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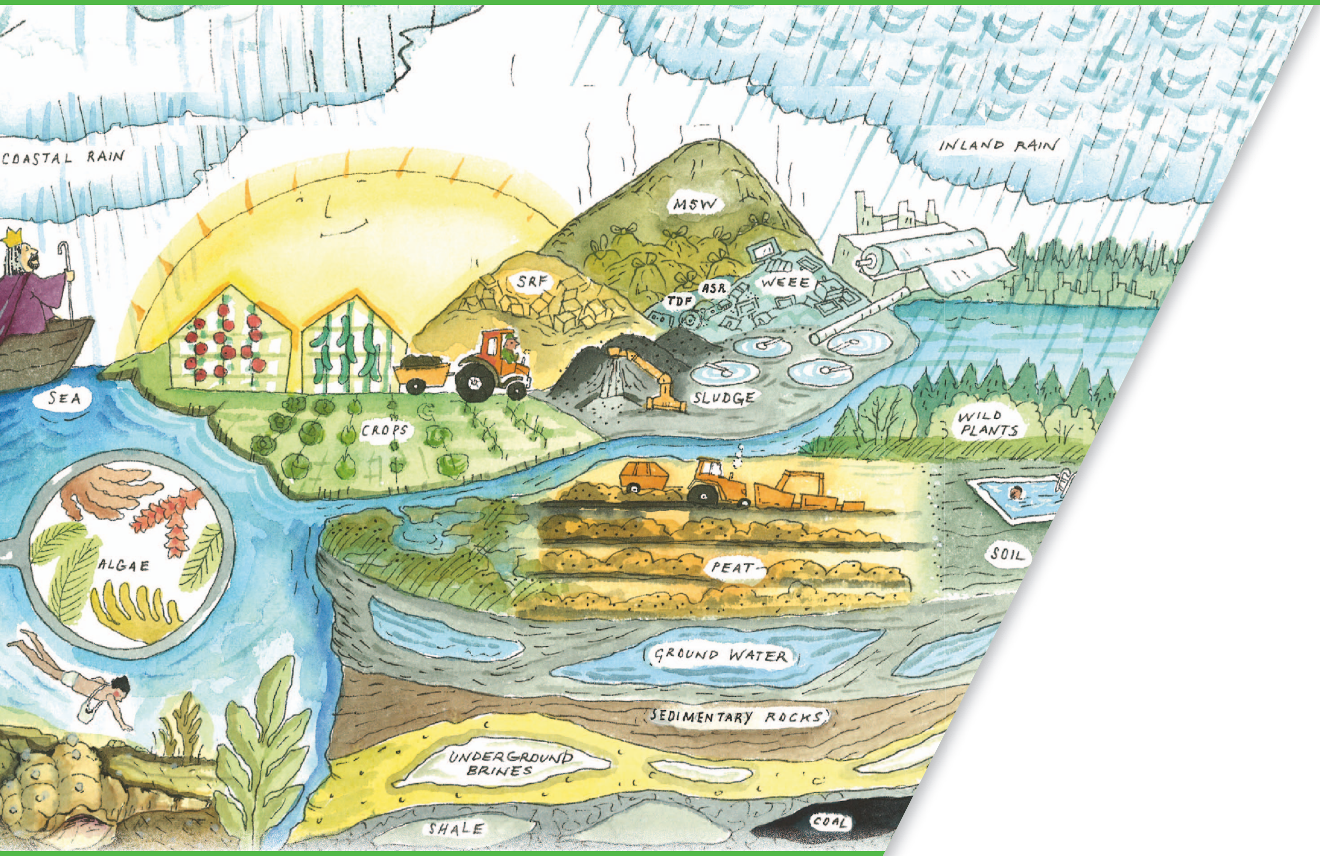

Pasi Vainikka

Occurrence of bromine in fluidised bed combustion of solid recovered fuel

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Figure on the front page: *Artist’s view of the natural and anthropogenic occurrence of bromine in solid fuels. By Pasi Vainikka & Heli Pukki.*

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Pasi Vainikka. Occurrence of bromine in fluidised bed combustion of solid recovered fuel [Förekomst av brom vid förbränning av returbränsle i fluidiserade bädd; Bromin esiintyminen kierrätyspolttoaineen leijukerrospoltossa]. Espoo 2011. VTT Publications 778. 118 p. + app. 134 p.

Keywords bromine, bromide, combustion, ash, corrosion, aerosol, vapour

Abstract

Corrosive ash species are the single most important factor limiting the electric efficiency of steam boiler plants fired with waste or biomass. Chlorine has been found to have a central role in the chemistry involved as it reduces the melting temperature of ash, forms corrosive vapour and gas species in the furnace and halogenated deposits on boiler heat transfer surfaces. In this context chlorine has been extensively researched.

At the time of writing this thesis there was hardly any published data available on the occurrence of bromine (Br) in the aforementioned context. The objective of this work was to review the occurrence of bromine in solid fuels and characterise the behaviour of bromine in full-scale fluidised bed combustion. The central questions in the context of ash chemistry were: In which fuels bromine can be found and in which form, what is the speciation of bromine in the furnace and fly ash, what role bromine may have (if any), and finally, which are the practical implications?

The review on the occurrence of bromine in solid fuels revealed that in anthropogenic wastes bromine is mainly found in connection to flame retarded substances. Several weight percentages of bromine can be found in plastics treated with brominated flame retardants (BFRs). Bromine is typically found some 100–200 mg kg^{-1} in mixed municipal solid wastes (MSW). Bromine may be enriched in fuels with high share of plastics, such as solid recovered fuel (SRF) or refuse derived fuel (RDF). Up to 2000 mg kg^{-1} was found as a monthly average in SRF, typical levels being 20–200 mg kg^{-1}. Wastewater sludge from paper mills may contain bromine 20–100 mg kg^{-1} due the use of bromine based biocides. In other fuels bromine may be found in significant amounts in marine influenced coal deposits and peat as well as in biomass treated with brominated pesticides.

In the experimental part SRF, spruce bark and wastewater sludge from a paper mill were co-fired in a full-scale bubbling fluidised bed (BFB) boiler, and the collected fuels, aerosols and waterwall deposits were analysed with the focus on the fate of bromine. Bromine was mainly found to form water soluble high vapour pressure alkali metal halides in the furnace – in the form of KBr(g) and NaBr(g) as estimated by thermodynamic equilibrium modelling. A positive correlation was observed between the halogen (Br, Cl) and the metal (Cu, Pb, and Zn) concentrations in the lower furnace vapours when measured next to the waterwalls. Further, bromine was observed both in the wall deposits and in the corrosion front of the waterwall tubes. This was found to take place even if the bromine content in the SRF was less than 60 mg kg^{-1} in SRF. Laboratory scale oven tests with commercial boiler steels showed that a bromine containing salt induced a higher corrosion rate than the corresponding chloride.

Pasi Vainikka. Occurrence of bromine in fluidised bed combustion of solid recovered fuel [Förekomst av brom vid förbränning av returbränsle i fluidiserade bädd; Bromin esiintyminen kierrätyspolttoaineen leijukerrospoltossa]. Espoo 2011. VTT Publications 778. 118 s. + bil. 134 s.

Nyckelord bromine, bromide, combustion, ash, corrosion, aerosol, vapour

Sammanfattning

Korrosiva askföreningar är den viktigaste enskilda faktorn som begränsar den elektriska effektiviteten hos ångpanneanläggningar som eldar avfall eller biomassa. Klor har visats ha en central roll i askkemin då den sänker askans smälttemperatur, bildar korrosiva ång- och gasföreningar vid förbränning och förorsakar halogenerade avlagringar på pannans stålytor. Omfattande forskning har ägt rum om kloren i dessa sammanhang.

Vid tidpunkten då denna avhandling skrevs fanns det knappt om data gällande förekomsten av brom (Br) i ovannämnda sammanhang. Målet med detta arbete var att granska förekomsten av brom i fasta bränslen följt av karakterisering av bromens roll i fullskalig förbränning i fluidiserade bäddar. De centrala frågorna gällande askkemin var: i vilka bränslen kan brom hittas och i vilka former, i vilka former finns brom i pannan och flygaska, vilken roll har brom (om någon) och slutligen; vilken är den praktiska innebörden.

Undersökningen av bromförekomsten i fasta bränslen visade att brom i antropogent avfall huvudsakligen hittas i samband med brandförhindrande substanser. Flera viktprocent brom kan hittas i plast som behandlats med bromerade flamskyddsmedel. I blandat kommunalt fast avfall (MSW) finns det brom typiskt mellan 100 och 200 mg kg^{-1}. Brom kan vara anrikad i bränslen med hög plasthalt som t.ex. fasta återvunna bränslen (SRF, solid recovered fuel; RDF refuse derived fuel). Upp till 1000 mg kg^{-1} hittades som månadsmedelvärde i SRF och typiska nivåer var 20–200 mg kg^{-1}. Avfallsvattenslam från pappersbruk kan innehålla brom 20–100 mg kg^{-1} på grund av användning av brombaserade biocider. I andra bränslen kan brom hittas i betydande mängder i maritima kol- och torvförekomster samt i biomassa som behandlats med brominnehållande bekämpningsmedel.

I den experimentella delen i detta arbete samförbrändes SRF, granbark och slam från avfallsvatten i en fullskalig bubblande fluidiserad bädd (BFB) och bränslena, aerosolerna och avlagringarna från pannväggarna analyserades med

fokus på bromens öde. Vid förbränning fanns brom huvudsakligen bilda vattenlösliga metallhalider med högt ångtryck. Termodynamiska jämviktsberäkningar visade att haliderna förekom som KBr(g) och NaBr(g). En positiv korrelation observerades mellan halogen- (Br, Cl) och metallkoncentrationerna (Cu, Pb och Zn) i pannans nedre delar invid de vattenkylda pannväggarna. Vidare observerades brom i avlagringarna på väggarna och vid korrosionsfronten på vattenväggens rör. Detta visades äga rum även om bromhalten var lägre än 60 mg kg^{-1} i SRF. Korrosionsexperiment i laboratorieskala med kommersiella pannstål visade att brominnehållande salt förorsakade allvarligare korrosion än motsvarande klorsalt.

Pasi Vainikka. Occurrence of bromine in fluidised bed combustion of solid recovered fuel [Förekomst av brom vid förbränning av returbränsle i fluidiserade bädd; Bromin esiintyminen kierrätyspolttoaineen leijukerrospoltossa]. Espoo 2011. VTT Publications 778. 118 s. + liitt. 134 s.

Avainsanat bromine, bromide, combustion, ash, corrosion, aerosol, vapour

Tiivistelmä

Korrosiiviset tuhkayhdisteet ovat suurin yksittäinen sähköntuotannon hyötysuhdetta rajoittava tekijä biomassaa ja jätettä polttavissa höyryvoimalaitoksissa. Tähän liittyvässä kemiassa kloorilla on havaittu olevan keskeinen rooli, sillä se laskee tuhkan sulamislämpötilaa ja muodostaa tulipesässä korrosiivisia höyry- ja kaasuyhdisteitä sekä halogenoituja kerrostumia lämmönsiirtopinnoille. Tässä yhteydessä klooria on tutkittu laajasti.

Tätä opinnäytettä kirjoitettaessa saatavilla oli hyvin vähän julkaistua tietoa bromin (Br) esiintymisestä edellä mainitussa yhteydessä. Tämä työn tarkoituksena oli koota tietoa bromin esiintymisestä kiinteissä polttoaineissa ja luonnehtia bromin käyttäytymistä täyden mittakaavan leijukerrospoltossa. Keskeiset kysymykset tuhkakemiaan liittyen olivat: mistä polttoaineista bromia voidaan löytää ja missä muodossa, minä yhdisteinä bromi esiintyy tulipesässä ja lentotuhkassa, mikä bromin rooli on (jos mikään), ja mitkä ovat käytännön seuraukset.

Katsaus bromin esiintymiseen kiinteissä polttoaineissa osoitti, että ihmisen toiminnassa syntyvistä jätteistä bromia löydetään enimmäkseen palosuojattuihin materiaaleihin liittyen. Bromia voidaan löytää useita painoprosentteja bromatuilla palosuoja-aineilla käsitellyistä muoveista. Sekalaisessa yhdyskuntajätteessä bromia on tyypillisesti noin 100–200 mg kg^{-1}. Bromi voi rikastua polttoaineisiin, joissa muovien osuus on suuri, kuten kiinteät kierrätyspolttoaineet (SRF, solid recovered fuel; RDF refuse derived fuel). SRF-polttoaineesta löydettiin jopa 2 000 mg kg^{-1} kuukausikeskiarvona, kun tyypillinen pitoisuustaso on 20–200 mg kg^{-1}. Paperitehtaan jätevesiliete voi sisältää bromia 20–100 mg kg^{-1} bromiin perustuvien eliöntorjunta-aineiden käytön vuoksi. Muissa polttoaineissa merkittäviä bromipitoisuuksia voidaan löytää meriympäristön vaikutuksen alaisista kivihiiliesiintymistä ja turpeesta sekä bromatuilla tuholaistorjunta-aineilla käsitellystä biomassasta.

Kokeellisessa osuudessa kierrätyspolttoainetta, kuusenkuorta sekä paperitehtaan jätevesilietettä rinnakkaispoltettiin täyden mitan kerrosleijukattilassa, ja kerätyt polttoaineet, aerosolit ja kattilaseinäkerrostumat analysoitiin keskittyen

bromin esiintymisen määrittämiseen. Tulipesässä bromin havaittiin muodostavan pääasiassa vesiliukoisia korkean höyrynpaineen alkalimetallihalideja – termodynaamisen tasa painomallinnuksen perusteella arvioidut esiintymismuodot ovat kaasumaiset KBr ja NaBr. Tulipesän alaosassa, tulipesän seinien vierestä mitattujen halogeeni- (Br, Cl) ja metallihöyryjen (Cu, Pb ja Zn) pitoisuuksien välillä havaittiin positiivinen korrelaatio. Lisäksi bromia havaittiin sekä seinäkerrostumissa että kattilaseinäputkien korroosiorintamassa. Näin tapahtui, vaikka kierrätyspolttoaineen bromipitoisuus oli keskimäärin alle 60 mg kg^{-1}. Laboratoriomittakaavassa suoritetut uunikokeet kaupallisilla kattilateräksillä osoittivat bromia sisältävän suolan aiheuttavan jopa suuremman korroosionopeuden kuin vastaava kloridi.

Preface

I hope this thesis provides a small step forward in the knowledge, science and chemistry around fuels, wastes, boilers, furnaces, vapours, high-temperature corrosion and more specifically bromine. A major part of the experimental work in this work was in fact the measurements, analyses and results' interpretation regarding vapours and fine particles. This could also be branded under the umbrella of nanoscience, but this term was not used in the thesis.

There were initially three people who made this thesis to realise. These were Dr Jouni Hämäläinen and Prof Kai Sipilä both at VTT, and Prof Mikko Hupa at Åbo Akademi. These were the people who unquestionably supported me in all forms from the very beginning in planning, in actual execution and substance through funding and project development and finally in job arrangements. I am truly grateful for the support. I hope I can return some of the trust you gave to me.

Establishing all this work required huge amount of knowledge covering a very long chain of individual actions and processes. The full scale campaigns I could have never, never and never again accomplished alone. Part of my work was to build up such a team who could do this together. This core group included Päivi Hakkarainen, Juho Kauppinen, Sari Kauppinen, Marko Räsänen, Meiju Sinkkonen, Kauko Tormonen, Raili Taipale, Hannu Vesala and Martti Aho. We did spend sleepless nights at the campaigns, and all we got was a few micrograms of fine particles. This required from the colleagues some thousand hours of preparing, execution and after-processing. After all this was done there was a fair chance for research scientist like me to write a scientific paper on the issue. Well, what to say? Thank you all!

At laboratory Åbo Akademi I have received support, help and guidance particularly from my co-authors Daniel Lindberg and Dorota Bankiewicz as well as Tor Laurén and my supervisor Patrik Yrjas. Without them the backbone of this thesis, the journal papers, would simply not be there. It was a pleasure to work with you, your extraordinary contribution and commitment made the puzzle to become a complete picture.

A major part of the work was the literature review on bromine. Here by far and foremost the credit on supporting that part of the work goes to Pirjo Muhonen at VTT. No matter which document I asked, I received it in a few moments. Hannu Luoma supported me through the database search.

I am grateful for the companies and people from the industry who supported the work – actually made also part of it – and beard a major part of the cost too. These people are Ari Frantsi, Teemu Heinänen, Jukka Nuutinen and Pekka Ruuskanen from Stora Enso; Lassi Hietanen and Janne Hannula from Lassila&Tikanoja; Jaani Silvennoinen and Sonja Enestam from Metso Power and Markku Karlsson from UPM-Kymmene.

It was actually Sonja Enestam and colleagues at Top Analytica who first observed the bromine to be a possible issue. With the help of Ari Frantsi and Jaani Silvennoinen we could gather effort to go after this halogen. Thank you Sonja, Jaani and Ari!

Dr Heikki Ollila, Prof Minna Tiainen and Antero Moilanen are acknowledged for their support with SEM-EDX data on the SRF.

Tekes – the Finnish Funding Agency for Technology and Innovation is acknowledged for funding through BIOSAFE and ADCOF projects and the Seventh Framework Programme through a research and demonstration project RECOMBIO TREN/FP7EN/239530. Also the Graduate School in Chemical Engineering (GSCE) is acknowledged for financial support.

I regret some of the time I had to spend away from my family, especially my little daughters. I hope, Siiri and Sara, you do not mind. I hope I could plant a seed in your minds to observe and appreciate what nature provides with us. On the other hand, I have learned from you to try not to let education to spoil my mind. I thank my wife Tuuli for keeping all the pieces together, also when I was away. Thank you girls! We have also got support from our families in the course of the work, this has been priceless.

Finally, I am thankful to all those not specifically mentioned above by name but who know they supported me and my work.

Be careful about what you want –
because you will get it.
- Andy McCoy

Academic dissertation

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Institute of Chemical Engineering
Vienna University of Technology
Vienna, Austria

List of papers

I Vainikka, P. & Hupa M. Review on bromine in solid fuels. Part 1: Natural Occurrence. Acc. for publication in Fuel.

II Vainikka, P. & Hupa M. Review on bromine in solid fuels. Part 2: Anthropogenic occurrence. Fuel (in press).

III Vainikka, P., Enestam, S., Silvennoinen, J., Taipale, R., Yrjas, P., Frantsi, A., Hannula, J. & Hupa M. Bromine as an ash forming element in a fluidised bed boiler combusting solid recovered fuel. Fuel 90(3), pp. 1101–1112 (2011).

IV Vainikka, P., Bankiewicz, D., Frantsi, A., Silvennoinen, J., Hannula J. & Hupa M. 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. In: Fuel 90(5), pp. 2055–2063 (2011).

V Bankiewicz, D., Vainikka, P., Lindberg, D., Frantsi, A., Silvennoinen, J., Yrjas, P. & Hupa M. 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. Fuel Processing Technology 2011 (in press).

VI Vainikka, P., Lindberg, D., Moilanen, A., Ollila, H., Tiainen, M., Silvennoinen, J. & Hupa, M. Trace elements found in the fuel and in-furnace fine particles collected from 80 MW BFB combusting solid recovered fuel. Fuel Processing Technology (2011). (In press)

Author's contribution

I Vainikka carried out the review work and writing of the paper.

II Vainikka carried out the review work and writing of the paper.

III Vainikka planned the experimental work, carried out part of it, and finally wrote the manuscript with the exception of the SEM-EDX study on waterwall tubes which was prepared by Sonja Enestam.

IV Vainikka planned the experimental work, carried out part of it, and finally wrote the manuscript with the exception of the SEM-EDX study on waterwall deposits which was prepared by Dorota Bankiewicz.

V Vainikka planned the work in co-operation with Dorota Bankiewicz and Daniel Lindberg. Vainikka wrote together with Daniel Lindberg the interpretation of the thermodynamic equilibrium modelling results in connection to the vaporised ash-forming matter in Part 1. The corrosion work as a whole was carried out by Dorota Bankiewicz and the modelling by Daniel Lindberg.

VI Vainikka planned the experimental work, carried out part of it, and finally wrote the manuscript. The SEM-EDX analyses on the fuels was done by Heikki Ollila and the thermodynamic equilibrium modelling by Daniel Lindberg.

Contents

Appendices

Papers I–VI

Paper II is not included in the PDF version.
Please order the printed version to get the complete publication (http://www.vtt.fi/publications/index.jsp).

1. Introduction

1.1 Waste – classification and denotation

Even in the developed countries the waste sector is by every measure a grey area. It is highly regulated, but the regulations are often overcome by common practices and exemptions. It is also a sector full of specific terminology with less precise definitions.

In this work anthropogenic wastes are defined according to the EuroStat and relevant European Union directives [1–3]. The denotation used is as follows:

- HHW: Household Waste. With or without source separation.
- CIW: Commercial and Industrial Waste. Typically packaging and other types of waste from commerce, offices, public buildings collected in a similar way as HHW.
- MSW: Municipal Solid Waste = HHW + CIW [4].
- SRF: Solid Recovered Fuel. Fuels classified and certified according to CEN-TC 343 [5,6]. SRF can be prepared from HHW and/or CIW through various optional processes [7].
- RDF: Refuse Derived Fuel. In this work is meant by 'SRF' (above) that does not meet the CEN-TC standards.
- WEEE: Waste Electric and Electronic Equipment.

MSW originates from households, commerce and trade, small businesses, office buildings and institutions (schools, hospitals, government buildings). It includes waste collected door-to-door through traditional 'kerbside collection', and fractions collected separately for recovery operations (through door-to-door collection and/or through voluntary deposits). The common practices, whether industrial or communal, can be categorised in three:

i) Mixed waste collection where no sorting is done (mixed household waste).

ii) Commingling where all recyclables are collected together but kept separate from other waste.

iii) Source separation.

MSW can be categorised into two fractions depending upon the point of collection: HHW and CIW.

SRF can be regarded as a waste derived fuel the quality of which is monitored and controlled by processing. It falls into specified quality categories based on heating value and chlorine and mercury content [6]. SRF can be prepared from CIW and/or HHW which may be collected as a separate 'energy waste' fraction or processed from CIW/HHW by various mechanical and biological processes and/or their combinations [7]. Figure 1 shows schematically, with references to the relevant European Union directives, the classification of SRF.

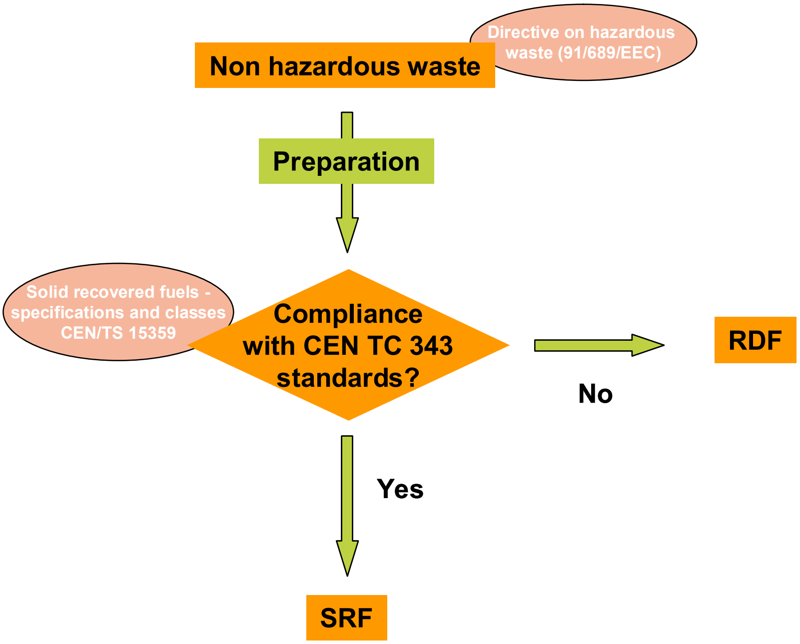


Figure 1. Classification of SRF. Courtesy of Thomas Glorius, REMONDIS GmbH.

In comparison to MSW, SRF is typically enriched in high calorific value plastics [8] and often consists also of specific homogeneous sources of combustibles such as industry process residues, textiles or materials from demolition. Table 1 presents the typical composition of MSW and SRF. SRF production typically consists of several consecutive unit processes aiming at separating non-wanted fractions such as food residues or recyclables such as metals, polymers, clean wood, glass, paper, cardboard etc. The unit processes are typically [9,10]:

- Pre-treatment to cut open plastic bags, first stage crushing.
- Manual sorting to recover large plastics, paper, cardboard, clean wood.
- Crushing, grinding to control particle size.
- Screening (e.g. star, disc, trommel), wind shifting and ballistic separation to separate heavy-light (e.g. glass-paper) and large-fine fractions.
- Ferrous metal separation by means of magnets and non-ferrous metal separation by means of eddy current.
- Polymer (other item) recovery by means of infrared (IR).

Table 1. Composition of SRF and MSW in weight percent (as received) and lower heating value (LHV) in MJ kg^{-1} [11]. The composition data has been compiled from various sources [7,12–14] and values should be taken as indicative.

	SRF, wt-%	MSW, wt-%	LHV, MJ kg^{-1}
Organics	NA*	30–40	6
Paper/Cardboard	40–50	15–25	14
Textiles	10–14	1–5	14
Plastics	25–35	7–15	33
Metals	2	3–4	0
Glass		4–7	0
Wood	3–10	NA*	16
Other	5–10	18–30	5
LHV, MJ kg^{-1}	19	11	
Renewable energy, %	39%	52%	

* Organic residues in SRF included in 'Other'

** Wood in MSW included in 'Organics'

The heating values of the different waste fractions are also listed in the table. Different processing options result in different SRF yields, recovery rates and mass break of different fractions and contaminants [8]. The ash-forming elements relevant for waste combustion are discussed in Paper VI and Chapter 2.2 of this thesis.

1.2 Halogens in combustion: ash deposition and high temperature corrosion

From a technical point of view, replacing conventional fuels with waste or biomass tends to lead in increased chlorine-induced corrosion rates and to ash melting problems in boiler furnaces [15–17]. Regarding biomass combustion the main initiators of ash melting and corrosion are attributed mainly to the salts of Na, K, Ca, S and Cl [18–20] as well as P [21–24]. For waste incineration or co-incineration the aforementioned list of main contributors is commonly complemented with Zn, Pb and also Sn [25–28]. It is essential to avoid high concentrations of corrosive gases, vapours and molten salts, particularly chlorides, in combustor furnace in order to reduce the risk for high temperature corrosion of heat transfer surfaces.

At the present time, in purely waste-fired units, corrosive gases and ash-forming elements have limited the steam temperature to 420–470 °C, and consequently the electric efficiency to 20–24% [29]. This is discussed further in Chapter 2.4 in this thesis.

Even if the corrosion of biomass and waste fired boilers is often attributed to chlorine, in terms of corrosion risk for boilers, most of the salts of bromine are in physical and chemical properties similar to those of chlorine [30–34]. Prior to this thesis only few indications were found in the literature indicating that bromides could eventually contribute in corrosion equally as chlorine [31].

The melting points of bromides are only some tens of degrees centigrade lower or higher than those of the corresponding chlorides. It is relatively clear from the few publications available that in waste combustion with typical level of Br in the fuel mix bromine is mostly found in the fly ash, and partially emitted in the form of HBr (possibly minor proportion as Br_2, too) in the flue gases [34–38].

1.3 Bromine properties

In this work the term ‘bromine’ is used generally to denote bromine as an element regardless of its speciation. This is abbreviated as Br. Where the term ‘bromide’ is used it is specifically meant by the bromide ion, Br^-. Regarding the content, ‘bromine’ typically means the total content of bromine and ‘bromide’ its common negative univalent form typically analysed as water soluble bromine.

Br is a halogen element with high reactivity. Naturally Br exists as 50.57 atom-% ^{79}Br and 49.43 atom-% as ^{81}Br [39]. Br is a dense (3.1 kg l^{-1}) red-brown dark liquid at room temperature. It freezes at -7 °C and boils at 58 °C. It is found in nature mainly in organic and dissolved bromide forms. The largest reservoirs are seawater with 65 mg l^{-1}, the atmosphere and organic soil. It is concentrated naturally in the Dead Sea (5000 mg l^{-1}), salt lakes and underground brines. Table 2 lists selected properties of bromine, complemented by the corresponding properties of chlorine for comparison.

Table 2. Comparisons of properties of bromine and chlorine. [40–42]

	Bromine	**Chlorine**
Molar weight, g mol^{-1}	79.90	35.45
Boiling point, °C	+58.8	-34.6
Melting point, °C	- 7.2	-101.0
Electro negativity	2.8	3.0
Standard reduction potential, °E (V)	1.066	1.358
Bond strength, kJ mol^{-1}	Br-Br 193.9	Cl-Cl 242.9
Van der Waals radii, Å	1.85	1.75
Solubility in water, g 100 ml^{-1} at 20°C	NaBr 90 CaBr 143	NaCl 36 CaBr 42
Acid dissociation constant, pK_a	HBr - 8.72	HCl - 6.2

1.4 Objective of the work

Chlorine has been extensively studied under the ash chemistry context in biomass and waste combustion. Very little has been published on bromine under the same context.

The objective of this work was to identify the occurrence of bromine in solid fuels and to characterise the occurrence of bromine in fluidised bed combustion of bromine bearing fuels.

The central questions concerning ash chemistry were: in which fuels bromine can be found and in which chemical forms, what is the speciation of bromine in the furnace and fly ash, what role bromine may have (if any) and finally which are the practical implications?

1.5 The approach

A review on the occurrence of bromine in solid fuels was prepared to understand the factors influencing bromine content in fuels and to collect data on the typical bromine content range. Bromine was found in the SRF and in the wastewater sludge used in the experimental work in this thesis, due reasons described in the review papers.

The experimental work was carried out in a BFB (bubbling fluidised bed) boiler co-firing the aforementioned fuels together with spruce bark. The experiments focused on determining the occurrence of bromine as an ash-forming element. Particularly the focus was on vaporised salts. The analysis of the bulk aerosol composition was complemented with thermodynamic equilibrium estimations carried out by Dr. Daniel Lindberg.

The full scale campaigns were complemented by SEM-EDX study on waterwall corrosion in the boiler and a study on the basic corrosion propensity of bromine salt in comparison to the corresponding chloride. These were carried out by Sonja Enestam and Dorota Bankiewicz, respectively.

Although, alkali metal chlorides and sulphates typically form the main bulk of vaporised/fine particle forming matter, the elements comprising the rest of the matter, and discussion on their origin in fuels, were also included in the work. These are often referred to as ‘trace elements’. This was to acknowledge the generic composition of vaporised ash, in addition to bromine.

1.6 Thesis organisation

This thesis consists of an introductory part annexed by six peer reviewed journal publications, Papers I–VI.

The Introduction Chapter is followed by Chapter 2 giving the relevant background to the subject. Chapter 3 presents a summary of the results from the review on the occurrence of bromine in solid fuels. Chapter 4 presents the main experimental procedures applied in the experimental part of this work. Chapter 5 presents results from the experiments with the focus on characterising bromine as an ash forming element. The conclusions in Chapter 6 summarises the main findings of the work and their relevance for solid fuel combustion. Also areas of future work are identified.

In Paper I is reviewed the literature on the natural occurrence of bromine in solid fuels. New illustrative graphs and summarising conclusions are drawn based on the literature. Paper II presents a review on the occurrence of bromine in solid fuels due anthropogenic use of bromine. Paper III presents results from an experimental campaign at a full scale BFB boiler where the occurrence of bromine in ash-forming matter is characterised alongside chlorine. Paper IV also presents experimental results from the BFB, but now just next to the waterwalls where high corrosion rates were detected. The focus is on connecting the composition of the vaporised ash forming elements to the composition of waterwall deposits. In Paper V the forms of bromine in the in-furnace vapours and deposit are modelled and the corrosion propensity of bromides on commercial boiler steels is determined by means of laboratory-scale oven tests. Paper VI presents the composition of vaporised ash-forming trace elements as a function of furnace height complemented with thermodynamic equilibrium modelling estimating the forms of the relevant ash-forming elements (including bromine) in the lower and higher parts of the furnace.

2. Background

2.1 The strategic role of waste

Due to the CO_2 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 (GHG) emissions in developed and developing countries by substituting fossil fuels, reducing landfilling and increasing recycling rates. In comparison to the potential adverse effects in utilising some biomass fuels, waste utilisation does not have any significant impact on the landuse, natural carbon stocks or sinks.

Globally, solid waste disposal is responsible for about 3–4% of anthropogenic GHG emissions [43]. The most significant GHG emission source regarding wastes is methane from landfills. It has been estimated that in the diversion of MSW in the EU from landfilling to composting, recycling and energy recovery could produce a reduction from 40 to over 100 Mt CO_2-equivalents (CO_2-eq.) per year which corresponds to 29% of the total CO_2-eq. reduction target under the Kyoto protocol for EU-15 [44,45].

Roughly half (49%) of the MSW is landfilled in the EU-25 [4] and 17% is incinerated. Approximately the same numbers apply to the US: landfilling accounts for 54% and incineration 13% [46] of the total MSW treatment. There are wide discrepancies between the EU Member States regarding waste management, ranging from those which recycle least (90% landfill, 10% recycling and energy recovery) to those where the recycling and recovery is well established (10% landfill, 25% energy recovery and 65% recycling) [45].

The EU-25 generates 241 million tonnes of MSW annually [47]. In theory, with an average electric efficiency of 25% [48] and a lower heating value of 11 MJ kg^{-1} [29,49] 184 TWh of electricity could be generated by MSW combustion.

This corresponds to 5.7% of the total electricity generation in the EU-25 [50] and approximately 20% of the electricity generation from coal and lignite [51]. In comparison, the US generates annually 250 Mt of MSW [46]. For many large cities in North America, it has been estimated that MSW could supply as much as 10% of the electrical demand [11].

In practice, the example of the most advanced countries in recycling and waste-to-energy (WtE) shows that some 40% of the MSW will end up in thermal treatment after recycling and recovery. There are country specific estimations for the potential for power generation from MSW in the EU member states [13]. Those range, with few exceptions, between 3 to 5% of the total power consumption if 20% electric efficiency is applied for the conversion. On the other hand the real figure for combustible waste volume is higher than the EuroStat numbers for MSW. This is due to private operations where, particularly some CIW and construction waste, go directly from the waste producers to SRF production and final users and never enters any transparent statistics [52].

2.2 Ash-forming elements in waste

Regarding wastes, with the exception of some textiles, kitchen waste and wood (as such, or as fibres e.g. in packaging paper and cardboard) the ash-forming elements originate from man-made products. During the course of this work it became obvious that waste fuels have to be characterised in two different dimensions:

i) through its elemental composition
ii) through its identifiable fractions.

In this thesis, the former is meant by waste's ash forming elements, whereas the latter is meant by the identification of the typical waste components: biogenic waste, textiles, leather, plastics, glass, metal, wood and the 'rest'. Figure 2 illustrates the main fractions found in MSW and SRF indicating also the most relevant elements when used as a fuel.

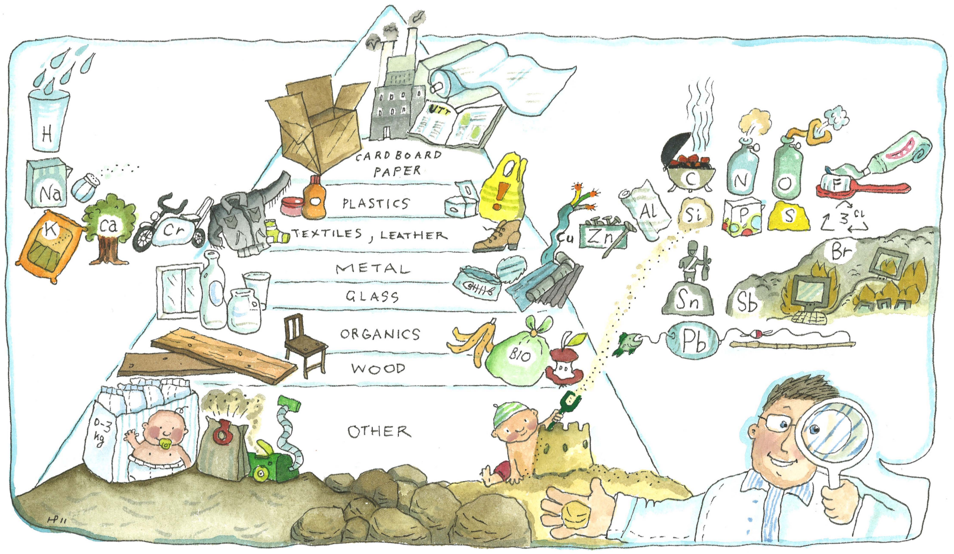


Figure 2. The main fractions in waste (pyramid, see Table 1) complemented with indications on the most relevant elements that define the waste quality. By Pasi Vainikka & Heli Pukki.

The ash-forming elements in biomass are a result of the plant's metabolic activity and the plants are therefore enriched in different nutrients [53,54] mainly K, Ca, P, Mn, Mg and possibly also S and Si. As with peat, ash-forming elements in coal are inherited from the vegetation and from the soil as a result of geological processes [55]. Typically the main elements are Al, Si, S, Fe and Ca complemented with alkali metals to a varying extent.

Waste fuels differ from all other fuels in that they are rich in 'trace' metals and halogens, possibly also in mercury. The chlorine contents of some biomass fuels such as straw are high, but both the fluorine and the bromine contents in wastes are typically higher than those in biomass. The Zn content may also be high in natural biomass, but the concentrations in mixed wastes may exceed those in biomass with over two orders of magnitude. Metallic aluminium is commonly found in waste and may cause boiler failures through so called 'thermite reaction'. In the reaction aluminium reduces vigorously the iron oxide in the boiler steels, and possibly also the oxides in the ash deposit [56], generating temperatures above 2000 °C melting the boiler steels. The other origin of Al is mineral matter (sand and clay) for example in concrete. In addition to Zn metals of anthropogenic source relevant for high temperature vapour formation are Pb, Cu, Fe. In terms of concentration found in waste these are followed for example by Ba, Cr, Sb and Sn. In addition to alloys, these elements can be found in plastics, rubber and various textiles as additives. A detailed discussion on the origin of these elements relevant for this work can be found in Paper VI.

As an example of the difference in elemental composition of biomass and waste, the ash-forming elements in SRF and Scandinavian spruce bark used in this work (Paper III) are compared in Figure 3. The chemical fractionation procedure was applied in the characterisation of the ash forming matter in the fuels. The fractionation is based on the consecutive leaching with water, ammonium acetate, and hydrochloric acid. The method was originally developed for the characterization of coal [57,58] and further modified for and applied to the characterization of biomass fuels[53,59,60].

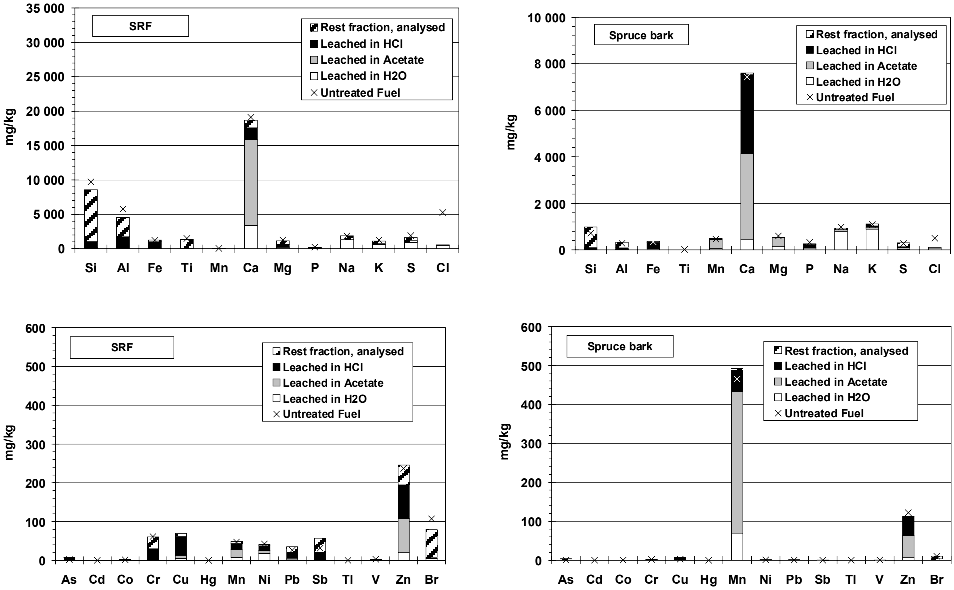


Figure 3. The ash-forming elements in SRF and spruce bark. Main elements (top), trace elements (bottom).

2.3 Options for Waste-to-Energy

In the waste-to-energy sector the terms ‘waste-to-energy plant’ and waste ‘incinerator’ are frequently used. These essentially mean the same thing, but the trend has been for some time to increase the share of energy recovery, also electricity, which has led to the re-branding of the ‘incinerators’ to ‘waste-to-energy plants’.

Other important terms include ‘incineration’ and ‘co-incineration’. They are differentiated from each other only by their primary purpose: whether a plant is dedicated to the thermal treatment of wastes with or without energy recovery (incinerator) or if the main purpose is the generation of heat and/or power or production of material products (co-incinerator). This has an important practical implication: incinerators are excluded from the EU emission trading scheme, co-incinerators are included. How is then the main purpose of a plant defined? According to The Court of Justice of the European Union ‘It is for the competent authorities to identify that purpose on the basis of an assessment of the facts existing at the time at which that assessment is carried out.’ [61]

Figure 4 shows the main options for WtE technologies. The grate incinerators (left) are dominating the sector with 95% share of the WtE market. The installed WtE capacity of the largest waste management companies in the EU shows that fluidised bed combustion may have a share of 3–7% of the treatment capacity [62,63]. Due to historic reasons Finland and Sweden are exceptions in this trend with a higher proportion of fluidised beds. Both fluidised bed combustion and gasification have been adopted (in the centre of Figure 4).

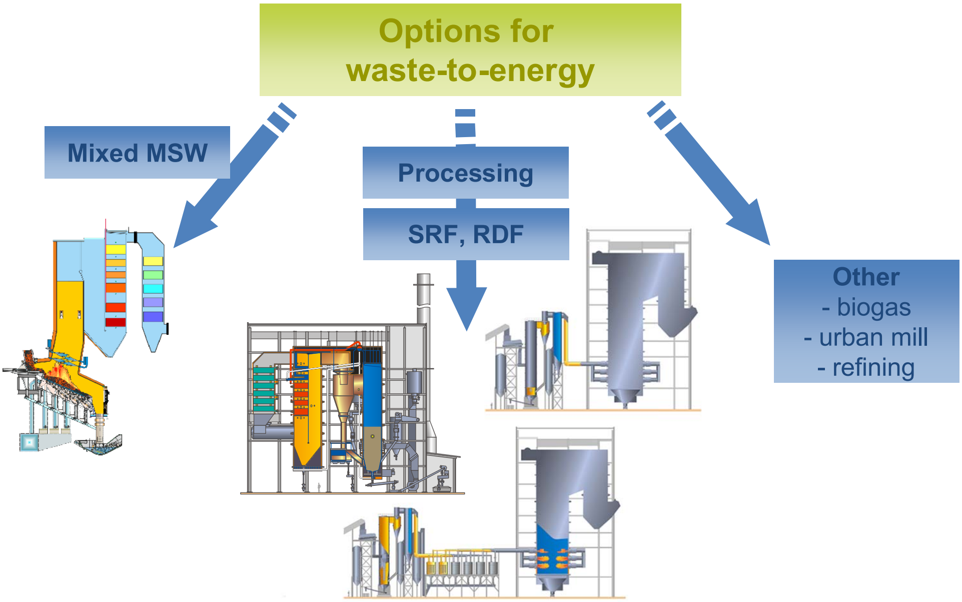


Figure 4. The main technical options for waste-to-energy. Courtesy of Martin GmbH, Metso Power and Kai Sipilä.

The fluidised bed systems require pre-treatment of waste in order to homogenise the particle size, reduce the amount of objects disrupting fluidisation and to reduce the amount of metallic aluminium. These pre-treated fuels can be called SRF or RDF depending upon the quality of the fuel. Processing adds cost to the fuel, and typically creates a residue to be landfilled or to be directed to grate incinerators. Another disadvantage with fluidised bed units is that currently they do not really provide any efficiency advantage when compared to the grate fired units. Also the residue management is unresolved as fluidised beds generate a soluble ash residue. In contrast, for the slag from a grate it is easier to find ash utilisation options, for example in land construction.

The advantage of the fluidised bed is the flexibility for inhomogeneous heating values, with wet sludge in one end and high calorific value plastics in the other end. Additionally, low – and in circulating fluidised bed (CFB) also uniform – combustion temperature does not generate large amounts of thermal NO_x, and sulphur retention in the ash is efficient [11]. Interestingly – and on contrary – the SO_2 slip from the grate combustion furnaces has recently been turned to a possible advantage through high temperature corrosion control technique [64].

The advantage in connection to SRF/RDF processing is the recovery of polymers, paper, cardboard, (ferrous/non-ferrous) metals, glass, and other recyclable materials in a material recovery facility (MRF). This improves paybacks for investments and ease complying with the recycling targets of the European Union.

In one extreme of the treatment options are the urban mill concepts where the wood fibres in the waste are recovered in wet pulpers and used in recycled fibre products or even in biomass-to-liquid concepts [65].

In the European Union the emission limits for waste fired units are tighter than those for other combustion plants. The regulated emissions concern heavy metals, chlorinated dioxins and furans, carbon monoxide (CO), dust, total organic carbon (TOC), hydrogen chloride (HCl), hydrogen fluoride (HF), sulphur dioxide (SO_2) and the nitrogen oxides (NO and NO_2). Regarding gasification and gas cleaning, if the product gas from a waste gasifier is not cleaned, combustion of such gas is treated as waste combustion. The required extent of gas cleaning in order the gas to be excluded from the waste status is not defined, however. [66]

2.4 Electric efficiency of waste combustion systems

Regarding solid fuel combustion high temperature corrosion has the most pronounced influence to the performance of the waste fired units. This is due the specific characters of the ash-chemistry as explained in Chapters 1.2 and 2.2. In Figure 5 is schematically illustrated the electric efficiency of state-of-the-art solid fuel fired power plants as a function of steam temperature and steam-side configurations.

According to the EU's Reference document on best available techniques for waste incineration [29], with the current state-of-the-art grate fired waste incineration system electric efficiency of 20% can be achieved and with fluidised bed systems 22.5% has been achieved. Higher figures with the installations have since been achieved, on the level of 25–27%, even up to 30%, depending on the case [48,67]. These units commonly operate with steam values close to 420 °C / 60 bar. For the biomass fired plants electric efficiencies up to 30% are considered high, but plants exceeding 40% are already commercially available. These latter units are those with as high steam values as 535 °C / 130 bar incorporating also steam reheat. For state-of-the-art coal fired units the steam values are in the proximity of 580 °C / 250 bar, possibly even incorporating double reheat. With state-of-the-art coal fired plants 43% electric efficiency is achieved, even up to 47% with double reheat.

From these figures it can be concluded that the largest space for improvement regarding electric efficiency are in those power generation technologies that utilise waste as a fuel.

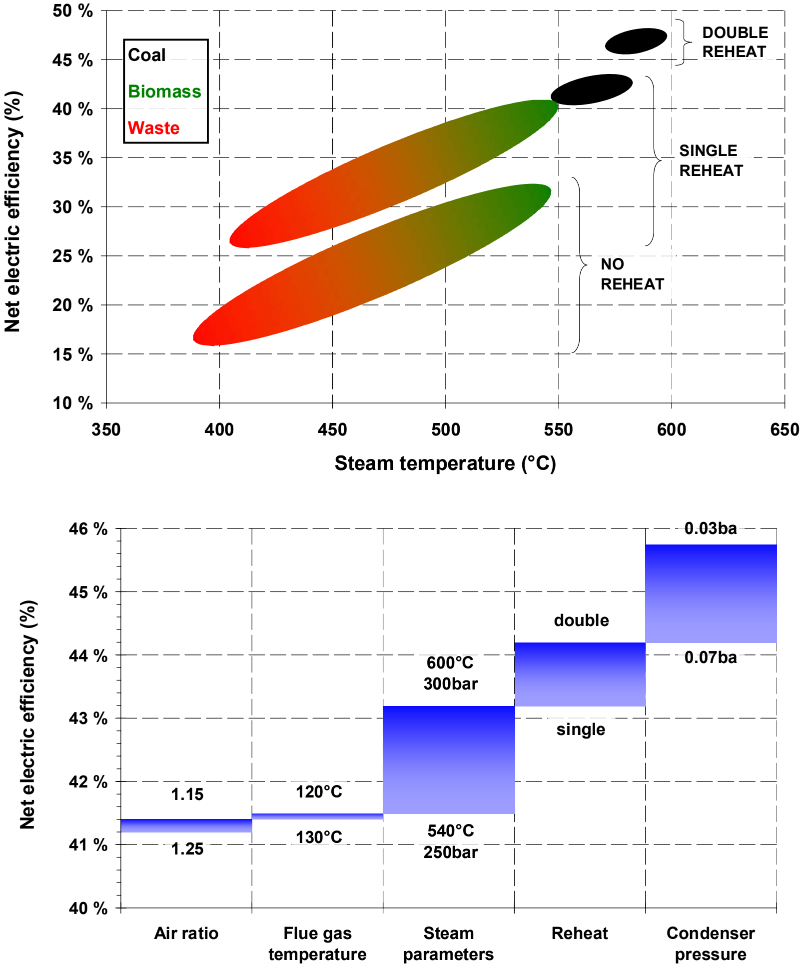


Figure 5. Electric efficiency of state-of-the-art solid fuel power plants as a function of fuel (top) and design/operation based improvement (bottom) (courtesy of Dr.-Ing. Klaus R.G. Hein).

2.5 Halogenated dioxins and furans

In this work dioxins and furans are not studied but as they are central compounds formed and tightly regulated in connection to waste treatment they are acknowledged in this thesis by means of a short review in the following and in Paper II. The US EPA finds polychlorinated dibenzodioxins (PCDDs, or simply 'dioxins') 'likely human carcinogen' [68,69]. In addition the PCDDs have been shown to bioaccumulate in humans [70].

There are very few experimental data on the physical and chemical properties of polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). According to the WHO report [70] PBDDs/Fs are not known to occur naturally in the environment. These are by their chemical structure exact homologues to the PCDDs and polychlorinated dibenzofurans (PCDFs). The characteristics are such that PBDDs/Fs have higher molecular weight than their chlorinated analogues, they also are characterised by high melting point, low vapour pressure, low water solubility and are typically soluble in fats and oils [70]. According to the WHO report [70] equimolar doses of the PBDFs and PCDFs result in comparable mortality rates.

The general understanding is that after the formation of PBDDs/Fs bromine is substituted (to varying degree) by chlorine to yield PXDDs/Fs (brominated/chlorinated dibentzodioxins, PXDDs; brominated/chlorinated dibenzofurans, PXDFs) which are the most common bromine bearing dioxins/furans [70]. It must be noted that only a fraction of the PXDDs/Fs exhibit 'dioxin-like toxicity'.

Bromine addition has been shown to increase the level of PCDDs/Fs from incomplete combustion, for a reason which is not exactly known [71]. Generally, due to its less stable carbon bond bromine is substituted with chlorine and brominated aromatics are more easily destroyed in well controlled incineration processes [41].

PBDD/Fs have been found in flame retardants and in brominated organic chemicals as contaminants [70]. Other main source for human exposure are in connection to thermal processes [41], namely thermal stress, pyrolysis/gasification, incomplete combustion as well as complete (well controlled) combustion of bromine bearing flame retarded plastics. Thermal stress may occur during production, where temperature can increase up to 270 °C, and in recycling processes. In these processes PBDD/F precursors may be formed. These are polybrominated diphenylethers (PBDE) from which PBDDs/Fs may be formed via a simple elimination, see Figure 6 for an example with decabromodiphenyl ether (DecaBDE), a common flame retardant. Mechanistically the formation of PBDFs from PBDEs may happen simply by intermolecular elimination of Br_2 or HBr, this has been observed above 500 °C. The presence of a common flame retardant synergist, Sb_2O_3, seems to even promote the yield of PBDD/Fs from their precursors due catalysing debromonation and hydrogenation.

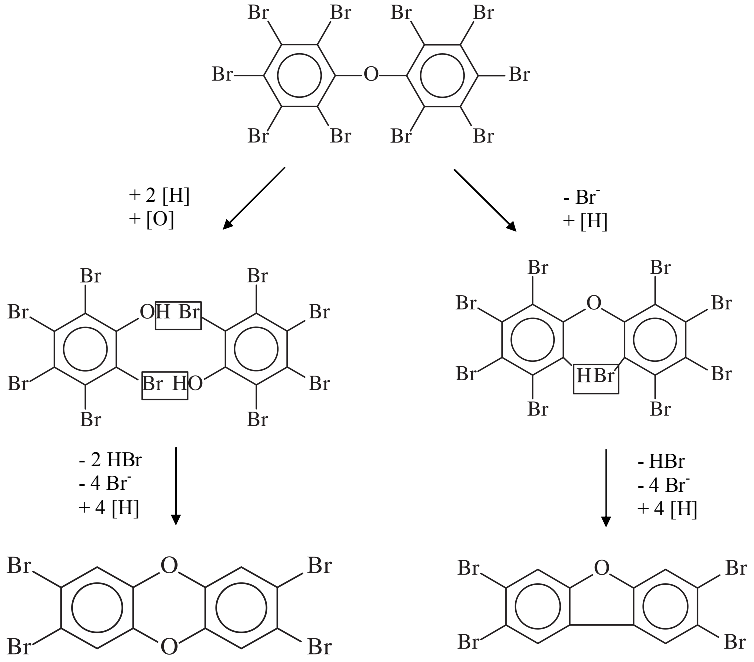


Figure 6. The principle of PBDD/F formation from decabromodiphenyl ether (flame retardant). Modified from [72].

Relevant for combustion systems it has been demonstrated, as summarised by Weber (2003) [41], that the PBDDs/Fs can be formed in the similar way as their chlorinated homologues:

- via the de novo synthesis [41, 73–75] (furnace back pass conditions with fly ash acting as a catalyst)
- via precursor compounds [72], namely brominated phenols and ethers.

The de novo synthesis has been suggested as the main route for PXDDs/Fs formation [41] demonstrated with MSW incinerator fly ash. The amount of formed aromatic compounds depends on the content of bromine. A maximum for the formation has been found at 350 °C [76].

Regarding waste incineration, in the co-combustion of waste electronic and electrical equipment (WEEE, treated with brominated flame retardants), Vehlow et al. (2000) [37] found 50% from the total PXDDs/Fs to be bromine containing. In Japan [77] in a measurement campaign at 75 waste incinerators PXDDs/Fs were found in almost every sample surveyed (effluent water, ash and flue gases) and the amount corresponded to approximately from 10 to 20% from the PCDDs/Fs. According to laboratory tests [78], the ratio of brominated, brominated-chlorinated and chlorinated aromatics might finally result in a Cl/Br ratio close to the proportions of chlorine and bromine present in the combusted material, or possibly higher bromination. According to pilot scale tests, activated carbon can effectively remove the PXDDs/Fs from flue gases [37].

