

Bromine as an ash forming element in a fluidised bed boiler combusting solid recovered fuel

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ABSTRACT

Plastic materials are the main sources of chlorine in solid recovered fuels (SRF). Chlorine is attributed to be the main initiator of slagging, fouling and corrosion in biomass and waste combustion as it lowers the melting point of ash forming matter and reacts chemically with the heat transfer surface steels. SRF may also contain sources of bromine in the form of brominated flame retardants (BFRs) applied in many plastics and textiles. Results presented in this paper from an experimental campaign at an 80 MW_{th} bubbling fluidised bed (BFB) boiler show that bromine is behaving in a similar manner as chlorine: bromine was found at the corrosion front in boiler membrane wall tubes, and as water soluble salts in aerosol samples collected from the furnace and electrostatic precipitator (ESP) ash. It is evident from these results and the data in the literature that most of the salts of bromine are, by both their fate and physical and chemical properties, similar to those of chlorine. It can be concluded that if there is a source of bromine in the fuel corrosive high vapour pressure bromides can be formed analogously to chlorides.

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1. Introduction

Due to the CO₂ emission trading scheme and rising prices of solid fuels and electricity, 'alternative' fuels for heat and power generation are receiving increasing attention in fuel markets. This applies not only to solid biomass fuels but also to wastes. Such wastes have a strategic role to play in reducing greenhouse gas emissions in developed and developing countries. Globally, solid waste disposal is responsible for about 3–4% of anthropogenic greenhouse gas (GHG) emissions [1]. In the EU, diversion of municipal solid waste (MSW) from landfilling to composting, recycling and energy recovery could produce a reduction from 40 to over 100 Mt CO₂-equivalents per year, which corresponds to 29% from the total CO₂-equivalent reduction target under the Kyoto protocol for EU-15 [2,3].

One of the options for energy recovery from waste is the preparation of solid recovered fuel (SRF). It can be prepared for example from waste from commerce and industry (WCI), mixed municipal solid waste (MSW) or even from source-separated household waste (HHW) [4]. SRF can then be used,

for example in fuel-flexible fluidised bed boilers, gasifiers or cement kilns.

From a technical point of view, replacing conventional fuels with waste or biomass tends to lead to increased chlorine-induced corrosion rates and to various ash related problems in boiler furnaces [5–7]. In biomass combustion the initiation of ash melting and corrosion is mainly attributed to the salts of Na, K, Ca, S and Cl [8–10] as well as P [11–15]. For waste incineration or co-incineration the aforementioned list of main contributors is commonly complemented with Zn, Pb and also Sn [16–20]. All these elements can be found in SRF, with the latter metals and halogens particularly in its plastic fraction. It is essential to avoid high concentrations of corrosive gaseous or molten salts, particularly chlorides, in a combustor furnace, in order to reduce the risk for corrosion of heat transfer surfaces. At the present time, in purely waste-fired units, corrosive deposits and ash melting have limited their live steam temperature to 420–470 °C, and consequently electric efficiency to 20–24% [21]. In SRF co-fired units, where electric efficiency is aimed at to be higher than in mixed MSW incineration, alkali chloride concentrations should be kept particularly low in order to allow for higher heat transfer surface temperatures.

In this article SRF is meant by fuels classified and certified according to CEN-TC 343 (European Committee for Standardization (CEN) – Technical Committee (TC) 343 for solid recovered fuels)

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[22]. SRF can be regarded as a waste derived fuel the quality of which is monitored, and controlled by processing, and falls into specified quality categories based on heating value and chlorine and mercury content [23]. MSW is defined according to the definitions of the Eurostat [24]. It includes household waste and similar waste from commerce and trade, small businesses, offices and institutions (mixed waste and separately collected fractions). The definition also includes street sweeping, content of litter containers, market cleansing waste, yard and parks waste, and bulky waste (old furniture, mattresses, etc.).

In comparison to mixed MSW or HHW, SRF is typically enriched in high calorific value plastics [25] and it often consists also of specific homogeneous sources of combustibles such as industry process residues, textiles or materials from demolition. In Table 1 the typical composition of MSW and SRF are compared.

Even if the corrosion of biomass and waste-fired boilers is often attributed to chlorine, in terms of corrosion risk to boilers most of the salts of bromine are in physical and chemical properties similar to those of chlorine [29–33]. However, there are only few indications in the literature that bromine could eventually contribute equally to chlorine in high-temperature corrosion [30]. Due to the very specific applications of bromine, its concentration in waste fuels can be assumed to be lower than chlorine and even negligible in biomass, but if there is a source of bromine in the fuel, based on its properties, its fate can be reasoned to be similar to that of chlorine.

In Fig. 1 are plotted the saturation pressures and in Table 2 are listed the melting points of selected bromides and chlorides. These metal salts have been selected for the listing based on the fact that the cations are those that can be found in waste fractions typically found in SRF, i.e. in packaging material such as cardboard and paper (K, Na, Ca) as well as plastics and plastics additives (stabilisers, acid scavengers, catalyst residues or colorants: Zn, Pb, Cu, Ba, Cd) [34,35]. Iron chloride and iron bromide are potential corrosion products.

