

High temperature corrosion of boiler waterwalls induced by chlorides and bromides – Part 2: Lab-scale corrosion tests and thermodynamic equilibrium modeling of ash and gaseous species

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ABSTRACT

In Part 1 of the work a measurement campaign was carried out to determine the occurrence of corrosive ash components in a bubbling fluidized bed (BFB) boiler combusting solid recovered fuel (SRF). It was found out that the main ash-forming elements that had been vaporized and subsequently condensed from the gas phase were Na, K, S and Cl together with minor amounts of Zn, Pb, Cu, and Br. Both, Cl and Br were found in the corrosion front of the waterwalls prior to the measurement campaign. In this work, the forms of ash forming elements in the combustion gases and in the waterwall deposits of the examined boiler were predicted by means of thermodynamic equilibrium modeling. Laboratory tests were also carried out to estimate the degree of corrosion of boiler steels under bromine containing deposits. A mixture of ZnBr_2 and K_2SO_4 was selected for high temperature lab-scale corrosion testing since Zn, Br and K as well as sulfates were present in the deposit and it was possible to compare these results to previously published results with ZnCl_2 – K_2SO_4 mixtures. The comparison showed that more severe material degradation was caused by the ZnBr_2 containing salt than by the corresponding chloride and corrosion was significant already at 400 °C.

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1. Introduction

This paper reports the second part of a study from a bubbling fluidized bed (BFB) boiler. The boiler subjected to research has been described in detail previously [1]. After a bed area revision, the boiler has been operating at a capacity of 140 MW_{th}. 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. The boiler is presented schematically in Fig. 1. In the first paper by Vainikka et al. [2] gas and aerosol measurements as well as waterwall deposits analyses were reported since the corrosion of the boiler waterwalls had earlier been observed [1]. The corrosion was then concluded to be induced mainly by Cl and to some extent also by Br which was found in the aerosols, deposits as well as in the corrosion front [1]. The ash-forming elements relevant to high temperature corrosion found during the measurement campaign, reported in the Part 1, were shown to be Na, K, S and Cl together with smaller amounts of Zn, Pb, Cu and Br.

While the objective of Part 1 was to determine the occurrence of corrosive elements in the fuel, in the furnace vapors and in the waterwall deposits, the purpose of the present work was to estimate the forms of these ash forming elements by applying thermodynamic equilibrium modeling. Further, laboratory tests were carried out to estimate the degree of corrosion of boiler steels under bromine containing deposits. A mixture of ZnBr_2 and K_2SO_4 was selected for high temperature lab-scale corrosion testing, making it possible to determine the relative corrosiveness of chloride and bromide salts compared to previously published results with ZnCl_2 – K_2SO_4 mixtures [3]. This is relevant for the full scale observations where K, S, Cl, Zn and Br had been found in boiler deposits [2].

1.1. Corrosion propensity of bromine

The amount of Br found in municipal solid waste (MSW) is usually quite low in comparison to Cl. Chlorine can be found in percentage levels whereas approximately 50–200 mg Br/kg fuel has been reported in MSW [4,5]. Vehlow and Mark [6] pointed out that materials such as insulating foams from the building sector, polymeric material used in automobiles, waste from electrical

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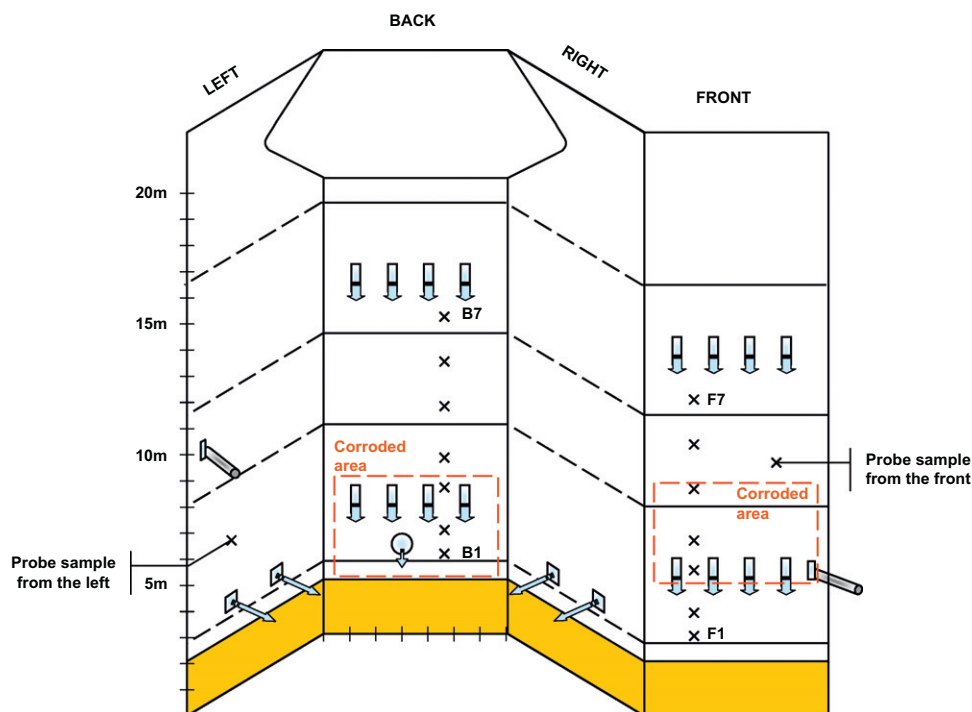