In well controlled combustion PBDDs/Fs are not an environmental risk [79]. They are potentially a substantial risk in uncontrolled combustion and accidental fires. In experimental fire tests simulating real fire conditions with electrical appliances such as television sets, printers, computer terminals, and their casings, PBDFs have been detected in the combustion residues in thousands of mg kg^{-1} [70].

3. Occurrence of bromine in solid fuels (Papers I and II)

In the following the occurrence of bromine in solid fuels, as published in Papers I and II, is presented. The occurrence is divided into natural and anthropogenic. 'Natural' is meant by the occurrence of bromine due natural bromine cycle in the ecosystem (summarised at the end of Chapter 3.1 in Table 4); and 'anthropogenic' by the occurrence due to the use of man-made brominated products.

3.1 Natural occurrence (Paper I)

The sea is the largest natural reservoir and source of organohalogens in the atmosphere. Organohalogens are formed through microbial processes in living organism. Enzymatic processes by haloperoxidases and halogenases taking place in algae and marine plants, are thought to be the main sources of halogenated organic compounds [80].

Sea spray, on the other hand, seems to be a major direct source of bromine in soil and plants. Sea spray is understood as a spray of water that forms when waves crash. This spray can then be transported varying distances by wind.

In sea water where bromine is mainly in the form of bromide the content ranges from 65 to 71 mg l^{-1} whereas Cl content is close to 19 000 mg l^{-1}. It has been observed that the Br^- content in sea water increases with the distance from coast due to the dilution effects of fresh waster rivers. [81]

Aerosols of marine origin have been shown to contain the two halogens in proportions different from the sea water and enrichment in bromine has been widely observed [82]. The ratio Cl/Br is usually several fold smaller in aerosols over land than in sea water or aerosols over open seawater where the Cl/Br ratio is in the order of 300 on mass basis [83].

Even if the properties of chlorine and bromine are very similar there is a difference in their solubility. As water is evaporated halite (NaCl) will precipitate first, leaving brine enriched in Br^- [84] with Cl/Br ratio (mass basis) of 50. This is an important factor regarding Br enrichment in brines.

In **fresh water** the reported bromine content ranges typically from 0.01 to 0.2 mg l^{-1} [85]. If higher values are observed they are likely to be due to soil fumigation or sea water 'contamination' [86]. The primary natural source of halogens in surface water is rainfall which derives them initially from sea spray [87]. Some minor contribution may originate from volcanic eruptions [88].

The Cl/Br ratio may vary over one order of magnitude in **groundwaters**. Slight change in Br/Cl ratio may occur during infiltration which may be due to the decayed organic matter which has been found to be enriched in Br.

In **rain** the Br concentratin is usually below 0.01 mg l^{-1}. However, in coastal areas 1.0 mg l^{-1} has been reported [85,89,90]. In precipitation (and fresh ground water) Cl/Br is on average 100 even though the variation is high (from 38 to 290) [91]. Lower Cl/Br ratios than in the sea water have been analysed also from **snow** [92].

It has been reported [[93] cited in [94]] that the content of bromine in rain seems to 'always' be some ten times higher in the coastal area than in the inland areas. This data can be combined with the annual precipitation and sear spray deposition which give the actual deposition rate of bromine in the soil. It is apparent that the content of bromine in rain water on the coast, and the (typically) higher precipitation on the coast in comparison to inland, results in high bromine deposition rate in coastal areas.

For **soils** there is a large variation in Br content. This is due to the marine influence on the coastlines compared to inland soil. The reported Br contents range from 0.3 to 852 mg kg^{-1} [95] (concentration in solid samples is always expressed on dry mass basis in this thesis). This has been found to be a function of organic matter content in the soil (see Figure 7) and Br deposition. Flury (1993) [85] concluded that seaborne aerosols are the main natural source of Br in the terrestrial ecosystem, and in referring to the Japanese original paper Yiuta (1973) [96] concluded that Br originates from the sea through rain, snow or directly as airborne salts. The analyses reported in that work [97] showed Br content to be halved in soil > 75 km inland. According to the literature sources [97] the 'World average' for Br in soils is 5 mg kg^{-1}. Igneous **rocks** have been characterised as containing approximately 1–10 mg kg^{-1} Br while for **sedimentary rocks** the scale is wider, from 1 to 140 mg kg^{-1} [95].

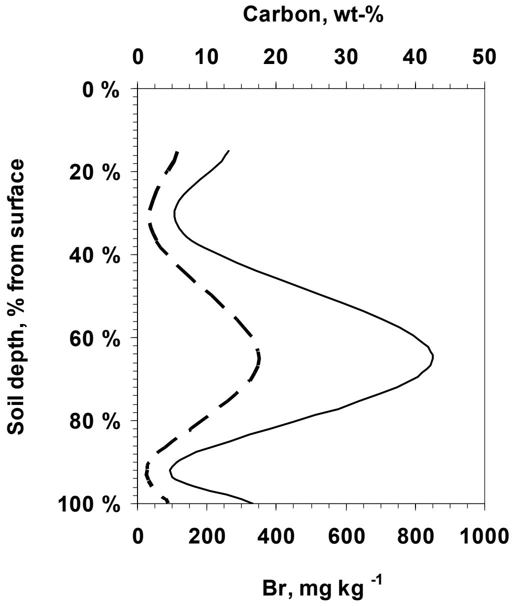


Figure 7. In soils sampled from Japan bromine content strongly correlates to carbon content. Data from [95]. Presented in Paper I.

It has been shown that bromine can be washed out from soil samples after a hydrogen peroxide wash [95], a process which has been used as the evidence for Br being located largely in soil humic acid (HA) fraction [98,99].

3.1.1 Biomass

Biomass here means living or recently living organisms, mainly plant matter that does not include residues from processes which may chemically alter the material such as fumigated biomass, manure or wastewater sludge. Bromine in the biomass can be categorised in five classes of occurrence:

i) Those terrestrial plants with less than 2 mg kg^{-1} bromine, natural bromine occurrence, no relevant bromine flux from the surrounding environment, chlorine is abundant in the soil.

ii) Those containing between 2 to 20 mg kg^{-1} bromine (‘World average’), exposed to a typical and natural flux of bromine in continental conditions.

iii) Those exposed to elevated natural (e.g. coastal organic soil) bromine flux, up to a maximum of 100 mg kg^{-1}.

iv) Those exposed to anthropogenic (fumigant, pesticide) bromine flux, starting from 200 up to 200–10 000 mg kg^{-1} Br.

v) Those assimilating bromine by taking advantage of haloperoxidase, marine algae and seaweeds, with bromine up to 60 000 mg kg^{-1}.

Algae assimilate inorganic bromide from the sea. The uptake is associated with bromoperoxidase (BPO) enzymes [100]. Peroxidases oxidise the bromide ion with hydrogen peroxide to bromine (namely hypobromite, BrO^-) where bromine is in oxidation state +1. This is the main mechanism how bromide initially starts to be bound in organic matter [101] and it results in a large array of organobromine metabolites in marine organisms. The description of the bromine cycle in nature is available in reference [100]. The main types of naturally occurring organobromides have been extensively mapped [102] and exhaustive listings have been established according to what is known today [100,103,104].

Bromine seems to be relatively abundant in the organohalogens: from the known 3200 naturally occurring organohalogen compounds, 1600 contain bromine. By far the most abundant are bromoform ($CHBr_3$) and methyl bromide (CH_3Br, MeBr). It seems evident that the bromine content of the surrounding water is not the controlling factor in algae bromine content, and nor could it be attributed to wastewater influence [105].

In **seaweeds** in the seas of Japan bromine has been found in concentrations varying up to 32 000–37 000 mg kg^{-1}, depending on the location and algae species [106]. The red and brown species were the richest in bromine. The typical Br content varied between 200 and 1000 mg kg^{-1}, with the absolute minimum found at 150 mg kg^{-1}. According to the Russian literature [[107] cited in [106]] 1 500 mg kg^{-1} has been found in a freshwater green alga, which has some 80 000 times greater concentration of Br in comparison to the surrounding water (with approximately 0.007 mg l^{-1} bromine).

In contrast to marine algae, hundreds of organochlorine compounds have been identified from **terrestrial plants**, but only a few organobromine compounds are known [103]. The emission of MeBr is a characteristic of terrestrial plants. It is produced in significant amounts by such plants as rapeseed, cabbage, broccoli, turnip, radish etc. from bromide available in the soil. The emission increases with increasing bromide content in the soil. MeBr production by terrestrial higher plants is potentially a large source for atmospheric MeBr [108]. Br emission from biomass burning has also been brought up in the literature as a potential Br source in the atmosphere [109].

Another major difference between the marine and terrestrial species is the Br take-up. Several studies have noted that bromide is fractionated relative to chloride by vegetation [82,89,110]. Bromine is taken up as a bromide and it may replace the nutrient chlorine [111–113]. It is clear from the plant nutrition literature that plants prefer chloride over bromide as a nutrient despite the fact that controversial results have been published. Typically, the addition of chloride in soil inhibits bromide up-take. If only bromide is available it depends on the species how much bromine is taken up from the soil, and if the plant can substitute Br for Cl. Three classes of plants can be identified: [114–118]:

i) Those in which Br can substitute for Cl.

ii) Those other plants in which Br cannot substitute for Cl, and Br eventually results in toxicity at higher concentrations.

iii) Plants with Cl deficiency where Br can displace Cl from less essential functions (roots) to provide essential functions higher in the plant (leaves, shoots).

However, the above can be stated based only on the very limited number of studies on only a handful of plant species. There still might be unknown factors influencing the Br content in plants, such as Mycorrhizal inoculation, which has been shown to elevate bromide and chloride concentrations in plant tissue [119].

It seems that if both halogen ions are available in the soil the required chloride uptake of plants is so low that sufficient chloride is in practice always available. Therefore ‘Cl preference’ results in low Br content in plants. Although the Br available in the soil has a positive correlation with Br content in different parts of the plant, the affinity with Cl is so high that absolute Br content remains low. It must be the case that the exceptionally high Br contents reported in the literature claimed as natural have been as a result of anthropogenic Br sources [95].

In naturally occurring terrestrial plants, bromine content is approximately 5 to 15 mg kg^{-1}. The same applies to **foodstuff** and **greenhouse residues** (growth on non-fumigated soil, no pesticide treatment) where less than 10 mg kg^{-1} can be expected [85]. As a general rule the typical natural level of bromide in plants can be taken to be below 50 mg kg^{-1} [101].

Japanese wild plants have been found to contain on average from 6 to 30 mg kg^{-1} bromine, rice plant 21 mg kg^{-1} and soya bean 79 mg kg^{-1}. The average content of bromine in leaves of Japanese wild plants has been reported as 12 mg kg^{-1}. The leaves were influenced by untypically high bromine content in the soil [94,97]: Chlorine content found in those soils in Japan (from which the wild plant samples were collected) [94] was in the same range as the reported World average, around 100 mg kg^{-1}, but the bromine content was found to be significantly higher than the 'World average', up to 152 mg kg^{-1} [97]. In the data of Yuita (1983) [94] the coastal/inland ratio of chlorine in rainwater was higher than for bromine, but the ratio was lower in the soils and plants. The chlorine content in the soils was not particularly higher than the bromine content, even if the content in the rainwater was some 100 times higher. Therefore it is postulated that chlorine is eluviated from the soil to a greater extent than bromine.

Br concentration in red pine, cedar, cypress and white oak in Japan was found on average to be 10 mg kg^{-1} in the coastal area and 1.7 mg kg^{-1} inland [94]. In grasses from the corresponding areas (pampas grass, fern, bamboo) 12 mg kg^{-1} was found in the coastal area and 8 mg kg^{-1} in inland (excluding one sample where there was a discrepancy). In those forest and grassland soils in the coastal area 16 to 157 mg kg^{-1} Br was found and the values inland (125 km from coast) ranged from 9 to 68 mg kg^{-1}, which are approximately half to those on coast.

Saw dust (presumably Scandinavian) has been analysed to contain < 20 mg kg^{-1} Br [120]. Other plants (radish, turnip, potato, cabbage, egg-plant) contained approximately 10 mg kg^{-1} bromine in a Japanese study, whereas for onion and tomato approximately 30 mg kg^{-1} were analysed [95]. The average bromine content in sub-Saharan biomass, including grasses, shrubs and branches, maize stalks, was found to be 4 mg kg^{-1} with a maximum of 11 mg kg^{-1} [121].

3.1.2 Peat

The sea is the largest natural source of bromine. On the other hand, it has been estimated that peat lands, which cover approximately 2–3% of the total land area, are one of the largest active terrestrial reservoirs of halogens [122].

Peat formation is decomposition of vegetation in stagnant water with small amounts of oxygen, under conditions intermediate between those of putrefaction and those of mouldering [123]. Unlike most other ecosystems, the dead plants in peatlands do not decompose completely. This is because of the waterlogged conditions where the lack of oxygen prevents micro-organisms such as bacteria and fungi from rapidly decomposing the dead plants [124].

Peat is generally regarded to have more than 30 wt-% (dry basis) dead organic material. As an energy source peat is used mainly in Europe, where it is used in more than 100 power plants. In the EU, 50% of the harvested peat is utilised as fuel. From the total explored volume in Europe, Finland produces 41%, Ireland 21% and Germany 13% followed by Estonia, Sweden and the other countries in the Baltic region. In Finland and Ireland peat constitutes some 5–6% of primary energy, whereas in Estonia and Sweden the corresponding proportion is 1–2%. In these latitudes peat has accumulated in the order of one millimetre per year over thousands of years after the withdrawal of the glaciers. [123,125]

Br is strongly enriched in peats [105] and it has been relatively well studied through geology research.

The depth profile analyses from peat bogs show that the concentration of the halogens (Cl, Br, I) are a function of the peat C/N (carbon/nitrogen) ratio [80,126]. A decreasing C/N ratio indicates an increase in peat decomposition. It is therefore suggested that the depth profile of the halogens does not illustrate the atmospheric deposition, but rather the hydrological condition over time. As the humification process is accompanied with great mass loss (80–90%), the enrichment of halogens during peat formation indicates that organohalogen formation and degradation of organic material are concurrent processes. It has been found that the highest bromine content in peat is detected from periods of relative high dryness when peat bog decomposition is high. Another explanation is simply that if the bog falls temporarily dry it may increase the organohalogen concentration in the peat due to the loss in mass of organic matter. [122]

The bromine content data, as a function of peat bog depth, from three Nova Scotian [127] and two Swiss peat bogs [128] has been plotted in Figure 8. The maximum bromine content was 62 mg kg^{-1} for the Nova Scotian and 27 mg kg^{-1} for the Swiss peat. For the peat bogs it is typical, even if exceptions exist, that the bromine content maximum is found close to, but not on, the bog surface. This depth is typically 30 to 50% of the total bog depth. A water extraction test for the Nova Scotian samples showed that < 0.1% of the bromine was found in water extractable form. From the Swiss samples it was found that approximately 40% of bromine was associated with humic acids [128].

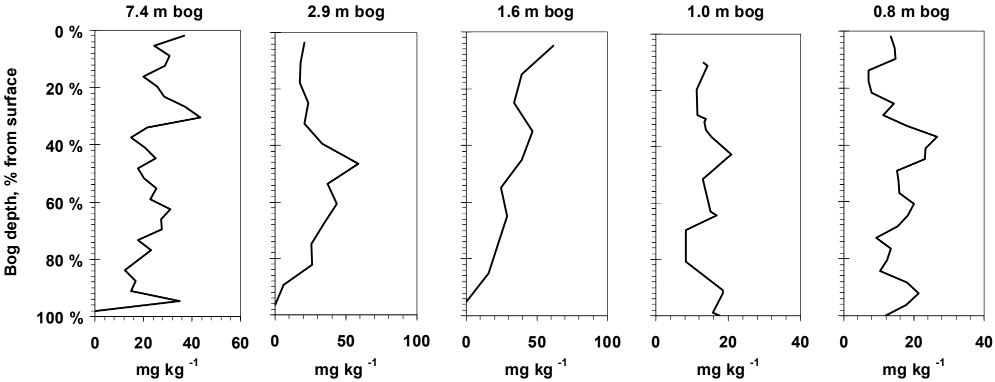


Figure 8. The variation of bromine content according to depth in three Nova Scotian [127] and two Swiss (two cores, far right) ombrotrophic peat bogs [128]. 0% = bog top, 100% = bog (silt) floor. Paper I.

The intense concentration gradient in the peat bogs may be interpreted to imply that the diffusion of the halogens in the peatbog is not significant [122,127]. Patterns different from the ones shown in Figure 8 can be found. In those cases it is likely that a detailed study of the diagenesis of such bogs, in connection with the pattern of chlorine, reveals the bogs to have been minerotrophic, at least at some stage of their history. The elevated halogen content in the lower parts of bogs may originate from marine silts in the floor of the bog. [129]

The retention rate for Br in peat has been found to be up to 50%, whereas for Cl it has been found to be up to 2.4%. The conclusion is that the higher retention of bromine in comparison to chlorine may be due to the physicochemical difference between the halogens, resulting in the favouring of bromine in the formation of organohalogens. [80]

From the data in Figure 9 (top) it can be seen that there is hardly any correlation between the total (TX) and total organic (TOX) bromine and chlorine content in peats. In the plot in the bottom the correlation between the total content and total organic content for the both halogens is shown. It can be seen that the organic bromine content is proportional to the total bromine content in the peats, though for chlorine the correlation is less evident.

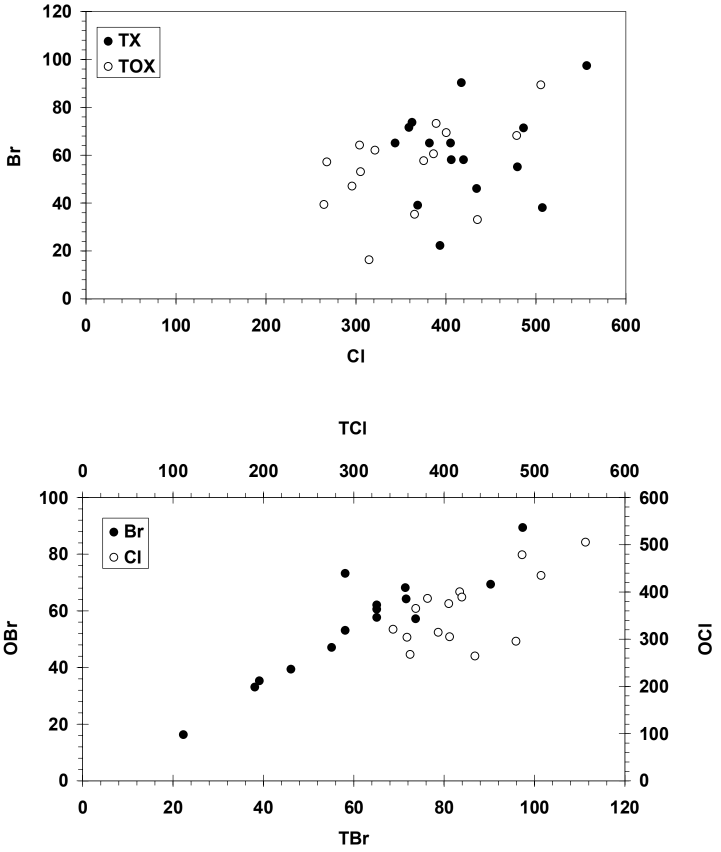


Figure 9. Correlation between total bromine and chlorine (TX) and total organic bromine and chlorine (TOX) content in peat bogs. Data from [105], Paper I.

When analysing peat bog porewater it has been frequently found that the halogen content may be some 15 to 30 times higher in the porewater than in the rainwater [122,130]. The peat bog is a source of bromine in the porewater, and this depends on the stage of diagenesis which in turn determines the adsorption and desorption process of halogens in peat. The more dissolved organic matter is released from the peat, the more Br can be found in the porewater. For chlorine this relationship is weak.

It seems that approximately 50 to 70% of the bromine in porewater exists in organic forms (soluble organohalogens or halogenated dissolved organic matter), whereas for example in rainwater bromine exists predominantly in inorganic form. In Chilean bogs the proportion of bromine found in the porewater was up to 1–2% of the total bromine in the moist peat sample. For Cl the proportion was 10–15%. [122].

Bromine content in peat has not generally been reported in connection with the use of fuel; rather it has been of interest to geologists studying the atmospheric deposition of elements where the preservative characteristics of peatlands are taken advantage of. Two studies were found on the comparison of bromine content in peats from different countries [99,131]. Peats acquired from Canada, Finland, Ireland, Latvia, Lithuania, Poland and England for horticultural use were also analysed for water extractable bromine. The water extractable form was found to represent only < 1% of the total bromine.

Table 3. The total bromine concentration in peats from different countries and continents. Paper I.

Origin	**Br, mg kg^{-1}**	**Ref.**
Canadian	25–60	[129]
	130–530	[129]
	42	[99]
Finnish	12	[99]
Norwegian	50–80	[131]
Swiss	7–27	[128]
Chilean	202	[80]
	< 60	[80]
	22–122	[105]
Latvian	20	[99]
Lithuanian	11	[99]
English	116	[99]
	61	[99]
Irish	110	[99]
Scottish	270	[130]
	< 600	[130]
Polish	21	[99]

From Table 3 it can be seen that the bromine content in the Irish, English, Scottish and Canadian peat is the highest, while the continental European peats Br content is 10–30 mg kg^{-1}. Only the peats with the highest total bromine concentration had detectable amounts of water extractable bromine. In studies on Chilean ombrotrophic peat bogs [80] which experience high and low annual precipitation, it has been found that the bromine concentration in the peat land is a function of the influx of bromine in rainfall. This is not the only explanatory factor of peat bromine content as a high load of bromine can also come from sea spray.

3.1.3 Coal and shale

Coal is the most important of the solid fuels, providing 40% of the electricity and one fourth of the primary energy in the World. An extensive literature can be found on chlorine in coal and it has been recently summarised in review publications [132,133]. Relatively few summarising papers can be found on bromine however [134–138]. This is in addition to the coal trace element studies where bromine has been included. Bromine has caught less attention than chlorine due to its typically lower content and postulated similar behaviour [135].

The typical bromine content in coal is approximately 20 mg kg^{-1} ranging from 0.5 to 90 mg kg^{-1} [134,139,140]. A listing by continent can be found in Swaine (1990) [139]. Clearly the highest figures have been found in Canada, the UK and in some parts of Australia. High values have since been found in Bulgarian and Ukrainian coals [135,136].

Eskenazy and Vassilev (2001) [135] analysed 219 samples from 8 coal mines in Bulgaria including coal, coaly shales and sandstone enriched in carbonates. The highest bromine content deposit had on average 128 mg kg^{-1} Br. It was postulated that this was due to the high bromine content in the ground waters (70 mg l^{-1}, typically < 0.1 mg l^{-1}). Particularly high bromine content, as a function of depth, was found locally in the Pirin deposit, 256 mg kg^{-1} [136], the mean content being 72 mg kg^{-1}. The content in all the 219 samples varied mainly between 10 and 30 mg kg^{-1}, which is similar to that for the US coals.

The exact origin of bromine in coal and the processes involved during coalification are unclear. For nearly all the other elements there is a good understanding of the main processes involved [138,141]. At least some of the bromine is inherited from the plant matter whereas the high concentrations may be due to the influence of underground brines [136].

The bromine content does not depend upon the rank of coal. Typically the content is higher than the average for soil. This has been characterised by the negative correlation between ash and bromine content in coal [135] (see later Figure 10). In addition, different coal macerals have been analysed separately for bromine [135], and bromine has been shown to be associated particularly with vitrinite macerals [142]. Vitrinite group macerals are coalification products of humic substances [143] originating from cellular plant material such as roots, bark, plant stems and tree trunks. With some US, English and Australian coal samples it was found that the bromine content in vitrinite were 1.2–2.7 times higher than in the coal samples overall [[144] cited in [135]]. Out of 34 elements analysed bromine was found to be the only one associated with vitrinite in all samples.

A study of UK coals suggests that chlorine and bromine differ from nearly all other trace elements in that they are not present in significant concentrations in mineral matter or bound within organic matter [138,141]. They are thought to be incorporated in the porewaters of coal and they are considered to be preservative, i.e. the original marine deposition imprint has been preserved in the coal. The forms of bromine are therefore suggested to be analogous to chlorine. For chlorine it has been suggested that the organic-associated chlorine predominates. It consists of two different types [132]:

i) A minor proportion as a ’true’ Cl_{org} as covalent-bonded Cl in coal organic macromolecules.

ii) The major proportion of organic chlorine is present as ’ semi-organic‘ Cl as anion sorbed on the coal organic surface in pores.

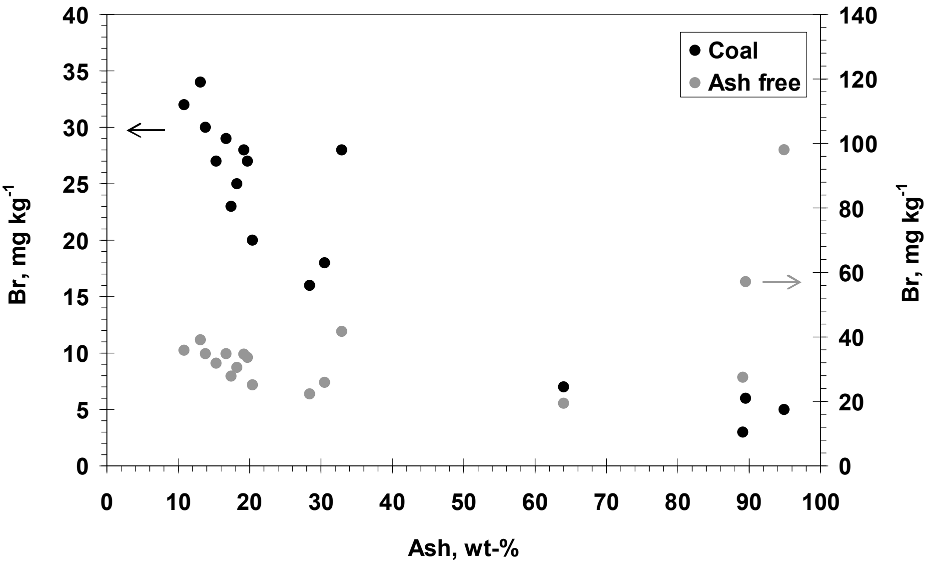
The latter is not ‘true’ Cl_{org}, because in moisture the anions are anchored to the polar organic functional groups on the surface of micropores in coal macerals by ionic attraction [145] and not in the coal macromolecular organic structure. On the other hand it is not ’truly’ water-soluble because it persists after pore water release, at up to 300 °C in coal drying. Preliminary XAFS (X-ray absorption fine structure) experiments confirm this speciation for bromine, too. [145]

For South African coals it has been found that elements which tend to be more concentrated in marine-derived sediments, e.g. boron, chlorine, lithium and bromine, occur in greater concentrations in the top of coals overlain by marine strata than in coals overlain by non-marine fluvial sequences. The latter do not show enrichments of these elements [146]. This is supported by the suggestion that bromine may originate from marine connate (relic water) which is depleted in Cl/Br ratio.

The brines in the coalfields of the north east of England show considerable depletion in Cl/Br ratios compared to sea water [82]. The Cl/Br ratio may be influenced also by the thermal history of the coal deposit, as the devolatilisation of coal beds may result in fluids with low Cl/Br relative to most hydrothermal fluids [142]. The Cl/Br ratio in UK coals is about one fourth of that in the sea water. The same ratio was found for water soluble proportions of Cl and Br, a finding which supports their similar association in coal. The ratio in coal porewater is at the same level (70, mass basis) as brine after halide precipitation. [138]

From the high bromine Bulgarian coals 13% of the bromine was leached in water [135,136]. In the high chlorine coals the water soluble NaCl chlorine association was pronounced, whereas the corresponding inorganic association of bromine has not yet been identified. For the high bromine coal samples collected by Vassilev (2000) [137] water extraction was carried out. Up to 35% of the chlorine could be leached, while < 1% of Br was always leached. This finding is in alignment with the findings for US coals [147]. But, even if it is a simple method, water extraction leaves room for speculation on halogen speciation. It has been found that if coals contained above about 0.25 wt-% carbonate, the percentage of chlorine extraction approaches 100%. The reason is that chlorine (bromine) is held in anion exchange sites and is exchanged when carbonates dissolve. Fine grinding will over-emphasise this ion exchange capacity. [138,141]

Coals, coaly shales and partings were analysed for Br by Eskenazy and Vassilev (2001) [135]. This data can be used in two different dimensions: firstly, in assessing the affinity of Br to organic matter (coal) in one deposit, and secondly, in evaluating the Br content in different mining ‘products’ from several mines as a function of ash content. Figure 10 shows the bromine content in coal, coaly shales and partings as a function of ash content. From the chart on top it can be seen that in one deposit there seems to be a negative correlation between the ash and Br content of the ‘coal’. This supports the findings on the organic affinity of bromine in coals.



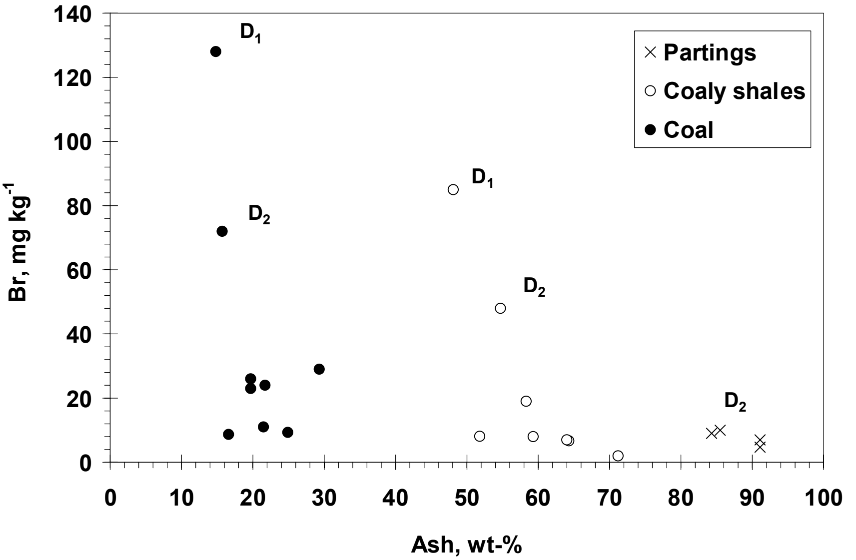


Figure 10. Correlation between the ash and bromine content in coals and coaly shales from the Dobroudzha deposit, Bulgaria (top) and different mining products from 7 Bulgarian mines (bottom). On the chart on top the x-axis for data drawn on ash-free basis corresponds to the ash content of the original sample. Drawn based on data in [135]. Paper I.

On the bottom in Figure 10 the correlations between different mining products collected from 7 different mines in Bulgaria are shown. This plot divides the 'products' into three classifications, where the coals with a mean 20 wt-% ash content have the highest bromine content. The next class in the order of ash content are the shales, and the third partings. In two deposits (labelled D_1 or D_2) the bromine content is always higher in the coal than in the shales (or partings in D_2) from the same deposit.

In addition to the coal in Figure 10 (top) the bromine content in the coal samples calculated on ash free basis is plotted. The finding is that the bromine content is in the proximity of 30–35 mg kg^{-1} in the macerals, whereas from the chart on the bottom it is evident that the bulk of shales contain some 8 mg kg^{-1} Br. In Canadian oil sands a similar pattern can be observed where the raw bitumen separated from the sand is enriched in Br in comparison to the oil sand. [148]

To conclude [137] the bromine (and chlorine) enrichments are 'associated with favourable coal-forming vegetation, marine influence, arid and stable conditions of deposition, volcanic activity, diagenetic and epigenetic solutions enriched in halogen elements and metamorphic progression accompanied by optimum pore-size distribution in coal'. Significant proportion of bromine may be associated with the inherent moisture of coal porosity. How much this fractionates chlorine and bromine is not known. [137,138]

Table 4. Summary of the natural content and forms of bromine in solid fuels. Paper I.

Fuel	**Content, mg kg^{-1}**	**Form/Function**
Biomass		
Terrestrial plant, inland	2–20	Mobile nutrient bromide
Terrestrial plant, coastal	≤ 150	
Marine algae and plants	150–1000	Organically bound bromine, over 1600 compounds identified
Marine, highly concentrating	30 000–60 000	
Peat		
Inland	10–20	Sorption of Br to humic acids, possibly mediated by microbial activity
Coastal	50–150	
Coal		
'Standard'	5–20	'Semi organic', bound in maceral micropres by ionic attraction
Marine influence	100–200	Water soluble proportions can be found
Shales	< 10	Bound in the macerals of the shale

3.2 Anthropogenic occurrence (Paper II)

3.2.1 Bromine refining, anthropogenic use and toxicity

The estimated world bromine production totalled 669 Mt in 2006 and has not changed significantly since then. Some production has come on-line in Jordan and some has shut down in the US, events which have led to the need for proprietary data requirements and definite production figures are currently not available [149]. Figure 11 shows the estimated breakdown of bromine production and consumption by country.

Bromine is a corrosive substance and it is often transported in the form of intermediate products. Lead has been shown to the best in handling elemental bromine: bromine forms a dense lead bromide superficial coating in containers which prevents further corrosion. [150]

Bromine is found principally in and **refined** from seawater, salt lakes, and underground brines. The largest bromine producer is the US [149] and the largest market China [151]. In US bromine is recovered from brine wells in Arkansas and Michigan. In Arkansas the concentrated brines contain up to 5 000 mg l^{-1} bromide and the Michigan brines about half of that. For Arkansas bromide has become the single most valuable mineral commodity produced [152]. In Arkansas brine is drilled from a depth of 2 400 m [149], whereas in Israel bromine is refined from the Dead Sea brine. In Dead Sea the bromine concentration is close to 5 000 mg l^{-1}. The Dead Sea bromine is enriched up to 13 000 mg l^{-1} in the end-brine after precipitation of sodium, magnesium and calcium chloride [153].

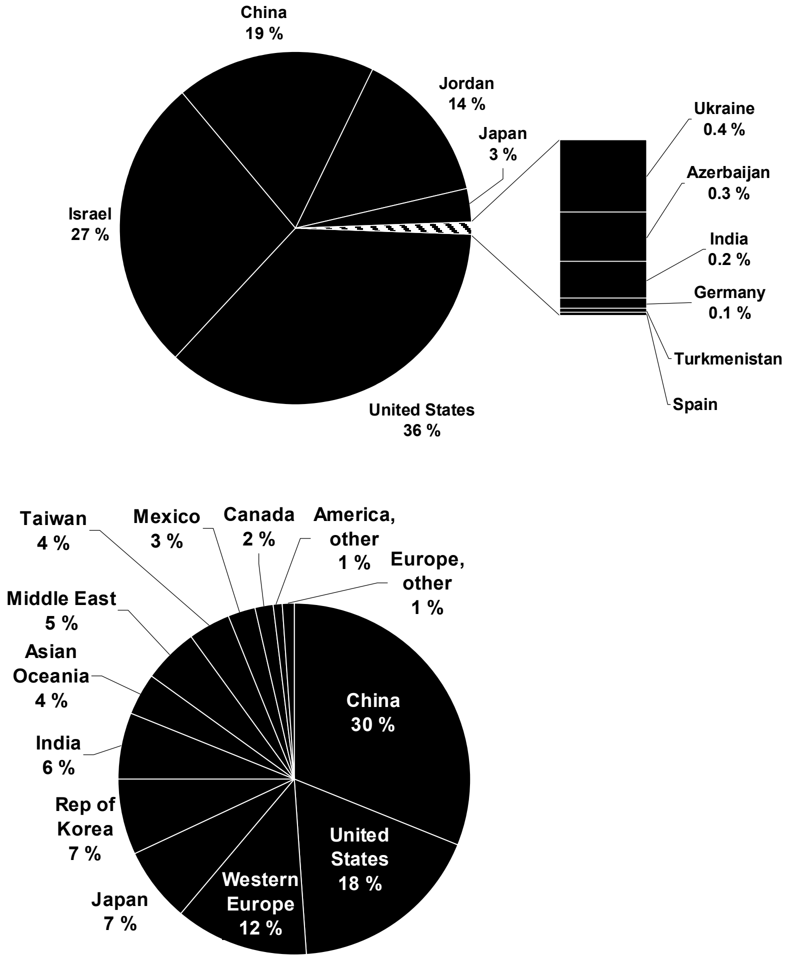


Figure 11. The estimated World bromine production [149] (top) and the consumption by country [151] (bottom). Paper II.

The anthropogenic **bromine utilisation** can be divided in five categories:

i) flame retardants
ii) drilling fluids
iii) pesticides
iv) biocides and water treatment chemicals
v) others (dyes, photography, additive).

The current consumption of bromine by end use has been estimated in Figure 12. Approximately 50% from the refined elemental bromine is used for brominated flame retardants (BFRs). Up to 7% annual increase in BFR use has been reported from the Asia Pacific region [154]. In the past 10 years the global market has grown from 3 to 5% annually. The gasoline additive use has been phased out [155,156]. The drilling fluid market projections fluctuate with the oil drilling industry. About 4–5% annual growth is expected in the biocide market, half of which comes from the industrial water treatment market [152]. Detailed discussion also on the minor uses of bromine can be found in Paper II.

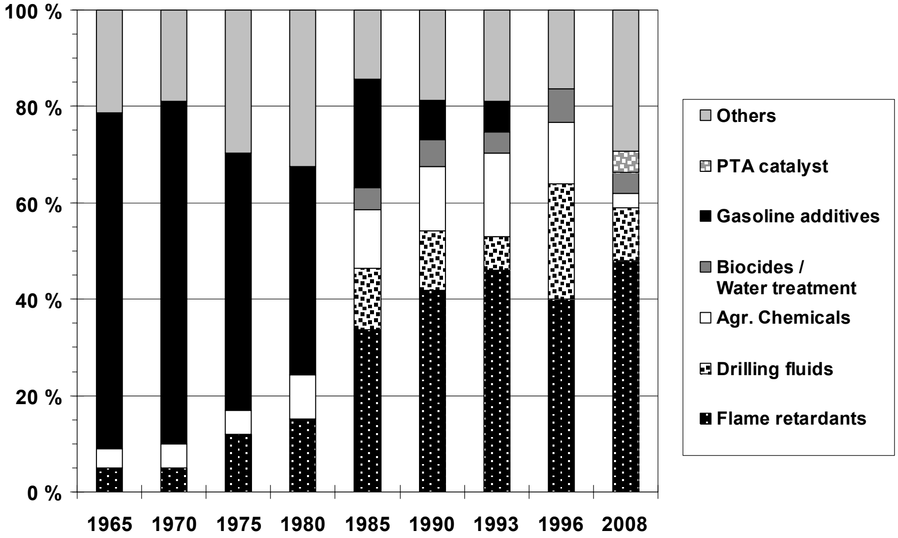


Figure 12. Consumption of bromine divided by end-use. The data is based on a compilation from several sources [151,152,154,157–159]. PTA = purified terephthalic acid. Paper II.

Bromide is toxic to humans in high doses, but humans are exposed to bromine on a daily basis. Bromine can be found in commercial crude and refined salts [160]: Dead Sea crude salt has been found to contain 358 mg kg^{-1}, Dead Sea refined salt 174 mg kg^{-1}, wet mined crude 35 mg kg^{-1} (definite source not given) and wet mined refined salt 29 mg kg^{-1}. During industrial times the highest concern has been due the utilisation of bromine bearing fumigants which have been shown to increase the bromine concentrations in plants grown on treated soils.

Van Leeuwen (1987) [101] provides a comprehensive overview on the **toxicity of the bromide ion**, and particularly describes the medical symptoms of bromism.

It should be noted that the review focuses on the toxicity of the bromide ion while the vast amount of bromine bearing compounds, particularly organic compounds, exhibit another type of toxicology. Yet, the study is of major relevance, as regardless of the likely organobromide origin, human exposure is often due to the bromide ion released from organohalogens e.g. soil fumigants.

Currently the main human exposure for bromide comes from foodstuff due to the use of fumigants or postharvest biocide residues. Bromine compounds (methyl bromide and ethylene dibromide) are used for storage, handling and processing of the food against nematodes, fungi and bacteria. The WHO recommendation for the acceptable daily bromide intake (ADI) is 1 mg (kg bodyweight)$^{-1}$ [39] which is not in practice realised unless bromine contamination has taken place in foodstuff. The typical bromide intake is close to 10 mg day^{-1} per person [101].

Bromine's biological half-life in humans has been shown to be approximately 12 days. The half-life is strongly dependent upon the chlorine intake due to the competition of the two halogens Cl and Br, which is also taken advantage of in the treatment of bromism. With a salt-free diet the bromine half-life can be extended ten times. In blood plasma, bromide seems to replace chloride only if chloride is not available. [101]

Even if Br is abundant in nature, WHO concludes that in non-contaminated drinking water, including desalinated water, bromine content does not pose a health risk [39].

3.2.2 Fumigated biomass

The main path for anthropogenic bromine contamination relevant for solid biomass is the decomposition of organic bromine bearing fumigants and pesticides and the consequent take-up by plants as bromide. This has been comprehensively studied within the context of soil science [158,161, 162]. Specific biomass residues such as greenhouse residue used as solid fuel may contain significant amounts of bromine.

Methyl bromide (CH_3Br, MeBr, bromomethane) is the main bromine containing pesticide used worldwide. It is used as soil fumigant in agriculture, fruit growing, and a multipurpose pesticide used in soil sterilisation, the control of nematodes, pathogens, pest insects, rodents, and weeds. [154]

MeBr use has been declining due to the ban imposed by the 1987 Montreal Protocol as it is a class I ozone-depleting substance alongside the well-known chlorofluorocarbons (CFCs). Bromine is on an atomic basis 40 times more efficient than chlorine in destroying stratospheric ozone, and MeBr is the single largest source of stratospheric bromine due to human activity. However, according to the US EPA, MeBr has been proven to be difficult to replace. Despite the Montreal protocol, in 2008 the US EPA authorised the use of 19% of the 1991 MeBr utilisation level [154]. This represented 79% of the World usage in 2009. [159]

Soil fumigation may contribute to some 20–30% of the MeBr emissions in the atmosphere. The largest source is the sea, followed by MeBr formed by terrestrial plants and biomass burning [163]. For this reason MeBr is likely to be the main reservoir of atmospheric bromine. MeBr has been identified in laboratory experiments of biomass combustion and smoke plumes from wildfires in savannas, chaparral, and boreal forest. [109,158,164]

From the literature it is evident [101], that the bromide content in plants grown on soil treated with bromine derivatives is significantly higher than in those grown on non-contaminated/treated soil. In soil fumigation the methyl bromide fate is depressing: on average over a year about 14% of the MeBr applied for soil fumigation is converted to bromide ion [81] and consequently dissolved in water. In this form bromine can be taken up by plants. Approximately 70 to 90% of the MeBr is evaporated from the soil. Even if the fumigated soils are typically covered with polyethylene film it is relatively permeable to MeBr and significant emissions can occur [165–167]. Greenhouse soils sometimes even have to be leached after fumigation in order to avoid large Br^- uptake by plants. These leaching (in addition to water treatment, see Chapter 3.2.4) waters may act locally as a large bromide source. Upstream of the river Rhine 6 to 32 $\mu g\ l^{-1}$ and in the Danube 15 $\mu g\ l^{-1}$ bromide has been reported. The corresponding values downstream were found to range from 200 to 800 $\mu g\ l^{-1}$ [101] and are most definitely due to industrial pollution. Soil type and water content also influence MeBr transport and transformation: the total volatilization from soil with high organic matter content may be drastically reduced relative to that from a low organic matter soil.

Regarding solid fuels bromine may have practical meaning if residues from greenhouses are used. Since most of the research work has been carried out regarding foodstuff, residual plant bromine content is often omitted in the literature. Regarding foodstuff the bromine content in biomass can be categorised in three ways:

i) Those foodstuffs with less than 2 mg kg^{-1} bromine, beverages and fruits.

ii) Those containing between 2 to 8 mg kg^{-1} bromine, such as root vegetables, milk, dairy products, meat and sugars.

iii) Those with clear contamination through bromine treatment containing > 200 mg kg^{-1}, such as leafy vegetables, lettuce, spinach etc.

The highest level of bromine has been found in leafy vegetables. Naturally it is less than 10 mg kg^{-1}, however after MeBr fumigation up to several thousands of mg kg^{-1} has been found in the plants [168]. The Br uptake has been observed to increase with [169–171]:

- the rates of fumigation application
- the bromine content in the soil (whether or not fumigated)
- the organic content of the treated soil (with equal bromine application rates).

In tomato plant leaves up to 2 200 mg kg^{-1} has been analysed after fumigation. The concentration of bromide decreased from the base to the leave tip, and increased with the age of the tissue [172]. It was shown with tomato plants that the concentration of bromide in leaves and fruit were directly proportional to the bromide concentration in the soil. After MeBr fumigation the tops of beans and cabbage contained about 1 000 mg kg^{-1} bromine. Up to 18 000 mg kg^{-1} has been measured from citrus leaves. At this concentration the bromine already exhibits toxic effects, which resulted in a significantly reduced growth (90% reduction). Carrot seems to be very tolerant to bromine, as it did not suffer growth reduction even with a 25 000 mg kg^{-1} bromine content in the leaves [173]. In a study on soil fumigation 1.8–13 mg kg^{-1} (fresh) bromide was analysed from a reference lettuce plant, and, after fumigation up to approximately 650 mg kg^{-1} (fresh) corresponding to about 13 000 mg kg^{-1} in dry matter [174]. In a work with 828 lettuce samples collected from growers in England and Wales 83% of the plants had been grown in bromine treated soils. 71% exceeded 100 mg kg^{-1}, 30% 500 mg kg^{-1} and 12% 1 000 mg kg^{-1} [156]. These were reported on a fresh weight basis. Lettuce contains approximately 96% water, wherefrom it can be calculated that on a dry mass basis 1 000 mg (fresh kg)$^{-1}$ corresponds to 25 000 mg (dry kg)$^{-1}$. In a Japanese study samples of carrot leaves from a plantation utilising bromine-bearing nematocide were reported to contain 615 mg kg^{-1} bromine

[95]. In the same work tobacco leaves were found to contain from 10 to 50 mg kg^{-1} Br, while cigarettes were found to have from 91 to 450 mg kg^{-1} bromine due to bromine treatment.

Comparing the magnitude of the bromine content in bromine contaminated biomass to the naturally occurring concentration it is clear that some of the values reported as 'natural' have actually been influenced by anthropogenic bromine. Values as high as 200 to 1 000 mg kg^{-1} have been reported [85,175,176] for biomass – these cannot be natural concentrations.

Figure 13 shows the concentration of bromine in tomato plant leaves as a result of soil fumigation. Analyses have been carried out after growing tomato plants for 9.5 weeks on methyl bromide treated soil. The interval between planting and fumigation was varied. Also the rate of fumigation (g m^{-2}) was varied but the time that had elapsed from the last fumigation seemed to be the main determining factor. [172]

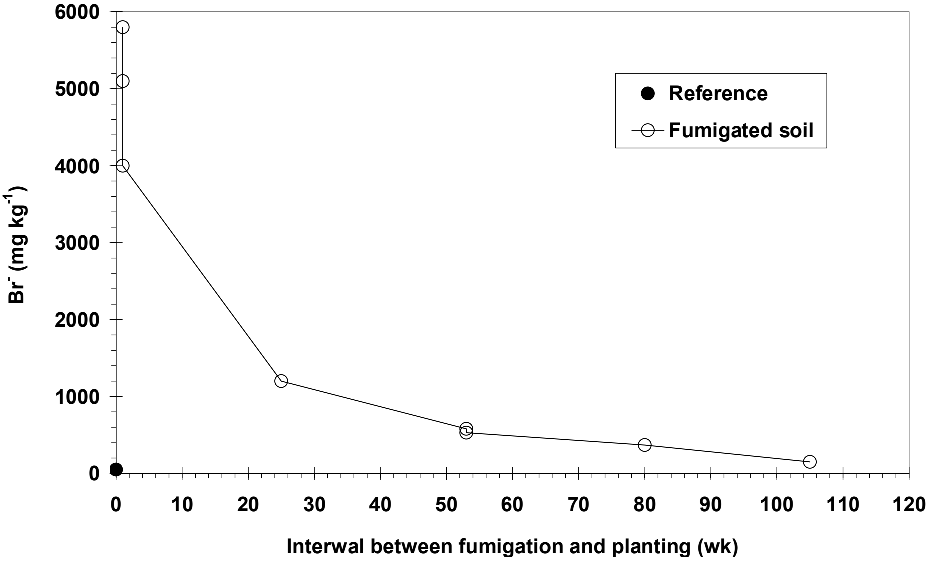


Figure 13. Concentration of bromine in tomato plant leaves as a result of methyl bromide soil fumigation. Drawn based on data in [172]. Paper II.

3.2.3 Municipal solid waste

The largest use of Br with 50% from bromine market is in flame retardants [151,177–179] with an annual market value of 2 billion €. Figure 14 shows the proportions in different flame retardants from worldwide consumption in 2006 [178]. The total flame retardant consumption amounted to 1.59 million tonnes out of which 18%, i.e. 290 kt, were BFRs. In the bar chart the distribution of the BFRs (Br) by final applications is shown.

It has been shown [8] that when SRF is prepared from MSW, it may eventually be enriched in chlorine due to a higher plastics content in SRF (or RDF). Approximately 70% of the Cl in MSW has been estimated to originate from plastics, particularly polyvinylchloride (PVC) [7,180]. In addition to PVC, chlorine is used in flame retardants [181]. The rest in MSW originates mainly from food residues which contain dietary salt. This is indicated by the small water soluble portion of chlorine in waste [182].

Plastics and textiles are used in applications and products where flame retardancy is often required. Therefore the sources of bromine in SRF can be traced to brominated flame retardants (BFRs) [30,181,183]. In BFRs bromine is bound in organic matrix and is readily available for reactions [184] in a similar way as Cl in PVC plastic.

By far the largest amount of BFRs is utilised in electronic and electric equipment (EEE), i.e. circuit boards, TV and PC housings. About 90% of all electrical components contain BFRs [154]. Building and construction applications include construction and insulation boards and extruded foams. Textile applications are to a large extent in synthetic and natural fibre drapery, upholstery, fabrics and furniture cushioning. Transportation applications include the plastics and elastomers used in cars. [185,186]

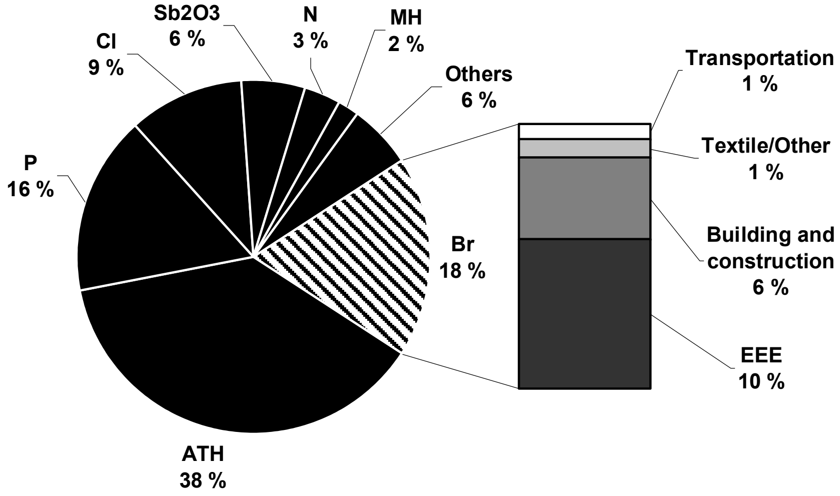


Figure 14. The proportions (mass basis) of different flame retardants from total worldwide consumption in 2006 (pie chart). In the bar chart the distribution of BFRs ('Br') by final applications is shown [178,187]. ATH = Alumina trihydrate, P = Phosphorus compounds, Cl = Chlorine compounds, N = Nitrogen compounds, MH = Magnesium hydroxide, Br = Bromine compounds, EEE = Electronic & electrical equipment. 'Others' include borate, B, and tin, Sn, and zinc, Zn, -based compounds, from which the most important are zinc hydroxystannate and zinc stannate [188].

The requirement for consumer products and construction materials to comply with both national and international fire safety regulations leads to the use of various types of flame retardants [189]. Halogenated flame retardants have traditionally been used because of their efficiency and suitability with various types of plastics and textiles. The form of action of BFRs is such that Br is eventually released as HBr from the flame retarded heated object [183] and will end up in combustion gases predominantly as HBr analogously to HCl from PVC [79,190]. Halogenated flame retardants (containing chlorine or bromine atoms) act effectively by removing the H· and OH· radicals in the gas flame phase, thereby reducing heat generation and the production of further gaseous flammable material.

The effectiveness of the halogenated flame retardants depends on the halogen atoms they contain, and also on the control of the halogen release [191]. Bromine is generally preferred over chlorine because it requires lower quantities of flame retardant and minimizes the impact of the additive on the polymer's performance. All four halogens are in principle effective in eliminating free radicals, and the trapping efficiency increases in the order I > Br > Cl > F. Therefore, all organohalogen compounds could in principle be used as flame retardants, but fluorinated compounds are very stable and decompose at much higher temperatures than most organic matter burns, delivering their halogens too late to be effective as a flame retardant, and iodinated compounds are unstable already at slightly elevated temperatures. With a higher trapping efficiency and a lower decomposing temperature, organobromine compounds are favoured over their organochlorine homologues [181].

Halogenated flame retardants are not used in PVC as it is inherently resistant to fire [189]. Neither in the applications indicated in Table 5 PVC is (mainly) used, but they take advantage of other polymers, mainly epoxy resins and high impact polystyrenes (HIPS). High Cl concentrations can still be found in these materials, indicating that chlorine based flame retardants have been applied.

There are two main options for incorporating BFRs in the plastics: either additive or reactive. Additive BFRs are those that do not react with the application – here plastic polymer – but are simply blended with the polymer. These type of BFRs are those most likely to leach out of the products [192,193] and may lead to human exposure. When used as a reactive the BFR becomes covalently bound in the polymer and is essentially lost. The potential for BFR exposure is from unreacted BFR which may exist if excess has been added during the production [186].

The three most widely used BFRs today and over the past 10 to 20 years of the plastics era are Tetrabromobisphenol A (TBBPA), Decabromodiphenyl Ether (DecaBDE) and Hexabromocyclododecane (HBCD). Even if tens of different BFRs are available on the market [194] these three compounds account for some 94% of the used BFRs [187]. In the past also Polybrominated biphenyls (PBBs) were used but were banned due to their chemical similarity to Polychlorinated biphenyls (PCBs) which are toxic. PBBs existence in waste fuels is possible, even if not likely, as the life cycle of the applications can be longer than the time since they were banned in the late 1970s [192].

