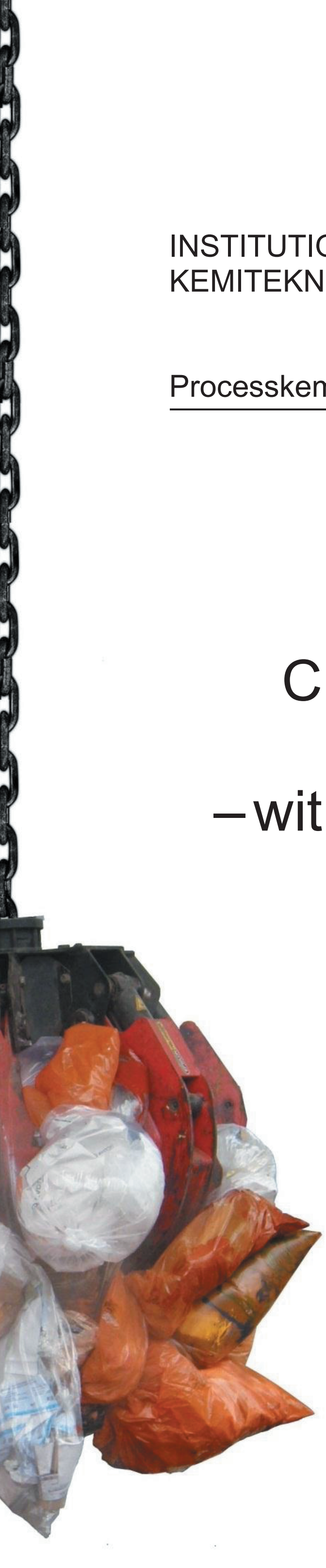

ÅBO AKADEMI

INSTITUTIONEN FÖR
KEMITEKNIK

DEPARTMENT OF CHEMICAL
ENGINEERING

Processkemiska centret

Process Chemistry Centre

REPORT 13-04

Characterisation of Waste for Combustion – with Special Reference to the Role of Zinc

Frida Jones

Doctoral Thesis

Laboratory of Inorganic Chemistry

Characterisation of Waste for Combustion

– with Special Reference to the Role of Zinc

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Doctoral Thesis
Laboratory of Inorganic Chemistry
Process Chemistry Centre
Department of Chemical Engineering
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2013

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ISSN 1459-8205
ISBN 978-952-12-2979-4 (paper version)
ISBN 978-952-12-2980-0 (pdf version)

Printing by Painosalama Oy

Åbo, Finland, 2013

The one man team is a complete and total myth

- *Don Shula*

Preface

The work described in this thesis has been carried out in co-operation between Åbo Akademi University and SP Technical Research Institute of Sweden. During the first three years (2007-2010) there was also a co-operation with the University of Borås and for a seven-month period (2011/2012) I had the pleasure to work in Canada at the University of Toronto. I am ever so grateful to be working with so many experts, always surrounded by people that can answer my questions. I especially would like to point out the support from Professor Mikko Hupa at Åbo Akademi University for taking me in as one of his students, although the majority of my work has been carried out in Sweden. Likewise, the seven months spent in Toronto, guided and encouraged by Professor Honghi Tran, will always be a dear memory and ever so important part of my PhD-work. During my first three years co-operating with the University of Borås, I worked with Professor Tobias Richards and Associate Professor Bengt-Åke Andersson, two very inspiring men helping me on my way. Here I also met Dr. AnnaLena Elled, then a co-supervisor and now a very close and dear friend.

The process of writing my articles and this thesis would not have been such a smooth and positive experience if it was not for the help from Dr. Daniel Lindberg whose wise comments and priceless aid kept me going. In addition, Docent Benco Skrifvars is greatly acknowledged for his support during my first three years as a PhD-student. To all my other co-authors on my articles: Thank you for your commitment and your contributions to the work!

As a part-time industrial PhD-student there are a lot of balls to juggle and without my boss at SP Energy Technology, Dr. Andreas Johansson, some of the balls surely would have fallen to the ground. He has been a supporting rock, always keeping my back, for which I will be eternally grateful. By allowing me to work part-time in other projects and also work in Toronto for several months, he has kept me sane. Another important person I would like to thank is Dr. Anders Hjörnhede for giving med the structure and security I needed to be able to focus on this work.

The list of all colleagues that mean a lot to me would be too long to write out, so all you guys at SP that I interact with on a daily basis, a huge thank you for making me laugh during the coffee breaks and love being at work. In addition, all the people I have met during my PhD-time in Åbo and Toronto, you are all great friends and I feel lucky to have met you all. A special thanks to Dr. Dorota Bankiewicz, for helping me with everything, all the time.

No research can be carried out without funding. I have so many to thank for financing and/or supporting my work; KK-stiftelsen (The Swedish Knowledge Foundation), The Hans Werthén foundation through IVA-The Royal Swedish Academy of Engineering Sciences, Waste Refinery, Avfall Sverige (Swedish Waste Management), The Swedish research school POWRES, the Nordic research school BioFuels-GS2, ÅFconsult, The Swedish Energy Agency, Profu AB, Metso Power, Renova, Borås Energi och Miljö, Dalkia, Umeå Energi, EOn, Fortum, Sysav, Tekniska Verken, National Technology Agency of Finland (Tekes), Andritz, Foster Wheeler, UPM-Kymmene, Clyde Bergemann GmbH, International Paper Inc., and Top Analytica. In addition to this, parts of my work are funded by my employer SP, by University of Toronto, and by Åbo Akademi University. Thank you all for investing in me!

Outside work my lovely network of friends are making sure I stay myself. A special thanks to David Antonsson, Camilla Olsson, Johanna Lövebrant, Emelie Fritz, Jennie Andersson, and Moa Larsson, where ever we are in the world we are close!

For many years of my life I have had the pleasure to reside and compete in the world of Track and Field, a sport I love deeply. This has brought special people into my life, you all know who you are, and even if I am not on the track anymore I still cheer for you whatever you may do in life, on or off track. Track and Field teaches you how to plan, structure and set goals to achieve your dreams, a lesson for life in general. Dwight D. Eisenhower once said “Plans are nothing, planning is everything”. I have learnt how to plan my time around training, school, work, family, and friends and still enjoy life. But most importantly Track and Field has taught me to fight even when times are hard, and no one fought harder than my dear high jumping friend Mattias Grundberg. Even though he lost his fight in the end, his determination and strength is an inspiration to me and in some ways he won; you cannot jump higher than to heaven.

No person is stronger than the love that surrounds them and I have been blessed with plenty. I have many people to thank for this; first and foremost my beloved parents, role models in every aspect of life and whom I love dearly. My older sister, aunts and uncles, cousins and all other family members, you all keep my life stable. My wonderful extended family of in-laws in England and other countries around the world, thank you for all your encouragement!

Last, but not at all least, my dear husband Ashley. Without you I would never have considered a career within research but your endless undoubted belief in me made me stronger. With you by my side the world is at my feet and where I would be without you is something I never want to find out. The future is bright for you, me, and the little one we will meet next year.

Thank you all for being on “Team Frida” ♥

Frida Jones, Borås, November 2013

Abstract

Waste combustion has gone from being a volume reducing discarding-method to an energy recovery process for unwanted material that cannot be reused or recycled. Different fractions of waste are used as fuel today, such as; municipal solid waste, refuse derived fuel, and solid recovered fuel. Furthermore, industrial waste, normally a mixture between commercial waste and building and demolition waste, is common, either as separate fuels or mixed with, for example, municipal solid waste.

Compared to fossil or biomass fuels, waste mixtures are extremely heterogeneous, making it a complicated fuel. Differences in calorific values, ash content, moisture content, and changing levels of elements, such as Cl and alkali metals, are common in waste fuel. Moreover, waste contains much higher levels of troublesome trace elements, such as Zn, which is thought to accelerate a corrosion process. Varying fuel quality can be strenuous on the boiler system and may cause fouling and corrosion of heat exchanger surfaces.

This thesis examines waste fuels and waste combustion from different angles, with the objective of giving a better understanding of waste as an important fuel in today's fuel economy. Several chemical characterisation campaigns of waste fuels over longer time periods (10-12 months) was used to determine the fossil content of Swedish waste fuels, to investigate possible seasonal variations, and to study the presence of Zn in waste. Data from the characterisation campaigns were used for thermodynamic equilibrium calculations to follow trends and determine the effect of changing concentrations of various elements. The thesis also includes a study of the thermal behaviour of Zn and a full—scale study of how the bed temperature affects the volatilisation of alkali metals and Zn from the fuel.

As mixed waste fuel contains considerable amounts of fresh biomass, such as wood, food waste, paper etc. it would be wrong to classify it as a fossil fuel. When Sweden introduced waste combustion as a part of the European Union emission trading system in the beginning of 2013 there was a need for combustion plants to find a usable and reliable method to determine the fossil content. Four different methods were studied in full-scale of seven combustion plants; ^{14}C-analysis of solid waste, ^{14}C-analysis of flue gas, sorting analysis followed by calculations, and a patented balance method that is using a software program to calculate the fossil content based on parameters from the plant. The study showed that approximately one third of the coal in Swedish waste mixtures has fossil origins and presented the plants with information about the four different methods and their advantages and disadvantages.

Characterisation campaigns also showed that industrial waste contain higher levels of trace elements, such as Zn. The content of Zn in Swedish waste fuels was determined to be approximately 800 mg kg^{-1} on average, based on 42 samples of solid waste from seven different plants with varying mixtures between municipal solid waste and industrial waste. A review study of the occurrence of Zn in fuels confirmed that the highest amounts of Zn are present in waste fuels rather than in fossil or biomass fuels. In tires, Zn is used as a vulcanizing agent and can reach concentration values of 9600-16800 mg kg^{-1}. Waste Electrical and Electronic Equipment is the second Zn-richest fuel and even though on average Zn content is around 4000 mg kg^{-1}, the values of over 19000 mg kg^{-1} were also reported. The increased amounts of Zn, 3000-4000 mg kg^{-1}, are also found in municipal solid waste, sludge with over 2000 mg kg^{-1} on average (some exceptions up to 49000 mg kg^{-1}), and other waste derived fuels (over 1000 mg kg^{-1}). Zn is also found in fossil fuels. In coal, the average level of Zn is 100 mg kg^{-1}, the higher amount of Zn was only reported for oil shale with values between 20-2680 mg kg^{-1}. The content of Zn in biomass is basically determined by its natural occurrence and it is typically 10-100 mg kg^{-1}.

The thermal behaviour of Zn is of importance to understand the possible reactions taking place in the boiler. By using thermal analysis three common Zn-compounds were studied ($ZnCl_2$, $ZnSO_4$, and ZnO) and compared to phase diagrams produced with thermodynamic equilibrium calculations. The results of the study suggest that $ZnCl_2$(s/l) cannot exist readily in the boiler due to its volatility at high temperatures and its conversion to ZnO in oxidising conditions. Also, $ZnSO_4$ decomposes around 680°C, while ZnO is relatively stable in the temperature range prevailing in the boiler. Furthermore, by exposing ZnO to HCl in a hot environment (240-330°C) it was shown that chlorination of ZnO with HCl gas is possible.

Waste fuel containing high levels of elements known to be corrosive, for example, Na and K in combination with Cl, and also significant amounts of trace elements, such as Zn, are demanding on the whole boiler system. A full-scale study of how the volatilisation of Na, K, and Zn is affected by the bed temperature in a fluidised bed boiler was performed parallel with a lab-scale study with the same conditions. The study showed that the fouling rate on deposit probes were decreased by 20 % when the bed temperature was decreased from 870°C to below 720°C. In addition, the lab-scale experiments clearly indicated that the amount of alkali metals and Zn volatilised depends on the reactor temperature.

Svensk sammanfattning

Avfallsförbränning har gått från att vara en volymreducerande bortskaffningsmetod till en energiåtervinningsprocess för oönskat material som inte kan återanvändas eller återvinnas. Olika fraktioner av avfall som används som bränsle idag är till exempel; fast kommunalt avfall, bränslekross och fasta återvunna avfallsbränslen. Dessutom är industriavfall, ofta en blandning av mellan verksamhetsavfall och bygg- och rivavfall, vanligt förekommande, antingen som enskilda bränslen eller blandat med kommunalt avfall.

Jämfört med fossila bränslen och biobränslen är avfall extremt heterogent, vilket gör det till ett komplicerat bränsle. Skillnader i värmevärde, askhalt och fukthalt samt skiftande koncentrationer av till exempel Cl och alkalimetaller är vanliga i avfallsbränslen. Avfall innehåller också mycket högre nivåer av besvärliga spårelement, såsom Zn som tros kunna accelerera en korrosionsprocess. Varierande bränslekvalitet kan vara påfrestande för pannsystemen och orsaka beläggningsbildning och korrosion av värmeväxlande ytor.

Denna avhandling presenterar studier från olika vinklar av avfallsbränslen och förbränning av avfall med målet att ge en bättre förståelse för avfall som ett viktigt bränsle i dagens bränsleekonomi. Flera långtidsbaserade (10-12 månader) kemiska karaktäriseringskampanjer har använt för att bestämma det fossila innehållet i svenska avfallsbränslen, för att undersöka eventuella årstidsvariationer, samt för att studera förekomsten av Zn i avfall. Data från karaktäriseringskampanjerna användes också för termodynamiska jämnviktsberäkningar för att se trender och bestämma effekten av förändrade halter av olika kemiska element. I avhandlingen ingår också en undersökning av det termiska beteendet hos Zn och en fullskalig studie av hur bäddtemperaturen kan påverka volatiliseringen av alkalimetaller och Zn från bränslet.

Eftersom blandat avfallsbränsle innehåller en hel del färsk biomassa, såsom trä, matavfall, papper etc, skulle det vara fel att klassificera det som ett fossilt bränsle. Då Sverige inkluderade avfallsförbränning i Europeiska Unionens system för utsläppsrättigheter i början av 2013 fanns ett behov för förbränningsanläggningar att hitta en användbar och tillförlitlig metod för att bestämma fossilandelen i avfallsbränslet. Fyra olika metoder studerades i fullskala vid sju förbränningsanläggningar; ^{14}C-analys av fast avfall, ^{14}C-analys av rökgasprover, plockanalyser följt av beräkningar samt en patenterad balansmetod som använder ett mjukvaruprogram för att beräkna fossilandelen baserat på pannparametrar. Studien visade att ungefär en tredjedel av kolet i svenska avfallsbränslen har fossilt ursprung och gav anläggningarna underlag med för- och nackdelar med de olika metoderna.

Karaktäriseringskampanjer användes också för att visa att industriavfall innehåller högre halter av spårelement, såsom Zn. Halten av Zn i svenska avfallsbränslen bestämdes till ca 800 mg kg^{-1} i gensomsnitt, baserat på 42 fasta avfallsprover från sju olika anläggningar med varierande mängder hushålls- och industriavfall. En litteraturstudie bekräftade att förekomsten av Zn i bränslen är betydligt högre mängder än i fossila bränslen eller i biomassa. I däck används Zn som vulkaniseringsmedel och kan nå koncentrationer mellan 9600 och 16800 mg kg^{-1}. Fraktionen el- och elektronikavfall är den näst Zn-rikaste med ett medel på cirka 4000 mg kg^{-1} men med värden så höga som 19000 mg kg^{-1} har också rapporterats. Höga koncentrationer av Zn återfinns också i fast kommunalt avfall (3000-4000 mg kg^{-1}), i avloppsslam med över 2000 mg kg^{-1} Zn i genomsnitt (med några undantag upp till 49000 mg kg^{-1}) och i andra typer av behandlat avfall (mer än 1000 mg kg^{-1}). Zn finns också i fossilt bränsle, i kol är medelvärdet för Zn i nivå med 100 mg kg^{-1} men värden mellan 20 och 2680 mg kg^{-1} har rapporterats för oljeskiffer. Halten Zn i biomassa bestäms av dess naturliga förekomst i växten och ligger typiskt i intervallet mellan 10 och 100 mg kg^{-1}.

Det termiska beteendet hos Zn är av betydelse för att förstå de möjlige reaktioner som sker i en förbränningsanläggning. Detta utreddes genom att använda termisk analys av tre vanliga Zn-ämnen ($ZnCl_2$, $ZnSO_4$ och ZnO) och jämföra med fasdiagram konstruerade med termodynamiska jämviktsberäkningar. Resultaten från studien visar att $ZnCl_2$(s/l) inte kan existera i pannan på grund av dess flyktighet vid höga temperaturer och dess omvandling till ZnO under oxiderande förhållanden. Studien också att $ZnSO_4$ sönderfaller vid ca 680°C medan ZnO är relativt stabilt inom temperaturområdet som råder i en förbränningsanläggning. Genom att exponera ZnO för HCl i en varm miljö (240-330°C) kunde studien påvisa att det är möjligt att klorera ZnO med HCl-gas.

Avfallsbränsle innehåller relativt höga koncentrationer av element som är kända för att vara korrosiva, till exempel Na och K i kombination med Cl, och även betydande mängder av spårelement såsom Zn, vilket är påfrestande för hela pannsystemet. En fullskalig studie av hur flyktavgången av Na, K och Zn påverkas av bäddtemperaturen i en förbränningsanläggning med fluidiserad bädd utfördes parallellt med en laboratoriestudie med samma villkor. Studien visade att tillväxten av beläggningar på en korrosionssond minskade med 20 % när bäddtemperaturen sänktes från 870°C till under 720°C. Dessutom visade de laborativa försöken tydligt att flyktavgången av och mängden alkalimetaller och Zn som avgår från bädden beror på reaktorns temperatur.

Nomenclature

AMS	Accelerator Mass Spectrometry
BFB	Bubbling Fluidised Bed
BI	Beta-Ionisation
CCA	Copper-Chromium-Arsenic (pressure-treated wood)
CFB	Circulating Fluidised Bed
Dp	Aerodynamic particle diameter
DS	Dry substance
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
ETS	Emission Trading System
FB	Fluidised Bed
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
IW	Industrial Waste
JJA	June-July-August (European summer)
LHV	Lower Heating Value
LSC	Liquid Scintillation Counting (also known as PSM)
MSW	Municipal Solid Waste
pmC	percentage modern Carbon
PSM	Proportional Scintillation counter Method
RBT	Reduced Bed Temperature
RDF	Refuse Derived Fuel
RWW	Recovered Waste Wood
SD	Standard Deviation
SRF	Solid Recovered Fuel
TDF	Tyre Derived Fuel
TGA	Thermogravimetric Analysis
THC	Total Hydrocarbon
WEEE	Waste Electrical and Electronic Equipment
WtE	Waste-to-Energy
Wt%	Weight%

Contribution of the author

Paper I

“Determination of fossil carbon content in Swedish waste fuel by four different methods”

Jones, F.C., Blomqvist, E.W., Bisaillon, M., Lindberg, D.K., Hupa, M.

Jones had the main responsibility when organising the sampling and analysis campaign, and also taught personnel at the grate-fired boilers how to perform the samplings by performing one at each plant (five in total). She also took participated in the sorting analysis. Together with co-authors she evaluated all the results from the study. Jones is the main author of the paper.

Paper II

“Chemical characterization of waste fuel for fluidized bed combustion”

Claesson, F., Skrifvars, B-.J., Elled, A-.L., Johansson, A.

Jones (Claesson at the time) performed the evaluation of the results from the sampling campaign with the other co-authors. She planned and performed the thermodynamic equilibrium calculations with support from co-author Elled. Jones (Claesson) was the main writer of the paper.

Paper III

“Occurrence and sources of Zn in fuels”

Jones, F., Bankiewicz, D., Hupa, M

Jones and Bankiewicz performed the literature review and co-authored the paper.

Paper IV

“The presence of zinc in Swedish waste fuels”

Jones, F., Bisaillon, M., Lindberg, D., Hupa, M.

Jones had the main responsibility when organising the sampling and analysis campaign, and also taught personnel at the grate-fired boilers how to perform the samplings by performing one at each plant (five in total). Jones evaluated the results and is the main author of the paper.

Paper V

“Thermal stability of zinc compounds”

Jones, F, Tran, H., Lindberg, D., Zhao, L., Hupa, M.

Jones planned and performed all experiments together with co-author Tran and Zhao. Jones made the evaluation of the results and is the main author of the paper.

Paper VI

“Effects of Reduced Bed Temperature in Laboratory- and Full-Scale Fluidized-Bed Boilers: Particle, Deposit, and Ash Chemistry”

Jones, F., Niklasson, F., Lindberg, D., Hupa, M.

Jones was active during the full-scale experimental campaign and performed some of the samplings alongside co-author Niklasson. She was involved in the planning and organising of the lab-scale experiments and performed it together with co-author Niklasson. Jones and Niklasson evaluated the results together. Jones is the main author of the paper.

Related publications not included in this thesis

The following publications are related to this thesis; however, they are not included. The author of this thesis can be found in the list below either as Jones, F. or Claesson, F.

Publications in peer-reviewed international scientific journals

Andersson, S., Blomqvist, E.W., Bäfver, L., **Jones, F.,** Davidsson, K., Froitzheim, J., Karlsson, M., Larsson, E., Liske, J.; *"Sulfur recirculation for increased electricity production on Waste-to-Energy plants."* Waste Management, online 16 Oct, 2013. (http://dx.doi.org/10.1016/j.wasman.2013.09.002)

Bäfver; L. S., Rönnbäck, M., Leckner, B., **Claesson, F.,** Tullin, C.; *"Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin"* Fuel Processing Technology 90 (2009) 353–359. (http://dx.doi.org/10.1016/j.fuproc.2008.10.006)

Publications in conference proceedings

Claesson, F., Wikström Blomqvist, E., Johansson, A., Skrifvars, B-J., Andersson, B-Å.; *"Annual Variation In Elemental, Dioxin And PCB Content Within Swedish Waste Fuels – Results From Two Plants"* Proceedings of the 12th International Waste Management and Landfill Symposium, October 5-9, 2009, Sardinia, Italy

Rönnbäck, M., Johansson, M., **Claesson, F**.; *"Combustion tests of pellets from ash rich biomasses in residential pellet burners"* Proceedings of the International Conference on Solid Biofuels, August 12-14, 2009, Beijing, China

Claesson, F., Johansson, L., Rönnbäck, M., Johansson, M., Tullin, C.; *"Particle emissions from combustion of oat grain with additives"* Proceedings of the 4th Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute, November 5-6 2007, Åbo/Turku, Finland

Rönnbäck, M., Arkelöv, O., Johansson, M., Johansson, L., Tullin, C., **Claesson, F**.; *"Methods to reduce sulphur dioxide, hydrogen chloride and particle emissions from small-scale combustion of energy grain"* Proceedings from the 15th European Biomass Conference & Exhibition, May 7-11, 2007, Berlin, Germany

Research reports

Hermansson, S., Victorén, A., Niklasson, F., **Jones, F.**; "*Pre-treatment of waste fuel with low-speed shredding and screening for fluidized bed incineration*" Waste Refinery-rapport, WR-52, 2013 (In Swedish)

Davidsson, K., Gustafsson, G., Herstad Svärd, S., **Jones, F.**, Niklasson, F., Ryde, D.; *"The importance of ash for the favourable properties of sewage sludge in co-firing"* Waste Refinery-rapport, WR-38, 2012 (In Swedish)

Blomqvist, E.W., **Jones, F**.; *"Determination of fossil content in combustible waste in Sweden"* Avfall Sverige Rapport 2012:02, 2012 (Main report in Swedish, also available in English)

Niklasson, F., Pettersson, A., **Claesson, F**., Johansson, A., Gyllenhammar, M., Victorén, A., Gustafsson, G.; *"Reduced Bed Temperature in FB-Boilers Burning Waste – Part II"* Waste Refinery-rapport, WR-19, 2010 (In Swedish)

Andersson, S., Blomqvist, E., Bäfver, L., **Claesson, F**., Davidsson, K., Froitzheim, J., Karlsson, M., Pettersson., J., Steenari, B-M.; *"Sulphur recirculation for reduced boiler corrosion"* Waste Refinery-rapport, WR-07, 2010 (In Swedish)

Niklasson, F., **Claesson, F**., Haraldsson, C.; *"Online measurements of non-organic components in flue gas"* Waste Refinery-rapport, WR-29, 2010

Pettersson, A., **Claesson, F**.; *"Chemical Fractionation of Waste Fuels – A comparison of methods"* Waste Refinery-rapport, WR-18, 2009 (In Swedish)

Niklasson, F., Haraldsson, C., **Claesson, F**., Bäfver, L., Ryde, D.; *"Reduced bed temperature at thermo-chemical conversion of difficult fuels"* Värmeforskrapport A08-812, 2009 (In Swedish)

Claesson, F., Blomqvist, E.; *"Optimised waste management in Viared Business region Association"* Energiteknik, SP Rapport 2009:06 (In Swedish)

Rönnbäck, M., Johansson, L., **Claesson, F**.; *"ERA-Net Evaluation of technology status for small-scale combustion of pellets from new ash rich biomasses- combustion tests in residential burners"* SP Energy Technology, SP Report 2008:31

Rönnbäck, M., Johansson, L., **Claesson, F**., Johansson, M.; *"Characterization and reduction of dust during combustion of energy grain"* Energiteknik, SP Rapport 2008:04 (In Swedish)

Contents

1 Introduction

Disposal of waste through combustion has been used for thousands of years; it has been an easy way to reduce the volume of waste. However, most development has taken place during the past few decades, resulting in the advanced combustion technology and state-of-the-art flue gas-cleaning equipment of today.

