Many biomass- or waste-fired plants have problems with high temperature corrosion especially if the steam temperature is greater than 500°C. An increase in the combustion of waste fuels means that an increasing number of boilers have had problems. Therefore, there is great interest in reducing the costs associated with high temperature corrosion and at the same time there exists a desire to improve the electrical efficiency of a plant by the use of higher steam temperatures. Assuming that the fuel is well-mixed and that there is good combustion control, there are in addition a number of other measures which can be used to reduce superheater corrosion in biomass and waste fired plants, and these are described in this paper. These include the use of fuel additives, specifically sulphur-containing ones; design aspects like placing superheaters in less corrosive positions in a boiler, using tube shielding, a wider pitch between the tubes; operational considerations such as more controlled soot-blowing and the use of better materials.

Keywords: Biomass, waste, superheaters, corrosion

1. Introduction

In recent years there has been a considerable increase in the amount of heat and electricity generated from the combustion of biomass or waste due to the drive to reduce CO₂ emissions and legislation forbidding the deposition of waste at landfill sites. One of the main problems with biomass and waste combustion is the production of low melting point chloride-containing deposits, which build up on heat-exchange surfaces, for example superheater tubes, and cause corrosion. The considerable corrosion problems increase the operation and maintenance costs, therefore leading to a higher cost for electricity and heat produced by these fuels. Energy companies are actively trying to reduce costs to make bio-fuels and waste more competitive sources of energy. At the same time there exists a driving force towards improving the electrical efficiency of a plant by the use of higher steam temperatures.

This paper describes some examples of methods for reducing corrosion, or achieving higher temperatures with acceptable corrosion. It is not intended to be an exhaustive or comprehensive list of methods, rather those that have come to the attention of the authors or that have been investigated by us. We assume that the fuel is well mixed and that there is good combustion control and instead focus mainly on the fuel chemistry and flue gas temperature and the effects that these have on critical components like superheaters. The paper looks at three main techniques for reducing corrosion:-

- Use of additives to change the flue gas and deposit chemistry
• Design and operation considerations
• Use of better materials. (A table giving the chemical composition of all the materials mentioned in this paper is given in the Appendix at the end)

2. Additives

Fuel additives can be used to alter the chemical environment in the boiler and make it less corrosive. Problems with corrosion and large amounts of deposits are to a great extent caused by chlorine compounds, especially alkali chlorides (NaCl, KCl), but also e.g. lead chloride (PbCl₂) and zinc chloride (ZnCl₂). These compounds have low melting points and are therefore partially or completely molten at the temperatures on heat transferring surfaces in the boiler. This makes them form sticky deposits where more particles can easily accumulate and in this way the deposits grow quickly. Molten phases on the tube surfaces are also much more corrosive than solid compounds. Some theories state that chlorine takes a major part in the corrosion process, by so-called “active corrosion”, [1, 2], whereby chlorine is not consumed but circulates within the oxide. Other theories give potassium and sodium more central roles in the corrosion process, [3, 4], causing the breakdown of the protective chromia layer in stainless steels by the formation of potassium (or sodium) chromate K₂CrO₄.

2.1 Sulphur-containing additives

In the 1980’s additions of sulphur made during waste incineration caused a substantial reduction in the chlorine content of the superheater deposits, [5]. Short-term (8 hour) corrosion probe tests also showed that the corrosion rates of low alloy and stainless steels were greatly reduced. It was concluded that, in the case of low alloy steels, sulphur additions must be sufficient to reduce the chloride content of the initial deposit to ~0.1 percent to achieve low corrosion rates. A deposit containing only alkali sulphates has a higher first melting point than a deposit containing alkali chlorides [6] and, as molten phases increase the corrosion rate, alkali sulphates are preferred to alkali chlorides in the deposits.

It is known that co-firing wood fuel with sulphur containing fuels like coal decreases the corrosion rate, [7]. It has been shown that the addition of SO₂ led to a decrease in corrosion under deposits made from waste incinerator fly-ash and that no chlorides were found in the deposits after the experiments, [8] and also that the addition of SO₂ to pure oxygen reduced the oxidation rate of T22 in the range 500-600°C, [9]. In this case the suppression of oxidation was suggested to be due to the formation of small amounts of iron sulphate, which interfered with the oxidation process.

