Resource recovery from waste incineration residues

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Preface

The work presented in this PhD thesis was conducted at the Department of Environmental Engineering of the Technical University of Denmark (DTU) under the supervision of Associate Professor Thomas Fruergaard Astrup and the co-supervision of Senior Researcher Alessio Boldrin. The work was conducted from September 2011 to September 2014. Funds for the PhD were provided by the graduate school 3R (Residual Resources Research), AFATEK Ltd., Energinet.dk (project PSO-10627) and the Danish Research Council as a part of the IRMAR (Integrated Resource Management & Recovery) initiative.

The PhD thesis summarises the findings published in four scientific journal papers, each of which is referred to throughout this study by their Roman numerals (e.g. "Allegrini et al. (**I**)").

I **Allegrini, E.**; Boldrin, A.; Jansson, S.; Lundtorp, K.; Astrup, T.F. Quality and generation rate of solid residues in the boiler of a waste-to-energy plant. *Journal of Hazardous Materials 2014, 270, 127-136.*

II **Allegrini, E.**; Maresca, A.; Olsson, M.E.; Holtze, M.S.; Boldrin, A.; Astrup, T.F. Quantification of the Resource Recovery Potential of Municipal Solid Waste Incineration Bottom Ashes. *Waste Management 2014, 34(9), 1627-1636.*

III **Allegrini, E.**; Butera, S.; Kosson, D.S.; Van Zomeren, A.; Van der Sloot, H.A.; Astrup, T.F.; Life cycle assessment and residues leaching: importance of parameter, scenario and leaching data selection. S*ubmitted to Waste Management.*

IV **Allegrini, E.**; Vadenbo, C.; Boldrin, A.; Astrup, T.F. Life Cycle assessment of resource recovery from municipal solid waste incineration bottom ash. *Submitted to Journal of Environmental Management.*

In addition, and not included in this thesis, during this PhD study four internal reports for AFATEK Ltd. and Energinet.dk were concluded, as well as five contributions in the proceedings of international conferences.

In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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I am very happy to be part of such a friendly and inspiring community as our *Waste Group* and I am particularly grateful to Laura for translating the Danish summary and to Alberto for the great help he gave me during the first year.

I would also like to thank Bertrand, the poppels and my friends (vicini e lontani), and especially, I would like to say a big THANKS to Stefania and Veronica who took care of me since the very first working day, as great colleagues and even better friends.

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Summary

Municipal solid waste incineration (MSWI) is nowadays an important waste treatment technology and results in the production of approximately 40,000,000 Mg of solid residues every year in Europe. Approximately 90% of the residue is bottom ash (BA), while the rest includes boiler ash, fly ash and residues from flue gas cleaning systems. MSWI residues have the potential to be an important resource, as they are enriched by valuable materials present in the residual waste flow sent to incineration and has characteristics that make it suitable for reuse in the construction sector. Recovery activities addressing MSWI solid residues can increase the sustainability of waste-to-energy (WtE) systems, and hence they are addressed in this thesis which focuses on BA and boiler ash.

Currently, most WtE plants implement sorting systems (more or less advanced), in order to recover scrap metals from BA. However, the quantification of the potential content of scrap metals in BA and recovery efficiencies is often not a clearly defined process. This study combines BA sample characterisation, material flow measurements at a full-scale recovery facility and the elaboration of historical data on plant operations, to quantify potential scrap content in BA and related recovery efficiencies. The potential content of non-ferrous (NFe) and ferrous (Fe) scrap resulted in 2.2% and 7.2% of wet BA, respectively, while recovery efficiencies were 61% for NFe and 85% for Fe scrap.

After recovery activities, the remaining fraction of BA can be utilised in construction works as aggregate because of its physical properties and the low leachability of harmful compounds. Any other solid residues from MSWI are generally classified as hazardous materials and are often disposed of after stabilisation processes. Boiler ash was investigated in order to assess the possibility of increasing material recovery by managing specific ash fractions together with BA. Boiler ash was sampled at a WtE plant at ten points along the energy recovery system of the plant. However, based on the concentration and leachability of substances of environmental concern in the samples, the recovery of selected fractions in this instance could not be supported.