In Sweden, waste combustion started in the 1970s as a result of new legislation giving the municipalities a monopoly on household waste [1]. The amounts of generated waste had increased enormously during the 1960s and landfilling was the dominant treatment method. At the same time, the first worldwide oil crisis forced society to welcome a complementary technique to meet the demand for heat in the district heating systems.

In addition to this, research has shown that landfilling of waste significantly contributes to the release of methane gas [2, 3], a known greenhouse gas, which has a warming potential in the atmosphere that is 21 times more powerful than CO_2 [4]. As well as contributing gaseous emissions to the atmosphere, landfills release a number of chemical compounds in the form of leachates and particulate matter, some of them hazardous to the environment [5, 6]. Combustion of waste can therefore serve several purposes: mass and volume reduction of waste, production of heat and power, and a reduction in the emission of methane and leachates from landfills. As a consequence, more and more countries nowadays are opting to prohibit or reduce the flow to landfills of materials such as organic and combustible waste.

The EU's Council Directive 99/31/EC on landfills (agreed on 26th April 1999) [7], aimed to prevent, or reduce, the possible negative effects on the environment from the landfilling of waste by introducing stringent technical requirements for waste and landfills. Directive 06/12/EC of the European Parliament and of the Council of 5th April 2006 on waste elucidates the EU waste treatment hierarchy [8]. It encourages all member countries to prevent, reuse, and recycle waste as far as possible and then use waste as an energy source, e.g. in Waste to Energy (WtE) plants. Improvement and expansion of waste combustion is taking place worldwide and progress within the technical areas has refined the cleaning technologies and eliminated a greater part of the emissions [9, 10]. Figure 1 shows great potential for energy recovery within the EU-27 by using combustion instead of landfilling as a treatment method for Municipal Solid Waste (MSW) [11].

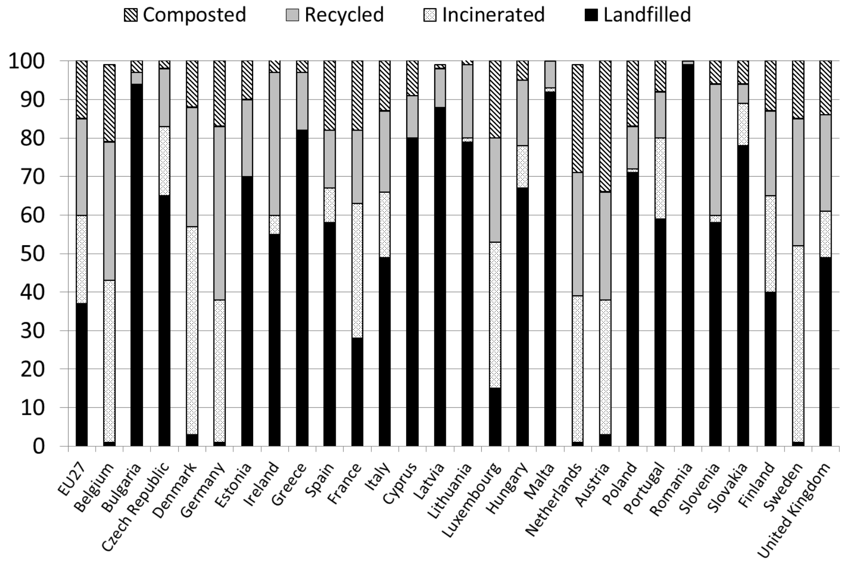


Figure 1. Treatment methods for MSW in EU27 countries in 2011. Data for the EU27, Germany, Ireland, Spain, France, Italy, Cyprus, Luxembourg, Austria, Poland, Portugal, Romania, and the United Kingdom are estimated [11].

However, combustion of waste fuels is more challenging compared to most other fuel in combustion plants owing to the heterogeneity and the content of various problematic compounds. Several studies done over recent decades, such as Uberoi [12] and van Lith [13], have pointed out that fuel composition is a determining factor during combustion, and that it has a substantial effect on the occurrence of fouling and corrosion. High levels of certain problematic elements, such as alkali metals and Cl, are present in waste. They are known to affect the formation of deposits, cause lower boiler efficiency, lead to an increased need for maintenance and shorten boiler lifetime. Induced by high temperatures, Cl-containing deposits are known to cause severe corrosion of heat exchangers. To minimise these problems today, waste boilers are operated at a significantly lower steam temperature than, for example, fossil fuel boilers, to extend the steel lifetime [14]. A lower steam temperature means that the electricity production is decreased as well, and the full energy potential of the fuel is not acquired.

Fuel characterisation gives valuable information about the combustion properties of the fuel. Studying waste mixtures used for combustion provides an opportunity to find ways to reduce or avoid unwanted chemical reactions. Long-period studies can also provide information about possible time-related variation patterns in the fuel composition, such as the political economic climate, which affects consumption patterns, or seasonal variations. Furthermore, the introduction of waste combustion in the CO_2 Emission Trading System (ETS) [15] in Sweden requires a good knowledge of waste and its origin to be able to determine the fossil content.

1.1 Purpose of this thesis

The purpose of this work was to support the further use of waste derived fuels in energy conversion by deepening the understanding of some important chemical aspects of waste fuels and the combustion process. The work presented in this thesis is threefold, considering: (i) different ways of characterising fuel, (ii) occurrence and sources of Zn in fuels, and its behaviour during combustion, and (iii) the effects due to reduction of the bed temperature in boilers.

Suitable waste fuel sampling processes facilitates proper characterisation of elemental composition as well as a possibility to determine the shares of carbon with fossil origin in waste. Both of which are important factors for modern combustion plants, striving for an efficient combustion process with no or little problems and also expecting tougher regulations regarding emissions of fossil CO_2. The occurrence and behaviour of Zn in waste fuels is of importance for increased understanding of fuel related issues, as Zn may play a role in deposit and corrosion problems. However, more studies are needed in this area. One way of reduce the formation of corrosive products, such as $ZnCl_2$ and alkali chlorides could be to reduce the bed temperature of a fluidised bed boiler, and the effects of such a change is part of the study for this thesis.

This thesis is based on six papers, which will henceforth be referred to by the roman numerals below:

I. ”Determination of fossil carbon content in Swedish waste fuel by four different methods”
Jones, F.C., Blomqvist, E.W., Bisaillon, M., Lindberg, D.K., Hupa, M.
Waste Management & Research 31:10 (2013) 1052-1061.
(http://dx.doi.org/10.1177/0734242x13490985)

II. “Chemical Characterization of waste fuel for fluidized bed combustion”
Claesson, F., Skrifvars, B-.J., Elled, A-.L., Johansson, A.
Published in the proceeding of the 20th International Conference on Fluidized Bed Combustion (2010) 1116-1122.Conference held in Xi’an, China May 18-21, 2009.
(http://dx.doi.org/10.1007/978-3-642-02682-9_174)

III. “Occurrence and sources of zinc in fuels”
Jones, F. Bankiewicz, D. Hupa, M.
FUEL 117 (2014) 763-775.
(http://dx.doi.org/10.1016/j.fuel.2013.10.005)

IV. ”The presence of Zinc in Swedish waste fuels”
Jones, F., Bisaillon, M., Lindberg, D., Hupa, M.
Waste Management 33:12 (2013) 2675-2679.
(http://dx.doi.org/10.1016/j.wasman.2013.07.023)

V. ”Thermal Stability of Zinc Compounds”
Jones, F, Tran, H., Lindberg, D., Zhao, L., Hupa, M.
Energy & Fuels 27:10 (2013) 5663–5669.
(http://dx.doi.org/10.1021/ef400505u)

VI. “Effects of Reduced Bed Temperature in Laboratory- and Full-Scale Fluidized-Bed Boilers: Particle, Deposit, and Ash Chemistry”
Jones, F., Niklasson, F., Lindberg, D., Hupa, M.
Energy & Fuels 27:8 (2013) 4999–5007.
(http://dx.doi.org/10.1021/ef400836e)

2 Background

This chapter describes different combustion technologies and sampling techniques, as well as techniques for chemical analysis of waste fuel samples. In addition to the chemical analyses, this chapter describes the presence of Zn in fossil, biomass, and waste fuels. The chapter also includes the behaviour of Zn during combustion. Furthermore, this chapter features descriptions of thermal analysis, analytical techniques for determining the fossil content in waste used for combustion, and thermodynamic equilibrium calculations.

2.1 Combustion technologies for waste

In 2012, there were a total number of 455 waste combustion plants in Europe, of which approximately 80 are located in the Nordic countries (Denmark, Finland, Norway, and Sweden) [16]. There are two dominating combustion technologies typically used for waste combustion, Fluidised Bed (FB) boilers and grate-fired boilers. In Sweden, the latter is the dominating technique, used at approximately 75 % of the waste combustion plants. Brief descriptions of the combustion technologies are presented below.

2.1.1 Grate-fired boilers

Grate-fired boilers are a type of fixed-bed combustion boilers of which there are different types, mainly depending on the feeding systems for fuel and air: see the left part of Figure 2. The dominantly used commercial feeding method is cross-current feeding (showed to the right in Figure 2) where the fuel is fed on to a conveyor belt, the grate, and the air is inserted from a cross-current direction, from below the grate [17]. There are also different types of grates according to the movement of the rods in the grate: forward, backward, up-and-down or reciprocating. For complete combustion it is important that the air/fuel ratio is kept at oxidising conditions but avoiding cold passages. In a grate-fired boiler the primary air comes in at the grate and secondary, and possibly tertiary air, is introduced above the bed and further up in the boiler.
The moving grate has several tasks in the combustion system [18]:

- The mechanical transport of the fuel from the entering side, through the combustion process, and disposal of slag and ash to the slag transport system
- Mechanical distribution and mixing of the fuel to ensure optimal combustion conditions

- Mechanical adjustment of the fuel height across the grate depending on the stage of combustion the process is at
- Controlling the primary air addition.

The fuel used for waste combustion in Swedish grate-fired boilers most often consists of a mixture of MSW and IW. By logging the delivered waste based on specified codes entered by the lorry drivers at the weight-in point of waste, the plant can monitor an approximate ratio between the two. At a grate-fired boiler there is little or no pre-treatment of the waste before it is combusted, most of the lorries deliver their waste loads directly into the bunker from a dumping hall. From the bunker the untreated fuel is fed to the grate by an automated or man-operated overhead crane.

2.1.2 Fluidised bed boilers

There are two types of Fluidised Bed (FB) boilers, Circulating Fluidised Bed (CFB), and Bubbling Fluidised Bed (BFB), see Figure 3 for examples of both versions [19]. In both versions combustion takes place in a bed of fine sand particles, fluidised by primary air inlets in the bottom of the boiler.

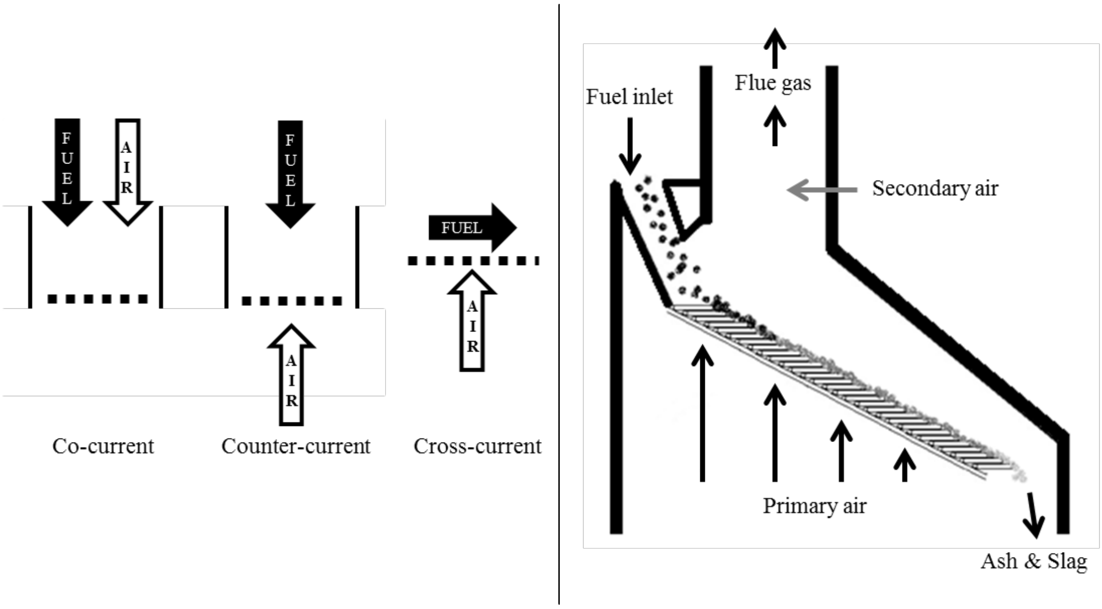
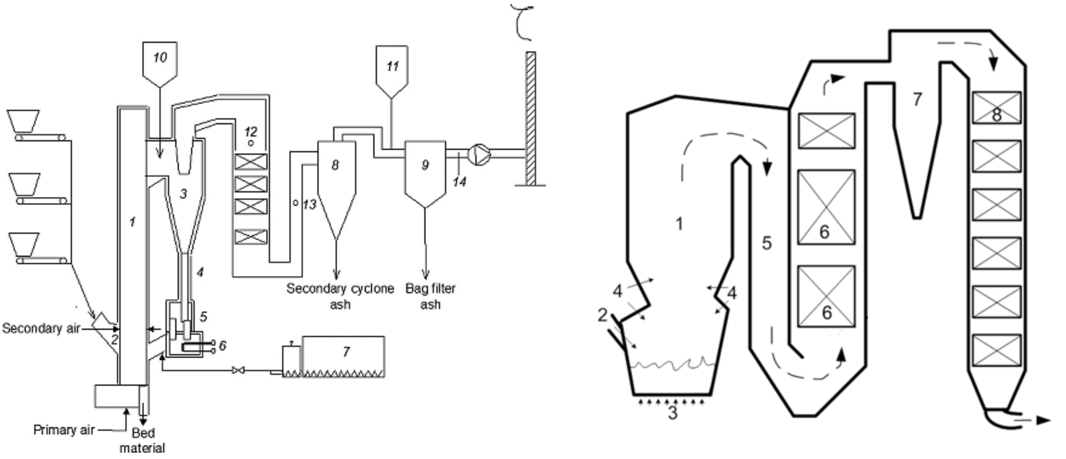


Figure 2. Left: Different types of feeding of fuel and air in grate-fired boilers. Right: the schematic view of a cross-current grate-fired boiler.

The BFB has a higher particle density due to lower air velocity than that in a CFB. In the CFB the fluidisation of the bed material is so powerful that the sand follows the flue gas and is separated in a cyclone and recirculated to the bed. Secondary and tertiary air is introduced further up in the boiler to ensure complete combustion. A normal bed temperature for a FB-boiler is around 800-900°C. The boiler design and bed temperature must facilitate the process that after the last point of addition of secondary air the flue gas temperature must keep a temperature of 850°C for at least two seconds, as determined by the EU for European waste combustion [20].

Fuel that is combusted in FB-boilers need to undergo pre-treatment before combustion, to ensure a particle size suitable for the combustion technology. As in the grate-fired boilers the incoming fuel for a waste-firing FB-boiler in Sweden is often a mixture between MSW and IW but both fractions are shredded and mixed at a preparation site before being placed in the bunker and are subsequently fed into the boiler via an overhead crane, which is often automated.



Scematic overview of a CFB: 1, combustion chamber; 2, fuel chute; 3, primary cyclone; 4, cyclone leg; 5, loop seal; 6, heat exchanger; 7, secondary cyclone; 8, bag house filter; 9, sludge pump; 10, ammonium sulphjate; 11, hydrated lime; 12, measurement location upstream of the convection pass; 13, measurement location in the convection pass; 14, measurement location downstream the convection pass; 15 measurement location of stack gases.

Schematic overview of a BFB: 1, combustion chamber; 2, fuel feed chute; 3, primary air; 4, secondary and tertiary air; 5, empty gas pass; 6, superheaters; 7, cyclone; 8, economiser.

Figure 3. The two types of FB-boilers: a Circulating Fluidised Bed Boiler (CFB) to the left (Figure from Elled et al. [19]), and a Bubbling Fluidised Bed Boiler (BFB) to the right (paper VI).

3 Methods

The sampling techniques (3.1) and fuel analysis methods (3.2) subsequently described were applied in the work for papers I, II, IV, and VI. The results in paper V are based on thermal analysis (3.3) and different methods were used to determine the fossil content in waste (3.4) for paper I. Thermodynamic equilibrium calculations (3.5) were performed to support the findings in papers II, V, and VI.

3.1 Sampling of waste

Sampling of waste for chemical analysis is a complicated process owing to the uncertainty of accuracy when taking just a few samples, especially when the sampling is performed on different occasions. The heterogeneous composition of waste produces great variation from time to time and therefore a single waste sample cannot be regarded as representative of a whole waste bunker in terms of ash-forming species and trace elements. One sample can be analysed and discussed but only with the proviso that it solely represents that particular waste and its unique composition. A better overview of the fuel can be gained by performing repeated samplings over a long period of time. The scattering of different species can then be correlated to, for example, political economic climate, seasonal variation, household consumption patterns, large batches of special industrial waste in a particular month, or problems that may arise in the boiler.

3.1.1 Sampling from a fixed bed grate furnace

Since most of the fuel is not treated before combustion, the process of sampling waste from a grate-fired boiler is complex. The heterogeneity of the fuel requires a representative sampling method. In this study a dividing method based on the standard CEN/TS15442 [21] has been employed for all solid waste samples. The sampling procedure starts some days before the actual extraction of a sample: the material is mixed in the dumping hall bunker using the overhead crane. This requires the involvement of an experienced overhead crane driver who has good knowledge of the waste streams in the bunker. After a few days of mixing of all incoming waste, a sample of two to seven tonnes is extracted from the bunker, depending on the capacity of the plant. The sample is then shredded and mixed at least twice, aiming at leaving the largest pieces a few centimetres in size. The shredded sample is spread on clean ground in the shape of a square of approximately 10x10 m, once again depending on how much waste that was extracted and the plant capacity. The square is divided into two halves; one half is disposed of and the remaining half is once again spread out on the same-sized area as the original square. As before, one half is removed and this dividing procedure is repeated until each half (four in total) has been removed once, which normally leaves a square about 20 cm high. Subsequently, the square is divided into smaller squares of approximately one square metre. From each square one sample is carefully taken with a shovel, with the aim being to secure samples all the way from the bottom to the top of the waste pile. The total weight of the final sample should be between 30 and 40 kg. Figure 4 shows a schematic overview of the dividing method used for fuel sampling for the grate-fired plant.

3.1.2 Sampling at a fluidised bed boiler

Owing to the fuel preparation the fuel sampling in FB-boilers is a simpler process than that applied in grate-fired boilers. In this study the FB-boilers included have had an accessible hatch placed where the fuel falls down towards the last pass to the FB. At this point the waste fuel samples were directly collected from the falling stream of prepared waste. This was done by repeatedly inserting a shovel into the falling waste stream in a specific pattern until all the sub-samples result in a total mass of 30-40 kg. The sub-samples can be extracted over a period of one or several days, depending on plant availability and capacity.

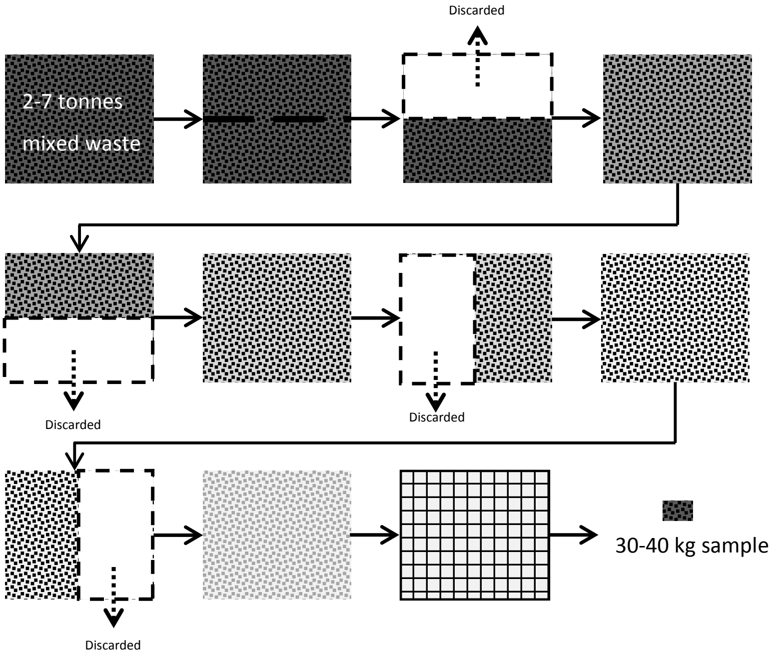


Figure 4. A schematic overview of the sampling procedure at grate-fired plants. The fuel sample is evenly spread over a quadrangular area and half of the square is discarded. The remains are once again spread over the same area and the halving and discarding-process is repeated for all four halves. The remaining square is divided into smaller squares and sub-samples are taken from each square.

3.2 Fuel analysis of solid samples

After collection the samples are chemically analysed at an accredited laboratory. The samples are first prepared for analysis at an accredited laboratory by grinding and mixing before a sub-sample is taken from the larger sample by using a coning and quartering method in accordance with CEN/TS15443:2006 [22]. For a full fuel analysis it is common to include a proximate analysis (Moisture, volatiles, char, and ash), an ultimate analysis (C, H, N, O, and S), and an elemental analysis (ash-forming elements that are present in a concentration of g/kg dry and trace element analysis, elements that are present in a concentration of $mg \cdot kg^{-1}$ dry). Table 1 shows the different methods of analysis for the components in the fuel.

Table 1. Analysis methods for waste fuel samples. Each method is described in the subsequent sections

Parameter	Method	Reference	
Moisture	Gravimetric analysis	SS-EN 14774-2	[23]
Ash	Gravimetric analysis	SS-EN 14775	[24]
S, Cl	Ion Chromatography	SS-EN 15289	[25]
C, H, N	Gas analyser	SS-EN 15104	[26]
Calorific value	Bomb calorimeter	SS-EN 14918	[27]
Ash-forming matter	ICP-OES	Modified ASTM D 3682	[28]
Trace elements	ICP-OES	Modified ASTM D 3683	[29]

3.2.1 Determination of moisture and ash content

The moisture is determined by weighing a sample before and after it has been treated at 105 ± 2°C until constant mass is achieved. The total moisture is then calculated based on mass change of the fuel [23].

Determination of the ash content is done by heating a cold fuel sample up to 250°C with a heating rate of 4.5-7.5°C/min. This temperature is then held for at least 60 minutes, which allows the volatiles to leave the sample before ignition. The sample is then heated by 10°C/min up to 500 ± 10°C and the temperature is maintained for 120 minutes. This is performed with at least two individual sub-samples from the original fuel sample. A calculation is then performed based on the loss of mass. Furthermore, the standard used for determining the ash content shows that carbonates are present in the ash owing to the low temperature used to avoid loss of alkali [24].

3.2.2 Determination of S, and Cl content

To determine the content of S and Cl (calculated from measuring Cl^- and SO_4^{2-}) the samples are processed and then analysed with Ion Chromatography (IC) and a Conductivity Detector (TCD) [25]. The method is based on a separation process where the sample is eluted thorough a separator column. The stationary phase (the inside phase of the column) has different affinities for different ions; this means that some ions in the solute will remain in the column longer, i.e. the column causes retardation. In this work anion exchange columns were used. In this type of column the stationary phase consists of positively charged groups, which attract solute anions.

3.2.3 Determination of C, H, and N content

The principle when analysing C, H and N content is that a known mass of the sample is burned in oxygen or in an oxygen/carrier gas mixture, which converts the sample into ash and gaseous combustion products [26]. These products are treated to ensure that H is liberated as water vapour (rather than associated with S or halides). Products that could interfere with the gas analysis are removed. Nitrogen oxides are reduced to elemental nitrogen and the mass fractions of nitrogen, CO_2 and water vapour are determined quantitatively by a gas analyser.

3.2.4 Determination of calorific value

The method used to determine the calorific value is based on burning the sample at a constant volume at 25°C in a bomb calorimeter [27]. The result obtained is the gross calorific value of the sample at a constant volume.

