat exchangers

Corrosion of heat exchangers is strongly related to ash-deposition on the tubes. In hot water fire tube boilers where the flue gas passes inside the tubes no or little direct impaction of sticky fly-ash particles occurs on the tube walls. Instead, the initial deposits are formed due to thermophoretic forces. These forces are caused by the high temperature gradient between the hot flue gas and the tube walls in the boiler and are most dominant for small particles (<1µm) formed through vapour nucleation, condensation, chemical reaction and agglomeration processes [2, 3].

During combustion of biomass, large amounts of Cl and S together with volatile alkali metals such as K (mainly) but also Na are released as vapours to the flue gas. At high concentrations of vaporised species and high cooling rates in the heat exchanger new very small sub-micron particles are formed through homogenous and subsequent heterogeneous nucleation and agglomeration [4]. In addition, ash forming vapours condense on or react with fly-ash particles with decreasing flue gas temperature in the boiler section.

For all relevant mechanisms (nucleation, condensation, chemical reaction) the highest concentrations of vaporised and subsequently condensed K-, Cl- and S-species are to be expected in the smallest particles. Field measurements of fly-ash particles from biomass combustion units agree with this prediction and reveal increasing concentrations of K, S and Cl with decreasing particle size [4, 5, 6, 7]. The measurements also reveal that these elements are the major constituents of sub-micron particles (smaller 1 µm), while refractory elements, like Ca and Si, dominate in larger particles.

The temperature at which condensation, chemical reaction or nucleation of K, S and Cl vapours occurs depends on which species are present in the flue gas. Moreover, the impact of fly-ash layers deposited on tube walls on corrosion is also related to the K-, S- and Cl-species present.

If equilibrium is assumed in the flue gas at the high temperatures before boiler inlet (>900°C), potassium primarily exists as KCl(g) in straw combustion units (Figure 1) and as KOH(g) in bark and wood chips combustion units (Figure 2), while sulphur and excess chlorine are present as SO₂(g) and HCl(g) respectively.

With decreasing temperature, KOH(g) is converted to K₂SO₄(g,s) and K₂CO₃(s) by gas phase reactions, while KCl(g) condenses as KCl(s). According to chemical equilibrium all sulphur should be bound as solid K₂SO₄ at temperatures below 900°C. However, according to
kinetic considerations, the formation of $K_2SO_4$ rarely reaches equilibrium in the gas phase and therefore only a part of the potassium follows this reaction path [4]. By considering this kinetic limitation and the high cooling rate of the flue gas in a hot water fire tube boiler, phase transformations without chemical reactions such as condensation of KCl in competition with formation of $K_2CO_3$ are more likely to occur. However, according to equilibrium $K_2CO_3$ is only formed when excess amount of K to S and Cl is present.

Kaufmann investigated single particles and deposition layers on heat exchanger tube walls from combustion of straw and woody biomass by means of X-ray diffraction analyses (XRD) and found crystalline KCl and $K_2SO_4$ to be the main constituents of the ash. No potassium carbonate was detected in crystalline form, which however not excludes the possibility of amorphous $K_2CO_3$ [3].

Figure 1: Chemical equilibrium for relevant ash forming elements in the flue gas passing the boiler – fuel: bark
Explanations: combustion air ratio $\lambda=1.44$ ($O_2 = 6.4$ Vol%, related to dry flue gas)

Figure 2: Chemical equilibrium for relevant ash forming elements in the flue gas passing the boiler – fuel: straw
Explanations: combustion air ratio $\lambda=1.88$ ($O_2 = 9.8$ Vol%, related to dry flue gas)
Discussion and Explanation of the corrosion mechanism - Active Oxidation

The enrichment of chlorine in the boilers of biomass combustion plants has two main reasons.
First, considerable amounts of alkali chlorides are formed in the flue gas during the combustion process, due to the fact that K, Na and Cl are relatively volatile elements [2, 9].
Second, alkali chlorides might result from pollution, especially from "salting" the biofuel in winter, to keep it from freezing during transport.
These alkali chlorides will condense/desublimate on the tube surfaces and will react with the flue gas under formation of sulphates and the release of chlorine according to reaction 1.

