



Sulfation of alkali halides in a bench-scale bubbling fluidized bed reactor



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HIGHLIGHTS

- Bench-scale investigations on sulfation of alkali halide aerosols.
- Indication of a higher tendency for sulfation of alkali chloride than alkali bromide.
- Consistent indications from both experimental results and thermodynamic calculations.

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ABSTRACT

During biomass and waste combustion, high levels of alkali halides in the flue gas often lead to increased deposit formation and accelerated superheater corrosion. These problems can be reduced either by co-combustion or by the use of sulfur-containing additives. A measurement campaign was carried out in a 20 kW_{th} bubbling fluidized bed (BFB) bench-scale reactor to characterize the sulfation behaviors of alkali chloride and alkali bromide. Spruce bark was used as the base fuel – serving as a source of alkali metals (mainly K). HCl and HBr gases were fed with the fluidization air to simulate co-firing of a halide-rich fuel with bark. SO₂ and elemental S powder were used as additives to convert the alkali halide aerosols to less corrosive alkali sulfates. The sulfation behavior of alkali halides was evaluated by means of several measurements including: FTIR (flue gas measurement), a low-pressure impactor (particle size distribution and chemical composition of extracted aerosol particles) and deposit probe sampling (deposit growth rate and chemical composition of the windward, 90° side and leeward deposits). The results indicated a higher tendency for sulfation of alkali chloride than of alkali bromide.

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1. Introduction

Certain biomass and waste fuels contain relatively high amounts of alkali metals (mainly K) and halogens (Cl, Br), but low amounts of sulfur (S). In waste fuels, Cl originates mainly from chlorinated plastics (e.g., polyvinyl chloride (PVC)) and from dietary salt (e.g., sodium chloride (NaCl)) in food residues [1–3]; Br is mainly found in certain wastes that are rich in flame-retarded plastics and textiles, as well as in industrial and municipal sewage sludge [4]. During biomass and waste combustion, the halogens (Cl, Br) released to the gas phase are mainly present as hydrogen halides (HCl, HBr) and alkali halides (KCl, KBr, NaCl, NaBr) [5,6]. Furthermore, HBr had earlier been found to be more reactive than HCl toward alkali metals to form alkali halides [7]. Potassium is mainly released into the gas phase as potassium halide and potassium hydroxide, and potassium halide is dominant when

the halogen content is high [8]. High levels of alkali halides in the flue gas often lead to increased deposit formation due to condensation and stickiness caused by their low melting temperatures [9], while high content of halogen in deposits can result in accelerated superheater corrosion [10]. These problems can be reduced either by co-combustion with fuels such as coal or peat, or by the use of elemental sulfur or other sulfur/sulfate-containing additives such as ammonium sulfate ((NH₄)₂SO₄) [8–10].

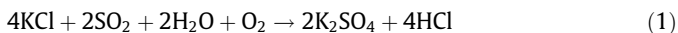
Glarborg [11] reported that the formation of alkali sulfates from alkali chlorides includes both homogeneous and heterogeneous mechanisms. In the heterogeneous mechanism, a gas phase alkali-containing precursor is transported to a surface where it is then sulfated by reactions in condensed or solid phases. The homogeneous mechanism involves the formation of alkali sulfate in the gas phase followed by condensation onto the deposition surfaces. The sulfation rate of KCl was found to be considerably faster in the gas phase than in the condensed phase [12].

Reactions (1)–(4) as shown below are the relevant reactions about sulfation of gaseous KCl. The sulfur required in reaction (1)

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can originate either from the fuel itself or from additives such as elemental sulfur. The sulfation rate in the gas phase was found to be limited by the presence of SO_3 , and the oxidation of SO_2 to SO_3 (reaction (4)) was claimed to be the rate-limiting step in the formation of alkali sulfate [8,13,14]



However, data on the sulfation of alkali bromide during biomass and waste combustion are not currently available. When alkali chloride and bromide coexist in the flue gas, the competition between both alkali halides for the available sulfur during sulfation process is not yet known. The objective of this work was to establish a basic understanding of the sulfation behavior of alkali chloride and bromide in BFB combustion conditions.

