Corrosion monitoring in waste-to-energy plants

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Abstract

A probe to online monitor the corrosive attack on superheater tubes in waste incinerators was constructed and applied in several WTE (waste to energy) plants. We present results obtained in these plants and attempt to compile the data into corrosion diagrams.

Introduction

Corrosion damage is a major issue in waste incineration plants: due to repair work and involved standstill it is highly expensive. That is why construction engineers as well as operators made numerous attempts in the past to reduce corrosion both by using optimized materials and by adding additives to the flue gas. Nevertheless, solutions based on material did not succeed when superheaters were concerned. As the condition of a plant can not be rated while operating, effects on corrosion of a changed fuel composition, of additives and of a changed process control normally are difficult to quantify. Therefore it often takes more than six months until a second examination can be made.

As was shown in a number of other projects, corrosion is mainly due to high temperature chlorine attack, either through gaseous species like HCl or Cl_2 or by chloridic particles, which are deposited on the superheater tubes. By conversion into sulfates these particles release chlorine towards the superheater material, leading to strong damage by acceleration of oxide formation.

Within a research project, the department for Experimental Physics of the Augsburg University has designed a probe to monitor corrosion online. The aim is to observe and examine variations in the corrosion rate of plants with temporal resolution for a better understanding of the mentioned effects and correlations. Furthermore this approach allows to position steel samples of the material used in the plant's superheaters into the fuel gas and to cause their corrosion under normal or under controlled changed conditions.

Methods for measuring

The new probe design consists of a water cooled support lance made from a nickel base superalloy with an air cooled probe head (see fig. 1). The head itself is composed of a variable number of sample rings that are separated by ceramic rings. Those sample rings, made of the same material used as the superheater's tubes, have to be held at a constant temperature. They are electrically contacted to take the electrochemical measurements.

The major aim of the measurements is monitoring the corrosive attack in its temporal process. This was obtained by measuring the polarization resistance. The polarization resistance is the ratio of the applied potential and the resulting current response; it is proportional to the current corrosive degradation. By quantifying the loss of weight at the end of the measurements, the electronic measurement signal can be calibrated. Additionally, our method allows taking samples for offline examination. For further description of the method and results see [1], [2] [3], [4], [5], [6].

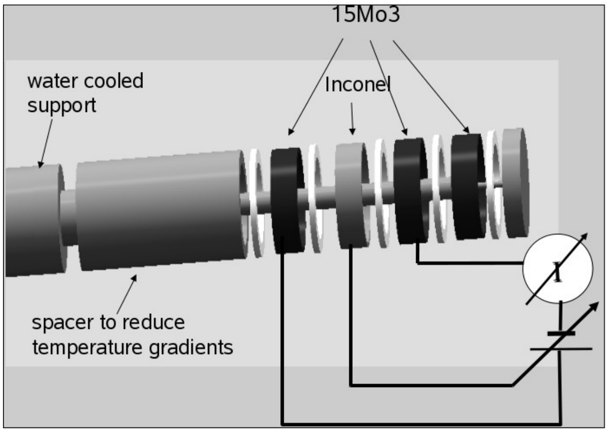

Figure 1: Schematic view of the probe head with electrical wiring

The controlled air cooling of the probe head and enhancements in the cooling system makes it possible to adjust the temperature of the sample rings within a range from 50 up to some hundred degrees Celsius below the temperature of the fuel gas. So it is even possible to position the probe in the first pass of the waste incineration plant – within the direct radiation zone of the firing where fuel gas temperature will rise up to 900 degrees Celsius and the additional heat flux by direct radiation - and therefore to take continuous measurement for several months.

Results from different plants

In order to compare the corrosion processes in WTE plants with a wide range of different corrosion rates, measurements were performed in four plants covering a range in corrosive attack. In the following we present results from such measurements to show the capabilities of the probe system.

Plant 1 (low corrosion)

In Plant 1, a WTE plant with comparably low corrosion rate, we measured in two different positions, in the second pass (probe 1) at a flue gas temperature of approximately 750°C and in the third pass (probe 2) at a temperature of 600°C. Both probes were installed at 25m height. Fig. 2 shows the results for the polarization conductance. As expected, the probe at the lower flue gas temperature shows a lower signal, which was later confirmed by weight loss determination. Distinctive features are the sudden increase of the signal of probe 1 for periods of several days, with only one appearing also on probe 2 (see fig. 3).

Possibly, special conditions of the combustion are visible only up to the second pass, but damped out in the third pass.