BA used in construction works after metal recovery still holds precious and valuable metals which could be recovered using methods from the metallurgical sector. To assess current losses of valuable metals, the total contents of a wide range of elements were analysed for individual grain size

fractions of BA and boiler ash samples. Most elements could be detected in the samples; however, only a few elements such as Cu and Zn were found in concentrations suitable for recovery. Moreover, the enrichment of elements between different boiler ash and BA fractions was, overall, negligible.

To assess environmentally the recovery of resources from BA (i.e. scrap metals and aggregates), a life cycle assessment (LCA) was used. The holistic nature of the LCA methodology provides an overview of the impacts and benefits of a system, revealing possible burdens shifting or breakeven points. With the direct emission of metals into the environment through leaching being the main concern of utilising MSWI BA, the importance of leaching in LCA was evaluated. A large set of leaching data was used as an input into three LCA studies of a waste management system with increasingly large system boundaries. Specifically for leaching, crucial parameters such as the liquid-to-solid ratio, pH and metal speciation varied. The results showed that toxic impacts from leaching could not be disregarded in any of the LCA scenarios considered, and they were dominant when the sole utilisation phase of BA was included.

The LCA of a MSWI BA recovery system was carried out based on a full-scale MSWI BA treatment system. Ten scenarios were defined in line with increasing recovery efficiencies for scrap metals (from zero recovery of NFe scrap to efficiencies over 90%), various utilisation options for the treated BA were considered (i.e. disposal in a landfill and being used as aggregate in road construction or concrete) and leaching emissions were based on experimental results. The quality of the recovered scrap metals was of crucial importance for the LCA results. Particularly for aluminium scrap, recovery efficiencies were complemented by the quality of the scrap in terms of oxidation levels and yield at the recycling facility. Recycling of aluminium scrap resulted in large benefits from a global warming perspective because of avoiding the production of primary aluminium. However, the assumption of 100% substitution of primary aluminium with incineration scrap was brought into question, and the substitution ratio was changed accordingly. The results showed that, with current recovery efficiencies, the recycling of low quality scrap might outweigh the benefits of metal recycling against the effort involved in sorting, transporting and upgrading the scrap.

Dansk sammenfatning

Affaldsforbrænding er en vigtig affaldsbehandlingsteknologi i mange lande og resulterer i en årlig produktion af restprodukter på ca. 40,000,000 tons per år i Europa. Omtrent 90% af restprodukterne udgøres af slagge, mens de resterende asker inkluderer kedelaske, flyveaske og reaktionsprodukter fra røggasrensningen. Indholdet af værdifulde metaller i affaldet til forbrænding medfører, at restprodukterne har et stort potentiale som ressource, ligesom den mineralske/inerte del af askerne er velegnet til udnyttelse ved bygge- og anlægsarbejder. Øget genanvendelse og udnyttelse af restprodukter fra affaldsforbrænding kan øge den miljømæssige bæredygtighed af forbrænding. Denne afhandling har dermed fokus på udnyttelsen af disse restprodukter, specifikt på slagge og kedelaske.

De fleste forbrændingsanlæg inddrager i dag sorteringssystemer (som er mere eller mindre avancerede) til udsortering og genanvendelse af metalskrot fra slaggen. Kvantificeringen af det potentielle indhold af metalskrot i slaggen samt genanvendelseseffektiviteten er dog sjældent klart defineret. I denne afhandling kombineres karakterisering af slaggeprøver, målinger af materialestrømme i et fuldskala slaggesorteringsanlæg samt historiske data for anlæggets drift med kvantificering af ressourcepotentialet i slaggerne og kvantificering af de tilhørende sorteringseffektiviteter. Resultaterne dokumenterede et indhold af ikke-magnetisk og magnetisk metal på henholdsvis 2,2% og 7,2% per våd vægt af slaggen. Sorteringseffektiviteterne var 61% for ikke-magnetisk og 85% for magnetisk metalskrot.