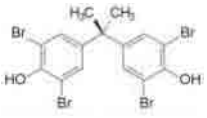
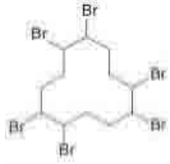
Table 5 shows selected physicochemical properties and applications of the three most widely used BFRs. There are basic differences in the forms and targets of their application. The main uses of TBBPA are as a reactive flame retardant in epoxy and polycarbonate resins for applications such as circuit boards. It may also be used as an additive flame retardant, for example in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins, HIPS and phenolic resins. Where TBBPA is used as an additive flame retardant, it is generally used alongside antimony trioxide for maximum performance. Antimony trioxide is generally not used in conjunction with TBBPA in reactive flame retardant applications [186]. DecaBDE is mostly used in applications in the plastics and textile industries. It is an additive flame retardant. HBCD can be used on its own or in combination with other flame retardants e.g. antimony trioxide and DecaBDE [185]. HBCD is used in four principal product types: expandable polystyrene (EPS), extruded polystyrene (XPS), HIPS and polymer dispersion for textiles.

In addition to the mentioned BFRs 2,4,6-Tribromphenol is also used in flame retardant applications as well as a wood preservative and fungicide. Flame retardant use includes use in nylon and polyethylene terephthalate (PET) [194]. The use as a wood preservative may result in the release to the environment. No data has been reported to be available on the possible leaching of unreacted brominated phenols from BFR plastics containing 2,4,6-TBP derivatives. [195]

The high content of bromine, chlorine and heavy metals in WEEE has led to the need for establishing separate collection and recycling scheme for this type of waste in order to reduce environmental impact [196]. For this reason, this type of material is not found in large quantities in waste fuels. This category also includes other opportunity fuels such as automotive shredder residue (ASR) and tire derived fuel (TDF) that can have significant bromine content. More detailed information on these can be found in Paper II.

But, flame retarded plastics can be found everywhere where thermal stability is required, also in waste fractions commonly found in SRF. These are: polystyrene foams in construction; textiles in sofas, chairs and upholstery; decorative profiles; construction and protective films; polyamide or nylon based heat protective hoods and pipes; different types of polypropylene (lamp, gadget) holders, sockets and kitchen hoods etc.

Table 5. Selected physico-chemical properties and applications of Tetrabromobisphenol A (TBBPA), Decabromodiphenyl Ether (DecaBDE) and Hexabromocyclododecane (HBCD) with indications of the resulting Br contents (as wt-%) in various final products. [185,186,197]

	TBBPA	**DecaBDE**	**HBCD**
Structural formula			
Chemical formula	$C_{15}H_{12}Br_4O_2$	$C_{12}Br_{10}O$	$C_{12}H_{18}Br_6$
Molecular weight	543.9 g/mol	959.2 g/mol	641.7 g/mol
Bromine content	58.80 wt-%	83.30 wt-%	74.71 wt-%
Melting point	~180°C	~305°C	~190°C
Boiling point	Decomposes at > 200°C	Decomposes at > 320°C	Decomposes at > 190°C
Main use type	Reactive, additive	Additive	Additive
Main applications	70% reactive in epoxy resins for printed circuit boards 15% additively in HIPS for TV, PC, electric equipment casing materials 10% for the production of TBBPA derivatives 5% as additives for other polymers such as ABS and thermoplastic polyesters	80% in HIPS, PP, LD-PE, ABS, thermoplastic elastomers found in TV, PC, electric equipment casings, wires, cables and rubber like plastics 20% in PP and cotton drapery, nylon, upholstery, fabrics	90% in EPS, XPS used in construction & insulation boards 2% HIPS (see left for applications) Textiles
Typical Br content of final product	Epoxy resin 20–48 wt-% (reactive) Circuit board 10–20 wt-% (reactive) Electric appliance casing 12% (additive)	HIPS electrical equipment casings 5–12wt-% PP drapery and upholstery fabric, carpets (not clothing) up to 25–35wt-%	EPS, XPS boards 2–30 wt-% HIPS casings 1–5 wt-% Textiles up to 20 wt-%
Used as pure or additive	Pure as reactive, with Sb synergist when additive	Additive use only, always with Sb synergist	Additive use only, always with Sb synergist in typically 2:1 mass ratio

In addition to plastics, flame retardancy has been one important area in (natural fibre) textile developments. In fibres and fabrics there are basically two options to incorporate flame retardancy: to use inherently flame-retardant fibres or flame-retardant finishes. Regarding cotton the most widely used flame retardants seem to be phosphorus based systems, whereas for wool systems that are based on hexafluorotitanates and hexafluorozirconates (Zirpro) seem to be widely applied. The use of bromine is focused on flame retardation of conventional textile fibres where specific (technical use) flame retardancy is required. Up to several weight percentages of brominated finishing agent can be applied in such cases [150,198]. Halogen and particularly bromine derivatives and phosphorus-containing co-monomers have been found to be the most effective ones. These add cost: flame retarded cotton or wool costs 20–50% more than untreated fabric.

Out of the brominated flame retardants used in packaging in Europe 55–85% is estimated to end up in incineration within the final products, 10–25% is recycled and the rest is landfilled [199].

3.2.4 Wastewater sludge

Ultraviolet (UV), ozonation and halogen treatment – alone, or in combination – are widely used water sanitation methods. UV has been applied in disinfection of drinking water and wastewater. UV disinfection is a physical process which induces photobiochemical changes in microorganisms, providing that the microorganism's DNA absorbs energy from the applied range of the electromagnetic spectrum [150]. Ozone is one of the strongest oxidants, and also disinfectants, and is widely used in water sanitation [150].

Ozone treatment also has a connection to waterborne bromine: most water sources, whether natural or industrial, contain at least some level of bromide, and ozone treatment has been shown to result in the formation of bromate (BrO_3^-) in addition to the main Br form hypobromous acid (HOBr). As these both are strong oxidants, they are likely to react with organic matter, leaving bromide as the result [200,201]. Bromate is a highly toxic substance [200]. The formation requires dissolved ozone to be present in the water which then reacts with hypobromite ions (OBr^-) present naturally in water. The reacted bromide can be found as bromate to a varying extent. It can be the major bromine species converted from bromide, whereas some studies indicate up to 70% of the bromine can be found to form organic bromine [202,203]. This proportion depends for example on bromide content, TOC (total organic carbon), pH and alkanity in water. Regarding wastewater treatment, bromate can be removed by ferrous iron (ferrous sulphate) where iron is oxidised to ferric iron and bromine is reduced to bromide [204].

During the last 20 years, the use of brominated water treatment programs has become standard practice to control algae and bacterial growth in industrial processes. In fact bromine-chlorine biocides are considered as the mainstream products for cooling water systems, preservatives, disinfectants, slimicides, pesticides and algaecides in the agriculture, pulp and paper industries, in industrial (cooling) water treatment, the chemical industry, as brewery pasteurizers, and for commercial and residential spas/pools [149]. The halogens are available in many different compositions and forms.

Chlorine and bromine are strong oxidants that react with organic materials. As the halogens oxidize the cell walls or other cell components the organism dies. It has been observed that some bacterial suspensions become sterile when they lose the power to oxidize glucose enzymatically. Enzymes, on the other hand, are oxidized by the halogens eliminating their action and causing unbalanced growth. The inactivation mechanisms include also unabling reproduction. The effectiveness of disinfecting agents is a function of the rate of diffusion through the cell wall and the reactivity with cells walls, enzymes (proteins) and nucleic acids. The rate and extent of inactivation are known to depend upon [150]:

- the type and concentration of organisms to be inactivated
- the disinfectant species present
- the concentration of disinfectant
- contact time
- temperature
- pH
- interfering substances.

Generally, increasing the halogen dose or extending the contact time results in higher effectiveness [150]. Chlorine is widely used due to its effectiveness and economy of operation. Chlorination started to be employed as it accomplished the purpose for which it was used, not because its mode of action was understood [150]. Waterborne diseases were common in the past: there are statistics that more than 25 000 typhoid deaths occurred in 1900 in the US but due to the onset of water chlorination this reduced to 20 in 1960 [205]. Approximately 5% of anthropogenic chlorine is currently used in water treatment. It can be used for various purposes in taste and odour control, algae and slime control, water disinfection etc. On the other hand concerns have been raised due to the by-products of the disinfection as these may be carcinogenic. [205]

Bromine (and its derivatives) is more expensive than chlorine but bromine based products can be cost-effective due to their effectiveness [206]: they tend to kill microbes more quickly and they are safer due to the lower volumes needed [149]. Bromine is less than half as volatile and three times as soluble in water (31 g l^{-1} at 30°C) as chlorine – this allows smaller dosing and a less corrosive environment. Also, bromine systems are in practice effective over a wider pH range than chlorine systems. In alkaline cooling/process water environments [206] bromine use allows 1.0 unit higher pH in disinfection than chlorine. In pool treatment bromine may produce less odour than the corresponding chlorine treatment due to the reduced presence of volatile smelly compounds, namely brom- and chloramines. These are formed in the presence of various nitrogen compounds. Bromamines are relatively unstable in comparison to chloramines and (re-)hydrolyze to HOBr which is the active form of Br. [150]

One of the disadvantages of bromine is that it cannot be easily stabilized against ultraviolet light [207]. Also, if a purely oxidizing effect is required HOCl is preferred due to the fact that it is a stronger oxidizer, even if bromine is more 'effective' in killing microbes [206]. Accordingly, chlorine may cover most of the halogen demand in industrial cooling systems, leaving then the bromine to act as a disinfectant. The oxidation potentials (25°C) (relative to the hydrogen electrode) are 1.49 for HOCl and 1.33 for HOBr.

When bromine dissolves in water it hydrolyzes quickly to hypobromous acid (HOBr) which is the active form of bromine as a disinfectant

$$Br_2 + 2H_2O \leftrightarrow HOBr + H_3O^+ + Br^- \qquad (1)$$

The HOBr dissociates to produce a mixture of HOBr, hypobromite ions (OBr^-) and hydronium ions (H_3O^+)

$$HOBr + H_2O \leftrightarrow H_3O^+ + OBr^- \qquad (2)$$

HOBr is a weak acid and dissociates only partially in water. The relative proportions of HOBr and OBr^- depend heavily on the pH [150]. The fraction of bromine present as HOBr in different pH at 20 °C is illustrated in Figure 15. Between pH 7 and 8 the speciation of aqueous chlorine changes quickly with the pH [208] and the same happens with bromine between pH 8 and 9. At approximately pH 7.5 the proportions HOCl and OCl^- are equal and HOBr and OBr^- at pH 8.5. Thus the pH of the solution has to be kept in an optimal pH window.

Where higher operational pH has to be used bromine-based oxidisers are more suitable. [206]

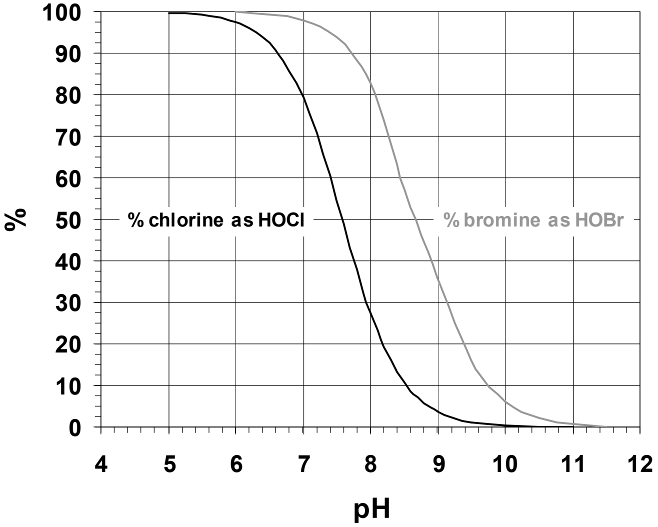


Figure 15. Dissociation of hypobromous acid (HOBr) and hypochlorous acid (HOCl) as a function of pH at 20 °C. Drawn based on data in [150,206,209,210]. Paper II.

The generation of HOBr can be achieved by several means. There are in principle three options: [206]

i) Generation of HOBr from Bromine Gas.

ii) Generation of HOBr from NaBr by applying an oxidant. These can be for example mixing with chlorine gas or sodium hypochlorite. This method is widely used in general industrial cooling systems where it is necessary to have a permanent source of oxidant available to promote HOBr formation [207].

iii) Generation of HOBr from brominated organic compounds. These are typically granules, sticks, and tablets.

All the available bromine is not lost by biocidal reaction. When acting as a disinfectant hypobromous acid produces bromide ions as a result

$$\text{HOBr} + \text{living organism} \rightarrow \text{Br}^- + \text{oxidised debris} \qquad (3)$$

In actual systems there is recycling of the bromide back into HOBr. This is because HOCl oxidizes bromide to HOBr in the pH range of 7–9. Oxidation can be carried out for example by supplying NaOCl or 1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) in water. When BCDMH dissolves in water bromide reacts with the HOCl formed to produce HOBr

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (4)$$

Therefore chlorine concentration in the solution is also a factor influencing bromine disinfection and an optimum halogen balance can be found [207].

When bromide-containing water is treated with oxidants (chlorination and ozonation) disinfection by-products (DBPs) are formed. This involves the conversion of bromide ion to trihalomethanes (THMs), halogenated acetic acids (HAAs), and other halogenated organic compounds as well as bromate (BrO_3^-). These are claimed to be even more harmful than their chlorinated analogues [202]. The THMs have even been identified as possible carcinogens [205].

THMs are the most common DBPs in halogen treated waters, and they are also used as indicators for the total DBPs. THM formation has been found to be enhanced when water contains bromide. Bromide is not efficiently removed in water treatment processes, a factor which results in increased bromide/TOC ratio in the process and the increased formation of brominated DBPs. It is evident that bromide ion concentration decreases in water treatment processes but the total bromine concentration is conservative [202]. Chloroform is typically the dominant THM species in bromide-free waters, but in bromine containing waters brominated THMs can account for 60 to 100% of the total THM. Typically bromoform is the predominant compound with approximately half of the THMs but also bromodichloromethane and chlorodibromomethane can be the main bromine species. It has been shown that bromochloro-, bromodichloro-, and dibromochloroacetic acid are formed when bromide is added to humic substances that have been extracted from surface water or groundwater [211]. It seems that the active part of the organics are humic and fulvic acids that originate from decaying matter [212].

Bromoform formation can be higher than chloroform formation with low bromide concentrations. The highest concentrations for brominated THMs have been found as a result of water chlorination alone or in combination with ozonation or UV treatment [202]. Bromoform and dibromochloromethane have been detected in chlorinated swimming pools [213].

Also halonitromethanes (HNMs) have been observed to be formed. Increase in pH and bromide concentrations increases HNM and THM formation during ozonation-chlorination. [214]

In one study dealing with surface and ground water treatment, bromine was found to be incorporated (in pH 6.5) 25% in THMs, 10% in HAAs and 12% in BrO^{-3}, but these proportions were dependent on the pH [203]. The THM proportion was increased and HAA proportion decreased when the pH was increased to 8.5.

Pools and spas are the most widespread use of bromine as a disinfectant in non-industrial use [150]. The co-use in compounds with chlorine is increasing in this sector as bromine is perceived as a gentler disinfectant than chlorine [149]. With an effective oxidizer only small amounts of bromine can be used [194].

The presence of microbes in paper machine circulation waters is inevitable. They are in principle of two different types: sessile (attached to the surfaces) or planktonic (free-swimming) [210]. The environment in paper mills is favourable for microbial life [215]. Grinding of wood releases carbohydrates and the processes often use starch (used as an adhesive and sizing agent to improve strength and printing properties). These are utilised as nutrients by micro-organisms. Temperatures of paper machine waters are typically between 30 and 55 °C in pH from 4 to 8. These conditions are similar to those used in micro-organism incubators. [210]

Almost all microorganisms live in aggregates that are also called biofilms. In paper machines biofilms lead to spots and holes in paper and cause web breaks when slime lumps come off from the machine surfaces. These slime deposits can be several centimetres thick. Microorganisms interfere also by causing smell problems and corrosion in anaerobic conditions as well as by degrading additives; polymers, starch, fillers and furnish [210]. Products such as food and liquid packaging must be free of microbes and spores.

For these reasons biocides are used in the fresh water, in the recirculation loop (short circuit), in the recovered water (long circuit) and in the additive (filler, coating, colorant) treatment [210]. They prevent microbial growth or kill the organisms. The biocidal operations include long term biocide use in the process waters as well as ‘shock treatment’ [216]. The paper industry is estimated to spend about 200 million Euros annually on slime control [210].

There are two fundamentally different classes of biocides; oxidizing and non-oxidizing. Oxidizing biocides are divided in two: halogenated and non-halogenated. Oxidants are characterised by quick-killing biocides. These cause damage non-specifically to any organic substances in the process waters. Oxidants can also decrease anaerobic bacteria and odour problems. The majority of paper machines use oxidation in fresh water treatment. Machines are increasingly using halogen based oxidants also in the recirculation loop (short circuit) and recovered water (long circuit) machines. The pH of the process waters favour the use of HOBr than HOCl since HOBr dissociates at a higher pH. [210]

The treatments are typically halogen based via hypochlorite, sodium bromide, 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) combinations. Some of the treatment locations in paper machine include the wet end showers or addition of biocides in storage tanks. Biocides such as 2-bromo-2-nitropropane-1,3-diol (Bronopol) and 2,2-dibromo-3-nitrilopropionamide (DBNPA) work much more effectively in an oxidising environment than in reducing conditions.

In cooling water applications the most common bromine compounds are BCDMH and mixtures of sodium bromide with sodium hypochlorite. [149]

Brominated agents are also used in cosmetics, sunscreens, shampoos, shower gels and wet-wipe hand towels. From those uses they inevitably end in the sewage system and also sludge. Other relevant products include dishwashing liquids, household cleaning detergents, wax and other polishing preparations for floors. The most commonly used preservatives and biocides, for example in skin creams or domestic cleaning agents, are Bronopol, 5-bromo-2-nitro-1,3-dioxane (Bronidox) and 1,2-dibromo-2,4-dicyanobutane (Methyldibromo glutaronitrile, MDBGN). [217–223]

Only very few figures were found regarding bromine content of wastewater sludge. These values indicate the content in the range of 20–120 mg kg^{-1}. These sludges originated mostly from paper mill wastewater treatment where bromine was used at least for treatment of mill process water [120,182,224–226]. In domestic sewage sludge samples between 45 and 70 mg kg^{-1} Br was found and in industrial sludge < 10 mg kg^{-1} in one study [120]. In wastewater sludge samples from 5 thin film transistor-liquid crystal display (TFT-LCD) factories bromine was found from 2 300 to 4 400 mg kg^{-1} [227].

4. Experimental procedures (Papers III–VI)

4.1 Bubbling fluidised bed boiler

Stora Enso Anjalankoski co-incineration plant, where the combustion experiments discussed in Papers III–VI were carried out, started as a pulverised coal fired boiler in 1971 with a small fixed grate for bark combustion. The first commercial size bubbling fluidised bed (BFB) boiler in Finland was connected to this coal boiler in 1983 to combust wet sludge from the adjacent paper mill's wastewater treatment. The grate of the coal boiler was converted to a BFB in 1995. A wet scrubber was also installed after the electrostatic precipitator (ESP) to improve flue gas cleaning and establish heat recovery from the flue gases. With this flue gas cleaning system the plant could comply with the EU Waste Incineration Directive (WID) [3] emission limits.

After the start-up of the 80 MW_{th} BFB, co-combustion of SRF was initiated in order to manage the paper mill's waste treatment, and was later widened to the use of acquired package wastes which could not be recycled. Simultaneously, the boiler live steam values were reduced to the level of 500 °C / 80 bar from 525 °C / 87 bar. The lowered superheater temperature was to allow a safety margin for more corrosive combustion gases in comparison to coal firing. In the current steam conditions the boiler waterwall fluid temperature is estimated to be close to 300 °C and the waterwall gas-side surface close to 350 °C (see Paper III and Chapter 5.4 of this thesis).

Plant invested in an indirect thermal sludge dryer in the year 2000 in order to combust all the paper mill's waste water sludge with a dry matter content of about 90%. This also made it possible to increase the amount of SRF in the fuel mix, due to the sludge's favourable influence on chlorine-induced corrosion. In 2006 the boiler received a new environmental permit according to the WID with an annual SRF capacity of 50 000 tonnes. The SRF share in the fuel mix was increased to 60% (on energy basis) after long term tests and investigations.

The boiler utilises on average 30% Scandinavian spruce bark and 10% dried paper mill sludge together with SRF on energy basis. All the fuels are introduced in the boiler house in separate streams. From the fuel receiving pocket outside the boiler house (wherefrom the bark was sampled), bark is fed by a conveyor belt in the boiler house where it is forwarded to a scraper conveyor. From there it is discharged through screws into two parallel 5 m^3 buffer fuel hoppers. The bark feed in the fuel mix is adjusted by discharge screw feeders under the two hoppers which feed bark into the furnace through two parallel fuel chutes equipped with rotary feeders. SRF is forwarded after crushing and an intermediate storage silo in the boiler house by a series of scraper conveyors. Fuel sampling during the experimental campaigns was carried out from the discharge of the intermediate silo. In the boiler house SRF is then discharged from the scraper conveyor by screws which forward the fuel in the same two fuel chutes where bark is fed on the left wall (Papers III and VI) and on left and right wall (Papers IV and V) of the furnace (in Paper III and VI experiments there was fuel feeding through the left wall only). Both, the bark and the SRF discharge screws have been calibrated for the volumetric production per revolution which enables accurate fuel proportioning in the two parallel fuel chutes, and eventually in the furnace.

The paper mill wastewater sludge is supplied from the wastewater treatment to a drying process. This consists of a series of mechanical (press) and thermal driers. The final indirect thermal drier feeds a pneumatic transportation line (at this location the sludge was sampled), which takes the dried sludge into the boiler house in a dry matter content of approximately 90 wt-% and the line blows the sludge directly into the furnace through the front wall.

The furnace size is approximately 8 x 8 x 30 m. Fuel feeding takes place at the height of 3.5 m form the grate, secondary air feeding 5.5 m and tertiary air 15 m height from the grate. The secondary (radiative) superheater is located after the nose at the height of 21 metres from the grate. This is followed by tertiary superheater and primary superheaters in combustion gas flow direction. In the second pass are located the economizers and air pre-heaters. In the experiments the target for air distribution was 50%–35%–15% fluidizing-secondary-tertiary air, respectively and the operating capacity close to 80 MW_{th}.

The ESP consists of two parallel lines in the flue gas flow direction, both with two sequential fields. Ash is forwarded from a hopper below each of the four sections of the ESP by pneumatic transportation to a discharge platform. As the hoppers reach a certain level of fill-up, pneumatic transportation takes place automatically. Fly ash was sampled form each of the four lines during the pneumatic sending procedure. Samples were sucked from the line by a vacuum cleaner and combined into one sample.

4.2 Formation of fine particles

In this work the terms ‘fine particle’, ‘aerosol’ and ‘vapour’ are used in parallel. ‘Fine particles’ are meant by particles with a diameter (dp) less than 1 μm. Often in the literature this is also meant by particles with dp < 2.5 μm. Aerosol is generally meant by a suspension of particles or droplets in gas. Therefore a suspension of fine particles is often referred to as aerosol. In this work vapours are meant by gases close to their saturation pressure and temperature. All these terms are interlinked in high temperature sampling of ash forming elements: in the conditions prevailing in a combustor furnace the ash-forming elements (in focus in this thesis) are in the gas phase as vapours. These form fine particles when supercooled in the convection pass or in the extraction from the furnace by aerosol sampling probe. This results in the formation of an aerosol. Fine articles relevant for combustion can be divided in two classes:

i) Those particles that are emitted from the combustion unit as particles. These are defined as ‘primary particles’.

ii) Those particles that are formed in atmospheric processes from the plume of flue gases, defined as ‘secondary particles’.

In this work the focus is only on the primary particles, and their gas-phase precursors. Primary fine particles can be divided in three classes: ash, soot (elemental carbon) and organic material [228,229]. In this work only the inorganic ash forming fine particles are discussed.

The size classification used in this work is based on the aerodynamic diameter corresponding to a spherical particle with standard density that has the same settling velocity as the particle in question [230].

As the measure of fine particle concentration the number and mass-size distributions are frequently used. In this work where the composition of the inorganic vapours and their concentrations in the aerosol are of interest, the mass-size distribution charts are used.

Homogeneous nucleation, or simply ‘nucleation’, is the formation of new particles from the gas phase due vapour-molecule collisions. These clusters grow to form particles in supersaturated conditions where the growth rate of the particle clusters is faster then the dissociation. Supersaturation may take place in combustion systems for example by temperature decrease, oxidation or through chemical reactions. The particles formed are very small, in the range of 0.01–0.1 µm. In heterogeneous nucleation preferential sites assist in the formation of molecular clusters by reducing the energy needed to form a stable (spherical) cluster.

The typical particle growth mechanism after the formation of particles by nucleation are condensation and agglomeration [231]. Also chemical reaction on the surface and adsorption of molecules may take place. Condensation is meant by heterogeneous condensation where submicron particles grow by condensation of vapours on particle surface. Generally the saturation ratios required for condensation are smaller than for the homogeneous nucleation [229]. In agglomeration the submicron particles stick together to form irregular clusters [232].

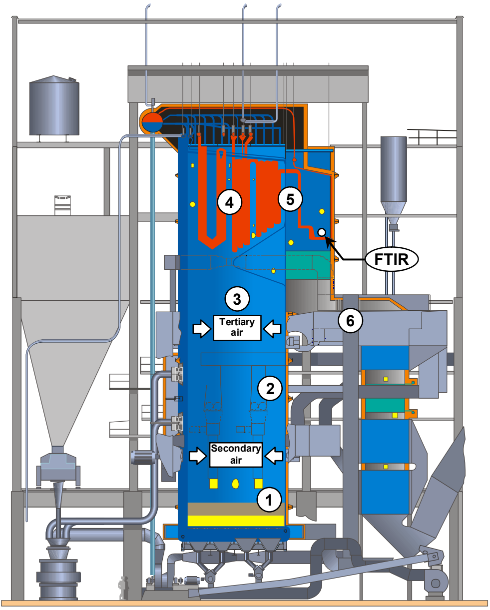
The formation of fine particles from volatilised ash-forming matter is qualitatively well known [231,233–235], but all detailed phenomena involved in nucleation are still not resolved [236]. Fine particle formation sampled from high temperatures has been reported for different combustion systems [232,237–241] where it has been shown that the fine particles formed from vaporised ash-forming elements are clusters with primary particle size of dp = 0.05–0.25 µm.

4.3 Fine particle and gas sampling

In the experiments fine particle samples were collected from the locations indicated in Table 6. The sampling was carried out with a combination of an air cooled gas permeable tube probe and two consecutive ejector diluters.

The sample gas is sucked into the probe and immediately diluted and quenched within a 200 mm long gas permeable tube diluter. This dilution stage was carried out with nitrogen with a target dilution ratio of DR = 8. The sample gas was taken from the probe to a second dilution stage carried out by means of an ejector diluter with DR = 3 and then divided between two parallel Dekati type Low Pressure Impactors (DLPI) and an Electric Low Pressure Impactor (ELPI). At the location of the division a third gas stream was taken to an FTIR gas analyser for determining the dilution ratio based on H_2O and CO_2 (target value DR = 24). The reference H_2O and CO_2 concentration for determining the total dilution ratio was taken from the FTIR located in the second pass. This means that the concentrations in combustion gases presented for the different species are all reduced to the conditions prevailing at the second pass FTIR. Both aerosol sampling lines (for DLPI & ELPI) included a cyclone separator with 10 µm cut-size. The two DLPIs were connected in parallel and were collecting sample after this cyclone and ELPI after the third stage dilution that was carried out by means of an ejector diluter with DR = 11. All the dilution stages utilised 5.0 nitrogen for dilution. A schematic picture of the sampling arrangement is shown in Figure 16. The collection membranes in the impactor were Nuclepore polycarbonate membranes which were greased by spraying Apiezon L on the particle collection sites positioned below the DLPI jet plates in order to enhance particle adhesion. The filters after the impactor stages were PTFE Pall Teflo type filters.

Table 6. Description of the measurement locations, with reference to the schematic boiler picture. Paper VI.

	Description	**T_{gas}, °C**	
FTIR	2^{nd} pass.	480	
6	In the 2^{nd} pass, downstream from the first economizer.	371	
5	Downstream from the superheaters.	580	
4	In between the superheater tube banks.	740	
3	Downstream from the tertiary air feed.	940	
2	Downstream from the secondary air feed.	950	
1	Above the bed / splash zone.	835	

After the sampling of fine particles the impactor membranes were placed in sample tubes. To determine the water soluble elements the samples were first extracted for five days with water at room temperature. The tubes were shaken every now and then. Then the sample tubes were hold two hours in ultrasonic bath and two hours on a vertical-shaft mixer before extraction to the analyser.

The concentrations of Na^+, K^+ and Ca^{2+} in the solutions were determined by Flame Atomic Absorption Spectrometry (FAAS) and the concentrations of Cl^-, Br^- and SO_4^{2-} by Ion Chromatography (IC). Also ICP-MS was used for the water soluble elemental analyses in the results reported in Papers IV and VI. The acid soluble composition was determined by means of ICP-MS after HF-HNO_3 digestion. In the digestion the samples were let to digest for a total of 48 + 48 hours and were shaken in between. The samples were shaken well again and the composition was determined by means of Perkin-Elmer Sciex Elan 6 000 ICP-MS.

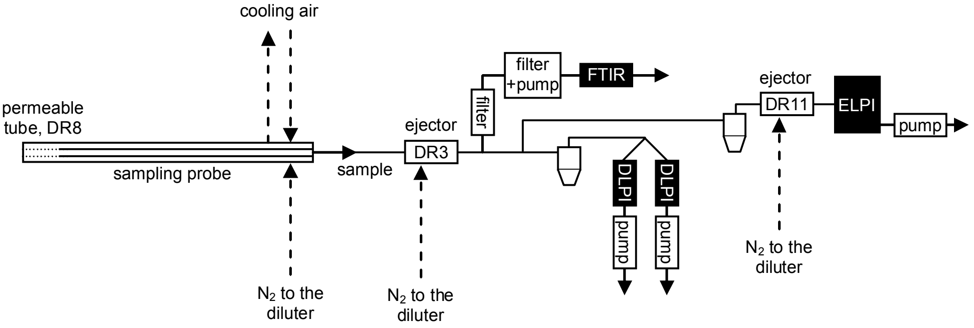


Figure 16. A schematic picture of the aerosol sampling installation.

For the determinations of gaseous species in the combustion gases such as CO, CO_2, NO, NO_2, N_2O, HCl, HBr, H_2O the FTIR [242] was used. In the work reported in Papers IV and V a gas sample was collected also to chromatograph analysis [243,244] from the exhaust of the FTIR. The possible reduced gaseous species, shown to be mainly H_2S, were measured my means of Photovac Voyager [245] gas chromatograph equipped with Photo Ionization Detector (PID) [244].

Particle losses in such sampling setup are discussed here thorough establishing the chlorine balance for the measured BFB boiler based on data in Paper III. Figure 17 shows the chlorine balance for the superheater region of the boiler. This is convenient as Cl is the main element in the fine particles/aerosols ($dp < 1.6$ µm), it is present in relatively large concentration in the fuel and its conversion to gas the phase is typically close to 100%. It can be seen that the Cl balance is satisfactorily closed. The horizontal line gives the maximum theoreticl Cl concentration in the combustion gases providing that all the Cl forms gaseous MCl where M is typically K, Na or H. The anion-cation ratio (atomic basis) (Cl+Br+2S)/(Na+K+2Ca) for the $dp < 1.6$ µm aerosol fraction were between 1.0 and 1.1. The ratio (Cl+Br)/(Na+K) ranged between 0.8 and 1.0.

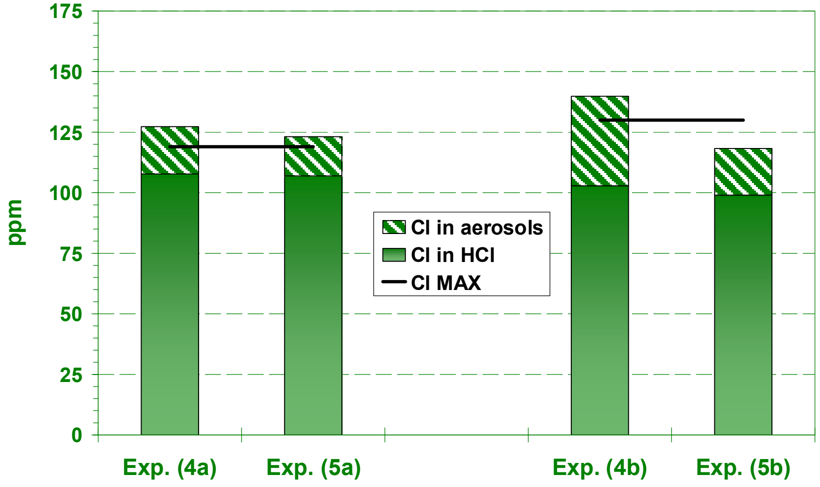


Figure 17. Chlorine balance in the superheater of the BFB boiler. Location (4): entrance, Location (5): exit of superheater are. Y-axis in ppm on volume basis.

4.4 The fuels used

The chemical fractionation procedure was applied in the characterisation of the ash forming matter in the fuels. The fractionation is based on the consecutive leaching with water, ammonium acetate, and hydrochloric acid. The method was originally developed for the characterization of coal [57,58] and further modified for and applied to the characterization of biomass fuels [53,59,60]. Increasingly aggressive solvents, i.e., water (H_2O), 1 M ammonium acetate (NH_4Ac), and 1 M hydrochloric acid (HCl) leach samples into a series of four fractions (including the insoluble residue) for analysis. Typical ash-forming components which are leached out by water include alkali metal salts: sulfates, carbonates, and chlorides. Elements leached out by NH_4Ac are believed to be organically associated, such as magnesium, calcium, potassium and sodium, or weak acid soluble salts. HCl leaches the carbonates and sulfates of alkaline earth and other metals. Typically silicates and other minerals remain in the insoluble residue; however, chemical reactions of the ash forming matter during digestion may alter the speciation. Therefore the results should be used with caution and to complement other available analysis data.

The spruce bark used originates from the paper mill adjacent to the BFB where the stem wood is used for mechanical pulping. The wood is Norway Spruce (*Picea abies* L.) of which a detailed study regarding its ash forming matter can be found in the literature [54]. The main ash forming elements are Ca, K and Na, see Figure 3. Compared to stem wood bark is rich in these nutrients. In the bark K and Na exist mainly as water soluble salts, and Ca in equal proportion as ion exchangeable ions and HCl soluble included mineral, namely calcium oxalate [54]. Br and S content in the bark are very small. During the experimental campaign bark, and the mixture of bark and sludge in Experiment (b) (see Table 7), were collected from the conveyor belt taking the fuel into the boiler house.

The paper mill wastewater sludge consists of wood fibre residue, paper filler and coating rejects which are mainly kaolin and calcium carbonate as well as residues of flocking agents. In the wastewater treatment some 30– 40 kg of iron(III) sulphate per ton of dry sludge is added to the wastewater stream to precipitate out non-settleable solids. In addition, ash forming matter in the sludge originates from alum, namely aluminium(III)sulphate, which is used in pH control and as a sizing agent in paper making [215]. Regarding the main salt forming matter, Ca is the main component, originating either from the filler/coating residues or from wood fibre reject. In contrast to the bark, the sludge contains Ca mainly (80%) in NH_4Ac soluble form. This is probably due to the partial dissolution of calcium carbonate already in the weak acid; this step does not dissolve all the carbonate, however. The residual $CaCO_3$ is dissolved in the mineral acid, HCl, as no insoluble Ca residue was found. Regarding the acid soluble fraction, it is noteworthy that calcium oxalate is absent from the stem wood, which essentially forms the wood fibre reject, but is abundant in the bark [54], which implies that almost all the HCl soluble Ca originates from the $CaCO_3$ paper filler/pigment. Na exists mainly as water soluble and K as insoluble compounds. The interpretation for the sulphur fractionation result is not fully clear or well established. It is likely that sulphur in the sludge is bound in a reduced form as a result of the activity of sulphur reducing bacteria (SRB) [246,247]. If all the S in the iron(III)sulphate added in the wastewater treatment is calculated back to be a concentration per unit of dry sludge, it results in residual S concentration of 0.68 wt-% which already is quite close to the concentration found in the sludge (0.73 wt-%, see Figure 18, p. 79). This indicates that a high proportion of the S in the sludge originates from the flocking agent ferric sulphate.

The SRF utilised at the BFB plant originates from offices, wholesale business and small and middle scale industry in southern Finland [9]. Suitable wastes are source-separated package and other solid industrial non-recyclable wastes, which are separately collected by the SFR supplier. In offices and commerce the source of this fuel can be identified from the waste bins labelled ‘energy fraction’. The labelling instructs the consumer to sort in this fraction the following items: packaging plastics (not PVC), contaminated paper & cardboard, wooden packages, plastics (not PVC), expanded polystyrene, paper towels and clothes & textile. Naturally, in the collection of the waste it is ultimately the consumer decision at the trash bin that dictates which items end up in the energy fraction. The fractions collected from commerce (shopping centres, supermarkets) are mostly packaging materials, i.e. paper, cardboard and plastics in various forms. Industry sourced energy fractions are different types of demolition and packaging discards with production wastes from furniture manufacturing. These contain mainly textiles, wood and plastics. In the SRF preparation plant the material is crushed to 50–100 mm particle size and magnetic materials are separated. SRF is transported to the BFB plant as wrapped bales or fluff.

SRF is the main source of Cl and Br in the final fuel mix. The leaching behaviour of Br and Cl is similar: both are found mainly in the insoluble residue. SRF is also the main source of Na in the fuel mix, which is bound in water soluble form. This is likely to be residual dietary salt from disposed food packages. K and S are almost equally distributed between water soluble and insoluble fractions, with a minor proportion found in Ac and HCl fractions. Ca is found mainly in the Ac soluble fraction with small but equal proportions in water and acid soluble fractions. This is in alignment with the high proportion of Ca found in Ac soluble form in the sludge: the main Ca source in SRF is packaging material i.e. paper and cardboard: see Table 1, which contains only the stem wood fibres as well as $CaCO_3$ applied as paper & cardboard filler and coating material. The other sources include gypsum from construction and demolition waste, as well as calcium carbonate in plastics additives (surface treatment and filler). However, the latter two must be small in comparison to paper and cardboard fillers and coatings.

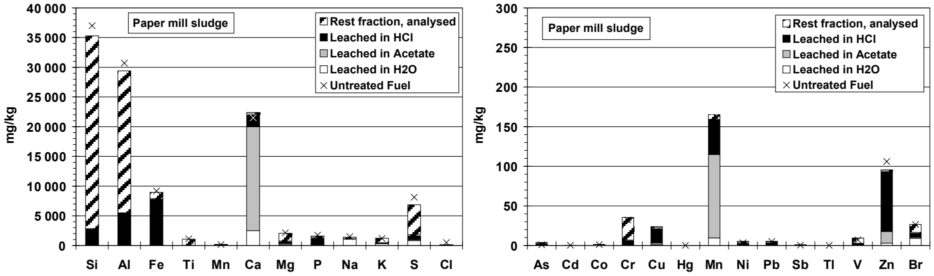


Figure 18. Chemical fractionation result of the paper mill sludge.

Three fuel mixtures were used in the experiments, see Table 7. Papers III and VI present results from Experiments (a) and (b), and Papers IV and V from Experiment (Wall). During the Experiments (a) and (b) fine particle sampling was carried out at several different locations in the boiler, and in the Experiment (Wall) only the conditions just next to the waterwalls were measured.

The SRF-Bark proportion was kept as constant as possible in all experiments, on a dry mass basis of 50%–50%. The proportion of the sludge from the total fuel mix was approximately 15% in Experiment (a) and 4–5% in Experiments (b) and (Wall), respectively, and the rest was composed of the SRF-Bark mix. In Experiment (b) wet sludge was fed in the boiler by mixing it with the SRF-Bark. In other experiments the pneumatic system was used.

Table 7. The properties of the fuel mixes used in the experiments. On dry mass basis the fuels consisted of: Experiment (a) 42%–43%–15%, Experiment (b) 51%–45%–4% and Experiment (Wall) 48%–46%–5% SRF-bark-sludge, respectively. Papers III–VI.

	Exp.(a)	Exp. (b)	Exp. (Wall)
Moisture (wt-%, ar)	38.6	42.7	36.5
Ash (wt-%, ds)	7.2	5.6	9.9
IN DRY SOLIDS (wt-%)			
C	51	52.4	52.2
H	6.5	6.7	7.1
N	0.69	0.43	1
S	0.18	0.12	0.16
O	34.4	34.6	29.2
IN DRY SOLIDS (mg kg^{-1})			
Al	7093	4343	1900
Ba	289	270	170
Br	25	110	80
Ca	13908	13925	17100
Cd	0	0	0
Cl	2100	2300	5280
Cr	68	33	40
Cu	151	17	140
Fe	2070	1158	2080
K	1470	1445	1470
Mg	1213	1004	1260
Mn	247	241	160
Na	1042	1186	1860
Ni	61	22	10
P	476	337	500
Pb	19	14	70
Sb	16	16	150
Si	10065	6814	9090
Sn	3	1	5
Zn	302	179	280
HEATING VALUE (MJ kg^{-1})			
LHV, db	20.54	21.17	21.1
LHV, ar	11.68	11.08	12.5

5. Experimental results (Papers III–VI)

5.1 Bromine in the fuels used (Papers III and IV)

The bromine and chlorine contents in the SRF during the Experiment (a) and Experiment (b) published in Paper III are shown in Figure 19 (labelled as experiments I and II, respectively, in Paper III). The bromine content varies from about 20 up to 520 mg kg^{-1} during the campaign but is mainly below 100 mg kg^{-1}. Chlorine content in the corresponding samples is also shown. It is obvious from the chart that the Br content is fluctuating highly in the feedstock which is typical for SRF.

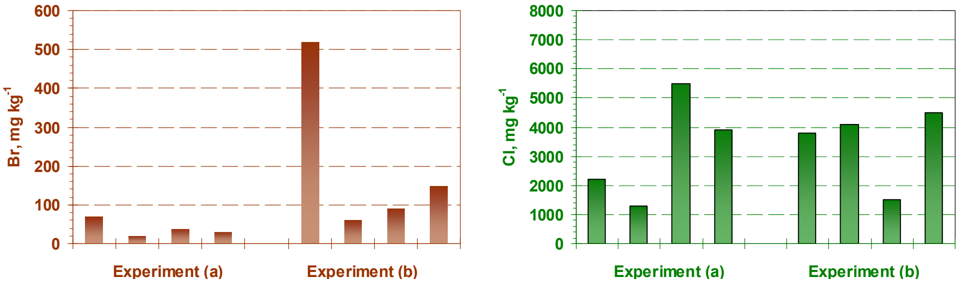


Figure 19. Bromine (left) and chlorine (right) content in the SRF during the Experiment (a) and (b). Four representative samples were collected during both experiments.

Figure 20 shows the bromine content variations in three different Finnish SRF qualities for a period of two years as sampled from SRF production facilities. Regarding corrosion and long term use of SRF in full scale boilers the long term concentrations are more relevant and representative than those obtained in a short campaign. The Br content 60 mg kg^{-1} is used as the average value for the

SRF used in the experimental campaign in Paper IV as the SRF originates from the SRF plant 3.

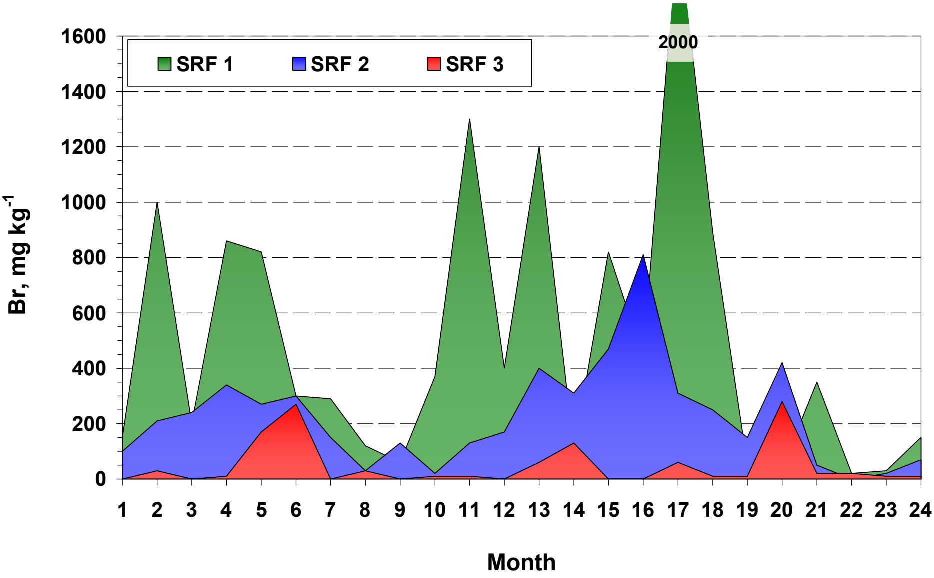


Figure 20. Bromine content in monthly quality control samples of three Finnish SRFs. Courtesy of Lassila&Tikanoja Oyj.

Cl in SRF originates mainly from chlorinated plastics such as PVC or food residues which contain dietary salt [7,180]. As explained in Chapter 3.2 chlorine is used in flame retardants [181]. With reference to the work published in Paper II and summarised in Chapters 3.2.3 and 3.2.4 of this thesis regarding the sources of bromine it has been shown [8] that the proportion of plastics and textiles in SRF can be significantly higher than in MSW. Both of these fractions are used in applications and products where flame retardancy is required. Therefore, the likely sources of bromine in solid wastes are brominated flame retardants [183]. In SRF bromine is bound in the organic matrix and is in a reactive form [184] in a similar way than Cl in PVC plastic.

Regarding the fuel mixture it is also possible that Br can originate to a large extent from the sludge, as Br is commonly used in water treatment [150,206,210], particularly in the pulp, paper and cardboard mills in slime control [215,216].

Figure 21 shows chemical fractionation results for bromine in the wastewater sludge and in the SRF. These were given in Paper II. It can be seen that the bromine is not predominantly in water soluble form in the SRF, neither in the sludge, but rather in insoluble form. This indicates organic bromine speciation which supports the association in flame retardants as concluded in Paper II.

The bromine content in the sludge was found to vary between 30 and 110 mg kg^{-1}. In the case of the sludge bromine is also to a large extent in insoluble form. This supports the findings in the Paper II where bromine was concluded to be found in the halomethanes and haloacetic acids in addition to the hypobromous ion (BrO^-) and hypobromous acid (HOBr). The speciation of bromine is strongly correlated with the pH, also the association in organic matter [248]. It is left unclear after the fractionation to what extent the soluble bromine is due to dissolved organic matter.

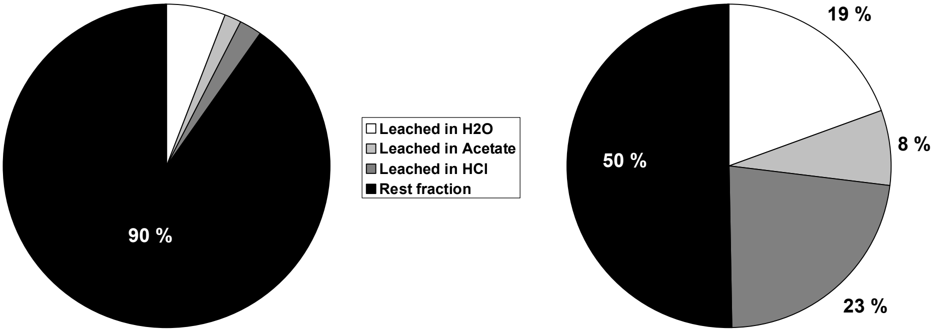


Figure 21. Chemical fractionation results for Br. SRF (left) and paper mill wastewater sludge (right). Data taken from [224].

5.2 Bromine in the fly ash (Paper III)

In Figure 22 (Paper III) curves for the saturation pressures are shown and in Table 8 the melting points of selected bromides and chlorides are listed. Data of these specific salts were selected based on the fact that the cations are those that typically can be found in fractions 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) [249,250]. Iron chloride and iron bromide are potential corrosion products.

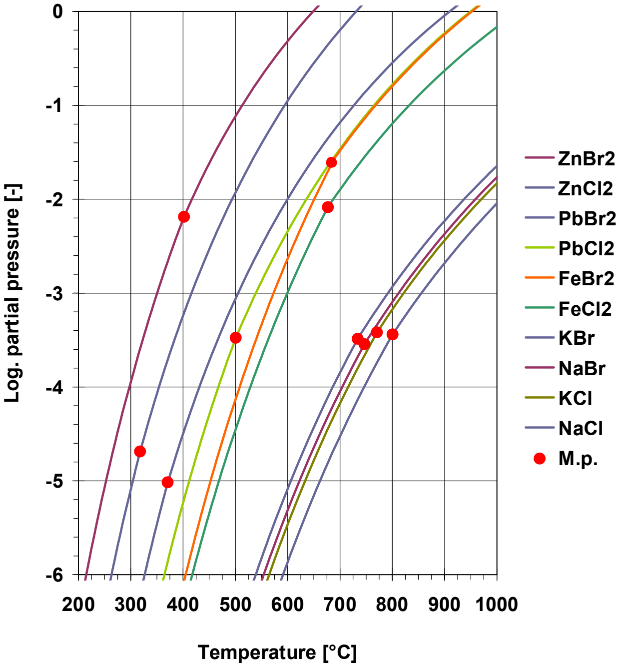


Figure 22. Calculated saturation pressures and melting points (M.p.) for selected chlorides and bromides [251]. Paper III.

From the saturation curves it can be seen that bromine forms compounds with K, Na, Zn, Pb and Fe with a very similar volatilisation character to corresponding chlorides. 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 8 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.

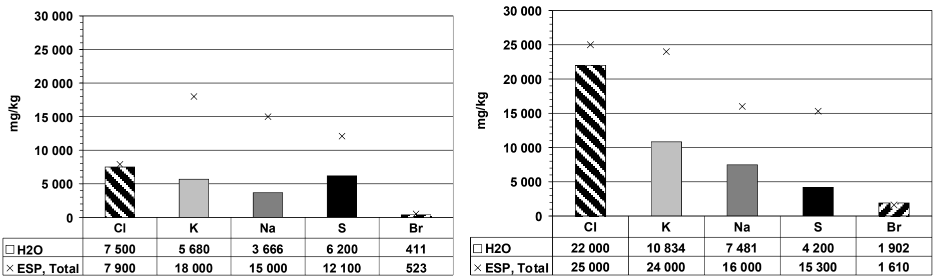
The deposits in boilers are always mixtures of different salts. The first melting temperature of a salt mixture is in most cases lower than the melting point of the pure salts that the mixture consists of. Chlorides are known to lower the first melting point of sulphate rich deposits, and it is reasonable to expect a similar effect of bromides.

Table 8. Melting points [40,251] of selected chlorine and bromine salts relevant to SRF co-firing [31,40,252]. Paper III.

Compound	Melting point, °C	Compound	Melting point, °C
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 character of the two halogens (Cl and Br) present in the fly ash is similar in terms of the solubility in water, see Figure 23. The same chemical fractionation method was applied for the fly ash as for the fuels (described in Paper III).

The halogens are forming compounds that are water soluble. Excluding Ca, the atomic ratios (Cl+Br)/(Na+K) for the water soluble fractions in fly ash were 0.7 and 1.0 for Experiments (a) and (b), respectively. To account for the S, the anion-cation balance can be rewritten to (Cl + Br + 2S)/(Na + K) which gives 1.9 and 1.4 for Experiments (a) and (b), respectively. These indices indicate that more sulphates were formed in Experiment (a) than in Experiment (b), and that there are enough halogens in Experiment (b) for all Na and K to form the corresponding halides. In Experiment (a) some 30% of the Na+K seem to have formed sulphates. Br is found in higher concentration in the fly ash in Experiment (b) than Experiment (a). This is due to two complementing reasons: Br was found in higher concentration in the SRF during Experiment (b), and, due to the reduced proportion of the high sulphur sludge in the fuel mix, higher concentrations of halogen salts are formed in relation to sulphates. The higher concentration of the elements in the fly ash can not only be explained due to the higher overall ash content in the fuel mixture in Experiment (a), i.e. dilution of fly ash by sludge ash. Cl concentration in the SRF, and consequently in the fuel mix, was on average the same on both days.



	Cl	K	Na	S	Br
☐ H2O	7 500	5 680	3 666	6 200	411
× ESP, Total	7 900	18 000	15 000	12 100	523

	Cl	K	Na	S	Br
☐ H2O	22 000	10 834	7 481	4 200	1 902
× ESP, Total	25 000	24 000	16 000	15 300	1 610

Figure 23. Total concentration (cross) and water solubility (bar) of the main aerosol forming elements in the ESP ash (dry solids). Left: Experiment (a), right: Experiment (b).

5.3 Bromine bearing salt vapours (Papers III–VI)

Chlorides have been frequently in the focus when thermodynamic equilibrium modelling has been applied in ash behaviour characterization [28,253–256]. As the fine particle sampling procedure applied in this work can only give the bulk composition of the particulate matter the objective in the modelling was to estimate the most likely forms of the fine particle forming elements at the conditions prevailing in different sampling locations. The thermodynamic software package Factsage version 6.1 [257] was used in modelling of the ash chemistry in Paper VI. The FACT53 database for stoichiometric condensed phases and the gas phase was used. All compounds in the database were considered, except for nitrogen compounds, where N_2 was the only nitrogen compound considered. It is known that thermodynamic equilibrium modelling does not predict nitrogen chemistry at combustion conditions satisfactorily. No non-ideal liquid solutions, such as a molten salt, were included.

Regarding the vapours, three conditions were used in the modelling in Paper VI: 1) 950 °C reducing, 2) 950 °C oxidizing and 3) 750 °C oxidizing. These were selected to represent the conditions in the lower and upper furnace in a simplified manner (with reference to Table 6). For the calculations of the oxidizing conditions, air was added to the elemental input at an air-fuel ratio of 1.4, which results in roughly 5 vol-% O_2 in the wet flue gas. In the reducing case, no air was added.

Figure 24 shows the estimated forms of bromine in different furnace conditions. Based on the equilibrium modelling at 950 °C gaseous KBr is the dominating Br species, complemented by NaBr(g). This applies for both reducing and oxidizing conditions. While the combustion gases are cooled down $CuBr_3(g)$ is estimated to be formed, dominating the speciation of bromine at 750 °C followed by KBr(g) and NaBr(g). Considering the trace element chemistry, if Na and K are excluded, $CuBr_3$(g) is by far the dominating Br bearing compound followed by HBr(g) and Br(g). Minor amounts of $BaBr_2$(g) and $ZnBr_2$(g) were also estimated to be formed.