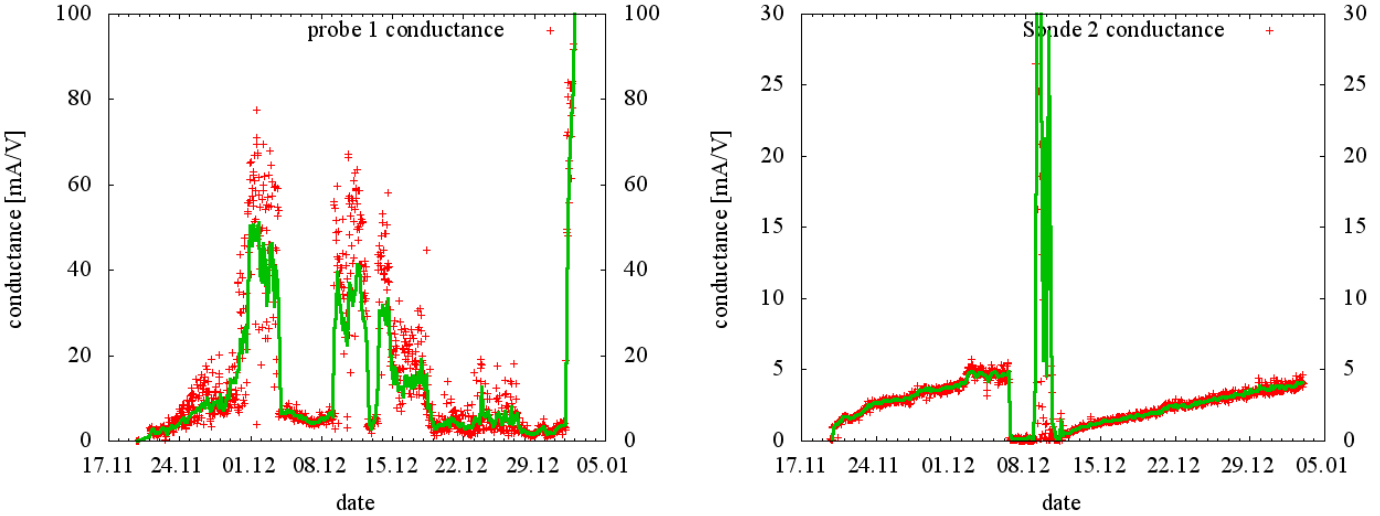

Figure 2: Polarization conductance of plant 1. Left hand part: second pass, right hand part: third pass (different scaling)

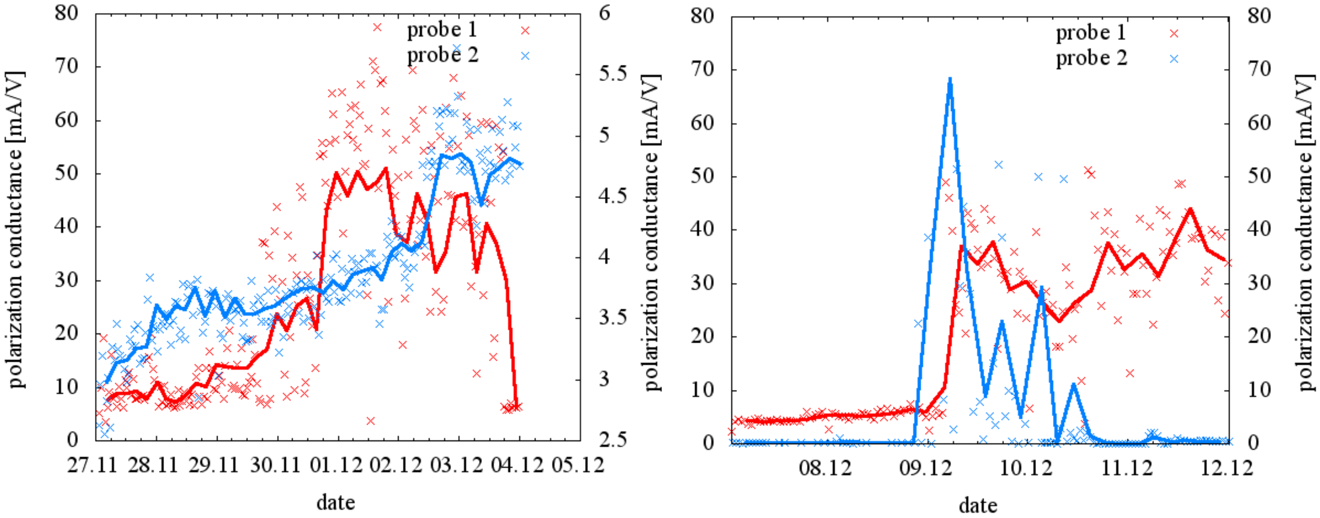

Figure 3: Probe 1 and 2, plant 1, special events

Integration of the polarization conductance with respect to time yields a quantity, which is directly proportional to the total material loss. If the latter is determined after the measurement either by wall thickness or weight loss measurement of a special control ring, one obtains a calibration factor which can be used to convert the measured values of the polarization conductance into material loss rate. Fig. 4 shows the integrated values (red and green) of probe 1 and 2 and the converted values (right axis).

