INVESTIGATION OF THE MECHANISMS OF HEAT EXCHANGER CORROSION IN A MUNICIPAL WASTE INCINERATION PLANT BY ANALYSIS OF THE RAW GAS AND VARIATION OF OPERATING PARAMETERS

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ABSTRACT

The detailed mechanism of high temperature chlorine corrosion, the dominant cause of corrosion in a municipal solid waste incinerator (MSI), has still to be clarified (Schroer, 2002). Upon its way through the boiler the raw gas is subject to various physical and chemical processes and interactions. Of these, sulphation of chlorides is supposed to have the major impact on chlorine corrosion (Neumann, 1997).

The physical and chemical mechanisms of corrosion were investigated at a municipal solid waste incinerator. Both, the particulate and gas phase of the flue gas, were chemically and physically analyzed during their way through the boiler, at temperatures from close to 1000 °C down to 200 °C. The raw gas composition was analyzed during normal operation and soot blowing cleaning routine. Additionally, operating parameters of the plant were varied, and deposition processes were evaluated with the aim to find out primary measures to reduce corrosion rates.

The particle mass concentration exhibits a bimodal size distribution with maxima at approximately 0.5 µm – growing by duration of travel – and 100 µm. First results show that sulphation of the particles can be observed upon travel through the boiler and on the fouling. Sulphur containing additives increased the sulphation of the particles during flight though not to completion.

INTRODUCTION

High temperature chlorine corrosion of superheaters is one of the main cost factors of municipal solid waste incineration plants. In contrast to coal, waste has a high content of alkaline, earth alkaline and chlorine compounds which cause, in combination with high temperature, high corrosion rates.

Fig. 1: Cross section of the MSI boiler investigated. It has four vertical passes with the superheater packages (5) and (6) placed at the beginning of the 3rd pass.

Whereas the principle mechanisms of corrosion have been understood nowadays, there are still open questions
regarding kinetics and raw gas evolution, one of the reasons for a broad range of corrosion rates in similar plants that still cannot be explained completely (M. Spiegel, 1994 and Warnecke, 2003).

A study has been started to setup a comprehensive model for corrosion in a municipal solid waste incineration plant (MSI). The plant investigated has an annual operational capacity of 180,000 tons, operating with three lines each equipped with a vertical-4-pass boiler.

The raw gas has a mean load of approx. 2-4 g/m³ of particulate matter, which consists of particles of different physical condition (liquid or solid), different shape (spherical, cubic, flat, fractal, etc.) and different size (nuclei of some nanometres up to ash pieces of some millimetres in diameter) (Deuerling, 2005). Deposition of particulate matter is supposed to play the major role in exposing metal surfaces inside the boiler to corrosive substances (Schroer, 2002 and W. Spieglel, 2003). The aerodynamic diameter of depositing particles ranges from some nanometres to several hundreds of micrometers. The small particles are deposited by diffusion and thermophoretic effects, the larger ones due to inertial impaction (estimation of inertial deposition predicts a lower aerodynamic diameter of approximately 20 µm for high chance of impaction at the geometry of superheater tubes) (Benker, 2005).

The raw gas components are subject to various physical and chemical processes and interactions of particulate and gas phase during passage through the boiler. Thermodynamic equilibrium predictions do not represent the real situation in the boiler due to very short residence times of the raw gas at a given temperature level (Deuerling, 2005 and Maguhn, 2003). Therefore, the kinetic of most of the reactions has to be considered. Hence, nucleation of particles, e.g. alkali salts, from the gas phase might appear at a lower temperature (further in the flue-gas duct) than thermodynamically calculated. The progression of the single reactions, however, plays a major role in understanding corrosion processes and setting up a concise corrosion model.

**METHODS**

Particles from 30 nm to 3 mm were sampled, transferred to off-stack instruments, size fractionated and analyzed regarding chemical composition and mass concentration. Additionally, acidic components of the gas phase were analyzed. Measurements were performed in the first pass (900 °C) and second pass (700 °C), straight behind the first two superheater bundles in the third pass (500 °C) and finally in the forth pass (300 °C). As the composition of the fuel exhibits considerable temporal variation, each measurement was carried out in parallel at the reference point (2nd pass) and at the measuring point in question. According to this, two identical measurement systems were set up.