3.2.5 Determination of ash-forming matter and trace elements

To determine the ash-forming elements the fuel sample is analysed dry but for some elements (Fe, Al, Si, Ti, Mg, Ca, Ba, Na, K and P) the analysis is performed after treating the sample at 500°C [28, 29]. The ash-forming matter is then analysed by Inductively Coupled Plasma- Optical Emission Spectroscopy, ICP-OES. ICP is a type of atomic spectroscopy where the sample is atomised by a plasma. The plasma is much hotter than a combustion flame (~ 6000 – 8000°C) and it is used in a stable, inert argon environment that reduces interferences that is otherwise common in flames [30]. The ICP can perform simultaneous multi-element analysis. The waste samples are vapourised and decomposed into ions in the plasma. The OES is used to determine the ions present in the solution. This is done by measuring the concentration of atoms in the vapour by emission of characteristic wavelengths of radiation [30].

3.3 Thermal analysis

Thermal analysis is a group of techniques that monitor the physical and chemical properties of a substance or material as they change with temperature. The properties that can be studied by using thermal analysis include mass change, enthalpy, thermal capacity, and the coefficient of heat expansion. In solid state chemistry thermal analysis is a tool for studying thermal degradation, phase transitions, and phase diagrams. Three of the conventional thermal analysis techniques are Thermogravimetric Analysis (TGA) measuring mass changes, Differential Thermal Analysis (DTA) measuring temperature difference, and Differential Scanning Calorimetry (DSC) measuring heat difference [31].

TGA measures changes in mass associated with heating, cooling, or a given temperature to determine material composition, material purity, thermal stability of a material, and/or humidity [32]. Mass is plotted as a function of temperature at a constant heating or cooling rate, or as a function of time under isothermal conditions [33]. Mass change is caused by physical (gas adsorption, gas desorption, vaporisation, or sublimation) or chemical (decomposition, solid/gas reactions, chemisorption) phenomena. Figure 5 shows an example of a TGA curve.

DTA measures the temperature difference by studying the substance/material and an inert reference by using the exact identical thermal cycles and records any temperature difference between the sample and the reference. DSC is a method of measuring the amount of heat that is absorbed or released to produce a zero temperature difference between a sample and a reference, as a function of temperature or time [33]. It requires both the sample and the reference to operate under the same experimental conditions. The instrument has independent thermocouples (platinum/platinum-rhodium) under each sample holder (one for the reference and one for the studied substance/material), which provide heat separately. First, the sample and the reference are heated or cooled at a constant rate. If there is any temperature difference, the power input for the reference will be adjusted to eliminate the difference. This continuous and automatic power adjustment is directly proportional to the amount of heat required during the process by the sample and reference [34].

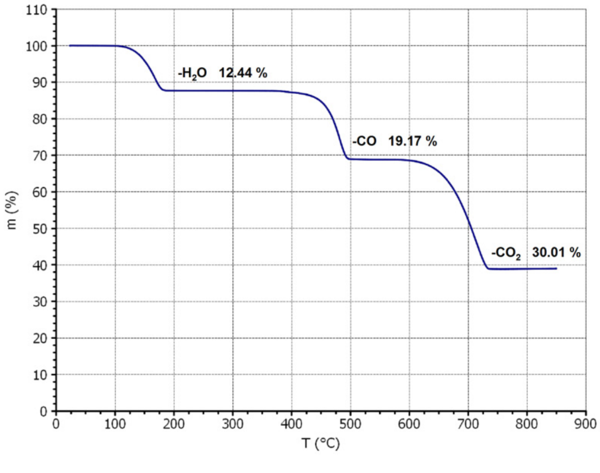


Figure 5. Example of TGA-results: The decomposition of calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$). Three mass changes are exhibited as the sample is heated in an inert atmosphere, for example, N_2. The changes represent the loss of H_2O to form CaC_2O_4, loss of CO to form $CaCO_3$, and loss of CO_2 to form CaO, respectively.

An exothermic process corresponds to an increase in heat flow, which is indicated as a positive peak in the results, while an endothermic process has a decreasing heat flow, showing a drop in the resulting curve. Changes in temperature or heat could be caused by several different phenomena, either physical (adsorption, desorption, melting, vaporisation, sublimation, crystallisation, and change in crystal structure), or chemical (oxidation, reduction, solid state reactions, decomposition, and chemisorption).

Several instruments are available for Simultaneous Thermal Analysis (STA), for example, the instrument SDT Q600TM that simultaneously can generate TGA and DSC data for each sample.

3.4 Determination of the fossil content of waste

As regards fossil content in waste used for combustion there is not yet a determined standard in Sweden. However, it is expected that Swedish waste combusting operations will face changes in instruments of control. For example, the Swedish Environmental Protection Agency (EPA) introduced the fossil share of MSW into the European ETS during 2013, based on guidelines from the European Commission [15]. The methods used for determining the fossil share in waste prior to 2013 included sorting analyses followed by calculations that involve several assumptions, a plausible source of error. With the upcoming changes there was a need for a study of Swedish waste as well as a comparison of different methods available for Swedish waste plants.

3.4.1 Calculation method based on sorting analyses

By using input data from sorting analyses it is possible to calculate the carbon with fossil origin content in waste. In Sweden there is a sorting analysis instruction manual recommended by Avfall Sverige –Swedish Waste Management [35]. The application of the method in this manual means that a waste sample considered to represent the bunker is divided into nine primary fractions. The results of the sorting are then used as input data for the calculation of the proportions of carbon with fossil origin. All primary fractions consist of secondary fractions but for determining the carbon with fossil origin it is enough to follow through with sorting for two of the primary fractions; Plastics and Other. The fractions are shown in Table 2. All sorting analyses are performed manually, meaning the sorting itself is time-consuming and hence expensive.

The sorting analysis results are then used as input data in a calculation model that links each fraction from the sorting analysis to an assumed chemical composition of the fraction. In this study, the calculations have been performed together with Profu AB and the chemical composition information has been taken from Profu AB's database *AvfallsAtlas* (in English: *WasteAtlas*), which contains chemical analyses of various waste fractions such as paper, plastics and glass. A description of the parameters in Table 2 can be built up for each fraction using the database.

Table 2. Waste fractions used in sorting analyses when using Avfall Sverige –Swedish Waste Management's manual [35]. There are nine primary fractions listed to the left and two of them (Plastics and Other) are further divided into secondary fractions listed in italics to the right

Sorting analysis waste fractions	
Biowaste	
Paper	
Plastics	
	Soft plastics
	Expanded plastic foam
	Hard plastics packaging
	Other plastics
Glass	
Metal	
Other inorganic	
Hazardous waste	
Electrical and electronic waste	
Other	
	Woods
	Textiles
	Absorbent hygiene products
	Miscellaneous

Table 3. Parameters that can be described by calculations in a calculation model with the database AvfallsAtlas

Fuel parameters
Moisture content
Dry solids content (DS)
Carbon content (C) as % of dry solids (both biogenic and fossil contents)
Hydrogen content (H) as % of dry solids
Oxygen content (O) as % of dry solids
Nitrogen content (N) as % of dry solids
Sulphur content (S) as % of dry solids
Ash as % of dry solids

Combining data on the composition of each sorting analysis (percentage by weight) and the chemical composition of each fraction enables the chemical composition of the waste as a whole to be calculated, from which the biogenic and fossil carbon proportions can be determined. If it is assumed that all carbon is oxidised to CO_2, then the biogenic, fossil and total emissions of CO_2 can be calculated. An effective calorific value of the entire body of waste is also calculated in order to be able to relate emissions to the quantity of energy delivered from the waste.

An advantage with this calculation method is that when all the basic work is done (calculations structure, deciding what chemical composition each fraction should have, etc.) it is easy to insert the result from the sorting analyses to get the calculated results. The method is easily adapted to the sorting analysis data available. The cost for the evaluation itself is low, but the total cost could increase dramatically depending on how often the sorting analyses have to be performed in order to get a representative overview of the waste that is going to be burned. This is a disadvantage/challenge for the method. Another challenge is whether the chemical composition that is assigned to each fraction gives a correct description of the current fraction. In calculations like this the description of the plastic fraction is of major importance since it plays such an important role when it comes to the resulting emission of fossil CO_2. One other important parameter is the moisture content, since it affects both the share of carbon (higher moisture content leads to a lower share of carbon) and the LHV (higher moisture content leads to a lower LHV).

3.4.2 The radiocarbon (^{14}C) method

The ^{14}C-method, also known as the radiocarbon method, can be used on both solid waste samples and on flue gas samples. The ^{14}C analysis method is based on the same concept as radiocarbon dating; determination of decay events of the unstable carbon isotope ^{14}C per time unit (half-life about 5,730 years).

The solid samples need to be as representative as possible and in this study the sampling procedures described above in section 3.1 were implemented. This laboratory prepared sample of about 30 g is then used for ^{14}C analysis in accordance with CEN/TS 15747:2008 [36]. The standard allows three different methods of transforming the carbon in the sample into a sample suitable for ^{14}C-determination; conversion by combustion in a calorimetric bomb, conversion by combustion in a tube furnace, and conversion by combustion in a laboratory scale combustion apparatus. In all three methods the CO_2 formed is absorbed in a suitable solution, depending on the subsequent ^{14}C analysis method. The choice of final ^{14}C-determination method is between Liquid Scintillation Counting, LSC (also known as PSM), Beta-Ionisation (BI), and Accelerator Mass Spectrometry (AMS).

The biogenic share of solid waste samples could also be analysed using a method that is different from the ^{14}C-method, namely the selective dissolution method. This method is described in Annex B of CEN/TS 15440:2006 [37]. It includes treatment with concentrated sulphuric acid topped with hydrogen peroxide. The biomass in waste will selectively dissolve and oxidise while all material consisting of non-biomass components will remain in the residue. The sample should be weighed before and after the selective dissolution procedure. The biomass content by weight is corrected for the content of carbonates by measuring the ash content before and after dissolution [38].

For flue gas samples there is a standard method and it is described in ASTM D7459-08 [39]. In this sampling method flue gas is extracted into a gas-proof bag, for example, a Tedlar® bag. The method is based on sampling with a constant flow over time so the plant must be operated with an even load. The standard specifies permissible limits for the variation of the flow in the plant for the sampling to still be considered equal to flow proportional sampling. To ensure that the sampling follows the recommendations at least one parameter that can be directly related to the stability of the operation, such as flue gas flow or fuel flow, is logged during sampling. It is also stated in the standard that sampling should be performed after the flue gas cleaning system and for at least one hour, resulting in a minimum sample of 2 cm^3. The flue gas samples are analysed using the same method as the solid samples standardised in CEN/TS 15747:2008.

In other sampling methods the flue gas is bubbled through a solution of 4 M KOH or 4 M NaOH, which is then analysed using a standard method. Another method is to use an organic reagent solution (3-methoxypropylamin “Carbosorb-E”) to absorb the flue gas in directly at the sampling point. This solution is then analysed with respect to a density analysis, giving the total carbon content, and by LSC, giving the ^{14}C-activity. From these two analyses the biogenic and fossil share of the fuel can be determined by calculation.

Instead of using age equations as in radiocarbon dating, a ratio is derived from the amount of radiocarbon present in an unknown sample to a modern reference standard, giving a distinction of carbon with fossil origin, where all the originally existing ^{14}C is completely decayed. Thus, the fossil content in the samples is reported as percentage modern Carbon (pmC). However, due to anthropogenic activities the background level of ^{14}C changes over time, complicating interpretation of the results. One observed effect is the Suess-effect: dilution of atmospheric ^{14}C over time due to the admixture of fossil fuel derived CO_2, containing no ^{14}C-isotopes described by Suess [40]. Furthermore, the thermonuclear-weapon tests performed during almost two full decades after the Second World War nearly doubled the ^{14}C concentration in the atmosphere. Levin and Kromer have shown that the decrease in ^{14}C since the bombing stopped in the mid-1960s has gone slowly and is primarily due to buffering in the oceans [41]. This means that this method of analysis requires an atmospheric correction factor, making up for the changes in ^{14}C in the atmosphere, which is also implied in the standard. This is also called the ^{14}C-background value representing the ratio of the $^{14}C/^{12}C$-isotopes in the atmosphere during the time the material in the samples grew and absorbed CO_2. This ratio has been measured since the 1950s and its change due to the Suess-effect and the atmospheric bombings can be seen in Figure 6 [42].

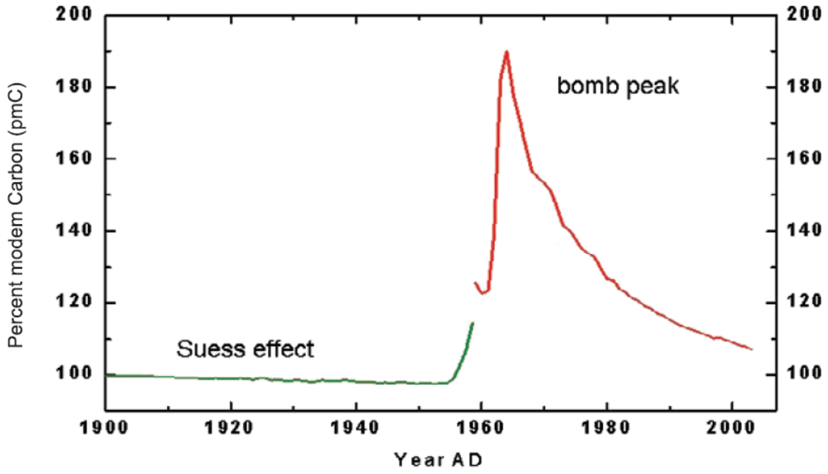


Figure 6. The ^{14}C concentration in the atmosphere, figure from Reinhardt and Richers [42].

This change in atmospheric ^{14}C means that a fossil material will have a pmC of zero while a young biomass, such as fruit or grass, will have a pmC-value reflecting the present value in the atmosphere, circa 107 pmC. Older biomass, for example a 40-year-old tree, would have a background value starting at approximately 130 pmC but would have been growing during the slow dilution of ^{14}C. For a fuel consisting of a homogeneous material of known age, it is possible to calculate with a fairly good accuracy. However, for a heterogeneous sample, such as MSW and IW, it is hard to determine an exact value for the material. In the standard [36] it is recommended that 113 pmC should be used for SRF but values ranging from this down to the biomass value of 107 pmC are used for waste samples with a large proportion of MSW. Mohn et al. [43] calculated a correction factor of 1.113 ±0.038 for mixed household, commercial, and bulky waste, for the year 2010 which was also used in a later publication by Mohn et al. [44]. By using a similar approach Fellner and Rechberger [45] suggested 1.156 ± 0.034 for the then current European waste. Swedish waste mixtures contain large shares of biological waste, paper/cardboard waste, and wood waste; all of these materials have correction factors of 1.12 or lower according to Mohn et al. [43]. For determining the fossil content in Swedish waste the lower limit could be set to 1.07, as suggested for fresh biomass in CEN/TS 15747 [36], and the upper limit could be 1.12, as suggested by both Mohn et al. [43] and Fellner and Rechberger [45]. It is likely that the true carbon with fossil origin content value in Swedish waste mixtures is found within these limits, as a large share of the waste mixtures are waste fractions with a content of 1.12 or lower as suggested by Mohn et al.[43].

To investigate the capability of flue gas sampling with subsequent ^{14}C analysis, Hämäläinen et al. experimented with seven different fuels, both fossil and biogenic, at different combustion plants [46]. They also included methane gas as an alternative to the solid fuels. The samples were extracted from the flue gas stack, stored in Tedlar® bags and subsequently analysed by AMS. Their study shows that the method is reliable and that the contamination risks with the sampling method and the storing of the samples are low but that they increase the smaller the size of the total sample. To evaluate the method they compared their results from the methane gas sampling to available literature values of ^{13}C and found their measured sample was within the range. During experiments with biogenic samples, saw dust and wood chips, they thought the measured values were quite low owing to the fact that the trees used would have been growing during a time of high pmC in the atmosphere. Further investigations showed that even though sawdust contains all the parts of a tree, the wood chips consisted mostly of the younger parts of the tree, hence the lower pmC. To verify this theory they performed laboratory-scale tests with a wood material with a known age and found, as expected, that the old material gave a higher pmC. In the more complicated fuel mixes they used their results are still satisfying compared with calculated values (somewhat based on assumptions). The article states that flue gas sampling with subsequent ^{14}C analysis is an adquate method of determining the biogenic share of material in fuels. However, they also point out that there is uncertainty with regard to background levels of ^{14}C in the atmosphere in mixed fuels.

Other studies of the fossil content in flue gas include Mohn et al. [44] who performed a yearlong sampling campaign with 24 samples from five plants and were able to show that the bag sampling procedure proved to be simple and straight-forward when it came to obtaining temporally integrating exhaust samples. In the study, they also combined the bag sampling with direct $^{14}CO_2$ analysis by AMS, improving quality control. In an earlier study by Mohn et al. [43] the CO_2 from the flue gas was sampled directly into washing bottles with KOH solutions. The same method was used by Calcagnile et al. [47] and both studies confirm the high potential of this approach in the analysis of industrial CO_2 emissions. Furthermore, Palstra and Meijer [48] performed similar sampling (but in NaOH instead of KOH) of flue gas samples from a combustion plant burning pulverised coal and pulverised wood pellets. The experiments had known input and output data of carbon in the fuel providing the possibility of calculating a carbon balance [48]. The study also included flue gas samples from a waste combustion plant. All samples were collected in a solution and analysed in a laboratory using AMS. The approach to reach finalised calculation results differ slightly from other studies since the coal combustion plant shared a stack with a natural gas combustion plant, meaning there is an extra source of CO_2 to be taken into consideration. The results of the measurements show that the method is reliable by comparing the carbon mass input and output data from the power plants with the results they obtained. They point out the importance of using clean chemicals and also a suitable flow of flue gas through the absorbing chemical (in this case NaOH) [48]. An unsuitable flow, in relation to the volume of the NaOH, could result in a loss of CO_2. It is not possible to assume the leaking CO_2 is homogenous since ^{12}C and ^{13}C are more soluble than ^{14}C, thus dissolve to a greater degree than ^{14}C in the NaOH solution and the sample is ruined [48]. Furthermore, the authors state that the uncertainties in flue gas sampling and ^{14}C analysis are not related to the laboratory analysis but rather to the extraction method. In summary the study shows that flue gas samples are suitable for determining the biogenic shares of various fuels. Nevertheless, they also specify that with fuels consisting of less than 10 % biogenic material other sources of CO_2, such as atmospheric CO_2, should be taken in to consideration as well so as to properly determine the biogenic emissions [48].

3.4.3 The balance method

The balance method was developed at the Vienna University of Technology [49]. It is a calculation method based on mass balances and energy balances that together give an overdetermined equation system, i.e. the number of equations > the number of unknowns [49, 50]. The Vienna University of Technology has developed a software program, BIOMA©, that performs all calculations on-line - it is a commercial product available on the market for combustion plants to buy. The method utilises the operating data from the existing control system at the plant. The most important input data is the balance between the oxygen consumption and the CO_2 formation in the process. The method is based on the fact that there are several fundamental differences between how biogenic and fossil carbon reacts in a combustion process, making it possible to separate these reactions. Some of the differences are:

Carbon/oxygen ratio: Fossil fuels, such as plastics, have a high carbon:oxygen ratio. In some cases it is extreme, for example, polyethylene, where the ratio is infinite since polyethylene does not contain any oxygen at all. A typical biomass, for example, cellulose $(\text{-C } C_6H_{10}O_5)\text{-}_n$, can have a carbon:oxygen-ratio of almost 1.

Oxygen consumption: Due to the high share of oxygen in a biogenic material, it consumes less free oxygen (available in the combustion air) during combustion.

Energy content: A fossil material generally has a higher energy content since biogenic material contains more water and less inert material per mass.

During waste combustion CO_2 is produced while free oxygen from the surrounding air is consumed according to two general equations specific to the two carbons sources:

Biogenic (cellulose): $(\text{-}C_6H_{10}O_5\text{-})_n + 6nO_2 \rightarrow 6nCO_2\ 5nH_2O$ (R-1)

Fossil (Polyethylene plastic): $(\text{-}CH_2\text{-}CH_2\text{-})_n + 3nO_2 \rightarrow 2nCO_2 + 2nH_2O$ (R-2)

As can be seen from the equations above, the two reactions consume different amounts of oxygen. Reaction (1) consumes 1 mole of oxygen per each produced mole of CO_2, while reaction (2) consumed 1.5 moles of oxygen per each produced mole of CO_2. This means that the difference between the oxygen consumption during combustion of biogenic and fossil material is 50 %.

By starting from the two extreme cases, 100 % biogenic material and 100 % fossil material, it is possible to calculate theoretical values for the heating value (HV_{waste}, kJ/kg) and the oxygen consumption ($O_2{}^{C}{}_{waste}$). The balance method also includes the possibility of doing a "plausibility test" to control whether the calculated values are reasonable, i.e. are within the limits of what is possible.

Information on the following process parameters (listed in Table 4) is required in order to perform the calculations. Of the parameters in the table, it is the measured O_2 and CO_2 concentrations in the flue gas that are the most important for the calculations.

Purely mathematically the balance method is based on the solving of five theoretical balance equations, one energy balance equation (for mass, element and energy), and measured data. The measured data is conventional measurement data available on waste combustion plants (for example, flue gas volume, O_2, and CO_2 concentrations, steam production, ash and slag production).

Table 4. The process parameters used in the balance method

Continuous input data	**Predefined input data**
- O_2 and CO_2 concentrations in the flue gas (actual value, dry, %) - Waste quantities (tonne/h) - Masses of bottom ash, filter ash and filter cake - Flue gas quantity (Nm^3/h) - Steam production (tonne/h) - Steam pressure and temperature (bar and °C) - Feed water temperature (°C) - Quantity of additional fuel (oil [tonne/h], gas [Nm^3/h] or *[for example]* sludge [tonne/h])	- Water content in the bottom ash (slag), % - Water content in the fly ash, % - Slag content in the waste, excluding metals, % - Energy efficiency of the boiler, (%) - O_2 content of the combustion air, %. (Normally atmospheric air, but there are sometimes occasions when it is enriched or changed.)

The equations solved are the following (parameters listed in Table 5)

Mass balance: $m_B + m_F + m_I + m_w = 1$ (Eq-1)

Ash balance: $m_I = a_{waste}$ (Eq-2)

Carbon balance: $c_B * m_B + c_F * m_F = C_{waste}$ (Eq-3)

Energy balance: $HV_B * m_B + HV_F * m_F - 2.45 * m_W = HV_{waste}$ (Eq-4)

O_2-balance: $O_2{}^{C}{}_{,B} * m_B + O_2{}^{C}{}_{,F} * m_F = O_2{}^{C}{}_{Waste}$ (Eq-5)

The unknown parameters from the equations are the mass fractions of inert, biogenic, and fossil material as well as the share of water (m_i, m_B, m_F, and m_W). The coefficients in the equations for these parameters (HV_B, C_B, etc.) can be extracted from the chemical composition of the fuel (here: waste). The chemical composition used by the balance method software is described below. A more detailed description of the equations and the method to solve them can be found in Fellner et al. [49] and in the Austrian patent A539/2005 (in German) [50].

Table 5. Explanation of the parameters in equation 1-5

Parameters for equation 4-9			
m_B	the share of biogenic material in the waste, %	HV_F	the lower heating value of fossil material, kJ/kg
m_F	the share of fossil material in the waste, %	HV_{waste}	*the lower heating value of waste, kJ/kg
m_I	the share of inert material in the waste, %	$O_2{}^{C}{}_{,B}$	the oxygen share in biogenic material, %
m_w	the share of water in the waste, %	$O_2{}^{C}{}_{,F}$	the oxygen share in fossil material , %
a_{waste}	*the mass of ash in the waste, kg	$O_2{}^{C}{}_{Waste}$	*the oxygen share in waste, %
c_B	the carbon share in biogenic material, g/kg ash free	ΔOC_B	the difference between oxygen consumption and CO_2-production for the biogenic share
c_F	the carbon share in fossil material, g/kg ash free	ΔOC_F	the difference between oxygen consumption and CO_2-production for the fossil share
C_{waste}	*the carbon share in the waste, g/kg ash free	ΔOC_{waste}	* the difference between oxygen consumption and CO_2-production for the waste
HV_B	the lower heating value of biogenic material, kJ/kg		

*Marked parameters are input data from the combustion plant

Table 6. The chemical composition of the biogenic and fossil share in waste used in the Balance method

Share	**C g/kg ash free**		**H g/kg ash free**		**S g/kg ash free**		**N g/kg ash free**		**O g/kg ash free**	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Biogenic	483.3	3.2	65.0	0.8	1.2	0.3	8.0	2.9	441.4	5.3
Fossil	768.6	20.2	109.0	7.0	3.0	1.1	13.3	5.5	87.7	21.8

Some simplifications and assumptions are included in the software program that it might be important to take into consideration as waste fractions change over time. For example, bioplastics are still considered fossil in the calculations. At present this is not of major concern since the share of bioplastics in the total plastic so far is so small it is negligible [49]. The Vienna University of Technology is constantly improving the software and special request by the plants can be arranged if required; for example, it is now possible to include oxidations of metals and calcination of limestone, something that was not possible a few years ago [51].

