1. Occurrence of corrosion

Corrosion effects on refuse fired boilers have already been investigated for a long time. In many cases, chlorine was found to be one of the major players in the role of corrosion. It would be too simple to just correlate the corrosion rate to chlorine content in the fuel. Alkali metals and heavy metals contribute to corrosion as well as molten salts. Various corrosion mechanisms can be triggered. A brief overview is given here [10].
Gaseous corrosion

HCl content in the raw gas varies typically in the range of 1,000 mg/Nm³ or higher. In RDF concentration, it can be much higher. From the investigation described in [1], HCl from raw gas doesn’t contribute to metal chlorination as the above stated content is by far too low to be a major refuse or RDF incinerators. A further reason why HCl is not directly acting from the gas phase is that no condensing conditions are reached. Mechanisms known from wet chemistry are likely not to be valid for high temperature gas atmosphere. A further compound which is likely to trigger gaseous corrosion would be H₂S, triggering sulphide corrosion. This mostly occurs in reducing atmospheres, which is accompanied by higher CO concentration. Therefore, H₂S corrosion is widely described as CO corrosion.

Deposit-induced corrosion

The deposit on the boiler tubes consists of ash and salts [11]. The deposition of the salts can occur on ash particles and on other surfaces by vapour condensation, physical desorption or the impact of condensed salts. Depending on the salt composition and the amount of inert ash the melting point of the is influenced and this has an impact on the hardness of the depositions. Corrosion triggered by the deposit can occur under dry conditions (see section 1.1 where this topic is specifically discussed) or due to molten salts. The corrosiveness of the salt derives from the characteristic feature that a molten salt contains a high concentration of charge carriers [6]. Molten salts as electrolytes on a metallic surface can be seen as half cells, triggering electrochemical processes. The driving force for electron transfer are concentration gradients of salt and also temperature differences. With increasing heat flux temperature, gradients also increase and thus corrosion effects are also increasing. The correlation between heat flux and corrosion is described in [8].

In [10], melting temperatures of various salts are summarized. The specific melting point is seen as an important factor concerning corrosion – in short: the lower the melting point, the higher the corrosion. It is further stated that the chloride containing compounds are more aggressive in terms of molten salt than sulphate salts. In [2], it is shown that electrochemical corrosion from both, sulphates and chlorine, can occur. In [17], it is stated that sulphate induced corrosion is more likely at higher material temperatures than corrosion by chloride salts.

In which manner the playing field of corrosion including chlorine, sulphur, oxides metals, temperatures, residence times, type of combustion system, velocity, and turbulence of flue gas occurs is quite complex and not jet finally explained and describable.

Mechanically-assisted corrosion

Effects like abrasion and erosion surely assist resp. accelerate corrosion [10]. When inspecting boilers, which were taken out of operation for maintenance, it can be seen that not many parts in the boiler are free from deposits by pure flue gas velocity.
Mechanically-assisted corrosion would be most likely to be found in areas where non-suitable online cleaning measures are in operation. These can in be online water cleaning devices in the radiation passes or soot blowers in the convective part of the boiler. Damaging the stable oxide layers and exposing fresh metal surface to the raw gas would result in high losses of material thickness.

1.1. High temperature chlorine corrosion on superheaters

As described before, a special type of corrosion mechanism will be explained in further details although studied in several objects in the past, e.g. in [2], [3], [4], [9], [16], [17].

The scheme from Figure 1 shows temperature and gradient of gaseous species in the scale and deposit on a super heater tube.

It is important to mention that the O₂ and H₂O concentration is low (basically zero close to the scaling on the tube and increasing until reaching flue gas conditions.
As described before, chlorine can be cycled in the described mechanism. The original source of chlorine is the high partial pressure of chloride salts [10]. In the salt, decomposition occurs and \( \text{Cl}_2 \) is formed due to high temperatures. A substantial amount of chlorine is formed when the partial pressure of the salt reaches more than \( 1 \times 10^4 \) atmospheres. It is important to mention that the oxygen and vapour content strongly differ in the scaling and the deposition (Figure 1). The deposit is much less tight to diffusion compared to the scale.

1.2. Molten salts

In [2], [9], [10] and [18], the molten salt attack is described. It is generally stated that sulphate containing salts have higher melting points than the corresponding chloridic salts (Figure 3, the same range of different melting temperatures can be found for lead salts).

The example of Figure 4 shows that either the temperature or the concentration difference can cause electric current. Both, temperature and concentration can be recognised as non-homogeneous when deposits occur on the tube. The finding in [13] states that higher corrosion rates occur together with higher heat fluxes.

![Figure 2: Chlorine cycle in the interface layers between tube scale and deposits (not true to scale)](image)

![Figure 3: Melting temperatures of sodium zinc chloride and sodium zinc sulphate](image)
This finding can be explained when assuming that temperatures gradients in the deposit are increasing by increasing heat flux.