To minimize sampling artifacts, a high temperature resistant probe was constructed which instantaneously dilutes and tempers the raw gas to 300 °C in a range of 250 – 1000 °C of boiler temperature. To retain the particulate matter in its current state, rapid but smooth dilution of the raw gas was accomplished by a porous tube diluter. The porous tube is positioned directly behind the swan neck inlet of the sampling probe and is provided with preheated clean air. The probe is kept to a constant temperature of 300 °C by air cooling, independent from the varying ambient temperature (Baron, 2001; Deuerling, 2005; Lyyränen, 2004; Mikkanen, 2000; Mikkanen, 2001 and Turrek, 2004).

The temperature of the aerosol sample is kept at 300 °C until the first ejection diluter (see fig. 3). This temperature was chosen to prevent condensation of water until final dilution. Additionally, the physical condition of several eutectics of metal chlorides melting beneath 300 °C could thus be maintained throughout the sampling path.

![Sample Suction](image)

**Fig. 2: Cross section of the porous tube diluter (PTD) probe**
The coarse particle fraction is deposited in a tailored cyclone. Subsequently the branch for analysis of the gas phase and main pump is separated. After a further dilution by a factor of 100 by a two ejector dilutor cascade, the fine particles (30 nm – 12 µm) are size fractionated by an ELPI (Dekati Oy, Finland) and collected for chemical analysis in a Berner low-pressure impactor cascade (60 nm – 10 µm). For analyzing the size distribution of particles from 0.8 µm to 20 µm an Aerodynamic Particle Sizer (TSI Inc., USA) was employed (see fig. 3) (Deuerling, 2005).

**RESULTS**

**Mass balance**

The total mass concentration was determined by summing the sampled data of all instruments and taking into account the losses. In summary, the mass concentration is approx. 3.2 g/m³ in the first and second pass, 2.6 g/m³ in the third pass behind the first two superheater packages and 2.1 g/m³ in the middle of the forth pass after the aerosol has passed all superheaters and half of the economisers.

The deposits inside the inlet of the probe varied in mass from pass to pass. Chemical analysis showed a good correlation with the particular content of the cyclone, implying that primarily coarse particles were deposited in the bend of the inlet. Consequently, its content was merged with that of the cyclone. Figure 4 shows the different mass concentration fractions of the components of the sampling system.

**Fig. 4: Total mass balance of the four passes**

In total, the mass concentration is reduced over the course of the boiler; however, this total trend is only reflected by the fraction of the inlet. The content of the inlet contributed nearly half of the whole sampled mass concentration in the first pass. This portion is drastically...
reduced to a finally negligible value in the 4th pass. Vice versa, the content of the cyclone has tendency to increase from pass to pass, so, when added, the inlet and cyclone show a good compliance with the total trend.

**Chemical composition**

Fifteen particle size fractions and the inlet content were chemically analysed. Looking at the relevant elements only, the particles can be divided into two main groups, < 20 µm and > 20 µm, where the chemical composition differs significantly.

The fraction < 20 µm has a high content of chlorine, potassium and sodium, indicating their origin from NaCl and KCl. The sulphur content is about 5 %, but only few silicon and calcium is present in this fraction.

The fraction > 20 µm has a much higher content of silicon and calcium, which are typical constituents of ash set free directly from the fire.

Fig. 6: Chemical composition of the four main particle fractions in the 3rd pass during normal operation. The coarse fraction is displayed in its two fractions, the content of the cyclone (= ”> 20 µm”) and the inlet.

Fig. 5 a-d: Chemical composition of all size fractions (in micrometers) from 1st pass (a) to 4th pass (d). Column 9 shows the composition of the inlet. The so called “Rest” is the sum of minor present elements (like titanium, bromine etc.) and the oxygen of the oxides of the shown elements.

