



Theory and practice of corrosion related to ashes and deposits in a WtE boiler



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ABSTRACT

Corrosion of heat-exchanging components is one of the main operational problems in Waste-to-Energy plants, limiting the electrical efficiency that can be reached. Corrosion is mainly related to the devolatilization and/or formation of chlorides, sulphates and mixtures thereof on the heat-exchanging surfaces. Theoretical considerations on this corrosion were already put forward in literature, but this paper now for the first time combines theory with a large scale sampling campaign of several Waste-to-Energy plants. Based on the outcome of elemental and mineralogical analysis, the distribution of Cl and S in ashes sampled throughout the plant during normal operation is explained. Cl concentrations are high (15–20%) in the first empty pass, decrease in the second and third empty pass, but increase again in the convective part, whereas the S concentrations show an inverse behavior, with the highest concentrations (30%) observed in the second and third empty pass. Sampling of deposits on specific places where corrosion possibly occurred, gives a better insight in the mechanisms related to corrosion phenomena in real-scale WtE plants and provides practical evidence for some phenomena that were only assumed on the basis of theory or lab scale experiments before. More specific, it confirms the role of oxygen content, temperatures in the different stages of the boiler, the presence of polysulphates, Pb and Zb, and the concentrations of HCl and SO₂ in the flue gas for different types of boiler corrosion.

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1. Introduction

One of the main operational problems in Waste-to-Energy (WtE) boilers is high temperature corrosion of steel heat-exchanging surfaces, such as membrane walls and economizer, superheater and evaporator tubes. Typically, the hot gases that originate from the incineration of the waste, pass through several stages of the WtE boiler. The first stage is the radiation part, and consists of one or more (up to three) empty passes, where heat is transferred to membrane waterwall tubes. Flue gas temperatures range from 1000 °C right after incineration, to around 650 °C at the end of this stage. The temperature of the (surface) of the water-wall tubes is typically 265 °C. The second stage is the convective part and is comprises superheater, evaporator and economizer bundles. The flue gas that passes through this section is cooled from 650 °C to 145 °C. The water is flowing countercurrent to the flue gas, and is heated from 105 °C in the economizer tubes to 400 °C in the superheater tubes.

Steel corrosion in the boiler is mainly caused by interaction of chlorides, sulphates, polysulphates and sulphides with iron or iron oxides on the tube surfaces, and limits the steam temperature that can be reached in WtE plants, and as a result also the electrical energy efficiency. These corrosive species originate from the waste that is incinerated and are devolatilized onto the colder tube surfaces as the temperature decreases further down the boiler. Many chlorides are volatile at the temperatures prevailing in the furnace and are easily transferred from the waste to the flue gas during incineration. The main sources of chlorides are PVC containing materials (packaging, plastics) and chloride salts (e.g. NaCl) (Ma et al., 2010). Chlorides appear in the flue gas as HCl, mostly transported to the flue gas cleaning downstream, or as salts of alkali metals (Na, K) or heavy metals (Zn, Pb). These salts can be deposited in the furnace and boiler section wherever the surface temperature is below the devolatilization temperature of the respective chlorides (Andersson et al., 2014; Viklund et al., 2013). In the gas phase, HCl can also be converted to the highly corrosive chlorine gas (Cl₂) via the Deacon reaction (Reaction (1)):



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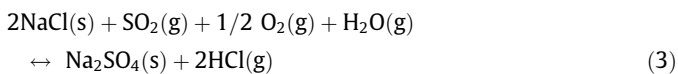
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The overall conversion rates are only below 2% in the absence of catalysts and at the temperatures typically prevailing in WtE-plants (Liu et al., 2000).

Sulphur is mainly found in the flue gas as SO₂, and most of it is transported to the flue gas cleaning downstream. The direct oxidation of SO₂ to SO₃ with oxygen in the gas phase is thermodynamically feasible, but in practice, at the conditions prevailing in large parts of an incinerator furnace/boiler system, the kinetics of this gas phase reaction are unfavorable for a substantial amount of SO₃ to be formed (Belo et al., 2014; Krüger, 2009). Fly ash and Fe₂O₃ that can be present in the fly ash can catalyze the conversion, but the conversion rates remain nevertheless low. A maximum conversion of about 2% was found at 700 °C and a residence time of about 1s (Belo et al., 2014). SO₃ can be formed alternatively, via the Griffin reaction (Reaction (2)), in which SO₂ reacts with Cl₂ formed in the Deacon reaction (Reaction (1)) (Krüger, 2009):



Information on conversion rates of this reaction are however scarce to non-existent in literature. The most likely option for SO₂, is a gas-solid reaction to sulphates, in/on the deposits present on heat exchanging surfaces, known as the “sulphation reaction”. (Reaction (3)):



In more detail, SO₂, O₂ and H₂O first adsorb on wall deposits, where SO₂ can react with O₂. The formed SO₃ then reacts with adsorbed H₂O to form H₂SO₄ that in turn reacts with NaCl (or similarly, KCl) already present in the deposit. As a result, solid Na₂SO₄ and gaseous HCl are formed as final products (Schroer and Konys, 2002).