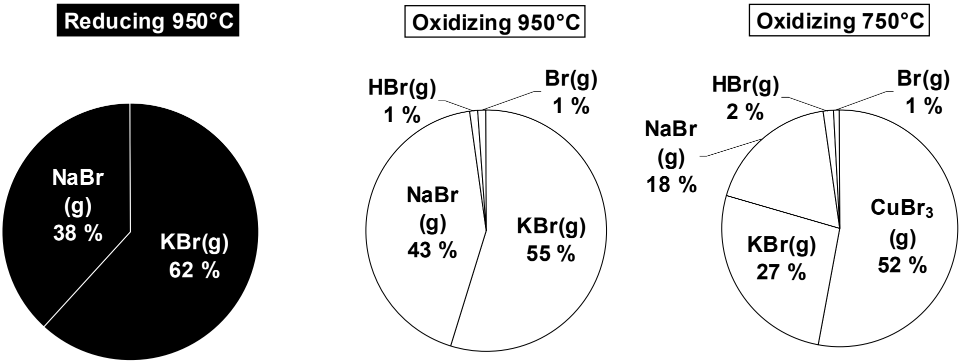


Figure 24. Estimated forms of bromine in the combustion gases in the conditions and with the fuel mixtures used in the experiments presented in Paper VI.

Aerosol samples were collected (as presented in Paper III) from the superheater region in locations indicated in Table 6, i.e. location (4) and (5). Water soluble Br, SO_4, Na, K, Ca and Cl were analysed from the impactor sample membranes and the corresponding concentrations for the superheater region samples are shown in Figure 25 (from Paper III). The fine mode, i.e. here particles with an aerodynamic diameter less than 1.6 µm, consisted mainly of Cl, K, Na and SO_4. Sulphate was found in higher concentration in Experiment (a) than in Experiment (b). This is also in alignment with the findings from the ESP ash leaching results. Sulphur is shown in these figures in the form of sulphate as a realistic picture is obtained of the total elemental yield on each membrane stage. If the same figures are redrawn on an molar basis the proportion of sulphur is visually reduced due to the high molar mass of sulphate.

The atomic ratio (Cl+Br)/(Na+K) for the submicron fraction in Experiment (a) (location 4 and 5, respectively) is 0.8 and 0.9. For Experiment (b) the corresponding value is 1.0 for both locations. These are in good alignment with the findings in the ESP ash where the (Cl+Br)/(Na+K) ratio also had values at 1.0 for Experiment (b) and 0.7 for Experiment (a). Based on the aerosol sampling at least some 10 to 20% of the alkali metals have formed sulphates in Experiment

(a) and the rest are halides. (Cl+Br+2S)/(Na+K) values were 1.1 and 1.3 for Experiment (a) (location 4 and 5, respectively) and 1.2 for both locations in Experiment (b). This indicates that some two thirds of sulphur is bound in Na-K sulphates in location 4 and one fourth in location 5 (Experiment (a)). The rest is mainly bound as $CaSO_4$ if no $CaCl_2$ formation is assumed [258]. (Cl+Br+2S)/(Na+K+2Ca) ratio has values of 1.0 and 1.1 for location 4 and 5 submicron fractions, respectively, for both experiments. Based on these indices $CaSO_4$ formation is likely in the upper part of the furnace.

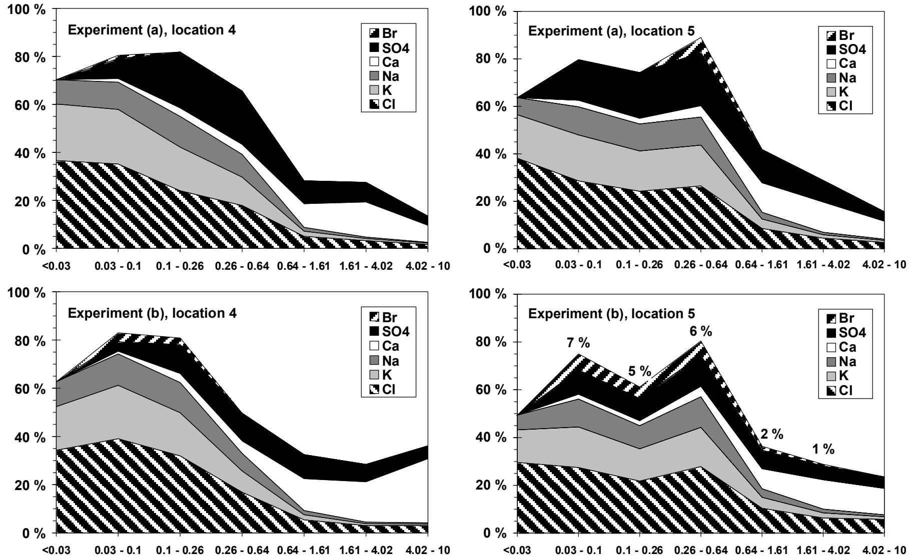


Figure 25. Composition as wt-% (on the vertical axis) of different particle size fractions (µm, horizontal axis) collected with the LPI. In the chart at bottom right the numbers indicate the weight percentage for Br in the corresponding particle size fraction. From Paper III.

Regarding bromine in Experiment (b), location (5) Br is one of the main elements in the aerosols. It can be calculated that approximately 10% on atomic basis of the halogens in submicron particles are bromides. In the fuel the proportion of Br from Cl+Br was 2% on atomic basis which indicates that Br is efficiently converted into vaporised salts. Figure 26 presents the conversion-% of fuel bound bromine and chlorine to vapours. Here the highly fluctuating Br content in the fuel must induce error in the results. However, particularly the conversion figures for the Experiment (b) are satisfactory, taking into account that the maximum concentration of Br in the combustion gases – based on full conversion of Br from fuel into gas phase – was less than 3 ppm. Conversion of Cl into vapours was relatively stable during the experiments.

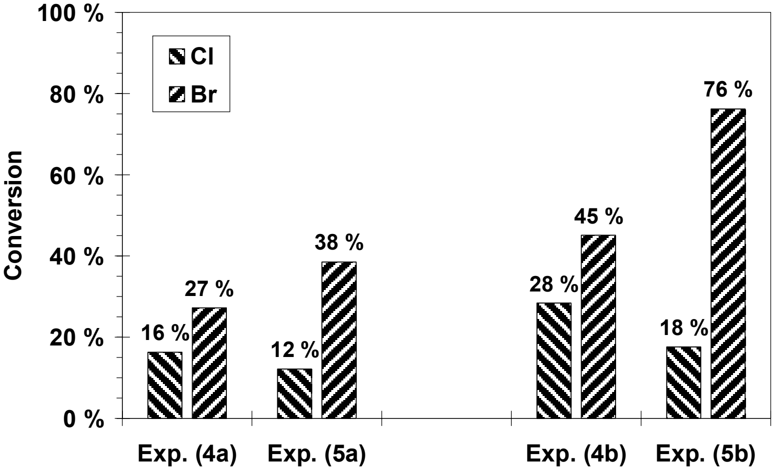


Figure 26. Conversions of Cl and Br into vapours (the submicron fraction of aerosols) in the superheater region of the BFB boiler. Paper III. X-axis: Each number refers to the sampling point and each letter to the experiment, see Table 6 and Table 7.

Excluding the main fine particle forming elements S, Na, K, and Cl in Paper VI the composition and concentration Br was discussed together with the ‘ main trace’ elements. By these are meant elements with the highest concentration in the fine particles after the above-mentioned main elements. Those elements were found to be Ba, Cr, Cu, Fe, Pb, Sb, Sn and Zn. Also thermodynamic equilibrium modelling was done to estimate the forms of these elements in the combustion gases.

The concentrations of fine particle forming elements in different locations of the BFB are presented in Figure 27. The concentrations are expressed in conditions prevailing at the 2nd pass FTIR (see Table 6), which makes the graphs directly comparable to each other. Bromine is found in the fine particle forming vapours already above the bubbling bed and the concentration was relatively consistent over the whole furnace height. This is supported by the modelling results in Figure 24 where Br is estimated to form alkali bromide in the conditions prevailing in the lower furnace and not significantly to change speciation before the exit of the superheater region.

Antimony, Sb, is found in bimodal distribution in the fine particles. It is found in the highest concentration when Br is also present, particularly in the fine mode. Sb is a commonly used flame retardant synergist [181]. For example in the US 42% of Sb was used in flame retardant applications in 2008 [259]. Nakamura et al. (1996) [260] found approximately 80% of the Sb originated from textiles and plastics in waste fuels. Some 10% could be allocated to glass. In flame retardants antimony [261] is in the form of antimony trioxide, Sb_2O_3, and in glass applications sodium antimonite, $NaSbO_3$, is used initially. Despite the likely co-existence of Br-Sb in the fuel, and appearance in the fine particles, the modelling does not suggest that they form salt together. Sb-halides exhibit very low melting points, as do the oxides (Sb_2O_3 655°C) which facilitate the occurrence in the fine mode. Thermodynamic modelling (Paper VI) suggests $Sb_2(g)$ and $Sb(g)$ for the main forms in reducing and $Sb_4O_6(g)$ and $SbO_2(s)$, $Sb_2O_4(g)$ as well as $Sb(OH)_2(g)$ in oxidizing conditions. [36]

Copper seems to have particular affinity to Br. Cu is found in all the sampling locations in the fine particles. On average Cu is found in the fuel mix concentrated in one order of magnitude higher in Experiment (a) than in Experiment (b) but this does not show through in the fine particle measurements. The conversion to aerosols seems not to be directly proportional to the amount in fuel, even if there is excess of Cl/HCl in the combustion gases. Actually the proportion of Cu, when compared to other vaporised elements, is higher in Experiment (b) than in Experiment (a). It may be that in Experiment (a) the higher Cu content in the fuel is due to large metallic Cu impurities, or Br actually promotes Cu volatilisation as the equilibrium modelling estimates.

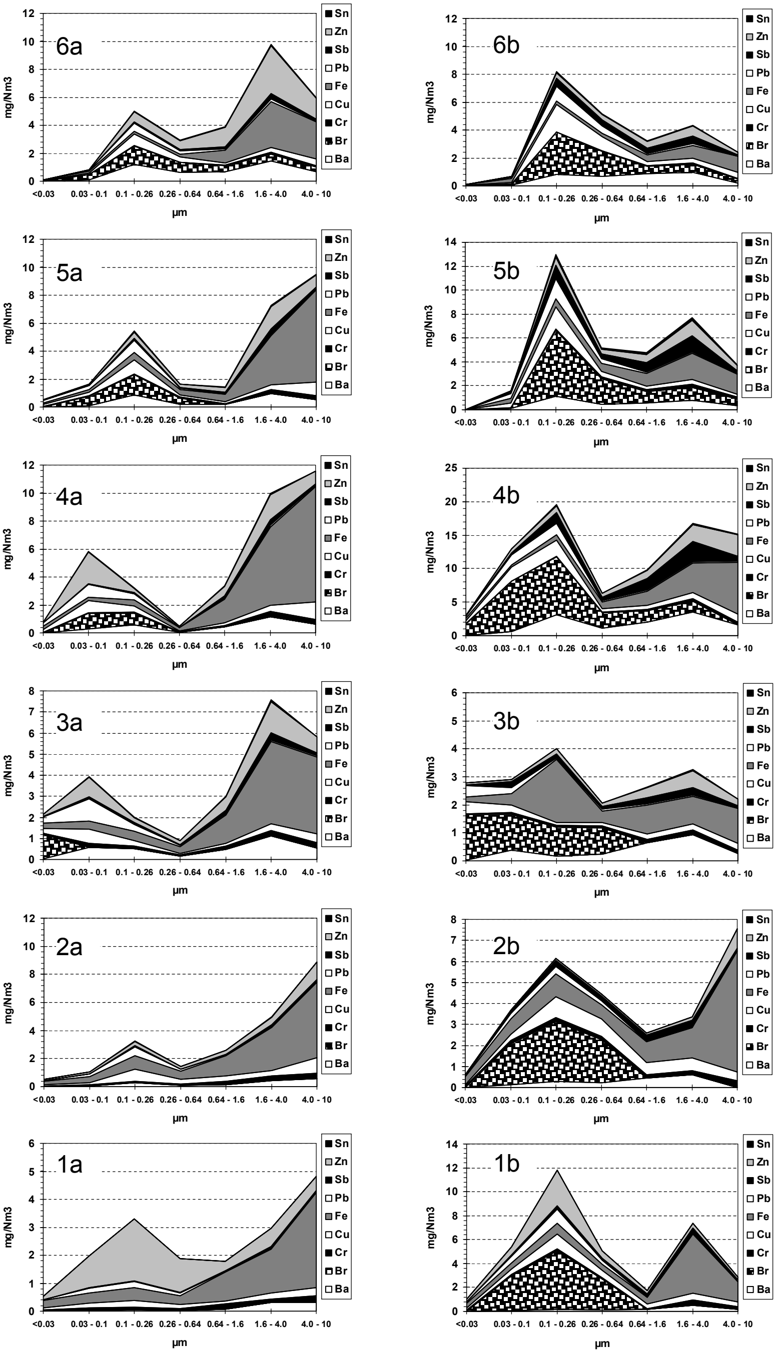


Figure 27. Concentration of selected fine particle forming elements in the combustion gases. From Paper VI.

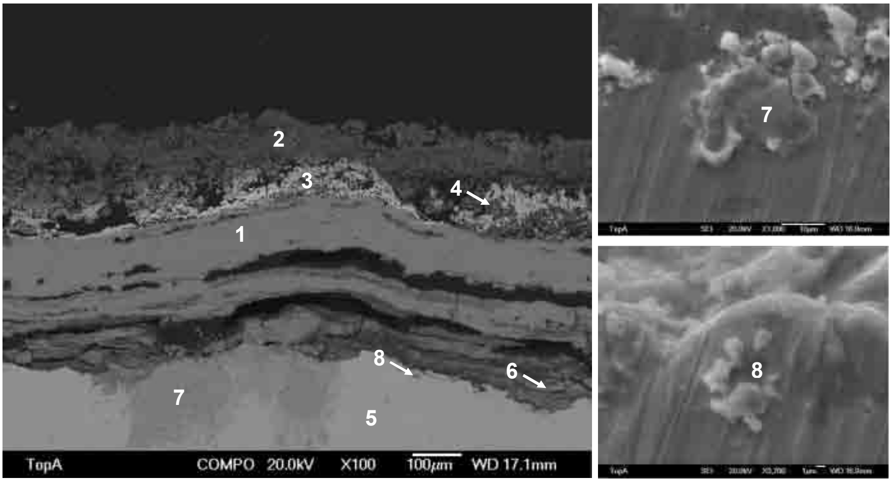
In oxidizing conditions in and after the superheater region it is suggested, based in the modelling in this work, that $CuBr_3(g)$ is formed. Cu was found to be the main cation reacting with Br in addition to K and Na. Cu is relatively evenly distributed in the fine and coarse mode of the particles. In reducing conditions $Cu_2S(s)$ and Cu(l), and in oxidizing conditions CuCl(g) and CuO(s), have been suggested as the main stable forms [255,256].

The sources and estimated speciation of the other elements, with no assumed direct connection to bromine, found in the vapours are discussed in detail in Paper VI.

5.4 Corrosion indications (Papers III–V)

The boiler studied in this work experienced rapid membrane (water) wall corrosion. An SEM back-scatter image from a cross section of one of the corroded waterwall tubes is shown in Figure 28 (Paper III). The top layers of the cross-section indicated with numbers 2, 3 and 4 are deposit layers and the light grey section at the bottom of the image is the tube material (number 5). The scaled layers (1) in the middle of the image are the corrosion products (mainly iron oxide). The image is a back scatter electron image, which means that different elements are displayed with different degrees of darkness in the image, the heavier the element the lighter the hue of grey. The composition of the numbered spots as analysed by the means of EDX are presented in the adjacent data table. The analyses were made as area analyses and were chosen to be representative for each part of the sample.

The tube surface was covered by a relatively thin deposit. The outermost layer of the deposit (2) consisted mainly of potassium, sodium, calcium and sulphur, probably as sodium, potassium and calcium sulphate. The lighter grey layer closer to the metal (3) consisted of sulphur, potassium, lead, sodium and chlorine. The amount of lead found is considerable (8.5% on atomic basis) which can be seen as the light grey colour in the image. The layered area in the middle of the image (1 and 6) is the corrosion product layer (Fe_2O_3 based on atomic ratios).



	1	2	3	4	5	6	7	8
S	1.2	11	14	15				
K	0.9	7.1	8.9	20				
Na	1.3	6.2	4.8	6.7				
Cl	0.6		4.8	0.1			6.8	6.1
Br							16	
Ca	0.4	7		0.3				
Mg		1.2						
Si	0.6	2.8		0.2	0.5	0.3		
Al	0.8	2.0	0.4					
Zn		0.8						
Pb	0.2	0.3	8.5	0.2				
Fe	32	0.5	1.4	1.4	98	48	38	46
P		0.5						
Mn	0.3	0.4						
Ti		0.3						
Mo					1.5	0.8	0.4	0.5
O	61	60	58	57		50	39	47

Figure 28. An SEM back-scatter image (left) of the cross section of the corroded water-wall tube with the elemental composition (at-%) at the numbered locations. The right hand side pictures show magnifications from locations 7 (top) and 8 (bottom). From Paper III.

Clear indications of chlorine induced corrosion and the formation of iron chloride can be seen in areas 7 and 8. Area 7 consists of iron, oxygen, bromine and chlorine. Assuming that all chlorine and bromine is present as iron compounds gives 3.4 at-% $FeCl_2$ and 8.0 at-% $FeBr_2$, which would leave 13.4 at-% Fe_2 and

12.9 at-% O_3 to form Fe_2O_3. The corresponding mass proportion for bromine in this location is 30 wt-%. Area 8 represents a typical trace of chlorine induced corrosion consisting of iron, oxygen and chlorine, indicating the presence of iron chloride and iron oxide. The small traces of molybdenum in both locations originate from the steel.

The waterwall surface temperature is not definitely known and can be only roughly estimated from the steam values. The temperature of saturated steam at 80 bar (which is the live steam pressure for which the boiler is designed) is 296 °C. According to the plant data the steam drum pressure is some 1.5 bar higher than this and there is also the influence of the static head from the feed water down comers, which increases the saturated steam temperature about 2 °C. The tube wall thickness was originally 5.6 mm. There are indications in the literature [262–264] that the wall temperature may be some 15 °C higher than the saturated fluid inside the riser tubes, and this is excluding the possible influence of water/steam side scaling. With a compact oxide layer thickness of 300 µm on the water/steam side, the gas side temperature has been estimated to increase with about 30–40 °C [264]. Also the local heat flux is a major variable which is not exactly known in the BFB boiler. To conclude, it is not reasonable to assume the wall temperature would have been very much below 350 °C.

High temperature corrosion tests in lab-scale tube furnaces were carried out to characterise the corrosion propensity of bromide salt - in comparison to the corresponding chloride mixture. Results with salt mixtures consisting of K_2SO_4 with $ZnBr_2$ or $ZnCl_2$ are given in Paper V and the method used is described in detailed in [265,266].

Zinc salt mixtures were selected for the test as there is no reason to expect the observed waterwall corrosion (if to be due deposits) is caused by a purely alkali metal, for example K or Na, halide-sulphate salt mixture. The corrosion caused by those salt mixtures initiates typically at > 450°C [267,268]. Zinc chloride has been shown to cause high temperature corrosion of boiler steels already at > 350 °C [266] and it is convenient to compare the results with corresponding bromides to the published data on chlorides.

The average corrosion layer thicknesses calculated for the sample steels tested are shown in Figure 29. The results with these salt mixtures show that bromide is inducing corrosion which is at least comparable to that of the corresponding chloride. In some of the tested conditions the bromide was found to be even more aggressive than the corresponding chloride. The bromide salt corrosion measured on 10CrMo9-10 steel exceeded significantly the attack caused by the corresponding chloride mixture.

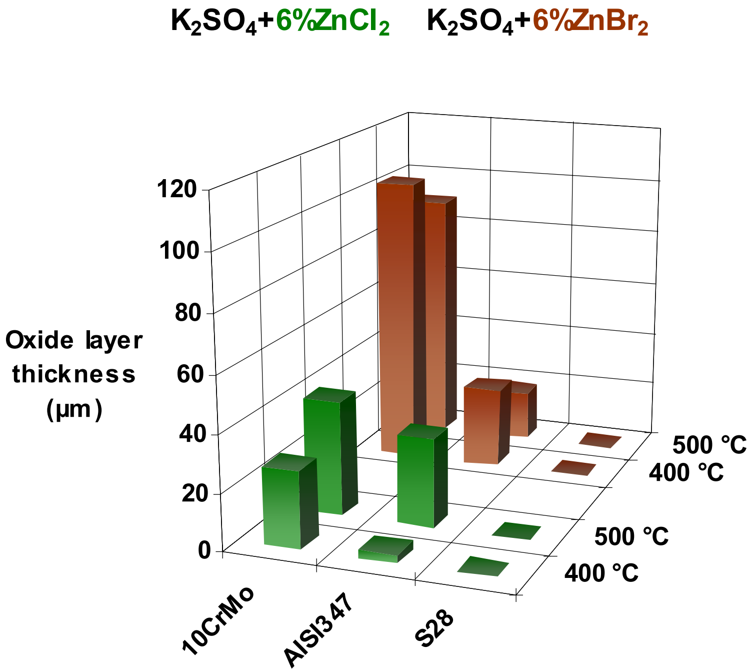


Figure 29. Oxide layer thicknesses measured in laboratory tests as described in Paper V.

5.5 Vapours next to boiler waterwalls

In the previous chapters bromine was shown to induce high temperature corrosion of boiler steels, the corrosion propensity to be (in these tests and conditions) even higher than the corresponding chloride and that bromide is found as a vaporised salt in the furnace. Paper IV gives data on the measured conditions to which the boiler waterwall shown in Figure 28 is exposed to. Figure 30 shows the concentration of water soluble fine particle forming matter in the combustion gases touching the waterwall. Regarding solubility, the halides of Cl and Br are likely to be dissolved in water, although Pb halides only slightly, whereas the metallic form of Zn, Pb and Cu dissolve in the acid. The elemental analyses of the fine mode (vapours) showed that approximately 40% of Pb, 50% of Zn and 35% of Cu has formed water soluble compounds. For Na and K the proportions were 80% and 100%, respectively. Cu is reported here alongside with Pb and Zn as it was found in surprisingly high concentrations, also in the deposits (Paper IV).

The main bulk of fine particle is formed of alkali metal halides. The concentration of K in the combustion gases (bound in the fine mode) was measured to be approximately 11 mg Nm^{-3}, Na 7 mg Nm^{-3} and Cl 20 mg Nm^{-3}. The Br concentration was approximately 2–3 mg Nm^{-3}. The concentrations of Zn, Pb and Cu were found to be up to 1 mg Nm^{-3}. Based on the analyses some 80% of the fine mode particles were formed of the elements discussed here. The rest of the elements were mainly Al, Fe, Ca, Ba, Cr and Mg.

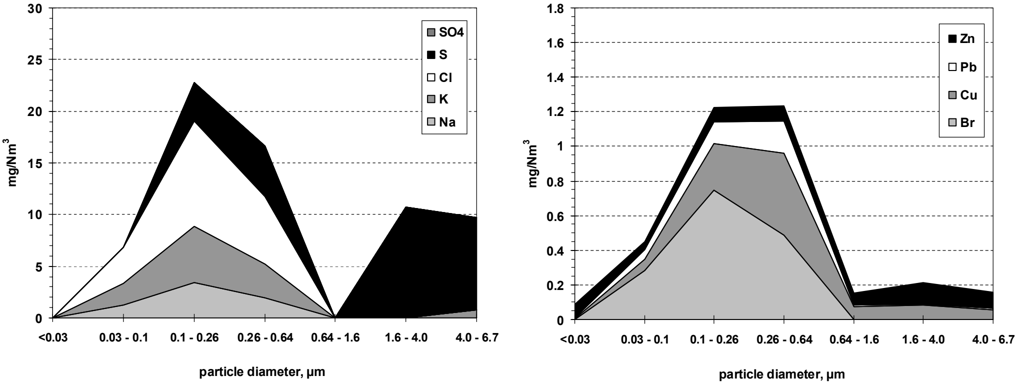


Figure 30. Concentrations of the water soluble fine particle forming elements flowing on the waterwall where bromine induced corrosion had been detected. SO$_4$ denotes the amount of sulphur in the form of sulphate calculated as elemental sulphur. S denotes elemental sulphur in a form other than sulphate. Paper IV.

From the atomic ratios it can be calculated that Zn, Pb, and Cu can bind approximately 10% of the halogens. The rest are Na and K halides that are able to bind > 85% of the halogens. This, additionally, indicates that the formation of sulphates was negligible at this level in the boiler.

The forms of the ash-forming vapours next to the wall were estimated by means of thermodynamic equilibrium modelling in Paper VI. Potassium was predicted to be present almost completely as gaseous KCl in both reducing and oxidizing conditions with only minor amounts of gaseous KBr and KOH. Sodium on the other hand, in the present case, is distributed evenly between two species, gaseous NaCl and solid NaAlSiO$_4$. Minor amounts of gaseous NaOH and NaBr was also predicted to form. The predicted formation of solid NaAlSiO$_4$ may explain why potassium is enriched in relation to sodium in the sampled aerosols as compared to the overall contents of potassium and sodium in the fuel mixture, as shown in Paper IV. Sulphur was predicted to form mainly

H_2S and minor amounts of SO_2 and COS in the gas phase at reducing conditions and SO_2 at oxidizing conditions. Chlorine was estimated to form predominantly HCl and also gaseous NaCl and KCl. Cu, Zn, and Pb show different behaviour at reducing and oxidizing conditions. Cu was predicted to be present mainly as solid Cu_2S at reducing conditions but mainly as gaseous CuCl at oxidizing conditions. Pb on the other hand was predicted to be in a gaseous form at both reducing (Pb and PbS) and oxidizing conditions (PbO), while Zn was predicted to be volatilized as gaseous Zn at reducing conditions and to form a solid silicate at oxidizing conditions with a minor fraction volatilized as gaseous $ZnCl_2$. Bromine was predicted to form gaseous NaBr, KBr and HBr at both oxidizing and reducing conditions with minor amounts of gaseous Br and $CuBr_3$ at oxidizing conditions.

When comparing the equilibrium estimations to the experimental observations Figure 30 shows that the water soluble alkali metal chlorides form the large bulk of the vapours. Sulphate as the sulphur species was negligible in the sampled aerosols, neither modelling results indicated sulphate formation. Cu was found in high concentrations (in comparison to Zn and Pb) in the vapours and the modelling predicts gaseous Cu to be mainly in the form of CuCl(g). Water soluble alkali metal bromides are the most likely form of Br in the sampled vapours. In addition to alkali metals Br was predicted to form a compound with Cu, namely $CuBr_3$(g). Approximately half of the Zn and Pb were found in water soluble form in the vapours. It supports at least the modelled speciation of Zn of which some part was estimated to be present also as $ZnCl_2$(g).

6. Conclusions

The most important natural source of bromine is the sea, by means of sea salt deposition and rain. Bromine content exhibits large variation in fuels. In marine algae - as potential future fuels - bromine can be found up to several weight percentages in a large variety of organic compounds but only a few mg kg^{-1} is found in terrestrial plants where bromine is in the form of (mobile) bromide. Peat exhibits varying physical and chemical properties as a function of diagenesis, which facilitates the enrichment of bromine in comparison to chlorine. The total bromine content is in the order of 20 mg kg^{-1} for inland peats and up to 200 mg kg^{-1} for coastal peats. In coal, bromine content is inherited from the plant matter and peat. Typical content is < 20 mg kg^{-1}, but due to ground water influence bromine content can be one order of magnitude higher than that. In coal bromine is assumed to be bound mainly as anion sorbed on the coal organic surface pores. Shales are depleted in bromine.

The most important anthropogenic source of bromine in solid fuels is the utilisation of brominated flame retardants (BFRs). Nor can the influence of various brominated chemicals such as pesticides or disinfectants be disregarded. The BFR treated plastics can contain several weight percentages of bromine whereas some 100–200 mg kg^{-1} Br is typical in mixed municipal solid wastes (MSW). Bromine may be enriched in fuels with high share of plastics, such as solid recovered fuel (SRF) or refuse derived fuel (RDF). Up to 2 000 mg kg^{-1} was found as a monthly average in SRF, typical levels being 20–200 mg kg^{-1}. Industrial and residential water treatment (sanitising, slime control) may involve the use of brominated biocides which resulted in the paper mill sludge to contain 20–100 mg kg^{-1} Br in this work. Bromine is applied in other selected uses such as colorants, rubber additives and in photographic paper which may be found in solid waste fuels, too.

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. In this work it was shown that bromine can be found in significant concentration in SRF and wastewater sludge, bromine predominantly forms alkali metal halide (KBr and NaBr) vapour in the furnace, bromine bearing salts induce high-temperature corrosion of boiler steels and the corrosion propensity may even exceed that of the corresponding chloride. Br was found in the fine particles already in the lower furnace; therefore KBr and NaBr are suggested to be formed already above the bed of the BFB, and staying as the stable forms of Br through the furnace. This is supported by thermodynamic equilibrium estimations. Presence KBr and NaBr facilitate the formation of corrosive Br bearing deposits analogously to chlorine. This takes place with only some hundred mg kg^{-1} Br in the fuel.

In addition to Na and K, according to thermodynamic equilibrium estimations Cu was found to be the most likely cation to form a salt with Br in the form of $CuBr_3$(g). In addition to Pb and Zn, Cu was found in the in-furnace vapours in high concentrations in the work. The main fine particle forming elements found after the exclusion of the typical main elements Na, K, Cl and S were Ba, Br, Cr, Cu, Fe, Pb, Sb, Sn and Zn. These originate mainly from plastics, rubber and alloys in solid recovered fuel. These elements are vaporized predominantly as metallic, oxide or halide forms depending upon the local conditions in the boiler and were found in the fine mode ($d_p < 1$ µm) of the fine particles.

Future work should focus on establishing inventory data on bromine in solid fuels in order to obtain a better understanding on its occurrence in solid fuels. This can be simply done by including bromine in the conventional fuel analysis procedures. These should then be complemented with experimental studies on the practical influence of bromine particularly on high efficiency power generation systems.

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PUBLICATION I

Review on bromine in solid fuels

Part 1: Natural Occurrence

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Review on bromine in solid fuels. Part 1: Natural Occurrence

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Bromine seems to have similar behaviour to chlorine during thermal conversion: bromine forms high vapour pressure salts in the furnace, bromine contributes to high temperature corrosion of boiler steels and brominated dioxins and furans have been detected in combustion plant effluents. This paper presents a review of the natural origin, content and modes of occurrence of bromine in solid substances used as fuel. The most important natural source of bromine is the sea, by means of sea salt deposition and rain. In some marine algae bromine can be found up to several weight percentages in a large variety of organic compounds but only few mg kg^{-1} in terrestrial plants where bromine is in the form of (mobile) bromide. Peat exhibits varying physical and chemical properties as a function of diagenesis, which facilitates the enrichment of bromine in comparison to chlorine. The total bromine content is in the order of 20 mg kg^{-1} for inland peats and up to 200 mg kg^{-1} for coastal peats. In coal, bromine content is inherited from the plant matter and peat. Typical content is < 20 mg kg^{-1}, but due to ground water influence bromine content can be one order of magnitude higher than that. In coal bromine is assumed to be bound mainly as anion sorbed on the coal organic surface pores. Shales are depleted in bromine.

Keywords: Bromine, bromide, biomass, peat, coal

Contentns

1. Introduction

There is a limited amount of data available on bromine in solid fuels. This is understandable due to its typically low content in comparison to the main halogen, chlorine. However, bromine can be found in solid fuels in all the abundance classes, i.e. major (> 1 wt-%), minor (1–0.1 wt-%) and trace (< 0.1 wt-%).

The implications of bromine for solid fuel conversion systems are under research and not well established but qualitatively understood. From the experimental data available it can be concluded that bromine and chlorine behave in a similar manner to each other and their implications for combustion systems are comparable [1–3]: bromine seems to form high vapour pressure salts in the furnace, it contributes to high temperature corrosion of boiler steels, and brominated dioxins and furans have been detected in combustion plant effluents.

In the context of literature on fuels, data regarding bromine can be found for coal and anthropogenic wastes. For biomass the literature originates currently from plant science, nutrient publications and handbooks. For peat, bromine studies can be found within the context of bog geology. Bromine science can be evaluated as the second best established for peat after the anthropogenic wastes. Regarding coals, while reviews have been published on bromine, they none the less still leave a surprisingly much for speculation – less for bromine content, but more on bromine speciation.

The occurrence and concentration of bromine in the natural environment has been studied. The environment includes natural waters, soil and the atmosphere. Another main research area concerning bromine relevant for solid fuels has been the environmental fate and health concerns of brominated soil fumigants and brominated flame retardants (BFRs).

The purpose of this paper is to present a comprehensive review of the origin, concentration and forms of bromine occurring naturally in solid fuels. In the paper chlorine is sometimes discussed alongside bromine as a ‘reference’ due to their chemical similarity. The occurrence of bromine in natural environment and bromine refining for industrial purposes are the starting-points for understanding the reasons for possibly high bromine content in some fuels. This essential background for natural systems is given in Part 1 and for anthropogenic use in Part 2. The atmospheric behaviour and fate of bromine [4] is not discussed in depth. Implications on thermal fuel conversion are only shortly referred to in Part 1.

1.1 Properties of bromine

In this paper the term ‘bromine’ is used generally to denote bromine as an element regardless of its speciation. This is abbreviated as Br. Where the term ‘bromide’ is used it is specifically meant by the bromide ion Br^-. Regarding the content, ‘bromine’ typically means the total content of bromine, and ‘bromide’ its common negative univalent form typically analysed as water soluble bromine.

Br is a halogen element with high reactivity. Naturally Br exists as 50.57 atom-% ^{79}Br and 49.43 atom-% as ^{81}Br [5]. Bromine is one of the two elements which are found in liquid form at room temperature. Br is a dense (3.1 kg l^{-1}) red-brown dark liquid at room temperature. It freezes at -7 °C and boils at 58 °C. It is found in nature in mainly organic and dissolved bromide forms. The largest reservoirs are seawater with 65 mg l^{-1}, the atmosphere and organic soil. It is concentrated naturally in the Dead Sea with 5000 mg l^{-1}, salt lakes and underground brines. Table 1 lists selected properties of bromine, complemented by the corresponding properties of chlorine for comparison.

Table 1. Comparisons of properties of bromine and chlorine. [2,6]

	Bromine	**Chlorine**
Molar weight	79.90	35.45
Boiling point	+58.8	-34.6
Melting point	-7.2	-101.0
Electro negativity	2.8	3.0
Standard reduction potential, °E (V)	1.066	1.358
Bond strength (kJ/mol)	Br-Br 193.9	Cl-Cl 242.9
Van der Waals radii (Å)	1.95	1.8
Solubility in water, g 100 ml^{-1}, 20°C	NaBr 90 CaBr 143	NaCl 36 CaBr 42
Acid dissociation constant, pK_a	HBr -8.72	HCl -6.2

1.2 Occurrence in the natural environment

Sea water. The sea is the largest natural reservoir of bromine. It is a dynamic system and the most significant source of organohalogens in the atmosphere. Organohalogens are formed through microbial processes in living organism. Enzymatic processes, namely halopreoxidases and halogenases taking place for example in algae and marine plants, are thought to be the main sources of halogenated organic compounds [7]. The total annual flux of organic Br to the atmosphere has been estimated to 500 kt. Most of this flux arises from the ocean but apparently also from terrestrial plants. The main Br sinks are atmospheric reactions, oceans and soils. The importance of the direct take-up by plants is not definitely known [8].

Sea spray, on the other hand, seems to be a major direct source of bromine in soil and plants. Sea spray is understood as a spray of water that forms when waves crash. This spray can then be transported varying distances by wind. In sea water where bromine is mainly in the form of Br- the content ranges from 65 to 71 mg l^{-1} whereas Cl content is close to 19 000 mg l^{-1}. It has been observed that the Br- content in sea water increases with the distance from coast due to the dilution effects of ending fresh waster rivers [9]. Typically in natural fluids as well as in most solids chlorine is from 40 to 8000 times more abundant that bromine [10].

Interestingly, aerosols of marine origin have been shown to contain the two halogens in relative proportions different from the sea water and enrichment in bromine has been widely observed [11]. The ratio Cl/Br is usually several fold smaller in aerosols over land than in sea water or aerosols over open seawater where the Cl/Br ratio it is in the order of 300 [12].

Even if the properties of chlorine and bromine are very similar there is a difference in their solubility. As water is evaporated halite (NaCl) will precipitate first, leaving brine enriched in Br^- [13] with Cl/Br ratio (mass basis) of 50. This is an important factor regarding Br enrichment in brines. The ‘naturally’ low Cl/Br ratio has previously been doubted due to anthropogenic Br uses such as additives used in gasoline (as lead scavengers), fumigants (methyl bromide) or halons (extinguishants) and the consequent elevated anthropogenic bromine content in the air [14]. These uses are being phased out following the Montreal protocol as these compounds are strongly ozone depleting [15].

Fresh waters. The primary natural source of halogens in surface water is rainfall which derives them initially from sea spray [16]. Some minor contribution originates from volcanic eruptions [17]. In fresh water the reported bromine content ranges typically from 0.01 to 0.2 mg l^{-1} [18]. If higher values are observed they are likely to be due to soil fumigation (see Part 2 of the paper) or sea water 'contamination' [19].

In Finland [20] surface waters have been reported to contain on average 0.06 mg l^{-1} bromide. On the west coast of Finland the bromide content was approximately three times higher than inland. Infiltration waters from cultivated soils can be as high as 6 mg l^{-1} in bromine. This may be due bromine residues in fertilisers: 716 mg kg^{-1} has been analysed from a KCl fertiliser and 230 mg kg^{-1} from road salt [18].

The European average for river water bromide is approximately 0.15 mg l^{-1} [20], and similar values have been reported from the US river waters. Some reports give for the bromine range 0.01–1.0 mg l^{-1}[21] but in the US a study of 150 waterworks revealed that the bromide range is mostly between 0.05 and 0.1 mg l^{-1} [22].

Rainfall. In rain the Br content is usually below 0.01 mg l^{-1}. However, in coastal areas 1.0 mg l^{-1} has been reported [15,18,23]. Similar figures have been reported for Wales [15]. In Japan corresponding figures have also been found, where the concentration of bromine in the rain water ranged up to 0.034 mg l^{-1}. The average on the coastal area was 0.01 mg l^{-1} and in the inland 0.0028 mg l^{-1}.

Samples from the UK indicate that they all have lower Cl/Br ratio than sea water [11]. In precipitation (and fresh ground water) Cl/Br is on average 100 even though the variation is high (from 38 to 290) [10]. Lower Cl/Br ratios than in the sea water have been analysed also from snow [14]. For cloud water (mist collected over river water) 0.16 mg l^{-1} has been reported [11] and that was found to be one order of magnitude higher than in rain water [11,15]. In that study similar figures were reported for river water as for the rainfall, i.e. approximately 0.02 mg l^{-1}.

It has been reported [[24] cited by [25]] that the content of bromine in rain seems to 'always' be some ten times higher in the coastal area than in the inland areas. This data can be combined with the annual precipitation which gives the actual deposition rate of bromine in the soil. It is apparent that the content of bromine in rain water on the coast and high precipitation on the coast in comparison to inland results in high bromine deposition rate in coastal areas through rainfall.

Soil. For soils there is a large variation in Br content. This is due to the marine influence on the coastlines compared to inland soil. The reported Br contents range from 0.3 to 852 mg kg^{-1} [26]. This has been found to be a function of organic matter content in the soil and Br deposition (see Figure 1). Particularly in coastal areas the latter is a major subject in the discussion regarding bromine in peat. Flury (1993) [18] concluded that seaborne aerosols are the main natural source of Br in the terrestrial ecosystem, and in referring to the Japanese original paper Yiuta (1973) [27] concluded that Br originates from the sea through rain, snow or directly as airborne salts. The analyses reported in that work [28] showed Br content to be halved in soil > 75 km inland.

According to the literature sources [28] the 'World average' for Br in soils is 5 mg kg^{-1}. Igneous rocks have been characterised as containing approximately 1–10 mg kg^{-1} Br while for sedimentary rocks the scale is wider, from 1 to 140 mg kg^{-1} [26]. In UK soils bromide content is at a level of 5 mg kg^{-1}, whereas in coastal regions 100 mg kg^{-1} has been reported [29]. In one study the chlorine content found in soils in Japan [25] was in the same range as the reported World average, around 100 mg kg^{-1}, but the bromine content was found to be significantly higher than the World average. This was up to 152 mg kg^{-1} in single sample analysis and on average up to 81 mg kg^{-1} depending upon the soil type [28].

Regarding different soil types, a large number of soil and plant samples from Japan [25,28,30] were analysed for Br. It was found that in forest soils the bromine content (and iodine) were some 10 times higher than reported in the literature from other continents. In paddy soils, characteristic of Japan, the bromine (chlorine and iodine) contents were similar to those reported in the reviewed literature. The forest soils had 63 mg kg^{-1} bromine content on average, while in paddy soils the average was as low as 3.3 mg kg^{-1}. This was explained by eluviation from the soil of Br in a submerged condition after forest land is converted to paddy fields.

Very high bromine content was found on the east coast of Japan in Kawaminami on the island Kyushu [26]. The concentration analysed by means of x-ray fluorescence and Neutron Activation (NAA) was 850 mg kg^{-1}. These values were equal to the values for chlorine. This area is characterised by annual precipitation higher than 2500 mm m^{-2}. In these soil samples Br was shown to correlate positively with the carbon content, see Figure 1.

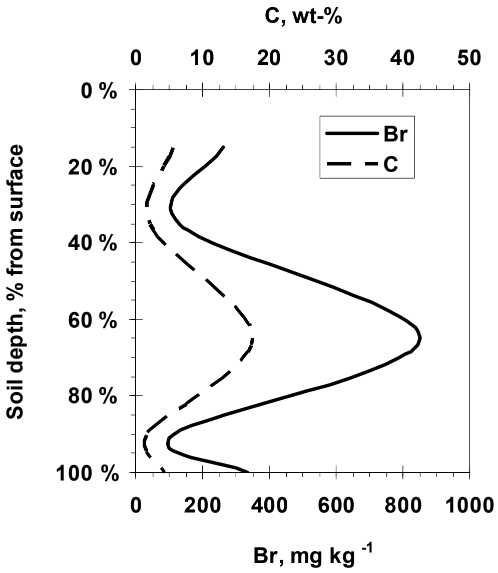


Figure 1. In soils sampled from Japan bromine content strongly correlates to carbon content. Data from [26].

Combining the data on soils and the literature on Br in peat, it can be concluded that there is no direct correlation between total Br and Br^- in soil. The otal bromine content seems to be a function of the organic matter content in soil and the annual Br deposition (coast proximity) event though it is not always evident from the data [18]. The depth profiles for the bromine content in soil are in alignment with the findings for peat bogs: the maximum is close to, but not actually on, the surface of the soil, and the chlorine and bromine content patterns do not follow each other [28]. It has been shown that bromine can be washed out from soil samples after a hydrogen peroxide wash [26], a process which has been used as the evidence for Br being located largely in soil humic acid fraction [31,32].

Bromine content in rain and its influx in soils, and further in plants, varies with the distance from the coastline. In Japan it was observed that the chlorine content did not change with the distance, but bromine content was higher on the coast. This has been found out also in Norwegian forests with high humus content where the bromine content was approximately four times higher on the coastal forest humus layer when compared to the content in 120 km inland [25,33].

It has been suggested in the literature that volcanic ash soil contributes to the bromine content in soil. This has been discussed in a study including such soils [25] and misleadingly emphasised by other authors since then. In the light of other literature published since, this influence can be doubted. In the original work it was concluded that volcanic ash soil is not the original source of bromine in the soil [25], a conclusion which leaves the soil properties as the main determining factor. The main natural source of bromine in soil was again concluded to be the sea rather than the parent rocks or sediments. This conclusion was justified by the postulation that bromine, alongside chlorine and iodine, are easily eluviated during the weathering process and it is very unlikely that these elements originate from the rocks.

Fresh ground water. The Cl/Br ratio may vary over one order of magnitude in groundwaters. Slight enrichment in Br relative to Cl occurs during infiltration which may be due to the decayed organic matter which has been found to be enriched in Br. Bromine has been used as a tracer in soil science as it has been postulated to be conservative (as chlorine). These results should be evaluated with great caution [34] as bromine retention by organic soil will be a cornerstone in the discussion of bromine/bromide in peat.

The different behaviour of chlorine and bromine in (particularly high organic carbon) soils is supported by the findings that in river stream flow there is no correlation between the content of these two elements (as compared with rainfall). Bromine content in river water increases in rainy periods when organic matter releases bromine after re-wetting [11,15,35].

The concentrations of bromine in potable groundwater in the United Kingdom range from 0.06 to 0.3 mg l^{-1} [11]. In Sweden it has been found that Br^- content in ground water is higher than in surface waters [36]. Concentrations up to 2.26 mg l^{-1} have been found in groundwater in coastal areas of England [[37] cited in [18]] and values reaching up to 7.3 mg l^{-1} have later been reported [11]. In Taiwan 5.0 mg l^{-1} for ground waters has been reported due to contamination by seawater as a result of excessive pumping that exceeds the natural recharge rate [38].

Typically the groundwater bromine content is < 0.1 mg l^{-1}. In Finland the average can be estimated to be close to 0.13–0.27 mg l^{-1}. In bromide and bromine mapping for 18 Finnish ground water treatment plants supplying drinking water the content was on average 0.05 mg l^{-1} and 0.11 mg l^{-1}, respectively [20]. From the dataset it can be concluded that on average half of the bromine was in the form of bromide in the waters. Interestingly the fresh river water feeding into a surface water treatment (for drinking water) contained < 0.01 mg l^{-1} bromine, but the treated water 0.24 mg l^{-1}.

Underground brines, Dead Sea. Underground brines are known to be concentrated in bromine and some of them are commercially explored as a source of bromine. In Arkansas, US, concentrated brines contain up to 5000 mg l^{-1} bromide and Michigan brines about half that. In Arkansas, brine is drilled from a depth of 2400 m [39]. The upper concentration limit is not definitive and depends on the aquifer stone type. In Israel bromine is refined from Dead Sea brine. In the Dead Sea bromine concentration is close to 5000 mg l^{-1}. From the Dead Sea bromine is enriched from the end-brine after precipitation of sodium, magnesium and calcium chloride when bromine is enriched up to 13 000 mg l^{-1} [40].

2. Biomass

Biomass here means living or recently living organisms, mainly plant matter that does not include residues from processes which may chemically alter the material such as fumigated biomass, manure or wastewater sludge. In this paper biomass fuels are divided into two: terrestrial and marine. Regarding terrestrial plants the role of bromine is very plant specific and the content of bromine is dominated, as in all terrestrial systems, by the exposure to bromine. Marine plants and organisms concentrate by far the highest concentrations of bromine, on a percentage level on dry mass basis. In marine plants and algae the bromine content depends rather upon the species than the bromine content in the sea.

Bromine in the biomass can be categorised in five classes of occurrence:

- Those terrestrial plants with less than 2 mg kg^{-1} bromine, natural bromine occurrence, no relevant bromine flux from the surrounding environment, chlorine is abundant in the soil.
- Those containing between 2 to 20 mg kg^{-1} bromine (‘World average’), exposed to a typical and natural flux of bromine in continental conditions.

- Those exposed to elevated natural (e.g. coastal organic soil) bromine flux, up to a maximum of 100 mg kg^{-1}.
- Those exposed to anthropogenic (fumigants and pesticides, see Part 2 of the paper) bromine flux, starting from 200 up to 200–10 000 mg kg^{-1} Br.
- Those assimilating bromine by taking advantage of haloperoxidase, marine algae and seaweeds, with bromine up to 60 000 mg kg^{-1}.

2.1 Marine

As a potential future solid fuel, marine biomass is discussed separately from terrestrial plants. This is because marine plants can have very high bromine content, easily up to percentage level on dry mass basis. This content is mainly in the form of organic compounds, which may be difficult to remove cost efficiently.

Algae are a large and diverse group of simple organisms between unicellular to multicellular. Algae are often referred to as 'simple' as they do not have many of the organs found in land plants, actually similarities between algae and plants are much fewer than their differences: Plants exhibit higher level of differentiation (roots, leaves, stems. etc.) than algae, plants have exclusively a sexual reproduction and algae occur in many dissimilar forms such as microscopic single cell or filmy conglomerations contradicted by the uniformity of vascular plants. The largest and most complex marine algae are called seaweeds, which are photosynthetic. [41]

Algae assimilate inorganic bromide from the sea. The uptake is associated with bromoperoxidase (BPO) enzymes [42]. Peroxidases oxidise the bromide ion with hydrogen peroxide to bromine (namely hypobromite, BrO^-) where bromine is in oxidation state +1. This is the main mechanism how bromide initially starts to be bound in organic matter [43] and it results in a large array of organobromine metabolites in marine organisms. The bromine cycle in nature is not discussed in detail in this paper but details are available in the references [42]. It seems evident that the bromine content of the surrounding water is not the controlling factor in algae bromine content, and nor could it be attributed to wastewater influence [44].

Modes of occurrence. The main types of naturally occurring organobromides have been extensively mapped [45] and exhaustive listings have been established according to what is known today [42,46,47]. Bromine seems to be relatively abundant in the organohalogens: from the known 3200 naturally occurring organohalogen compounds, 1600 contain bromine. By far the most abundant are bromoform ($CHBr_3$) and methyl bromide (CH_3Br, MeBr): see Table 2. They are produced by marine and terrestrial plants, as well as (marine) animals. These include sponges, tunicates, bryozoans, gorgonians, sea hares, nudibranchs, bacteria, fungi, some higher animals, and a few mammals including humans.

Even if contamination due to anthropogenic organobromine use has been a major concern the naturally produced forms are more common than their anthropogenic counterparts. The knowledge is relatively recent as while 60 organobromine compounds had been identified in 1973, 25 years later the number has increased to more than 1600. Yet only a handful of the marine species has been examined up till today. [42,46,47]

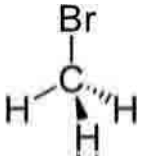
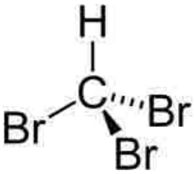
One of the first organobromine compounds 'found' was Tyrian purple (Egyptian dye, royal purple, imperial purple, 6,6′-dibromoindigo), which is found in several Mediterranean molluscs. This colorant is briefly discussed in Part 2 of this work. The main bromophenols identified in marine algae are 2- and 4-bromophenol, 2,4- and 2,6-dibromophenol, and 2,4,6-tribromophenol [48].

An extreme example of bromoform is that it comprises 80 % by weight of 'limu kohu', an edible seaweed of native Hawaiians, known for its flavour and aroma. This single alga contains more than 50 organobromine compounds. Toxic compounds are also produced by algae, including those known to cause the 'swimmer's itch'. These organobromides have been speculated also to be related to the defence of some marine species against predators. In the past bromoform was used by industry as a solvent against dirt and grease and for making other chemicals. It was also used as a medicine to help children with whooping cough get to sleep, but it resulted in several deaths from overdosing. Currently, bromoform is used in small quantities in laboratories and in geological and electronics testing. [49]

The marine emission of MeBr is estimated to be 56 000 tons per year^{-1}, with biomass burning accounting for a further 50 000 tons per year^{-1}. Marine production of bromoform (95 % Br by weight), is estimated at 1–2 million tonnes annually. Some algae have been found to emit more bromoform than they held in their tissue [50] and the emission can be about twice as much in light than that in the dark.

Another brominated organic compound reported in mammals is the bromoester, which is associated with REM (rapid eye movement) sleep and may have a significant role in sleep [45].

Table 2. Properties of methyl bromide and bromoform. [51]

	Methyl bromide	Bromoform
Structural formula		
Chemical formula	CH_3Br	$CHBr_3$
Molecular weight	94.95	252.8
Bromine content	84.2 %	94.8 %
Appearance	Colourless gas	Colourless to yellow liquid
Solubility in water	Soluble	Soluble
Anthropogenic use	Pesticide, soil fumigant, fire extinguishers	Laboratory use, pharmaceuticals, solvent
Status	Still utilised per exemption (ozone depleting)	Probably the main from of atmospheric bromine

Bromine content. In seaweeds in the seas of Japan bromine has been found in concentrations varying up to 32 000–37 000 mg kg^{-1}, depending on the location and algae species [52]. Seaweeds that grow at greater depths showed increased bromine content. The samples included red, brown and green seaweeds and two species of higher water plants. The red and brown species were the richest in bromine. The typical Br content varied between 200 and 1000 mg kg^{-1}, with the absolute minimum found at 150 mg kg^{-1}. According to he Russian literature [[53] cited in [52]] 1500 mg kg^{-1} has been found in a freshwater green alga, which has some 80 000 times greater concentration of Br in comparison to the surrounding water (with approximately 0.007 mg l^{-1} bromine). The most valuable commercial species was Laminaria Japonica, whose biomass attains as much as 100 kg m^{-2} [[54] cited in [52]]. It has been suggested that these species could be cultivated commercially cultivations to obtain bromide [52].

2.2 Terrestrial

Role of Bromine. In contrast to marine algae, hundreds of organochlorine compounds have been identified from terrestrial plants, but only a few organobromine compounds are known [46]. The emission of MeBr is a characteristic of terrestrial plants. It is produced in significant amounts by such plants as rapeseed, cabbage, broccoli, turnip, radish etc. from bromide available in the soil. The emission increases with increasing bromide content in the soil. MeBr production by terrestrial higher plants is potentially a large source for atmospheric MeBr [55]. Br emission from biomass burning has also been brought up in the literature as a potential Br source in the atmosphere [56].

Another major difference between the marine and terrestrial species is the Br take-up. Several studies have noted that bromide is fractionated relative to chloride by vegetation [11,15,35]. Bromine is taken up as a bromide and it may replace the nutrient chlorine [57–59]. It has also been published, but not widely supported by other literature, that if the air is contaminated by bromine plants can absorb it through the leaves [60]. This has been found in connection to high traffic areas where high concentrations of bromine have been present as pollutants from engine exhausts: 40 times higher bromine content was found in the leaf of the poplar tree in Athens, Greece, than in rural areas. [60]

Instead, it is clear from the plant nutrition literature that plants prefer chloride over bromide as a nutrient despite the fact that controversial results have been published. Typically, the addition of chloride in soil inhibits bromide up-take. If only bromide is available it depends on the species how much bromine is taken up from the soil, and if the plant can substitute Br for Cl. Three classes of plants can be identified: [34,61–64]:

- Those in which Br can substitute for Cl.
- Those other plants in which Br cannot substitute for Cl and eventually results in toxicity at higher concentrations.
- Plants with Cl deficiency where Br can displace Cl from less essential functions (roots) to provide essential functions higher in the plant (leaves, shoots).

However, the above can be stated based only on the very limited number of studies on only a handful of plant species. There still might be unknown factors influencing the Br content in plants, such as Mycorrhizal inoculation, which has been shown to elevate bromide and chloride concentrations in plant tissue [65].