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The summarizing graphs of figure 5 display the composition of the inlet as the ninth column. It is obvious – neglecting the 4th pass, where the inlet has nearly no content – that the inlet is very similar to the cyclone content. This observation was confirmed by correlation calculations. Consequently, for the considerations concerning mass concentration and chemistry, the content of the inlet was completely added to the cyclone content.

**Sulphation**

Sulphation of the chlorides is supposed to play a key role in corrosion processes. By this reaction alkali chlorides are converted to sulphates by sulphur dioxide. If sulphation occurs during the flight of chloride containing aerosol particles, chlorine is released mainly as indifferent HCl, as concerning corrosion (1).

\[
2 \text{KCl} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2 \text{HCl} \quad (1)
\]

The sulphation of particles already deposited on superheater tubes is supposed to result in the formation of “active” chlorine (2) that subsequently reacts with the iron of the tube steel (Kautz, 1972).

\[
2 \text{NaCl} + \text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{Cl}_2 \quad (2)
\]

The chemical composition of the aerosol particles shows a decrease of chlorine content in the three finest fractions, from the first to the third pass, accompanied by an increase of the sulphur content of these particles. Sulphation of the particles therefore occurs throughout the passes on-the-fly, so that already (partly) sulphated particles reach the superheaters. This conversion corresponds with a measured increase of the hydrogen chloride content of the raw gas (see fig. 7).

The composition of the inlet and the fouling of the superheater shows a slightly higher content of chlorines and sulphur than the content of the cyclone. This can be explained by an additional deposition of fine particles by thermophoresis or turbophoresis. For mass balance aspects, these additional amounts do not play a major role, though.

**Size distribution**

The aerodynamic particle size distribution appears bimodal through the way of the boiler. The first mode at approx. 0.5 µm should be merely created by secondary particles which are generated by the fire. The maximum of this fine mode shifts to slightly higher values during the travel of the aerosol (see fig. 8). This behaviour can be well understood by chemical and physical processes causing a growth of the particles. Nucleation from the gas phase occurs in the hot regions down to approx. 650 °C creating new particles in the 1st pass. Further condensation results in a quick growth of these ultra-fine particles as well as in growing of ash particles emitted from the fire. Furthermore, coagulation of particles increases the mean diameter of the particles in this size fraction up to 10 µm.

The second mode appears at approx. 300 µm and is mainly composed of primary particles like ashes and calcium oxide spherules. These particles are also growing by condensation. Because of the high initial particle diameter the coarse fraction does not change its size distribution significantly. The coarse fraction contributes to the particle mass concentration similarly as the first mode; however, it is more reduced on the way through the boiler.

Between the two modes there is a range of very low mass concentration which is increased from the 1st to the 4th pass, mainly by growing particles from the fine fractions.
Normal Operation, Mass Concentration, 1st - 4th Pass (mean values)

![Graph showing mass concentration distribution](image)

**Soot blowing**

Measuring the aerosol in the 3rd pass of the boiler during a cleaning (“soot blowing”) routine enables to look at particles, which were deposited on the superheater fouling surfaces at a temperature of approx. 490 °C and blown off after an eight hours interval.

Figure 9 gives a time resolved impression of the aerosol variation during soot blowing, which was recorded of the three soot blowers of the 3rd pass, each cleaning a superheater package by high pressure steam blowing from a rotating jet for a few minutes every 8 hours. The whole soot blowing procedure takes less than 15 minutes.

Fig. 8: Size distribution of the 4 passes during normal operation (mass concentration).

![Graph showing particle size distribution](image)

Fig. 9: 3D-Time (x-axis, total length equals 30 min) and particle size (y-axis, 0.8-20 µm) resolved mass concentration during a soot blowing routine. Measurement point is in the 3rd pass behind 3 soot blowers.

Fig. 10: Particle size distribution during normal operation (green) and soot blowing (black).

The chemical analysis shows that the chlorine content of all three fractions is significantly smaller and sulphur is slightly increased (fig. 11).

The aerosol sampled during soot blowing represents a mixture of current stack gas and remobilized deposits. The
two-dimensional mixture of the aerosol size fractions and of more or less sulphated particles from the deposits can be relocated by calcium as an indicator, as calcium relations are not changed on the superheater.