Efter udsortering af metal er slaggens fysiske og tekniske egenskaber velegnede til anvendelse som konstruktionsmateriale i bygge- og anlægsarbejder, ligesom udvaskning af problematiske stoffer (f.eks. tungmetaller) typisk er lavere end for frisk slagge. De øvrige faste restprodukter (kedelaske og flyveaske) fra affaldsforbrænding klassificeres typisk som farligt affald og kræver derfor særlig håndtering. Kedelasken er dog ikke nødvendigvis ligeså problematisk som flyveasken, og asken blandes i visse tilfælde sammen med slaggen. For at vurdere muligheden for at øge materialegenanvendelsen, blev kedelaskens kvalitet og ressourcepotentiale undersøgt specifikt. Prøver af kedelaske blev udtaget ti steder langs med kedlen på et affaldsforbrændingsanlæg. Baseret på koncentrationer samt udvaskningen af problematiske stoffer i askeprøverne, blev det dog konkluderet at selv udvalgte fraktioner af kedelasken ikke bør sammenblandes med slagge.

Den mineralske fraktion af slaggene, anvendt til bygge- og anlægsarbejder, kan stadig indeholde værdifulde ædelmetaller, idet slaggesorteringen ikke er 100% effektiv. Disse metaller kan potentielt stadig udvindes og genanvendes ved brug af metallurgiske processer. For at vurdere de nuværende tab af værdifulde metaller, blev det totale indhold af en lang række elementer analyseret i individuelle kornstørrelsesfraktioner af slaggen, men også af kedelasken. De fleste elementer kunne detekteres i prøverne; det var dog kun få elementer, såsom Cu and Zn, som kunne genfindes i koncentrationer af relevans for videre udvinding. Der blev ikke identificeret enkeltstående kornstørrelsesfraktioner af slagge og kedelaske, hvor specifikke elementer var betydeligt beriget.

For at vurdere de miljømæssige aspekter af genanvendelsen af ressourcerne i slagger kræves en helhedsvurdering, som inddrager alle trin i genanvendelsen. Livscyklusvurdering (LCA) blev anvendt som værktøj til dette. LCA muliggør en systematisk opgørelse af miljøpåvirkninger og -gevinster i relation til et ressourcesystem, og muliggør desuden identifikation af kritiske aspekter og eventuelt break-even mellem en samlet miljøbelastning og -gevinst. Udvaskning er generelt den primære bekymring ved udnyttelse af slagge fra affaldsforbrænding, da udvaskningen medfører en direkte emission af metaller til det omgivne miljø. Betydningen af udvaskning i relation til LCA har tidligere haft relativ lille bevågenhed, men blev her specifikt evalueret. En stor mængde data fra forskellige udvaskningstest blev anvendt som input til LCA modellering af en række affaldssystemer, som inkluderede genanvendelse af slagger. Forskellige systemafgrænsninger blev undersøgt og en række kritiske parametre blev varieret: væske/faststof forhold, pH og metal speciering i udvaskningsmediet. Resultaterne viste, at de toksiske påvirkninger fra udvaskningen potentielt kan have betydning for den samlede miljøvurdering og ikke bør udelades fra LCA modellering af affaldssystemer, hvor genanvendelse og udnyttelse af restprodukter er medtaget. Dette er særligt vigtigt ved fokus er på udnyttelse f.eks. af slagge til bygge- og anlægsarbejder, hvor udvaskningen dominerer LCA resultaterne.

Livscyklusvurdering blev anvendt til vurdering af fuldskala systemer til behandling af slagge fra affaldsforbrænding. Ti forskellige scenarier med stigende genanvendelseseffektivitet for metalskrot (fra ingen genanvendelse af ikke-magnetisk metalskrot til en effektivitet på over 90%) blev undersøgt. Forskellige muligheder for håndtering af den tilbageværende mineralske del af slaggen blev vurderet (deponering samt udnyttelse af slaggen som fyldmateriale i vejanlæg eller tilsætning til betonprodukter). Emissioner fra udvaskning i de forskellige håndteringsscenarier blev baseret på eksperimentelle resultater. Kvaliteten af det genanvendte metalskrot var yderst vigtig for resultaterne af LCA'en. Særligt for aluminium var den samlede effektivitet i genanvendelsen afhængig af metallets kvalitet, graden af oxidation og udbyttet fra metaloparbejdningen. Genanvendelse af aluminium bidrog med store miljøgevinster, da miljøbelastende primærproduktion af aluminium dermed undgås. Betydningen af substitutionsraten (antagelsen f.eks. om at det udsorterede aluminiumskot kan erstatte primærproduktion i forholdet 1:1) blev undersøgt. Resultaterne viste her, at hvor aluminiumgenanvendelsen generelt medfører store miljøgevinster, så er det ikke nødvendigvis miljømæssigt fordelagtigt at oparbejde metalskrot af meget lav kvalitet.