Furthermore, it is worth noting that the balance method software BIOMA© is very sensitive when it comes to input data. An increase of only 1 % CO_2 could cause changes of up to 9 % in the emitted CO_2 calculated.

In Fellner et al. [52] the inventors of the Balance method and distributors of the BIOMA© software made a long-term analysis of the biomass content in the fuel at a waste combustion plant. This particular combustion plant had oxygen-enriched combustion air which meant the balance method had to be modified for the special needs of the plant. The conclusions of the study are that the method is both adaptable and accurate. The writers argue that, with proper service and calibration of all measuring equipment, it is possible to produce reliable data 90 % of the operating time. However, the maximum error of the final results seems to be higher than when the method is used in a combustion plant with a conventional oxygen supply. No validation was performed in the study other than the plausibility test and a sensitivity analysis.

3.4.4 Comparisons between the ^{14}C-method and the balance method

Most available publications concerning determination of the fossil share of waste for combustion use the ^{14}C-method by analysing flue gas samples, rather than solid samples, or the balance method. There is still a need for more comparisons between the different methods [48]. However, it should be borne in mind that all comparisons of results are between single specific flue gas samples and data showing averages over time (often weekly or monthly averages) from the balance method.

In a comparative study by Mohn et al. [43] parallel measurements of flue gas samples and recording of data for the balance method were carried out in three different combustion plants in Switzerland. The sampling time was between three and four days during a month when the operational data was used for the balance method. The results from the two technically separate methods are highly comparable.

Obermoser et al. [53], welcomes the validation of the balance method but somewhat question the results from Mohn et al. [43], pointing out uncertainties that need to be incorporated, as described by Fellner et al. [45]. Here it is argued that a waste mixture is too heterogeneous to be determined by only using one pmC value, as suggested in standard methods. However, Obermoser et al. [53] present a simultaneous balance method measurement at two separate combustion lines being fed from the same bunker. By having separate lines, all parameters are separately and independently determined for each line. The results for the two lines are very similar but not identical; this is as expected since the waste fuel is heterogeneous [53].

Another comparison was carried out by Staber et al. [54] who compared flue gas samples with ^{14}C analysis to the balance method and an alternative method called the selective dissolution method for solid samples. The flue gas is absorbed directly into Carbosorb-E, which then undergoes a density analysis and an LSC analysis. The solid sample analysis is thought to be complicated due to the sample heterogeneity and the method has considerable limitations owing to the fact that the fuel makes it less user-friendly than the two other methods. The method standard was withdrawn in April 2011 [37].

More validations and comparisons of these methods are welcome. Naturally, many of the articles published about the balance method include authors from the Vienna University of Technology [45, 49, 50, 52-54], making the publications less independent, but evidently not unreliable since the balance method has been studied and validated by others, such as Mohn et al. [43]. The balance method software BIOMA$^{©}$ is now established a several combustion plants and a great advantage with the method is the on-line resolution of the fossil and biogenic share of the flue gas.

The different methods involved in extracting the flue gas for ^{14}C analysis make it hard to compare studies of the measurements of fossil/biogenic CO_2. The sampling of flue gas plus the handling and storage of the samples are of greater importance than the laboratory analysis method determining the accuracy of the sampling results. Nevertheless, the method has shown good comparability and repeatability when used with well-defined fuels. Compared with solid samples, the flue gas samples give a more absolute overview of the fossil emissions since the solid samples really only reflect the exact extracted samples, while the flue gas is collected for a minimum of one hour. Compared with the balance method the flue gas samples produce results for a shorter time period.

3.5 Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations have been widely used to better describe and understand inorganic reactions taking place during combustion processes [55-62]. They provide information that allows detailed studies of the mechanisms of, for example, bed agglomeration in fluidised beds, deposits and corrosion on heat transfer tubes, and emissions of particles. It is also valuable for building phase diagrams. It is a useful tool for studies of different fuels (different elemental concentrations) and evaluation of changes in temperature and/or pressure. The calculations will provide information about whether equilibrium lies in favour of reactants or products under certain conditions [63].

Thermodynamic equilibrium calculations are based on the minimisation of the total Gibbs free energy. The expression for Gibbs free energy at constant absolute temperature and pressure is shown in Equation 6 and the equation-parameters are explained in Table 7.

$$\frac{G^t}{R \times T} = \sum_{i=1}^{N} n_i \times \left(\frac{G_{f_i}^0}{R \times T} + \ln(a_i) \right) \qquad \text{(Eq-6)}$$

There are some limitations to thermodynamic equilibrium calculations. For example, the calculations exclude physical phenomena like kinetics, mass transfer and particulates (aerosol formation, surface reactions, absorption and adsorption). Furthermore, the local conditions (residence time and mixing) are not taken into account in the calculations. One of the most limiting factors is the quality of the thermodynamic data. For thermodynamic equilibrium calculations to be precise, consistent and accurate thermodynamic data is required for all the ash phases that may form in furnace and boiler conditions. These different phases include complex liquid and solid ionic phases, such as molten slats and silicate slags, as well as multicomponent gas phase [61].

Table 7. Calculation parameters for Gibbs free energy at constant absolute temperature and pressure

Parameters for equation 6	
G^t	total Gibbs free energy (kJ)
R	universal gas constant ($JK^{-1} \cdot mole^{-1}$)
T	temperature (K)
n_i	number of moles of component *i*
a_i	activity of component *i*
f_i	activity coefficient (fugacity) of component *i*
G^0	Gibbs free energy for the pure substance in the standard state (kJ)
N	total number of chemical elements

There are several available thermodynamic software programs used for modelling of ash chemistry, such as ChemApp, ChemSheet, HSC, MTDATA, Thermo-Calc and DICTRA, and FactSage [61]. Currently, FactSage is one of the most commonly used for calculating multicomponent, multiphase equilibria for metallurgical and thermochemical processes.

Expansion of databases is an on-going process, for example, the prediction of melting properties of alkali salt mixtures relevant to ash chemistry can be done with a high degree of accuracy while phosphate chemistry is harder to predict owing to the lack of required experimental data for the databases. However, although the databases, and therefore the calculations and predictions, are constantly improving, thermodynamic modelling has already been successfully used in combination with advanced fuel analysis, computational fluid dynamics and a stand-alone tool to predict ash deposition in full-scale boilers [55-62].

4 Results

This chapter describes the results from the papers this thesis is based on. Section 4.1 presents results from Paper I, and section 4.2, 4.3, 4.4, 4.5, 4.6 corresponds to Paper II-VI, respectively.

4.1 Determination of carbon from fossil fuels in Swedish waste mixtures

When this study was performed the methods in current use for determining the fossil share in waste included sorting analyses followed by calculations that include several assumptions, a possible source of error. With changes on the horizon, such as the impending introduction of Swedish WtE plants into the ETS, there was a need for a study of Swedish waste. Furthermore, there was a need for a comparison of the different methods available for Swedish waste plants to determine the fossil fraction in their waste mixtures.

In this study, four different methods were used and compared to determine the fossil share of waste mixtures going into seven different Swedish WtE-plants. Some plants burn 100 % MSW while others also include a share of IW. The findings are published in paper I.

The seven WtE plants in this study are geographically spread over the whole of Sweden. Table 8 describes the combustion technologies and MSW ratios for the participating plants. The study included six solid waste fuel samples taken at each combustion plant. In addition to the solid waste fuel samples, three 24-hour flue gas samples were taken simultaneously as solid waste samples for each combustion plant. Furthermore, three sorting analyses were performed at three different plants (C, D and F) to be used in calculations to predict fossil content in the waste. Data from plant E and F were also used for balance method equations.

The sampling of solid waste was performed as described in sections 2.1.1 and 2.1.2, for the grate furnaces and BFBs respectively. Sorting analyses and flue gas sampling were conducted as described in sections 3.4.1 and 3.4.2. The balance method used for the calculations is described in section 3.4.3.

Table 8. Participating plants, combustion technique and average mass ratio between MSW and IW as fired (paper I)

Plant ID	Combustion technique	Average MSW:IW-ratio during study
A	Bubbling Fluidised Bed	25:75
B	Bubbling Fluidised Bed	35:65
C	Grate	100:0
D	Grate	100:0
E	Grate	55:45
F	Grate	40:60
G	Grate	40:60

The results from the ^{14}C analysis of both solid samples and flue gas samples are shown in Figure 7. The x-axis represents the amount of industrial waste in the waste at the sampling time and the y-axis shows the percentage of carbon with fossil origin of the total carbon content in each sample. Two samples, one solid and one flue gas are statistically significant outliers, both outside 3 standard deviations, and will not be included in further evaluations. As both measurements had been carried out exactly as the others, there was no explanation for the outliers. In addition, the solid sample did not contain anything out of the ordinary according to the combustion plants delivery codes.

When investigating the effects of impact attributable to the share of IW, the samples can be divided into three groups, 0 % IW, 20-50 % IW and 50-80 % IW, as shown in Figure 7. A study of the mean values and standard deviations for the three groups reveals that they overlap. The trend is that a waste mixture consisting of 100 % MSW contains less carbon with fossil origin than a mixture with IW, but the results show no distinction in different shares of IW.

The same kind of analysis was performed with reference to when in the year the samples were collected (from October 2010 to August 2011). The analysis showed no correlation between fossil content and sampling date.

To illustrate the correlation between solid samples and flue gas samples taken simultaneously, Figure 8 shows the measured share of carbon with fossil origin in both a solid sample and a flue gas sample taken at the same time. The solid waste samples come to a mean average of 35 % (SD = 7) carbon with fossil origin out of the total carbon concentration. For the flue gas samples the mean average is 38 % (SD = 5) fossil CO_2 out of the total CO_2 concentration.

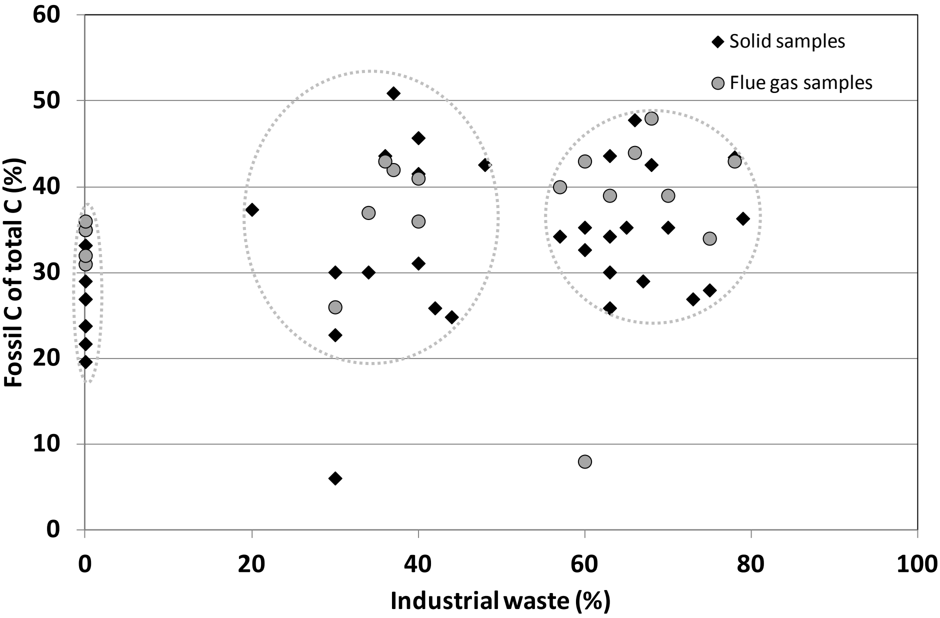


Figure 7. All solid samples and flue gas samples. The circles correspond to the three groups involving different share of IW used to analyse the correlation between the share of IW and carbon with fossil origin in the waste (paper I).

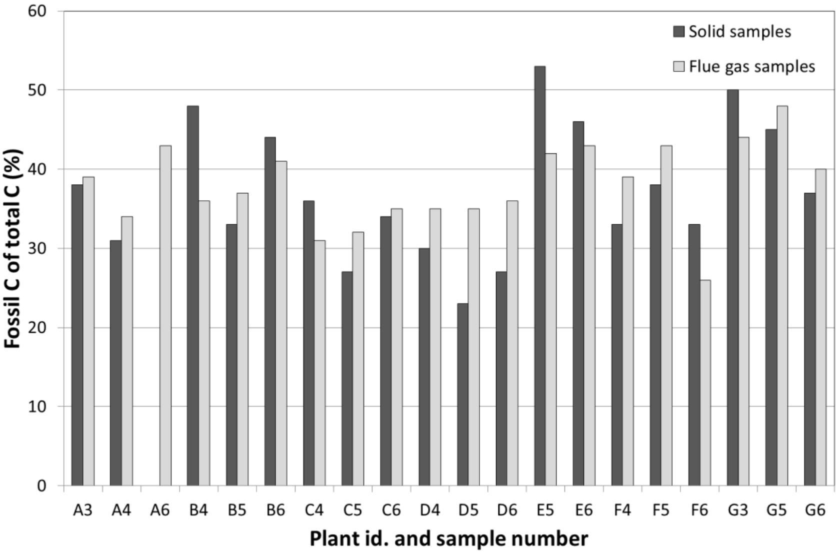


Figure 8. Analysis results of fossil share of carbon in solid fuel samples and flue gas samples taken simultaneously. NB. The solid sample corresponding to flue gas sample A6 was lost. Sample E4 and its corresponding flue gas sample are excluded from the graph beacuse the flue gas sample was an outlier (paper I).

When the two methods are compared by plotting the difference against the results from the solid samples, a systematic error appears that cannot be seen when using mean averages (see Figure 9). In this figure it is clear that the solid samples show a higher fossil content than what the flue gas samples do when the share of carbon with fossil origin is high and a lower content when the concentration is low. This information cannot be seen in the previous results due to the fact that the systematic error cancels itself out when using both high and low values.

Based solely on the data in this study, it is more likely that the flue gas results would be more accurate, corresponding to the full waste mixture over a 24-hour sampling. In addition, when the flue gas is measured the result will show the amount of carbon with fossil origin emitted rather than the amount of carbon with fossil origin of an extracted portion of waste. However, it has not been possible to determine the reason for the systematic error, or its source. It cannot be linked to either the share of IW or type of sampling.

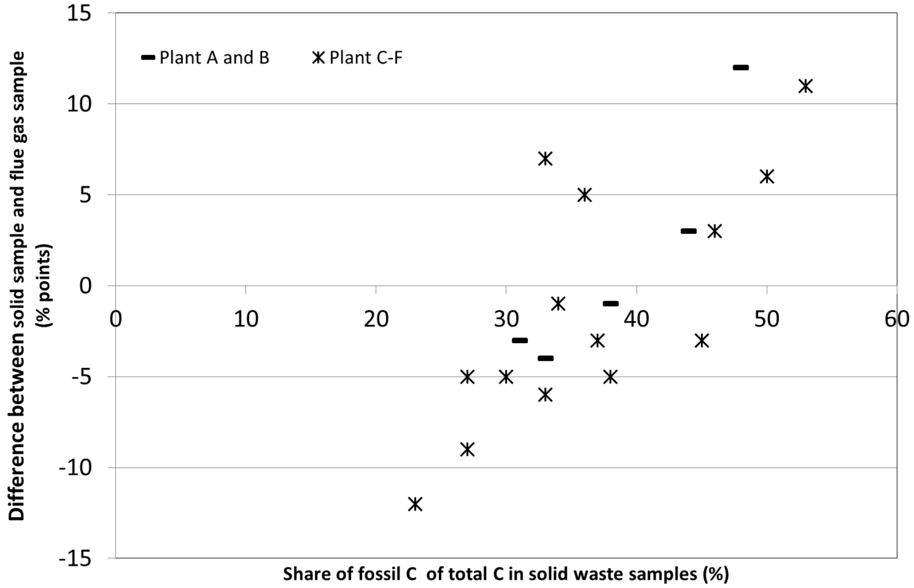


Figure 9. The difference between the carbon with fossil origin content in the solid waste samples compared with the parallel flue gas samples plotted as a function of the carbon with fossil origin content in the solid samples. The lines represent the fluidised bed plants A and B, and the stars represent the grate bed plants C-F (paper I).

The calculations based on sorting analyses were performed with the input data from Table 9. The calculations show that the fossil content is strongly connected to the plastic content in the input data, which explains the reason for plant C as a result having a higher share of carbon with fossil origin, 48 % compared to 38 % and 31 % for plants D and F, respectively.

For plants D and F where the plastic content was similar, other factors became significant. The major difference between the two plants was that the fraction "others" was dominated by hygiene products at plant D and wood at plant F. According to the calculation model used, hygiene products contain 64 % carbon with fossil origin while wood is 100 % biogenic.

Table 9. Input data for calculations and results from sorting analyses at plants C, D, and F (paper I)

Plant id.	C	D	F
Type of waste	100 % MSW	100 % MSW	40-45 % MSW 55-60 % IW
Composition (%)			
Biological waste	14.6%	31.4%	24.8 %
Paper	37.6%	23.2%	20.8 %
Plastics[a]	25.7%	13.8%	15.8 %
Soft plastics	*15.8 %*	*9.4 %*	*7.4 %*
Hard plastic packages	*0.5 %*	*0.3 %*	*0.4 %*
Polystyrene/styrofoam	*8.3 %*	*3.3 %*	*3.2 %*
Other plastics	*1.1 %*	*0.8 %*	*4.8 %*
Glass	3.4 %	1.4%	1.8 %
Metal	3.1 %	2.8%	3.8 %
Inorganic	0.4 %	2.7%	3.0 %
Hazardous waste	0.1 %	0.1%	0.1 %
Electric waste	0.1 %	0.3%	0.6 %
Others[b]	15.1%	24.5%	29.3 %
Wood	*1.6 %*	*0.4 %*	*17.3 %*
Textile	*4.5%*	*1.4 %*	*3.6 %*
Absorbent hygiene products	*6.7 %*	*16.0 %*	*1.6%*
Miscellanous/unidentifiable	*2.3 %*	*6.8 %*	*6.8 %*
Calculated results			
Share of fossil C	48 %	38 %	31 %

a) This fraction was further sorted into soft plastics, hard plastic packages, polystyrene/styrofoam, and other plastics, see numbers in italic representing the percentage of the total sum of waste.

b) This fraction was further sorted into wood, textile, absorbent hygiene products (such as nappies and feminine care products), and miscellaneous/unidentifiable, see numbers in italic representing the percentage of the total sum of waste.

The results of the balance method calculations with pre-logged data from plant E show that the average fossil share during this three-month period was 52 %. From the six solid samples and the two flue gas samples from plant E the averages for the fossil share are 38 % and 42.5 %, respectively. However, the calculations were performed with some uncertainties since not all the input data were logged but calculated based on assumptions.

The results from the online-installation at plant F are presented in Figure 10. During the three months of the study, weekly averages were calculated by the software. The average for all weekly samples is 43 %, compared to 34 % average for the solid samples and 36 % in the flue gas samples. However, it is clear that five of the weeks deviate from the others (see Figure 10). There is no visible relationship between the industrial waste content and the differences in carbon with fossil origin content. It turned out that the temporary use of a reserve O_2/CO_2-instrument during this week caused the differences. The instrument showed values increased by 0.2 percentage points for the O_2 and 0.9 percentage points for the CO_2, which produced a significant difference compared with when the more accurately calibrated ordinary instrument was used. When the weeks when the reserve instrument was used are excluded, the average for the whole period goes down to 36 %.

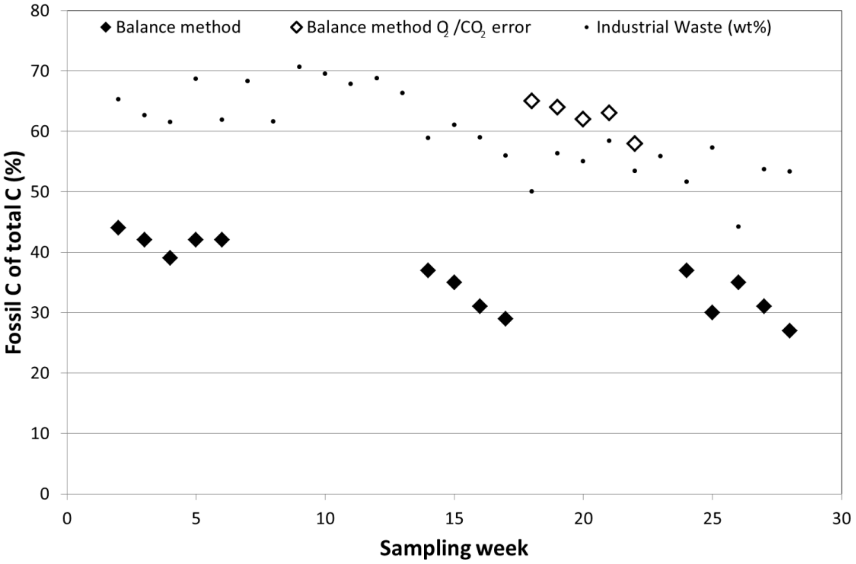


Figure 10. Weekly averages for the balance method showed together with the approximated share of industrial waste in the waste being combusted (paper I).

Table 10 collects together all the results from the study. Both the solid samples and the flue gas samples show that the majority of the samples have a share of between 30 % and 40 % carbon with fossil origin out of the total carbon content. The solid samples represent the waste composition from the original five-to-seven tonne samples extracted from the bunker, while the flue gas samples are averaged from a 24-hour continuous sampling. This should make the flue gas sample more homogenous and it also takes in all combusted waste rather than only one mixed extracted portion from the bunker. As discussed above, there is also a systematic error in the sampling of solid samples, which also points to the flue gas samples as being more trustworthy.

From the sorting analysis the results are somewhat similar. However, there are assumptions behind the calculations, making them dependent on predefined data. The balance method was only used at two of the plants: in plant E where old logged data was used, some of the input parameters had to be estimated, which resulted in a relatively high fossil share. In plant F the software program was installed and the results are in the same range as the results from other methods. Nevertheless, the software program turned out to be extremely sensitive and small changes in input data resulted in substantial differences in the results.

Overall, the results from this study suggest that approximately a third of the carbon in Swedish waste has fossil origin. This would correspond to a carbon with fossil origin share of approximately 10 wt% in a waste mixture. All methods provide data about the share of carbon with fossil origin in the waste mixtures but it is clear that the choice of method depends on the plant.

Table 10. All results from the four different methods presented together (paper I)

Plant id. / **Fossil C of total C. Averages per analysis method**	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Solid waste samples (%)	36	38	33	29	38[a]	34	43
Flue gas samples (%)	39	38	33	35	41[a]	36	44
Sorting analysis (%)	-	-	48	38	-	31	-
Balance method (%)	-	-	-	-	52	36[b]	-

a) This is calculated excluding outliers.

b) This is calculated without results from weeks with reserve instrument.

For example, sampling of solid waste is much more feasible and economically justified in a fluidised bed plant than in a grate-fired plant. The flue gas method seems to be more accurate than the solid samples but using solid samples also makes it possible to do a chemical fuel analysis of the waste mixture and retrieve information about its composition as well as the fossil share. The balance method provides online data, but requires that the plant log all the parameters required and it is very sensitive to changes. However, this sensitivity also makes the balance method a validation tool for all logged data and evaluates the quality of the logging instruments in the plants. Furthermore, the balance method provides information about the share of the produced energy that is fossil, which is of interest for other political decisions. The sorting analysis that has traditionally been used in Sweden is dependent on assumptions that produce great uncertainties but for two of the three plants it produced results in the same range as the other methods.

4.2 Chemical characterisation of waste fuel for commercial WtE boilers

The heterogeneous composition of waste makes both sampling accuracy and prediction of possible chemical reactions difficult to achieve. At the same time the variation in chemical composition is of great significance for the performance of the boilers in the WtE-plants in terms of availability and power efficiency. For example, the content of the alkali metals Na and K, in combination with the content of Cl and S, have a substantial effect on agglomeration, fouling and corrosion mechanisms, which often limits the steam data and requires counteractions such as soot blowing and outages. Increased knowledge on favourable levels and ratios of fuel components are therefore of great importance when retrofitting or developing waste combustors. Detailed knowledge of variations in waste composition over long periods is lacking and, as a consequence, it is also difficult to implement proactive measures to reduce unwanted reactions. The focus of this study was to characterise the waste fuel mixtures from two separate WtE plants, and achieve an overview of the composition as well as trying to identify seasonal variations.

This chapter presents the findings from a one-year chemical study of the waste streams of both MSW and IW to two commercial boilers, one grate-fired boiler and one BFB-boiler.