**Fig. 11:** Chemical composition of the particles during soot blowing routine (“SB net”), compared with normal operation (“NO”). “Net” composition means the calculated difference between normal and soot blowing operation.

### Variation of operating parameters

After characterisation of the normal operation and the deviations taking place in short term (size of fire), middle term (mixture of waste) and long term (seasonal changes, maintenance intervals), it was an important aspect to learn about the changes or different behaviour of the aerosol parameters when the operation parameters of the boiler were modified in a specific manner up to the limits of a safe run.

In a first experiment, the length of the fire was reduced by focussing the primary air to the first zones of the grate. By this the burning time for the waste was reduced parallely by an increase in fire temperature. This state was kept for three days, measurements being performed at the second and third day.

Whereas the particle fraction < 0.5 µm was nearly unaffected, the particle mass concentration of the particles above 0.5 µm nearly doubled, in the range of 1-20 µm, the mass concentration reached triple the value of normal operation (fig. 13). This can be explained by an increased halogenide (Cl, Br) release of a hotter fire. The halogenides condense as salt particles what is expected to create an increase of particles in the range one micrometer in the second pass.

The increased content of halogenides and alkalis compared to normal operation is also found in the chemical composition of the particles of the 3rd pass. Sodium and potassium in total are increased by more than five percent points, what means a doubling in the coarse particle fraction.

Another experiment was to decrease the recirculation gas addition in the boiler. The recirculation gas is taken from the flue gas after the cyclone, which is the first cleaning component behind the boiler, and reinjected above the burning zone. The injection optimises the mixing of the burning gas, and by taking flue gas an oxygen overload is avoided. A potential disadvantage of this procedure could be that the recirculation gas is already enriched of fine and chloride rich particles which are reinjected to the burning gas.

Due to the construction of the boiler, the recirculation gas had to be kept at a minimum flow rate of 33% of its standard value to prevent the ejectors from damage. So,
during the experiment the recirculation gas fraction was reduced from 12% to 5% of the total gas volume.

The measured mass concentration distribution and the chemical composition during reduced recirculation gas addition did not change significantly in any fraction. As the effect of the complete recirculation gas on the aerosol composition was expected to be small, this result was in agreement to the practical long-term experiences of the plant with this feature.

**Sulphur addition**

In a first series of experiments, sulphur pellets were added to the waste in differed amounts per hour (12 – 30 kg/h). Fig. 14 summarizes all measurements with sulphur pellets and compares them with normal operation. None of the four experiments exhibit significant changes in the particle size distribution.

**DISCUSSION**

The chemical analysis of the aerosol showed a higher corrosive potential of the fine fraction of the particles, as these particles contain high amounts of halogenides, mainly chlorides.

The fine fraction of the particles (<0.5 µm) contains a significantly higher content of alkali metals and chlorine, the smallest of the collected fractions (<0.2 µm) are nearly completely composed of Na, K and Cl. Looking at the present mass concentrations only, corrosion could be completely calculated by the present chlorine content of the fine fraction. The role of these particles with respect to fouling is, however, rather small. Though their mass concentration fraction is not yet negligible, the possible main deposition mechanisms – thermo- and turbophoresis – are by far less effective. Another argument against the fine fraction is the approved phenomenon that corrosion is much higher on the front side of superheater tubes. The deposition mechanisms of fine particles and condensables, however, show no significant differences around the tube and the percentage of fine fraction particles on the rear of a tube, as the coarse fraction mainly deposits on the front, is by far higher than on the front.

The fraction between the two modes, roughly at 10-20 µm, is seen to have already the appropriate properties to impact at the superheater tubes. This fraction, however, was only found in very small concentrations. From the point of view of particle origin, there should be a gap between primary and secondary particles, which would only be closed by agglomeration or condensation processes. Accordingly, this fraction is observed in a growing mass concentration from pass to pass, with an increase of some.
one order of magnitude in total, but still staying the minimum mass concentration by approx. one order of magnitude.