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Abbreviations

ADm	Abiotic depletion of mineral resource
APC	Air pollution control
BA	Bottom ash
CF	Characterisation factor
CLP	Classification, labelling and packaging of substances and mixtures
CTU	Comparative toxic unit
DOC	Dissolved organic carbon
ECS	Eddy-current separator
ET	Ecotoxicity to freshwater
EAA	European aluminium association
Fe	Ferrous metal
FU	Functional unit
GWP	Global warming potential
HNFe	Heavy non-ferrous metal
HTc	Carcinogenic human toxicity
HTnc	Non-carcinogenic human toxicity
ISS	Inductive sorting system
L/S	Liquid-to-solid ratio
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LME	London metal exchange
MFA	Material flow analysis
MSWI	Municipal solid waste incineration
NFe	Non-ferrous metal
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PGM	Platinum group metals
REE	Rare earth elements
RSD	Relative standard deviation
SFA	Substance flow analysis
SS	Stainless steel
TC	Transfer coefficient

WMS	Waste management system
WtE	Waste-to-energy
ww	Wet weight
XRF	X-ray fluorescence
XSS	X-ray sorting system

1 Introduction

1.1 Background

Municipal solid waste incineration (MSWI) is a mature and widespread waste treatment technology (Hulgaard and Vehlow, 2010; Eurostat, 2011a; Miljøstyrelsen, 2012) noted particularly for waste volume reduction and pathogen destruction. Energy recovery, the implementation of efficient technologies for flue gas cleaning and a new regulatory framework (European Commissions, 2008a) have driven the expansion of incineration capacity, which has seen steady growth in the last 20 years in Europe (Eurostat, 2001a).

During the last couple of decades, waste incineration has changed from a purely sanitary technology to an industrial technology, the major focus of which is the maximisation of energy and material recovery from waste. State-of-the-art incineration plants can achieve thermal efficiency above 90% (Hulgaard and Vehlow, 2010), and the resulting solid residues are either safely disposed of or utilised as secondary raw materials.

Solid residues from incineration processes include ash from the furnace (i.e. bottom ash, BA) and ashes and residues removed during flue gas cleaning. BA is generally classified as non-hazardous waste (European Commission, 2000), and it is either disposed of in a landfill or utilised as construction material (Crillesen and Skaarup, 2006). Other residues, such as boiler ash, fly ash and air pollution control residues, are often classified as hazardous materials and thus disposed of prior stabilisation treatment. Nonetheless, these residues are also utilised (Astrup et al., 2008).

MSWI residues have been investigated extensively for their potential release of toxic substances into the environment (Kosson et al., 1996; Chandler et al., 1997; Van der Sloot et al., 2001; Hjelmar, 2003). However, they also hold valuable materials, from scrap metals to mineral materials, which potentially could be recovered and used as secondary raw material. This resource potential in MSWI residues has recently become a source of interest for both economic and environmental reasons. In the scientific literature, an increasing number of studies have addressed the resource potential in MSWI residues, especially from the point of view of valuable metals (Hu and Rem, 2009; Muchova et al., 2009; Fedje, 2010; Grosso et al., 2011; Morf et al., 2013). Full-scale recovery systems are also being implemented, in order to recover an extensive and wide range of metals (Rem et al., 2004; De Vries et al., 2012; ZAR, 2014).

The current waste hierarchy (European Commission, 2008a), and the growing focus on resource availability (European Commission, 2010), has led to increasingly ambitious environmental targets for waste prevention and recycling (Miljøministeret, 2013). Post-incineration recovery and the recycling of materials is possible; however, recovery at this stage is not quantified by waste statistics, and optimising resource recovery from MSWI residues is the new primary objective for waste-to-energy (WtE) plants – not only from an economic perspective, but also for political and social acceptance.