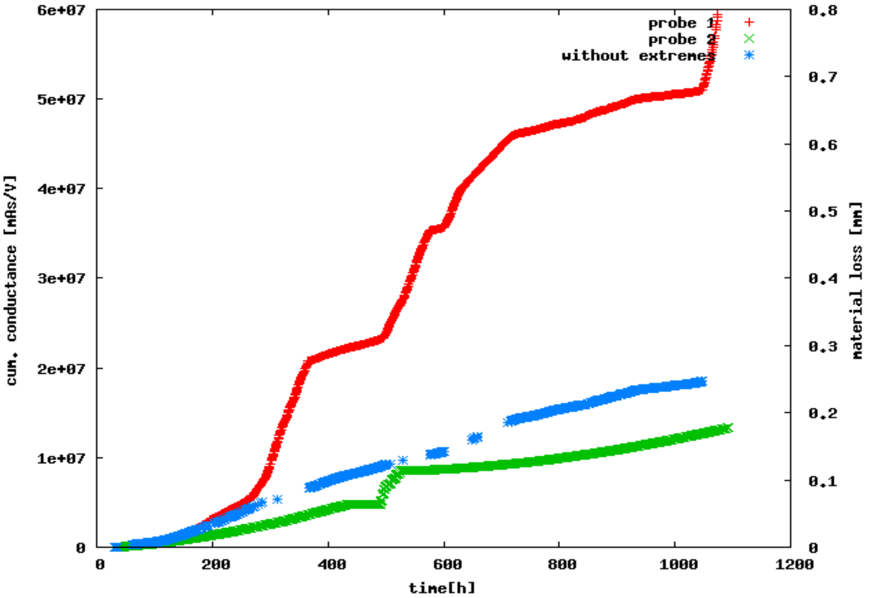

Figure 4: Probe 1 and 2 – anomalies of polariztion conductance: The integrated polarization conductance for both probes, (red, green) and a hypothetical curve for probe 1 without periods of extreme corrosion. Right scale: Conversion into material loss.

Additionally we computed a hypothetical curve, (blue) where periods of high corrosion (conductance > 30mA/V) were omitted to show what can be achieved under optimal control.

The calibration factors obtained from weight loss using this procedure are:

second pass:	1.39 10-8 Vm/As
third pass:	1.05 10-8 Vm/As

In a former measurement a similar value was obtained in the third pass:

plant 1 (2006):	1.32 10-8 Vm/As

Plant 2 (low corrosion)

In plant 2, another WTE plant with low corrosion rates, measurements were taken during a period of six weeks, again on two positions, one (probe 2, flue gas temperature 650°C) in the third pass on a height of 8.20m and in the fourth pass, a horizontal pass at a height of 12.80m at a flue gas temperature of 580°C.

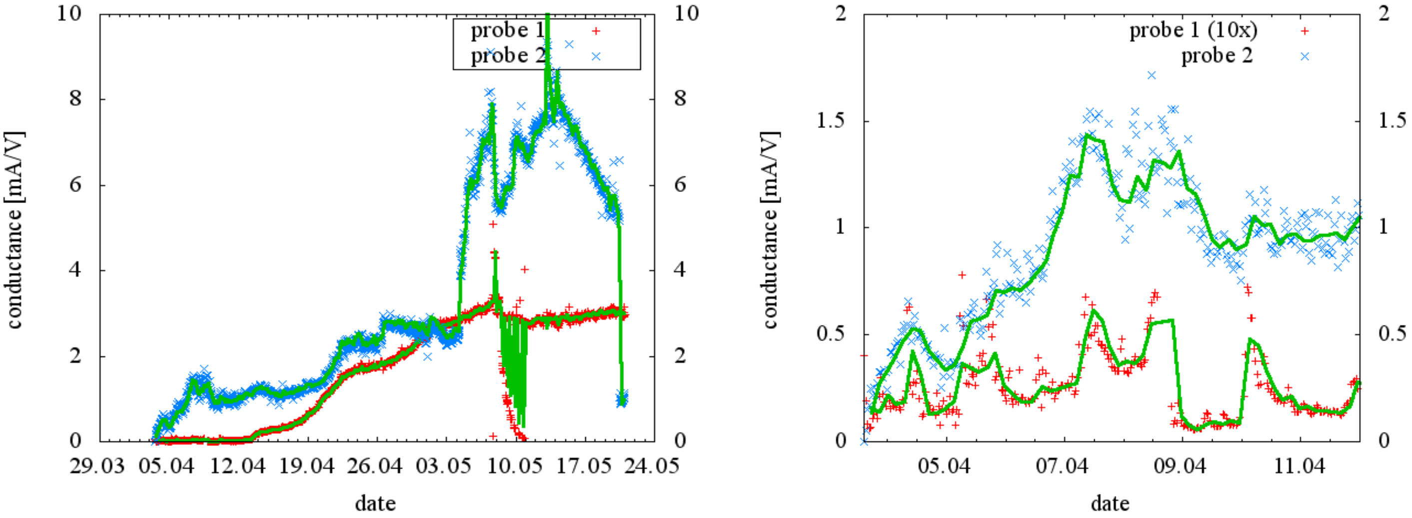

Figure 5: polarization conductance of probe 1 (fourth pass, flue gas temperature 580°C) and probe 2 (third pass, flue gas temperature 650°C). Right: initial phase, signal of probe increased by a factor 10x

Fig. 5 shows the corrosion signal (polarization conductance) for both probes, the green curves showing a signal averaged over ten values. As expected because of the lower flue gas temperature, the signal of probe 1 is far below that of probe 2. The right part of fig. 5 shows a close up of the initial period with even minor fluctuations (or variations) occurring simultaneously on both sensors. The variations during the time from 8/5/-10/5 were intended temperature variations to obtain the dependence of the corrosion signal as a function of the superheater tube temperature.