![Diagram showing driving forces for electric current in molten salt and aqueous solution.](image)

**Figure 4:** Driving forces for electric current in molten salt respective aqueous solution

### 2. Sulphur as counter measure to chloride induced corrosion

#### 2.1. Former investigations

As described above, it is recognised that sulphatic deposits are less aggressive in terms of corrosion compared to chloridic deposits. In an early research [9], it was discovered that adding high sulphur containing coals to waste incineration drastically reduces corrosion. The drawing from Figure 5 shows initial corrosion rates discovered during tests performed with different mixtures of waste and coal. Depending on the material temperature, initial rates between 0.15 and 0.2 mm/h can be lowered by the order of one magnitude. The high initial corrosion rate is not only of important concern for new boiler parts being in contact with combustion atmospheres. Moreover, the fresh metal surface can result from online cleaning as mentioned above. If wet online cleaning is performed in a way that the stable oxide layer is removed e.g. by a strong water jet, the high initial corrosion rate would occur by usage of online cleaning. In this case, the usage of the wet cleaning system must be optimised. As a second measure, the use of sulphur in the combustion is beneficial to avoid high corrosion rate.
It is very important to mention that the sulphur can only act in a positive way when occurring as sulphate. When injected in reducing atmospheres, sulphur can occur as sulphide which can trigger corrosion (Figure 6).

Seeing a benefit in terms of minimizing corrosion, a lower SO₂/HCl ratio in the raw gas was suggested in [10] (Figure 7).

A further interesting finding was discovered and described in [12]. A pyrite injection was performed in a WtE boiler and showed a difference on corrosion probes (Figure 8, test with corrosion monitor). Despite the effect from Figure 7 where an increasing SO₂/HCl ratio positively influences the corrosion, SO₃ is seen to trigger a sulphation reaction. Combined with increasing SO₂ content in the raw gas, SO₃ would also increase. I.e. the results from [12] and [10] basically do not contradict themselves.
Figure 6:

Initial corrosion rates with and without sulphur feeding to combustion


Figure 7:

SO₂/HCl ratio recommendation to minimize corrosion rate

2.2. Own accidental findings

From investigations carried out in the WtE plant of Schwandorf, Bavaria (commissioned in 1882), interesting results can be reported. Before revamping activities in 1992 took place, the boilers of the plant were equipped with heavy fuel oil burners. The heavy fuel oil contained approx. 1.5 to 2 % wt.-% of sulphur. HCl concentrations occurred in the raw gas during boiler start-up without waste combustion. The chloride content of heavy oil was checked and was too low to be the cause of HCl emissions. After the conversion of start-up burners to light heating oil, the corrosion rates in the membrane walls sharply increased.

At that time, the operator was not aware of the sulphation (re-salting of chloride salts to sulphate salts). The increasing corrosion was explained as a result of a change in the waste composition. During boiler start-up, 3.5 to 4 t/h heavy fuel oil was used. The sulphur mass flow was thus in the range of app. 60 kg/h.

Further findings occurred accidentally. Performance tests of a new semi-dry flue gas cleaning system were carried out in 1993. To create a high amount of SO₂, sulphur
powder was injected to the combustion chamber by pneumatic transport. The SO₂ increase was clearly below the stoichiometrically determined values. The sulphur seemed to vanish from the SO₂ measurement which can only take place when the sulphur reacts to SO₃ or H₂S. As injection took place in oxidising conditions with a high air excess from carrier air, the formation of H₂S could be excluded. SO₃ would be the only meaningful species to form under these conditions. The same amount of sulphur was added to the waste and burned in the reducing atmosphere on the grate. The increase of SO₂ was in the expected range.

The conclusion at this time was that it depends on the condition of dosing sulphur to the boiler. In the case that SO₃ is produced from elementary sulphur, it needs to be injected into an oxygen rich environment.

2.3. Sulphation of deposits

Comparing the results from the above cited researchers and our own findings, many conclusions are congruent. The main difference occurs when taking a closer look on the timing of dosing SO₃ to the boiler. From cited research, it is beneficial to have a continuous dosing of sulphur – to form SO₃ rather than SO₂ – in the boiler to force sulphation of salts before depositing on the walls. From our own findings and investigation, it is sufficient to feed SO₃ during the start-up period and after wet online cleaning of boiler. By this means the deposits close to the surface of the tube contain less chlorides. According to Figure 2, chlorine causes the above stated chlorine cycle (Figure 2). Less chlorine in the layer would cause a weaker pronounced chlorine attack. The scheme from Figure 9 shows a mechanism where chlorine is removed from the deposit by SO₃. This mechanism can only take place in an atmosphere containing small amounts of vapour. In this case, the deposits do not contain diffusion tight layers (compare Figure 1) and moisture is apparent.