Detailed and reliable data on resource in MSWI residues are needed to support residue management design. However, increasing the recovery of resource from MSWI residues requires additional efforts in terms of energy and materials, which could in turn result in increased burdens on the environment and eventually outweigh the environmental benefits of recovery. Hence, an overview of the system throughout its life cycle is necessary, in order to avoid burdens shifting and to support environmentally-sound decisions.

1.2 Aim of the thesis

The aim of this work is to provide a quantitative basis for assessing resource recovery from MSWI residues. BA will be the focus of the thesis; however, boiler ash will also be addresses as it can be mixed with BA for additional recovery. The specific objectives of the thesis are:

1) The quantification of resource potential in BA and boiler ash.

2) The quantification of current resource recovery and losses from BA and boiler ash, and the identification of possible improvement opportunities.

3) The quantification of the potential release of toxic substances into the environment from BA and boiler ash in view of their utilisation.

4) To carry out an environmental assessment of resource recovery from MSWI BA, by using life cycle assessment (LCA).

1.3 Structure of the thesis

This PhD thesis consists of a synopsis followed by four journal papers addressing in detail specific aspects of the topic. The synopsis is divided into four main sections in which the abovementioned objectives are addressed by summarising the findings of the journal papers.

- **Section 2** defines MSWI residues and the current management system and MSWI BA and boiler ash are selected for further investigation. The case study WtE plant and recovery system are described and an overview of the BA and boiler ash samples collected for experimental studies is presented [journal papers **I-II**].
- **Section 3** reports on the methods involved in and the results for the BA and boiler ash sample characterisation from a resource perspective. Resource potential in terms of scrap and valuable metals is then quantified in the BA and boiler ash samples and current recovery efficiencies are quantified [objectives 1-2; journal papers **I-II**].
- **Section 4** addresses BA and boiler ash as mineral resources that can be used as construction material. Material classification is discussed and the potential release of toxic substances is investigated [objectives 2-3; journal papers **I**, **II**, **III**, and **IV**].
- **Section 5** analyses resource recovery from MSWI BA from a LCA perspective, the results of which are applied to MSWI BA recovery systems and then discussed. Relevant aspects of the LCA methodology applied to the case study are identified and discussed, and recommendations are provided [objective 4; journal papers **III-IV**].

2 Waste incineration residues

2.1 The material

MSWI residues consist of residues extracted from the bottom part of the incineration furnace (bottom ash, BA), ash accumulating in the energy recovery section (boiler ash) and ash and residues formed and collected in the flue gas cleaning system (fly ash and air pollution control (APC) residues). Collectively they represent approximately 20 to 30% by weight of the waste input into an incinerator (Hjelmar et al., 2010). Based on the amount of waste incinerated in Europe (Eurostat, 2011b), a yearly production of up to 40,000,000 Mg of MSWI residues is estimated.

2.1.1 Bottom ash

BA accounts for 85 to 95% of MSWI residues (Chandler et al., 1997), representing 15% up to the 30% by weight of input waste (Hjelmar et al., 2010). BA consists mainly of coarse, non-combustible materials (such as ash, ceramics, glass, scrap metals), unburned materials and fine particles mainly collected from under the furnace grate (grate siftings), thus including fine materials and metals which have melted during the incineration process. Moisture content depends on the quenching technology applied at the incinerator and is approximately 25-30%w/w (the ratio between water weight and the weight of the wet BA) (Chandler et al., 1997).

Lithophilic elements in the waste (e.g. Al, Ba, Ca, Cr, Cu, Fe, K, Na, Ni and Mg) tend to stay in BA; however, minor to trace concentrations of volatile metals such as As, Pb, Sb and Zn are also found (Wiles, 1996; Chandler et al., 1997). Because of its physical properties and relatively low content of potentially harmful compounds, BA is often utilised in construction works (Crillesen and Skaarup, 2006; Van der Wegen et al., 2013), as long as it complies with country-specific environmental criteria (Hjelmar et al., 2013b).

