



# High temperature corrosion of boiler waterwalls induced by chlorides and bromides. Part 1: Occurrence of the corrosive ash forming elements in a fluidised bed boiler co-firing solid recovered fuel

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## ABSTRACT

In waste fired boilers high temperature corrosion has often been attributed to zinc and lead chlorides. In addition, bromine induced high temperature corrosion has been earlier observed in a bubbling fluidised bed (BFB) boiler co-firing solid recovered fuel (SRF) with bark and wastewater sludge. In Part 1 of this work a measurement campaign was undertaken to determine the occurrence of Cl, Br, Zn and Pb in the fuel, in the combustion gases as well as in the deposits on the boiler waterwalls. It was observed that Cl, Br, Zn and Pb originate to a large extent from the SRF, they are vaporised in the furnace, and may form waterwall deposits. This, complemented by fluctuations between oxidising and reducing atmosphere resulted in rapid corrosion of the waterwall tubes. Concentrations of Cl, Br, Zn and Pb in the fuel, in the furnace vapours and in the deposits are reported in this work. As there is lack of published data on the bromine induced high temperature corrosion, laboratory scale corrosion tests were carried out to determine the relative corrosiveness of chlorine and bromine and these results will be reported in Part 2 of this work. Furthermore, the forms of Cl, Br, Zn and Pb in the combustion gases as well as in the waterwall deposits were estimated by means of thermodynamic equilibrium modelling and these results will also be discussed in Part 2.

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## 1. Introduction

High temperature corrosion of heat transfer surfaces in waste fired boilers is well-known from practical experience [1,2]. However, the relative importance of the different corrosion ‘triggers’ on boiler waterwalls is still not well-known. These include, in combination with the steel composition: the deposit chemistry, the combustion gas composition next to the steel surface and the steel temperature. There are hardly any reported waterwall corrosion experiences from the combustion of ‘virgin’ biomass (wood, crops or their residues) while with the introduction of demolition wood into biomass combustion deposit formation related problems and waterwall/superheater corrosion have been observed [3–6]. Similar observations have been reported regarding municipal solid waste (MSW) incineration as summarised by Wright and Krause [7], and combustion of solid recovered fuel [8].

Regarding deposit chemistry high temperature corrosion in waste fired boilers, apart from Cl it is often attributed to the contribution of Zn and Pb. Zn and Pb are found in considerable amounts in waste combustor deposits, in addition to Ca, Na, K and S [1,2]. Other elements found frequently in the deposits, but less relevant regarding high temperature corrosion, are Al, Si, Mg and P [9].

In waste fired boilers the waterwall steel temperatures range typically from 300 °C to 400 °C [2]. Alkali chloride (KCl, NaCl) induced high temperature corrosion has not been reported to be particularly relevant in this material temperature range but rather at temperatures close to 500 °C and higher [10,11]. However, the presence of zinc and lead chlorides in the deposits can lead to the formation of low temperature melts which have been found to be corrosive already in the 300–400 °C temperature range [2,12–14].

The objective of the present work (Part 1) was to determine the occurrence of corrosive Cl-, Br-, Zn- and Pb-compounds in the fuel, in the furnace vapours and in the waterwall deposits in a bubbling fluidised bed (BFB) combusting SRF. Indications of bromine

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induced high temperature corrosion of the waterwalls in this boiler have been published earlier [8]. Since both Cl and Br were found in the corrosion front, Part 2 of the work focuses on determining the relative corrosiveness of chlorides and bromides by means of laboratory experiments. The experimental results are discussed together with the thermodynamic equilibrium modelling results in Part 2.

### 1.1. Sources of Cl, Br, Zn and Pb in the fuels

The fuels used in the BFB boiler are SRF, spruce bark and paper mill wastewater sludge. The elements Cl, Br, Zn and Pb originate mainly from the SRF (Table 1). Additionally, Zn also originates from the bark and Br from the sludge. The sources of these elements in the fuels are briefly reviewed.

#### 1.1.1. Chlorine

There is a general agreement that Cl in SRF originates mainly from chlorinated plastics, mainly polyvinylchloride (PVC), or food residues which contain dietary salt. Approximately 70% of the Cl in MSW has been estimated to originate from plastics, particularly PVC [15,16]. In addition to PVC, chlorine is used in flame retardants [17]. Less than 10% from the total Cl in the fuel mixtures used in this work has been shown to be soluble in water, indicating that about 90% of the Cl originates from plastics [8].

**Table 1**

Fuel compositions and heating values. The values for SRF are the long term minimum, average and maximum as analysed by the SRF supplier covering total 4.5 years. 'Mix' refers to the properties of the fuel mix combusted in the boiler.