As described above, the signals were calibrated after the end of the measurements using weight loss data. After 1246h we found a mass loss of 3.6% in the third pass and of 1.04% in the fourth pass. This corresponds to a material loss of 0.188mm/1246h=1.4mm/a and of 0.05mm/1246h=0.38mm/a, respectively.
Corresponding calibration factors were hence :

third pass:	1,36 10-8 Vm/As
fourth pass:	0.78 10-8 Vm/As

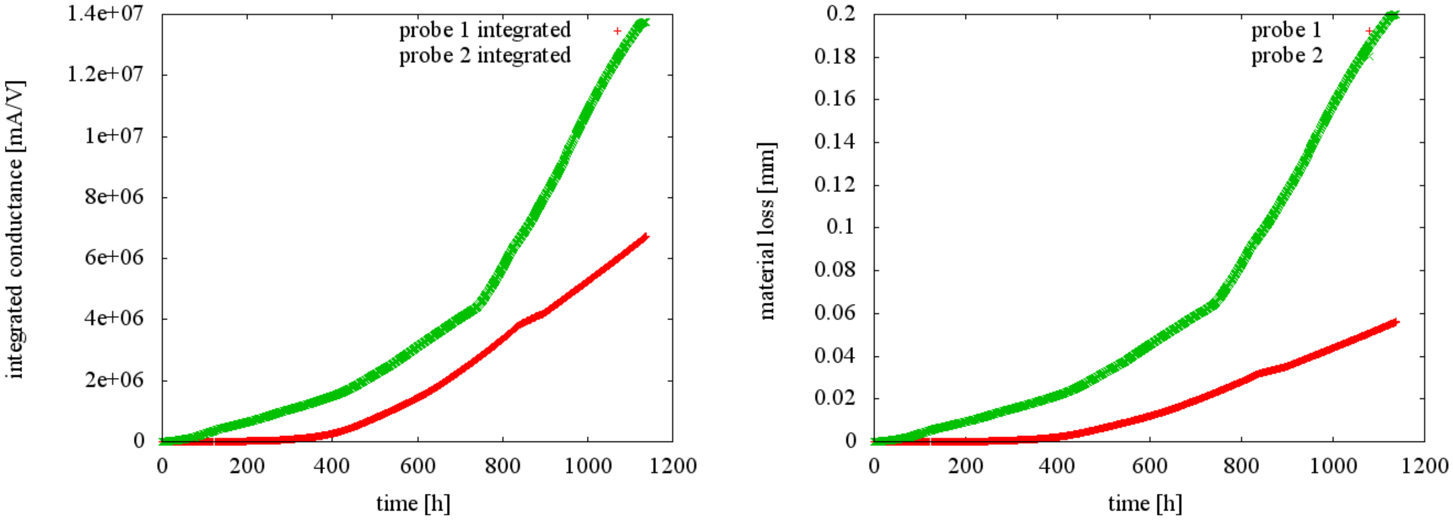

Figure 6: Time integrated corrosion signal for both probes (left) and signal converted into thickness loss (right)

Plant 3 (strong corrosion)

In plant 3 measurements are taken on the transition from first to second pass at a flue gas temperature of approx. 900°C. This plant has rather strong superheater corrosion, consistent with our results shown in fig. 7, where the signal was also converted into thickness loss (right hand scale). The right part of fig. 7 shows a short period of operation with an auxiliary burner. Visibly the signal drops nearly instantaneously to one third of its former value, essentially for two reasons: first chlorine supply is strongly reduced and secondly the flue gas temperature is presumably somewhat lower.

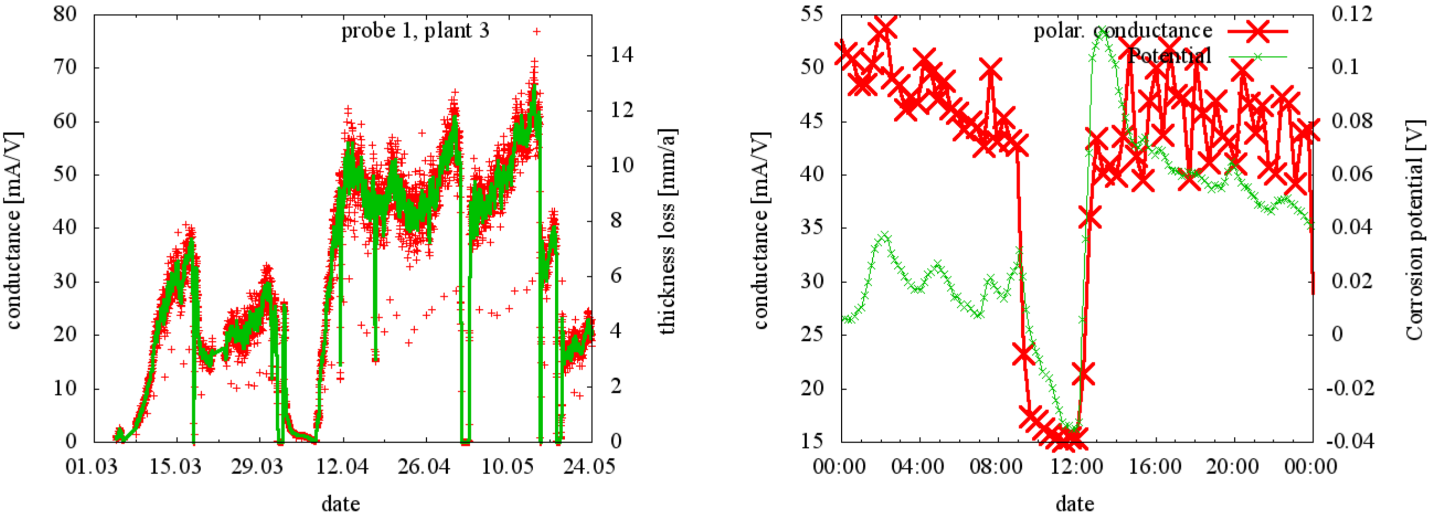

Figure 7: Polarization conductance (converted into material loss) in plant 3, right hand side a short period with auxiliary burner with corrosion potential

During a former measurement a calibration factor of 0.56 Vm/As was determined. The later measurements shown here yielded a calibration factor of 0.61 Vm/As, i. e. a value quite close to the first one. It is somewhat smaller than that found in other plants, but still in the same order of magnitude. The loss rate reaches maximum values above 15 mm/a, i. e. lifetimes of the superheater of less than half a year. Of course the average loss lies below this, but still is of the order 6mm/a.