BA is a highly alkaline material, with an initial pH value of approximately 12, and it is mainly controlled by the dissolution of $Ca(OH)_2$. At the initial pH level, the release into the environment of Cu, Pb and Zn is of major concern for the application of BA in construction works. However, weathering and ageing can effectively reduce the leaching of these metals into the environment. Because of the rapid quenching of BA after the incineration process, it is unstable under atmospheric conditions. Thus, when exposed to atmospheric agents, natural weathering reactions occur and change the mineralogical characteristics of the material (Meima and Comans, 1999; Chimenos et al., 2000). Due to carbonation reactions pH drops, and this, together with the neoformation of secondary minerals, affects the release of trace metals.

2.1.2 Other MSWI residues: boiler ash, fly ash and APC residues

Boiler ash, fly ash and APC residues are fine-grained residues consisting of ash particles in flue gas and reaction products from the neutralisation of acid components in the flue gas. Readily soluble salts and volatile metals condensing on ash particle surfaces are enriched in these residues, and they are therefore often classified as hazardous materials (European commission, 2000). Fly ash and APC residues, in general, are collected together at the WtE plant, treated and then disposed of (Astrup et al., 2008). Currently in Denmark, fly ash and APC residues are exported to Norway, to be stabilised and utilised for the neutralisation of waste acid, or to Germany, to be deposited/used in former or active salt mines as backfilling materials. Boiler ash is often collected together with fly ash and APC residues, while other management options such as mixing with BA are also found. Boiler ash represents the coarse fraction of ash particles transported by flue gas and can be up to 10% by weight of the input waste (Sabbas et al., 2003).

2.1.3 Resource in MSWI residues

MSWI residues contain two types of resources: metals and minerals. Metals are present in the residue in the form of scrap metals or as metals bound to the material matrix. Scrap metals are metals in metallic form, present as individual pieces in the residues. They are generally distinguished between ferrous (Fe) and non-ferrous (NFe) metals based on magnetic properties. Fe scrap is magnetic and magnetic separators are utilised in its recovery, while NFe scrap includes conductive metals characterised by low magnetic properties, examples of which include Al, Cu and Zn, as well some precious metals (e.g. Au, Pt). Stainless steel (SS) is often included in this category, as a large part of SS production consists of austenitic SS, which has non-magnetic properties. NFe scrap is sorted using eddy-current separators (ECS) which produce an alternating magnetic field inducing an opposite alternating magnetic field in the conductive material, which is then rejected proportionally to a ratio between metal conductivity and specific weight. In BA, the typical content of Fe and NFe is 7-15% and 1-2%, respectively (Grosso et al., 2011), but large variations in BA scrap content can be found, due to the strong correlation with input waste composition (Chandler et al., 1997). In other MSWI residues scrap metals are found in negligible amounts: a few studies have considered applying magnetic separation to boiler ash, but no satisfactory results have been achieved to date (e.g. De Boom et al., 2011). The recovery of Fe scrap from BA is common practice and high recovery efficiencies are achieved. NFe recovery is implemented to a lower extent, and recovery efficiencies vary considerably depending on the sorting system configuration (Crillesen and Skaarup, 2006; Muchová and Rem, 2006; Grosso et al., 2011; Heinrichs et al., 2012; ZAR, 2014).

Concerning metals or valuable substances not in scrap form, these can be found bound differently to the material matrix, e.g. oxides, hydroxides, metallic form, absorbed by $CaCO_3$ or other mineral phases (Fedje, 2010). However, it is generally difficult to identify their mineral phases, since metals of interest are present in the residues as minor or trace elements (Hykš, 2008). The recovery of such metals is specific to the individual metal and requires methodologies taken from the mining and metallurgical sectors (e.g. solvent extraction). These types of metals (e.g. Cu, Zn) are currently not recovered from MSWI BA, but applications are available for other MSWI residues. Several studies on fly ash have investigated the possibility of extracting metals such as Cu, Pb and Zn in view of their recovery (e.g. Vehlow et al., 1990, and Fedje et al., 2012); however, very few full-scale applications are currently in use. In Switzerland, though, the combination of the fly ash acid washing and recycling using the FLUWA and FLUREC systems (Schlumberger, 2010) allows for the recovery of 1,800 Mg of Zn per year (Meylan and Spoerri, 2014).