From the saturation curves it can be seen that bromide forms volatile compounds with K, Na, Zn, Pb and Fe in a very similar way as chlorine. There is a larger deviation between the curves, however, for Zn and Pb bromides and chlorides than for the halides of the other cations. From the data in Table 2 it can be seen that the melting point of the bromides can be some tens of degrees lower or higher than those of the corresponding chlorides. For alkali metal salts, KBr and NaBr, melting points are lower for bromides. Again, there is quite a large difference in the properties (melting points) of Zn and Pb bromides and chlorides. For Zn salts the melting point of the bromide is higher than that of the chloride, as opposed to the Pb salt where the bromide has a lower melting point than the corresponding chloride.

Table 1

Comparison of the composition of SRF and MSW in weight percent (as received). The data has been compiled from several sources [4,26–28] and values should be taken as indicative.

| | SRF | MSW |
|-----------------|-----------------|-----------------|
| Organics | NA ^a | 30–40 |
| Paper/cardboard | 40–50 | 15–25 |
| Textiles | 10–14 | 1–5 |
| Plastics | 25–35 | 7–15 |
| Metals | 2 | 3–4 |
| Glass | | 4–7 |
| Wood | 3–10 | NA ^b |
| Other | 5–10 | 18–30 |

^a Organic residues in SRF included in 'Other'.

^b Wood in MSW included in 'Organics'.

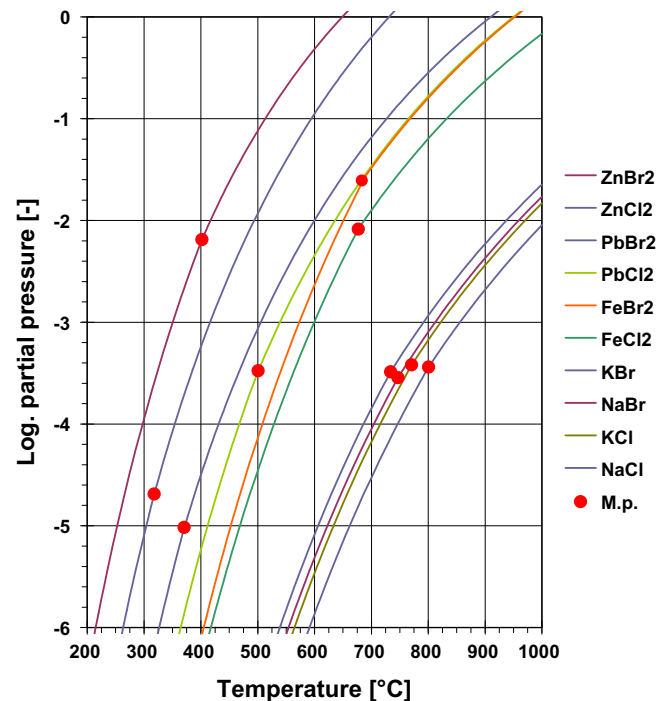


Fig. 1. Calculated saturation pressures and melting points (m.p.) for selected chlorides and bromides [36].

Table 2

Melting points [36,37] of selected chlorine and bromine salts relevant to SRF co-combustion [30,37,38].

| Compound | Melting point | Compound | Melting point |
|-------------------|---------------|-------------------|---------------|
| NaCl | 801 | CaCl ₂ | 772 |
| NaBr | 747 | CaBr ₂ | 742 |
| KCl | 771 | CdCl ₂ | 568 |
| KBr | 734 | CdBr ₂ | 568 |
| FeCl ₂ | 677 | SnCl ₂ | 247 |
| FeBr ₂ | 691 | SnBr ₂ | 232 |
| CuCl | 430 | SbCl ₃ | 73 |
| CuBr | 439 | SbBr ₃ | 95 |
| CuCl ₂ | 598 | PbCl ₂ | 501 |
| CuBr ₂ | 498 | PbBr ₂ | 371 |
| ZnCl ₂ | 318 | BaCl ₂ | 962 |
| ZnBr ₂ | 402 | BaBr ₂ | 857 |

The deposits in boilers are always mixtures of different salts. The first melting temperature of a salt mixture is in most cases lower than the melting point of the pure salts that the mixture consists of. Chlorides are known to lower the first melting point of sulphate rich deposits, and it is reasonable to expect a similar effect of bromides. Data on the melting behaviour of alkali salt mixtures containing bromides is not yet available, however.

In this paper the role of bromine as an ash forming element is characterised by means of samples obtained from an 80 MW_{th} BFB combusting SRF as the main fuel. The samples were obtained from two experimental conditions where two proportions of paper mill sludge feeding into the boiler were used. The results from the characterisation of the fuel, aerosol, and ESP ash samples are complemented with an SEM–EDX study on a corroded membrane wall sample. With the support of the physical and chemical properties presented for bromides and chlorides the occurrence of bromine and its role in high-temperature corrosion is discussed.

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