Plant 4 (extreme corrosion)

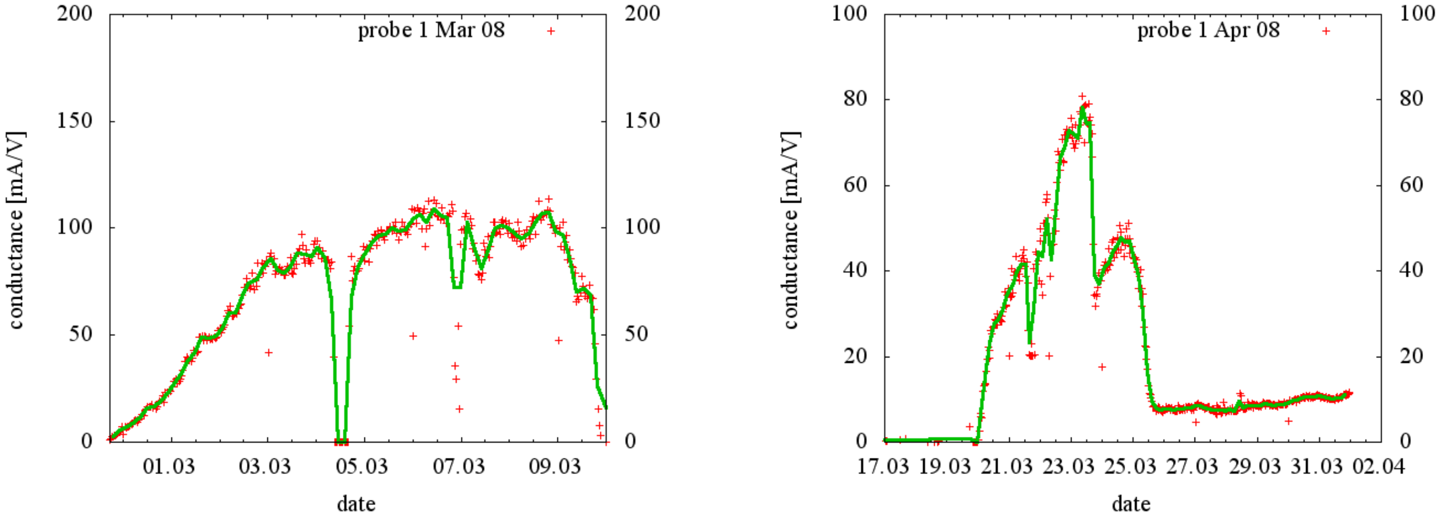

Figure 8: Probe 1 above superheater, two test series

In plant 4, a WTE plant with extremely high corrosion rates, we conducted several shorter test series. Again two probes were installed in different positions, both in the second pass close to the superheaters. Probe 1 was installed above the superheaters at a flue gas temperature of 850°C, probe 2 below at 700°C. Especially in the upper position, the signal reached values up to 150 mA/V, i. e. 10-20 times higher than in other plants.

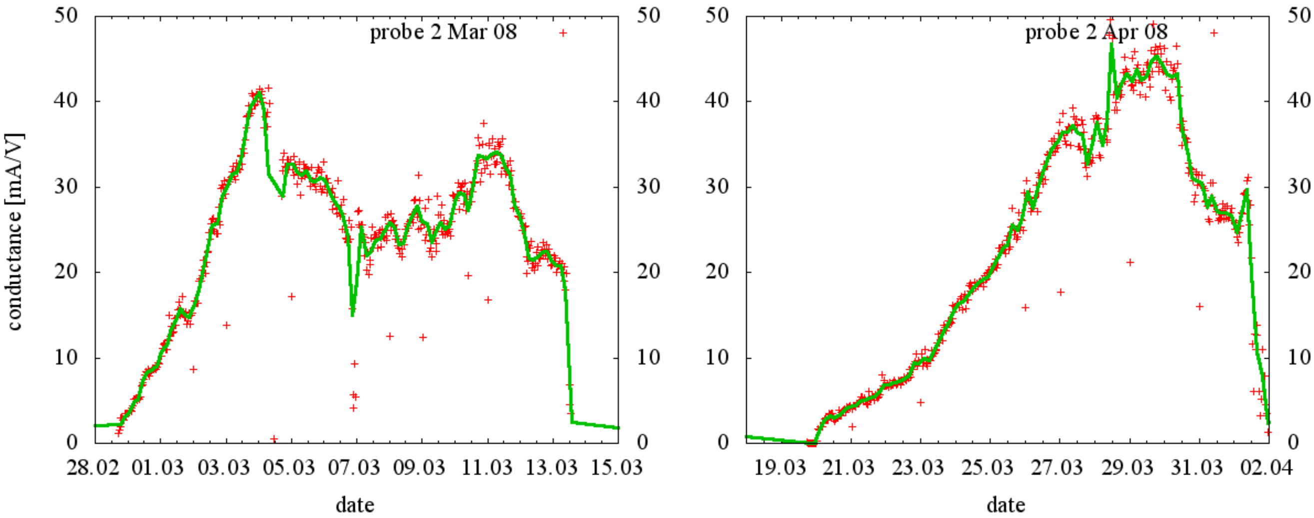

Figure 9: probe 2 below superheater, two test series

Until now, we were not able to determine calibration factors, but the results obtained so far would correspond (using the calibration from above) to material loss rates of about 9mm/a. This finding is confirmed by inspection of the measuring rings as well as from sparse information from the operators.