BA and the other MSWI residues also have resource potential as construction material. BA has been widely used as unbound aggregate in construction works (e.g. road bases, embankments) and increasingly in concrete production (Crillesen and Skaarup, 2006; Van der Wegen et al., 2013). However, pre-treatment of the material is necessary, for example to limit swelling processes due to Al oxidation or the formation of $Al(OH)_3$ gel (Pecqueur et al., 2001; Sorlini et al., 2011). Other uses for BA are under investigation as an additive in cement formulations (Bertolini et al., 2004; Onori et al., 2011), in the production of artificial aggregates (Jurič et al., 2006; Cioffi et al., 2011) and in mortar production (Saikia et al., 2008; Martens et al., 2010). Other MSWI residues have found very limited applications in the construction industry due to their hazardous nature; indeed, these residues are generally treated and then landfilled (Sabbas et al., 2003; Astrup et al., 2008). Nevertheless, many studies have investigated the utilisation of these residues in construction materials (Aubert et al., 2004; Del Valle-Zermeño et al., 2013), while some countries already allow this utilisation. For example, in the Netherlands, fly ash has been used as filler in asphalt for a number of years (Astrup et al., 2008).

2.2 Case study

Within the scope of this study, BA and boiler ash were characterised from a resource perspective. As such, material samples were collected and analysed, and the ensuing characterisation results are reported in the following chapters. One WtE plant and one BA treatment facility were selected for the case study, and sampling campaigns were carried out accordingly.

2.2.1 The BA recovery system

BA samples were collected at a Danish BA treatment facility managed by AFATEK Ltd., which receives BA produced by six WtE plants in Denmark. The system scheme is shown in Figure 1.

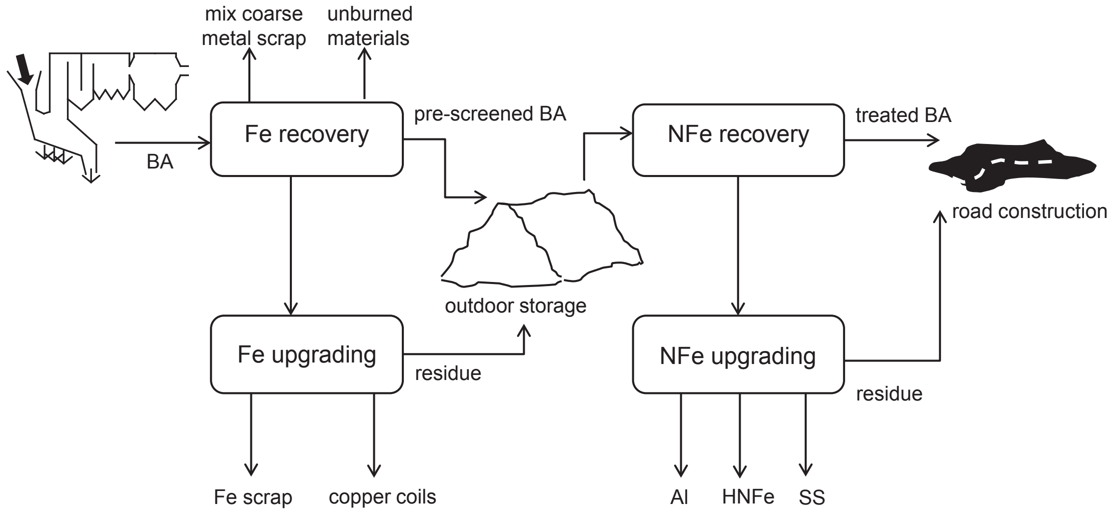

Figure 1: Schematic overview of the BA recovery system at AFATEK (BA: bottom ash; Fe: ferrous scrap metals; NFe: non-ferrous scrap metals; HNFe: heavy non-ferrous scrap metals; Al: aluminium scrap; SS: stainless steel scrap).