The findings for the BFB-boiler were published in "Chemical characterization of waste fuel for fluidized bed combustion" (Paper II). The study includes chemical analysis of the waste and thermodynamic equilibrium calculations to predict the chemical composition between 400 and 1000°C. The aim with the calculation was to predict unwanted reactions that shorten the boiler lifetime, such as the formation of corrosive alkali, and other metal, chlorides.

In the study plant A is a fixed-bed grate furnace, with fuel consisting of 60 wt% source-separated MSW and 40 wt% IW. Due to the decreasing heat demand in Sweden during the summer months, June, July, and August (JJA), the fuel consists of significantly less IW during these months. Instead, the IW is baled and saved for the colder months. The fuel at this plant is sampled according to the method described in section 3.1.1.

Plant B is a commercial BFB where the fuel normally consists of 30 % MSW and 70 % industrial waste. As at plant A, the IW is baled during the summer and the combusted fuel is close to 100 % MSW. The fuel at this plant is sampled according to the method described in section 3.1.2.

The fuel samples from both plants then underwent fuel analysis as described in section 3.2.
In paper I the results from the chemical analyses of the waste from plant B were used as input data to the thermodynamic equilibrium calculations. Three different cases were analysed;

- Case one (#1) a reference case with a normal combustion environment (oxidising) where the average values for all twelve samples were used as input data.

- Case two (#2) where the same average values on all species were used, except for Cl, which has been decreased to the lowest measured value from the samples to investigate how the Cl content affected the reactions.

- Case three (#3) where the content of S was increased to a Cl/S ratio of 1:4 to simulate the influence of a S additive. All other values were kept at the average for all twelve samples.

The program used was FactSage 5.5 and the databases FToxid, FTsalt and Fact53 were used with an oxygen level of 5 % in the flue gas, based on fuel consumption and combustion air.

Fuel sampling was performed twelve times for each plant between September 2007 and October 2008. Owing to some unscheduled shutdowns and planned maintenance periods the samplings did not take place once a month for a consecutive 12-month period, Table 11 shows the months when the fuel samplings were performed. Plant A has a maintenance period at the end of the summer, which means no sampling was performed for the boiler when it was shut down and during the start-up phase (August and September). At the end of 2007 two samples were lost from plant B (November and December). The second sample from plant A (October 2007) was divided into two plastic bags and analysed as two samples. Two samplings were performed at plant B in January 2008, one at the beginning and one at the end of the month.

The main differences in the chemical composition of these waste fuels and a biomass, such as wood pellets, are the moisture content and the ash content. Wood pellets normally have a moisture content around 8 wt% and less than 1 wt% ash. High ash content implies a high proportion of metals, which are often troublesome in combustion processes. The lower effective heating value relates to the high moisture content in the waste. Compared to wood pellets, the waste mixtures also contain an approximately 50 times higher proportion of chlorine, which is potentially corrosive, especially in combination with high alkali content, as in waste.

Both plants had a larger variation in the content of ash-forming elements which is evident in Figure 11 and Figure 12. The horizontal line at 1 represents the mean value for each element (the analysis result of each species is normalised against its mean value) and the distribution around this line shows the variation on the logarithmic y-axis. It is important when looking at the variation figures to take into account the differences in total content (wt%, g/kg, or mg·kg^{-1}). A low concentration, as for the trace elements, will make the variation larger. All samples are presented in the figures but for the fuel mixture from plant A there is no analysis for Sb, and for the fuel mixture from plant B there are no analyses made for Hg and Mn.

Table 11. Schedule for the fuel sampling. Each "x" marks one sampling

Year	2007				2008									
Month	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**March**	**April**	**May**	**June**	**July**	**Aug**	**Sep**	**Oct**
Plant A	X	XX*	X	X	X	X	X	X	X	X	X			X
Plant B	X	X			XX**	X	X	X	X	X	X	X	X	

*After sampling in October the sample was divided into two bags and analysed as two samples.
**Two samples were taken at plant B in January 2008, one at the beginning and one at the end of the month.

In Figure 12 (fuel mixture from plant B) there are bars on some of the species. These bars are given by the manufacturer of the boiler, and keeping the fuel composition within these guidelines (under the black one and above the white one) should give the durable performance of the boiler.

Both figures show that species such as Na, K, and Cl, which affect the corrosion risk, exhibit a larger spread from their mean value than for example C or N. Also S varies over the year, between 0.10 and 0.49 wt% ds in the fuel mixture from plant A and between 0.01 and 0.62 wt% ds in the fuel mixture from plant B. Furthermore, trace metals were present in low concentrations and show the widest relative variation (together with Ti and Ba). The figures also show that the spread from the average values is somewhat higher at plant A which could be related to the more heterogeneous fuel mixture. At plant B the fuel is shredded and then mixed several times, which gives a more homogenised fuel mixture than can be achieved when taking a 2-tonne sample from the bunker at plant A. However, there are no major differences so both sampling methods have to be seen as satisfactory.

4.2.1 Seasonal variations

The change of fuel mixture during the summer to close to 100 % MSW produces a notable change in fuel composition, most evident for the fuel mixture from plant B. In Figure 13 and Figure 14 the variation is presented again but with the summer months marked in black. For the fuel mixture from plant A (Figure 13) there are only two samples taken during the summer, June and July (JJ). The variation for the fuel mixtures from Plant B is shown in Figure 14 and it appears that the samples from the Swedish summer period contain less ash-forming material and predominantly fewer trace elements since they all lie on or under the annual average. A similar trend can be discerned for the fuel mixture in plant A but it is not as apparent as in the fuel mixture from plant B. This is an important observation supporting the conclusion above regarding the importance of repeated samplings of waste fuels, where one sample does not take into account possible seasonal (or other) variations.

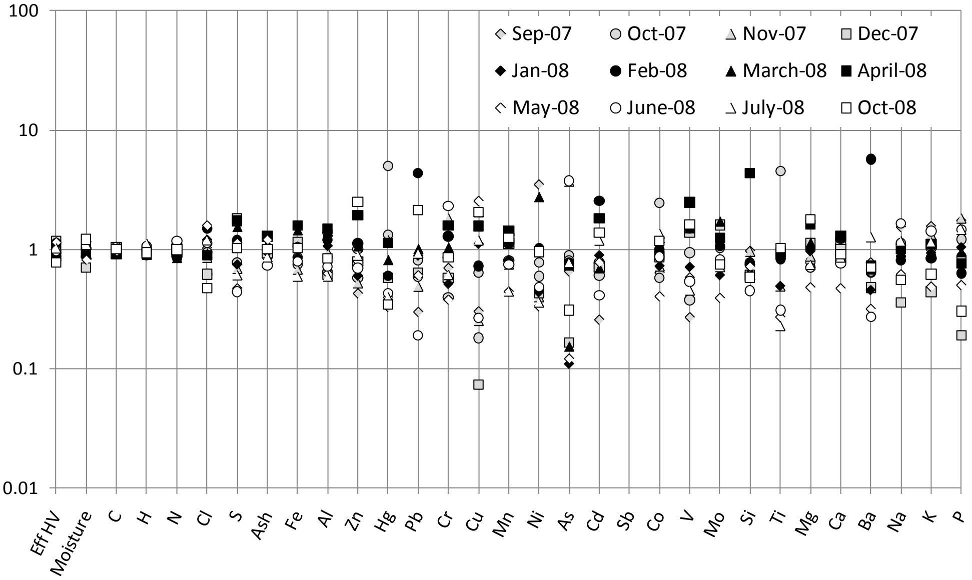


Figure 11. Variation over the sampling period in the fuel mixture from plant A. One Pb sample (April-08, 0.002 mg·kg^{-1} dry) is below the minimum in the diagram and not shown in the figure. The horizontal line at 1 represents the mean value for each element (the analysis result of each species is normalised against its mean value) and the distribution around this line shows the variation on the logarithmic y-axis.

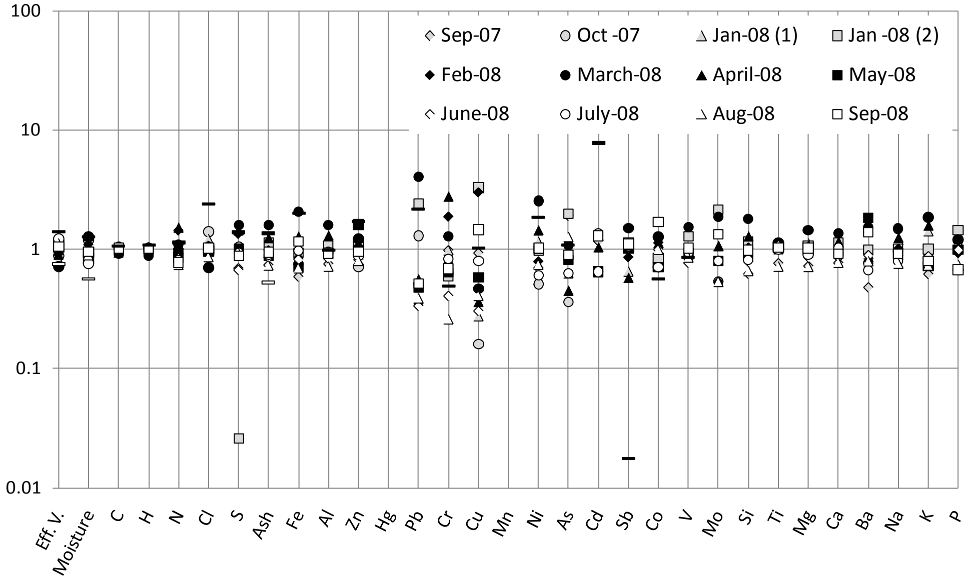


Figure 12. Variation over the sampling period in the fuel mixture from plant B. The small bars on some of the elements in the figure are given by the manufacturer of the boiler. There is a recommendation to keep the fuel composition of these elements within these guidelines (under the black one and above the white one) to get a durable performance from the boiler. The horizontal line at 1 represents the mean value for each element (the analysis result of each species is normalised against its mean value) and the distribution around this line shows the variation on the logarithmic y-axis.

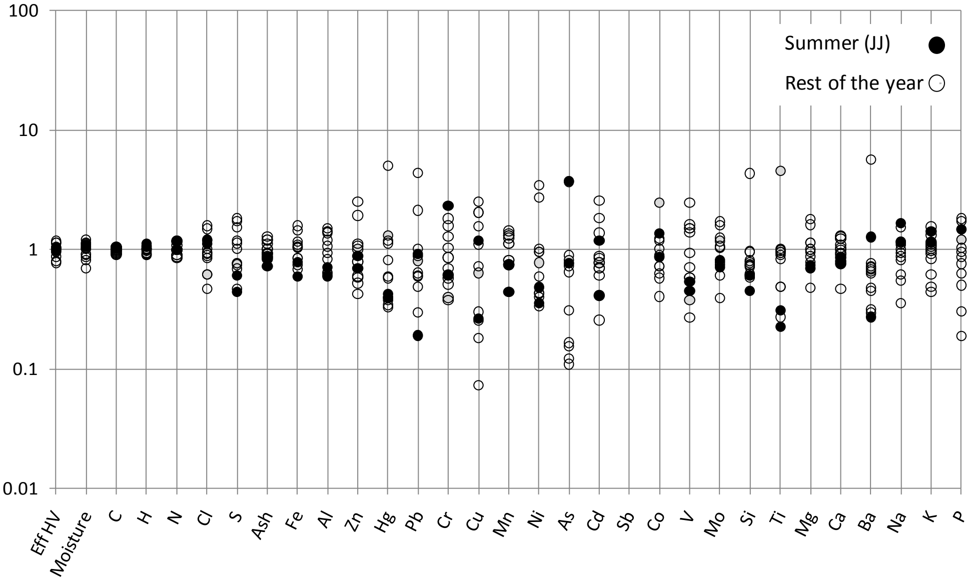


Figure 13. Comparison of the elemental composition in the summer months (JJ) and the rest of the year in the fuel mixture from plant A. The horizontal line at 1 represents the mean value for each sample (the analysis result of each species is normalised against its mean value) and the distribution around this line shows the variation on the logarithmic y-axis.

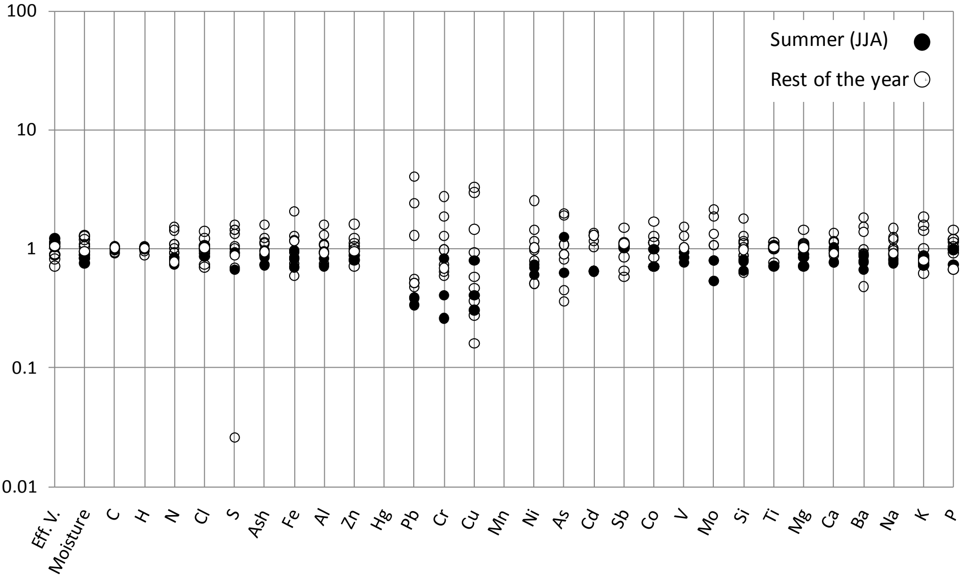


Figure 14. Comparison of the elemental composition in the summer months (JJA) and the rest of the year in the fuel mixture from plant B. The horizontal line at 1 represents the mean value for each element (the analysis result of each species is normalised against its mean value) and the distribution around this line shows the variation on the logarithmic y-axis.

4.2.2 Thermodynamic equilibrium calculations

The thermodynamic equilibrium calculations for paper II were performed with the average values for C, H, N, Cl, S, Fe, Al, Si, Mg, Ca, Na, K, P, Zn, and Pb from the twelve fuel samples from plant B used as input data. Equilibrium calculations like these are to be used as plausible scenarios, and are only implying possible outcomes in equilibrium at each temperature, which is not always the true scenario. In addition to this, the thermodynamic equilibrium calculations do not take into consideration kinetics or mixing.

The calculations suggested that most of the Na under these given conditions is bound in silicates but with increasing temperature, there is a formation of Na_2SO_4 and NaCl, while Cl is mostly found in the form of gaseous HCl. It is evident from the calculations that in the formation of corrosive alkali chlorides, NaCl is the favoured compound rather than KCl, showing the importance of Na in waste compared to biomass where K is often present in high concentrations. The superheater steam temperature in plant B is just above 400ºC, kept at this temperature to avoid superheater tube corrosion caused by condensed alkali chlorides on tube surfaces. This corrosion is known to be very temperature dependent and increase steeply at higher steam temperatures.

Of the twelve fuel samples taken, the sample with the least amount of Cl (sample 6) contained 0.35 wt% DS. compared with the average of all samples, 0.5 wt% DS. One calculation was performed with all values kept at their average but with the lower Cl content of 0.35 wt% DS. (a 30 % decrease). This minor shift in Cl content in the fuel, changes some of the outcomes of the inorganic reactions in the boiler, for example, decreasing the formation of NaCl significantly. Furthermore, another trend in this calculation is that there is an increase in the formation of $PbCl_x$ between 400ºC and 900ºC .

Since about 1/3 of the Na is bound in the less corrosive form Na_2SO_4(s) it could be possible that S contributes to a lower amount of NaCl by reacting with the Na. An increase of S was simulated in case 3 and the results show that the proportion of Cl bound in NaCl decreases with higher S in the fuel mix. Instead of forming NaCl, almost all Na is found in the solid sodium aluminium silicates in the lower temperature range, but no significant increase of Na_2SO_4 was noticed in this case. Instead a considerable increase in $CaSO_4$ occurred, leaving the Na still available for reaction with Cl. Moreover, this was another case where a minor increase in the formation of $PbCl_x$ was noted.

4.3 Evaluation of the presence of zinc in fuels

A comparative study on the content and sources of Zn in waste fuels is of interest towards an improved understanding of fuel related issues, where Zn may play a role in deposit and corrosion problems. The Zn content in common fossil fuels, common biomass fuels and different waste fuels used for power and heat production were presented in paper III. This section will describe the findings for the waste fractions included in the paper: Tyre Derived Fuel (TDF), Recovered Waste Wood (RWW), Waste Electrical and Electronic Equipment (WEEE), Municipal Solid Waste (MSW), Refuse Derived Fuel (RDF), Solid Recovered Fuel (SRF), and Industrial Waste (IW).

4.3.1 Tyre Derived Fuel

A Tyre Derived Fuel is generally called TDF and is refined scrap of shredded automotive tyres. The processing of TDF includes shredding into rubber chips of a certain size [64]. The tyre chips are rich in synthetic material and contain bead and radial wires, which in certain cases are removed [64, 65]. Tyres contain high amounts of Zn which is a vulcanising agent and is added to the rubber mainly as ZnO with just small amounts as different organozinc compounds [66, 67]. The high quantities of Zn can be found in both the tyres' tread (1.1-2.7 wt%) and wall (1-2.2 wt%). Smolders and Degryse [67] reported that the average amount of ZnO present in a car's tyre tread was estimated to be 1.2 wt%, while for lorry's tyres it was 2.1 wt-%. This gives between 12,000 and 21,000 $mg{\cdot}kg^{-1}$ of ZnO and since ZnO contains 80.3 % Zn, there are between 9,600 and 16,800 $mg{\cdot}kg^{-1}$ of Zn in the tyres. From the point of view of emissions problems, Zn is of special interest due to its relatively high volatility [65]. However, as indicated by Smolders and Degryse [67], ZnO has low volatility and this is the form of Zn present both in the tyres and in the ash remaining after combustion. It was noted that combustion of tyres may increase Zn-emissions by a factor of up to 20, which seems to be reasonable taking into account that the ash remaining after tyres combustion contains up to 60 wt% Zn [68].

4.3.2 Recovered Waste Wood

Recovered waste wood originates from stem wood and is composed to a great extent of different types of wood materials which result mainly from construction and demolition operations, and from commercial and industrial sources [69, 70]. In RWW there is a problem of heavy metal contamination. The biggest and particularly inextricable sources of contamination in terms of heavy metals such as Zn, Cd, Pb, Cu, Cr and Hg in waste wood are many kinds of surface treatments such as paints (white pigments), lacquers, siccatives, binders and preservatives [71, 72]. This work, however, focused on sources and quantities of Zn. Krook et al. reported, citing the example of Swedish RWW, that surface-treated wood is responsible for about 70 % of the Zn present in RWW. In paints, Zn is present as zinc oxide (ZnO) (white) or zinc chromates (yellow), some siccatives use Zn salts e.g. zinc carboxylate as a drying agent/accelerator, and in wood preservatives Zn can be found e.g. as ZnO, $ZnSO_4$ or ammoniacal copper zinc arsenate (ACZA). Many wood-plastic composites can also be treated with zinc borate [71, 73, 74]. Sorted waste wood also contains over 1 wt% of components other than wood such as plastics, metals, concrete, and gypsum, out of which the first two are potential sources of heavy metals including Zn. Galvanised fastening systems and metallic parts (nails, handles, screws, hinges, wires and different types of fittings) especially those made of brass (Cu-Zn alloy) in particular are the biggest source of Zn in waste wood. Krook et al. [71] established that the galvanised metal fraction in RWW contains over 14,000 $mg \cdot kg^{-1}$ of Zn and if the average amount of metal present in RWW is 0.5 wt%, assuming that all metal is galvanised, it equals on average 70 $mg \cdot kg^{-1}$ of Zn resulting just from metal fraction. The plastic parts such as flooring, wallboards, sheeting and electrical wires are usually well-integrated with the wood and may also, to some extent, be responsible for the increased presence of Zn. This is due to the fact that such PVC heat stabilizers as Ca/Zn, Ba/Zn and K/Zn have been incorporated and established in a wide range of applications such as cable covering, foil and sheet, flooring, wall coverings etc. [75]. Jermer et al. [76] reported that PVC represent roughly 40 % of the plastics present in RWW and the fraction of plastics reported in the available literature was estimated to be 0.1-2 wt%, as cited by Krook et al [71]. Overall the average total concentration of Zn in RWW is 400-600 $mg \cdot kg^{-1}$, but quantities over 1000 $mg \cdot kg^{-1}$ have also been reported. In comparison, the concentration of Zn in untreated stem wood (based on pine and spruce analysis) is <10 $mg \cdot kg^{-1}$ [69, 76, 77], while other studies show that spruce's heartwood contains 23-60 $mg \cdot kg^{-1}$, and sapwood 17-31 $mg \cdot kg^{-1}$ [78]. The amount of Zn found in pine was reported to be a little lower when compared to spruce. Ivaska and Harju [79] reported that the average concentration of Zn in Scots pine (*Pinus sylvestris*) ranges from 1-10 $mg \cdot kg^{-1}$. These data correspond well with the data reported by Pais and Jones [80] which show that the normal content of Zn in plants ranges from 10-100 $mg \cdot kg^{-1}$.

4.3.3 Waste Electrical and Electronic Equipment

Waste from electrical and electronic equipment (WEEE) means electronic and electrical equipment together with their non-electronic parts, which were discarded. Electronics being the world's largest and fastest growing business, the amount of WEEE waste is growing rapidly. WEEE contains a lot of combustible material, such as plastics, and hence a lot of energy; however, the presence of heavy metals, flame retardants and other harmful chemicals is an important environmental and health issue [81]. WEEE is a highly valuable waste fraction and the industry strives towards sustainable recovery of the many scarce and valuable metals that are present in complex electrical and electronic equipment today [82-88]. However, there are examples of WEEE not included in recycling laws [89] and therefore resulting in in MSW plants releasing Zn alongside other metals during combustion.

Zn is present in many different WEEE fractions due to its versatility in applications. For example, in addition to being used for galvanising, Zn is found in printed circuit boards [88, 90, 91], batteries [86, 92], and flame retardants [93]. Furthermore, Zn is also used as a filler, stabiliser, and/or pigment in plastics [83, 91, 94] and has traditionally been among the world's most used plastics additives [95].

4.3.4 Municipal Solid Waste, Refuse Derived Fuel, Solid Recovered Fuel, and Industrial Waste

Municipal Solid Waste (MSW), Refuse Derived Fuel (RDF), and Solid recovered fuel (SRF) are fuels derived from either domestic or industrial waste differing in composition and quality. Industrial Waste (IW) comes directly from industrial and commercial activities and also includes waste from the building and demolition sector. MSW is a very heterogeneous source of energy with little, if any, pre-treatment. MSW originates primarily from domestic and industrial sources and is typically household waste. The processed, partially sorted, high calorific fraction of MSW is called RDF. The other waste derived fuel with a similar composition to RDF is SRF. SRF is a high-quality fuel originating from MSW and industrial and commercial waste. The composition and quality of SRF are controlled, classified and certified by European standards. The maximum quantities of Zn allowed in RDF are e.g. 16 mg/MJ in Switzerland and 28 mg/MJ in Italy (as summarized in [96]). SRF is composed mainly of paper (40-50 %), plastics (25-35 %) and textiles (10-14 %) while RDF, in addition to SRF components, may also contain fractions such as organics or wood in amounts of around 1 % [97]. Unlike the above-mentioned RDF and SRF fuels, the main fraction of MSW are usually, but not exclusively, organics amounting to 30-40 %. Other fractions of MSW that are smaller in quantity are cardboard/paper, plastics, metals, glass, textiles and others (representing up to 30 wt%) [72]. Rotter et al. [96] reported (Table 12) the chemical composition of MSW from Germany with respect to Zn content, which gives a good general overview of the most Zn-rich fractions in waste derived fuels. The values in the table are sorted in descending order for Zn content in waste fractions. It is clear that, owing to the very heterogeneous character of MSW, any estimate, even on a rough basis, of the Zn content might be very difficult. If the general composition of MSW is known, the table gives an idea as to whether Zn is likely to be present in higher quantities. In the table, the largest source of Zn in MSW is spent batteries. Surprisingly, the report quantifying the percentage amount of batteries in MSW [98] showed that batteries are responsible for just 2 % of the Zn present in MSW. That indicates that even though batteries are rich in Zn, they are not responsible for the high amount of Zn in waste. However, due to the changeable composition, type of sorting, origin, etc. of MSW big variances are possible. If the values from Table 12 are recalculated so that they show the fractions responsible for the highest percentage of Zn in MSW, it is noticeable that fines <10 mm and 10-40 mm the largest problem, being responsible for almost 50 % of the Zn present in MSW. The second largest fraction responsible for high Zn content being batteries according to Table 12 does not seem to correlate with the data reported in [98] and described earlier. Non-ferrous metals also represent significant amounts of Zn in waste. Other fractions represent up to 4 % of the Zn. It should be remembered that the situation may change completely when investigating MSW coming from different cities or countries where segregation and recycling are at a different level. If the amounts of Zn from different fractions are added up, they come to over 4,000 mg·kg^{-1} of Zn present in MSW originating from rural housing and almost 3,000 mg·kg^{-1} of Zn being present in urban housing. These data can also be used to make rough estimates of the amount of Zn in SRF and RDF. As was noted earlier, RDF is composed of paper, plastics, textiles, organics and wood in proportions roughly 50/35/14/1 % respectively. In the table, there were two fractions of plastics that differed in their amount of Zn-content. Assuming that half of the Zn present in RDF plastics comes from packaging and the other half from other plastic products it was estimated that RDF may contain little over 1,100 mg·kg^{-1} of Zn. Removing organics and wood from the calculations gives an approximate amount of Zn in SRF, but the situation does not change much since those fractions were estimated to be present in amounts of only 1 %. Moreover, in this case the amount of Zn was not much above 1,100 mg·kg^{-1}.