Temperature dependence of corrosion

Two crucial parameters for high temperature corrosion in waste incinerators are the temperature of the superheater tube walls and the temperature of the flue gas. The former determines the energetic efficiency of the plant, the latter is controlled by constructive parameters, especially the mounting position of the superheaters.

Superheater wall temperature

Due to the separate temperature control of the probe head the surface temperature of the sensor rings can be varied over a broad range. The influence on corrosion is twofold: a short term variation of the ring temperature only modifies the kinetics of the corrosion processes but not the composition of the deposits nor the conditions at the corrosion front. A long term change, on the other hand, might also modify the structure and composition of the deposits and the morphology of the corrosion products.

Assuming a simple thermally activated reaction, the corrosion rate k should follow an arrhenius law

$$k = k_0 \exp\left(-\frac{\Delta G_1}{R T}\right)_{RW}$$

with an activation energy ΔG_1. Variation of the superheater temperature (or the temperature of the probe rings) allows to determine this activation energy. Fig. 10 (left) shows the polarization conductance as a function of temperature during short term temperature variations in the WTE plant GKS, Schweinfurt, Germany. Temperature was adjusted to a value different from the standard value of T=430°C for a time of 5h, than back to 430°C again for 5h. The lowest temperature that was achieved was 350°C, the highest 470°C. The slope of the green line corresponds to an activation energy of ΔG_1 =36 kJ/mol. A similar experiment was conducted in plant 2, where the activation energy was ΔG_1=75 kJ/mol.

In a second experiment in GKS temperature was lowered for a longer period (several days) to 250°C. The polarization conductance obtained there (1,7mA/V) is marked by a solid black square in the graph. When the temperature was raised back to 430°C, the measured corrosion signal first increased to 25mA/V, but dropped than during several days to the initial value of 15-20 mA/V (Solid and open black circle). This is a clear indication for a change in deposit composition or microstructure, presumably the formation of chloride deposits, which only sulphatized when the temperature was increased again.

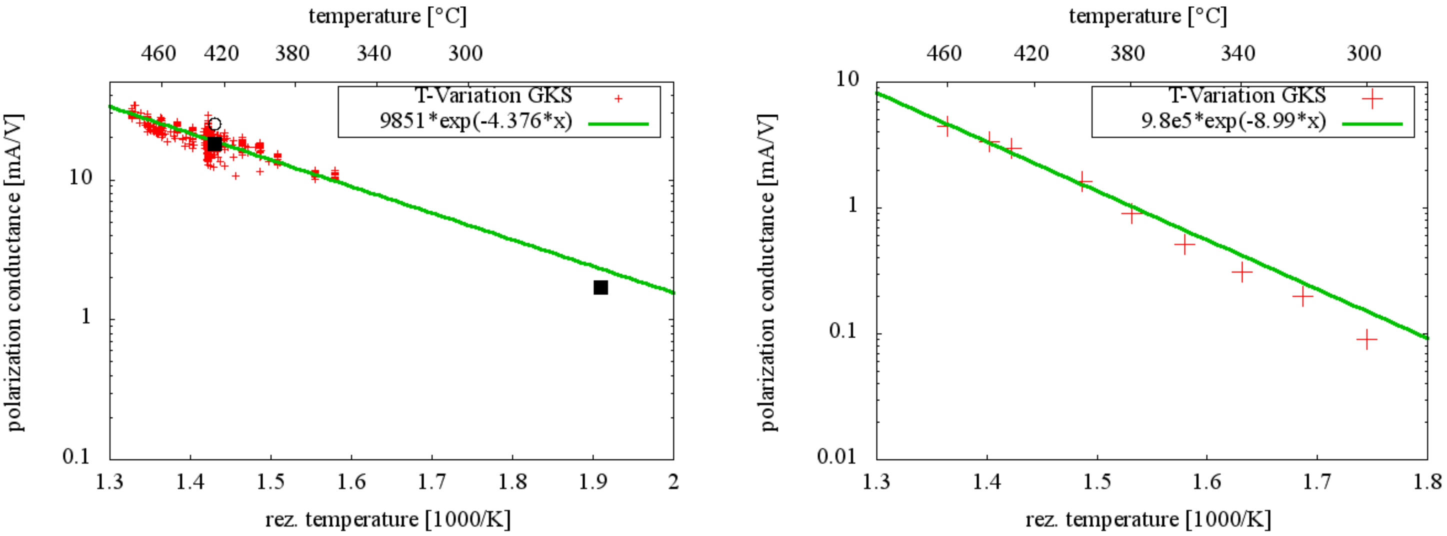

Figure 10: Arrhenius plot of the polarization conductance as function of the tube wall temperature. Left WTE plant Schweinfurt (GKS), right plant 2

Flue gas temperature

A compilation of the data obtained in the different WTE plants described above results in a slightly inconsistent picture (table 1, fig. 11): a plot of the data as a function of flue gas temperature shows a certain correlation between corrosion rate and flue gas temperature, but with strong scatter. This can be attributed to other factors like waste composition, control of combustion, design of the plant and others. Nevertheless we tried to plot the data again in an arrhenius like dependence (fig. 12).

$$k = k_0 \exp\left(-\frac{\Delta G_2}{R T_{RG}}\right)$$

Surprisingly this results in a similar activation energy of ΔG_2=37.2 kJ/mol. Bossmann [6] determined an activation energy of approximately ΔG_2=100kJ/mol.