Regarding wild plants, the enrichment factor for bromine (Br in plant leaves over Br in the soil) has been found to be 0.1, whereas for Cl 19 has been found [25,28]. In that study the corresponding values were 6.2 and 98 for rice plant. The interpretation was that this difference was due to the difference in the forms of the halogens in the soil: bromine was bound to a larger extent in organic matter than chlorine and therefore is not available for the plants as a nutrient. This is further emphasized by the differentiation in top soil retention of Br and Cl that has been observed also in other studies [66]. As discussed in length in the section concerning peats, the soil transportation studies show that Cl is more mobile and easily washed out by precipitation than Br [66]. The findings regarding nutrition and forms of Cl and Br in the soil both promote diminished take-up of bromine.

It seems that if both ions are available in the soil the required chloride uptake of plants is so low that sufficient chloride is in practise always available. Therefore ‘Cl preference’ results in low Br content in plants. Although the Br available in the soil has a positive correlation with Br content in different parts of the plant, the affinity with Cl is so high that absolute Br content remains low. The exceptionally high Br contents reported in the literature, sometimes claimed as natural, have been as a result of anthropogenic Br sources [26].

In conclusion of the knowledge today the Br concentration in plants depends upon their ability to take up bromide and on the bromide content in the soil.

Bromine content. In the literature it is not always clear if the reported values for biomass are on a fresh or dry mass basis but here, as throughout the paper, the values given are expressed on dry mass basis. In naturally occurring terrestrial plants, bromine content is approximately 5 to 15 mg kg^{-1}. The same applies to foodstuff and greenhouse residues (growth on non-fumigated soil, no pesticide treatment) where less than 10 mg kg^{-1} can be expected [18]. As a general rule the typical natural level of bromide in plants can be taken to be below 50 mg kg^{-1} [43].

Japanese wild plants have been found to contain on average from 6 to 30 mg kg^{-1} bromine, rice plant 21 mg kg^{-1} and soya bean 79 mg kg^{-1}. The average content of bromine in leaves of wild plants has been reported as 12 mg kg^{-1}. The leaves were influenced by untypically high bromine content in the soil [25,28]. Chlorine content found in those soils in Japan (from which the wild plant samples were collected) [25] was in the same range as the reported World average, around 100 mg kg^{-1}, but the bromine content was found to be significantly higher, up to 152 mg kg^{-1} [28]. In the data of Yuita (1983) [25] the coastal/inland ratio of chlorine in rainwater was higher than for bromine, but the ratio was lower in the soils and plants. The chlorine content in the soils was not particularly higher than the bromine content, even if the content in the rainwater was some 100 times higher. Therefore it is postulated that chlorine is eluviated from the soil to a greater extent than bromine being more easily available for plant take-up. Further, the ratios for the plant 'leaves/plough layer' (per dry weight) were 0.098 and 38 for bromine and chlorine, respectively.

Br concentration in red pine, cedar, cypress and white oak in Japan was found on average to be 10 mg kg^{-1} in the coastal area and 1.7 mg kg^{-1} inland [25]. In grasses from the corresponding areas (pampas grass, fern, bamboo) 12 mg kg^{-1} was found in the coastal area and 8 mg kg^{-1} in inland (excluding one sample where there was a discrepancy). In those forest and grassland soils in the coastal area 16 to 157 mg kg^{-1} Br was found and the values inland (125 km from coast) ranged from 9 to 68 mg kg^{-1}, which are approximately half to those on coast.

Saw dust (presumably Scandinavian) has been analysed to contain < 20 mg kg^{-1} Br [67]. Other plants (radish, turnip, potato, cabbage, egg-plant) contained approximately 10 mg kg^{-1} bromine in a Japanese study, whereas for onion and tomato approximately 30 mg kg^{-1} were analysed [26].

The average bromine content in sub-Saharan biomass, including grasses, shrubs and branches, maize stalks, was found to be 4 mg kg^{-1} with a maximum of 11 mg kg^{-1} [68].

3. Peat

The sea is the largest natural source of bromine. On the other hand, it has been estimated that peat lands, which cover approximately 2–3 % of the total land area, are one of the largest active terrestrial reservoirs of halogens [69]. One of the early evidences of this might be the combustion of coastal peats in the isles of Scotland during the eighteenth and nineteenth centuries which was a major source of chlorinated dioxins and furans [70]. Polychlorinated dibentzodioxins and furans are formed naturally also in peat bogs ‘in situ’ as their isomer patterns in the bog samples are different from those from atmospheric deposition [71].

Peat formation is decomposition of vegetation in stagnant water with small amounts of oxygen, under conditions intermediate between those of putrefaction and those of mouldering [72]. Unlike most other ecosystems, the dead plants in peatlands do not decompose completely. This is because of the waterlogged conditions where the lack of oxygen prevents micro-organisms such as bacteria and fungi from rapidly decomposing the dead plants [73].

Peat is generally regarded to have more than 30 wt-% (dry basis) dead organic material. As an energy source peat is used mainly in Europe, where it is used in more than 100 power plants. In the EU, 50 % of the harvested peat is utilised as fuel. From the total explored volume in Europe, Finland produces 41 %, Ireland 21 % and Germany 13 % followed by Estonia, Sweden and the other countries in the Baltic region. In Finland and Ireland peat constitutes some 5–6 % of primary energy, whereas in Estonia and Sweden the corresponding proportion is 1–2 %. In these latitudes peat has accumulated in the order of one millimetre per year over thousands of years after the withdrawal of the glaciers. [72,74]

Br is strongly enriched in peats [44] as it has been relatively well studied through geology research. In the following section a discussion on the sources, reasons for content variation and forms of bromine is followed by a summary of the concentration of bromine in peats obtained from different locations of the World.

3.1 Bromine influx and retention in peat

The exact mechanism of how bromine is incorporated in peat, or more specifically in humic acids (HAs), is not clear. For the speciation of organically bound bromine, bromophenols, or related derivatives have been proposed [32]. The binding efficiency for Br in peat organic matter seems to be higher than that for Cl.

Bromine depth profile. For soils it was suggested that the bromine content is a function of the organic content of the soil and Br is located largely in its humic acid fraction [31,32]. The depth profile analyses from peat bogs show that the concentration of the halogens (Cl, Br, I) are a function of the peat C/N (Carbon/Nitrogen) ratio [7,75]. A decreasing C/N ratio indicates increase in peat decomposition. Halogen concentration for all the halogens increases with the decrease in the C/N ratio. It is therefore suggested that the concentration of the halogens as a function of the depth in a bog depends on the degree of peat decomposition. Another conclusion is that the depth profile of the halogens does not illustrate the atmospheric deposition, but rather the hydrological condition over time. As the humification process is accompanied with great mass loss (80–90 %), the enrichment of halogens during peat formation indicates that orgaohalogen formation and degradation of organic material are concurrent processes. It has been found that the highest bromine content in peat is found from periods of relative high dryness when peat bog decomposition is high. One explanation is that if the bog falls temporarily dry it may increase the organohalogen concentration in the peat due to the loss in mass of organic matter. [69]

In Chilean peat bogs [7] the Cl/Br ratio decreases sharply in the outermost bog layer. This follows the C/N ratio which, it is postulated, indicates that bromine concentration increases to larger extent than chlorine when peat humification increases.

In Canadian bogs [76] a similar type of depth profile was found for bromine (and Cl and I). The reason was not fully explained. No relationship was found between the ^{14}C ageing test and peat halogen content. It was concluded that bromine originates from sea sprays as with regard to the geological history of the bog there is no evidence that the halogens could originate from ground water.

The bromine content data, as a function of peat bog depth, from three Nova Scotian [76] and two Swiss [77] (two cores, far right) peat bogs has been plotted in Figure 2. The maximum bromine content was 62 mg kg^{-1} for the Nova Scotian and 27 mg kg^{-1} for the Swiss peat. For the peat bogs it is typical, even if exceptions exist, that the bromine content maximum is found close to, but not on, the bog surface. This depth is typically 30 to 50 % of the total bog depth.

A water extraction test for the Nova Scotian samples showed that < 0.1 % of the bromine was found in water extractable form. From the Swiss samples it was found that approximately 40 % of bromine was associated with HAs. From the samples HAs were extracted and their bromine content was analysed. It was found that, in a bog depth of between 9 to 24 cm, 50 to 60 % of the total bromine in the peat was incorporated in the HAs. This proportion showed a decreasing trend towards the floor of the bog [77]. This may imply the breakdown of bromine to water extractable form during peat degradation [32].

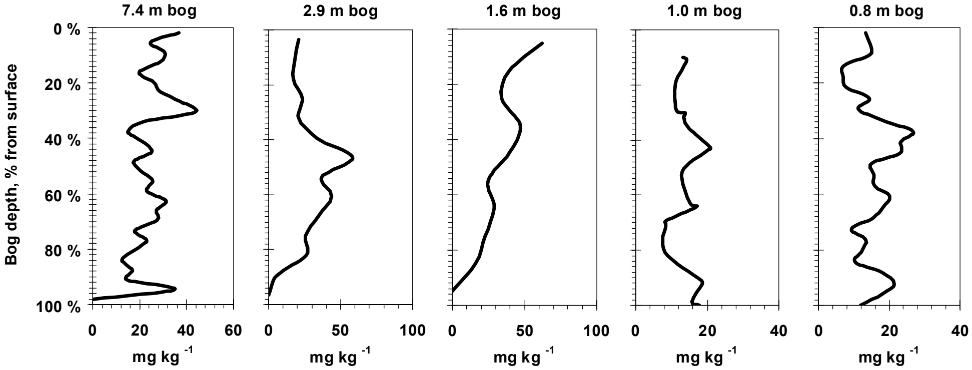


Figure 2. The variation of bromine content according to depth in three Nova Scotian and two Swiss ombrotrophic peat bogs. 0% = bog top, 100% = bog (silt) floor. Drawn based on data from [76,77].

The intense concentration gradient in the peat bogs may be interpreted to imply that the diffusion of the halogens in the peatbog is not significant [69,76]. The Br content in the uppermost layer can obtain high or low values in comparison to the concentrations found in the bog depth. The high Br content in the surfaces of a Chilean bog [7] was assumed be due to the plant type, as this bog had cushion plant dominance on the surface whereas the low Br (relative to the bog profile) concentrations were found in the sphagnum moss covered bogs. The halogen content variations found in the bogs were up to 22 fold as a function of depth. Another explanation for the high concentration of Br in the uppermost layer was the release of Br from decaying plants. This explanation can be doubted as Br release has not been shown to be significant from decaying matter, actually just the opposite. Typically the Cl/Br ratio is high in the uppermost peat layer, a fact which indicates that the release of chlorine is higher from decaying plat matter than for bromine.

Patterns different from the ones shown in Figure 2 can be found. In those cases it is likely that a detailed study of the diagenesis of such bogs, in connection with the pattern of chlorine, reveals the bogs to have been minerotrophic, at least at some stage of their history. The elevated halogen content in the lower parts of bogs may originate from marine silts in the floor of the bog. [78]

Peat bogs in the north Scottish mainland and the Shetland islands [79] show the same trends in concentrations as the Swiss and Nova Scotian bogs. The local Br concentration maximum was found to be at approximately 40 cm depth in the mainland bog and at 20 to 30 cm depth in the Shetland bog.

Bromine retention in peat. In studies on Chilean ombrotrophic peat bogs [7] which experience high and low annual precipitation, it has been found that the bromine concentration in the peat land is a function of the influx of bromine in rainfall. In the study the rainwater bromine concentration was up to 0.004 mg l^{-1} during the wet season and up to 26 mg l^{-1} in the dry season. In the wet season the bogs received high and halogen diluted precipitation relatively directly from the Pacific, whereas in the dry season the winds bring clouds with a high sea salt aerosol load through the Pampas from the Atlantic. The combination of the annual precipitation and halogen content in the rainfall resulted in a higher deposition rate of bromine in the bogs during the dry season. None the less, approximately three times higher bromine content was still found in the peat land closer to the coast line. The deposition rates for bromine were estimated to be from 6 to 16 mg m^{-2} yr^{-1} originating from the sea spray.

The organohalogen proportion from the total halogen content was found to be 82–91 % for Cl and 91–95 % for Br. The total and organic Br was found to have its lowest concentration in the uppermost layer of the bog and to have a sharp increase in concentration after a depth of some 50 cm, with a gradual slow decrease below that depth. It was suggested that the high total Cl concentration already at the surface of the bog was be due to the high uptake by plants of Cl relative to Br. It is therefore reasoned further that the plant uptake of Br is not as relevant as the retention of Br by humified plant matter just below the surface of the bog. It is postulated that this is due to the direct sorption of Br to HAs or else it is mediated by microbial activity [7].

Accumulation rates as mg m^{-2} yr^{-1} were also calculated [7], by determining the concentrations and age of the peat. As the concentration of halogens in peat has been shown to be a function of humic matter, the halogen accumulations were corrected by carbon accumulation rate. This accounts for the possible differences in retention in peats with a different humic fraction. The retention rate for Br was found to be up to 50 %, whereas for Cl it was found to be up to 2.4 %. The conclusion was that the higher retention of bromine in comparison to chlorine may be due to the physicochemical difference between the halogens, resulting in the favouring of bromine in the formation of organohalogens.

From the data in Figure 3 (left) it can be seen that there is hardly any correlation between the total (TX) and total organic (TOX) bromine and chlorine content in peats. In the plot on the right the correlation between the total content and total organic content for the both halogens is shown. It can be seen that the organic bromine content is proportional to the total bromine content in the peats, though for chlorine the correlation is less evident.

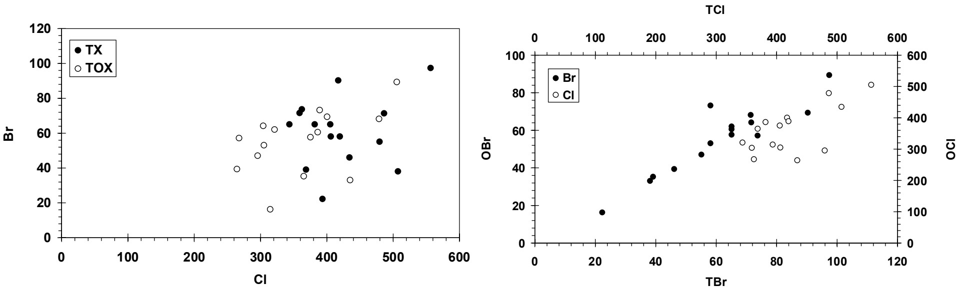


Figure 3. Correlation between total bromine and chlorine (TX) and total organic bromine and chlorine (TOX) content in peat bogs. Data from [44].

In peat bogs in the north Scottish mainland and the Shetland islands [79] the retention of Br in the peat (total Br concentration) was found to be 50 to 60 times higher than for Cl and the net retention of Br was found to be 1.5–4.3 % from the rainwater deposition. These results may involve some errors, however, as only the dissolved ions were analysed from the samples of liquid, thereby omitting the organohalogens. In comparison to the seawater Cl/Br ratio of 300, the ratio was 2.7–3.1 in the peat core. It was concluded that for Br there is no direct correlation between the Br supply and concentration in the bog due to biological transformations.

Bromine in porewater. Formation of organohalogens is suggested to be the key process in the retention of halogens. The proportion of released halogens has been found to be independent of the halogen concentration in the peat, a fact which indicates that there is another factor that controls the release from peat. It has been concluded [69] that it is due to the degree of peat humification and to the properties of the organic material at the different stages of humification.

When analysing peat bog porewater it has been frequently found that the halogen content may be some 15 to 30 times higher in the pore water that in the rainwater [69,79]. It has been assumed that this is due to additional inputs from seasprays or fog. Instead, the relationship between the porewater and the peat seems to be such that the peat bog is a source of bromine in the porewater, and this depends on the stage of diagenesis which in turn determines the adsorption and desorption process of halogens in peat. For chlorine this relationship is weak. The more dissolved organic matter is released from the peat, the more Br can be found in the porewater. It seems that approximately 50 to 70 % of the bromine in porewater exists in organic forms (soluble organohalogens or halogenated dissolved organic matter), whereas for example in rainwater bromine exists predominantly in inorganic form. In Chilean bogs the proportion of bromine found in the porewater was up to 1–2 % of the total bromine in the moist peat sample. For Cl the proportion was 10–15 %. [69].

As bromine is in the porewater mainly in organic form, dehalogenation of organohalogens is of minor importance for the release of bromine from peat. The atomic ratios of halogens in the porewater have been found to be independent of those in the rainwater. The mean atomic ratios are similar to those found in rainwater, but the high variation depending on the stage of peat decomposition indicates the influence of peat diagenesis on halogen sorption/desorption. Actually, the release of Br from peat correlates positively with dissolved organic matter (DOC) release and the C/N ratio. It is evident that the release of Br is controlled by the release of DOC, and that both parameters are dependent on the degree of peat humification (low degraded peat, high C/N ratio). [69]

To conclude, the Cl/Br ratio is lower for peat than for porewater or rain due to higher retention of bromine in peat in comparison to chlorine. This is complemented by the fact that more of the chlorine will stay in the ionic form (mobile in liquid phase) than the bromine does. Further, the Cl/Br and Cl/I ratio in porewater is generally higher than in peat, whereas Br/I ratio is similar in porewater and peat [69]. Regarding halogens, it is likely that the halogenation of organic matter proceeds in the order iodine-bromine-chlorine [80].

3.2 Bromine content

Bromine content in peat has not generally been reported in connection with the use of fuel; rather it has been of interest to geologists studying the atmospheric deposition of elements where the the preservative characteristics of peatlands are taken advantage of.

Peats acquired from Canada, Finland, Ireland, Latvia, Lithuania, Poland and England for horticultural use were analysed for water extractable bromine in a study comparing bromine contents in peats from different continents [32]. The water extractable form was found to represent only a part of the total bromine in the peat (and soil) samples. Table 3 shows the total and water soluble concentrations of bromine in the peat samples. For all the peats only < 1 % of the total bromine was found in water extractable form. From Table 3 it can be seen that the bromine content in the Irish and English peat is the highest, while the Canadian peat is intermediate in comparison to the continental European peats. Only the peats with the highest total bromine concentration had detectable amounts of water extractable bromine.

Table 3. The total (Br_t) and water extractable (Br_w) concentrations of Br in peat samples (mg kg^{-1}). [32]

Sample	**Type**	**Br_t**	**Br_w**
Canadian	Sphagnum	42	< 0.3
Finnish	Sphagnum	12	< 0.3
Irish	Sphagnum	110	0.9
Latvian	Sphagnum	20	< 0.3
Lithuanian	Sphagnum	11	< 0.3
Liverpool	Sphagnum	116	1.1
Polish	Sphagnum	21	< 0.3
Somerset	Sedge	61	0.4

In studies of areas with different annual precipitation it has been found that the overall Br concentration was due to the overall deposition rate and to retention efficiency as a function of peat degradation. In studies with two ombrotrophic southern Chilean peat bogs from high and low precipitation areas a distinct difference was found in the bromine content [7]. The peat from the high precipitation bog had an average as high as 202 mg kg^{-1} bromine, while the low precipitation area bog had up to 60 mg kg^{-1}. The peatlands experienced annual precipitation of 6000 and 1500 mm yr^{-1}, respectively. The local maximum in the high precipitation bog was approximately 300 mg kg^{-1}. In another study from Canada [78] of two peat hummocks from Bathurst Island in the High Arctic of Canada approximately 530 mg kg^{-1} bromine was found in one bog while the other contained up to 55 mg kg^{-1}. The bogs were only 30 km distance apart. Even though there was a relatively large difference between the bromine content of the two bogs, the content was concluded to be on average higher than in the bogs in Europe.

A Norwegian peat sample from a west coast ombrotrophic bog showed up to 100 mg kg^{-1} bromine content, mainly varying between 50 and 80 mg kg^{-1} as a function of bog depth. The bromine and lead content were studied in parallel in order to assess the extent of anthropogenic origin. A correlation was not definitely shown. [81]

Another set of 15 peat samples collected from Patagonia, Chile, contained a maximum of 122 mg kg^{-1} bromine [44]. The water extractable bromine was analysed separately, and the non-extractable proportion was interpreted to be organically bound. The proportion of organically bound bromine was on average 87 % of the total. The average content of bromine was 61 mg kg^{-1} and of organic bromine 55 mg kg^{-1}. The minimum values were 22 and 16 mg kg^{-1}, respectively. The Cl/Br ratio (mass basis) in the peat samples was on average 8, with a maximum and minimum of 18 and 5, respectively. This result is low compared to the average ratio of 300 in sea water and shows bromine enrichment.

Depth profiles from three cores sampled from a Nova Scotian peat bog within 1 km distance from each other [76] had a maximum content of 62 mg kg^{-1} bromine. Each core had a maximum content higher than 44 mg kg$^{-1,}$ while the bromine concentration varied 3.4 to 3.9 fold according to depth.

In two ombrotrophic peat bogs in the north Scottish mainland and the Shetland islands [79] the total bromine concentration in the peats was 271 mg kg^{-1} in the Shetland and 266 mg kg^{-1} in the mainland bog. The maximum bromine concentration analysed across the bog depth (up till 1 m depth) was found to be 600 mg kg^{-1} in the Shetland bog and 450 mg kg^{-1} in the mainland one. The annual precipitation in these areas ranged from 1000 to 1500 mm yr^{-1}, but the bromine concentration in the rainfall was not reported.

In a Swiss peat bog on average 14 mg kg^{-1} bromine was found. The annual precipitation into the ombrotrophic bog was 1300 mm yr^{-1} [77]. In the sampling of Swiss peat bogs the plants growing on the bog were found to contain 13 mg kg^{-1} bromine, while the peat at just 30 cm depth had up to 27 mg kg^{-1} bromine. [77]

A summary on the bromine content in peats from different continents is presented in Table 4.

Table 4. A summary of Br content in peats.

Origin	**Br, mg kg^{-1}**	**Reference**
Canadian	25–60	[78]
	130–530	[78]
	42	[32]
Finnish	12	[32]
Norwegian	50–80	[81]
Swiss	7–27	[77]
Chilean	202	[7]
	< 60	[7]
	22–122	[44]
Latvian	20	[32]
Lithuanian	11	[32]
English	116	[32]
	61	[32]
Irish	110	[32]
Scottish	270	[79]
	< 600	[79]
Polish	21	[32]

3.3 Concluding remarks

Bromine seems to be preferred over chlorine in the formation of organohalogens. This results in a higher proportion of organobromides over the chlorinated homologues, and this situation seems to be true even if there is many times more Cl available in the diagenesis in comparison to Br. The peat bog profiles found in the literature suggest that Br is incorporated in the organic matter during humification. Br is found to a lesser extent in the porewater but also there it is found primarily in organic matter. On average high Br loading through precipitation and sea sprays results in high Br content in peat, but the fluctuation in the Br content as a function of peat bog depth may be caused by changing climatic conditions.

From the data presented for the bromine content in peats it is evident that in the coastal regions of Canada, Ireland and Japan the soil and peat contain more bromine than inland/continental peats. In Figure 4 shows annual precipitation pictures for selected countries. The areas from which the highest bromine contents have been found are also the areas with 'the highest' coastal precipitation. As an example from the data in Table 3 the bromine content in the Irish peat is some 10 times higher than in the Finnish peat. The average annual precipitation in Ireland is approximately 1000 mm yr^{-1}, which is equivalent to the highest ever recorded in Finland [82]. This results in considerable difference in the flux of bromine in the soil and the peat bogs. Based on the literature on peat and rain water bromine contents, annual precipitation, coastal influence and data reported on soil with varying organic carbon content, it is clear that the favourable combination of these factors result in high bromine content in peat. This is not primarily due to plant uptake in natural conditions nor the influence of rocks or soil type surrounding the peatbog.

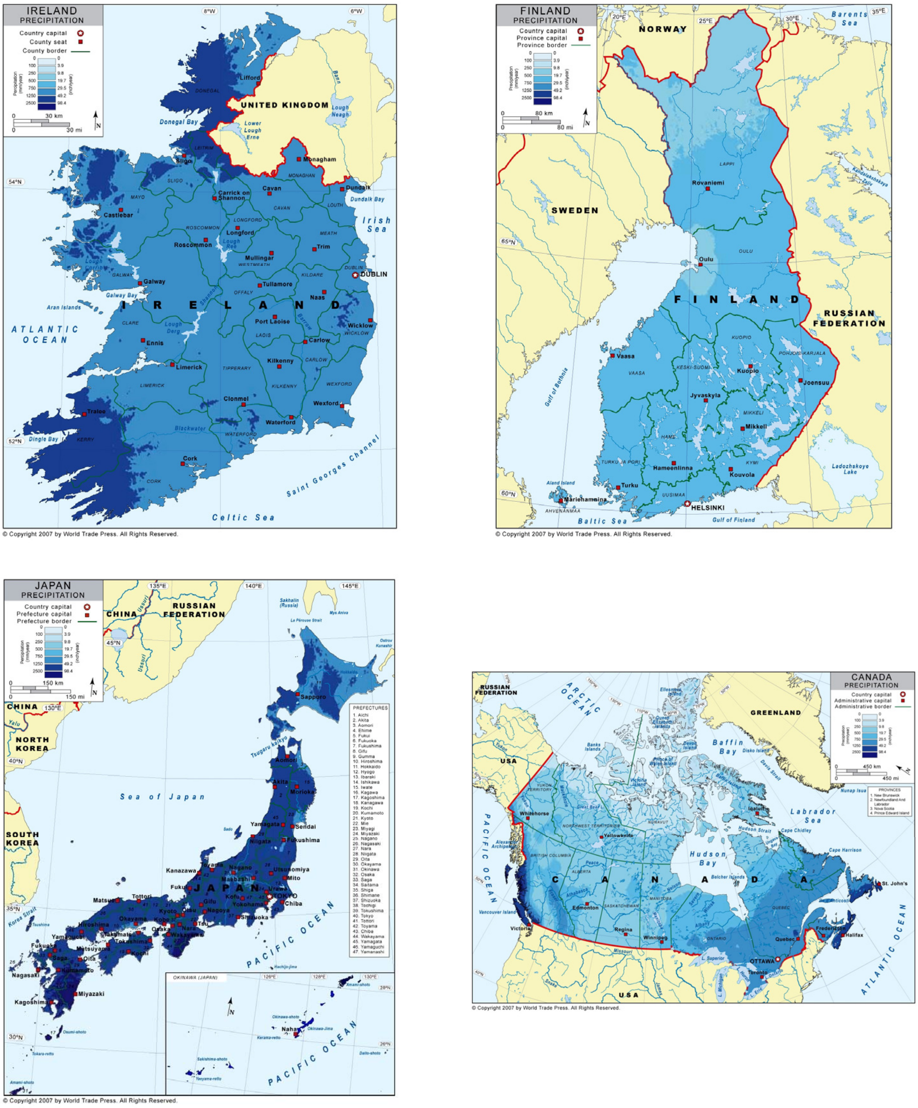


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Figure 4. Annual precipitation in Ireland, Finland, Japan and Canada.

4. Coal

Coal is the most important of the solid fuels, providing 40 % of the electricity and one fourth of the primary energy in the World. An extensive literature can be found on chlorine in coal and it has been recently summarised in review publications [83,84]. Relatively few summarising papers can be found on bromine however [85–89], in addition to the coal trace element studies where bromine has been included. Bromine has caught less attention than chlorine due to its typically lower content and postulated similar behaviour [86].

4.1 Bromine content

The typical bromine content in coal is approximately 20 mg kg^{-1} ranging from 0.5 to 90 mg kg^{-1} [85,90,91]. A listing by continent can be found in Swaine (1990) [90]. Clearly the highest figures have been found in the Canada, the UK and some parts of Australia. High values have since been found in Bulgarian and Ukrainian coals [86,87].

In samples from coals imported in Sweden [92] bromine was found from < 2 to 99 mg kg^{-1}. The highest value was found in UK coal, < 2 mg kg^{-1} in Australian coal, whereas the German, Polish, Soviet Union and US coal had contents between 5 and 23 mg kg^{-1}.

The average for coal in the US is 17 mg kg^{-1} [93], but for each deposit the content may vary greatly, the maximum being 160 mg kg^{-1} [93].

Eskenazy and Vassilev (2001) [86] analysed 219 samples from 8 coal mines in Bulgaria including coal, coaly shales and sandstone enriched in carbonates. The highest bromine content deposit had on average 128 mg kg^{-1} Br. It was postulated that it was due to the high bromine content in the ground waters (70 mg l^{-1}, typically < 0.1 mg l^{-1}). Particularly high bromine content, as a function of depth, was found locally in the Pirin deposit, 256 mg kg^{-1} [87], the mean content being 72 mg kg^{-1}. The mean content in all the 219 samples varied mainly between 10 and 30 mg kg^{-1}, which is similar to that for the US coal.

The Cl/Br ratio (mass basis) in the coals studied was on average < 100, occasionally exceeding 100 and only rarely exceeding 200 [86]. With a particularly high bromine content coal deposit at Pirin, the ratio was consistently below 2–3 throughout the deposit depth and only occasionally peaking at 10–50.

A ratio 'inorganic Br / organic Br' has been established [87] which is always one magnitude lower for bromine than the corresponding ratio for chlorine. This comparison is very interesting and possibly very important in differentiating the behaviour of chlorine and bromine. The analytical procedures were not described thoroughly, however, in that particular work [87].

In Chinese coals the average total bromine content has been estimated to be 9 mg kg^{-1} [94]. From those coals the identified brominated organohalogens were 2,4-dibromophenol and 2,4,6-tribromophenol.

In UK coals, which are on average relatively high in chlorine, 75 mg kg^{-1} bromine has been reported as an average value [89,95] with maximum values up to 195 mg kg^{-1}. These are often referred to as 'saline coals' and are associated with high chlorine content, which seems to show through also as high bromine content.

All together the 34 samples from Bulgaria, Australia, the US, Japan, Canada, South Africa, China and Ukraine that had been collected and analysed for bromine showed a mean bromine content of 170 mg kg^{-1} [88]. This average was raised however by two Bulgarian samples and one Ukrainian with 1130–1620 mg kg^{-1} Br. 74 % of the samples had bromine content < 21 mg kg^{-1}.

In Belgian coals bromine content has been reported to vary from 8 to 24 mg kg^{-1} [96]. From the Belgian samples the highest reported bromine content in coal, 6900 mg kg^{-1}, was reported.

4.2 Bromine origin and modes of occurrence

The exact origin of bromine in coal and the processes involved during coalification are unclear. For nearly all the other elements there is a good understanding of the main processes involved [89,95]. At least some of the bromine is inherited from the plant matter whereas the high concentrations may be due to the influence of underground brines [87].

The bromine content does not depend upon the rank of coal. Typically the content is higher than the average for soil. This has been characterised by the negative correlation between ash and bromine content in coal [86] (see Figure 5). In addition, different coal macerals have been analysed separately for bromine [86], and bromine has been shown to be associated particularly with vitrinite macerals [97]. Vitrinite group macerals are coalification products of humic substances [98] originating from cellular plant material such as roots, bark, plant stems and tree trunks. With some US, English and Australian coal samples it was found that the bromine content in vitrinite were 1.2–2.7 times higher than in the coal samples overall [[99] cited in [86]]. Out of 34 elements analysed bromine was found to be the only one associated with vitrinite in all samples.

A study of UK coals suggests that chlorine and bromine differ from nearly all other trace elements in that they are not present in significant concentrations in mineral matter or bound within organic matter [89,95]. They are thought to be incorporated in the porewaters of coal and they are considered to be preservative, i.e. the original marine deposition imprint has been preserved in the coal. The forms of bromine are therefore suggested to be analogous to chlorine. For chlorine it has been suggested that the organic-associated chlorine predominates. It consists of two different types [83]:

- A minor proportion as a ’true’ Cl_{org} as covalent-bonded Cl in coal organic macromolecules.
- The major proportion of organic chlorine is present as ‘semi-organic’ Cl as anion sorbed on the coal organic surface in pores.

The latter is not ‘true’ Cl_{org}, because in moisture the anions are anchored to the polar organic functional groups on the surface of micropores in coal macerals by ionic attraction [100] and not in the coal macromolecular organic structure. On the other hand it is not ’truly’ water-soluble because it persists after pore water release, at up to 300 °C in coal drying. Preliminary XAFS experiments confirm this speciation for bromine, too. [100]

For South African coals it was found that elements which tend to be more concentrated in marine-derived sediments, e.g. boron, chlorine, lithium and bromine, occur in greater concentrations in the top of coals overlain by marine strata than in coals overlain by non-marine fluvial sequences. The latter do not show enrichments of these elements [101]. This is supported by the suggestion that bromine may originate from marine connate (relic water) which is depleted in Cl/Br ratio. The brines in the coalfields of the north east of England show considerable depletion in Cl/Br ratios compared to sea water [11]. The Cl/Br ratio may be influenced also by the thermal history of the coal deposit, as the devolatilisation of coal beds may result in fluids with low Cl/Br relative to most hydrothermal fluids [97]. The Cl/Br ratio in UK coals is about one fourth of that in the sea water. The same ratio was found for water soluble proportions of Cl and Br, a finding which supports their similar association in coal. The ratio in coal porewater is at the same level (70, mass basis) as brine after halide precipitation. [89]

From the high bromine Bulgarian coals 13 % of the bromine was leached in water. In the high chlorine coals the water soluble NaCl chlorine proportion was pronounced, whereas the corresponding inorganic association of bromine has not yet been identified [86,87]. For the high bromine coal samples collected by Vassilev (2000) [88] water extraction was carried out for chlorine and bromine. Up to 35 % from the chlorine could be leached, while < 1 % of Br was always leached. This finding is in alignment with the findings for US coals [102]. Finkelman et al. (1990) [102] found, however, that from 17 to 54 % of bromine was removed in ammonium acetate solution from some coals. This finding supports the organic association in the micropores.

Even if it is a simple method, water extraction leaves room for speculation on halogen speciation. It has been found that if coals contained above about 0.25 wt-% carbonate, the percentage of chlorine extraction approaches 100 %. The reason is that chlorine (bromine) is held in anion exchange sites and are exchanged when carbonates dissolve. Fine grinding will over-emphasise this ion exchange capacity. [89,95]

4.3 Shales

Coals, coaly shales and partings were analysed for Br by Eskenazy and Vassilev (2001) [86]. This data can be used in two different dimensions: firstly, in assessing the affinity of Br to organic matter (coal) in one deposit, and secondly, in evaluating the Br content in different mining ‘products’ from several mines as a function of ash content. Figure 5 shows the bromine content in coal, coal shales and partings as a function of ash content. From the chart on the left it can be seen that in one deposit there seems to be a negative correlation between the ash and Br content of the 'coal'. This supports the findings on the organic affinity of bromine in coals.

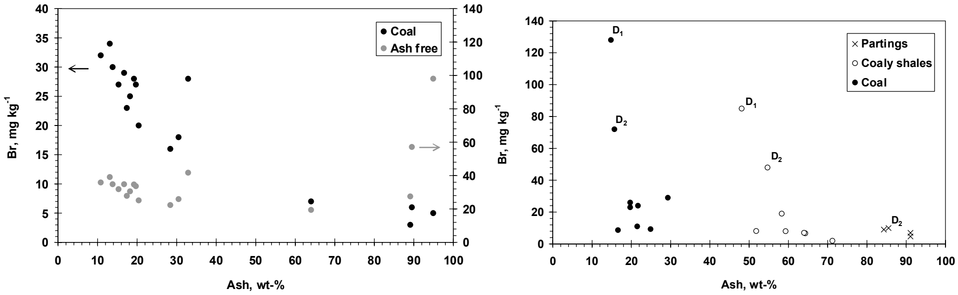

Figure 5. Correlation between the ash and bromine content in coals and coaly shales from the Dobroudzha deposit, Bulgaria (left) and different mining products from 7 mines (right). Data from [86].

On the right in Figure 5 the correlations between different mining products collected from 7 different mines in Bulgaria are shown. This plot divides the 'products' into three classifications, where the coals with mean 20 wt-% ash content have the highest bromine content. The next class is the shales, and the third partings. In one deposit (D$_1$ or D$_2$) the bromine content is always higher in the coal than in the shales or partings from the same deposit.

In addition to the coal in Figure 5 (left) the bromine content in the coal samples calculated on ash free basis is plotted. The finding is that the bromine content is in the proximity of 30–35 mg kg^{-1} in the macerals, whereas from the chart on the right it is evident that the bulk of shales contain some 8 mg kg^{-1} Br. In Canadian oil sands a similar pattern can be observed where the raw bitumen separated from the sand is enriched in Br in comparison to the oil sand. [103]

4.4 Concluding remarks

There is no direct correlation between Cl and Br contents in coals, though the coals highest in bromine have been found in continents with the highest chlorine content. The most influencing factor is the geographic location of coal deposits. The bromine (and chlorine) enrichments, as summarised in the literature [88] are ‘associated with favourable coal-forming vegetation, marine influence, arid and stable conditions of deposition, volcanic activity, diagenetic and epigenetic solutions enriched in halogen elements and metamorphic progression accompanied by optimum pore-size distribution in coal’.

Some of the general findings for coal [88] do not readily apply for UK coals [89]. In the light of the review presented in this paper regarding bromine association in biomass and peat, it seems that bromine has predominantly an organic association and it is not water extractable bromide. Some of the UK coals however are high in chlorine and they may represent another association of bromine. In UK coals a positive correlation was found between water soluble Na, Cl and Br. On the other hand the relationship between chlorine and moisture content was significant, whereas for bromine and moisture it was not significant.

As a conclusion, a significant proportion of bromine may be associated with the inherent moisture of coal porosity. How much this fractionates chlorine and bromine is not known. [88,89]

The assessment of the Br content as a function of ash content proves the organic affinity of bromine. It seems that the bromine content in coal within shale is relatively constant and comparable to coal. But due to the high ash content shales are depleted in bromine.

5. Conclusions

Bromine can be found naturally in solid fuels (if algae and marine plants are included) in all the abundance classes, i.e. major (> 1 wt-%), minor (1–0.1 wt-%) and trace (< 0.1 wt-%). It seems to have similar behaviour to chlorine during thermal conversion: bromine forms high vapour pressure salts in the furnace, bromine contributes to high temperature corrosion of boiler steels and brominated dioxins and furans have been detected in combustion plant effluents. This is understandable as the properties of chlorine and bromine are comparable even if they establish distinct differences, too. The single most important difference in their properties is their oxidation potential, which seems to lead in some significant differences in their behaviour.

The sea is the largest natural reservoir of bromine. Sea spray, on the other hand, seems to be a major direct natural source of bromine whereas the main Br sinks are atmospheric reactions, oceans and soils. Bromine is commercially explored from some underground brines and the Dead Sea where 5000 mg l^{-1} Br can be found. The soils showing high bromine deposition complemented by high soil carbon content are typically the highest in bromine.

Algae represent a potential solid fuel source in the future. They assimilate inorganic bromide from the sea. The uptake is associated with bromoperoxidase (BPO) enzymes. This may result in enrichment of bromine of up to several weight percentages in dry tissue. This is primarily in organic form.

Terrestrial plants may use Br as a nutrient, but only if chlorine is not available. In high concentrations bromine is toxic for plants. In some occasions bromine may displace chlorine to be available for more essential functions in the plant. Due to the use of bromine fumigants and pesticides one must be careful in considering high bromine content in plants as natural.

Peat enriches bromine and it is particularly efficient in bromine retention during the humification process. This was proven by assessing the depth profiles of bromine in peat cores. Bromine is bound in organic matter. With respect to peat, those peats with the highest bromine influx are also the highest in bromine content. However there is no correlation between chlorine and bromine content in peats.

In coals bromine seems to be inherited from plant matter but it may be possible to find Br in water soluble form as a result of underground brine influence. As bromine has primarily organic affinity, shales are depleted in bromine in comparison to coal.

In Table 5 the different fuel classes considered in this work are listed, together with the typical bromine content and the predominant form of bromine.

Table 5. Summary of the natural content and forms of bromine in solid fuels.

Fuel	Content, mg kg^{-1}	Form/Function
Biomass		
Terrestrial plant, inland	2–20	Mobile nutrient bromide
Terrestrial plant, coastal	–150	
Marine algae and plants	150–1000	Organically bound bromine, over 1600 compounds identified
Marine, highly concentrating	30 000–60 000	
Peat		
Inland	10–20	Sorption of Br to humic acids, possibly mediated by microbial activity
Coastal	50–150	
Coal		
‘Standard’	5–20	‘Semi organic’, bound in maceral micropres by ionic attraction
Marine influence	100–200	Water soluble proportions can be found
Shales	< 10	Bound in the macerals of the shale

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PUBLICATION III

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

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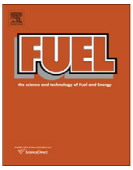

Bromine as an ash forming element in a fluidised bed boiler combusting solid recovered fuel

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Solid recovered fuel

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 it if there is a source of bromine in the fuel corrosive high vapour pressure bromides can be formed analogously to chlorides.

1. Introduction

Due to the CO_2 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 CO_2-equivalents per year, which corresponds to 29% from the total CO_2-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 an 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 if typically enriched in high calorific value plastics [25] and it often consist 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 .

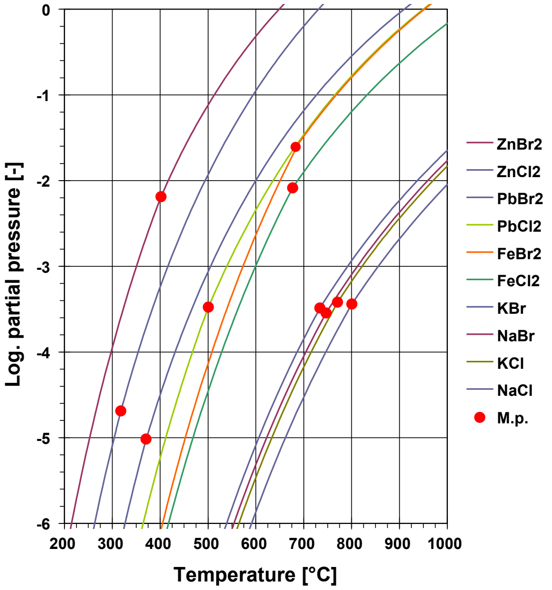


Fig. 1. Calculated saturation pressures and melting points (m.p.) for selected chlorides and bromides [36].

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.

2. Experimental

2.1. The BFB plant

Stora Enso Anjalankoski co-incineration plant started as a pulverised coal boiler in 1971 with a small fixed grate for bark combustion. The first commercial size bubbling fluidised bed (BFB) boiler in Finland was connected to this coal boiler in 1983 to combust wet sludge from the adjacent paper mill's wastewater treatment. The grate of the coal boiler was converted to BFB in 1995. A wet scrubber was also installed after the ESP to improve flue gas cleaning and establish heat recovery from the flue gases. With this flue gas cleaning system the plant can comply with the EU Waste Incineration Directive [39] (WID) emission limits. After the start-up of the BFB, co-combustion of SRF was initiated in order to manage the paper mill's waste treatment, and was later widened to the use of acquired package wastes which could not be recycled. Simultaneously, the boiler live steam values were reduced to the level of 500 °C/80 bar from 525 °C/87 bar in order to allow a safety margin for more corrosive combustion gases in comparison to coal firing. An indirect thermal sludge dryer was invested in the year 2000 in order to combust all the paper mill's waste water treatment sludge with a dry matter content of about 90%. This also made it possible to increase the amount of SRF in the fuel mix, due to the sludge's favourable influence on chlorine-induced risk of corrosion. In 2006 the boiler received a new environmental permit according to the WID with an annual SRF capacity of 50,000 tonnes. The SRF share from all fuels was increased to 60% (on energy basis) after long term tests and investigations.

The boiler utilises on average 30% Scandinavian spruce bark and 10% dried paper mill sludge alongside SRF on energy basis. All the fuels are introduced in the boiler house in separate streams. From the fuel receiving pocket outside the boiler house, bark is fed by a conveyor belt in the boiler house where it is forwarded to a scraper conveyor. From there it is discharged through screws into two parallel 5 m^3 buffer fuel hoppers. Bark proportion in the fuel mix is adjusted by discharge screw feeders under the two hoppers which feed bark into the furnace through two parallel fuel chutes equipped with rotary feeders. SRF is supplied after crushing and intermediate storage silo in the boiler house by a series of scraper conveyors. In the boiler house SRF is discharged from the scraper conveyor by screws which forward the fuel in the same two fuel chutes on the left wall of the furnace where bark is fed. Both, the bark and SRF discharge screws have been calibrated for the volumetric production per revolution which enables accurate fuel proportioning in the two parallel fuel chutes, and eventually in the furnace. The paper mill wastewater sludge is supplied from the activated sludge process to the drying. This consists of a series of mechanical (press) and thermal driers. The final indirect thermal drier feeds a pneumatic transportation line, which takes the sludge into the boiler house. The pneumatic line blows the sludge directly into the furnace through the front wall.

The ESP consists of two parallel lines in the flue gas flow direction, both with two sequential fields. Ash is forwarded from a hopper below each of the four sections of the ESP by pneumatic transportation to a discharge platform. As the hoppers reach a certain level of fill-up, pneumatic transportation takes place automatically. Each of the lines was sampled during the pneumatic sending procedure. Samples were sucked from the line by a vacuum cleaner and combined into one sample.

2.2. Fuels

The chemical fractionation procedure was applied in the characterisation of the ash forming matter in the fuels. The fractionation is based on the consecutive leaching with water, ammonium acetate, and hydrochloric acid. The method was originally developed for the characterisation of coal [40,41] and further modified for and applied to the characterisation of biomass fuels [42–44]. Increasingly aggressive solvents, i.e. water (H_2O), 1 M ammonium acetate (NH_4Ac), and 1 M hydrochloric acid (HCl) leach samples into a series of four fractions (including the insoluble residue) for analysis. Typical ash-forming components which are leached out by water include alkali metal salts: sulphates, carbonates, and chlorides. Elements leached out by NH_4Ac are believed to be organically associated, such as magnesium, calcium, potassium and sodium, or weak acid soluble salts. HCl leaches the carbonates and sulphates of alkaline earth and other metals. Typically silicates and other minerals remain in the insoluble residue; however, chemical reactions of the ash forming matter during digestion may alter the speciation. Therefore the results should be used with caution and to complement other available analysis data.

The spruce bark originates from the adjacent paper mill where the stem wood is used for mechanical pulping. The wood is Norway Spruce (*Picea abies* (L.)) of which a detailed study regarding its ash forming matter can be found in the literature [45]. The main ash forming elements are Ca, K and Na, see Table 3. Compared to stem wood bark it is rich in these nutrients. In the bark K and Na exist mainly as water soluble salts, and Ca in equal proportion as ion exchangeable ions and HCl soluble included mineral, namely calcium oxalate [45]. Br and S content in the bark are very small. During the experimental campaign bark, and the mixture of bark and sludge in Experiment II, were collected from the conveyor belt taking the fuel into the boiler house.

The paper mill wastewater sludge consists of wood fibre residue, paper filler and coating rejects which are mainly kaolin and calcium carbonate as well as residues of flocking agents. In the wastewater treatment some 30–40 kg of iron(III) sulphate per ton of dry sludge is added to the wastewater stream to precipitate out non-settleable solids. In addition, ash forming matter in the sludge originates from alum, namely aluminium(III) sulphate, which is used in pH control and as a sizing agent in paper making [46]. Regarding the main salt forming matter, Ca is the main component, originating either from the filler/coating residues or from

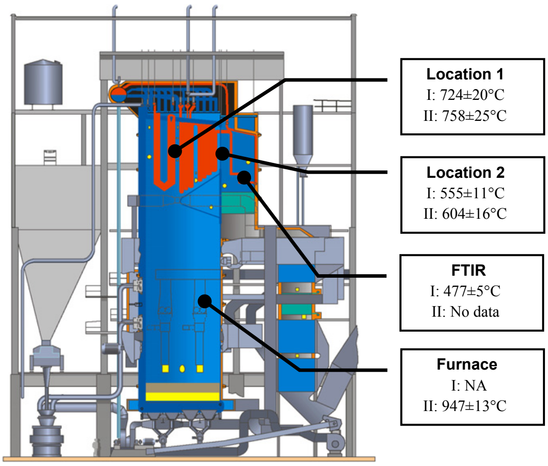


Fig. 2. Schematic picture on the Anjalankoski BFB boiler indicating the aerosol, FTIR and temperature measurement locations. The membrane wall sample was cut off at the same location as the "Furnace" measurement point is indicated in the picture. Gas temperatures and standard deviations at the measurement points are indicated for both experimental conditions.

Table 3
The properties for the fuels and fuel mixes used. Concentration of selected ash forming compounds relevant for this study has been included in the table. Analyses were carried out according to standardised CEN/TS, ASTM and ISO methods for biomass and SRF.

	SRF I	SRF II	Bark	Sludge	Experiment I	Experiment II
Moisture (wt%, ar)	18.3	18.1	54.8	8.3 (67[a])	38.6	42.7
Ash (wt%, db)	7.5	7.5	2.1	21	7.2	5.6
Ultimate analysis of dry solids (wt%, db)						
C	54.9	55.1	50.4	41.7	51.0	52.4
H	7.6	7.6	5.9	5.2	6.5	6.7
N	0.79	0.48	0.27	1.63	0.69	0.43
S	0.15	0.15	0.02	0.73	0.18	0.12
O	29.1	29.1	41.3	29.7	34.4	34.6
Ash forming compounds (mg/kg, db)						
Ca	17,800	19,100	7430	21,500	13,908	13,925
K	938	1270	1090	1200	1470	1445
Na	1960	1860	978	1490	1042	1186
Cl	4600	4400	150	210	2100	2300
Br	40	205	10	27	25	110
Heating value (MJ/kg)						
LHV, db	23.56	23.51	19.00	16.33	20.54	21.17
LHV, ar	18.80	18.81	7.25	14.77	11.68	11.08
Fuel proportions in the experiments (%, energy basis)						
Experiment I	51		36	13	100	
Experiment II		60	38	2		100
Fuel proportions in the experiments (%, dry basis)						
Experiment I	42		43	15	100	
Experiment II		51	45	4		100

[a] For wet sludge in Experiment II.

wood fibre reject. In contrast to the bark, the sludge contains Ca mainly (80%) in the NH_4Ac soluble form. This is probably due to the partial dissolution of calcium carbonate already in the weak acid; this step does not dissolve all the carbonate, however. The residual $CaCO_3$ is dissolved in the mineral acid, HCl, as no insoluble Ca residue was found. Regarding the acid soluble fraction, it is noteworthy that calcium oxalate is absent from the stemwood, which essentially forms the wood fibre reject, but is abundant in the bark [45], which implies that at least all the HCl soluble Ca originates from the $CaCO_3$ paper filler/pigment. Na exists mainly as water soluble and K as insoluble compounds. The interpretation for the sulphur fractionation result is not fully clear or well established. It is likely that sulphur in the sludge is bound in a reduced form as a result of the activity of sulphur reducing bacteria (SRB) [47,48]. If all the S in the iron(III) sulphate added in the wastewater treatment is calculated back to be a concentration per unit of dry sludge, it results in S concentration of 0.68 wt% which already is quite close to the concentration found in the sludge (0.73 wt%, see Table 3). This indicates that a high proportion of the S in the sludge originates from the flocking agent ferric sulphate.

The SRF utilised at Anjalankoski plant originates from offices, wholesale business and small and middle scale industry in southern Finland [49]. Suitable wastes are source-separated package and other solid industrial non-recyclable wastes, which are separately collected by the SFR supplier. In offices and commerce the source of this fuel can be identified from the waste bins labelled energy fraction . The labelling instructs the consumer to sort in this fraction the following items: packaging plastics (not PVC), contaminated paper and cardboard, wooden packages, plastics (not PVC), expanded polystyrene, paper towels and clothes and textile. Naturally, in the collection of the waste it is ultimately the consumer decision at the trash bin that dictates which items end up in the energy fraction. The fractions collected from commerce (shopping centres, supermarkets) are mostly packaging materials, i.e. paper, cardboard and plastics in various forms. Industry sourced energy fractions are different types of demolition and packaging discards with production wastes from furniture manufacturing. These contain mainly textiles, wood and plastics. In the SRF preparation plant the material is crushed to 50 100 mm particle size and magnetic materials are separated. SRF is transported to the BFB plant as wrapped bales or fluff.

Based on the data in Table 3 the quality of the SRF was comparable during the two experiments. The main salt forming compounds were Ca, followed by Cl, Na, S and K. Cl content in the SRF was at the same level in both experiments but Br content was higher in Experiment II than in Experiment I. SRF is the main source of both of these halogens in the final fuel mix. The source of Br and Cl in SRF are discussed in detail later in this paper. Their leaching behaviour is similar: both are found mainly in the insoluble residue. SRF is also the main source of Na in the fuel mix, which is bound in water soluble form. This is likely to be residual dietary salt from disposed food packages. K and S are almost equally distributed between water soluble and insoluble fractions, with a minor proportion found in Ac and HCl fractions. Ca is found mainly in the Ac soluble fraction with small but equal proportions in water and acid soluble fractions. This is in alignment with the high proportion of Ca found in Ac soluble form in the sludge: the main Ca source in SRF is packaging material, i.e. paper and cardboard: see Table 1, which contains only the stem wood fibres as well as $CaCO_3$ applied as paper and cardboard filler and coating material. The other sources include gypsum from construction and demolition waste, as well as calcium carbonate in plastics additives (surface treatment and filler). However, the latter two must be small in comparison to paper and cardboard fillers and coatings.

2.3. Sources of Cl and Br in SRF

There is a general agreement that Cl in SRF originates mainly from chlorinated plastics such as PVC or food residues which contain dietary salt [4,50]. In addition, chlorine is used in flame retardants [51]. Chlorine can also be found in other plastics than PVC where the source of Cl is somewhat different to that in PVC: Cl is used in the Ziegler Natta catalysts mainly in the form of $TiCl_3$ (most likely speciation of the residue in polymer) with $MgCl_2$ support for polymerisation of polyolefins, namely polypropylene (PP) and polyethylene (PE). These catalysts are able to carry out a repeated insertion of olefin units during polymerisation and produce high isotactic yields [35]. Literature indicates that residues of these catalysts may result in Cl concentration up to 300 1500 mg/kg in polyolefin plastics [35,52 54].

Acid forming anions, here namely Cl, can cause premature aging of the plastic and these are neutralised by acid scavengers which are introduced in the final products [35]. These include Zn/Ca stearates, zinc oxide, hydrotalcite and hydrocalumite [34] depending upon the plastic type and final application. Acid scavengers are added in plastic in excess to achieve sufficient scavenging capacity and therefore can act as a source of anions to neutralise the hydrogenhalides, HCl and HBr.

Like other members of group VII in the periodic table, bromine is a reactive element, and consequently it is mostly naturally found in the form of inorganic salts of the alkalis and alkaline earth metals in seawater, saline lakes, and the earth s crust. For industrial processing bromine is extracted from brines at different locations in the world [55]. Organic bromine and bromides are naturally formed in plants, food, and animal tissues including human blood. Brominated phenols and diphenyl oxides (ethers) are produced by some sponges, marine bacteria and algae [56]. The major source of dietary bromide is table salt.

The major areas of bromine production in the world are the Dead Sea in Israel and Jordan, salt brines found in the United States and China, and ocean water in the UK, France and Japan. In 2000, 470,000 tonnes of bromine was produced, for use in water purification (treatment in swimming pools), agriculture (pesticides), cars (batteries for electric cars), healthcare (analgesics, sedatives, antihistamines) and photography (black and white film) [57]. However, the largest use with indications in the proportion of 50% of bromine is in flame retardants [58,59].