2. Experimental

2.1. The 20 kW_{th} BFB reactor

In this work, an electrically stabilized 20 kW_{th} bubbling fluidized bed (BFB) reactor was used for the experimental runs. The BFB reactor has been described earlier in several publications [7,15–17]. Fig. 1 illustrates its construction. The reactor has a bed diameter of 0.16 m. The freeboard zone has a diameter of 0.23 m and height of 3.5 m. The interior walls that may have flame contact are made of ceramics and quartz. The bed material used in the tests was natural sand with a mean particle diameter of 0.33 mm (0.1–0.6 mm) and a composition (wt%) of Na_2O 3.0, K_2O 2.3, MgO 0.59, CaO 2.3, Al_2O_3 11.8, Fe_2O_3 1.4, SiO_2 77.5. The mean gas velocity in the reactor was about 0.5 m s⁻¹, corresponding to a total residence time of 7–8 s. This flow velocity is sufficient to transport particles of >100 μm to the cyclone, while larger particles will be deposited on the walls of the freeboard or stay in the bed. Fly ash particles of >10 μm will be separated by the cyclone. The total residence time

in the reactor is longer than in a typical BFB boiler since the upper half of the freeboard is designed to be a well-controlled zone for sampling and observation. The air staging was kept constant (primary/secondary/tertiary, 50:30:20). The bed temperature was kept between 850 and 870 °C.

2.2. Fuels and combustion tests

In the tests, spruce bark was used as the base fuel and served as a source of alkali metals (mainly K). HCl and HBr gases were fed with the fluidization air to simulate co-firing of a halide-rich fuel with bark, thereby forming alkali halide aerosols in the flue gas. SO_2 and elemental S powder were used as additives to convert the alkali halide aerosols to less corrosive alkali sulfates.

The properties and the composition of the main ash-forming elements in the bark are shown in Table 1. Bark A and Bark B were from the same source but from different batches. Table 2 illustrates the test matrix with different amounts of Br (HBr), Cl (HCl) and S (SO_2 or S). A total of nine experimental runs were done. Tests 1 and 2 burned only bark. Test 3 co-fired bark with equal amounts of HBr and HCl, and was considered as a reference test without sulfur addition. Tests 4 and 5 were performed with low and high doses of added SO_2 based on Test 3. In Test 6, a low dose of elemental S was used instead of the SO_2 used in Test 4. In Test 7 and Test 8, the dose of elemental S was the same as in Test 6, but only HCl or HBr was added.

2.3. Flue gas analysis

The dry flue gases (O_2 , CO_2 , CO, NO, SO_2) were analyzed with standard on-line analyzers. The wet and hot (180 °C) flue gases (H_2O , CO_2 , CO, NO, SO_2 , HCl) were measured by Fourier Transform Infrared Spectroscopy (FTIR). HBr, Br_2 , HCl and Cl_2 in the flue gas were sampled by absorption bottles and analyzed by means of ion chromatography, which was based on the EPA Method 26 – Determination of hydrogen halide and halogen emissions from stationary sources (non-isokinetic method) [18]. This has been well described in detail in an earlier publication [7].

2.4. Deposit sampling

Two air-cooled deposit probes were used in the tests. As shown in Fig. 1, the first probe was placed in the upper part of the freeboard (FB), where the gas temperature was about 870 °C; the second probe was placed in the flue gas channel (FGC) before the

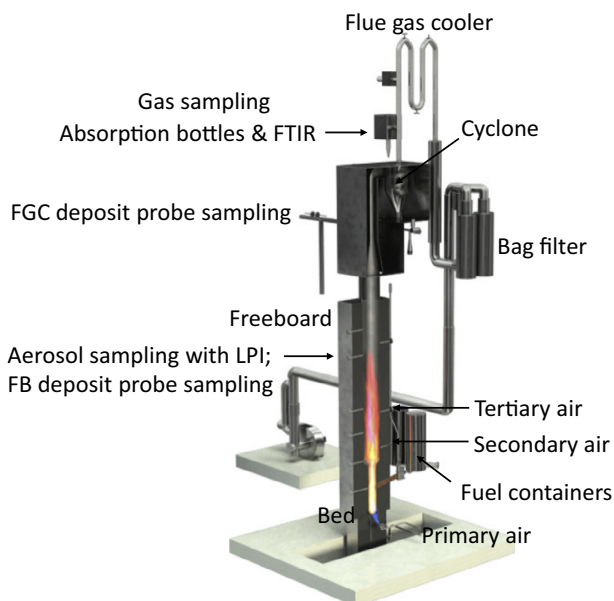


Fig. 1. The schematic diagram of the 20 kW_{th} BFB reactor. FB = freeboard, FGC = flue gas channel.

Table 1
Fuel properties.

	Bark A	Bark B
Moisture (wt%, ar)	30	30
Ash (wt%, db)	3.2	2.7
<i>Ultimate analysis of dry solids (wt%, db)</i>		
C	50.7	50.9
H	5.7	5.9
N	0.4	0.3
O	39.9	40.1
S	0.02	0.02
<i>Main ash-forming elements (mg/kg, db)</i>		
Ca	9100	10200
K	2300	2400
Na	140	79
Cl	140	140
Br	<10	<10
<i>Heating value (MJ/kg)</i>		
LHV, ar	12.4	12.5
LHV, db	18.7	18.8

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