Table 12. Zn content in different fractions of MSW from Eastern Germany, supplemented Table from Rotter et al. [96]

	Waste composition (wt%)		Chemical properties (mg ·kg$^{-1}_{DS}$)		Zn from certain source (mg·kg$^{-1}_{DS}$)			
	Rural housing	Urban housing	Zn	+/-	In rural housing		In urban housing	
					mg·kg$^{-1}_{DS}$	%	mg·kg$^{-1}_{DS}$	%
Batteries	0.7	0.4	176668	68045	1237	29.9	707	25.4
Non-ferrous metals	0.5	0.6	30446	12038	152	3.7	183	6.6
Rubber	0.1	0.2	14913	4562	15	0.4	30	1.1
Fines <10 mm	20.6	10.4	10034	285	2067	49.9	1044	37.6
Electronic waste	0.6	1.2	9113	3601	55	1.3	109	3.9
Other composite material	1.0	1.6	6361	3694	64	1.5	102	3.7
Other plastic products	0.6	1.5	4381	2801	26	0.6	66	2.4
Wood	1.8	1.5	4202	5829	76	1.8	63	2.3
Shoes	1.0	1.3	2918	1441	29	0.7	38	1.4
Leather	0.1	0.1	1296	1240	1	0.03	1	0.05
Fines 10-40 mm	21.5	17.6	1274	406	274	6.6	224	8.1
Packaging plastics	2.1	2.9	768	264	16	0.4	22	0.8
Non-packaging films	1.8	2.8	730	291	13	0.3	20	0.7
Textiles	3.5	5.4	520	235	18	0.4	28	1.0
Diapers	5.0	5.7	461	169	23	0.6	26	0.9
Paper and cardboard	5.6	14.0	424	296	24	0.6	59	2.1
Organic waste	18.5	17.1	241	99	45	1.1	41	1.5
Ferrous metals	1.7	3.4	214	118	4	0.1	7	0.3
Packaging composites	0.6	2.1	204	112	1	0.03	4	0.2
Glass	3.4	6.3	50	-	2	0.04	3	0.1
Minerals	8.2	2.8	n.d.	-	-	-	-	-
Others	1.1	1.0	n.d.	-	-	-	-	-
Total	100	100	-	-	4142	100	2777	100

Profu AB, an independent research and consultancy company in the areas of energy, environment and waste management, has developed a database called *AvfallsAtlas* [99]. Information from different waste fraction characterisation studies has been collected and summarised in this database, so that it is possible to show the waste fractions with the highest contribution to the proportion of Zn in waste. In Table 13 different waste fractions are listed with the minimum and maximum reported Zn content from *AvfallsAtlas*. The merging of different types of materials within each fraction, such as a summary of all plastic materials, also means that the origins of the waste fractions are merged. Therefore, all of the fractions presented in Table 13 include waste collected as MSW, but also Industrial Waste (IW) made up of mixtures of both industrial and commercial waste, and building and demolition waste.

The internal variation of Zn within each fraction also indicates how difficult it is to determine the Zn content in a waste mixture, for example in the textile/leather/rubber fraction where the Zn content varies from 31.5 up to 17,640 $mg \cdot kg^{-1}$ waste. Furthermore, although the difference between the materials in the Textile/leather/rubber-fraction is obvious, there is also a major difference within the glass fraction with reported measurements varying between 0 and 10,000 $mg \cdot kg^{-1}$. A study of the details behind Table 13 reveals that the materials contributing the most to the Zn content in waste are rubber tyres, glass, plastics treated with flame retardants, and PVC plastics. In PVC zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) is used as a heat stabiliser in combination with other elements such as calcium, barium, or potassium [100, 101]. Owing to the flexibility, mechanical properties, and electrical properties in materials stabilised with the Ca/Zn-combination, it is used in a variety of PVCs, such as potable water pipes, healthcare products, water bottles, cable covering, and toys [75]. In combination with barium the most common materials include flexible foils, flooring, wall coverings, fabric coating, and footwear while the K/Zn-combination is used as a stabiliser for foam layers in cushion flooring, foamed wallpaper and foamed fabric coating [75]. These are all common products that can be found in MSW, industrial and commercial waste, and building and demolition waste.

Table 13. Waste fractions and their zinc content, summarised information from the *AvfallsAtlas* database [99]

Waste fraction	Minimum (mg·kg^{-1}$_{DS}$)	Maximum (mg·kg^{-1}$_{DS}$)
Cardboard/paper/corrugated cardboard	13	160
Plastics	15	10 000
Kitchen and garden waste	14	125
Textile/leather/rubber	32	17 640
Glass	< 1	10 000
Wood/RWW*/CCA**/sleepers	26	539
Scrap/electronic waste	101	210
Sanitary products/nappies	13	29
Other combustible	150	322
Other non-combustibles	12	150

*RWW = Recovered Waste wood **CCA = pressure-treated wood with Cu, Cr, and As

4.4 Zinc in Swedish waste fuels

A more detailed study on the Zn content in Swedish waste fuels is published in paper IV. The study includes chemical analysis of 42 solid waste samples, investigating the presence of Zn in Swedish waste fuels.

To obtain a good overview of the Zn content in Swedish waste fuel, seven waste combusting plants spread over the whole of Sweden were used in this study, with 1,000 km between the southernmost and the northernmost plant. This provides the study with information about the waste content from different parts of Sweden as opposed to only being concentrated in one area. In total, there were two BFB-boilers and five grate-fired boilers. This distribution is in accordance with what the distribution of Sweden's waste combustion plants were at the time of the study, approximately 25/75 between plants with FB-boilers and plants with grate-fired boilers.

Six solid waste samples were collected at each plant over a 12-month period. The sampling was performed as described in sections 3.1.1 and 3.1.2 for the grate furnaces and BFBs respectively. Each sample underwent fuel analysis (according to the methods in section 3.2) to determine the Zn content as well as the content of Al, Si, Fe, Mn, Ti, Ca, Mg, Ba, Na, K, P, As, Pb, Cd, Cr, Cu, Co, Ni, V, Mo, and Sb.

In Table 14 the plants are described according to the type of combustion technique and the mean average of MSW during the sampling campaign; the table also shows the months in which the samples were taken. The time of sampling was based on plant availability, which leads to irregularity in times for some of the plants.

Table 14. The seven waste combusting plants included in the project and the time of sampling. Each "x" marks one sampling (paper IV)

Plant ID	Combustion technology	Mean Average MSW (%)	Sampling marked with x 2010 S	O	N	D	2011 J	F	M	A	M	J	J	A
A	BFB*	25			x	x		x		x	x			x
B	BFB*	35			x	x		x	x		x	x		
C	Grate	100			x	x	x		x	x	x			
D	Grate	100					x	x	x	x	x	x		
E	Grate	55		x		x	x	x		x		x		
F	Grate	40	x	x		x		x		x		x		
G	Grate	40			x	x			xxx			x		

4.4.1 Combustion technology, share of MSW and geographical relevance

The trace analysis results for Zn are presented in Table 15, which shows considerable differences between the samples, both between the seven plants and also within the plants. There is no clear difference between the waste mixtures from the two different combustion technologies. However, there is a lower mean average and median in the Zn content over the whole sampling campaign for the two plants with a fuel mixture of 100 % MSW (plants C and D). Furthermore, plant E has the lowest share of MSW and also the highest mean average and median, but also the highest standard deviation. This is related to the fact that plant E has one extreme sample, namely sample E6 containing 15,000 mg·kg^{-1} Zn, increasing both the mean and the median.

Considering all the samples, the mean average is 1,124 mg·kg^{-1} DS. owing to the outlier of 15,000 mg·kg^{-1} DS. from plant E. When excluding the min/max samples it goes down to 799 mg·kg^{-1} DS., which is much closer to the median of all samples, 825 mg·kg^{-1} DS.

The Zn analysis results suggest that the concentration of Zn in the waste fuel, over longer time periods is more related to the mixtures of IW, rather than the MSW.

Table 15. Results from the Zn analysis of each solid waste fuel sample. Minimum and maximum analyses for each plant are in italics. The mean and median are given for each plant and for all samples, as well as for all samples where the minimum and maximum analyses of all samples have been subtracted (paper IV)

Sample Plant Id.		1	2	3	4	5	6	Mean	Median
A	mg·kg^{-1} (DS)	960	*1000*	750	910	930	*630*	863	920
B	mg·kg^{-1} (DS)	830	*550*	860	*1020*	660	1000	820	845
C	mg·kg^{-1} (DS)	*950*	840	480	420	*260*	450	567	465
D	mg·kg^{-1} (DS)	*250*	*250*	380	300	*1250*	280	452	290
E	mg·kg^{-1} (DS)	850	*640*	1090	1405	950	*15000*	3323	1020
F	mg·kg^{-1} (DS)	630	*450*	*1600*	1500	840	580	933	735
G	mg·kg^{-1} (DS)	1100	820	*1800*	640	*450*	660	912	740
All samples								1124	825
All samples – min/max								799	825

4.4.2 Correlations with other elements

A correlation study was performed within each of the combustion plants where the Zn content were correlated to each of the other elements analysed in the waste samples. No clear pattern was apparent for correlations with Zn when comparing all waste mixtures. However, in three of the plants - C, D, and F - there were good correlations with one or more elements, suggesting the waste consisted of material combining the elements. The correlating elements are all metals, except the metalloid As. In both plants C and D the fuel mixture was 100 % MSW, meaning that neither waste from industrial and commercial activities nor major amounts of building and demolition waste has contributed to the proportion of metals. In addition, plants C and D are also the plants with the lowest mean average content of Zn. The elements occurring together with Zn in these two plants - Cu, Mn, Pb, and Fe - may originate from small WEEE that should have been excluded from the MSW by sorting at source.

With more than half of the waste mixture consisting of industrial and commercial/building and demolition waste in plant F it is hard to determine the dominating source of the Zn-Fe combination but the alloy is widely used in the automotive industry, for example, which indicates it originates from somewhere other than from MSW.

4.4.3 Variation over time

Owing to the significant difference in the mean average for all 42 samples when the clear outlier E6 (1124 compared to 799 $mg \cdot kg^{-1}$ DS.) is or is not included, the following data analysis is done by using the Zn content normalised against the mean average that is closest to the median, excluding the min/max of all samples.

Figure 15 presents the variation in Zn content over the year the sampling campaign was performed. The mean average for all samples is represented by 1 on the logarithmic scale and all variation around it is the scattering of the different Zn content in the samples. The first samplings took place in the Swedish autumn and the very last sample was taken in late summer, at the end of August.

For the two BFB-plants (A and B) and the two plants operating on 100 % MSW (C and D) the Zn content stays relatively stable over the sampling campaign. Two of the plants with the highest proportion of IW (E and F) both have a slightly higher Zn content during the winter, possibly indicating that the waste mixtures contain more Zn during this time period. However, no general trends of Zn either increasing or decreasing depending on the month of the year or season can be concluded with only a few samples from each plant and time period.

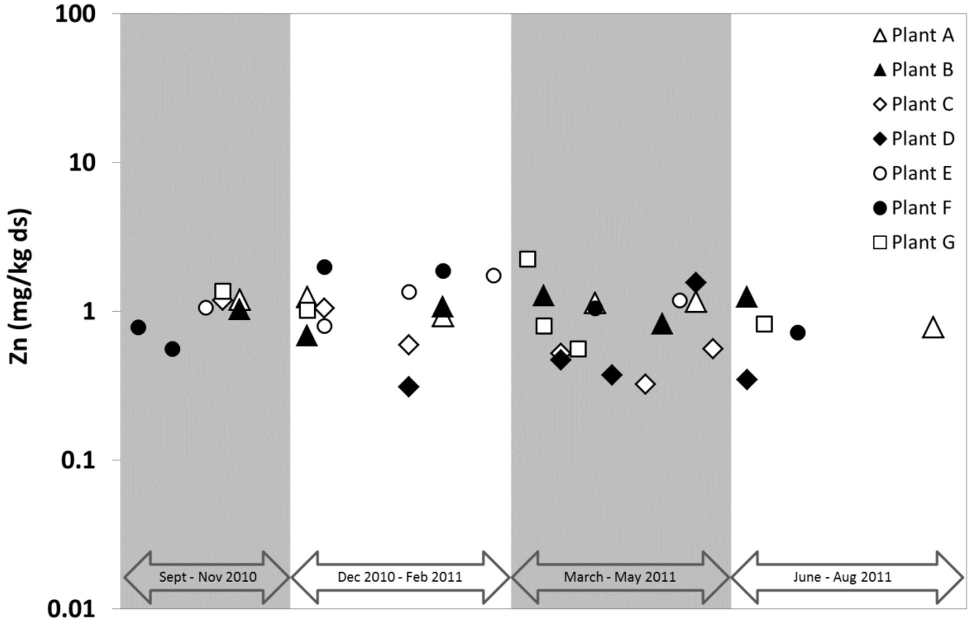


Figure 15. The variation in Zn in the waste fuel mixes during the full sampling campaign on a logarithmic scale. The figure is based on the normalisation of all samples by the mean average excluding the minimum and maximum samples. In the figure the four time periods are related to the Swedish autumn (Sept-Nov), winter (Dec-Feb), spring (March-May) and summer (June-Aug) (paper IV).

4.5 Thermal Stability of Zinc compounds

This study is focused on the thermal behaviour and stability of Zn compounds and how $ZnCl_2$ affects the thermal stability of alkali chlorides. The possibility of chlorinating ZnO and sulphating $ZnCl_2$ was also investigated. The results from this study are published in paper V.

4.5.1 Zinc Oxide (ZnO)

ZnO is thermally stable with a melting temperature above 1975°C and is insoluble in both water and alcohol [102]. However, ZnO does react with hydrochloric acid forming $ZnCl_2$. Verhulst et al [102] have shown by thermodynamic equilibrium calculations that the presence of HCl increases the volatility of Zn, and that the presence of water decreases the volatility of Zn by shifting the equilibrium to the right in reaction (3). In a study of Zn and lead (Pb) occurrence in aerosols and deposits Enestam et al. [103] doped wood chips with ZnO to increase the Zn content. They showed that ZnO can be chlorinated during the combustion process.

4.5.2 Zinc Chloride ($ZnCl_2$)

As a pure chemical, the anhydrous form of $ZnCl_2$ is highly hygroscopic, rapidly taking up moisture from the ambient air turning into one of five hydrates [104, 105]. The anhydrous form has a melting point of 318°C [106].

$ZnCl_2$ may react to form ZnO according to reaction (3) with oxygen or reaction (4) with H_2O. Stepwise it may also form $ZnSO_4$ with SO_2 or SO_3 according to reactions (5) and (6).

4.5.3 Zinc Sulphate ($ZnSO_4$)

The most common form of $ZnSO_4$ is the natural mineral goslarite, $ZnSO_4 \cdot 7H_2O$. This heptahydrate form of $ZnSO_4$ decomposes at around 280°C to form anhydrous $ZnSO_4$ [107]. The thermal decomposition of anhydrous $ZnSO_4$ has been thoroughly investigated and has been found to occur at temperatures between 610°C and 846°C. The highest temperature, 846°C, was determined in vacuum and with the decomposition temperature defined as the temperature where the equilibrium pressure of the gaseous decomposition products was equal to one atmosphere [108], while the lowest temperature, 610°C, was determined when heated on a thermobalance [109]. According to Ostroff and Sanderson [110], who studied the decomposition temperature with DTA-TGA, $ZnSO_4$ starts to decompose at 646°C and eventually forms ZnO. When the same experiments were repeated by Kolta and Askar [111], the decomposition temperature was found to be 675°C with TGA and 682°C with DTA. Mu and Perlmutter [112] carried out studies at different heating rates and intermediate phases. They showed that the heptahydrate form of $ZnSO_4$ is unstable at room temperature and is therefore often partially dehydrated. By back-calculation they determined the starting compound in their experiments to be $ZnSO_4 \cdot 5.44H_2O$. During the TGA experiment the $ZnSO_4$-hydrate then loses its water molecules stepwise, starting to form anhydrous $ZnSO_4$ above 230°C. It subsequently decomposes from $ZnSO_4$ to $ZnO \cdot 2ZnSO_4$ between 590°C and 712°C, and then forms ZnO above 900°C, see reaction (7).

The melting point of pure $ZnSO_4$ is difficult to measure owing to its decomposition reaction. Khaklova and Dombrovskaya [113] extrapolated the melting point of $ZnSO_4$ to 730°C from phase diagram data of the Na_2SO_4-K_2SO_4-$ZnSO_4$ system based on the liquidus temperatures of $ZnSO_4$-rich mixtures.

4.5.4 Chemical reactions of $ZnCl_2$, $ZnSO_4$, ZnO

Reactions involving $ZnCl_2$, $ZnSO_4$, and ZnO are given below. These reactions are bulk reactions and should not be treated as elemental reactions, as the detailed reaction mechanisms are much more complex.

$ZnCl_2 \text{ and } ZnO$

$$ZnCl_2(s) + H_2O(g) \rightleftharpoons ZnO(s) + 2HCl(g) \qquad \text{(R-3)}$$

$$ZnCl_2(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons ZnO(s) + Cl_2(g) \qquad \text{(R-4)}$$

$ZnCl_2 \text{ and } ZnSO_4$

$$ZnCl_2(s) + SO_3(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons ZnSO_4(s) + Cl_2(g) \qquad \text{(R-5)}$$

$$ZnCl_2(s) + SO_3(g) + H_2O(g) \rightleftharpoons ZnSO_4(s) + 2HCl_2(g) \qquad \text{(R-6)}$$

$ZnSO_4$ and ZnO

$$ZnSO_4(s) \rightleftharpoons ZnO(s) + SO_3(g) \qquad \text{(R-7)}$$

It should be noted that in reactions 5-7, SO_3 can be replaced by SO_2 and O_2 according to the following reaction:

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \text{(R-8)}$$

Thermodynamically, SO_3 is favoured at lower temperatures, while SO_2 is favoured at higher temperatures [114]. However, the conversion of SO_2 to SO_3 at low temperatures is very slow unless it occurs as a heterogeneous reaction in the presence of catalytic materials.

4.5.5 The fate of Zn during combustion

Findings of $ZnCl_2$ in fireside deposits in MSW-boilers as well as in deposits formed in industrial boilers that burn Zn-containing fuels has led to the belief that $ZnCl_2$ may play a role in corrosion of heat transfer tubes in these boilers owing to its low melting temperature and high corrosivity when molten [102, 115-122].

Elled et al. [55] performed an investigation of combustion of demolition wood contaminated with Zn by using thermodynamic equilibrium calculations and by studying deposits in a 12 MW_{th} circulating fluidised bed boiler. The results show that Zn in combination with chlorine do give rise to the formation of $ZnCl_2$ in the flue gas. Moreover, Elled et al. suggested that the formation is thermodynamically favoured between 450°C and 850°C under reducing conditions, while under oxidising conditions, the formation begins at 400°C and gradually increases with temperature. However, the calculations also show that reducing conditions increase the release of Zn to the flue gas but in the case of oxidising conditions, Zn is retained in the ash.

Furthermore, Elled et al. [55] summarised published knowledge about the influencing parameters on Zn behavior in combustion. They found that during oxidising conditions Zn is, in the absence of chlorine, retained in the ash within the temperature range usually encountered in solid waste combustion due to the formation of stable solid compounds, such as ZnO [115, 116]. In addition, the literature review suggested that limited access to oxygen (reducing conditions) promotes the volatility of Zn and increases the release of metallic Zn to the flue gas which may form, for example, ZnO and contribute to deposit formation [102, 116, 122]. It has also been concluded that an increase of available chlorine is an effective way to increase Zn volatilisation; the presence of HCl in the flue gas results in the formation of $ZnCl_2$ which is more volatile compared to the elemental and oxide form of Zn [102, 116]. The formation of alkali chlorides lowers the partial pressure of HCl in the flue gas and hence hinders the formation of $ZnCl_2$. On the other hand, S may react with alkalis to form alkali sulphates and by that reaction lower or hinder the formation of alkali chlorides and increase HCl in the flue gas, which may then increase the volatility of Zn by Cl [116].

4.5.6 Experimental set-up, results, and discussion

The thermal behaviour of the chemical compounds ZnO, $ZnSO_4$, $ZnCl_2$, and mixtures of $ZnCl_2$ and alkali chlorides (NaCl and KCl) was studied using simultaneous Thermogravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC) apparatus from TA instrument (Model SDT Q600TM). All samples were studied in N_2 and in air. The 110 µl crucible (6.5x4 mm) used for the experiments was filled with approximately 15 mg of powder-form sample, equalling about 2 mm particle bed thickness. The experimental conditions are listed in Table 16.

The same TGA-DSC was also used to investigate the possibility of chlorinating ZnO by introducing 500 ppm directly to the apparatus. A weight increase would be expected if condensed $ZnCl_2$ is formed from ZnO, due to the higher molecular weight of $ZnCl_2$ compared with ZnO. The chlorination experiments are included in Table 16 together with the other TGA-experiments.

As a hygroscopic substance, $ZnCl_2$ adsorbs moisture in air to form hydrates, which are released at the beginning of the heat-up. Aside from this, the DSC results show that in both air and N_2, $ZnCl_2$ melts at 320°C and remains molten below 400°C. Above this temperature, molten $ZnCl_2$ vaporizes and in air it is subsequently oxidised to ZnO. As $ZnSO_4 \cdot 7H_2O$ is heated above 230°C, all of its hydrates are released. The resulting anhydrous $ZnSO_4$ is stable up to 680°C at which it decomposes to form ZnO. ZnO is stable at much higher temperatures, than the one used in th analysis of pure ZnO, in both air and N_2, and no significant change can be seen.

Table 16. List of samples, gases and TGA-programs used for each Zn-compound or mixture (paper V)

Sample	Gases*			TGA-program
ZnO	N_2	air	HCl/N_2/air	In N_2 and air: heated 10°C/min up to 800°C. In HCl/N_2/air-mix: heated 10°C/min up to T°C, isothermal for 30 min. (T = 240, 270, 300, and 330°C).
$ZnCl_2$	N_2	air	-	Heated 10°C/min up to 800°C.
$ZnSO_4$	N_2	air	-	Heated 10°C/min up to 800°C.
NaCl	N_2	air	-	Heated 20°C/min up to 850°C.
KCl	N_2	air	-	Heated 20°C/min up to 850°C.
NaCl + $ZnCl_2$	N_2	air	-	Heated 20°C/min up to 850°C.
KCl + $ZnCl_2$	N_2	air	-	Heated 20°C/min up to 850°C.

*The gas flow for all samples was 100ml/min. The concentration of the HCl gas was 1000 ppm in N_2, and it was added to the TGA as 50 ml/min of the HCl/N_2-mix and 50 ml/min air. The gas flow equals a velocity of approximately 0.3 cm/min.

Experiments were also performed on mixtures of $ZnCl_2$ and NaCl and mixtures of $ZnCl_2$ and KCl. The results suggest that with an increasing $ZnCl_2$ percentage, the mixture becomes less stable and melts at a lower temperature for both NaCl and KCl (Figure 16 and Figure 17).

The melting temperatures of the mixtures were determined by DSC. Figure 18 and Figure 19 show phase diagrams for $ZnCl_2$–NaCl and $ZnCl_2$–KCl systems, respectively, constructed using FactSage. In the figures, results of experiments performed in air in this study are also represented by circles, and those of experiments performed in N_2 are represented by triangles. The experimental results are consistent with the calculated phase diagrams, particularly for the $ZnCl_2$-KCl system (Figure 19). For the $ZnCl_2$-NaCl system (Figure 18), however, the experimental results suggest that there is also a solid-solid transition of $2NaCl{\cdot}ZnCl_2$ at about 250°C. Small additions of $ZnCl_2$ to KCl or NaCl lower the first-melting temperature by several hundred degrees to around 400°C or even lower. These low-melting mixtures may be highly corrosive if they form deposits on heat-exchanger surfaces.