2.2 Sulphates – “ChlorOut additive”

Vattenfall has patented a method for the reduction of corrosion caused by high levels of alkali and chlorine in the fuel using sulphates, [11]. The method, called “ChlorOut” covers a number of sulphates, but ammonium sulphate, (NH₄)₂SO₄, is the most often used additive as it also
reduces NO\textsubscript{x} and the consumable costs of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and NH\textsubscript{3} are similar in terms of their NO\textsubscript{x} reducing potentials. The additive is sprayed into the flue gases after combustion, but before the superheaters, and changes gaseous alkali chlorides to sulphates, which are considerably less corrosive. A simplified reaction scheme during the injection of ammonium sulphate solution is described as follows:

(R1) The injected ammonium sulphate decomposes into ammonia and SO\textsubscript{3}.

(R2) SO\textsubscript{3} reacts with alkali chlorides and converts them into alkali sulphates and HCl. (Alkali sulphates are more stable and less corrosive than alkali chlorides. In waste incineration it is assumed that the most abundant alkali chloride is NaCl).

(R3) Ammonia reacts with NO which is consequently reduced by the so-called SNCR reaction.

(R1) \((\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_3 (g) + \text{SO}_3 (g) + \text{H}_2\text{O}\)

(R2) \(2\text{KCl} (g) \text{ (or NaCl)} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 (s) \text{ (or Na}_2\text{SO}_4) + 2\text{HCl} (g)\)

(R3) \(4\text{NH}_3 (g) + 4\text{NO} (g) + \text{O}_2 (g) \rightarrow 4\text{N}_2 (g) + 6\text{H}_2\text{O}\)

The level of alkali chlorides in the flue gases is measured with an IACM (In situ Alkali Chloride Monitor), [10].

![Fig. 1](image-url)  
Fig. 1 Results from bark and waste fired boiler in Munksund, showing corrosion rate versus metal temperature for a number of different alloys, [13].
The ChlorOut additive has been successfully used for a number of years in boilers firing wood, waste wood and wood-waste mixtures, [12]. Figure 1 shows the results of corrosion probe testing, with and without ChlorOut (ammonium sulphate), in a circulating fluidised bed (CFB) boiler in Munksund, Sweden, which fires a mixture of bark and 6% plastic waste, [13]. There was a temperature gradient of 430 to 550°C along the probe and five different materials were tested. The testing lasted four weeks and the two probes were exposed at the same time on different sides of the boiler. ChlorOut was sprayed in on one side of the boiler and affected only one of the probes. Chlorout greatly reduced the corrosion rates of all steels.

The figure also shows that X20 is a poor choice of steel for a biomass-and-waste fired boiler with a steam temperature of around 500°C (550°C metal temperature) and performed much worse than low alloyed steels. The austenitic stainless steel Esshete 1250 showed good corrosion resistance.

Within the EU project NextGenBioWaste, [14], a number of tests have been made by Vattenfall in boilers firing household waste or a mixture of household and industrial waste. Figure 2 shows an austenitic stainless steel after exposure for 4 hours at 500°C with and without ChlorOut in a CFB boiler owned by E.ON in Norrköping, Sweden, [15]. The fuel consisted of 30 - 50% household waste, 50 – 70% industrial waste.

*Fig. 2 Intergranular corrosion of the austenitic (Fe-18Cr-10Ni) steel 304L associated with chlorine ingress along the grain boundaries. Left and centre, reference case with no ChlorOut. Right, with ChlorOut. The extent of initial corrosion (right) is reduced with ChlorOut, [15]*

ChlorOut greatly reduced the amount of initial corrosion. The amount of chlorine in the deposit was reduced from 10-15 % to 1-3 %, by the use of ChlorOut and phase analyses showed that sodium, potassium and calcium chlorides decreased, (Figs. 3 and 4).

In low alloy ferritic steels corrosion was associated with the accumulation of iron chlorides at the metal oxide interface. Even though ChlorOut dramatically decreased the concentration of
chlorine in the deposit, chlorine-induced corrosion was not completely suppressed. The ferritic steel was clearly not able to form an oxide that sufficiently prevents chlorine ingress.

Austenitic steels did not suffer from chlorine accumulation at the metal/oxide interface to the same extent and the amount of corrosion was much less than in ferritic steels. The amount of corrosion was further reduced by additions of ChlorOut. The overall conclusion is that ammonium sulphate has the potential to reduce corrosion in waste-fired boilers and that higher alloyed austenitic steels are more likely to resist corrosion, [15].

3. Design and operation considerations

3.1 Final superheater in loop seal

In many new CFB boilers the final superheater is positioned in the sand-loop seal, in order to reduce corrosion. A number of steels were tested in corrosion probes in the boiler of the Nässjö Combined Heat and Power (CHP) station, situated in the southern part of Sweden, [16]. The boiler is a 30 MW CFB boiler, which produces steam at 80 bar/480°C and generates 9 MW electricity. The fuel used during the tests was 100% wood (logging residues). Probes were
exposed in two positions for 3360 h. One probe, metal temperature 600°C, was exposed near the top of the boiler at the superheaters in the flue gas passage and another, metal temperature 650°C, at the bottom in the cyclone loop seal. These both simulate the same steam temperature of 550°C. Corrosion was greatly reduced in the loop seal in spite of a higher metal temperature, (see Fig. 5).