By far the largest amount of BFRs are utilised in electronic and electric equipment (EEE), i.e. circuit boards and equipment casings for TV and PC housings. Building and construction applications include construction and insulation boards and extruded foams. Textile applications are to large extent synthetic and natural fibre drapery, upholstery, fabrics and furniture cushioning. Transport applications include the plastics and elastomers used in cars. [60,61].

The exact source of Br in the SRF used at the boiler plant is not definitively known. A commonly referred to source of Br in wastes are flame retarded plastics [31,51,55]. The data on Br content in SRF can scarcely be found in the published literature, with the maximum concentration reported in SRF being 520 mg/kg [62]. In MSW Br content of some tens of mg/kg has been reported [63].

Flame retarded plastics can contain several weight percentages of halogens [62,64]. There are two main options for incorporating BRFs in plastics: either additive or reactive. Additive BRFs are those that do not react with the application, here plastic polymer, but are simply blended with the polymer. These types of BRFs are those most likely to leach out of the products [65 67] and may lead to human exposure. Indications of this can be seen in fuel fractionation results illustrated in Fig. 3. Cl solubility can be a subject for discussion as it may also originate from inorganic salts in biomass and SRF, but as the Br is assumed to be only of anthropogenic origin in the form of BRFs, its solubility characteristics should represent the solubility of BFRs in the fractionation procedure. When used as reactive the BRF becomes covalently bound in the polymer and is effectively lost in the polymer.

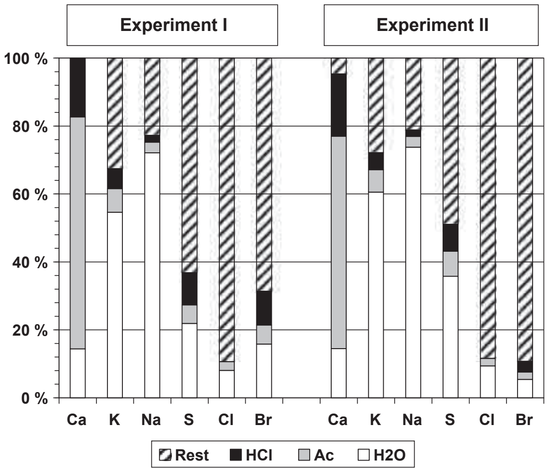


Fig. 3. Chemical fractionation results for the main ash forming elements in the fuel mixtures. The bars show the soluble fraction of each element in the corresponding solvent and the proportion of insoluble fraction (Rest).

The high content of bromine, chlorine and heavy metals in Waste Electrical and Electronic Equipment (WEEE) has led to the need for establishing separate collection and recycling scheme for this type of waste, in order to reduce environmental impact [68]. For this reason, this type of material is not found in large quantities in SRF. Flame retarded plastics can be found everywhere, however, where thermal stability is required, also in waste fractions commonly found in SRF. These are: polystyrene foams in construction; textiles in sofas, chairs and upholstery; decorative profiles; construction and protective films; polyamide or nylon based heat protective hoods and pipes; different types of polypropylene (lamp, gadget) holders, sockets and kitchen hoods etc. In the electronic equipment applications PVC polymer may also be applied, but in the main they take advantage of other polymers, mainly epoxy resins and high impact polystyrenes (HIPS). High Cl concentrations can nonetheless be bound in these materials, indicating that chlorine based flame retardants have been applied.

The three most widely used BFRs today and over the past 10 20 years of the era of plastics are tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (DecaBDE) and hexabromocyclododecane (HBCD). These three compounds account for some 94% of the used BFRs [57]. In the past also polybrominated biphenyls (PBBs) were used but were banned due to their chemical similarity to polychlorinated biphenyls (PCBs) which are toxic. PBBs existence in waste fuels is possible, if not even likely, as the life cycle of the applications can be longer than the time since they were banned from use in the late 1970s [65].

The main use of TBBPA is as a reactive flame retardant in epoxy and polycarbonate resins for applications such as circuit boards. It may also be used as an additive flame retardant, for example in the manufacture of acrylonitrile butadiene styrene (ABS) resins, HIPS and phenolic resins. Where TBBPA is used as an additive flame retardant, it is generally used alongside antimony trioxide for maximum performance. Antimony trioxide is generally not used in conjunction with TBBPA in reactive flame retardant applications [61]. DecaBDE is mostly used in applications in the plastics and textile industries. It is an additive flame retardant. The main uses of HBCDD are in the polymer and textile industries. HBCDD can be used on its own or in combination with other flame retardants, e.g. antimony trioxide and DecaBDE [60]. HBCDD is used in four principal product types: expandable polystyrene (EPS), extruded polystyrene (XPS), HIPS and polymer dispersion for textiles.

There is a continuous debate on the safety of BRFs for humans and the environment. Currently for DecaBDE and TBBPA no risks to human health or to the environment have been identified, and regarding HBCD the assessment is on-going [60,61,69,70].

2.4. Membrane wall

During a yearly shut down increased corrosion of the furnace membrane wall was observed above the fuel feeding chutes, starting from the top of the chutes reaching up 6 m from the top. A corrosion rate of up to 2 mm/year was measured with ultrasonic flaw detector. Due to the observed corrosion in the tubes, samples were removed from the wall. In order to study the corrosion mechanism cross-section samples were prepared of one of the removed tubes. The sample was cast in epoxy and polished with silica carbide sandpaper and isopropanol. The sample was then analysed with SEM EDX (Scanning Electron Microscope Energy Dispersive X-ray). The material of the furnace membrane wall was a widely used quality of carbon steel.

2.5. Aerosol and ESP ash sampling

Aerosol samples were collected from the locations indicated in Fig. 2. The sampling was carried out with a combination of an air cooled gas permeable tube probe and two consecutive ejector diluters. Sample gas is sucked into the probe and immediately diluted and quenched within a 200 mm long gas permeable tube diluter. This dilution stage was carried out with nitrogen in target dilution ratio of DR = 8. The sample gas was taken from the probe to a second dilution stage carried out by means of an ejector diluter with DR = 3 and then divided between two parallel Dekati type Low Pressure Impactors (DLPI) and an Electric Low Pressure Impactor (ELPI). At the location of the division a third gas stream was taken to an FTIR gas analyser for determining the dilution ratio based on H_2O and CO_2 (target value DR = 24). The reference H_2O and CO_2 concentration for determining the total dilution ratio was taken from the FTIR located in the second pass. This means that the concentrations found in combustion gases presented for the different species are all reduced to the conditions prevailing at the second pass FTIR. Both aerosol sampling lines (for DLPI and ELPI) included a cyclone separator with 10 μm cut-size. The two DLPIs were connected in parallel and were collecting sample after this cyclone and ELPI after the third stage dilution that was carried out by means of an ejector diluter with DR = 11. All the dilution stage utilised 5.0 nitrogen for dilution. A schematic picture of the sampling arrangement is shown in Fig. 4. The collection membranes in the impactor were Nuclepore polycarbonate membranes which were greased by spraying Apiezon L on the particle collection sites positioned below the DLPI jet plates in order to enhance particle adhesion. The filters after the impactor stages were PTFE Pall Teflo type filters. Before elemental analyses the impactor sample membranes were put in sample tubes and extracted for five days with water at room temperature. The tubes were shaken every now and then. Sample tubes were hold two hours in ultrasonic bath and two hours on a vertical-shaft mixer before extraction. Na, K and Ca concentrations of the solutions were measured by Flame Atomic Absorption Spectrometry (FAAS) and concentrations of chloride, bromide and sulphate by Ion Chromatography (IC).

After collecting the ESP ash samples they were fractioned chemically in a similar way as were the fuels based on the leaching test developed for biomass fuels [42,44] which has also been applied for fly ashes [71]. The total concentration of the cations in the ash was analysed by means of a Philips PW2404 X-ray Spectrometer complemented with Semi-Q software. For Br, Inductively Coupled Plasma Mass Spectroscopy (ICP MS) was used after HNO_3 HF digestion, and IC for Cl after HNO_3 digestion. S concentration was analysed by means of an ELTRA CS-500 carbon/sulphur determinator for both total and water soluble samples. IC was applied in determining Cl from the water solution and ICP MS for the cations and Br.

The aerosol sampling system has been applied in work published earlier [72,73]. Based on those experiments it is possible to evaluate the uncertainty involved in the sampling. This uncertainty comprises the error in weighing the DLPI membranes, elemental analyses and losses in the sampling system. The error from weighing of the membranes has been shown to be approximately 10% [72]. This is complemented with the error originating from the elemental analyses, which is estimated to be approximately 15%. These are complemented with the losses in the sampling system. This is in the case the results are calculated to be as the concentrations in the combustion gases as in Fig. 11. For this sampling system the chlorine balance has been closed with an accuracy of 6% [73] when chlorine bearing aerosols were used as the tracer compounds. If this uncertainty is used for the sampling specific fluctuation in the result, the total uncertainty can be estimated from:

$$\sqrt{10^2 \quad 15^2 \quad 6^2}\% \quad 19\% \qquad 1$$

2.6. Experimental campaign arrangements

In the experimental campaign for aerosol and fly ash sampling two experimental conditions were used. The SRF/Bark proportion was kept as constant as possible in both experiments, on a dry mass basis of 49%/51% and 53%/47% in Experiments I and II, respectively. The proportion of the sludge from the total fuel mix was 14.8% and 4.3% in Experiments I and II, respectively, and the rest, i.e. approximately 85% and 96%, was composed of the SRF Bark mix: see Table 3. In Experiment II the sludge drier had to be shut down as it cannot be run on partial loads due to the risk of fire. Wet sludge was therefore mixed with the bark by introducing it to the bark conveyor belt outside the boiler house through a fuel unloading line parallel to the bark receiving pocket. As the sludge is a high sulphur, high kaolin fuel it is postulated that it influences

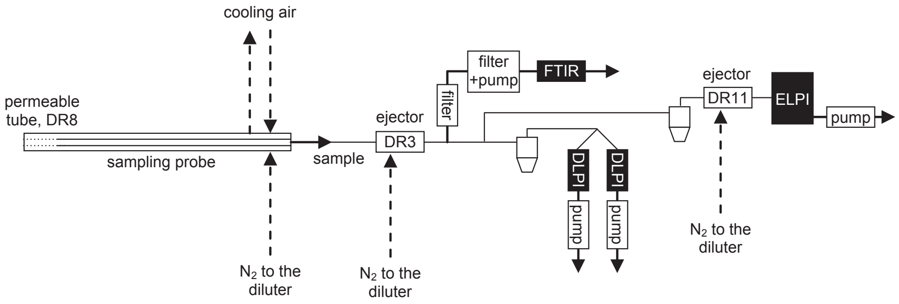


Fig. 4. Schematic picture of the aerosol sampling installation.

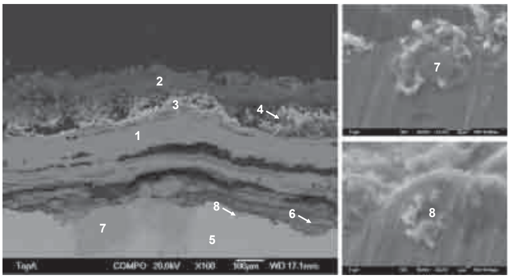
alkali halogen chemistry in the furnace through the formation of sulphates instead of halides, or adsorption of the halide vapours in the sludge bound kaolin.

3. Results and discussion

3.1. Membrane wall

An SEM image from a cross-section of one of the corroded membrane wall tubes is shown in Fig. 5. The top layers of the cross-section indicated with numbers 2–4 are deposit layers and the light grey section at the bottom of the image is the tube material (number 5). The scaled layers (1) in the middle of the image are the corrosion product (mainly iron oxide). The image is a back scatter electron image, which means that different elements are displayed with different degrees of darkness in the image, the heavier the element the lighter the hue of grey. The composition of the numbered spots as analysed by the means of EDX are presented in the adjacent data table. The analyses were made as area analyses and are chosen to be representative areas for each part of the sample.

The tube surface was covered by a relatively thin deposit. The outermost layer of the deposit (2) consists mainly of potassium, calcium and sulphur, probably as potassium and calcium sulphate. The lighter grey layer closer to the metal (3) consists of sulphur, potassium, lead, sodium and chlorine. The amount of lead is considerable (8.5% on atomic basis) and can be seen as the light grey colour in the image. The layered area in the middle of the image (1 and 6) is the corrosion product layer (Fe_2O_3 based on atomic ratios).



	1	2	3	4	5	6	7	8
S	1.2	11	14	15				
K	0.9	7.1	8.9	20				
Na	1.3	6.2	4.8	6.7				
Cl	0.6		4.8	0.1			6.8	6.1
Br							16	
Ca	0.4	7		0.3				
Mg		1.2						
Si	0.6	2.8		0.2	0.5	0.3		
Al	0.8	2.0	0.4					
Zn		0.8						
Pb	0.2	0.3	8.5	0.2				
Fe	32	0.5	1.4	1.4	98	48	38	46
P		0.5						
Mn	0.3	0.4						
Ti		0.3						
Mo					1.5	0.8	0.4	0.5
O	61	60	58	57		50	39	47

Fig. 5. SEM picture (left) of the cross-section of the corroded membrane wall tube with the elemental composition (at%) of the numbered locations. The right hand side pictures show magnifications from locations 7 (top) and 8 (bottom).

Clear indications of chlorine-induced corrosion and the formation of iron chloride can be seen in areas 7 and 8. Area 7 consists of iron, oxygen, bromine and chlorine. Assuming that all chlorine and bromine is present as iron compounds gives 3.4 at% $FeCl_2$ and 8.0 at% $FeBr_2$, which would leave 13.4 at% Fe_2 and 12.9 at% O_3 to form Fe_2O_3. The corresponding mass proportion for Bromine in this location is 30 wt%. Area 8 represents a typical trace of chlorine-induced corrosion consisting of iron, oxygen and chlorine, indicating the presence of iron chloride and iron oxide. The small traces of molybdenum in both locations originate from the steel.

The membrane wall surface temperature is not definitely known and can be estimated only roughly from the steam values. The temperature of saturated steam at 80 bar (which is the live steam pressure for which the boiler is designed) is 296 °C. According to the plant data the steam drum pressure is some 1.5 bar higher than this and at the location of the corroded membrane wall sample there is also the influence of the static head from the feed water down comers, which increases the saturated steam temperature in the order of 2 °C. The tube wall thickness was originally 5.6 mm. There are indications in the literature [74–76] that the wall temperature may be some 15 °C higher than the saturated fluid inside the riser tubes, and this is excluding the possible influence of water/steam side scaling. With a compact oxide layer thickness of 300 μm on the water/steam side, the gas side temperature has been estimated to increase for about 30–40 °C [76]. Also the local heat flux is a major variable which is not definitely known in the BFB boiler. To conclude, it is not reasonable to assume the wall temperature would have been very much below 350 °C.

The surface of the tube underneath the deposit and corrosion layer, as illustrated in Fig. 6, was also analysed with SEM–EDX. A SEM image and EDX maps of the exposed surface (on the right in Fig. 6) show that iron oxide is the main constituent of the analysed surface. Chlorine, bromine, lead and silicon can also be found, however, there is a correlation between the areas of chlorine, lead and bromine that does indicate the presence of lead chloride/lead bromide or a mixture of these.

It can be concluded from the SEM–EDX study that both bromine and chlorine are found in the corrosion front. The analysed deposit does not contain detectable amounts of bromine, but bromine can be found between the oxide scale and the tube surface. The EDX maps indicate that bromine would be in the form of lead bromine, possibly in combination with lead chloride. This implies that bromine could have formed $PbBr_2(g)$ in the furnace which then condenses on the tube surface according to the saturation curve in Fig. 1. The SEM–EDX analysis of the corrosion front indicates that bromine would then react with iron in the steel in a similar way as chlorine, forming $FeBr_2$. Bromine was found only in small spots in the corrosion front which can be due to (a) low overall concentration of Br in the furnace and (b) the high vapour pressure of $FeBr_2$, which leads to vaporisation of the iron bromide that is formed. If the Br long term concentration is as low as the fuel analysis results from the experimental campaign indicate, Br seems to be contributing already in low feedstock concentrations to high-temperature corrosion.

3.2. ESP ash

In Fig. 7 are show concentrations of the relevant gaseous species (for fly ash formation) in the second pass measured by means of

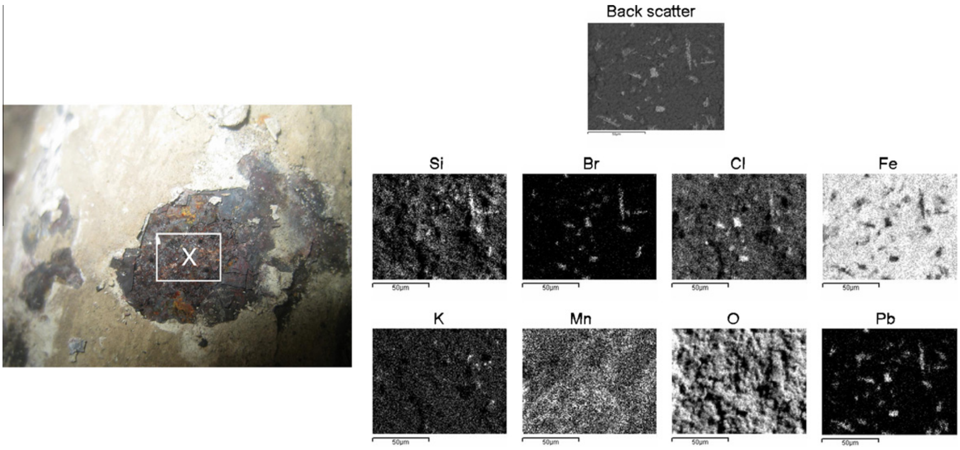


Fig. 6. The location of the analysed area on the tube surface (left) under the slag and corrosion product layer. To the right, EDX element mapping of the same area.

FTIR. Some 20 ppm SO_2 concentration was measured during Experiment I, but only occasional 1–2 ppm peaks during Experiment II. In the latter case majority of the sulphur is bound in the ash. HCl concentration is approximately the same in both experiments. The halogen speciation and balance between hydrogen halide and ash forming matter is discussed in Section 3.3.

Fly ash samples were collected from the ESP during both experiments. Results are presented in Fig. 7 for the total analysed concentration of Cl, K, Na, S and Br and their water soluble proportions in the ESP ash. The main water soluble element was calcium with 28,500 mg/kg in both experiments. Ca is the dominating element in the ESP ash with a total concentration of 22 wt% in Experiment I and 27 wt% in Experiment II. The water soluble fraction may be to large extent free lime, CaO [77]. This is supported by the Ca/S atomic ratio for the water soluble fractions, which was 3.7 and 5.4 for Experiments I and II, respectively. This already indicates a large excess of Ca over all the water soluble anions. Atomic ratio (Cl + Br + 2S)/(2Ca) for the water soluble fraction is 0.4 and 0.6 for Experiments I and II, respectively. These figures indicate that even theoretically all of the Ca cannot be bound in salts, and due to the low solubility of the corresponding carbonate and silicates, neither can it be in these forms.

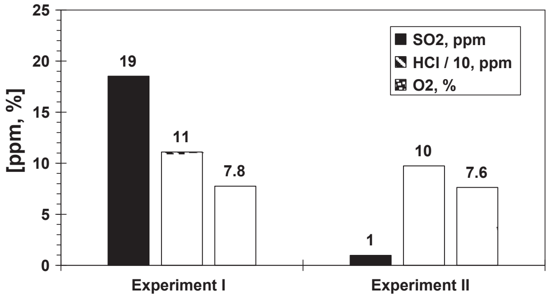
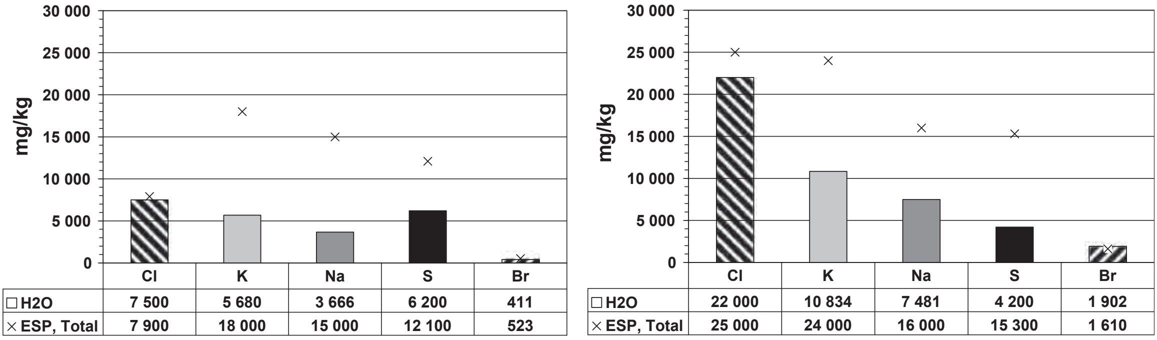


Fig. 7. The measured concentrations of gaseous species in the second pass relevant for this work.

The character of the two halogens considered, Cl and Br, are similar in terms of solubility. They are forming compounds that are water soluble. The water soluble fraction for Cl is slightly less than the total concentration; however, water soluble species clearly dominate. In contrast to the halogens, K, Na and S form to large extent compounds that are insoluble in water. Also it can be seen from Fig. 8 that the concentrations of all these elements are higher in Experiment II and their water soluble concentrations are approximately doubled, with the exception of S, when compared to Experiment I. This is an indication of a higher concentration of alkali halogen compounds in the furnace in Experiment II



	Cl	K	Na	S	Br
□ H2O	7 500	5 680	3 666	6 200	411
× ESP, Total	7 900	18 000	15 000	12 100	523

	Cl	K	Na	S	Br
□ H2O	22 000	10 834	7 481	4 200	1 902
× ESP, Total	25 000	24 000	16 000	15 300	1 610

Fig. 8. Total concentrations and water soluble fractions of Cl, K, Na, S and Br in the ESP ashes for Experiments I (left) and II (right).

than in Experiment I. This is even allowing for the lower ash content of the fuel mix in Experiment II than in Experiment I due to the lower proportion of sludge, i.e. fly ash dilution by sludge ash (see Table 3). If this is the case, it should show through also in the in-furnace aerosol sampling for vaporised ash forming compounds which are presented later in this paper.

Excluding Ca, the atomic ratios (Cl + Br)/(Na + K) for the water soluble fractions were 0.7 and 1.0 for Experiments I and II, respectively. To account for the S, the anion cation balance can be rewritten to (Cl + Br + 2S)/(Na + K) which values 1.9 and 1.4 for Experiments I and II, respectively. These indices indicate that more sulphates were formed in Experiment I than in Experiment II, and that there are enough halogens in Experiment II for all Na and K to form corresponding halides. In Experiment I some 30% of the Na + K seem to have formed sulphates.

Br is found in higher concentration in Experiment II than Experiment I. This is due to two complementing reasons: Br was found in higher concentration in the SRF during Experiment II, and, due to the reduced proportion of the high sulphur sludge in the fuel mix, higher concentrations of halogen salts are formed in relation to sulphates. Cl concentration in the SRF, and consequently in the fuel mix, was in practice the same on both days.

3.3. Aerosol samples

Aerosol samples were collected from locations indicated in Fig. 2, i.e. location 1, location 2 and the Furnace. Water soluble Br, SO_4, Na, K and Cl were analysed from the impactor sample membranes and the concentrations for the superheater region samples are shown in Fig. 9. The fine mode, i.e. particles with an aerodynamic diameter less than 1 μm, consists mainly of Cl, K, Na and SO_4. Sulphate is found in higher concentration in Experiment I than in Experiment II. This is also in alignment with the findings from the ESP ash leaching results. Sulphur is shown in these figures in the form of sulphate as a realistic picture is obtained of the total elemental yield on each membrane stage. If the same figures are redrawn on an atomic basis the proportion of sulphur is visually reduced due to the high molar mass of sulphate.

The atomic ratio (Cl + Br)/(Na + K) for the submicron fraction in Experiment I (locations 1 and 2, respectively) is 0.8 and 0.9. For Experiment II the corresponding value is 1.0 for both locations. These are in good alignment with the findings in the ESP ash where the (Cl + Br)/(Na + K) ratio also had values at 1.0 for Experiment II and 0.7 for Experiment I. Based on the aerosol sampling at least some 10 20% of the alkali metals have formed sulphates in Experiment I and the rest are halides. (Cl + Br + 2S)/(Na + K) values were 1.1 and 1.3 for Experiment I (locations 1 and 2, respectively) and 1.2 for both locations in Experiment II. This indicates that some two thirds of sulphur is bound in Na/K sulphates in location 1 and one-fourth in location 2 (Experiment I). The rest is mainly bound as $CaSO_4$ if no $CaCl_2$ formation is assumed [78]. (Cl + Br + 2S)/(Na + K + 2Ca) ratio has values of 1.0 and 1.1 for locations 1 and 2 submicron fractions, respectively, for both experiments. Based on these indices $CaSO_4$ formation is likely in the upper part of the furnace, particularly if this is combined with the data in Fig. 10 (see later in this paper) whence it is evident that the formation of sulphates in the furnace takes place only after the tertiary air.

In the bar chart in Fig. 8 it was shown that the bromine content in the fly ash was higher in Experiment II than in I. This seems to show through also in the aerosol samples as water soluble Br can

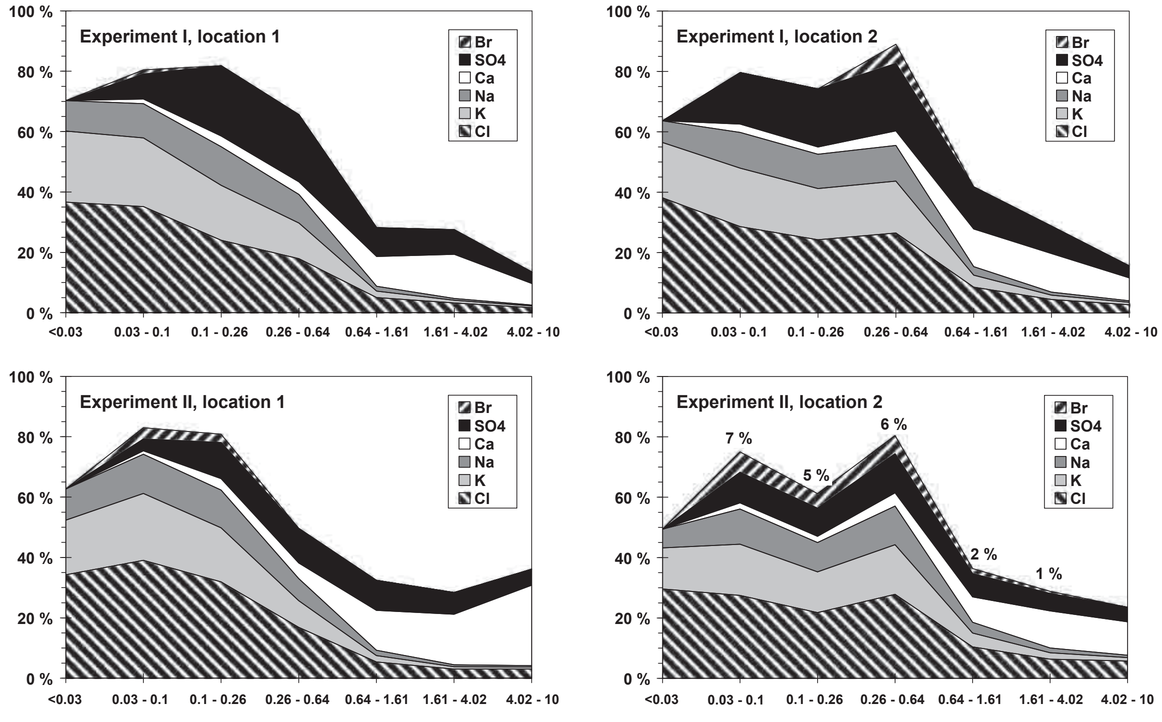


Fig. 9. Composition as wt% (on the vertical axis) of different particle size fractions (μm, horizontal axis) collected with the DLPI. In the chart at bottom right the numbers indicate the weight percentage for Br in the corresponding particle size fraction.

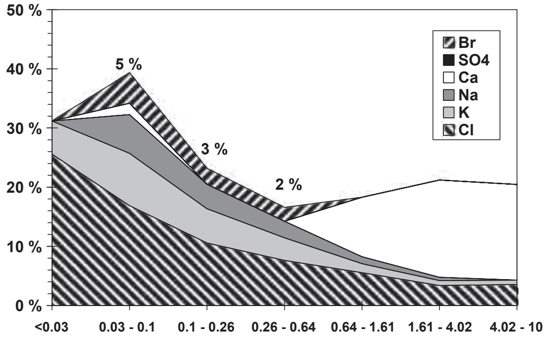


Fig. 10. Composition of water soluble elements as wt% (on the vertical axis) in different particle size fractions (μm, horizontal axis) collected with the DLPI.

be found in several weight percentages particularly in and during sampling in location 2 in Experiment II. In this case it can be stated that Br is becoming one of the major elements in the aerosols. It can be calculated that 9% on atomic basis of the halogens in submicron particles are bromides. In the fuel the proportion of Br from Cl + Br was 2% on atomic basis which indicates that Br, and specifically its acid form HBr, is more efficiently converted into vaporised salts than HCl as suggested in the literature [31].

Aerosols were also sampled during Experiment II at the location of the high corrosion rate in the furnace. This was to characterise the difference in the aerosol composition in comparison to the superheater region. The measurement was carried out 6.5 m above one of the two fuel feeding chutes at a penetration depth of 1 m in the furnace from the left wall. This location is perpendicular in the furnace to the location from which the membrane wall sample (Fig. 6) was cut off. The sampling point is located 3.5 m below the tertiary air openings. In Fig. 10 the elemental composition of the water soluble fraction in the aerosols is shown. The proportion of Br is now 11% of the halogens on atomic basis and there is a complete absence of sulphate anion from the samples as identified by means of IC. In this location combustion is incomplete and incombustible matter contributes heavily to the aerosol concentration. The total yield of water soluble elements reaches 37% at maximum, when up to 80% yields were reached at locations 1 and 2. The combustion gas temperature measured by the thermocouple was close to 950 °C, compensating the radiation due to the cold membrane walls the actual gas temperature is likely to reach 1000 °C. The high Cl content obtained in the filter sample may be due to retention of HCl acid in the Teflon filter placed after the impactor membranes [79]. However the Cl concentration collected in this fraction when calculated as concentration in the combustion gases (Fig. 11) is only 1 ppm in comparison to the total 29 ppm Cl found in the fine mode.

The absence of sulphates indicates that sulphate salt formation takes place higher in the furnace after the introduction of tertiary air. Taking into account the likely reduced from of sulphur in the sludge, which is the main source of sulphur in the boiler, it is therefore likely that sulphur is oxidised higher in the furnace where oxidising conditions are reached.

It has been found [64] in co-combustion experiments of flame retarded TV housing plastics with organic waste that some 25 40% of bromine ended up in fly ash. Some 5 10% was retained in the bottom slag of the grate fired unit and the rest was found in the gas phase mainly as HBr or in some cases Br_2. Br_2 was observed only when Br concentration in gas exceeded some 80 ppm. To reach this concentration in the gas phase even only theoretically would require in the case of the experiments presented in this paper a Br inventory of over 3000 mg/kg in the fuel mix. It was concluded from those experiments [31] that the higher tendency of Br than Cl to form alkali salts was due HBr being stronger acid than HCl. The acid dissociation constants, pK_a, for HBr and HCl, are −8.72 and −6.2, respectively [37] indicating that HBr takes part efficiently in neutralising reactions with basic elements. The practical meaning of this dissociation constant difference at this end of the scale amongst the strong mineral acids can, however, be small. In the experimental work presented in this paper HBr gas was included in the FTIR gas analyses but it was not present in the spectrum, with the exception of occasional 1 2 ppm peaks.

Fig. 11 shows the Cl and Br bound in submicron aerosols calculated as concentrations in the combustion gases at the different locations in the boiler. These values have been calculated to be concentrations in the conditions prevailing at the second pass FTIR, which enables direct comparison of the mass balance between different locations. Based on the concentrations found in the fuel mixtures the maximum possible Cl concentrations in combustion gases in Experiments I and II were 119 and 130 ppm, respectively, and 0.6 and 2.8 ppm for Br, respectively. The HCl concentrations measured in the second pass were 111 and 97 ppm for Experiments I and II, respectively. From these figures it can be concluded that the balance for both halogens is closed with relatively good accuracy.

In both experimental conditions the Cl concentration is less at location 2 possibly due to the lower gas temperature. This results in losses of the aerosols on the surfaces of large particles that are eventually seen in the concentration size distribution charts

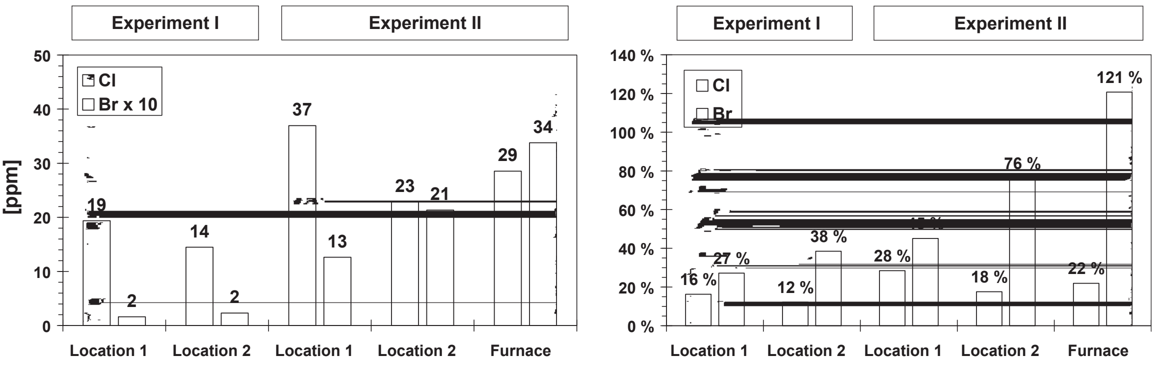


Fig. 11. Concentration and conversions of Cl and Br in the submicron fraction of aerosols at different locations in the boiler.

in Fig. 9 where the Cl distribution spreads towards the larger particle size fraction when moving from location 1 to location 2. The larger particle fraction is not accounted for in the ppm concentration calculations, as the sampling is not isokinetic.

The conversion percentages in the aerosols were quite stable for the Cl, whereas higher fluctuation was observed for the Br. Particularly in the Furnace measurement location the conversion is high at 121%. This can also be due to the fact that the fuel feeding in the furnace is established only through the left wall close to which the measurement took place. Due to non-ideal gas mixing the conversion may be over exaggerated. Based on these findings the possibility cannot be excluded that Br – through formation of HBr when released from plastics – is more efficient in forming salts in a BFB boiler furnace than HCl.

4. Conclusions

Traditionally, regarding ash forming matter, aerosol formation and high-temperature corrosion in biomass or waste-fired boilers have been attributed to the role of chlorine. In this work it was shown that Br is behaving in a similar manner to Cl in a BFB boiler combusting SRF.

In waste fuels Cl originates mainly from PVC plastics, but for Br it is suggested that products containing brominated flame retardants are the main sources. These include plastics, textiles and various other materials used in furnishing and construction.

By their physical and chemical properties the salts of Br are similar to the corresponding chlorides. In the furnace Br forms water soluble salts which are vaporised in a similar manner as chlorides. Based on the concentrations and conversions of Br in aerosols, it can be concluded that Br tends to form vaporised salts in at least comparable efficiency to that of Cl.

The maximum concentration of Br found in the ESP ash was 1900 mg/kg and 70,000 mg/kg in the aerosol samples. From the sum of water soluble halides found in the aerosols up to 10% were found to be bromides. These form Br bearing deposits which can induce high-temperature corrosion of boiler steels.

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PUBLICATION IV

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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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.

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
In dry solids (wt.%)						
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
In dry solids (mg/kg)						
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[a]	NA	18,500	NA	7300		16,910
Mg[a]	NA	1400	NA	600	590	1260
P[a]	NA	200	NA	320	2100	500
Al[a]	NA	5700	NA	280	830	1900
Si[a]	NA	9900	NA	720	11,800	9090
Fe[a]	NA	1270	NA	350	760	2080
Ba[a]	NA	430	NA	160	85	170
Sb[a]	16	24	36	0	3	150
Cd	0	0	14	0	0	0
Cr[a]	45	255	660	2	7	40
Cu[a]	25	45	200	2	15	140
Pb	6	45	270	1	3	70
Mn[a]	35	55	90	470	50	160
Ni[a]	7	120	320	1	2	10
Zn	2	420	2000	120	30	280
Sn	4	11	21	0	0	5
Heating value (MJ/kg)						
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).

[a] 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^{2+} or as $Zn(OH)_2$. Zinc is transported in the plant either as Zn^{2+} 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_{th}. 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].

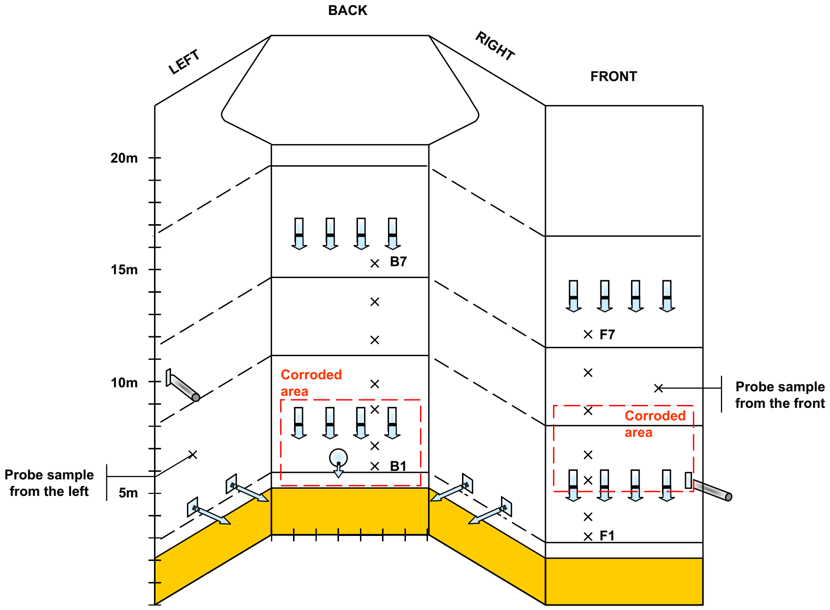


Fig. 1. Schematic picture of the aerosol and deposit sampling locations. In the picture the areas of the highest corrosion rate are illustrated. In the Fig. are shown the four fuel feeding chutes on the left and right wall (3.5 m elevation), the sludge feeding through the back wall (3.5 m) and the eight air feeding openings on the back and front wall (6 and 13 m elevations for secondary and tertiary air, respectively).

2.2. Fuel used

The fuels fired in the boiler are spruce bark, SRF and waste water sludge from the adjacent paper mill. The fuel proportions are on energy basis 56 37 7% SRF bark sludge, respectively. This corresponds to 48 46 5% on dry mass basis. The properties of the SRF, bark, sludge and their mix are summarised in Table 1. For the SRF the presented values are the values realised in a long term quality monitoring covering a continuous period of 4.5 years. For the bark and sludge the values are from samples collected during the experiments. This applies also to the ash forming elements in the SRF marked by asterisk. As the content of Pb, Zn, Cl and Br in the fuel mix is typically dominated by the content in the SRF, the fluctuation (minimum maximum) of those elements in the SRF is shown in Table 1. In the fuel mix, approximately 90% of the Cl and Br, 70% of the Zn and 95% of the Pb originate from the SRF.

Regarding the fuel mix, Cl content in the SRF varies highly (500 11,000 mg kg^{-1}). Also, the Br content in the SRF varies significantly and may, in contrast to Cl, originate to a large extent from the sludge (110 mg kg^{-1}). The Zn content in the SRF also varies and this indicates that specific metallic Zn sources cause occasional variations. Also the Pb content has large variation as indicated in Table 1. However, the concentration of Pb in SRF used in this work was quite low and usually varied between 40 and 50 mg kg^{-1} i.e. close to the average value.

2.3. Waterwall deposits sampling

During a boiler inspection increased corrosion at the bottom parts of the front and back walls was detected. The corrosion rates in the marked areas (Fig. 1) were as high as 3.4 mm per year as measured by Krautkramer USM 35X ultrasonic flaw detector. Samples of deposit were collected (by scratching) from seven levels of

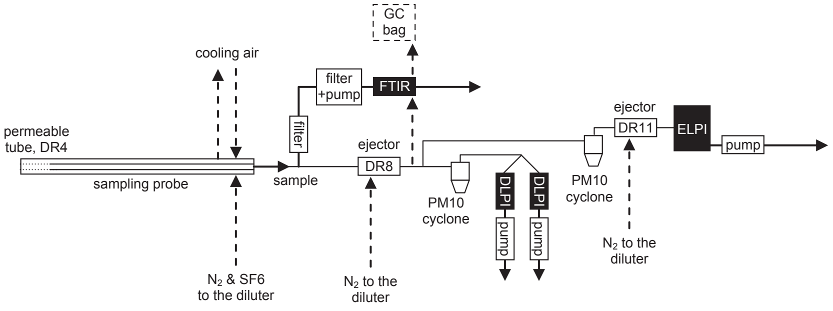


Fig. 2. Schematic picture of the aerosol sampling installation.

Table 2
The appearances of the deposit samples. Level 1 is the bottom part of the water wall just above the refractory.

Level	Front wall (F)	Back wall (B)
7	Brownish	Much lighter greyish
6	Light greyish	Light greyish
5	Greyish	Light greyish
4	Brown, rusty	Black-greyish (outer part lighter)
3	Brown, rusty	Black-greyish (outer part lighter)
2	Black, greyish	Brown, rusty
1	Black, greyish	Brown, rusty

the front (F1–F7) and the back (B1–B7) waterwalls. The sampling locations covered the corroded parts of both walls as well as the areas below and above and are marked by X in Fig. 1. The amount of deposit was fairly low in all the sampling locations and its thickness varied from 1 to 3 mm. The collected samples (deposit flakes) were cast in epoxy and cut in the middle in order to reveal the deposits' cross-sections and to analyse the composition across the depth of the flakes. The distribution of the elements in the deposits was studied by SEM images and EDX analyses. The purpose of the deposit analyses was to identify the corrosive elements, their compounds and to recognize eventual differences in the deposit compositions at different wall heights.

2.4. Aerosol sampling and chemical analyses

The aerosol sampling system has been described in detail earlier [8]. However, in distinction to the sampling system applied in the previous work, this set-up incorporated the use of a gas chromatograph (GC). Sample gas bags were filled with the gas from the exhaust of the FTIR analyser as illustrated in Fig. 2. Analyses were carried out to determine the reduced sulphur compounds, hydrogen sulphide (H_2S), carbonyl sulphide (COS), methyl mercaptan (CH_3SH), dimethyl sulphide ($(CH_3)_2S$) and dimethyl disulphide ($(CH_3)_2S_2$). The dilution ratio was determined by using SF_6 as a tracer gas.

From the DLPI (Dekati Low Pressure Impactor) membranes water soluble SO_4^{2-} and Cl^- were analysed by means of ion chromatography (IC) and the other elements by means of ICP-MS. As there are two DLPIs connected in parallel the second DLPI membranes were analysed by means of ICP-MS for the total concentration of the elements after HNO_3–HF digestion.

The reason for utilising the permeable tube–cascade impactor combination in the sampling is that the collected particles with an aerodynamic diameter of approximately $d_p < 1$ µm are assumed to be present as vapours in the furnace [34,35]. This particle size fraction (fine mode) corresponds therefore to the composition of the vaporised (corrosive) ash forming elements which can deposit on the waterwalls. By means of the DLPI the vapours can be collected as particles and subjected to chemical analyses. The fine mode cut-size in the DLPIs used in this work is $d_p = 1.6$ µm.

The DLPI and gas sampling were carried out on the front and the left wall of the BFB boiler. This was to measure the conditions on the heavily corroding front wall, and for reference purposes, the non-corroding left wall area. These were complemented by a third location with a 1.5 m distance perpendicularly from the left wall towards the boiler centre.

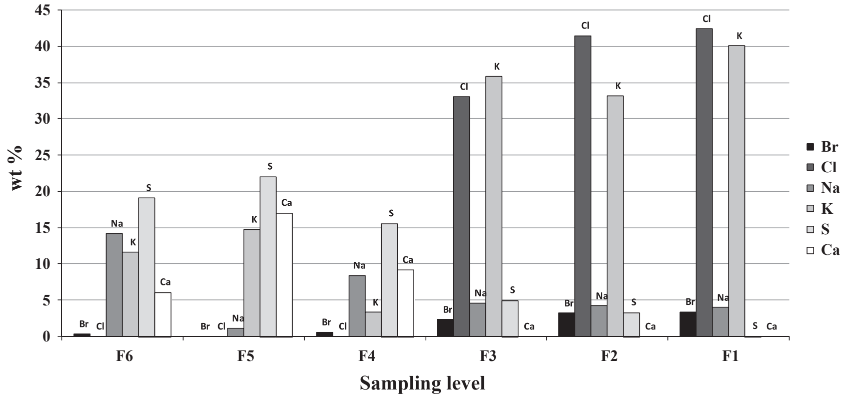
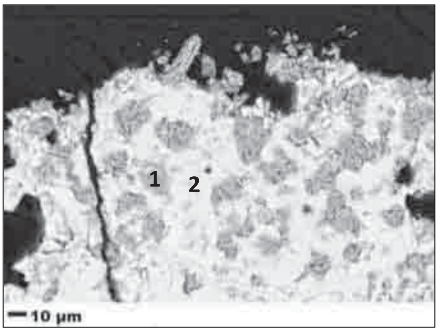
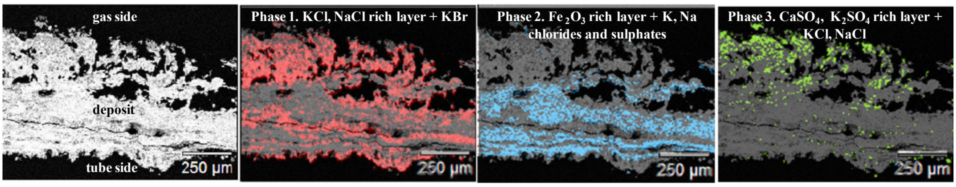


Fig. 3. Concentrations of most abundant elements in the waterwall deposits sampled from different levels of the front wall.



Wt.%	1	2
O	43.88	9.7
Na	0.18	4.02
S	22.33	0.17
Cl	0.44	44.66
K	15.51	38.17
Ca	17.34	-
Br	0.04	3.07

Fig. 4. BSE-SEM image of the cross-section of a deposit sampled from the bottom part of the heavily corroded area of the back wall and results of the EDX point analysis.



Atomic%	O	F	Si	S	Cl	K	Fe	Br	Na	Mg	Al	Ca	Zn
Phase 1 (red)	23.8	1.5	0.7	1.7	32.8	24.9	2.9	1.4	10.3				
Phase 2 (blue)	54.4		0.2	2.5	4.6	4.4	26.5		6.4		0.3		0.6
Phase 3	55.7		0.6	13.9	5.3	10.6	1.2		3.4	0.1	0.5	8.5	0.2

Fig. 5. Individual Xphase maps and atomic% of the elements in the deposit sampled from the bottom part of the back wall.

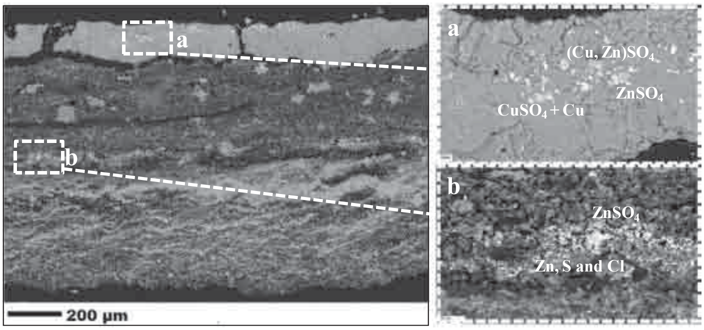


Fig. 6. BSE-SEM image of the cross-section of the deposit sampled from the bottom part of the front wall.

The sampling locations were chosen so that the adjacent wall could be reached when the probe is inserted through a wall at an angle (Fig. 1). The probe length (total 3 m) allowed approximately 2.3 m measurement distance from the corners of the furnace. This was confirmed by a cold test during a boiler shut down. The tip of the sampling probe was touching the waterwall in the wall measurements. Left wall was located some 1.5 m above the fuel feeding chutes on the left wall. On the front wall the measurement location was 5 m above this level. When the Left centre was sampled the probe was turned to a distance of 1.5 m perpendicular to the wall.

The gas temperature as measured by means of type K thermocouple at the DLPI sampling location next to the front wall was 850 °C and 880 °C next to the left wall. When the thermocouple was directed approximately 1.5 m distance perpendicular to the walls the gas temperatures measured were 980 °C and 1020 °C from to the front and leftwall, respectively.

3. Results and discussion

3.1. Waterwall deposit composition

The deposit samples from the corroded parts of the waterwalls had a dark brown and rusty colour suggesting presence of iron-based corrosion products while the rest had a light greyish colour with no indications of corrosion. Table 2 lists the appearance of the collected samples.

The analyses showed no significant differences in the deposit compositions between the corroded areas of the front and the back walls. Significant differences in the composition were observed, however, along the wall heights. Fig. 3 presents the concentrations of the most abundant deposit s elements at the different levels of the front wall. The concentration trends of the elements on the back wall were similar to that on the front. High concentrations of alkali (K, Na) chlorides and small amounts of Br, most probably in a form of KBr, were observed in the deposits present at the lower parts of both walls (levels 1 3). Nevertheless, only the back wall was corroded at this level. Accordingly, chlorine rich deposits could not have been the single cause for the corrosion behaviour observed in this area. Additionally, at the lower parts of the boiler, under the thin deposit, a noticeable layer of iron oxide was present.

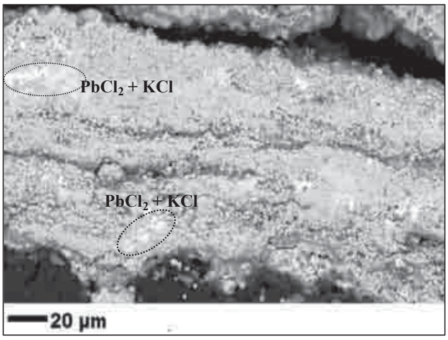


Fig. 7. BSE-SEM image of the cross-section of the deposit sampled from the bottom part of the heavily corroded area of the front wall.

At the 4th level and higher up the deposit was composed almost entirely of potassium, sodium and calcium sulphates, whereas Cl

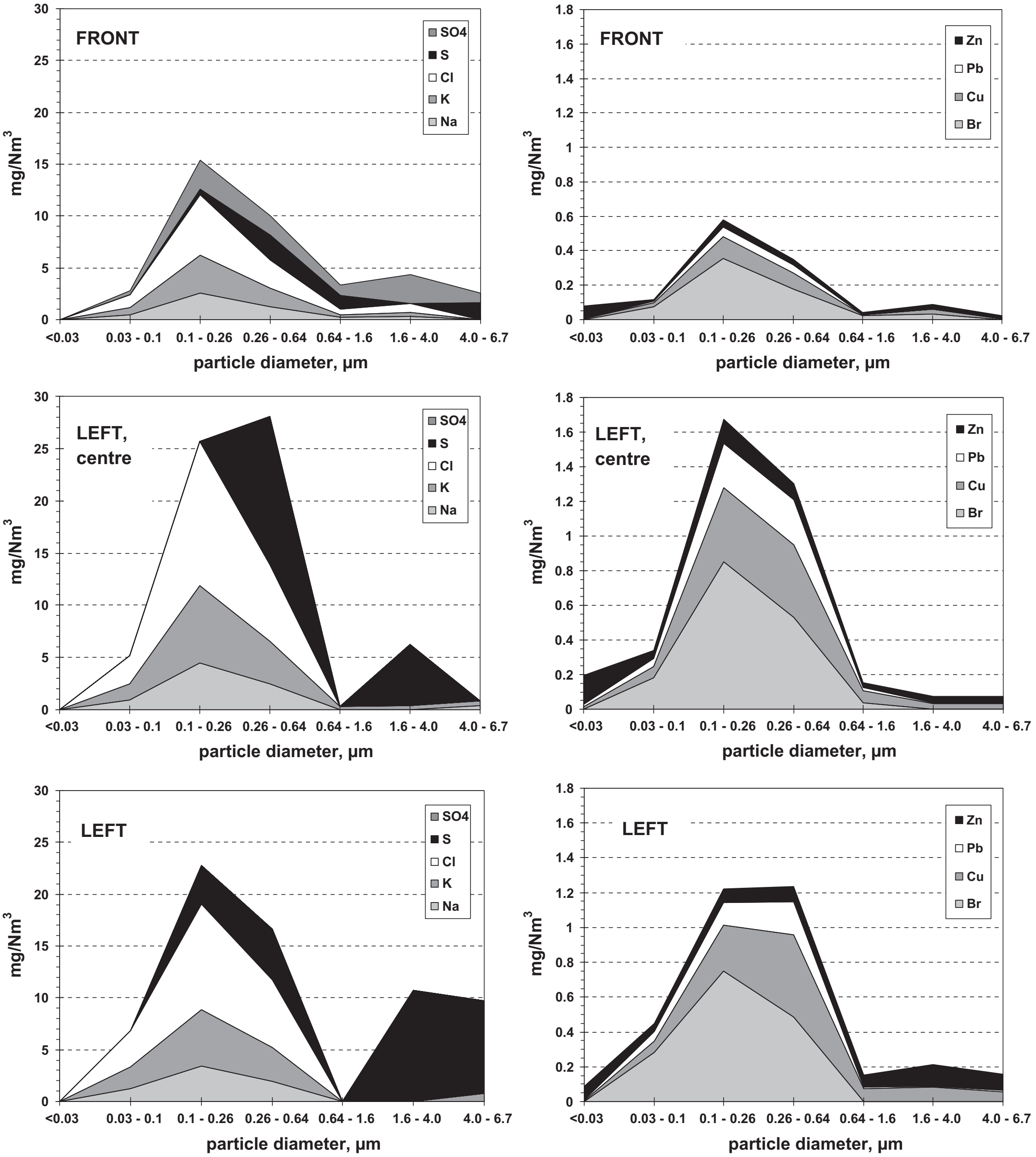


Fig. 8. Concentrations of the fine particle forming elements next to the waterwalls and towards the boiler centre from the left wall. SO_4 denotes the amount of sulphur in the form of sulphate calculated as elemental sulphur. S denotes elemental sulphur in a form other than sulphate.

and Br were almost absent. Also, the iron oxide layer decreased significantly in the upper levels. Bromine was found frequently in combination with potassium and/or sodium and was thus most likely present as KBr and/or NaBr (Fig. 4).