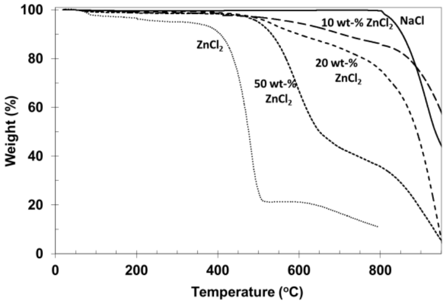


Figure 16. TGA curves of mixtures of three different amounts of $ZnCl_2$ in NaCl together with the TGA analysis of the pure substances in N_2 (paper V).

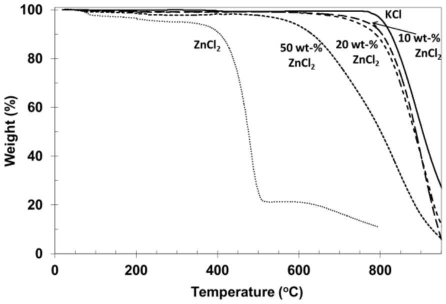


Figure 17. TGA curves of mixtures of three different amounts of $ZnCl_2$ in KCl together with the TGA analysis of the pure substances in N_2 (paper V).

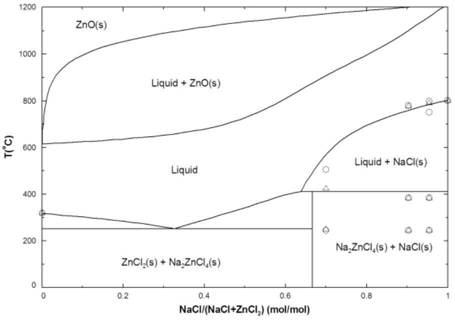


Figure 18. Calculated phase diagram of NaCl-$ZnCl_2$ with $p_{(O2)}$=0.21 bar. The circles represent the measured melting temperatures and phase transitions from experiments done in air and the triangles represent experiments done in N_2. The labels show the stable condensed phases for the phase diagram calculated for the air case (paper V).

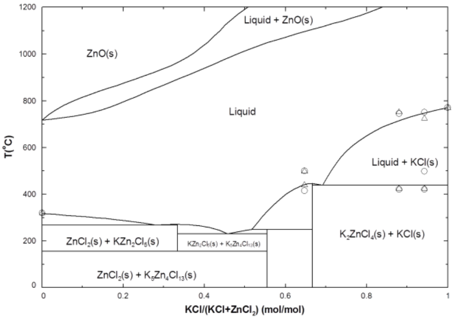


Figure 19. Calculated phase diagram of KCl-$ZnCl_2$ with $p_{(O2)}$=0.21 bar. The circles represent the measured melting temperatures and phase transitions from experiments done in air and the triangles represent experiments done in N_2. The labels show the stable condensed phases for the phase diagram calculated for the air case (paper V).

The results from the chlorination of ZnO at 4 different temperatures (240°C, 270°C, 300°C, and 330°C) suggest that $ZnCl_2$ can form by exposing ZnO to air containing 500 ppm HCl. At all these temperatures, the ZnO sample gained weight from the start (i.e. during the heat-up phase of approximately 20 to 30 minutes, depending on the final set temperature) and continued to gain weight during the isothermal period. Figure 20 shows the weight increase during the isothermal period after the system has reached its set temperature. The temperature dependence of this reaction appears to be quite complicated, with experimental results showing that the reaction rate (or weight gain) at 270°C was the highest, closely followed by that at 240°C, 300°C and then at 330°C. One way of explaining the results could be by the aid of Figure 21, which is the calculated phase stability of ZnO and $ZnCl_2$ as a function of temperature and HCl partial pressure. The figure indicates that below 270°C, the stability of $ZnCl_2(s)$ is high, while at temperatures above 270°C the chlorination of ZnO to $ZnCl_2$ is slowed down. In addition, it is possible that the vapour pressure of $ZnCl_2$ at the two higher temperatures causes the substance to vaporise and may therefore be lost from the sample. The complete reason for the differences between these different temperatures is not yet fully understood. All the experiments were repeated three times and the results all show the same trends. The stable phase above 400°C in 500 ppm HCl is ZnO, but no such experiments were performed since $ZnCl_2$ is highly volatile at this temperature, which is confirmed by TGA experiments.

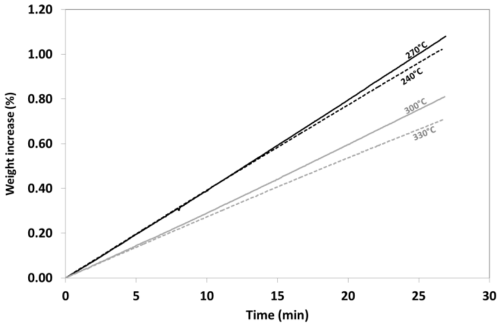


Figure 20. The exposure of HCl to ZnO kept isothermal at four different temperatures (240, 270, 300, and 330°C). The experiments were carried out in 500 ppm HCl mixed with air (paper V).

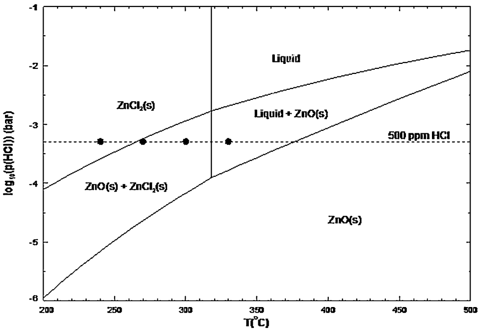


Figure 21. Calculated phase stability of Zn compounds as a function of temperature and p(HCl) with $P_{(O2)}$=0.1 bar. The dashed line represents the HCl concentration (500 ppm) and the four dots mark the experimental conditions at 240, 270, 300, and 330°C, and 500 ppm HCl (paper V).

The results of this study suggest that $ZnCl_2$(s/l) cannot exist without difficulty in the boiler due to its volatility at high temperatures and its conversion to ZnO in oxidising conditions. $ZnSO_4$ decomposes around 680°C, while ZnO is relatively stable in the temperature range prevailing in the boiler. Furthermore, the experimental data shows that chlorination of ZnO with HCl gas is possible. However, the total conversion only reached an increase of a few weight percentages (where 1 wt% corresponds to approximately 1.5 % conversion) during the heat-up phase and the 30-minute isothermal experiment. This could be related to the sample size in the TGA only allowing the HCl gas to react with the surface of the ZnO-particles in the crucible, not reaching into the core, and also to the limited experiment time of 30 minutes. A conversion as small as this cannot solely prove that ZnO can be chlorinated in a boiler but indicates that the conversion is possible and that further studies are needed.

4.6 Reduced bed temperature in a BFB-boiler

During combustion of MSW and IW, the chemical reactions that remove alkali chlorides from the flue gas are hard to predict and control owing to the fuel heterogeneity. The bed temperature of a FB- boiler is typically in the range of 750/780°C up to 900°C [120, 123], and is “normally” kept around 850°C in a waste boiler. Reducing this bed temperature is expected to change the behaviour of gas phase alkali metals, and hence reduce the formation of particles that may cause corrosive deposits on heat exchanging surfaces. The purpose of this study was to test this hypothesis with full-scale experiments in an industrial boiler and laboratory-scale experiments in a single-pellet fluidised bed reactor. The results from this study are published in paper VI.

The full-scale tests were carried out at a heat and power plant equipped with two parallel BFB-boilers of 20 MW_{th} each, delivering superheated steam at 49 bar and 405°C. The boilers will hereafter be referred to as B1 and B2. The fuel consists of a mixture of 30 % MSW and 70 % IW. A schematic sketch of one the boilers is presented in Figure 22. The bed temperature is normally kept around 870°C. In the event of this temperature being exceeded the bed will be cooled by means of flue gas recirculation mixed with the primary air (at (3) in Figure 22). Secondary and tertiary airs are introduced over the bed at a constriction of the combustion chamber (4). At the top of the combustion chamber, the flue gas temperature is normally between 900 and 950°C. After the combustion chamber, the flue gas passes through an empty gas pass (5) before reaching the superheaters (6). The flue gas temperature is around 350°C when it reaches the economiser (8), in which the gas is cooled to around 150°C. Finally, the flue gas passes through a cleaning system before leaving the plant or partly being recycled into the boiler to regulate the bed temperature.

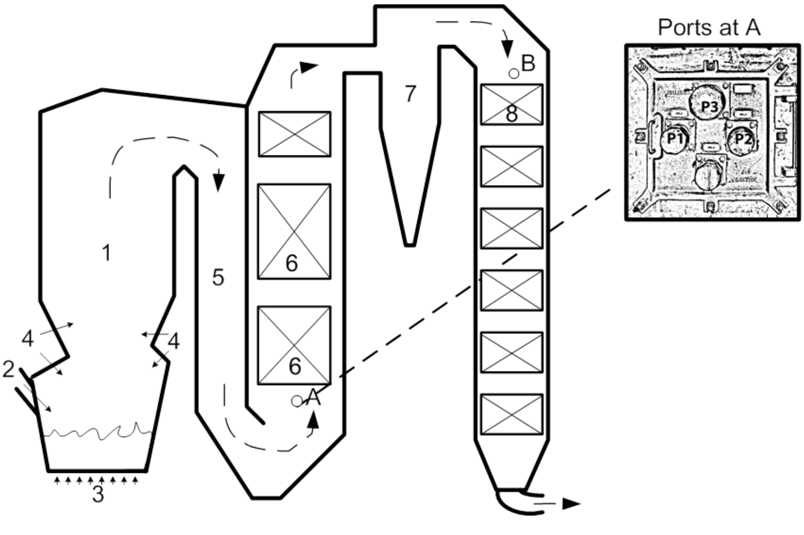


Figure 22. Sketch of one of two 20 MW_{th} waste combustors used for the experiments. (1) Combustion chamber, (2) Fuel feed chute, (3) Primary air, (4) Secondary and tertiary air, (5) Empty gas pass, (6) Superheaters, (7) Cyclone, (8) Economiser (paper VI).

4.6.1 Full-scale tests

In the experiments, a test case of Reduced Bed Temperature (RBT) has been compared to a reference case (Ref). For the RBT-case, the bed temperature was reduced by an increased flow of recirculated flue gas through the bed, while some of the primary air was diverted to secondary and tertiary airs. The measurements were carried out over two days, one day per bed temperature. The two boilers were operated under experimental conditions, given in Table 17, for approximately three days before the measurement campaign began. Figure 23 shows the load and temperature profiles of the boiler during the two cases.

Fuel from the boiler was sampled according to the method described in section 3.1.2. The fuel analyses are presented in Table 18 together with the analysis of the waste fuel used for the laboratory experiments described subsequently in section 4.6.2. The fuel used in the laboratory experiments was sampled from the same boiler but at a different occasion.

Table 17. Operating parameters during the measurements, including measured SO_2 and HCl contents* (Paper VI)

Parameter	RBT			Ref		
	Average	Min	Max	Average	Min	Max
T_{bed} (°C)	724	691	761	876	865	888
O_2 (vol-% wet gas)	6.1	5.9	6.3	7.3	7.0	7.7
CO (mg/Nm^3 dry gas, 11 % O_2)	12	2	60	6	4	9
Air_{Total} (Nm^3/s)	7.1	6.8	7.4	8.3	7.8	8.8
Recycled flue gas_{Total} (Nm^3/s)	4.2	4.0	4.5	4.4	3.6	5.0
HCl (mg/Nm^3, dry gas, 11 % O_2)	660*			530*		
SO_2 (mg/Nm^3, dry gas, 11 % O_2)	111*			114*		

*HCl and SO_2-analyses were done with a wet chemical method only providing an average in the sample

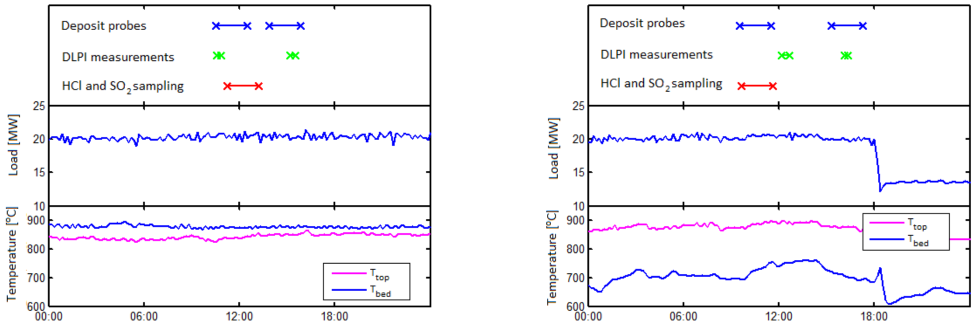


Figure 23. The figure illustrates the load and the temperature of the boiler during the Ref (left) and RBT (right) cases (Paper VI).

Table 18. Fuel analysis

		Ref	RBT	Lab-scale
Moisture	% by weight, a.r.	33.1	35.7	29.2
Ash	% by weight, d.f.	17.9	19	16.2
S	-"-	0.2	0.35	0.26
Cl	-"-	0.47	0.49	0.53
C	-"-	46.2	46	45.2
H	-"-	6.1	6	5.8
N	-"-	1.1	1.1	1
O (by diff.)	-"-	28	27	31
Al_2O_3	% by weight ash	11.61	10.94	9.33
SiO_2	-"-	41.83	50.67	38.30
Fe_2O_3	-"-	3.75	7.37	3.62
TiO_2	-"-	2.14	2.20	2.37
MgO	-"-	2.69	2.71	2.56
CaO	-"-	20.32	19.88	20.73
Na_2O	-"-	4.82	5.75	4.74
K_2O	-"-	2.96	2.28	2.31
P_2O_5	-"-	2.69	1.69	1.27
PbO	-"-	0.07	0.07	0.05
ZnO	-"-	0.37	0.39	0.37
Sum		93.26	103.94	85.64

a.r. – as received, d.f. – dry fuel

Fly ash particles were sampled at A, port "P3", in Figure 22, with a Quench/Dilution probe in combination with a Low Pressure Impactor, which is a cascade impactor separating particles according to their size. The method is further described by Johansson et al. [124]. Inside the impactor, the particles are collected on pre-weighed polycarbonate substrates mounted on collection plates. After sampling the polycarbonate substrates were weighed before the chemical analysis.

Deposit probes were used to study the deposit formation, and the temperature controlled by air cooling. The probes were two metres long with a diameter of 38 mm. On each probe, two high alloyed steel rings (253 Ma) were placed approximately 10 cm from the tip. At the superheaters (the position marked by "A" in Figure 22), two different material temperatures were used: 435°C, which corresponds to the material temperature at present operation, and 500°C, which is a goal for future waste combustion. Deposits were also sampled in the economiser (at B in Figure 22), using a material temperature of 230°C, roughly corresponding to the material temperatures of the economiser.

In addition to the particle and deposit samples, other types of ash samples were collected from different locations in the boiler during the tests: bottom ash, cyclone ash, ash from the empty gas pass, ash from the textile filter, and recycled sand.

Subsequent to the experiments, the deposit rings, particle samples, and ash samples were analysed according to section 3.2. The following elements were analysed: Cl, S, Al, Ba, Ca, Cu, K, Mn, Na, P, Pb, Ti, Zn and Si. Fe was not determined on the deposit probes since the analysis method would include deposit ring material.

Gaseous HCl and SO_2 were measured in the flue gas after the economiser. An extracted flow of the flue gas was bubbled through a solution of 0.1 M NaOH(aq) and 0.3 % H_2O_2(aq). The solution was analysed afterwards to provide average concentrations over the 2 h sampling period. Continuous measurements of CO_2, CO, and NOx, were done by FTIR (Fourier Transform Infrared spectrometry).

4.6.2 Laboratory experiments

The small-scale experiments were carried out in a laboratory fluidised bed reactor (see schematic overview in Figure 24). The reactor is made of quartz glass with an inner diameter of 60 mm and a length of 1.2 m. The reactor is placed in an electrically-heated oven with three individual temperature zones (up to 1,100°C). The fluidised bed rests upon a porous plate in the middle of the glass reactor. The bed consists of 180 g cleaned quartz sand where 90 % of the particles have a diameter between 0.1 and 0.3 mm. The inlet and outlet of the reactor is made of water cooled metal flanges attached to the glass reactor at the bottom (inlet) and at the top (outlet). The fluidising gas, a mixture of nitrogen and air, is controlled by mass flow regulators.

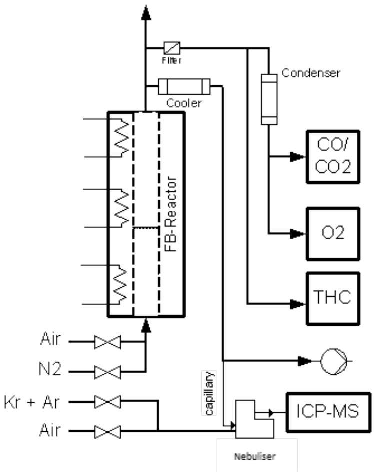


Figure 24. Laboratory set-up, schematics (paper VI).

The flue gas extracted at the top of the reactor was split between an on-line ICP-MS, and other gas analysing equipment (O_2, CO, CO_2, and total hydrocarbons). Before entering the gas analysing instruments, the flue gas passed through a heated ceramic filter and a condenser.

The flue gas diverted to the ICP-MS did not pass the heated filter; instead the gas was cooled and a sample was drawn through a capillary to a nebuliser, driven by a constant flow of Ar. The nebuliser controls the dosage of aerosol sample into the reactor. A controlled flow of Kr was used as an internal standard in the ICP-MS.

Single fuel pellets were dropped into the reactor from the top, after which the concentrations of the alkali metals and Zn in the flue gas were monitored online. The waste pellets used were made out of MSW collected from the full-scale boiler.

The results from the ICP-MS are presented as a relative mass weighted concentration $C_{x,rel}$ calculated from:

$$C_{x,rel} = \frac{1}{m} \frac{S_x}{S_{Kr}} \frac{F_{Kr}}{F_{rg}} \qquad \text{(Eq-7)}$$

where m is the mass of the fuel sample burned, S_x and S_{Kr} are the mass weighted signals from the instrument for element x and Kr respectively, and F_{Kr} and F_{rg} are the gas flows of Kr and flue gas to the instrument. In order to provide quantitative results, $C_{x,rel}$ should be multiplied with a constant that depends, among other things, on the element being studied. The values of such constants have not been determined in this study, implying that the results presented are qualitative values, proportional to the actual concentration.

4.6.3 Thermodynamic equilibrium calculations

The fuel compositions determined in the study for all three cases (RBT, Ref, and laboratory-scale) were used as input for the calculations in addition to air to achieve an air-to-fuel ratio of $\lambda=0.7$ for reducing conditions and $\lambda=1.4$ for oxidising conditions. Studies have shown that ash-forming matter can be divided in either reactive or inert ash-forming matter [125]. For example, silicates are usually considered less reactive whereas soluble alkali, Cl, and S are considered to be very reactive and are usually easily volatilised and prone to form volatile species. To be able to determine the distribution of inert and reactive elements a combination of standard fuel analysis, chemical fractionation, and literature information can be used. No further analysis was performed on the samples in this study but based on literature information a simplified calculation excluding the elements Mg-Fe-Al-Si was performed. When assuming these elements to be inert, the calculations can be used to study the behaviour of the alkali metals, Pb, Zn, and Ca compounds.

4.6.4 Results and discussion

The measurements of the two full-scale tests were made on separate days, one week apart, to minimise any memory effects in the bed. Fuel samples were extracted from the fuel feeder a few times daily during the measurements.

A higher concentration of HCl was detected in the flue gas during the RBT-case. The increase of gaseous HCl may be related to less alkali being released from the bed, but it could possibly also be an effect of temperature-dependent chemical reactions involving S-capture in the bed by Ca, which is abundant in the ash. If less S is captured by Ca in the bed, more sulphur will be available for other reactions, as with alkali metals, for example, resulting in reduced formation of alkali chlorides.

4.6.4.1 Particle samples

A comparison of the particle size distributions shows that the concentration of submicron particles (< 1 µm) decreased when operating the boiler with a reduced bed temperature, while the supermicron particles (> 1 µm) increased, see Figure 25. The increase in the coarser particles in the RBT case is not concluded, but it could be related to less agglomeration tendencies of the bed material at a reduced bed temperature.

In Figure 25 two size fractions are encircled: "fine" and "coarse". These samples were chemically analysed. Since O and C are not determined in the chemical analysis and it is plausible that they are present in the particle samples due to oxide and carbonate formation, there is no perfect balance between cations and anions. As expected from the chemical analysis, higher concentrations of alkali metals and Zn were detected in the fine particles, predominantly formed by condensation in the gas phase. The coarser particle fraction contained more Al, Ca and Mg. The same increase can be seen for the Pb content. Furthermore, the fine fraction from the RBT-case contained a slightly higher concentration of Cl than that found in the reference case. However, the total concentration of fine particles in the flue gas decreased, which means that the total concentration of particle-bound Cl decreased in the flue gas.

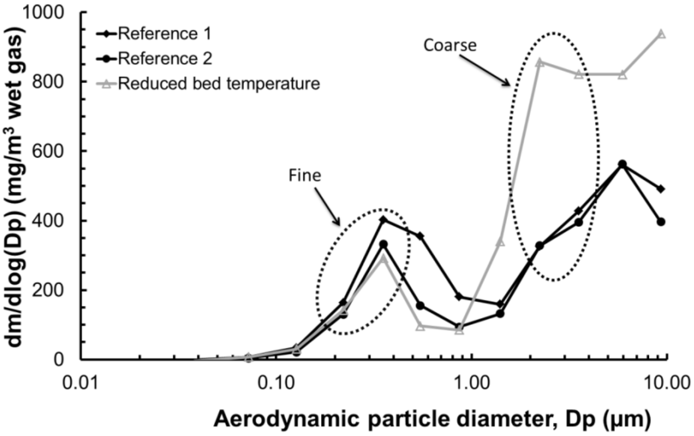


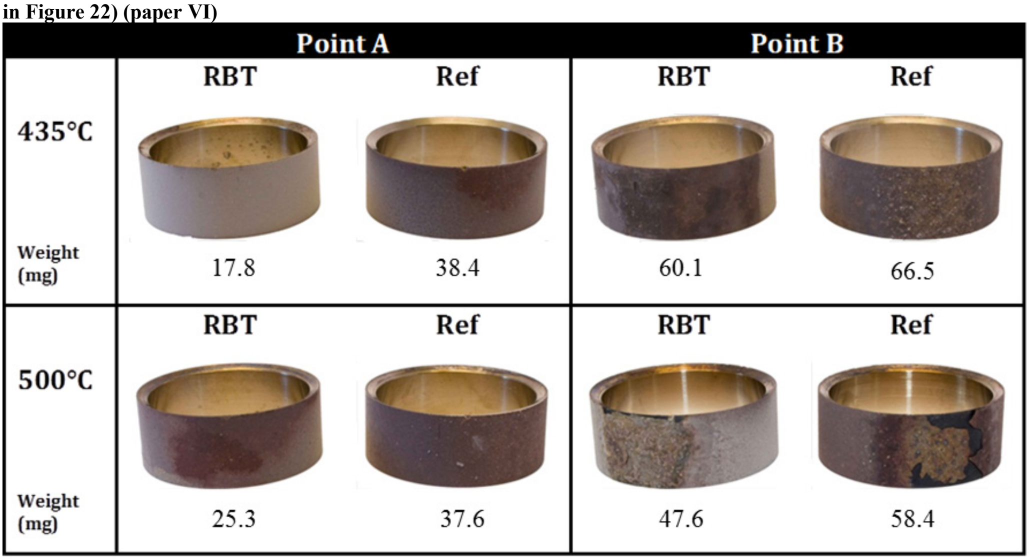
Figure 25. Measured particle size distributions using DLPI upstream of super heaters. The y-axis presents the Dp (aerodynamic particle diameter) in mg/m^3 (paper VI).

4.6.4.2 Deposit probe measurements

All deposit probe exposures were made for two hours and no soot blowing was carried out during the tests. Photos of the windward side of the deposit probes and the gained masses of the rings are presented in Table 19. The gained masses are recalculated into deposit growth rates in Figure 26 and Figure 27, in which the chemical compositions are also presented. The bars are balanced with an unaccounted part of the deposit ("others") referring to unanalysed elements, mostly oxygen but to a minor extent also other elements (P, Al, Mn, Ti, Ba, Cu, and Pb). It is notable that Cl is lower in all RBT cases when looking at comparable temperatures and positions. On average, the deposit growth decreased by 20 %, when the bed temperature was reduced.