\[
\begin{align*}
2 \text{NaCl} + \text{SO}_2 + \text{O}_2 & = \text{Na}_2\text{SO}_4 + \text{Cl}_2 \\
2 \text{KCl} + \text{SO}_2 & = \text{K}_2\text{SO}_4 + \text{Cl}_2
\end{align*}
\]

According to extensive thermodynamic equilibrium calculations alkali sulphate formation is favoured below 1000°C. In spite of this fact, mainly alkali chlorides are formed during biomass combustion, because of their higher rates of reaction [2, 8]

Although the thermodynamically stable sulphation reaction may be too slow in the gas phase, solid KCl or NaCl may have enough residence time to undergo heterogeneous reactions with SO\(_2\)(g) or SO\(_3\)(g) and form K\(_2\)SO\(_4\) respectively Na\(_2\)SO\(_4\) in the ash layer, reaction 1 in Figure 3.

During this sulphation reaction Cl\(_2\)(g) is released. Because this reaction takes place in the deposit it will cause a very high concentration of gaseous chlorine near the metal surface - higher than the concentration of Cl in the flue gas. Part of the chlorine set free can diffuse through the porous scale covering the tube. Iron chlorides are only stable, if the oxygen pressure is almost zero. This is possible at the iron/scale interface, where the chlorine may react to form iron dichloride, reaction 7 in Figure 3.

Because of the relatively high steam pressure of FeCl\(_2\) and depending on temperature and concentrations the iron dichloride formed will partly evaporate and diffuse through the surrounding scale in direction of the flue gas.

There, due to the higher oxygen partial pressure, the iron dichloride will react with oxygen and the iron oxides according to the reactions

\[
\begin{align*}
3 \text{FeCl}_2 + 2\text{O}_2 & = \text{Fe}_3\text{O}_4 + 3\text{Cl}_2 \\
2 \text{FeCl}_2 + 1,5\text{O}_2 & = \text{Fe}_2\text{O}_3 + 2\text{Cl}_2 \\
\text{FeCl}_2 + \text{O}_2 + \text{Fe}_3\text{O}_4 & = 2\text{Fe}_2\text{O}_3 + \text{Cl}_2
\end{align*}
\]

The chlorine set free, see reactions 2, 3 and 4 in Figure 3, can react with the pure metal again.

Consequently, chlorine can play a catalytic role in this process by transporting Fe from the tube wall and supporting severe corrosion.
In: Proceedings of the China International Corrosion Control Conference '99, paper Nr.90129, October 1999, Beijing, China, China Chemical Anticorrosion Technology Association (CCATA) (Ed.), Beijing, China

Figure 3: Principles of the corrosion mechanism by active oxidation

Possibilities to reduce active corrosion in biomass combustion plants

Very similar corrosion mechanisms are described for alloys based on nickel, cobalt and chromium. Therefore this type of corrosion can not be prevented by the selection of a common heat resistant or even high alloyed material.

Though the following measures will reduce or prevent corrosion:
- Avoid pollution with higher amounts of chlorides. Especially salt (NaCl) used to keep biomass from freezing has to be avoided.
- Reduction of the temperature by flue gas circulation in the secondary combustion zone.
- Change from discontinuous to continuous operation using frequency regulated fans. Continuous flow of the flue gas in the heat exchangers will be secured.
- In case the fuel is polluted with chlorine, the corrosion problem will not expire with time, because chlorine has got a catalytic function in the corrosion mechanism. In the case of "active oxidation" (characterised by the appearance of red rust and porous scale layers) of tubes the inner walls must be thoroughly cleaned (best by sandblast) to remove all the adhering FeCl2.
- Consequently the inner tube walls should be coated with a corrosion prohibiting layer. Protective graphite based coatings will dry to the wall and burn after start up. The "oil coal layer" formed will prevent diffusion and direct contact between the ash layers and the tube surfaces.
- Boiler cleaning should be carried out with an automatic and continuous cleaning system based on soot blowers for fire tube boilers seems to be of considerable advantage in comparison to manual cleaning with brush cylinders at longer intervals. The main reason for favouring the automatic and continuous cleaning system is that cleaning at short intervals reduces the dust and salt precipitation on the tube surfaces significantly. Moreover, protective graphite based coatings for boilers in order to prevent a direct contact between the tube surfaces and the ash layers will not be damaged by soot blowers but be destroyed by brushes.
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