Fig. 1. Schematic picture of the BFB subjected to gas and aerosol measurements and deposit analyses in Part 1 [2]. In the picture, the corroding areas are also marked.

and electronic equipment (WEEE) often contain brominated flame retardants. Their analyses showed that the amount of bromine in such waste can be elevated by a factor of 2000 when comparing to mixed MSW. Thus, in the case where a flame retardant rich waste is incinerated, the influence of Br on the combustion process needs to be taken into consideration. Also, as indicated in Part 1 of the work, already small amounts of bromine in the SRF are traceable and may be actively involved in the corrosion reactions.

Currently, experimental results on the differences in the corrosivity between heavy metal chlorides and bromides that can form ash deposits are not available. Also, the literature handling bromine-related high temperature corrosion is scarce. The possible influence of bromine on corrosion in waste incinerators was raised in the report by Rademakers et al. [5]. The problem of metals reacting with halogen gases (HCl, Cl₂, HBr, Br₂) was stressed in the report. It was described that steels which contain elements that tend to form low melting and/or highly volatile metal halides will most likely suffer accelerated corrosion at elevated temperatures. The melting temperatures of the most important metal halides (considering steel composition) and the temperatures at which their vapor pressure reaches 10^{−4} atm are presented in Table 1 [5].

Table 1

Melting points, temperatures at which chloride vapor pressure reaches 10^{−4} atm of Fe-, Cr- and Ni- chlorides and bromides. Taken from [5].

Metal halide	Melting temperature (°C)	Temperature at 10 ^{−4} atm (°C)
FeCl ₂	676	536
FeCl ₃	303	167
CrCl ₂	820	741
CrCl ₃	1150	611
NiCl ₂	1030	607
FeBr ₂	689	509
FeBr ₃	–	156
CrBr ₂	842	716
CrBr ₃	>800	615
CrBr ₄	–	516
NiBr ₂	965	580

Vehlow et al. [6,7] investigated the Br partitioning and the influence of Br on metal volatilization in a waste incineration process. In those experiments Br-bearing plastics were added to the waste resulting in a Br level of 30–3200 mg/kg fuel. Organically bound Br was claimed to be easily released during combustion and HBr was indicated to be the main form of bromine in the combustion gases when high Br content mixtures were incinerated. It was also shown [6] that Br seemed to promote zinc volatilization more than Cl. Moreover, Br apparently had a volatilizing effect also on other elements such as arsenic, cadmium and lead.

Only a few publications describe the corrosion resistance of alloys in HBr or Br₂ containing gas mixtures [8–10]. Zhuang et al. [10] exposed steel samples to a synthetic flue gas containing approximately 50 ppmv HBr. The tested temperatures were however quite low: 27 °C, 66 °C and 149 °C. At higher temperatures (above the dew point) HBr was suggested to diffuse through the oxide scale to the metal surface and then react with the iron to form iron bromide which then evaporates. Iron bromide was found on the metal/scale interface.

Önay and Saito [9] exposed Fe–20Cr and Ni–20Cr steel samples to a Ar–H₂O–HBr gas mixture at 727 °C. Bromine-rich products were found on the metal/scale interface on both steels. It was also shown that NiO crystals growing through the chromia on the Ni–20Cr significantly decreased the resistance of the steel. Protective Cr₂O₃ poorly adhered to the metal surface and Ni loss was substantial which was explained by the low stability of NiBr₂ in HBr containing gas. Also tests performed by Antill and Peakall [8] with pure Cr and Ni in a Br₂ containing gas at 750 °C showed heavy oxidation with markedly worse performance of Ni than of Cr.

2. Material and methods

2.1. Modeling procedures

In the thermodynamic equilibrium modeling a two-stage calculation procedure was applied to predict the forms of the ash forming elements that are volatilized at high temperatures and

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