![Figure 9: Proposed mechanism of action of SO₃ on a chlorine containing deposit](image-url)
2.4. Influence of sulphur injection on deposits

The influence of non-continuous SO$_3$ injection on the character of the deposits is not yet fully investigated. Thick deposits normally have a high overall concentration of sulphates. Coming closer to the relatively cold surface of the tube the concentration of sulphate is lower, chlorine content is increasing. A finding from operational testing (see section 3.2.) describes that the deposits become softer and more brittle when operating the sulphur injection. One can i.e. imagine that continuous sintering of deposits is disturbed by a discontinuously dosing of SO$_3$. This effect would require more detailed investigation to be fully described.

3. Field application of sulphur injection

3.1. Manual testing

In the WtE plant of Schwandorf, manual tests were conducted where sulphur is injected by a pressurized air jet to the boiler. Two positions in the boiler were available (hatch 1, hatch 2, Figure 10). By measuring the amount of sulphur injected to the boiler and the measured SO$_2$ increase in the raw gas, an evaluation of the conversion process can be conducted. It is assumed that the sulphur which does not react to SO$_2$ is oxidised to SO$_3$.

With a good injection setup – which depends not only on the injection settings, but also strongly on the combustion settings – chlorine could be released using sulphation reaction. The boiler was in operation several weeks before the manual injection was started. The chlorine release can be explained with the proposed mechanism from Figure 10.

Figure 10: Sulphur injection, manual test, WtE Schwandorf
3.2. Automated injection system

In the Klingele RDF boiler in Weener [14], a prototype of a full automated injection system was constructed and commissioned. The reason for the installation of the sulphur injector was strong corrosion. The sulphur injection is done – as proposed above – during the start-up of the boiler and also during resp. after online shower cleaning. The injection is done through the secondary air nozzles on the rear wall (Figure 11). In [14], the operator reported several findings. E.g. that HCl in raw gas increase after first start of injection and also when the injection is re-started after a longer non-operational period. The increase of HCl basically occurs due to same sulphation mechanism as described before. From the latest reports of the operator, the corrosion became significantly less. A further important finding is related to the characteristics of the deposits: The condition of the deposits changed from hard sticky character to soft and easy to remove characteristic. The sulphur injection is in operation since 2015.

A further installation of a fully automated injection system (Figure 12 left) was done in an MVV’s WtE plant (Devonport). The injection is done – similar as the installation in Weener – through the rear wall secondary air nozzles (Figure 12 right). The injection of sulphur was done during operation with only auxiliary burners (Figure 13) in operation and with waste-fired boiler in operation (Figure 14). During operations with oil-fired burners, similar findings were achieved as were reported in the mid 80ies in the WtE facility of Schwandorf. HCl occurred during the injection of sulphur. Obviously, the release of HCl occurred from sulphation of remaining the deposits. Operating with a
high oxygen content (app. 11% vol.-% wet at boiler exit) during oil firing, the yield from sulphur to SO₃ is relatively high – between 89 and 95 % of the sulphur converts to SO₃.

During combustion of the waste, the sulphur injection leads to an increase of SO₂ and HCl. By the increase of SO₂, it is possible to evaluate the efficiency of the reaction from sulphur to SO₃. In the case shown in the diagram of Figure 14, the yield for the oxidation reaction is between 70 and 85 %.

Before and after injection campaign, corrosion probes were installed in the boiler in the area of the superheater. The results are not available at that time.

Figure 12: Sulphur injection (sulphur burner), automated injection, MVV Plymouth WtE Plant

Figure 13: Results of sulphur injection during firing of fuel oil, MVV Plymouth WtE Plant
4. Summary

It is found that chlorine is a major player in the role of corrosion. The way chlorine is acting as a corrosive species is rather complex. Heavy metals like zinc and lead as well as alkalines like sodium and potassium are relevant for molten salt corrosion and also for dry deposit corrosion. Chlorine induced corrosion can be minimized by sulphation, i.e. conversion of chloride salts to sulphate salts. The less corrosive character of sulphate salts in comparison to chlorine salts is widely reported. The re-salting from chlorides to sulphates can be done by SO₃. SO₂ is not useful for sulphation. In cited publications, the effect of sulphation is described and it is recommended that the sulphation is done permanently and before the salts deposit on the tubes. These details of the proposed injection are contradicting to the cited theories which prefer sulphation in advance of depositing.
From the authors’ own investigations it was found that elementary sulphur can be used to produce SO₃ in a safe and cost-effective way directly inside the lower first radiation passes of boilers [7]. Furthermore, the field experiments show that a permanent injection of SO₃ is not necessary to minimize corrosion. A non-continuous dosing of SO₃ causes sulphation of already existing deposits, minimizing their corrosive character.

During test operation of the sulphur injection it was found that the character of the deposits changed from hard and sticky to softer and more brittle. The detailed mechanism behind this effect is not yet fully explained. One possible theory is that the continuous sintering structure is disturbed.

A relevant SO₂ increase – causing an increasing amount of consumables in the flue gas treatment – doesn’t occur. As the sulphur is not injected permanently, of dew point effects on the cold end of the boiler – the economizer – did not occur.

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5. Literature


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