During the RBT case the alkali content was reduced by approximately 25 %, while the S and the Ca contents increased compared to the reference case. In addition, also the Zn content decreased by approximately 25 %. Generally, the S/Cl ratios of the deposits increased when the boiler was operating with RBT.

Table 19. Photos and gained weight of sample rings after exposure at the superheaters in two different points (P1 and P2 in Figure 22) (paper VI)



	Point A		Point B	
	RBT	Ref	RBT	Ref
435°C Weight (mg)	17.8	38.4	60.1	66.5
	RBT	Ref	RBT	Ref
500°C Weight (mg)	25.3	37.6	47.6	58.4

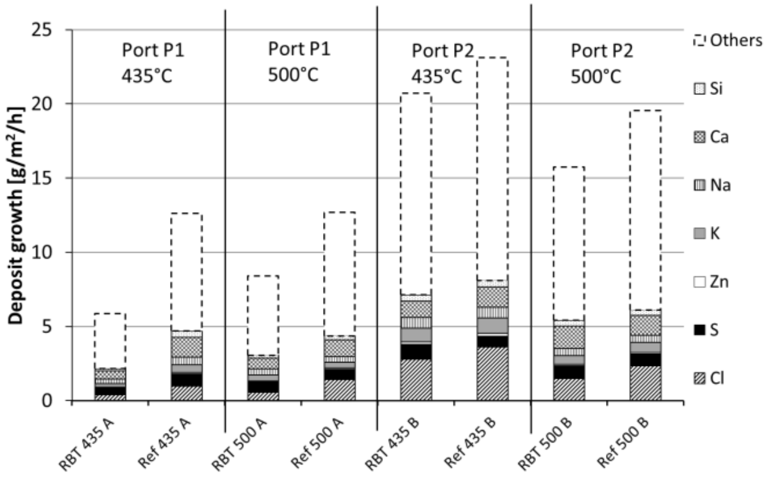


Figure 26. Deposit growth at superheaters (the whole bars). The different modes of boiler operation compared in pairs by position and material temperature (paper VI).

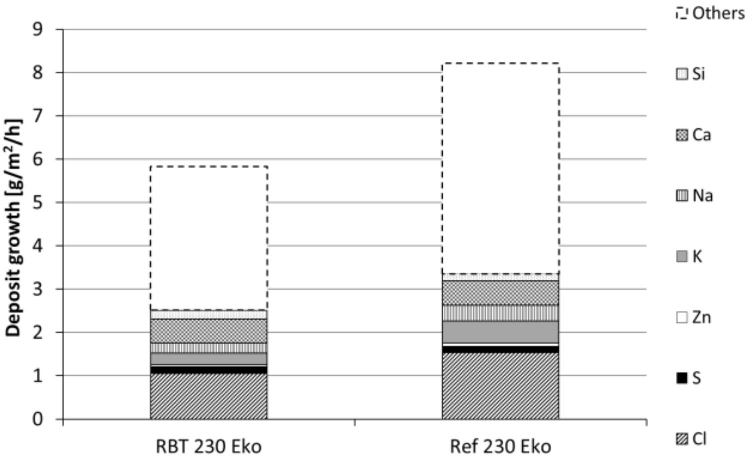


Figure 27. Deposit growth at the economiser (the whole bars). The content of the major elements in the deposit are shown as fractions of the bar (paper VI).

4.6.4.3 Bottom ash, cyclone ash, filter ash, and return sand

A visual inspection of the bottom ashes, Figure 28, shows that the Ref bottom ash contains a lot of small agglomerates and pieces of glass which has melted on the surface, allowing smaller sand particles to stick to it. The bottom ash from the RBT case does not contain agglomerates and the glass fragments had no sand particles stuck to them. Obviously, the glass did not become sticky under RBT conditions.

Figure 28. Photos of bed ash for the two different modes of operation of the boiler, Left: Reduced bed temperature case, Right: Reference case with agglomeration (paper VI).

Chemical analyses of the ashes show that the Cl concentration increases in the bottom ash and the recycled sand during the RBT case while it was unchanged in the ash from the empty gas pass and decreased in the ash collected both in the cyclone and the textile filter.

An enrichment of alkali chlorides in the bed could increase the risk of bed agglomeration but, on the other hand, the low bed temperature decreases the sintering tendencies of the bed. Another observation when looking at a longer perspective was that the sand consumption of the plant could be reduced by roughly 25 % when running the boiler under RBT conditions. This was a direct effect from the reduced sintering tendencies of the bed, resulting in less sand leaving with the bottom ash.

4.6.4.4 Laboratory-scale experiments

Experiments with single waste pellets, in the lab reactor (Figure 24), were performed to study the effect of varied reactor temperature on the release of alkali metals to the flue gas. During these tests, the reactor was operated with an atmosphere of 5 % O_2 in nitrogen. As an example of results from these tests, mass weighted signals of Na + K, and Zn measured by the ICP-MS instrument are shown in Figure 29. The horizontal axis shows the time from the start of each experiment, when a single waste pellet was dropped into the reactor. The vertical axis shows a mass weighted value of the signal from the ICP-MS instrument, scaled to the signal for the internal standard (here Kr) and to the weight of each pellet (in order of 0.8 g) as given by Equation (7). The lines illustrate the concentrations detected in three different test runs at different reactor temperatures.

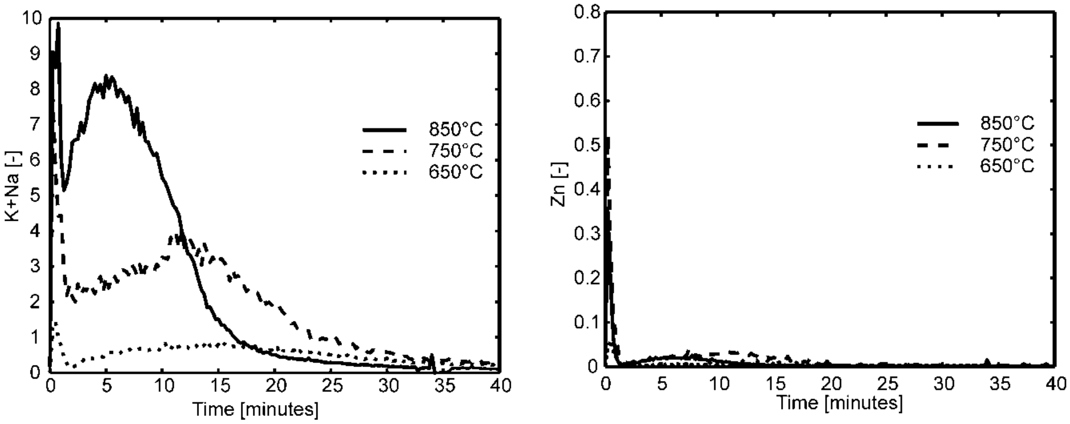


Figure 29. Accumulative measured mass released of to the left: alkali metals (Na + K) and to the right: Zn. Both graphs from combustion experiments of waste at 5 % O_2 and different temperatures (paper VI).

The initial peak, lasting about 1 minute, corresponds to the devolatilisation of the fuel, after which the char combustion occurs over a longer period. Alkali metals are released during both these stages of fuel conversion.

A comparison of the tests at 850°C and 650°C clearly illustrates that the amount of alkali metals released to the flue gas depends on the reactor temperature. In the case of Zn, there is a clear difference between the 850°C and 650°C, with a major decrease in the release of Zn. In contrast, for the 750°C the release of Zn continues over a longer time period and with more mass than in either of the other two cases. It should be mentioned, however, that the laboratory set-up is still under development in order to improve repeatability and to provide quantitative results. Nevertheless, the results of these experiments support the full-scale results, proposing that a lower bed temperature reduces the emission of alkali metals.

4.6.4.5 Thermodynamic equilibrium calculations

Calculations were performed for each of the three fuel compositions determined in the study. No major differences were noted between the three different fuels, behavioural trends were similar and therefore only one fuel is presented in figures, the fuel sampled during the reduced bed temperature case.

Under oxidising conditions (Figure 30) the calculations predict that the volatilisation of alkali chlorides increases with increasing temperature, confirming the hypothesis that a lower bed temperature would result in less release of potentially corrosive elements. At the same time as the alkali chlorides decrease with reduced temperatures the HCl formation increases, suggesting that more Cl forms HCl when less alkali is available from the fuel. The formation of gaseous $ZnCl_2$ takes place at much lower temperatures and increases with a maximum release peaking around 800ºC, then decreasing with temperatures above this. At temperatures higher than 1000ºC, gaseous Zn is the main volatile Zn-species. After 800ºC the formation of SO_2 increases significantly, being the dominant gaseous species close to 1000ºC while HCl decreases due to the formation of other chlorides, such as alkali chlorides.

For the same fuel mixture in reducing conditions there is an even higher concentration of alkali chlorides formed around 850°C, see Figure 31. Under these reducing conditions no SO_2 is formed and $ZnCl_2$ behaves similarly to how it does under oxidising conditions (too low concentration to be seen in the figure). However, there is a significant formation of gaseous Zn at 700°C with a sharp increase up to 800°C and then stabilising, showing a steady level at higher temperatures. The trends from the calculations suggest that reducing conditions give rise to the release of corrosive elements in higher concentrations than the oxidising conditions. They also show that a temperature drop from 850°C to 650°C significantly reduces the alkali chlorides in favour of the formation of HCl.

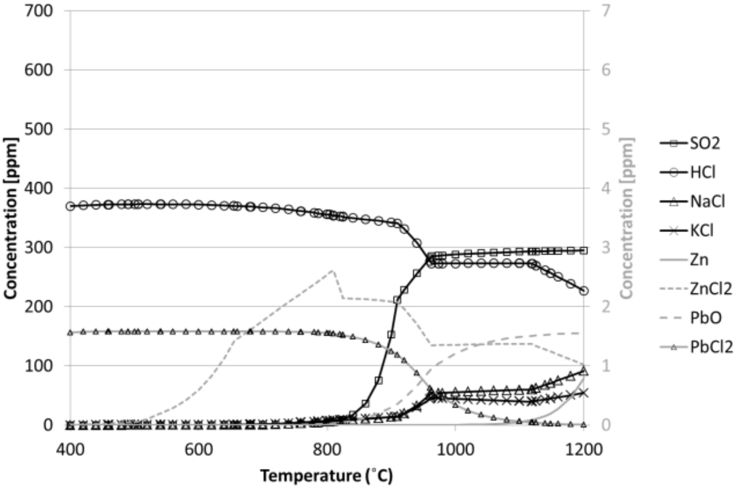


Figure 30. Predicted concentration of selected gaseous compounds at oxidising conditions with all elements included in the calculation. All compounds correspond to the primary y-axis on the left except the Zn-compounds that correspond to the secondary y-axis on the right. Under reducing conditions (b), Zn reaches a stable level of just over 40ppm at 800°C (above axis) (paper VI).

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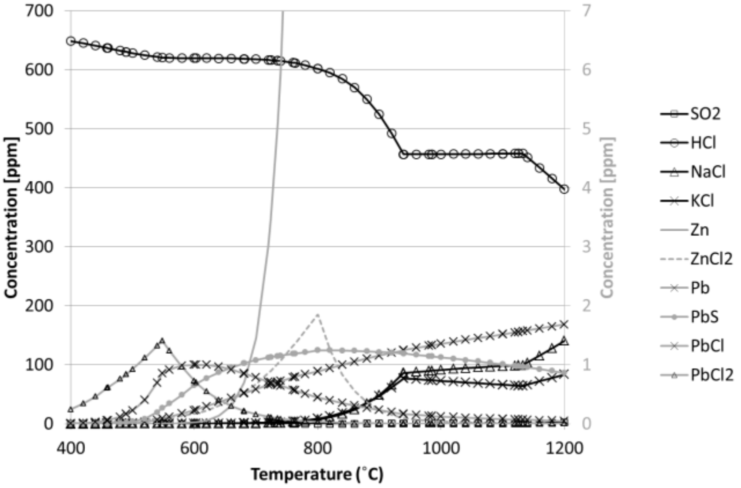

Figure 31. Predicted concentration of selected gaseous compounds at reducing conditions with all elements included in the calculation. All compounds correspond to the primary y-axis on the left except the Zn-compounds that correspond to the secondary y-axis on the right. Under reducing conditions (b), Zn reaches a stable level of just over 40ppm at 800°C (above axis) (paper VI).

The simplified calculations exclude Si, which then prevents the formation of alkali silicates. This affects the calculations in that alkali is now available for reaction with chlorine, inhibiting domination of gaseous HCl. This is visible in Figure 32 (please note the difference in scale of the secondary y-axis compared with Figure 30 and Figure 31) where the HCl concentration stays rather low throughout the temperature range. However, at lower temperatures the alkali chlorides are in solid state and gaseous alkali chlorides are increasing with temperatures as in the calculations with all elements, but being formed at lower temperatures and at higher concentrations. In addition to the alkali chlorides, alkali hydroxides are formed in noticeable amounts just under 900ºC and increase with temperature, which is also the behaviour of gaseous Zn. The calculation also shows the formation of PbO at 500ºC and stabilising from approximately 770ºC and upwards. In a reducing environment (Figure 33, please note the difference in scale of the secondary y-axis compared with Figure 30 and Figure 31) the increased formation of gaseous Zn and Na above 900ºC is significant. Around 1,100ºC the formation of alkali hydroxides sharply decreases and SO_2 is formed. Pb and PbS are formed in low concentration and fluctuate with one another from 500ºC and upwards. As in the calculations with all elements, the simplified calculations show that a reducing environment gives rise to a higher concentration of potentially corrosive substances.

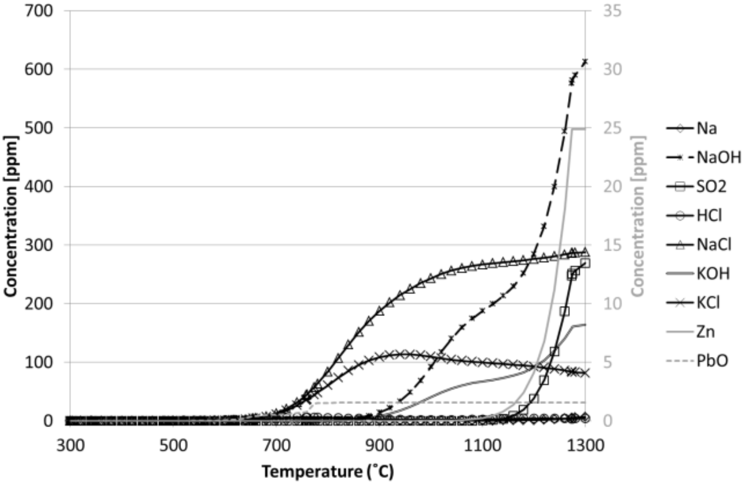

Figure 32. Predicted concentration of selected gaseous compounds under oxidising conditions for the simplified calculation. All compounds correspond to the primary y-axis on the left except Zn, and Pb compounds that correspond to the y-axis on the right. Under reducing conditions (b), Zn reaches a stable level of just over 40ppm at 780°C (above axis) (paper VI).

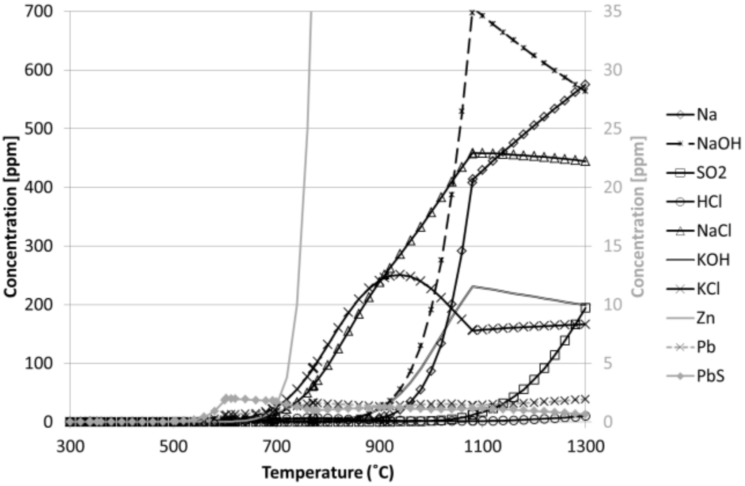

Figure 33. Predicted concentration of selected gaseous compounds under reducing (b) for the simplified calculation. All compounds correspond to the primary y-axis on the left except Zn, and Pb compounds that correspond to the y-axis on the right. Under reducing conditions (b), Zn reaches a stable level of just over 40ppm at 780°C (above axis) (paper VI).

5 Conclusions

The work presented in this thesis is threefold, considering: different ways of characterising fuel, Zn and its presence and behaviour in combustion, and the effects due to reduction of the bed temperature in boilers. Chemical characterisation of waste fuels is an important tool for determining concentration and presence of chemical compounds that have impact on the combustion process. Furthermore, the possibility of determining the fossil carbon content in the waste fuels is of great importance as the EU is now starting to include Waste-to-Energy plants in the Emission Trading System, with Sweden as the first entrant country.

Two different sampling methods, one for grate-fired boilers and one for fluidised bed boilers, have been used for taking samples from full-scale commercial boilers geographically spread over the whole of Sweden. The samples were used for chemical analysis, such as analysis of ash-forming matter and trace elements, and analysis of ^{14}C to determine the fossil content. The results from ash-forming matter and trace element analyses have been used for thermodynamic equilibrium calculations. Also, the analyses have been used for mapping of chemical content, determination of seasonal variations, and to study the presence of certain elements of interest during combustion. In addition, sorting analyses have been performed to calculate fossil content and a software program doing fossil content calculations based on on-line data was evaluated. Alongside a characterisation of the Zn content in Swedish waste fuel, a laboratory-scale evaluation of ZnO, $ZnSO_4$, and $ZnCl_2$ was performed to study the thermal behaviour. The thesis also includes a study of the effects of a reduced bed temperature in both full-scale and small-scale fluidised bed boilers. The study included sampling of waste fuel, particles, deposits, and ash from different positions in the boiler to investigate whether a reduced bed temperature would lower the volatilisation of elements from the fuel that can affect the combustion process.

From the ^{14}C analyses it was concluded that about a third of the carbon in mixed Swedish waste (municipal solid waste and industrial waste collected at Swedish industry sites) is fossil. The two other methods (the balance method and calculations from sorting analyses), based on assumptions and calculations, gave similar results at the plants where they were used. Furthermore, the results indicate that the difference between samples containing as much as

80 % industrial waste and samples consisting of solely municipal solid waste was not as large as expected.

In the 12-month study where solid waste samples were taken from two commercial boilers (one grate-fired boiler and one bubbling fluidised bed boiler) the ultimate analyses, (C, H, N, S and O) show that the waste fuel composition was rather similar. As expected, there was a larger variation between the samples in the content of ash-forming elements, such as Na, K, and Cl, which affect the corrosion risk. Furthermore, trace metals were present in low concentrations and showed the widest relative variation. It is concluded here that repeatable fuel samples are necessary to get a good overview, as single samples can divert significantly from an average over a longer period. One notable seasonal change was that the waste fuel contained less ash during the summer months of June, July, and August. This is related to the change of fuel mixture to only consisting of municipal solid waste. This is also an important observation supporting the conclusion above about repeated samplings of waste fuel, where one sample will not take in possible seasonal (or other) variations. The grate-fired boiler had a larger spread of the ash forming material around the average value for this plant. This is explained by the fact that the fuel mixture was more heterogeneous since it was not pre-treated (shredded). The fuel treatment in the bubbling fluidised bed boiler not only fragments the fuel but also mixes the shredded fuel, thus homogenising the fuel.

The sampling of waste fuel also provided information on the presence of Zn in fuels and showed a relationship between the content of municipal solid waste and Zn content; high municipal solid waste content produces lower Zn content. When studying the correlations between Zn and other chemical elements no general pattern was observed when considering all waste mixtures. However, for three of the plants there was a clear correlation between Zn and other elements; in one plant there was a strong correlation with Cu, in another a correlation between Zn and Fe, and in the third a correlation between Zn and the following three elements: Mn, Pb, and As. This suggests that Zn together with these other elements often originate from the same waste fraction in these particular WtE plants. Furthermore, it is concluded that the different seasons do not appear to affect the Zn concentrations significantly.

Experimental results suggest that $ZnCl_2$ is unlikely to form deposits in a boiler due to its instability when molten, particularly in an oxidising atmosphere. In addition the study confirms the literature data and shows that $ZnSO_4$ and ZnO are less volatile than $ZnCl_2$ in temperatures up to about 700°C. $ZnSO_4$ decomposes around 680°C while ZnO is stable at much higher temperatures. The experimental findings also show that chlorination of ZnO to $ZnCl_2$ is possible at temperatures between 240 and 330°C when it is exposed to 500 ppm HCl. This also tallies with thermodynamic equilibrium calculations. It means that it is theoretically possible to form $ZnCl_2$ from ZnO. Furthermore, a TGA analysis of mixtures of $ZnCl_2$ and NaCl and KCl, respectively, shows that the melting temperatures are lowered with increasing $ZnCl_2$ concentration compared with those of the pure alkali chlorides. Furthermore, the results show that the presence of $ZnCl_2$ in combination with alkali chlorides increases the risk of corrosion, owing to the decrease in melting temperatures of the alkali chlorides when mixed with $ZnCl_2$.

A full-scale campaign investigating a reduced bed temperature in a bubbling fluidised bed boiler showed that by reducing the bed temperature, the sand consumption of the plant could be reduced by roughly 25 %. The measurements also showed that the number of submicron particles decreased and the fouling rate on deposit probes was reduced by about 20 %. The measured concentration of HCl in the flue gas increased as the bed temperature was reduced, while the SO_2 concentration remained almost unchanged. This may be a consequence of the reduced formation of alkali chlorides. In addition, results from the laboratory-scale tests illustrate a trend of reduced alkali emission from the fluidised bed with reduced temperature.

6 Future work

Continuous mapping and characterisation of waste fuels is necessary in order to be able to control and influence fuel quality as the demands on sorting and recycling of material from the waste stream in Europe hardens owing to targets for 2020 within the waste framework. By sorting out fractions like paper, plastics, and food waste many parameters that affect combustion will be changed. A decrease in heating value due to lower paper/plastic content could be expected but at the same time the moisture content will decrease due to the minimisation of food waste. By changing the composition of the fuel with these anticipated changes it is very likely that the fossil content will be affected as well. When excluding fractions of "young" material, such as food waste, the fossil content is likely to increase. To be able to keep the waste combustion within the European Emission Trading System for CO_2 the precision and availability of methods to measure the fossil content needs to improve and be continuously validated.

It is a possibility that the European waste market might increase the import/export of waste. Owing to many export regulations and transportation possibilities, it is fair to assume that most waste fractions exported/imported will be of RDF-type excluding, for example, food waste. How the waste fuel will be affected by this should be of interest for future studies.

Still of great importance, the sorting of electronic and hazardous waste will be further targeted in the future, both to recover materials and valuable metals, and to avoid the presence of unwanted elements in the boilers. The content of trace metals, such as Zn, will continue to be of great importance and the behaviour during combustion still requires study. How new future waste fuel mixtures develop will be of interest both for plant owners and plant designers.

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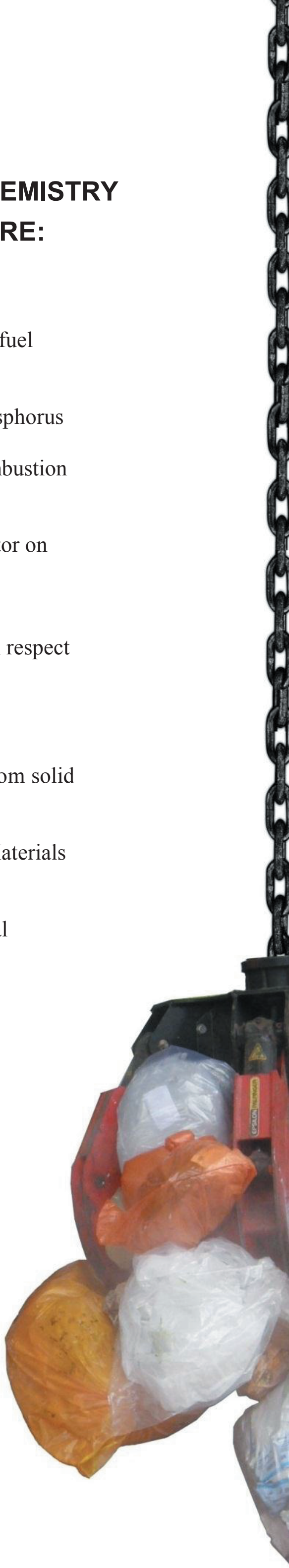

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PROCESS CHEMISTRY CENTRE

ISSN 1459-8205
ISBN 978-952-12-2979-4 (paper version)
ISBN 978-952-12-2980-0 (pdf version)
Åbo, Finland, 2013