Gas analyses showed that HCl levels were broadly similar in the range of 2-6 ppm at both testing positions. Levels of H$_2$O in the flue gas at the final superheater were in the range 22-25% (by volume) as opposed to 3-6 % in the loop seal. SO$_2$ levels were 13-20 ppm at the superheaters and 3-7 ppm in the sand loop seal. O$_2$ levels were 3-5 % at the superheaters and 5-15% in the loop seal. The environment is considerably less aggressive there, from a chemical point of view, although erosion problems would be expected to be greater. However, Fig. 5 clearly shows that the loop seal is an ideal position for a final superheater and sand erosion does not seem to be a problem. In addition, the deposits collected on probes in the loop seal were much thinner than those collected at the superheaters. It is possible that sand erodes the deposits, thereby removing a corrosive source. Another advantage to be gained, in addition to reduced corrosion, is that the superheater can be considerably smaller in size (about a third of the size of a conventional superheater) since the heat transfer per unit area of tube surface is more intensive in the loop seal, [16]. This leads to savings in material and manufacturing costs.

Fig. 5  Comparison of erosion-corrosion rates for steels exposed in probes near the superheaters at 600°C and in the cyclone loop seal at 650°C, simulating the same steam temperature of about 550°C, [16].
3.2 Soot-blowing

Extensive deposit growth is a well-known problem in biomass and waste-fired boilers and a number of soot-blowing methods are available for removal of the deposits. However, soot-blowing too intensively or badly adjusted soot-blowers can remove protective oxide layers along with the deposits or damage the oxide layers by causing cracking, thereby making it easier for corrosive melts or gases to react with the metal, [17]. Commonly used measures for reducing material damage during soot-blowing are, reduced soot-blowing steam pressure, reduced frequency, and tube shielding to protect the tubes nearest the blower, [17]. Tests on a variety of tube shielding in a waste-fired plant found that Sicromal 10, Sicromal 12 and 15Mo3 were good choices for shielding material (better than austenitic stainless steels) when considering a combination of cost and lifetime, [18].

Danish straw-fired boilers are designed with an increased pitch between superheater tube bundles which allows a thicker build-up of deposits before the flue-gas passage becomes blocked, [19]. The high temperature superheaters are operated at a temperature where there is equilibrium between deposit growth and deposit melting, thus removing the need for soot-blowing. The deposits help to insulate the tubes and reduce the heat flux, which also reduces the corrosion rate.

“Non-stick” or “inert” coatings on superheaters have also been considered as a means of reducing the amount of soot-blowing, by reducing the amount of deposit that sticks to the tubes in the first place, [20]. Plant tests showed that a tube surface coated with a nickel-based alloy can reduce the formation of chlorine-rich, partly melted deposits, but no effect was shown on the chlorine-free deposits of a biomass plant. A ceramic coating showed a similar effect, but the coating did not remain on the tubes long enough for a long-term evaluation, [20].

3.3 Other design and operation considerations

Within the EU project NextGenBioWaste, [14], a “Chlorine trap” or “cold finger” has been installed and evaluated in the household waste fired boiler in Schweinfurt, Germany, [21]. The trap is a heat exchanger with narrow distances between the tubes and operated at a low temperature in front of the superheaters. (In order to compensate for the extra heat extracted there, some heat exchangers were eliminated from the second pass.) Chlorine-rich deposits condense from the flue gas at the trap. Preliminary results showed a reduction of 25% in the corrosion rate of the final superheater and differences in ash particle size distribution in pass 3 after installation, [21]. However, more long-term data are needed before these improvements can be attributed solely to the action of the trap, [21].

Reducing the flue gas temperature at the superheaters, by designing boilers with an extra empty pass, or by regular cleaning of membrane walls is another proven method of reducing superheater corrosion. The disadvantages are the increased investment cost in the first case
and the increased risk for wall corrosion in the second. As a last resort, the final steam temperature can be reduced. These methods, though, are commonly used.

And last, but not least, a cost-effective and simple way of increasing the lifetime of superheaters is by increasing the wall thickness when ordering replacements or designing new plant. A corrosion allowance of 1 mm is common in superheaters, but this should be increased to 2 mm. This method is popular in Danish straw-fired plant, [19], and has been used effectively in waste incineration plant, [22].