Table 1: material loss rate on superheater tubes measured in different plants

	Wall temperature	Flue gas temperature	Material loss rate [mm/a]
plant 0	430	580	2
plant 1 a	430	600	1,4
plant 1 b	430	750	6,4
plant 2 a	430	650	1,5
plant 2 b	430	580	0,5
plant 3	430	900	6,9
plant 3	430	900	5,7
plant 4 a	430	850	9
plant 4 b	430	700	

Taking the measurements inside a single plant on different positions one can estimate (with some uncertainty, since temperature differences are not too high) the activation energy as ΔG_2=74 kJ/mol for plant 1 and ΔG_2=121 kJ/mol for plant 2.

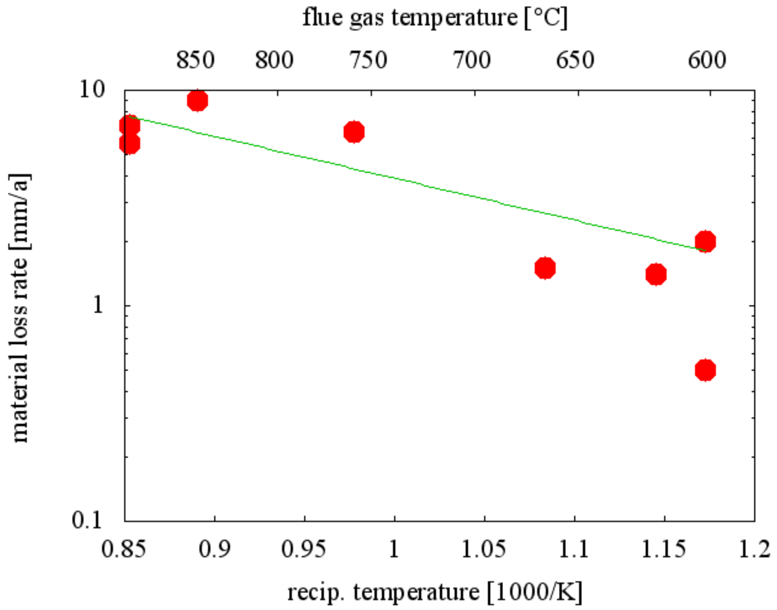

Figure 11: The data from fig. 11 in an arrhenius plot. Green: straight line fitted to the data yielding an activation energy of 37.2 kJ/mole

Constructing a corrosion diagram

Empirically a corrosion diagram, i. e. a plot of regions of high and low corrosion rate in the parameter plane of flue gas and tube wall temperature, was developed in 1994 [7] and augmented by Warnecke in 2004 [8], see fig. 12. Our results for the dependence of corrosion rate *k* on those temperatures can be inserted into this graph (red and green line in fig. 12, see also [9]), if for both dependencies thermally activated processes are assumed:

$$k = k_0 \exp(-\Delta G_1 (\frac{1}{RT_W} - \frac{1}{RT_W^0})) \cdot \exp(-\Delta G_2 (\frac{1}{RT_R} - \frac{1}{RT_R^0}))$$

Here T_W denotes the wall temperature, T_R the flue gas temperature and T_W^0, T_R^0 are reference temperatures of 430°C and 600°C, respectively.
The red line is obtained for an activation energy ΔG_1=36kJ/mol and ΔG_2=100kJ [6], which does not reproduce the empirical data, while the green line is computed with $\Delta G_{2=}$=40kJ/mol, the value which is close to the one obtained from the compilation of data above.

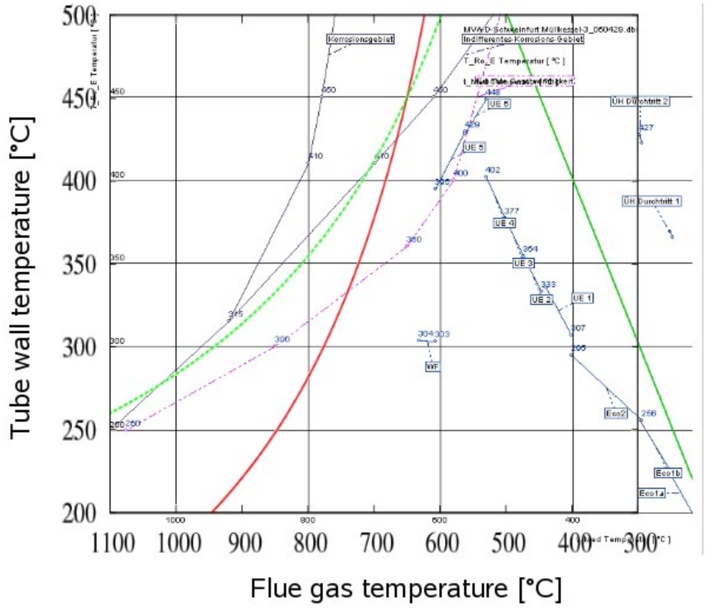

Figure 12: corrosion diagram after Kümmel [8] ("Flingern corrosion diagram") enhanced by Warnecke. Red and green lines obtained from our probe measurements (see text).