Fig. 5 presents the different areas of about same elemental composition found in the deposit s cross-section, identified and visualised by applying Xphase spectral imaging software. The deposit sampled from the bottom part of the front wall is oriented in the SEM images so that the waterwall facing surface is at the bottom part of the figures.

The three main areas recognized in the deposit sample are marked with different colours and the EDX elemental composition of these is presented in the table in Fig. 5. The atomic ratio of the red colour area fits well with the stoichiometric atomic ratio of NaCl and KCl as the main compounds with small amount of alkali bromides. The alkali halide rich area is mixed with iron oxide

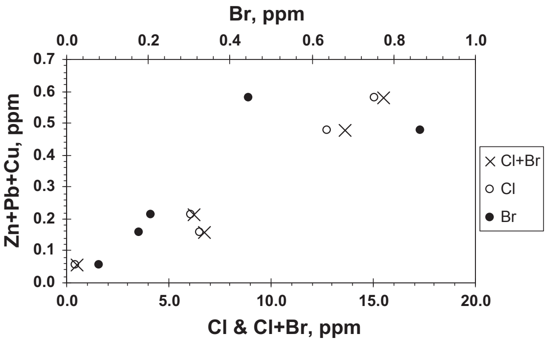


Fig. 9. Correlation between the sum of the water soluble Zn + Pb + Cu, Cl and Br in the combustion gases (analysed as particles $d_p < 1.6$ um.

(marked with blue) indicating/confirming an active role of halides in corrosion processes. The outer layer (gas side) of the deposit was enriched with K-, Na- and Ca-sulphates.

Also Zn and Pb were detected as well as some Cu could be identified, however, the overall amounts of these in the bulk deposit samples were small due to a very local occurrence. Zn and Cu were found most often in the form of sulphates and rarely also as chlorides (Fig. 6).

The spot analyses of Pb precipitates showed also some enrichment with Cl indicating the presence of $PbCl_2$. This was found especially in the deposit sampled from the corroded part of the front wall (Fig. 7). The presence of $PbCl_2$ in the deposit is expected to increase the corrosion rate [12,36]. Pb was also found at the higher wall levels (not corroded), however the amount of Cl present in these parts was negligible.

3.2. Vapour and gas composition next to the waterwalls

Fig. 8 shows the concentration of fine particle forming matter in the combustion gases based on water soluble wet chemical analyses. Regarding solubility, the halides of Cl and Br are likely to be dissolved in water, although Pb halides only slightly, whereas the metallic form of Zn, Pb and Cu dissolve in the acid. The elemental analyses of the fine mode (vapours) showed that approximately 40% of Pb, 50% of Zn and 35% of Cu has formed water soluble compounds. For Na and K the proportions were 80% and 100%, respectively. Cu is reported here alongside with Pb and Zn as it was found in surprisingly high concentrations also in the deposits (Fig. 6).

The concentration of the main elements (mg Nm^{-3}) in the fine mode is consistent next to the left wall and centre . The measured concentration next to the front wall was approximately half of that on the left wall. Another difference between the front and left wall was that sulphate was identified only in the samples collected next to the front wall. The measurement time next to the front wall was approximately 1 h 30 min and 20 min next to the left wall. Longer sampling time next to the front wall was required due the smaller vapour concentration.

The concentration of K in the combustion gases (bound in the fine mode) varied from 6 to 13 mg Nm^{-3}, Na from 4 to 7 mg Nm^{-3} and Cl from 10 to 24 mg Nm^{-3}. The smaller concentrations refer to those measured on the front wall. Br was measured in detectable amounts but its concentration was always less than 2 mg Nm^{-3}. The concentration of Zn, Pb and Cu were found to be present upto 1 mg Nm^{-3}. Based on the analyses some 80% of the fine mode particles were formed of the elements discussed here. The rest of the elements were mainly Al, Fe, Ca, Ba, Cr and Mg. The possible forms of these elements are discussed in-depth in Part 2 together with thermodynamic equilibrium modelling results of the ash forming elements.

In Fig. 9 the correlation between the (fine mode bound) sum of the water soluble Zn + Pb + Cu, Cl and Br is shown. The sum of Cl + Br is dominated by the Cl concentration, but both Cl and Br correlate positively with the concentration of the Zn + Pb + Cu. From the atomic ratios it can be calculated that Zn, Pb, and Cu can bind approximately 10% of the halogens. The rest are Na and K halides that are able to bind >85% of the halogens. This, additionally, indicates that the formation of sulphates was negligible at this level in the boiler. The concentration of the sulphate anion identified in the samples from the front wall was 1 2 ppm in the combustion gases.

The gas composition next to the front and left wall is shown in Table 3. In the Table the average values as well as the measured minimum and maximum values are shown. It can be seen that the average values may give a wrong indication as to the actual concentration the walls are exposed to: the fluctuation in the concentrations can be several times the measured average value. On the left wall close to the fuel feeding the concentration of the combustion gas components is higher, with the exception of HCl. Based on these results it may be too ambiguous to draw conclusions on the differences in the concentrations between the front and left wall. Instead, these values may be used as the range of conditions that the waterwalls are exposed to.

The GC was applied only to the measurements next to the left wall, as on the front wall SO_2 concentration was frequently close to zero and it may not have been reasonable to establish the sulphur balance. Some 75% of the gaseous sulphur was found as SO_2, 25% as H_2S and the rest in the form of COS. The other reduced sulphur compounds were identified in the gases but their concentrations were negligible.

If the particle and gaseous analyses are assessed together it can be noticed that there is a continuous partial pressure of SO_2 next to the waterwalls as particle bound sulphate formation is not consistent with this. Sulphate was found in the DLPI samples from the front wall as the pneumatic injection of the dried sludge with high sulphur content may have made the conditions in this respect

Table 3

Gas composition as measured by means of FTIR, GC and oxygen analyser. The sampling times correspond to those in the vapour sampling. The values are expressed in dry gases with the exception of H_2O which is given in wet gases. For O_2 the oxidising condition is given as a percent of the time. This is the percent of time with measurable oxygen concentration.

		CO_2 (vol-%)	CO (ppm)	SO_2 (ppm)	H_2S (ppm)	HCl (ppm)	H_2O (vol-%)	COS (ppm)	O_2 (vol-%)	Oxidising % of time
Front	Avg	5	2000	20	NA	100	1.7	0	1.6	80
	Min. max.	2 8	50 10,000	0 150		65 125	1 3	0 1	0.0 4.1	
Left centre	Avg	10	20,000	200	80	10	3.0	5	0.1	7
	Min. max.	8 12	7000 40,000	80 1000		0 20	2.5 3.3	2 10	0.0 0.8	
Left	Avg	9	7000	100	NA	5	2.3	1	0.2	17
	Min. max.	5 14	500 20,000	10 200		1 10	1.5 3.2	0 2	0.0 1.0	

different between the different walls. Also, the conditions on the front wall were predominantly oxidising in contrast to the left wall which was predominantly exposed to a reducing atmosphere.

4. Conclusions

The high temperature corrosion of waterwalls is an important operational issue and a limiting factor in increasing the steam values, and consequently the electric efficiency, of waste fired boilers. The main ash forming elements attributed to induce such corrosion are Cl, Br, Zn and Pb. A measurement campaign was carried out to determine the occurrence of these elements in a SRF fired bubbling fluidised bed boiler.

The occurrence of chlorine is well established in the literature, but less is known about the occurrence of bromine. It is likely that Br originates mainly from plastics in the form of brominated flame retardants, but also from wastewater sludge. The possible sources of Br in the sludge are water treatment chemicals containing bromine. Br was found enriched in the waterwall deposits and as ash forming vapours in the furnace. The fuel mix contained only tens of mg kg^{-1} Br but it was found in several weight percentages in some deposit areas. Already such amounts of bromine in the deposit can increase the high temperature corrosion rates, and that is the subject of research in Part 2.

Also Zn and Pb which have been shown to be corrosive in the operating temperature range of boiler waterwalls, were found in the deposits and aerosols. The fact that they were found in both water soluble and water insoluble forms in the fine particles indicates the co-existence of gaseous halides and elemental forms of these elements.

Based on these results, the conditions to which the waterwalls in such a boiler are exposed to can fluctuate between oxidising and reducing. As the conditions are considerably different in the higher part of the furnace in comparison to the lower part, deposit composition changes along the boiler height.

In the upper part of the boiler the waterwall deposits composed mainly of K-, Na- and $CaSO_4$ but significant concentrations of alkali chlorides and some bromides were additionally detected in the bottom parts on both the front and the back walls. The heavy metals found in the deposits were mainly Zn, Pb, and Cu present as sulphates, but also as chlorides. Br was found upto 3 wt.% and was most likely present as KBr and/or NaBr.

The fluctuating gas phase composition, complemented with the halogen enriched deposit in the lower part of the furnace has led to a rapid high temperature corrosion of the waterwalls. In the lower part of the furnace the deposit mainly composed of the elements found as vapours in the gases in contact with the walls. The forms of these elements will be estimated by means of thermodynamic equilibrium analyses in Part 2.

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PUBLICATION V

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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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 boiler (BFB) 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.

Keywords: bromine, chlorine, waterwall, corrosion, solid recovered fuel

1. Introduction

This paper reports the second part of a study from a bubbling fluidised 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 MWth. 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 Figure 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].

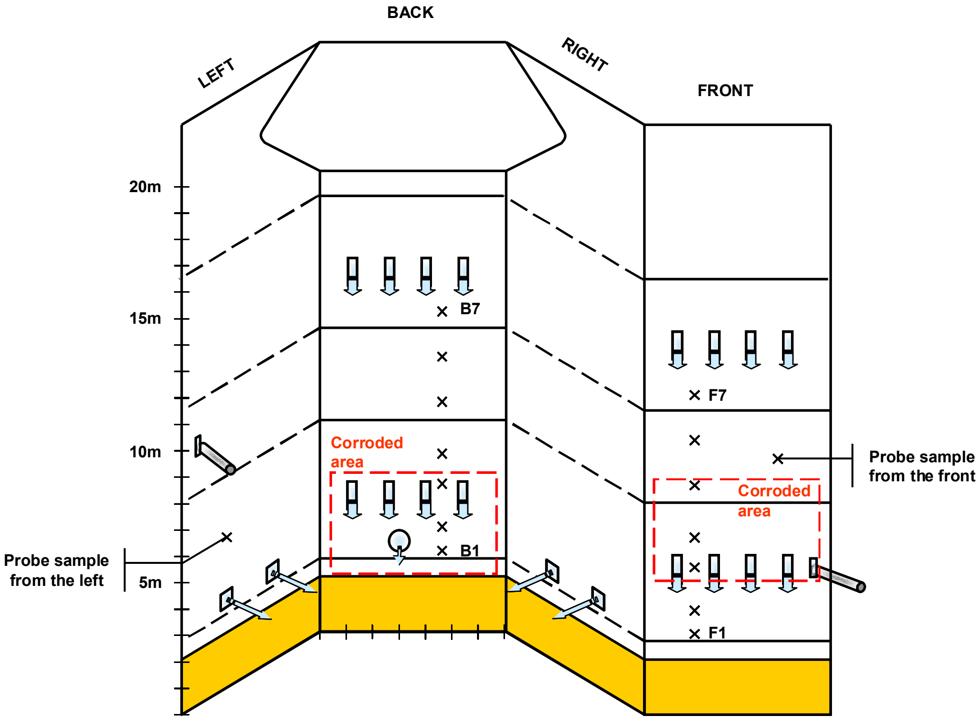

Figure 1. Schematic picture of the BFB subjected to gas and aerosol measurements and deposit analyses in Part 1 [2]. In the picture, the corroding areas are also marked.

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 et al. [6] pointed out that materials such as insulating foams from the building sector, polymeric material used in automobiles, waste from electrical 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, Cl_2, HBr, Br_2) 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 Br_2 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 et al. [9] exposed Fe-20Cr and Ni-20Cr steel samples to a Ar-H_2O-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 Cr_2O_3 poorly adhered to the metal surface and Ni loss was substantial which was explained by the low stability of $NiBr_2$ in HBr containing gas. Also tests performed by Antill et al. [8] with pure Cr and Ni in a Br_2 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 subsequently form aerosol particles at lower temperatures and may condense on the waterwalls in the examined boiler. The fuel input was a mix of SRF, bark and sludge (48–46–5% on dry mass basis, respectively) as given in Table 2.

This is the same fuel mixture used in the BFB during the measurement campaign as described in Part 1 [2]. 1100 °C is an approximated temperature of the combustion gases in the reference boiler used in this work [2] and 400 °C is an approximation for the waterwall deposit temperature.

Table 2. Composition of the fuel mixture used in the thermodynamic equilibrium modeling. Taken from [2].

Moisture (wt-%, ar)	36.5
Ash (wt-%, ds)	9.9
IN DRY SOLIDS (wt-%)	
C	52.2
H	7.1
N	1.0
S	0.16
O	29.2
IN DRY SOLIDS (mg/kg)	
Cl	5280
Br	80
Na	1860
K	1470
Ca	16 910
Mg	1260
P	500
Al	1900
Si	9090
Fe	2080
Ba	170
Sb	150
Cd	0
Cr	40
Cu	140
Pb	70
Mn	160
Ni	10
Zn	280
Sn	5
HEATING VALUE (MJ/kg)	
LHV, db	21.1
LHV, ar	12.5

The thermodynamic software package Factsage version 6.1 [11] was used for the modeling. The FACT53 database was used for the calculations of the stoichiometric condensed phases and the gas phase, while the SGTE database [12, 13] was used in the calculations of some gaseous heavy metal compounds (e.g. SbCl, $PbBr_4$) that are not present in the FACT53 database.

All compounds in the database were considered, except for nitrogen, where N_2 was the only nitrogen compound considered. It is well known that thermodynamic equilibrium modeling does not predict nitrogen chemistry at combustion conditions satisfactory. The only solution phases included were the rock salt-type alkali halide solid solution (Na, K)(Cl, Br), and a liquid solution for molten salts containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}//S^{2-}, SO_4^{2-}, CO_3^{2-}, Cl^-. The thermodynamic data for the liquid solution are taken from references [14–16], however, the liquid solution was not stable at 400 °C or 1100 °C. Calculations for the vapor pressure and stability of various metal bromides and chlorides were also made.

The chemical equilibrium at 1100 °C in both oxidizing and reducing conditions was calculated in the first step. The equilibrium gas phase at 1100 °C was used as input for the second step where, to simulate the formation of ash phases condensed from the gas phase, the equilibrium was calculated at 400 °C. The flow chart in Figure 2 describes the approach used.

Two main cases were considered:

2a: cooling of the 1a gas phase formed at reducing conditions ($\lambda = 0.8$) from 1100 °C to 400 °C

2b: cooling of a 1a gas phase formed at reducing conditions ($\lambda = 0.8$) from 1100 °C to 400 °C and adding air to correspond to 3 vol-% O_2 in the equilibrium gas phase.

Two other cases were also calculated, however, the results did not show any significant differences.

2c: cooling of the oxidized gas 1b from 1100 °C to 400 °C

2d: cooling of the oxidized gas 1b from 1100 °C to 400 °C and setting activity of O_2 to correspond to the reducing conditions in 2a.

The same compounds estimated for cases 2a and 2b are formed in cases 2c and 2d, but the proportions of the formed compounds differ slightly, and the results from 2c and 2d are not discussed further in the this paper.

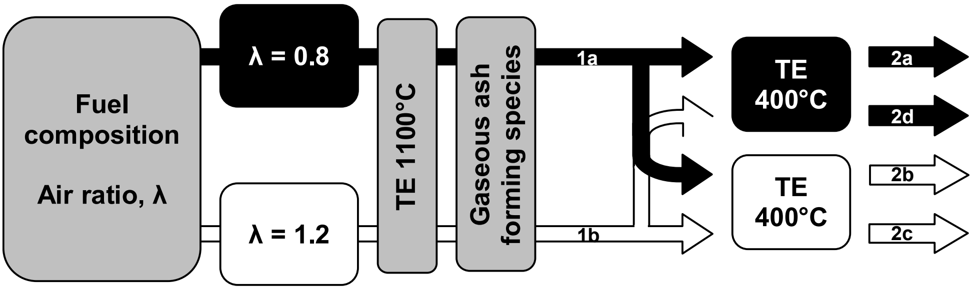

Figure 2. Flow chart describing the calculation procedure, λ = air ratio, TE = thermodynamic equilibrium.

2.2 The laboratory corrosion test method

The laboratory tests were performed in a horizontal silica tube furnace at 350 °C, 400 °C, 500 °C and 600 °C for 168 h in air and in reducing atmosphere. The furnace for the tests under reducing conditions was equipped with a tightly closed, inner glass reactor. The gas composition under reducing conditions was 5% CO and 95% N_2 with a flow of 2.0 l/min. When the tests in reducing atmosphere were performed, activated carbon (2 wt-% of the salt) was additionally weighted on the top of the salt, to ensure that eventually present O_2 would be converted to CO_2.

Four commercial waterwall and superheater materials were tested. The materials can be classified as two low alloy steels: carbon steel – St.45.8/III and ferritic steel – 10CrMo9-10, high alloy: austenitic stainless steel – AISI347 and high nickel austenitic stainless steel – Sanicro 28. St.45.8/III was tested only under reducing conditions. Table 3 presents the detailed steel compositions.

Table 3. The detailed compositions of the tested steels (wt-%).

	Fe	Cr	Ni	Mo	Mn	Si	C	Nb	P	S
St.45.8/III	95.85	0.19	-	-	0.81	0.30	2.85	-	-	-
10CrMo9-10	95.96	2.24	-	1.00	0.45	0.25	0.07	-	0.01	0.01
AISI347	68.74	18.08	10.92	-	0.92	0.46	0.04	0.81	0.02	0.01
Sanicro28	36.11	27.36	31.38	3.51	1.15	0.46	0.01	-	0.01	0.01

The steel specimens had a size of 20 x 20 x 5 mm. Before the tests each specimen was polished, and pre-oxidized, while the salt mixtures were pre-melted, cooled down, crushed, and sieved. After the pre-treatment the salt was placed on the steel specimen (0.25g/specimen). The chemical composition of the synthetic ashes used in the tests were as follows:

6 mol-% $ZnBr_2$ – 94 mol-% K_2SO_4
10 mol-% $ZnBr_2$ – 90 mol-% K_2SO_4
6 mol-% $ZnCl_2$ – 94 mol-% K_2SO_4 [3]
10 mol-% $ZnCl_2$ – 90 mol-% K_2SO_4 [3].

After the furnace test, the samples were cold-mounted in epoxy, then cut off in the middle. For the analysis and characterization of the specimens' cross-section a SEM/EDX was used. The oxide layer thickness on each specimen was evaluated based on a panorama SEM technique, which together with the experimental methodology has been used widely before and described in detail elsewhere [3, 17–20].

3. Results and discussion

3.1 Thermodynamic modeling results at 1100 °C

The deposit and aerosol measurement results reported in Part 1 of this work, give only limited indications of the actual compounds existing in a furnace during boiler operation. The equilibrium results from Step 1 at 1100 °C predict the composition of the gas phase to which the boiler steels are exposed [2]. The calculated composition of the combustion gas and the predicted stable condensed phases at 1100 °C for

$\lambda = 0.8$ (Case 1a) and $\lambda = 1.2$ (Case 1b) are given in Table 4. Figure 3 shows the relative proportions of some chosen compounds that were predicted to form at 1100 °C, based on Table 4a. The condensed phases predicted at 1100 °C (Table 4b) were removed from the input data for the second step calculations.

Table 4. Calculated a) gas phase composition and b) condensed phases, at 1100 °C for $\lambda = 0.8$ and $\lambda = 1.2$.

a)

$\lambda = 0.8$		**$\lambda = 1.2$**	
Species	**Vol-%**	**Species**	**Vol-%**
N_2	58.9	N_2	66.2
H_2O	21.3	H_2O	18.7
CO_2	12.0	CO_2	12.1
CO	4.1	O_2	2.9
H_2	3.6		
	ppm_v		
HCl	260	HCl	190
H_2S	200	SO_2	170
NaCl	150	NaCl	120
KCl	140	KCl	100
SO_2	20	OH	20
Zn	16	CuCl	5.9
COS	7.4	SO_3	2.2
Sb	1.8	NaOH	1.5
KBr	1.7	KOH	1.2
NaOH	1.6	$CrO_2(OH)_2$	1.2
NaBr	1.5	KBr	1.0
HS	1.4	PbO	1.0
$Fe(OH)_2$	1.4	Cl	0.9
CuCl	1.3	NaBr	0.9
KOH	1.3	Sb_4O_6	0.8
Sb_2	0.9	$ZnCl_2$	0.5
Pb	0.9	CO	0.4
Na	0.8	H_2	0.3
H	0.6	HBr	0.3
S_2	0.6	Br	0.3
Cu	0.5	$(NaCl)_2$	0.1
HBr	0.5	(SbO_2H_2)	0.1

b)

Phase ($\lambda = 0.8$)	**Phase ($\lambda = 1.2$)**
	$Ca_3Si_2O_7$
$Ca_3Si_2O_7$	$Ca_2Al_2SiO_7$
$Ca_2Al_2SiO_7$	$Ca_3Fe_2Si_3O_{12}$
$Ca_2FeSi_2O_7$	$Ca_3MgSi_2O_8$
$Ca_3MgSi_2O_8$	$NaAlSiO_4$
$NaAlSiO_4$	Mn_3O_4
Mn_2SiO_4	$BaSiO_3$
$BaSiO_3$	$Ca_3(PO_4)_2$
$Ca_5(PO_4)_3OH$ $FeCr_2O_4$	$MgCr_2O_4$
Cu_2S	$NiFe_2O_4$
Ni	$Ca_2Zn_2Si_2O_7$

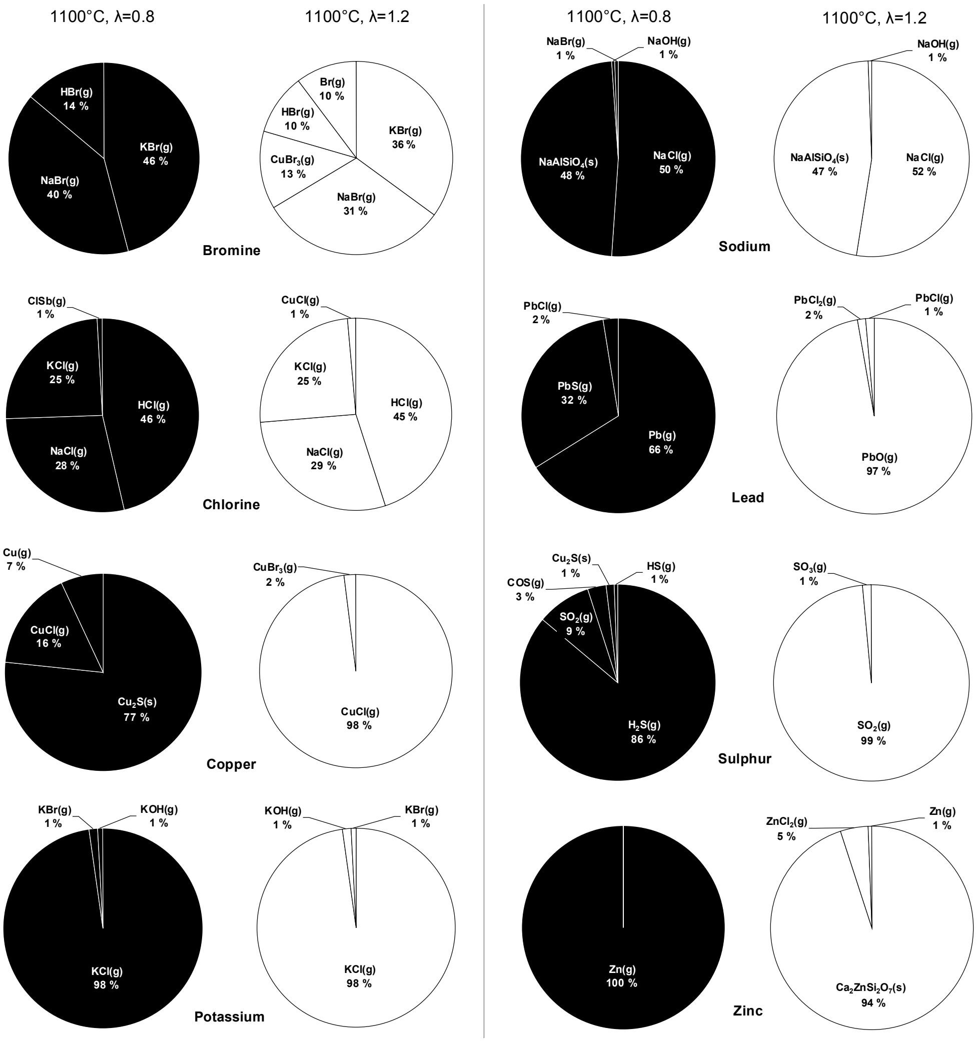

Figure 3. The predicted forms of selected ash forming elements at 1100 °C in the SRF fired BFB boiler [2]. The proportions with less than 1% are excluded from the charts.

Speciation of Na, K, Cl, and S

Potassium is predicted to be present almost completely as gaseous KCl in both reducing and oxidizing conditions with only minor amounts of gaseous KBr and KOH. Sodium on the other hand, in the present case, is distributed evenly between two species, gaseous NaCl and solid $NaAlSiO_4$. Minor amounts of gaseous NaOH and NaBr are also predicted to form. The predicted formation of solid $NaAlSiO_4$ may explain why potassium is enriched in relation to sodium in the sampled aerosols as compared to the overall contents of potassium and sodium in the fuel mixture, as shown in Part 1 of the paper [2]. Sulfur is predicted to form mainly H_2S and minor amounts of SO_2 and COS in the gas phase at reducing conditions and SO_2 at oxidizing conditions. Solid Cu_2S is predicted to form in small amounts in the reducing conditions but no solid or liquid sulfates are stable at oxidizing conditions. $CaSO_4$ may form if there is 'free' calcium available during the combustion processes and if the SO_x levels are high, but in the present predictions calcium is mainly bound as silicates or phosphates. Chlorine forms HCl and gaseous NaCl and KCl. Small amounts of other gaseous metal chlorides, such as SbCl and CuCl are also predicted to be formed.

Speciation of Cu, Pb, Zn, and Br

Cu, Zn, and Pb show different behavior at reducing and oxidizing conditions. Copper is predicted to be present mainly as solid Cu_2S at reducing conditions but mainly as gaseous CuCl at oxidizing conditions. Lead on the other hand is predicted to be in a gaseous form at both reducing (Pb and PbS) and oxidizing conditions (PbO), while zinc is predicted to be volatilized as gaseous Zn at reducing conditions and to form a solid silicate at oxidizing conditions with a minor fraction volatilized as gaseous $ZnCl_2$. Bromine is predicted to form gaseous NaBr, KBr and HBr at both oxidizing and reducing conditions with minor amounts of gaseous Br and $CuBr_3$ at oxidizing conditions.

Comparison to the in-furnace measurements

In the vaporized ash-forming elements sampled from the combustion gases from the front and left wall in the BFB as described in Part 1 [2] the water soluble alkali metal chlorides were found to form the large bulk of the vapors. This is in alignment with the modeling results in which Cl was predicted to be present in the combustion gases in the form of HCl(g) as well as KCl(g) and NaCl(g). Sulfate as the sulfur species was negligible in the sampled aerosols [2], neither modeling results indicated sulfate formation. In the combustion gases sampled from the boiler by means of FTIR and gas chromatography [2] 75 % of the S was found as SO_2(g) and the rest as H_2S(g) and COS(g). Cu was found in high concentrations (in comparison to Zn and Pb) in the vapors and the modeling predicts gaseous Cu to be mainly in the form of CuCl(g). Br was estimated to form to a large extent alkali metal bromides, which was also the most likely form of Br in the sampled vapors [2]. In addition to alkali metals Br was predicted to form a compound with Cu ($CuBr_3$(g)). Approximately half of the Zn and Pb were found in water soluble form in the vapors. It supports at least the modeled speciation of Zn of which some part was estimated to be present also as $ZnCl_2$(g).

3.2 Thermodynamic modeling results at 400 °C

The predicted condensed ash phases at 400 °C for the reducing case (2a) and the oxidizing case (2b) are given in Table 5. The condensed phases predicted at 1100 °C (Table 4b) were removed from the input data for the second step calculations. The relative proportions of some chosen compounds that were predicted to form at 400 °C are shown in Figure 4.

Table 5. The predicted condensed ash phases at 400 °C for the reducing and the oxidizing case.

Phase ($\lambda = 0.8$)	Wt-%	Phase ($\lambda = 1.2$)	Wt-%
(K,Na)(Cl,Br)	51.3	$K_3Na(SO4)_2$	58.7
(Na,K)(Cl,Br)	39.0	Na_2SO_4	30.9
ZnS	7.0	$CuSO_4$	4.1
PbS	1.4	Sb_2O_5	2.8
Cu_2S	0.7	$PbSO_4$	1.5
FeS	0.6	$Cr_2(SO_4)_3$	1.3
MnS	0.1	$ZnSO_4$, $NiSO_4$	< 0.5
Total	5.9 g / kg dry fuel		7.1 g / kg dry fuel

Speciation of Na, K, Cl, and S at 400 °C

Na and K are predicted to form mainly chlorides and bromides under reducing conditions, while under oxidizing conditions they are present as sulfates. It must be noted that it is assumed that the elements have not had the possibility to interact with ash phases that were predicted to be the condensed phases at 1100 °C, such as Ca-silicates and $NaAlSiO_4$. Cl forms almost solely alkali chlorides under reducing and HCl under oxidizing conditions. Sulfur forms mainly H_2S as well as Zn, Pb and Fe sulfides in the modeled deposit in reducing conditions. In oxidizing conditions the metals are predicted to predominantly form sulfates.

Speciation of Cu, Pb, Zn, and Br

Cu_2S(s) is the main form of Cu in reducing conditions. In oxidizing conditions the main solid form of Cu is estimated to be Cu_SO_4 and some gaseous $CuBr_3$. At the wall temperature, lead seems to form stable PbS(s) in reducing and $PbSO_4$(s) in oxidizing conditions. In reducing conditions PbC_{12}(g) is also stable. Regarding bromine, the solid forms are KBr and NaBr in the alkali halide solid solutions, while the gaseous form is predominantly HBr under reducing conditions. Under oxidizing conditions Br is predicted to form $CuBr_3$. In distinction to the situation at 1100 °C the forms of the Pb and Zn at 400 °C are very similar to each other. They are estimated to form sulfides and sulfates under reducing and oxidizing conditions, respectively.

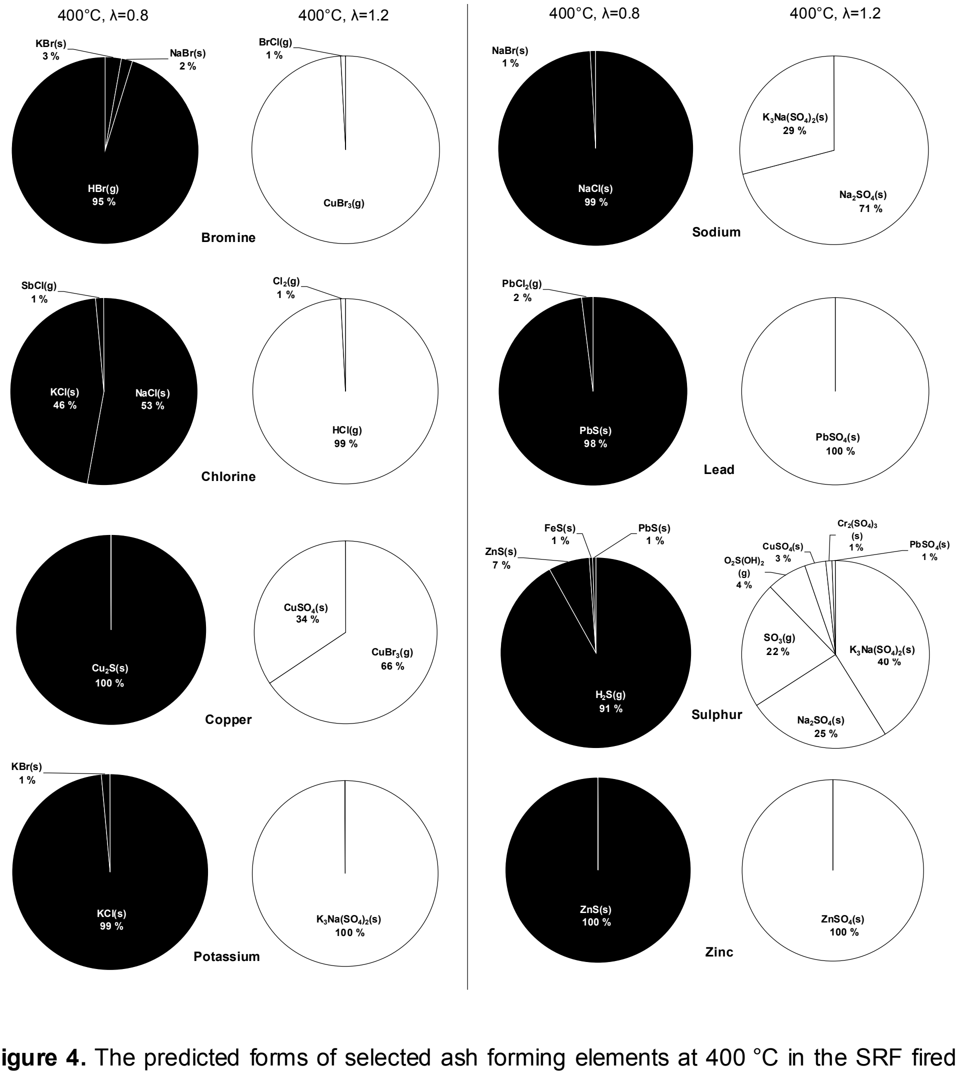

Figure 4. The predicted forms of selected ash forming elements at 400 °C in the SRF fired BFB boiler [2]. The proportions with less than 1% are excluded from the charts.

Comparison to the deposit analyses

There is a clear difference in the predicted phases in reducing and oxidizing conditions. At reducing conditions about 90 wt-% of the condensed phases are KCl- and NaCl-rich alkali halide solid solutions containing small amounts of alkali bromides. Two separate alkali halides are stable at 400 °C but these phases are fully miscible at higher temperatures. The rest of the predicted condensed phases are sulfides, mainly ZnS and minor amounts of PbS, Cu_2S and FeS.

In Part 1 [2], the analysis of the waterwall deposit showed a clear pattern. In the lower parts of the boiler the deposit was enriched in alkali (K, Na) chlorides and small amounts of Br, most probably in the form of KBr, and the deposit collected from the upper parts composed mainly of alkali metal and calcium sulfates. Zn and Cu were found in the form of sulfates but the presence of ZnS could not be excluded. The thermodynamic equilibrium modeling corresponds with these findings: according to the predictions, alkali metals are present as chlorides and bromides in reducing conditions and most likely in the form of sulfates when the conditions change to oxidizing. Also Zn, Pb and Cu are predicted to form sulfates.

The conditions in the BFB are likely to fluctuate between reducing and oxidizing since both alkali halides and smaller amounts of sulfates were found at the same elevations and those species were indicated by modeling to be stable at 400 °C in reducing and oxidizing conditions respectively. The occurrence of fluctuating conditions was also observed in Part 1.

The only discrepancy found between the modeled deposit composition and the analyzed composition concerned Pb which was predicted to be present either as PbS in reducing or $PbSO_4$ and oxidizing conditions. In the SEM-EDS analysis, however, Pb was found typically in connection to Cl suggesting the occurrence of $PbCl_2$. Small amounts of $PbCl_2$ were also predicted to be stable under reducing conditions, however, only in gas phase. Thus, the presence of $PbCl_2$ in the wall deposits suggests that at least in the case of lead, equilibrium has not been attained or that local conditions are different than the conditions that were considered in the modeling.

The predictions at 400 °C can also be discussed together with the aerosols measured in Part 1 (Figure 8 in [2]) where the ash-forming vapors are let to form fine particles in the cooled quench probe. The condensed phase consisted mainly of K, Na, Cl as well as S. The potassium content was slightly higher than the sodium content on mass basis, which is also supported by the predictions. The measurements suggest that KCl and NaCl are the main species in the fine particle fraction. Sulfur is mainly in a reduced form in the measurements, which is also supported by the calculations, where metal sulfides (ZnS, PbS, FeS) are predicted to form at 400 °C. The main difference between the measurements and the predictions are that ZnS is predicted to condense in higher amounts than PbS, Cu_2S, and FeS, while the measurements show that the amount of formed Cu_2S is higher than of ZnS and PbS. The reason for this may lay in the fluctuations between oxidizing and reducing conditions in the boiler, as Zn can stay condensed or as solid ZnO or Zn-silicates at oxidizing conditions and high temperatures. Cu on the other hand shows the opposite behavior, where solid Cu_2S may stay stable at reducing conditions at high temperature, but volatilize at oxidizing conditions as CuCl(g) (see Figure 3). The measurements show that the fine particles contain some bromine together with K and Na, which is supported by the calculations, where KBr and NaBr are predicted to form.

3.3 Laboratory experiments

The average corrosion layer thicknesses calculated for the samples tested are presented in Figure 5. Similarly to the previously tested $ZnCl_2$ containing salt mixtures [3], heavy corrosion was observed when exposing the samples to a corresponding bromide salt mixture. The mixtures with $ZnBr_2$ were found to be, however, more aggressive in some cases. The heavy corrosion measured on 10CrMo9-10 exceeded significantly the attack caused by the salt containing $ZnCl_2$. Also, for AISI347 the resistance was deteriorated in the presence of zinc bromide. A corrosion attack was observed already at 400 °C.

While at temperatures above 400 °C corrosion measured after exposures to both salt mixtures was very comparable, at temperatures around 400 °C differences were substantial especially when comparing performance of the low alloy materials. Such materials are typical materials used for boiler waterwalls and 400 °C is close to the waterwall material temperature in waste fired boilers [21]. The results imply that deposit enriched in Br can lead to even more severe material degradation, compared to a Cl rich deposit.

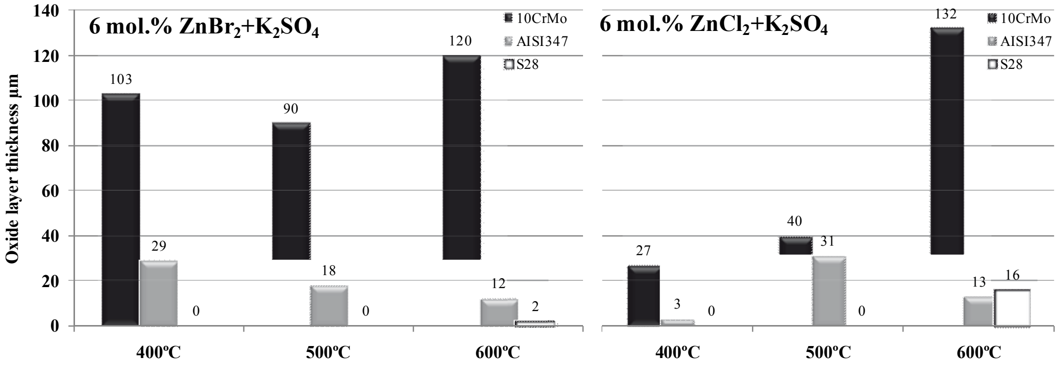

Figure 5. Oxide layer thicknesses measured on 10CrMo9-10, AISI347 and S28 steels after 168 h exposure in air with 6 mol-% $ZnBr_2$+K_2SO_4 and 6 mol-% $ZnCl_2$+K_2SO_4 mixtures at 400 °C–600 °C.

At 400 °C an internal degradation of the steel (10CrMo9-10) together with the oxide layer growth was observed. The steel surface was bromine rich indicating the formation of $FeBr_2$ (Figure 6). Also, the oxide layer was poorly adhering to the metal surface. Poor adherence and oxide layer spallation due to the formation of volatile metal bromides on the metal/oxide interface was also observed and described by Önay et al. [9] and Zhuang et al. [10]

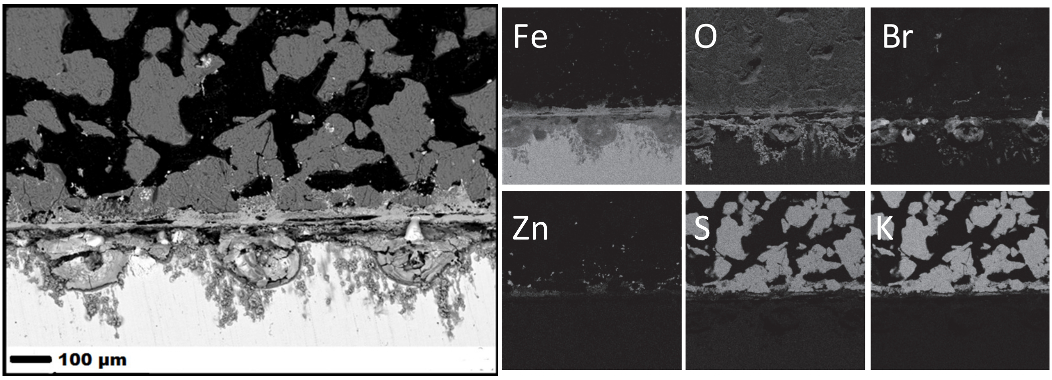

Figure 6. SEM image and X-ray maps of the 10CrMo9-10 steel after 168h exposure with 6 mol-% $ZnBr_2$+K_2SO_4, 400 °C.

At 500 °C the formed oxide layer was thick and quite compact but detached from the steel surface. At this temperature a clear decomposition of $ZnBr_2$ was observed. On the contrary to what was observed at 400 °C, most of the bromine was found in a form of quite large KBr crystals localized close to the oxide layer surface (Figure 7). The analysis of the steel/oxide layer interface (Figure 7, points 1 and 2) showed a small enrichment in Br.

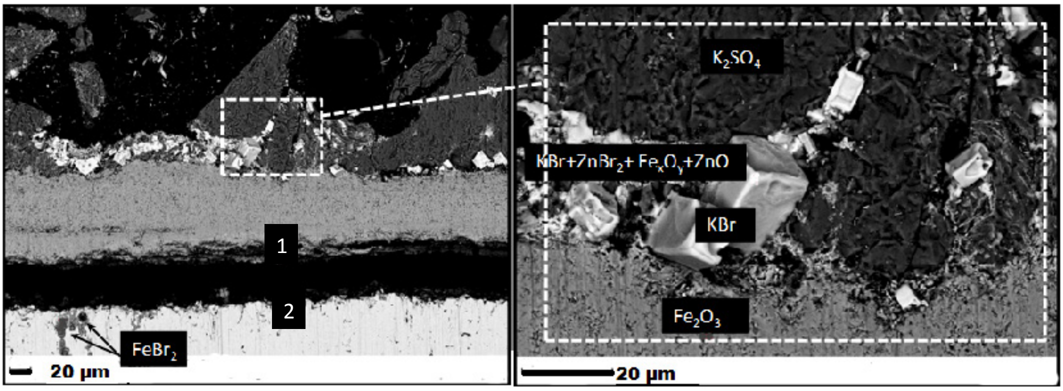

Figure 7. SEM image of the 10CrMo9-10 steel after 168h exposure with 6 mol-% $ZnBr_2+K_2SO_4$, 500 °C.

It has been suggested [10] that at higher temperatures, the active oxidation is a prevailing type of corrosion responsible for degradation of metals in the Br-rich environment, similarly to chlorides. That means that the reactions of metals e.g. Fe with Br species will be analogue to those with Cl: HBr(g), or rather Br_2(g), can diffuse through the oxide scale to the metal surface. The analogue reactions with HCl and Cl_2 were described by e.g. Zahs et al. [22]. The metal surface can also simultaneously undergo direct reaction with a Br containing salt. As a result highly volatile $FeBr_2$ will be formed.

Since $FeBr_2$ has a slightly higher vapor pressure than $FeCl_2$ (Figure 8) and the partial pressure $p(O_2)$ required to oxidize $FeBr_2$ to Fe_2O_3 (at 400 °C) or Fe_3O_4 (at 500 °C) is noticeably lower than for $FeCl_2$, $FeBr_2$ will be oxidized closer to the steel surface. This situation can be observed on the calculated phase stability diagrams for the Fe-Br_2-O_2 and Fe-Cl_2-O_2 systems at 400 °C (Figure 9). In practice this means that a larger fraction of the released Br_2 (or HBr) may still be available for further reactions with the metal. In contrast, $FeCl_2$ is more stable and will diffuse further out through the deposit before the required amount of O_2 needed for oxidation is present. Such a behavior may lead to the situation that larger amount of Cl, than of Br, may be released from the deposit into the flue gas.

The stability and partial pressure differences between $FeBr_2$ and $FeCl_2$ may be an explanation on why Fe-based steels showed worse resistance against bromine than chlorine.

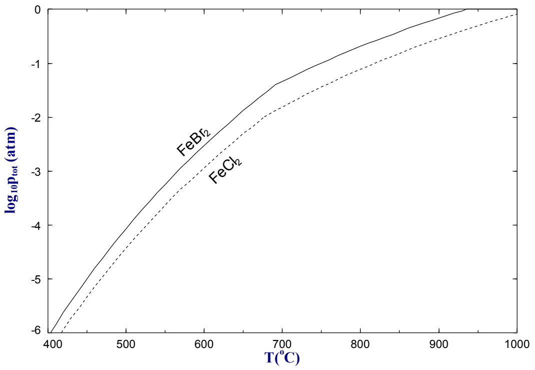

Figure 8. Partial pressure of $FeBr_2$ and $FeCl_2$ as a function of temperature.

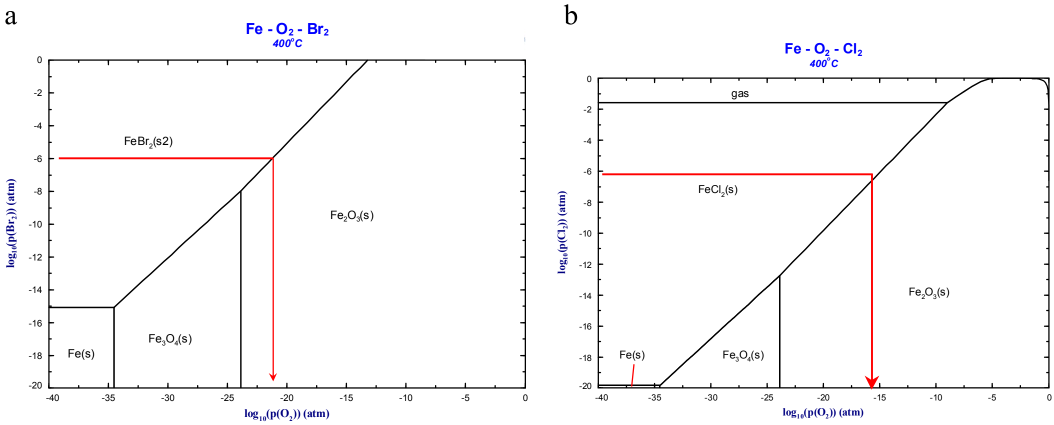

Figure 9. Phase stability diagrams for a) $Fe-Br_2-O_2$ at 400 °C, b) $Fe-Cl_2-O_2$ at 400 °C systems.

Since the reducing atmosphere was considered to occur at the lower parts of the boiler [2] a few tests were performed in the simulated reducing atmosphere. All four materials were tested at 350 °C and 400 °C. The results are presented in Figure 10. The tests at 350 °C resulted in a thin oxide layer growth on the low alloy steels. The oxide layer thickness on the both austenitic steels was under the detection limit. At 400 °C all the materials experienced similar oxide layer thickness growth (12–16 µm).

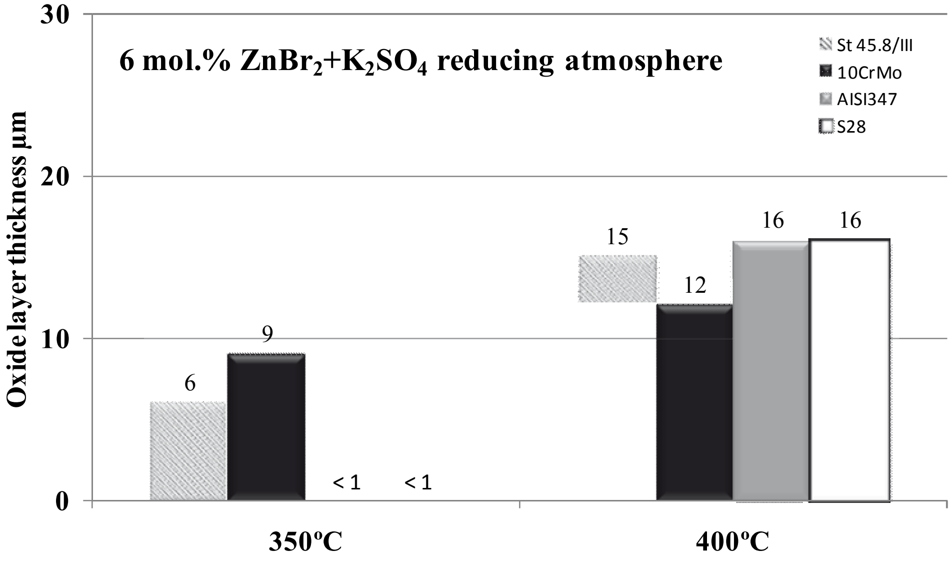

Figure 10. Oxide layer thicknesses measured on St 45.8/III, 10CrMo9-10, AISI347 and S28 steels after 168 h exposure with 6 mol-% $ZnBr_2$+K_2SO_4 mixture at 350 °C and 400 °C in reducing atmosphere.

In the test in reducing atmosphere, the corrosion layer seemed to be less porous and appeared to adhere quite well to the steel surface in most of the cases (Figures 11 and 12). The better adherence can be caused, but has not been proven to be the only reason, by the different cooling process compared to the tests in air. In these tests, the samples were slowly cooled down in the furnace with a continuous gas flow, while after the tests in air the samples were taken out straight from the high temperature oven and cooled down.

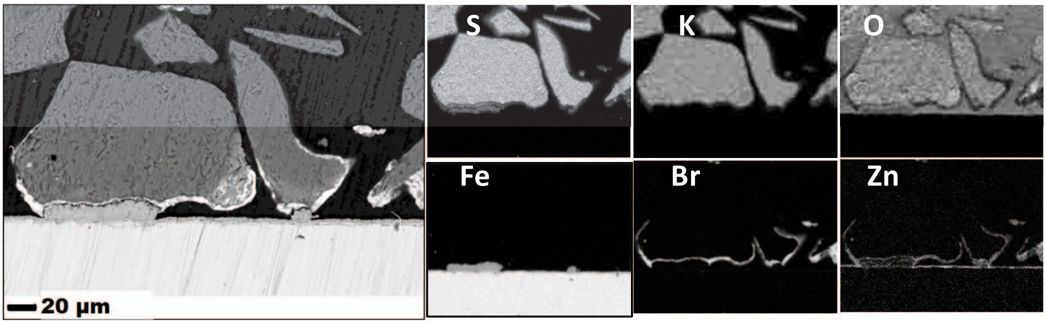

Figure 11. SEM image and X-ray maps of the St 45.8/III steel after 168h exposure with 6 mol-% $ZnBr_2+K_2SO_4$ at 350 °C in reducing atmosphere.

The formed corrosion layer was different in composition (mainly Fe, Zn and S) and the oxide layer was slightly thicker in places where the salt particles were in a direct contact with the steel surface. Otherwise the corrosion layer was quite thin, and even (Figure 11). These results go very well with the thermodynamic predictions which showed that in reducing conditions sulfur should mainly form Zn, Pb and Fe sulfides in the deposits. The formation of a Fe-Zn-S system with some oxygen was clearly observed.

In the work by Önay et al. [9] it was mentioned that Ni containing steels suffered accelerated attack due to the low stability of $NiBr_2$ and chromia being destroyed by NiO crystals growth in the oxygen lean atmosphere (Ar-H_2O-HBr). Since the currently tested environment was reducing, more attention was put to the Ni containing samples. The analysis of the S28 which contains 31 wt-% of Ni showed formation of Ni rich corrosion products. NiO crystals are clearly visible in the mixed salt/Fe-Cr oxide scale (Figure 12). The Ni rich formations above the chromia were also observed in AISI347 which contains 10 wt-% of Ni.

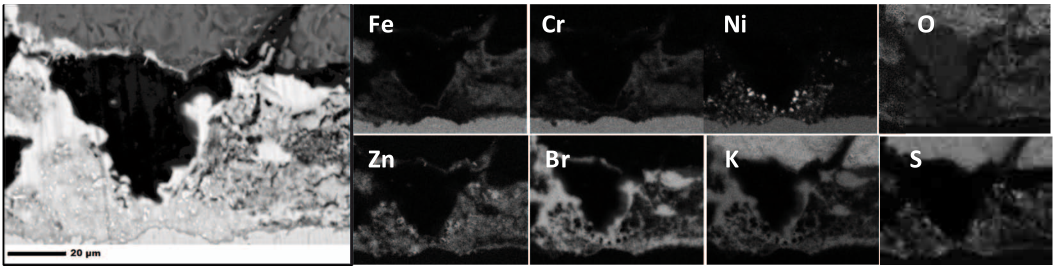

Figure 12. SEM image and X-ray maps of the S28 steel after 168h exposure with 6 mol-% $ZnBr_2$+K_2SO_4 at 400 °C in reducing atmosphere.

Also in reducing atmosphere the formation of KBr was observed, however, no clear crystalline form was observed as in the case in the tests with O_2 present. This could have it reasons in the differences in the cooling process of the test pieces under oxidizing versus reducing conditions, as mentioned earlier.

4. Conclusions

In Part 1 of the work it was found out that the main vaporized ash forming elements in the BFB combusting SRF were Na, K, S and Cl together with minor amounts of Zn, Pb and Cu and Br. Cl and Br have previously been suggested to induce high temperature corrosion of the boiler waterwall steels.

In the present work, tools such as theoretical equilibrium calculations and laboratory corrosion tests under relevant conditions were used to explain and evaluate results obtained from measurements in the lower furnace of a full-scale BFB boiler.

The detailed modeling results for this case indicated that at the in-furnace combustion gas temperatures (1100 °C) both Cl and Br form mainly gaseous alkali metal halides. Also Zn and Pb were estimated to be present to large extent in the gas phase. Zn- and Pb-chlorides have earlier been shown to cause corrosion at temperatures typical for waterwall surfaces. The modeling results showed also that in the examined BFB boiler at the waterwall deposit temperatures (400 °C) Zn and Pb can be present mainly as solid sulfides or sulfates in reducing and oxidizing conditions, respectively. In reducing conditions Cl, Na and K were estimated to be found mainly in the form of solid alkali metal chlorides. In oxidizing conditions Cl was estimated to be present as HCl(g) and the alkali metals as sulfates. Taking into account the large difference in the concentrations of Cl and Br in the modeled fuel mixture, at 400 °C the stable bromine compound was predicted to be mainly HBr(g) and some solid alkali metal bromides in reducing conditions. At this temperature the main difference in the Cl and Br behavior was that in oxidizing conditions Br seemed to have a particular affinity to Cu forming $CuBr_3$(g).