4. Materials

4.1 Biomass boilers

In coal-fired boilers increasing the chromium content of the superheaters leads to a decrease in the corrosion rate. This is not always the case in biomass-fired boilers. Figure 6 shows the results of corrosion probe testing in the 98 MW\textsubscript{tot} CFB boiler in Munksund, Sweden, which has a final steam temperature of 480°C and pressure 60 bar. The boiler is fired mainly with bark (>80%), but also sawdust, woodchips and approximately 6% of waste. The waste is mostly plastic from tape and packaging, obtained from the reprocessing (recycling) of cardboard cartons. Fig. 6 shows that increasing the chromium content of steels from the 0% of 15Mo3 to 1% in 13CrMo44, 2% in 10CrMo910 or even 10% in X20CrMoV12 1 did not lead to a reduction in corrosion rates. However the stainless steel Esshete 1250, containing 15% Cr and 10% Ni, showed very low corrosion rates, [16].

![Corrosion rates for various steels tested at 520°C in Munksund, [6].](image-url)

*Fig. 6. Corrosion rates for various steels tested at 520°C in Munksund, [6].*
Increasing the metal temperature of a superheater steel does not always lead to an increase in the corrosion rate. Tests performed in a bubbling fluidised bed (BFB) boiler running on 100% waste wood showed that for stainless steels a maximum corrosion rate was reached at a metal temperature of 540-560°C, [23]. An example of the results obtained for Esshete 1250 is given in Table 1. The decrease in corrosion rates at higher temperatures were explained on the basis of decreasing Cl levels in the deposits with increasing temperature and increasing diffusion allowing a protective Cr-rich oxide to be formed more effectively.

Table 1. Average metal loss at various metal temperatures for Esshete 1250 in a boiler firing waste wood, [23]

<table>
<thead>
<tr>
<th>Av. Metal Temperature (°C)</th>
<th>505</th>
<th>536</th>
<th>568</th>
<th>585</th>
<th>598</th>
<th>601</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. Metal loss (µm per 1000 h)</td>
<td>77</td>
<td>100</td>
<td>94</td>
<td>78</td>
<td>39</td>
<td>23</td>
</tr>
</tbody>
</table>

A steam loop for corrosion testing was constructed in a BFB boiler firing biomass and 15% packaging waste. At 500°C steam the alloys with the best corrosion resistance were the ones with the highest Ni and Cr contents, namely Haynes 230, HR11N, AC 66 and HR3C. The corrosion rate of X20 was unacceptably high and was totally unsuitable for this fuel mix. At 600°C Haynes 230 showed the lowest corrosion rates, followed by (surprisingly) TP 347 HFG, HR3C and AC66. The full results are presented elsewhere in the proceedings, [25].

4.2 Waste-fired boilers

Within the NextGenBioWaste project, [14], corrosion testing with cooled probes was performed by the authors in the boiler of a waste fired power plant, Müllverwertung Borsigstrasse, (MVB), in Hamburg, Germany. The maximum steam temperature was 380°C and the fuel consisted of 70% household waste and 30% industrial waste. Two probes were installed at the plant and were exposed for 1550 hours directly in front of the first set of superheater tubes that the flue gases meet on their way through the boiler. The flue gas temperature at this position was in the range 600-650°C and the metal temperatures of the probes were 440°C and 490°C, corresponding to steam temperatures of about 410°C and 460°C. The previously unpublished results are shown in Figs. 7 and 8.

The probe testing performed in this case represents a “worst case” form of corrosion testing. The probes were placed in a rather exposed condition before the first bank of superheaters and therefore subjected to a slightly higher than normal flue gas temperature and erosion rate. The first bank of superheaters that the flue gases meet do not contain the highest steam temperatures. The superheaters with the highest steam temperature are placed further along the flue gas passage at a lower gas temperature.
Fig. 7 Maximum and average metal loss (per 1000h) measured on probe rings with a temperature of 440°C in MVB. 317L and Alloy 625 were weld overlay coatings.

Fig. 8 Maximum and average metal loss (per 1000h) measured on probe rings with a temperature of 490°C in MVB. 317L and Alloy 625 were weld overlay coatings.
13CrMo44, Super 304, 15 Mo3 and HCM12A show the highest rates of metal loss, although 15Mo3 performed surprisingly well considering the low alloying content. All these four alloys have a nickel content of less than 10% and a molybdenum content of less than 0.5%. Super 304, which contains no Mo, performed very badly.