Instead of only plotting fields of „high“ and „low“ corrosion, our data allow to give a three dimensional representation or a field of „iso-corrosion-lines“, as is shown in fig. 13 for plant GKS and in fig. 14 for plant 2. Despite the considerably values for the corrosion rate measured in this plant, the higher value for ΔG_1 in plant 2 results in a much steeper increase, so one can conclude, that increased superheater temperatures would lead to stronger corrosion as e.g. in GKS.

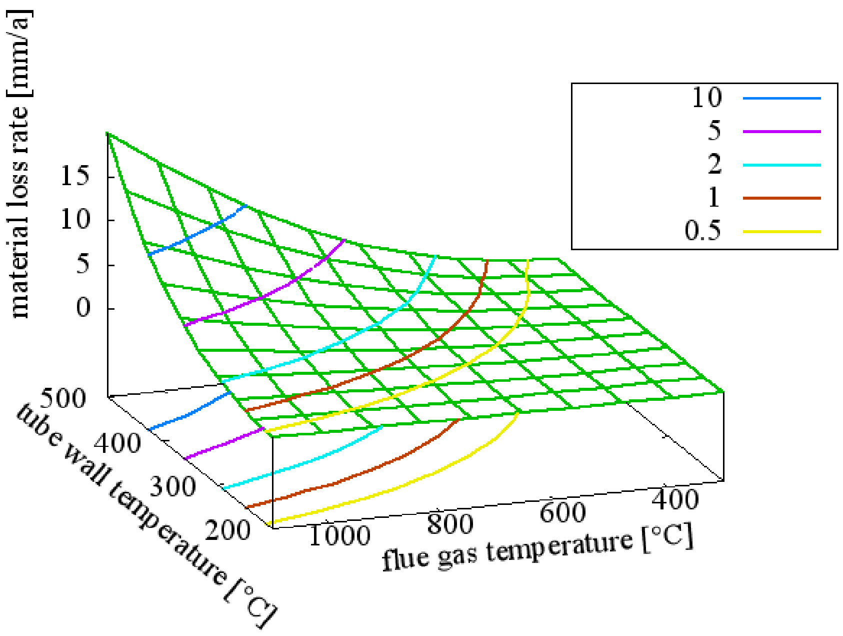

Figure 13: Three dimensional plot of a corrosion diagram for the data obtained in GKS. Colored lines are lines of constant corrosion rate in mm/a.

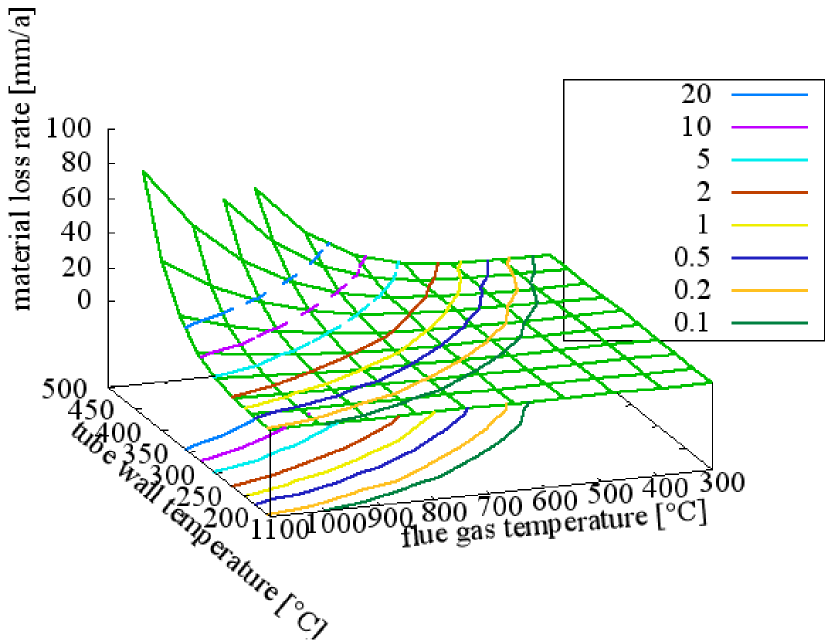

Figure 14: Same as fig. 13 but for activation energies obtained from the data in plant 2

Conclusion

The measurements shown above result in a rather simple picture for the corrosion rate in a given plant, if superheater or flue gas temperature are varied. Apparently the process is dominated by thermal activation with activation energies depending on the plant. Nevertheless it should be clear that differences of different plants not only stem from different temperatures but also from numerous other parameters like e. g. waste composition, control of combustion, design of the plant or amount and availability of chloride compounds. However our results confirm the importance of those thermal parameters (especially given by the position of the superheaters in the plant). To further quantify these correlations and the influence of other parameters, but also to further clarify the processes during this type of high temperature corrosion, we plan to vary more systematically both the position of our probe in one plant and the temperature of the probe, and furthermore to modify locally the composition of the flue gas by injection of aerosol particles in the vicinity of our probe.

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