The bromine containing salt mixtures were shown in the lab-scale corrosion test to cause severe corrosion. Four different steel types (10CrMo9-10, St.45.8/III, AISI347, S28) and two bromine containing salts mixtures (6 mol-% $ZnBr_2$-K_2SO_4 and 10 mol-% $ZnBr_2$-K_2SO_4) were tested in air and in reducing atmosphere. The highest corrosion attack was observed on low alloy steel 10CrMo9-10 at all tested temperatures with both salt mixtures. At 400 °C, internal degradation of the steel together with the oxide layer growth was observed. The steel surface was bromine rich indicating formation of $FeBr_2$. The degradation of the austenitic stainless steel – AISI347 started already at 400 °C. Similar levels of degradation were observed at higher temperatures (500 °C and 600 °C). The corrosion attack on 10CrMo9-10 and AISI347 at 400 °C caused by a $ZnBr_2$ containing salt exceeded significantly the damage observed in corresponding tests with $ZnCl_2$ mixtures. This may be explained by the difference in a) the higher partial pressure of iron bromine in comparison to iron chloride and b) the lower oxygen partial pressure required to oxidize iron bromide. Adversely, S28 stood well all the exposures with salts containing Br but suffered increased corrosion when exposed to Cl containing salts at 600 °C. Two tests done under reducing conditions, performed at 350 °C and 400 °C, resulted in an oxide layer less than 20 μm thick for all tested materials. The measured oxide layer thickness indicates limited corrosion resistance of the tested materials in the tested environment. Formation of Zn-Fe sulfides was observed in reducing conditions. In oxidizing and reducing (> 350 °C) conditions, transformation of $ZnBr_2$ to KBr was observed.

Consistency between the aerosols measurements and deposit analyses performed in Part 1 of the work and the laboratory tests and thermodynamic calculations in the current work was observed.

Acknowledgements

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PUBLICATION VI

Trace elements found in the fuel and in-furnace fine particles collected from 80 MW BFB combusting solid recovered fuel

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Trace elements found in the fuel and in-furnace fine particles collected from 80MW BFB combusting solid recovered fuel

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ABSTRACT

The main fine particle ($d_p < 1$ μm) forming elements found in combustion gases of anthropogenic waste or biomass fired boilers are typically K, Na and Cl, possibly complemented with S. When these are excluded, in solid recovered fuel (SRF) combustion the main elements were found to be: Ba, Br, Cr, Cu, Fe, Pb, Sb, Sn and Zn. Fine particle composition is presented for 6 different furnace heights of a bubbling fluidized bed (BFB) boiler. As the fine particles are formed of vaporized ash species the experimental results are discussed with the support of thermodynamic equilibrium modeling for estimating the forms of the gaseous elements in the furnace. The occurrence of bromine was found to be similar to chlorine as the main forms of bromine in the furnace were estimated to be KBr(g) and NaBr(g) complemented with $CuBr_3$(g). It is proposed that the trace elements mentioned originate mainly from plastics and rubber where they are used as production additives, stabilisers, dyes, colorants and flame retardants. Cr, Cu and Zn may originate to a large extent from alloys and other metallic impurities. SEM-EDS analyses carried out for the SRF supports the postulated origin of the elements.

1. Introduction

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 [1–3]. In waste-fired boilers the main areas of failures, caused by gases and ash forming vapors, are the refractory lining, water walls and superheaters [4]. Regarding biomass combustion, the salts of Na, K, S and Cl are attributed to be the main initiators of ash melting and corrosion [5–7]. These are also the compounds that are easily vaporized during combustion, forming fine particles [8–14]. For waste combustion the aforementioned list of main contributors is commonly complemented with Zn and Pb with regard to both high temperature corrosion [15–19] and fine particle formation [20–22]. All these elements can be found in SRF, the mentioned metals and halogens particularly in plastic fraction [23–25]. Regarding bromine the few studies found in the literature indicate that it has a similar influence on the volatilization of the named cations as chlorine [26–32]. But due to the very specific applications of bromine its concentration in waste fuels can be assumed to be lower [33] than that of chlorine and even negligible in biomass.

In addition to inorganic salts, other bromine bearing species relevant for waste combustion are polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are likely human carcinogens which can be formed in thermal processes such as uncontrolled combustion. Analogously PBDDs/Fs can be formed in the presence of bromine. These are by their chemical structure exact homologues to the PCDDs/Fs. The general understanding is that after the formation of PBDDs/Fs bromine is substituted (to varying degree) by chlorine to yield PXDDs/Fs (brominated/chlorinated dibenzodioxins (PXDDs) and brominated/-chlorinated dibenzofurans (PXDFs) which are the most common bromine bearing dioxins/furans. In this paper these organohalogens are not discussed further [34–37].

The objective of this paper is to determine the composition and concentration of fine particle forming matter (aerosols) in different locations of a BFB (bubbling fluidized bed) boiler combusting solid recovered fuel (SRF). The focus is on the inorganic elements, with the largest concentration in aerosols, after excluding K, Na, Cl and S. These were found to be Ba, Br, Cr, Cu, Fe, Pb, Sb, Sn and Zn. The occurrence of these elements in the fuel and combustion gases is discussed. The discussion is supported by thermodynamic equilibrium modeling for the elements.

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2. Materials and methods

2.1. The BFB plant and fuels used

A detailed description on the BFB boiler and the general arrangements during the experiments can be found in another publication [38]. In the experimental campaign two experimental conditions, (a) and (b), were used in varying the proportions of the three fuels used. The fuels were SRF, spruce bark and wastewater sludge from a paper mill. The SRF-Bark ratio was kept as constant as possible in both experiments, on dry mass basis of 49%–51% and 53%–47% in experiment (a) and (b), respectively. The proportion of the sludge on dry mass basis from the total fuel mix was 14.8% and 4.3% in experiment (a) and (b), respectively, and the rest consisted of the SRF-Bark mix. The properties and composition of the fuel mixtures are summarized in Table 1.

The spruce bark originates from a paper mill adjacent to the boiler plant where the stem wood is used for mechanical pulping. The wood is Norway Spruce (*Picea abies* (L.)) of which a detailed study regarding its ash-forming matter can be found in the literature [39]. The paper mill wastewater sludge consists of wood fiber residue, paper filler and coating rejects which are mainly kaolin and calcium carbonate as well as residues of flocking agents. In the wastewater treatment some 30–40 kg of iron(III)sulfate per ton of dry sludge is added in the wastewater stream to precipitate out non-settleable solids. In addition, ash-forming matter in the sludge originates from alum, namely aluminium(III) sulfate, which is used in pH control and as a sizing agent in paper making [40]. A high proportion of the Fe and S in the sludge originates from the iron sulfate [38].

The SRF utilized in the BFB boiler originates from offices, wholesale business and small and middle scale industry in southern Finland [41]. Suitable wastes are source-separated packaging and other solid industrial non-recyclable wastes which are separately collected by the SFR supplier. In offices and commerce the source of this fuel can be identified from the waste bins labeled 'energy fraction'. The labeling instructs the consumer to sort in this fraction the following items: packaging plastics (not PVC), contaminated paper & cardboard, wooden packages, plastics (not PVC), expanded polystyrene, paper towels, clothes and textiles. The fractions collected from commerce (shopping malls, supermarkets) are mostly packaging materials, i.e. paper, cardboard and plastics in various forms. Industry sourced energy fractions are different types of demolition and packaging discards with production wastes from furniture manufacturing. These contain mainly textiles, wood and plastics. In SRF preparation plant the material is crushed to 50–100 mm particle size and magnetic materials are separated. SRF is transported to the BFB plant as wrapped bales or fluff.

Table 1
Fuel properties [38].

	SRF (a)	SRF (b)	Bark	Sludge	Exp.(a)	Exp. (b)
Moisture (wt.%, ar)	18.3	18.1	54.8	8.3 (67[a])	38.6	42.7
Ash (wt.%, ds)	7.5	7.5	2.1	21	7.2	5.6
In dry solids (wt.%)						
C	54.9	55.1	50.4	41.7	51.0	52.4
H	7.6	7.6	5.9	5.2	6.5	6.7
N	0.79	0.48	0.27	1.63	0.69	0.43
S	0.15	0.15	0.02	0.73	0.18	0.12
O	29.1	29.1	41.3	29.7	34.4	34.6
In dry solids (mg/kg)						
Ba	488	381	162	90	289	270
Br	40	205	10	27	25	110
Ca	17,800	19,100	7430	21,500	13,908	13,925
Cl	4600	4400	150	210	2100	2300
Cr	148	62	2	32	68	33
Cu	348	30	2	18	151	17
Fe	1330	1210	345	9180	2070	1158
K	938	1270	1090	1200	1470	1445
Na	1960	1860	978	1490	1042	1186
Pb	43	26	1	5	19	14
Sb	37	31	< 1	< 1	16	16
Sn	8	2	< 1	< 1	3	1
Zn	552	237	122	106	302	179
Heating value (MJ/kg)						
LHV, dry basis	23.56	23.51	19.00	16.33	20.54	21.17
LHV, as received	18.80	18.81	7.25	14.77	11.68	11.08

[a] For wet sludge in Experiment (b).

2.2. Fine particle sampling

In this paper the denotations 'aerosol' and 'fine particle' are used parallel to each other. Aerosol is generally meant by a suspension of solid or liquid (fine) particles in gas. In the fine particle collection system used in the current work the low pressure impactor (LPI) size segregates particles found in the combustion gases. These are complemented with vaporized ash-forming elements, such as halides, which form fine particles in the dilution probe used. The fine particle sampling system has been described in detail in an earlier publication [38]. The elemental composition of the samples collected by means of LPI was determined with ICP-MS after HNO_3-HF digestion.

The sampling locations in the boiler are illustrated and described in Fig. 1. There were all together 6 sampling locations. They were situated above the bed, in between each air feeding stage, in the superheater region and in the 2nd pass. The air split in the boiler was 50%–35%–15% fluidizing-secondary-tertiary air, respectively. The combustion gas temperature measurements were carried out by means of thermocouples with the same penetration depth of approximately 1.5 to 2 m in the furnace as the tip of the fine particle sampling probe. The boiler was operating with a constant load of 80 MW_{th}.

The concentrations of the fine particle forming matter in the combustion gases are reported in the normal pressure and temperature of the conditions prevailing at the corresponding moment in the 2nd pass FTIR (Fourier transform infrared) gas analyzer. The total dilution factor for the sampling has been defined based on the water vapor concentration in the 2nd pass and each fine particle sampling location as defined by means of FTIR.

2.3. Thermodynamic equilibrium modeling

Chlorides have been frequently in the focus when thermodynamic equilibrium modeling has been applied in ash behavior characterization [18,42–45]. In the current work alkali metal chlorides were also the main fine particle forming species [38]. The thermodynamic software package Factsage version 6.1 [46] was used in modeling of the ash chemistry. The objective was to estimate the most likely forms of the fine particle forming elements at the conditions prevailing in the sampling location. The FACT53 database for stoichiometric condensed phases and the gas phase was used in the calculation. All compounds in the database were considered, except for nitrogen compounds, where N_2 was the only nitrogen compound considered. It is known that thermodynamic equilibrium modeling does not predict nitrogen chemistry at combustion conditions satisfactorily. No non-ideal liquid solutions, such as a molten salt, were included. The elemental input for the fuel was taken from Table 1, exp. (a). Si and Al were not included in the modeling; it is assumed that regarding aerosol formation Si and Al are inert elements mainly originating from the sludge and that they would only form solid SiO_2 or Al_2O_3. These elements may however interact with the main ash-forming elements Ca, K, Na, and Fe and in turn affect S or Cl speciation. Interactions of Ca with Si and Al were identified in the aerosol sampling but mainly for the non-vaporized large particles, see Fig. 4, originating from the sludge. The melting of sludge ash particles were then modeled using the FToxid database, which contains data for complex oxide/silicate melts and other complex solid phases.

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Location	Description of location	T_{gas}, °C
FTIR	2nd pass.	480
6	In the 2nd pass, downstream from the first economizer.	371
5	Downstream from the superheaters.	580
4	In between the superheater tube banks.	740
3	Downstream from the tertiary air feed.	940
2	Downstream from the secondary air feed.	950
1	Above the bed / splash zone.	835

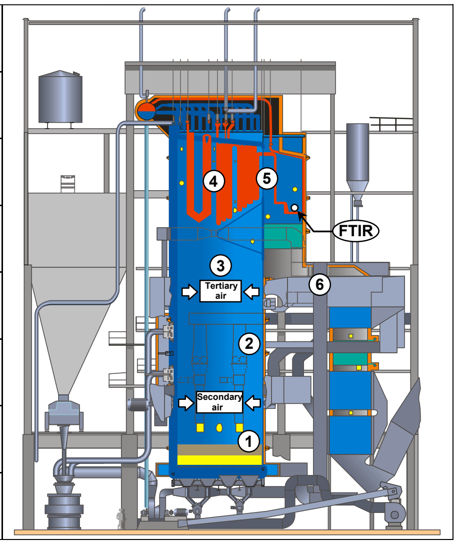

Fig. 1. Description of the measurement locations, with reference to the schematic boiler picture.

Regarding fine particle forming elements three conditions were used in the modeling: 1) 950 °C reducing, 2) 950 °C oxidizing and 3) 750 °C oxidizing. These were selected to represent the conditions in the lower and upper furnace in a simplified manner [47]. For the calculations of the oxidizing conditions, air was added to the elemental input at an air-fuel ratio of 1.4, which results in roughly 5 vol.% O_2 in the wet flue gas. In the reducing case, no air was added.

2.4. SEM-EDS for fuel

To find out in which form the ash-forming elements exist typically in SRF scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (EDS) was applied. This method has been described and applied for SRF in earlier work [48–51]. In the method pulverized fuel samples were mounted with Struers Epofix resin, cross-sectioned, and ground with 250, 600 and 1000 mesh grinding paper to produce an even surface. The surface was coated with a thin carbon layer and pre-selected areas of the sample surface were scanned with a focused electron beam using a Jeol JSM-6400 SEM. The elemental composition was determined with a Link ISIS EDS. The acceleration voltage of 15 kV and a beam current of 12×10^{-8} A were used in the SEM-EDS-analyses.

3. Results

3.1. Forms and concentration of fine particle forming elements in combustion gases

Fine particle composition and concentration in combustion gases are illustrated in Fig. 2. From the distribution K, Na, Cl and S are excluded. They have been discussed in a previous paper [38]. The mg/Nm^3 concentrations are expressed in conditions prevailing at the 2nd pass FTIR, which makes the graphs directly comparable to each other.

With the exception of sample (4b) the total concentration of PM2.5 (particles with aerodynamic diameter $d_p < 2.5$ µm) is roughly on the same level in every location. In (4b) the total concentration of the elements is the highest amongst the measured values. It seems at the moment of measurement at this location, being a single point measurement, the concentration was for some reason higher that in the other locations. From the particle size distribution it can be seen that the coarse mode ($d_p > 1$ µm) concentration in (4b) is not particularly high when compared to (4a); instead the fine mode ($d_p < 1$ µm) is pronounced in (4b).

The total concentration sum of the cations in the fine mode is approximately the same in both experiments (with the exception of (4b)). The inclusion of Br results in higher total concentration of the fine mode in the experiment (b) where it was identified as the only anion after the exclusion of Cl and S. Zn concentration is slightly higher in the fuel in experiment (a), a factor which also results in higher total concentration of fine mode Zn bearing particles in experiment (a) than in (b).

3.1.1. Barium

Ba is found in bimodal particle size distribution. Regarding the fine mode the likely compounds with sufficiently low melting point to generate significantly high vapor pressure are $BaCl_2$ and $BaBr_2$. In the modeling in the current work the only gaseous form found was $Ba(OH)_2$ (g) and only less than 1% from the total Ba, see Fig. 3. It is noteworthy that amongst the elements discussed here (excluding Fe) Ba is found the largest amount in the fuel, approximately the same concentration in both experiments. The main form of Ba based on modeling is BaS(s) in reducing and $BaSO_4$(s) in oxidizing conditions. $BaCrO_4$(s) was also estimated to be formed particularly in temperatures lower than 950 °C.

3.1.2. Bromine

In experiment (b) the Br concentration is higher in the fuel, and also in the aerosols than in experiment (a). In the fuel mix the concentration was on average 110 mg/kg, peaking as high as 520 mg/kg in the SRF [52]. In aerosols Br is found in higher concentration together with the increase in Sb concentration. Bromine is clearly enriched in the fine mode, indicating it has formed vaporized salt. In the superheater region samples Br is found in both experimental conditions. Similarly to Cl [38], Br size distribution expands towards a larger particle size when the gas temperature decreases.

Based on the equilibrium modeling at 950 °C gaseous KBr is the dominating Br speciation, complemented by NaBr(g). This applies for both reducing and oxidizing conditions. While the combustion gases are cooled down $CuBr_3$(g) is estimated to be formed, dominating the speciation of bromine at 750 °C followed by KBr(g) and NaBr(g). Considering the trace element chemistry, if Na and K are excluded, $CuBr_3$(g) is by far the dominating Br bearing compound followed by

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HBr(g) and Br(g). Minor amounts of $BaBr_2$(g) and $ZnBr_2$(g) were also estimated to be formed.

3.1.3. Copper

Cu is found in every experiment in the fine particles. On average Cu is found in the fuel mix concentrated in one order of magnitude higher in experiment (a) than in experiment (b) but this does not show through in the fine particle measurements. It may be that in experiment (a) the higher Cu content in the fuel is due to large metallic Cu impurities. Their conversion to aerosols seems not to be directly proportional to the amount in fuel, even if there is excess of Cl/HCl in the combustion gases. Cu is relatively evenly distributed in the fine and coarse mode. For reducing conditions Cu_2S(s) and Cu(l) have been suggested as the main stable forms in oxidizing conditions CuCl(g) and CuO(s) [44,45]. In oxidizing conditions in and after the superheater region it is suggested, based in the modeling in this work, that $CuBr_3$(g) is formed. Cu was estimated to be the main cation reacting with Br in addition to K and Na.

3.1.4. Chromium

Cr is found relatively evenly distributed between the fine and coarse mode in the reducing conditions and mainly in the coarse mode in oxidizing conditions. Cr_2O_3(s) has been suggested as the stable form in these conditions [53]. In the modeling in the current work, solid Cr bearing oxides were estimated to be formed in reducing and oxidizing conditions (not illustrated in Fig. 3). The suggestion that gaseous Cr chlorides are formed [53] supports the occurrence in the fine mode even if in the current work chlorides were not estimated to be formed.

3.1.5. Lead

Pb is found concentrated in the fine mode throughout the furnace. Pb(l,g) (l, liquid), PbCl(g) and $PbCl_2$(g) have been suggested for the stable forms in reducing conditions [44,45]. In this work modeling suggests also the formation of PbS(g). In oxidizing conditions PbO(g) and $PbCl_2$(g) are the main estimated forms of lead.

3.1.6. Antimony

Sb is found in bimodal distribution. It is found in the highest concentration when Br is also present, particularly in the fine mode. The connection of Sb and Br in the fuel is discussed later in this paper. Despite the likely co-existence of Br-Sb in the fuel and appearance in the fine particles, the modeling does not suggest that they form salt together. Sb halides exhibit very low melting points, as do the oxides (Sb_2O_3 655 °C) which facilitate the occurrence in the fine mode.

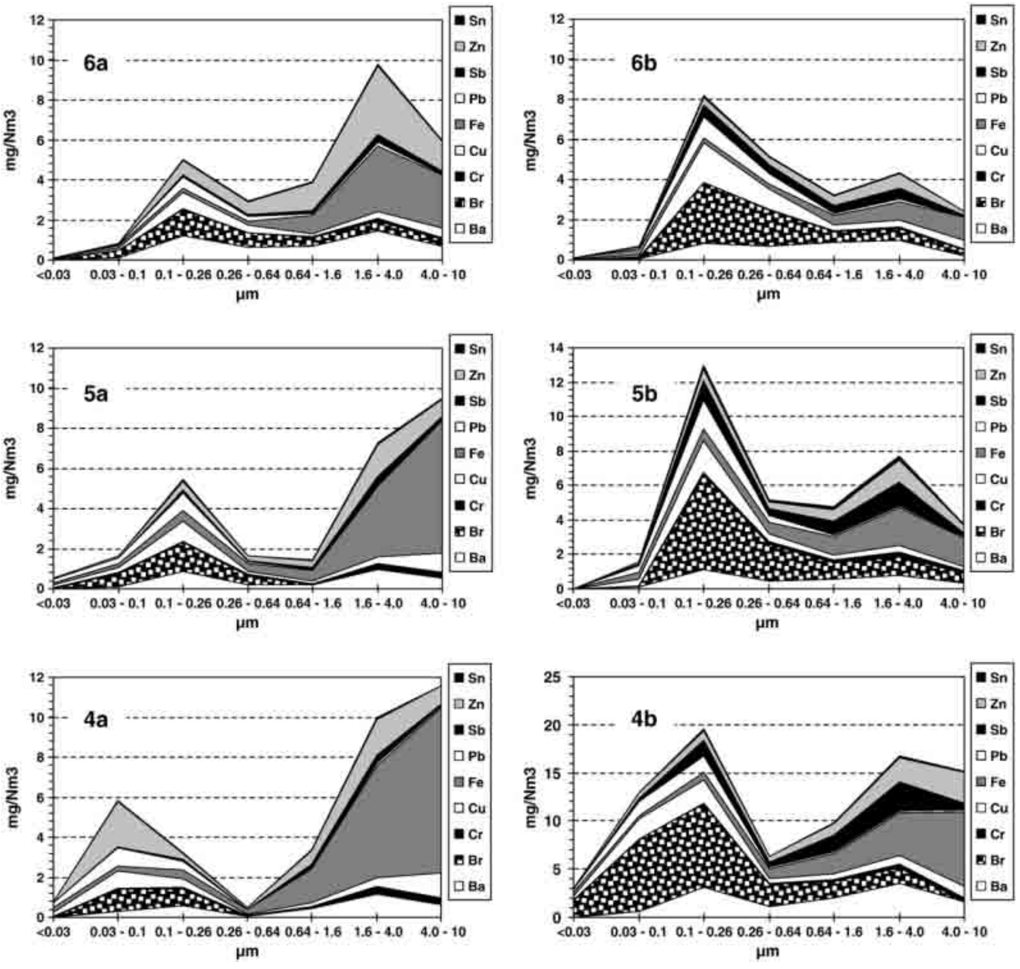

Fig. 2. Concentration of selected fine particle forming elements in the combustion gases.

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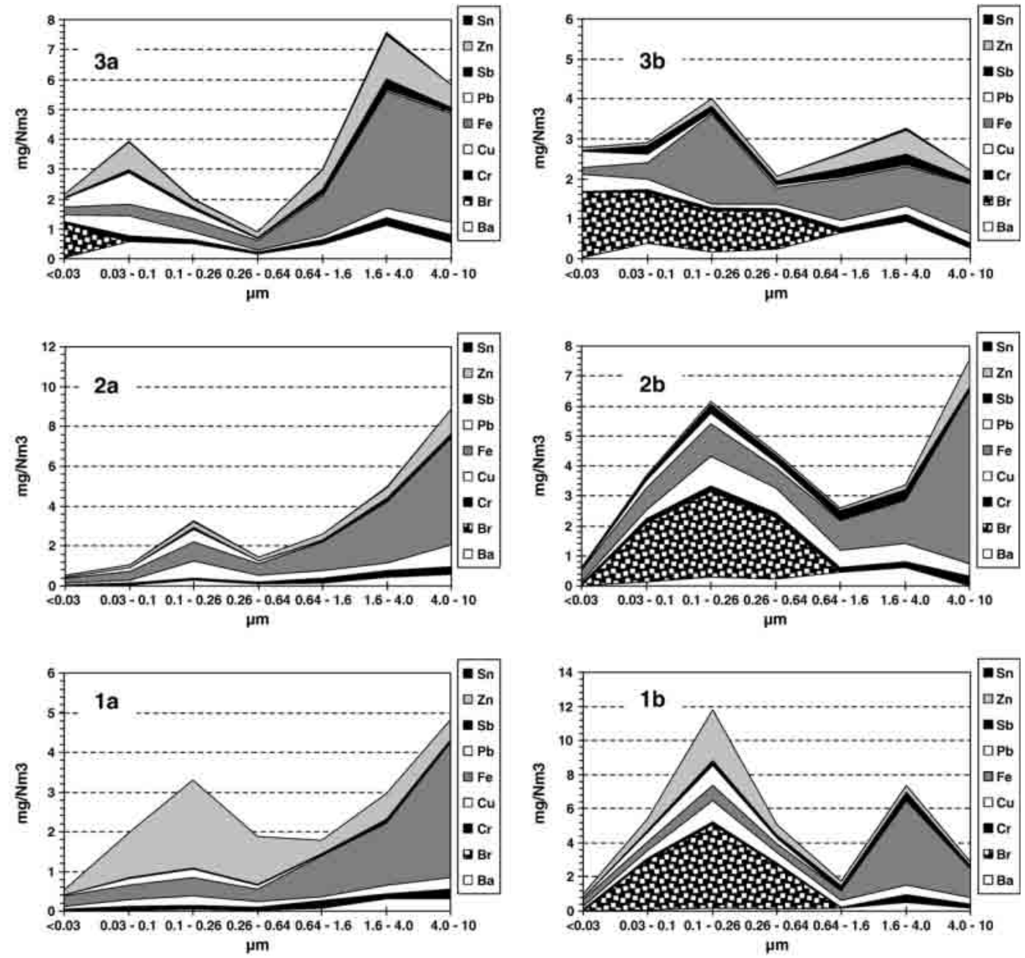

Fig. 2 (*continued*).

Thermodynamic modeling suggests $Sb_2(g)$ and Sb(g) for the main forms in reducing and $Sb_4O_6(g)$ and $SbO_2(s)$, $Sb_2O_4(g)$ as well as Sb$(OH)_2(g)$ in oxidizing conditions[32].

3.1.7. Tin

In comparison to the other elements considered here, Sn is found in the fine particles in small amounts. Particularly, it is found in both fine and coarse mode in locations 4 to 6 in experiment (b). According to the modeling results SnS(g) is the main form of tin in reducing and $SnO_2(s)$ in oxidizing conditions. It has been postulated that reducing conditions promote the volatilization of Sn [33].

3.1.8. Zinc

The highest concentration of Zn is found above the bed in both experiments. In these conditions the possible main speciation for Zn is gaseous elementary zinc, denoted as Zn(g), or chloride $ZnCl_2(g)$ [44,45]. According to the modeling in this work 100% of Zn was found as Zn(g). Zn is also found to large extent in the coarse fraction ($d_p > 1$ µm), to which ZnO(s) (s, solid) and silicate $2ZnO \cdot SiO_2$ have been suggested for the stable forms [53]. In oxidizing conditions ZnO(s) was estimated to be the form of zinc in the modeling in this work. The change in the form of Zn along the furnace height seems to show through in the fine particle sampling: in reducing conditions just above the bed Zn is clearly enriched in the fine mode (location 1), whereas above this location the fine mode Zn is clearly suppressed. Above the secondary air the furnace conditions are already primarily oxygen rich, a factor which already seems to facilitate the shift from Zn(g) to ZnO(s). It has been estimated that $ZnCl_2$ formation correlates positively with the HCl (residual) concentration in the furnace [54–56] but that it requires a relative large increase in Cl inventory in order for this effect to be clearly seen. Also a distinct difference was observed between Zn and Pb behavior where Pb was found more easily volatilized as chloride than Zn (Fig. 3).

3.1.9. Iron

Fe is by far the most abundant element found in the fuel mix amongst the elements considered here. In comparison to the other elements iron is found at high concentration in the fine mode particularly in the lower part of the boiler. This implies that Fe bearing species have been in the gas phase at some stage during combustion, possibly also involving molten phases. In reducing conditions and with HCl concentration of approximately 110 ppm (as measured in the 2nd pass) Fe may be present as halide, and in oxidizing condition as oxide [57]. This is seen as the suppression of the Fe in fine mode in locations 4–6 in comparison to 1–3. Based on the modeling in this work

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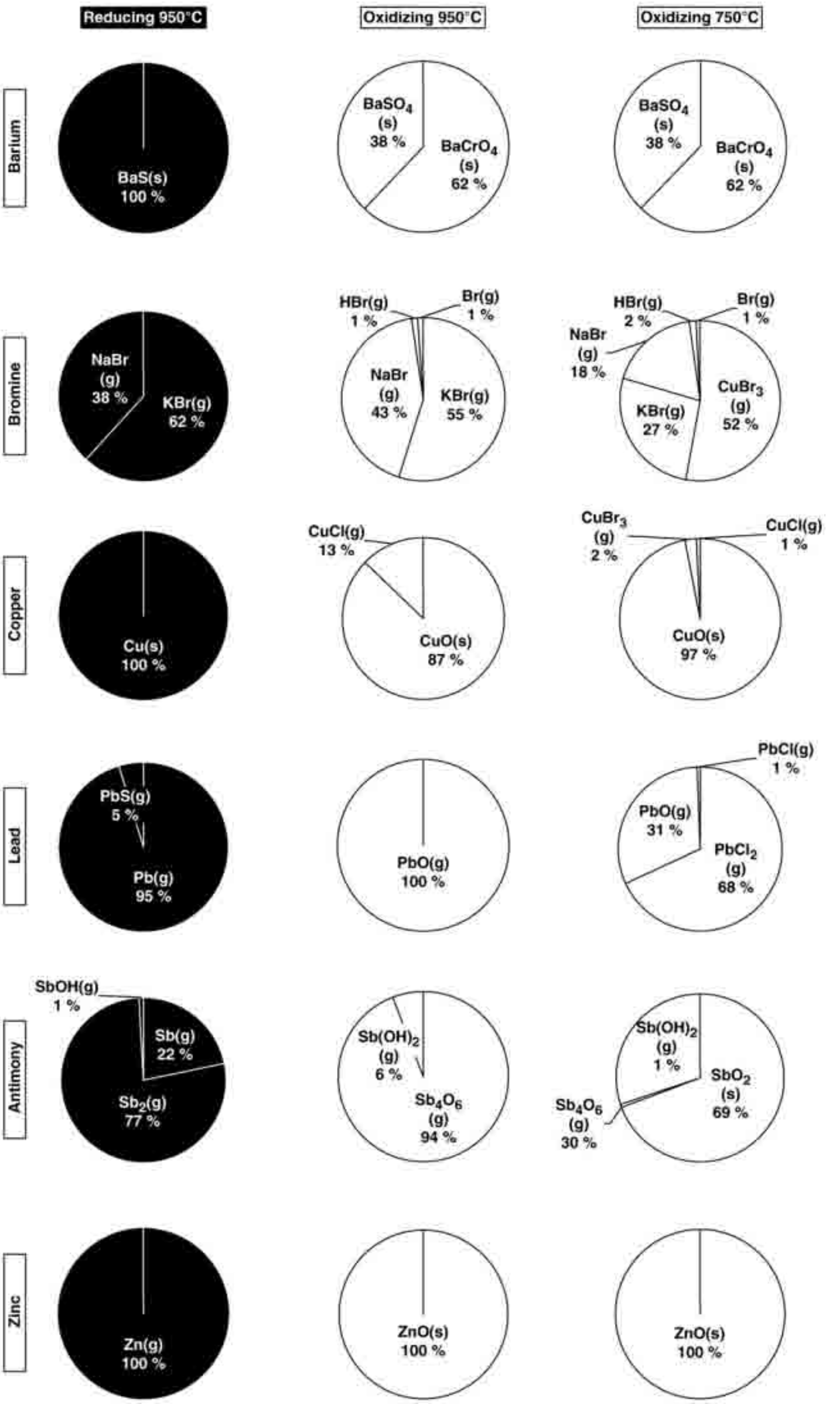

Fig. 3. Estimated forms of selected ash-forming elements in the combustion gases. The conditions have been selected in a simplified manner to represent those prevailing at the fine particle sampling locations.

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$Ca_2Fe_2O_5$(s) is estimated to be formed in oxidizing conditions and Fe(s) in reducing conditions. Halides were not estimated to be formed.

From the cyclone pre-separator of the fine particle sampling system, particles that had apparently undergone partial melting were found. These particles were analyzed by means of SEM-EDS and compared to the SEM-EDS analysis result of 815 °C laboratory ashed (oxidizing conditions) sludge. They are characterized by a relatively high Fe content. The results with SEM images are shown in Fig. 4. The composition of the ashed sludge resembles the composition of the particles found in the cyclone. The approximately 200 μm fiber agglomerates commonly found in such sludge [58] and their ash residue seem to keep their shape surprisingly well in the furnace. Apparently the particles shown in Fig. 4 have been partially molten, and the smallest sludge particles seem to have been completely molten in the furnace, as they have a ball shape. In the SEM backscatter image labeled 'Ash' the laboratory ashed sludge is shown, and in the corresponding bar chart its bulk composition. In '1a' is shown the image of a ball shaped particle from sample (1a) and the elemental composition from spots 1 and 2 are shown in the bar chart. In '4a' is shown the composition from spots 1–3 from particles in experiment/location (4a).

The thermodynamic modeling suggests the first melting point for the sludge ash composition to be 950 °C in reducing conditions, where most Fe is in the Fe^{2+} form, and around 1050 °C in oxidizing conditions, where Fe is mainly in the Fe^{3+} form. More relevant may be the amount of melt in reducing and oxidizing conditions at combustion gas temperatures. The amount of melt at 1000 °C in reducing conditions was found to be 20%, and in oxidizing conditions 0%. At 1100 °C, the amount of melt is 35% in reducing conditions and 15% in oxidizing conditions. This supports the visual characteristics of the particles found as they have undergone melting at some stage during combustion. Local reducing conditions in the fluidized bed may be the most favorable for the melting of the sludge ash particles.

3.2. Sources of aerosol forming elements in the fuels

The most significant difference in SRF compared to other fuels (coal, peat, biomass) is the character of the impurities: in SRF impurities often originate from specific materials which can contain high amounts of specific elements. Therefore impurities are distributed discretely, while in conventional fuels they are relatively evenly distributed. Typically, impurities in wastes are various man-made materials such as pieces of various metals, plastics, impregnated wood, textiles, treated leather, rubber etc.

3.2.1. Barium

Identifying the barium sources is perhaps the most challenging amongst the elements considered here. Ba/Cd mixed metal, barium stearate and barium laurate stabilisers are well known from PVC stabilization [23]. In PVC Ba content can in principle be thousands of ppm, and hundreds of ppm have been found in mixed wastes [59]. Ba is also used in the form of barium sulphate (barite) in paints, rubber and paper. Barite is used in acid resistant rubbers and as high gravity filler. It is also used in white sidewalls for tires, and in floor mats, PVC and polyurethane foam backings for carpeting and sheet flooring. Ba forms dense coatings due to its high specific gravity and ability to be used at high loadings. Paper applications include bristolboard, playing cards, and heavy printing papers [60,61].

3.2.2. Bromine

Regarding halogens, there is a general agreement that Cl in SRF originates mainly from chlorinated plastics such as PVC or food residues which contain dietary salt [62,63]. In addition, chlorine is used in flame retardants [64]. Regarding the sources of bromine it has been shown [65] that the proportion of plastics and textiles in SRF can be significantly higher than in MSW. Both of these fractions are used in applications and products where flame retardancy is required. Therefore, the likely

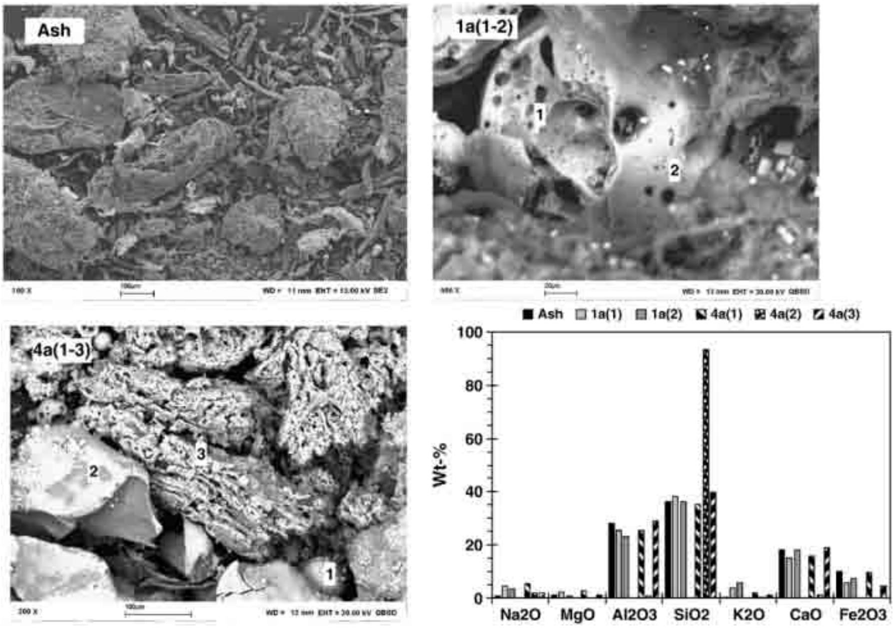

Fig. 4. SEM backscatter image on 815 °C ashed sludge, particle trapped in cyclone pre-separator from location 1a (spots 1–2) and location 4a (spots 1–3).

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sources of bromine in solid wastes are brominated flame retardants (BFRs) [66]. In BRFs bromine is bound in organic matrix and is readily available for reactions [67] in a similar way than Cl in PVC plastic. In the SEM-EDS study for the fuels Br could not, however, be identified. Often the bulk analysis corresponded to the SEM-EDS particle analysis, but not always. This may be simply due to no particles rich in the elements being present in the sample, or to the content being relatively evenly distributed in SRF.

Flame retarded plastics contain significant amounts flame retardant metal based synergists and stabilisers: antimony, Sb, most likely in the form of Sb_2O_3; tin, Sn, most likely from of zinc hydroxystannate ($ZnSn(OH)_6$) and its anhydrous analogue, zinc stannate (ZnSnO); zinc, Zn, as acid scavenger zinc stearate (ZnSt), zinc oxide or stannate [68]; and lead, Pb, in lead stearate stabiliser or lead carbonate colorant (white lead $(PbCO_3)_2 \cdot Pb(OH)_2$) or mixed metal colorant) [23].

Regarding the fuel mixture it is also possible that Br can originate to a large extent from the sludge, as Br is commonly used in water treatment [69–71], particularly in pulp, paper and cardboard mills in slime control [40,72].

The aerosol composition and literature on flame retardants [64] both support the postulation that Br and Sb originate from flame retardants. Sb was present in every fine particle sampling location, but was pronounced in the fine mode only in connection with the appearance of Br.

3.2.3. Copper

Cu seems to originate predominantly from brass in the SRF (with reference to the paragraph on Zn). But nor can Cu originating from electric wiring be neglected. Also, Cu is used in the impregnated wood (CCA, chromium, copper, arsenic) but this is collected separately and is not a significant source of Cu in the SRF. Cu may also originate from plastics where it is used in colorants and stabilizers in organic and salt forms [23,73]. In the SEM-EDS if Cu was present only at a single measurement point it was interpreted as copper metal or possibly copper oxide.

3.2.4. Chromium

On Cr rather scattered information was obtained through the SEM-EDS. The CCA association was indentified, but only in very few particles. Based on the SEM-EDS work Cr association in different alloys is the most likely main source of Cr. Chromium sulfate residues (from leather tanning [74]) were not identified.

3.2.5. Iron

Based on the SEM-EDS Fe in SRF is present mainly as metal or rust. However, the main Fe source in the boiler, as well as in aerosols, is the wastewater sludge. The Fe originating from ferric sulfate is likely to be found in the oxide form in this sludge, as the majority of it dissolved in acid.

3.2.6. Lead

Nakamura et al. (1996) [75] found up to 90% of the Pb in waste to originate from lead batteries, glassware and electric appliances, light bulbs etc. The proportion of paints was 0.1%. With the possible exception of paints these fractions are minor in high quality SRF. For the SRF used in this work the base material originates from commerce and industry where plastics, packaging (cardboard, paper) and wood are the main groups. If the highly Pb contaminated items (batteries, glass, light bulbs) were excluded from the data of Nakamura et al. (1996) [75], approximately 50% of the Pb originated from plastics, textiles, rubber and leather. The main compounds were suggested to be lead oxide, PbO, and lead stearate. The latter is commonly used metal soap in PVC stabilization [23]. The most commonly used PVC stabilizers (Pb bearing) are, however, tribasic lead sulfate and dibasic lead phosphite [23,76].

Pedersen et al. (2010) [77] found mixed PVC plastics to contain 3530 mg/kg Pb and 49 wt.% Cl. Further, approximately 90% of the Cl in the SRF used in this work originates from plastics (PVC) [38]. The combination of these results indicates approximately 0.39% PVC content in the fuel mixture used in this work. Also, these concentrations may result in theoretical Pb content of 14 mg/kg in the fuel mix due to PVC. Based on this observation, and with reference to Table 1, PVC can be reasoned to be the main source of Pb in the SRF. In the SEM-EDS Pb containing particles seemed to originate either from lead white pigment (oxide) or lead metal, and from PVC stabilized with lead, if it existed together with Cl. Nor can the use in solders be ruled out [78].

3.2.7. Antimony

Sb is a commonly used flame retardant synergist [64]. For example in the US 42% of Sb was used in flame retardant applications in 2008 [79]. Nakamura et al. (1996) [75] found approximately 80% of the Sb originated from textiles and plastics in waste fuels. Some 10% could be allocated to glass. In flame retardants antimony [80] is in the form of antimony trioxide, Sb_2O_3, and in glass applications sodium antimonite, $NaSbO_3$, is used initially. In the SEM-EDS study a clear main characterization for Sb speciation was not accomplished. Sb occurred in high concentrations in particulates together with Ca and Sn. This may indicate applications such as cable sheathing, plastics or rubber where Ca compounds may have been used as fillers, Sn as a stabilizer and Sb to provide flame retardant properties. Another source of Sb may be soldering tin or various other alloys.

3.2.8. Tin

Sn is used as soldering tin, which is typically an alloy of several metals. The co-existence of for example tin, copper, silver, zinc and antimony in varying combinations was seen in the particle analysis. Sn was found in connection to Cu and Zn, as it is used in alloying element in bronze and brass. Sn was also frequently observed in combination with Al, Si, Ca and Sb, which may indicate association with the plastic additive system (organotin stabilizers [23]).

3.2.9. Zinc

The appearance of Zn alone could originate in Zn plating such as galvanized nails. For example in the US more than half of stocks of bulk zinc is used in galvanizing [81]. According to the SEM-EDS observations, however, the most Zn rich particles were found in connection to the most Cu rich particles. This is assumed to be brass which is an alloy of Cu and Zn. Zn is also used in plastics as an acid scavenger and filler [23]. Cu and Zn rich particles were also found in connection to Si, which may indicate tinted glassware application [82]. Zn was also found in connection to other metals such as Fe and Ni, suggesting incorporation in alloy. In the fuel mixture Zn may also originate to a large extent from the bark in which Zn is absorbed by roots primarily as Zn^{2+} or as $Zn(OH)_2$[83–85].

In Table 2 (non exhaustive) the aforementioned elements are listed along with their purpose of application.

Table 2
Possible sources and purpose of application of selected elements found in SRF.

Ba	Plastic stabilizer, colorant, additive
Br	Flame retardant, sanitizing agent, disinfectant
Cu	Brass, impregnation, catalyst, colorant pigment
Cr	Alloys, color (yellow and green), impregnation, chromium plating, leather tanning
Fe	In this work the main Fe source is the wastewater sludge
Pb	Brass, soldering tin, pigment ("lead white"), PVC stabilizer, polymer catalyst, glass
Sb	Metal alloys, flame retardant, yellow and orange pigment in paints, vulcanizing agent and impregnation substance
Sn	Metal and alloys, plastic stabilizer, soldering tin
Zn	Brass, zinc plating, impregnation, flame retardants, vulcanizing agent, pigment, oil hardener, rust prevention, plastic stabilizer, acid scavenger

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4. Conclusions

Vaporized ash-forming compounds may form corrosive deposits on boiler waterwalls and superheaters. These ash species form fine particles when combustion gases are cooled down. In this work the main fine particle forming elements after the exclusion of the typical main elements Na, K, Cl and S were found to be Ba, Br, Cr, Cu, Fe, Pb, Sb, Sn and. Zn. These originate mainly from plastics, rubber and alloys in solid recovered fuel. Fe in this work originated mainly from wastewater sludge co-combusted with the SRF. These elements are vaporized predominantly as metallic, oxide or halide forms depending upon the local conditions in the boiler and were found in the fine mode ($d_p < 1$ μm) of the fine particles.

The most likely forms of Br in SRF combustion gases are KBr(g) and NaBr(g). HBr(g) and Br(g) are also estimated to be formed but only in minor amounts. Br was found in the fine particles already in the lower furnace; therefore KBr and NaBr are suggested to be formed already above the bed, and staying as the stable forms of Br through the furnace. This facilitates the formation of corrosive Br bearing deposits analogously to chlorine. If Na, K and Ca are excluded, copper was found to be the most likely cation to form a salt with Br in the form of $CuBr_3(g)$. Cu was found, in fact, in the fine mode particles in high concentrations (amongst the trace elements). Minor amounts of $BaBr_2(g)$ and $ZnBr_2(g)$ were formed at 950 and 750 °C, respectively. Sb was found in increasing amount in fine particles with bromine, but they were not estimated to form a compound together. Regarding the occurrence of iron, it was found that the iron-rich fibers that agglomerate in the wastewater sludge seem to keep their shape relatively well in the furnace, and that they are partially molten in it. Zn was estimated to be in the Zn(g) form in the lower furnace where it was also found to be most enriched in the fine mode particles. Pb was found in the fine mode particles. It seems to originate predominantly from plastics, forming mainly elemental, oxide or halide vapors in the furnace. Cr and Sn were found in the fine particles only in small amounts. They are assumed to originate mainly from alloys.

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Title

Occurrence of bromine in fluidised bed combustion of solid recovered fuel

Abstract

Corrosive ash species are the single most important factor limiting the electric efficiency of steam boiler plants fired with waste or biomass. Chlorine has been found to have a central role in the chemistry involved as it reduces the melting temperature of ash, forms corrosive vapour and gas species in the furnace and halogenated deposits on boiler heat transfer surfaces. In this context chlorine has been extensively researched.

At the time of writing this thesis there was hardly any published data available on the occurrence of bromine (Br) in the aforementioned context. The objective of this work was to review the occurrence of bromine in solid fuels and characterise the behaviour of bromine in full-scale fluidised bed combustion. The review on the occurrence of bromine in solid fuels revealed that in anthropogenic wastes bromine is mainly found in connection to flame retarded substances. Several weight percentages of bromine can be found in plastics treated with brominated flame retardants (BFRs). Bromine is typically found some 100–200 mg kg^{-1} in mixed municipal solid wastes (MSW). Bromine may be enriched in fuels with high share of plastics, such as solid recovered fuel (SRF) or refuse derived fuel (RDF). Up to 2000 mg kg^{-1} was found as a monthly average in SRF, typical levels being 20–200 mg kg^{-1}. Wastewater sludge from paper mills may contain bromine 20–100 mg kg^{-1} due the use of bromine based biocides. In other fuels bromine may be found in significant amounts in marine influenced coal deposits and peat as well as in biomass treated with brominated pesticides.

In the experimental part SRF, spruce bark and wastewater sludge from a paper mill were co-fired in a full- scale bubbling fluidised bed (BFB) boiler, and the collected fuels, aerosols and waterwall deposits were analysed with the focus on the fate of bromine. Bromine was mainly found to form water soluble high vapour pressure alkali metal halides in the furnace – in the form of KBr(g) and NaBr(g) as estimated by thermodynamic equilibrium modelling. A positive correlation was observed between the halogen (Br, Cl) and the metal (Cu, Pb, and Zn) concentrations in the lower furnace vapours when measured next to the waterwalls. Further, bromine was observed both in the wall deposits and in the corrosion front of the waterwall tubes. This was found to take place even if the bromine content in the SRF was less than 60 mg kg^{-1} in SRF. Laboratory scale oven tests with commercial boiler steels showed that a bromine containing salt induced a higher corrosion rate than the corresponding chloride.

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Författarna
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Förekomst av brom vid förbränning av returbränsle i fluidiserade bädd

Referat

Korrosiva askföreningar är den viktigaste enskilda faktorn som begränsar den elektriska effektiviteten hos ångpanneanläggningar som eldar avfall eller biomassa. Klor har visats ha en central roll i askkemin då den sänker askans smälttemperatur, bildar korrosiva ång- och gasföreningar vid förbränning och förorsakar halogenerade avlagringar på pannans stålytor. Omfattande forskning har ägt rum om kloren i dessa sammanhang.

Vid tidpunkten då denna avhandling skrevs fanns det knappt om data gällande förekomsten av brom (Br) i ovannämnda sammanhang. Målet med detta arbete var att granska förekomsten av brom i fasta bränslen följt av karakterisering av bromens roll i fullskalig förbränning i fluidiserade bäddar.

Undersökningen av bromförekomsten i fasta bränslen visade att brom i antropogent avfall huvudsakligen hittas i samband med brandförhindrande substanser. Flera viktprocent brom kan hittas i plast som behandlats med bromerade flamskyddsmedel. I blandat kommunalt fast avfall (MSW) finns det brom typiskt mellan 100 och 200 mg kg^{-1}. Brom kan vara anrikad i bränslen med hög plasthalt som t.ex. fasta återvunna bränslen (SRF, solid recovered fuel; RDF refuse derived fuel). Upp till 1000 mg kg^{-1} hittades som månadsmedelvärde i SRF och typiska nivåer var 20–200 mg kg^{-1}. Avfallsvattenslam från pappersbruk kan innehålla brom 20–100 mg kg^{-1} på grund av användning av brombaserade biocider. I andra bränslen kan brom hittas i betydande mängder i maritima kol- och torvförekomster samt i biomassa som behandlats med brominnehållande bekämpningsmedel.

I den experimentella delen i detta arbete samförbrändes SRF, granbark och slam från avfallsvatten i en fullskalig bubblande fluidiserad bädd (BFB) och bränslena, aerosolerna och avlagringarna från pannväggarna analyserades med fokus på bromens öde. Vid förbränning fanns brom huvudsakligen bilda vattenlösliga metallhalider med högt ångtryck. Termodynamiska jämviktsberäkningar visade att haliderna förekom som KBr(g) och NaBr(g). En positiv korrelation observerades mellan halogen- (Br, Cl) och metallkoncentrationerna (Cu, Pb och Zn) i pannans nedre delar invid de vattenkylda pannväggarna. Vidare observerades brom i avlagringarna på väggarna och vid korrosionsfronten på vattenväggens rör. Detta visades äga rum även om bromhalten var lägre än 60 mg kg^{-1} i SRF. Korrosionsexperiment i laboratorieskala med kommersiella pannstål visade att brominnehållande salt förorsakade allvarligare korrosion än motsvarande klorsalt.

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Bromin esiintyminen kierrätyspolttoaineen leijukerrospoltossa

Tiivistelmä

Korrosiiviset tuhkayhdisteet ovat suurin yksittäinen biomassaa ja jätettä polttavien höyryvoimalaitosten sähköntuotantohyötysuhdetta rajoittava tekijä. Tähän liittyvässä kemiassa kloorilla on havaittu olevan keskeinen rooli sillä se laskee tuhkan sulamislämpötilaa, muodostaa tulipesässä korrosiivisia höyry- ja kaasuyhdisteitä sekä halogenoituja kerrostumia lämmönsiirtopinnoille. Tässä yhteydessä klooria on tutkittu laajasti.

Tätä opinnäytettä kirjoitettaessa saatavilla oli hyvin vähän julkaistua tietoa bromin (Br) esiintymisestä edellä mainitussa yhteydessä. Tämä työn tarkoituksena oli koota tietoa bromin esiintymisestä kiinteissä polttoaineissa ja luonnehtia bromin käyttäytymistä täyden mittakaavan leijukerrospoltossa.

Katsaus bromin esiintymiseen kiinteissä polttoaineissa osoitti että ihmisen toiminnan aikaansaamissa jätteissä bromia löydetään enimmäkseen liittyen palosuojattuihin materiaaleihin. Bromia voidaan löytää useita painoprosentteja bromatuilla palosuoja-aineilla käsitellyistä muoveista. Sekalaisessa yhdyskuntajätteessä on bromia tyypillisesti noin 100–200 mg kg^{-1}. Bromi voi rikastua polttoaineisiin joissa muovien osuus on suuri, kuten kiinteät kierrätyspolttoaineet (SRF, solid recovered fuel; RDF refuse derived fuel). SRF polttoaineesta löydettiin jopa 2000 mg kg^{-1} kuukausikeskiarvona, tyypillinen pitoisuustaso on 20–200 mg kg^{-1}. Paperitehtaan jätevesiliete voi sisältää bromia 20–100 mg kg^{-1} johtuen bromiin perustuvien eliöntorjunta-aineiden käytöstä. Muissa polttoaineissa merkittäviä bromipitoisuuksia voidaan löytää meriympäristön vaikutuksen alaisista kivihiiliesiintymistä ja turpeesta sekä bromatuilla tuholaistorjunta-aineilla käsitellystä biomassasta.

Kokeellisessa osuudessa kierrätyspolttoainetta, kuusenkuorta sekä paperitehtaan jätevesilietettä rinnakkaispoltettiin täyden mitan kerrosleijukattilassa, ja kerätyt polttoaineet, aerosolit ja kattilaseinäkerrostumat analysoitiin keskittyen bromin esiintymisen määrittämiseen. Tulipesässä bromin havaittiin muodostavan pääasiassa vesiliukoisia korkean höyrynpaineen alkalimetallihalideja – termodynaamisen tasapainomallinnuksen perusteella arvioidut esiintymismuodot ovat kaasumaiset KBr ja NaBr. Tulipesän alaosassa, tulipesän seinien vierestä mitattujen halogeeni- (Br, Cl) ja metallihöyryjen (Cu, Pb ja Zn) pitoisuuksien välillä havaittiin positiivinen korrelaatio. Edelleen, bromia havaittiin sekä seinäkerrostumissa että kattilaseinäputkien korroosiorintamassa. Näin havaittiin tapahtuvan vaikka kierrätyspolttoaineen bromipitoisuus oli keskimäärin alle 60 mg kg^{-1}. Laboratoriomittakaavassa suoritetut uunikokeet kaupallisilla kattilateräksillä osoittivat bromia sisältävän suolan aiheuttavan jopa suuremman korroosionopeuden kuin vastaava kloridi.

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OCCURRENCE OF BROMINE IN FLUIDISED BED COMBUSTION OF SOLID RECOVERED FUEL

Due to the CO_2 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.

Corrosive ash species are the single most important factor limiting the electric efficiency of steam boiler plants fired with waste or biomass. Chlorine has been found to have a central role in the chemistry involved, and in this context chlorine has been extensively researched.

This thesis shows bromine is forming corrosive vapours during combustion and it can be even more aggressive than chlorine in inducing high-temperature corrosion of boiler steels. This work includes a comprehensive review on the occurrence of bromine in solid fuels, as well as experimental and modelling results on bromine behaviour in in-furnace conditions.

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