In summary, the efficiency of deposition mechanisms of particles on superheater tubes and the main regions of corrosion point to the coarse fraction, to particles of at least 20 µm in aerodynamic diameter. Only this size and above is impacting on the tubes with a probability of more than 50%. Experimentally, this phenomenon could be proved by the composition of the deposits of investigated tube fouling, special fouling experiments and the inlet of the sampling probe, which all showed a high correlation with the coarse fraction of the particles from the cyclone.

Thus, though their chemical composition seems rather passive compared to the fine particles, the coarse particles play the most important role in creating the fouling on the tubes and keeping the corrosion running.

The question is arising how the chlorine supply to the corrosion front is maintained. In fouling investigations, the porosity of the deposits was approx. 50%, however, no fluid regions or fine particle transport options could be observed. The porosity is rather suitable for molecular diffusion transport processes than for any even smallest particle size.

In contrast to the sodium concentration, a good correlation was found between the sodium load of the fouling and the corrosion rates of the various ranges of a single tube. Even more, after preliminary data analysis, there seems to be also a correlation between the sodium load of different MSI and their specific corrosion rate.

The study also shows that sulphation is not completed during the flight of the particles and is progressing on the deposits. However, the increase of sulphur in remobilized particles and therefore the degree of sulphation taking place on the deposits is less than expected.

The addition of sulphur – by pellets or sulphur dioxide – did improve the situation of the important fraction of coarse particles, in agreement with other experiences (Grundmann, 2007; Hunsinger, 2004; Kautz, 2003 and Pettersson, 2005). The sulphur content did not only increase in the particles retained by the cyclone – representing the free particles – but also in the inlet – representing the deposited particles. Thus, addition of sulphur supports the sulphation during the flight phase, but also on the fouling. The desired effect of complete sulphation during the flight could not be achieved. However, the inlet content was almost free of chlorine. As the inlet is made of silica glass, the chlorine was not consumed by any corrosion reaction, so in fact a lack of chlorine was produced on the deposits what might impact the corrosion rate during a long-term addition of sulphur.

The experiments with a shorter fire geometry confirmed that a higher fire temperature causes more salt being ejected resulting in an increase of particles in the aerodynamic size range of 0.5 µm and above. This combination of chlorine containing salts and particles sizes which are likely to impact at the superheater tubes seems to impair the corrosion situation of the tubes by a higher concentration of chlorine containing coarse particles (Deuerling, 2006).

CONCLUSIONS

1. The comprehensive physical and chemical investigation of the gas phase and the complete particle phase through the whole boiler of a MSI has generated an impression of the composition and dynamics as a base for understanding fouling processes.
2. The fouling mainly consists of coarse particles deposited by impaction. Only a minor mass fraction derives from fine particles.
3. It was measured that sulphation takes place during the flight of the particles and in the fouling. However, the measures applied to influence the speed of sulphation did not afford clear changes.
4. The total chlorine being present at a certain place can be estimated by the lasting amounts of sodium and to a certain extent of potassium.
5. The corrosion rate is merely linked to the absolute amount of chlorine transferred than to the present chlorine concentration. This explains why the higher concentration of chlorine at the rear of a superheater tube does not cause a higher corrosion rate than at the front side of the tube, where the concentration of sodium (chlorine indicator) is less, but the total amount by far higher.
6. The presence of sodium seems also to be suitable for comparing the various MSI corrosion rates. This has to be further investigated and proven. If this correlation is confirmed, measures can be generated to influence the corrosion rates of superheaters.
7. The design of the PTD sampling probe proved to be suitable for the broad range measurements. However, the deposits in the inlet turned out to have a major impact on the mass balances. The inlet design itself is therefore subject to consideration about possible future improvements.

NOMENCLATURE

MSI Municipal solid waste incineration plant
PTD Porous tube diluter
REFERENCES


ACKNOWLEDGEMENTS:

This project is funded by the Bayerisches Staatsministerium für Umwelt, Gesundheit und Verbraucherschutz within the scope of the European Regional Development Fund (ERDF).

The first author would like to thank the Buchner Foundation for their kind financial support.