Sanicro 41, Alloy 625, C-22, C-276, C-2000 and San 28 performed very well with average metal losses below 100 mm/1000h at 490°C. All these alloys contain more than 30% nickel and 2% molybdenum. Sanicro 41, C-22, C-276 and C-2000 actually showed lower corrosion rates at 490°C than at 440°C.

In the same plant, MVB, protective coatings of 317L and Alloy 625 were applied to tubes with Pulse Spray Gas Metal Arc Welding and these tubes were welded into a superheater where the metal temperature was 300-350°C and the flue gas temp 500°C. After nearly two years (14000 hours) no material loss could be detected on Alloy 625, but an average of about 0.3mm metal loss was measured on 13 CrMo44 and 317L and 0.22 mm on 15Mo3, [24]. At these low temperatures the cheapest alloy, 15Mo3, showed the lowest corrosion rates of the steels and explains why 15Mo3 is a good choice in many waste applications at lower temperatures.

### 4.3 Cost of components

The corrosion resistance is of course not the only parameter to be considered when choosing a material. The cost is of prime importance. As a rule of thumb, if 15Mo3 has a cost factor of 1; 9-12% Cr steels cost 2 times; austenitic stainless steels, like TP 347H FG, cost 4-5 times; super austenitics like AC66, cost 10 times and nickel-base alloys cost 15-20 times. The cost of expensive alloys can be reduced by weld cladding on a low alloy ferritic steel if steam-side oxidation is not a problem.

Manufacturing costs must not be neglected though. As an example a superheater made of 2500 metres of tubing has a material cost of about 100 kEuro if made in a 9-12% Cr steel or 250 kEuro if made in an austenitic steel like 347 or Esshete. However the manufacturing costs are similar in both cases, around 150 kEuro. For a biomass application where 9-12% Cr steels corrode several times as fast as a stainless steel (see for example Figs 1 and 6) the austenitic steel is the obvious choice.
5. Conclusions

In addition to good mixing of the fuel and uniform combustion, measures that can be taken to reduce corrosion in biomass- and waste-fired boilers are:

- Use of sulphur-rich fuel additives which convert highly corrosion alkali chlorides into less corrosion alkali sulphates. Sulphates which are sprayed into the flue gas after combustion are particularly effective.
- Placing the final superheaters in a less aggressive environment, e.g. in the loop seal in a CFB boiler
- Reducing the amount of soot-blowing as much as possible, either in intensity or frequency. Excessive soot-blowing damages or removes the protective oxide scale from a superheater and leads to an increase in the corrosion rates.
- Use of tube shielding to protect components exposed to soot-blowers
- Use of non-stick (inert) coatings so that deposits accumulate at a lower rate on superheaters (more research is needed in this area)
- Superheaters with a wider pitch between the tubes and allowing thicker deposits to build up. The deposits may reduce the corrosion by reducing the heat flux (needs to be considered at the plant design stage)
- Use of a thicker corrosion allowance
- Use of a “chlorine trap” or “cold finger”
- Reducing the flue gas temperature at the final superheaters
- Use of “better” materials; “better” meaning combination of cost and corrosion resistance.

Ferritic or martensitic steels from 0 to 12\% Cr showed similar corrosion rates under similar conditions in biomass or waste-fired boilers, which means there is no advantage from a corrosion point of view in using X20CrMoV121 over 15Mo3. At higher steam temperatures in biomass applications austenitic- or super austenitic stainless steels are a good choice, and for waste boilers at higher temperatures alloys with high nickel contents and some Mo are needed. As it is often difficult to know which alloy will perform best, probe testing to simulate the superheater conditions of temperature and flue gas chemistry is highly recommended.

6. References

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19. Maribo-Sakskøbing and Amager. Private communications

7. Acknowledgements

The authors acknowledge with thanks the contribution to the research work presented here made by their former and present colleagues at Vattenfall.
8. Appendix

*Chemical composition, in weight percent, of the materials mentioned. The balance is Fe.*

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Other</th>
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<td>0.1</td>
<td>0.3</td>
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<td>0.9</td>
<td>0.1</td>
<td>0.5</td>
<td>0.5</td>
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<td>0.89</td>
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<td>0.32</td>
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<td>--</td>
<td>--</td>
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<td>9</td>
<td>--</td>
<td>0.8</td>
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<td>11.9</td>
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<td>1.5</td>
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<td>3.1</td>
<td>1.7</td>
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<td>--</td>
<td>--</td>
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<td>20.0</td>
<td>--</td>
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<td>0.5</td>
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<td>2.1</td>
<td>0.5</td>
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<td>8.5</td>
<td>0.4</td>
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<td></td>
<td>21.5</td>
<td>56</td>
<td>13.0</td>
<td>0.25</td>
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<td>0.5</td>
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