	SRF			Bark	Sludge	Mix
	Min.	Average	Max.			
Moisture (wt.%, ar)	7.9	16.7	40.4	55	13.8	36.5
Ash (wt.%, ds)	4.5	8.9	20.2	2.2	9.1	9.9
<i>In dry solids (wt.%)</i>						
C	43.4	54.7	63.8	50.4	48.2	52.2
H	5.9	7.7	9.3	5.6	6.0	7.1
N	0.31	0.71	1.24	0.27	1.28	1.0
S	0.05	0.18	0.56	0.02	0.57	0.16
O	50.3	36.7	25.1	43.7	34.9	29.2
<i>In dry solids (mg/kg)</i>						
Cl	500	4100	11,000	500	130	5280
Br	<10	60	320	10	110	80
Na	660	1400	2500	980	2100	1860
K	450	870	2300	1100	950	1470
Ca <sup>a</sup>	NA	18,500	NA	7300		16,910
Mg <sup>a</sup>	NA	1400	NA	600	590	1260
P <sup>a</sup>	NA	200	NA	320	2100	500
Al <sup>a</sup>	NA	5700	NA	280	830	1900
Si <sup>a</sup>	NA	9900	NA	720	11,800	9090
Fe <sup>a</sup>	NA	1270	NA	350	760	2080
Ba <sup>a</sup>	NA	430	NA	160	85	170
Sb <sup>a</sup>	16	24	36	0	3	150
Cd	0	0	14	0	0	0
Cr <sup>a</sup>	45	255	660	2	7	40
Cu <sup>a</sup>	25	45	200	2	15	140
Pb	6	45	270	1	3	70
Mn <sup>a</sup>	35	55	90	470	50	160
Ni <sup>a</sup>	7	120	320	1	2	10
Zn	2	420	2000	120	30	280
Sn	4	11	21	0	0	5
<i>Heating value (MJ/kg)</i>						
LHV, db	16.2	23.2	28.5	19.0	18.3	21.1
LHV, ar	13.3	19.0	24.2	7.3	15.4	12.5

NA – Not applicable (establishing a variation range is not relevant due to the small number of samples).

<sup>a</sup> Not included in the long term fuel quality monitoring, values from samples collected in the experiments.

#### 1.1.2. Bromine

It has been shown that SRF typically comprises of 35–50% textiles and plastics [18,19]. In both of these fractions flame retardancy is often required. Therefore, the likely sources of bromine in solid wastes are brominated flame retardants (BFRs) [20]. In SRF, Br has the same water solubility characteristics as Cl [8]. In BFRs bromine is bound in the organic matrix, which readily decomposes during combustion [21] as also PVC does.

Bromine is also used for water purification and disinfection purposes, as an alternative to the use of chlorine. Bromine has been found to be safer than its substitutes because bromine has a higher biocidal activity level for the same volume of product [22]. Brominated compounds are used in both commercial and residential water treatment which can be a source of Br in both industrial and municipal sewage [23–25].

#### 1.1.3. Lead

Nakamura et al. [26] found that upto 90% of the Pb in waste originates from batteries, glassware and electric appliances, light bulbs etc. The proportion originating from paints was only 0.1%. With the possible exception of paints the aforementioned items are minor in high quality SRF. For the SRF used in this work the base material originates from trade, commerce and industry where plastics, packaging (cardboard, paper) and wood are the main groups [27]. If the highly contaminating items (batteries, glass, light bulbs) are excluded from the data of Nakamura et al. [26] approximately 50% of the Pb would originate from plastics, textiles, rubber and leather. The main Pb-compounds in these products were suggested to be lead oxide (white pigment) and lead stearate [26]. Pb-stearate, tribasic lead sulfate and dibasic lead phosphite are common metal stabilisers used in PVC [28].

#### 1.1.4. Zinc

One of the largest industrial applications of Zn is in galvanising [22]. Zn is also used in plastics as an acid scavenger and filler in the form of ZnO [28]. According to SEM-EDX analyses of untreated SRF [29] most of the Zn rich particles in the fuel were found in connection to Cu rich particles. This was assumed to be brass which is an alloy of Cu and Zn. Cu and Zn rich particles were also found in connection to Si, which may indicate tinted glassware application [30]. Additionally, Zn was found in combination with other metals such as Fe and Ni, suggesting incorporation in alloys.

If the Zn content in the SRF is low, the content of Zn (naturally present) in the bark may be equal to that in the SRF. Plants, here meaning spruce, utilise Zn as a nutrient. In plants Zn appears to be absorbed by the roots primarily as Zn<sup>2+</sup> or as Zn(OH)<sub>2</sub>. Zinc is transported in the plant either as Zn<sup>2+</sup> or bound to organic acids. Zn seems to accumulate in root tissues but is translocated to the shoots when needed and is partially translocated from old leaves to developing parts of the plant. Depending on the plant species, between 60% and 90% of the zinc in a plant can be in a water soluble form (low molecular weight complexes and free ions) [31–33].

## 2. Material and methods

### 2.1. The BFB boiler

The boiler subjected to research has been described in detail previously [8]. Since then, the boiler has been through a bed area revision, now operating at a capacity of 140 MW<sub>th</sub>. In addition, the boiler has fuel feeding through the left and right walls from two chutes on both walls. The boiler steam values are 80 bar/500 °C. It has been estimated that the waterwall temperature in this boiler is close to 350 °C [8].

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