This paper starts by characterizing ashes and deposits sampled in different stages of full-scale WtE plants to gather insight in the speciation, the transport and the distribution of corrosive Cl and S compounds. Ash and deposits analysis are then related to the abovementioned reaction mechanisms. It is not the aim of this work to fundamentally unravel the formation (and corrosion) mechanisms of Cl and S compounds since this requires strict control of the parameters that influence these mechanisms, which cannot be obtained in full-scale installations in which the operational conditions may vary but rather requires lab experiments in controlled conditions.

2. Materials and methods

2.1. On-site sampling

A large sampling campaign was set up to collect samples from several European and non-European WtE plants. In this paper, the results of two European WtE plants and one non-European WtE plant are presented, each with several incineration lines. The selected plants incinerate mixed, non-hazardous waste with an average lower heating value (LHV) between 8 and 12 MJ/kg, and are equipped with a water- or air-cooled grate. For reasons of confidentiality, no further specific details on the location of the plants, and on the exact composition of the waste being incinerated, can be disclosed.

Samples were collected during plant operation and during shutdown periods. To obtain representative results, samples were taken at similar sampling spots from all lines of the incineration plants. During plant operation, ash samples were taken from the hopper below the second and third empty passes, and from hoppers underneath the convective (i.e. fourth) pass. During shutdown, deposit and ash samples were collected at several

locations in the first, second, third and fourth (empty) passes, including superheater, evaporator and economizer tubes.

2.2. Chemical and mineralogical analysis

Prior to the chemical and mineralogical analysis, the ash and deposit samples were milled (<2 mm) and homogenized. The representative sample was then further milled (<0.5 mm) and prepared for analysis. The chemical analysis was performed with X-ray Fluorescence (XRF) using a Bruker S4 Pioneer. The mineralogical analysis was performed with X-ray Diffraction (XRD) using a Philips PW1830 with monochromatic Cu Kα radiation, generated at 45 kV and 30 mA. Measurements ranged from 2θ = 5° to 75°, with a step size of 0.02°. Quantification was done using the Rietveld refinement method.

3. Results and discussion

The composition of ashes and of the deposit samples is given and discussed simultaneously. Thereby, the ash composition is considered representative for the normal operation of a waste incineration plant, whereas the deposits are seen as representative for a problematic situation. For both the ashes and the deposits, a chemical and a mineralogical analysis was performed and compared.

3.1. Elemental composition of ashes and deposits

Table 1 shows the elemental concentrations of ash samples collected during shutdown on the walls of the first, second and third empty pass of the steam boiler of the same line in one of the selected WtE plants. Analysis of samples taken in the boilers of the other lines showed that their compositions were comparable. For the ease of comparison, only the 15 most abundant elements are shown in the table; they make up for 98% of the total sample mass.

The relative concentrations of the main corrosive species S (expressed as SO₃) and Cl already change significantly in these first sections of the boiler. In the early stages of the WtE boiler (the first empty pass), the Cl/SO₃ ratio is high; the concentrations of Cl and SO₃ are almost equal (15–20%). The more downstream in the empty passes, the less chlorine, and the more sulphur is present in the ashes. There is not much literature available to compare these results with, as most literature is focused on deposits on the heat-exchanging surfaces and not on ashes, certainly not from the first empty pass. Results from Lai et al. (2014), Chen et al. (2015) and Krüger (2009) show comparable S and Cl concentrations, and a

Table 1
Elemental (expressed as oxides, except Cl) concentrations (%) of ash sampled in the first, second and third empty pass of the boiler of a WtE incineration line.

	1 st pass	2nd pass	3rd pass
CaO	26.7	22.2	18.3
SO ₃	17.5	24.4	37.3
SiO ₂	9.4	9.1	5.6
Al ₂ O ₃	4.1	4.1	2.9
Na ₂ O	6.9	6.1	8.7
Cl	17.7	7.9	7.3
K ₂ O	6.7	4.8	8.2
Fe ₂ O ₃	2.0	14.2	2.4
TiO ₂	1.8	1.4	1.0
MgO	1.2	1.2	0.9
ZnO	4.1	3.1	3.7
BaO	0.1	0.1	0.1
MnO	0.1	0.1	0.1
PbO	1.8	1.4	3.5

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