BA is produced at grate-based mass-burn WtE plants, and quench tanks are utilised for cooling the material, which is then transported to a treatment site and processed through the following steps:

- ***Fe recovery***: the material is screened with a 50 mm sieve, and the two resulting fractions (coarser and finer than 50 mm) go through magnetic separation in order to sort Fe scrap. The remaining coarse fraction is rich in inert materials, unburned materials (e.g. paper, textiles) and NFe scrap metal. Unburned materials and NFe scrap metals are manually sorted and respectively sent back to the incinerator or sold for recycling. The remaining inert material is crushed and recirculated into the Fe recovery unit.

- ***Fe upgrading***: Fe scrap sorted from BA in the first unit is upgraded. The scrap is loaded into a rotating drum followed by a 10 mm drum screen to separate extraneous material sticking on the scrap surface. The material then passes through two magnetic separators in series, purifying the scrap to a quality suitable for secondary steel production. The rejected material from the magnets is a scrap stream enriched in copper coils, which are then hand-sorted to recover the copper.
- ***Outdoor storage***: the fraction of BA below 50 mm output from the Fe recovery unit is stored in outdoor heaps approximately 5,000 Mg in weight for a few months. During storage, mild ageing and weathering occur, and the resulting release of toxic substances complies with Danish regulatory limits for waste materials utilisation in construction works (N. 1662:2010).
- ***NFe recovery***: after outdoor storage, the aged BA is screened to remove any fine fractions (approximately below 2 mm) which are not treated further. The remaining material is classified in three grain size fractions, and each separately undergoes sorting for NFe scrap by means of ECS and inductive sorting systems (ISSs). The fine BA and the remaining BA after ECS and ISS treatment are collected together in one output flow (treated BA) for further utilisation.
- ***NFe upgrading***: NFe scrap from the previous unit is transported to an indoor upgrading unit where the scrap is treated by a complex combination of ECS, ISS and X-ray sorting systems (XSS) to remove non-metallic particles. Clean scrap is divided into SS, light NFe (i.e. Al scrap) and heavy NFe (HNFe) scrap consisting of a mixture of copper, brass and other metals. Individual metal fractions are sold for secondary metal production.

Mineral residues from the scrap upgrading units are added up to the treated BA (material output from the NFe recovery section). The material is then sampled and analysed to verify compliance with environmental criteria set by the Danish Statutory Order N.1662:2010. After a quality check, the BA is utilised as aggregate in road construction.

BA samples

BA samples were collected from various points, together with AFATEK, over a one-year period (2011-2012):

- Thirty-seven samples of BA below 50 mm were taken after the pre-screening section (Fe recovery section).
- Ten samples of the total treated BA output were taken after the NFe recovery section.
- Twenty-three samples of the fine fraction were taken after the NFe recovery section.

Samples taken after the NFe recovery section were collected by manually intercepting the falling stream of fine BA bypassing metal recovery, and by means of an automatic sampler installed at the final output section of the system. Samples of pre-screened BA were mainly collected from temporary storage BA heaps. Sampling was done following the requirements set out in the Danish Statutory Order N.1662:2010, whereby 50 increments of 2 kg were collected from various parts of the heap to form a primary sample of 100 kg, which was then mass-reduced by quartering the sample into secondary samples for analysis.

Additionally, four samples of the pre-screened BA and four of the treated BA were taken in larger amounts than previous samplings: increments were collected from the falling stream output from the pre-screening section during the treatment of 100 Mg of BA and from the automatic sampler at the output of the NFe recovery section during the treatment of a specific BA heap. Cumulative primary samples were mass-reduced by quartering into a secondary sample of approximately 200 kg. These wet material samples were then sieved into four fractions (0-2 mm; 2-8 mm; 8-16 mm; 16-50 mm) by using large plastic sieves (produced ad hoc for this study), in order to obtain samples of individual BA grain size fractions.

2.2.2 The WtE plant and boiler ash collection points

Line 4 of the AffaldPlus WtE plant in Næstved (Denmark) was chosen for collecting the boiler ash samples. The WtE facility is a grate-based mass-burn furnace, followed by a boiler with three vertical radiant passes, a horizontal superheater and an economiser section. Flue gas temperature within the boiler ranges from 700°C to 160°C. As schematised in Figure 2, the boiler presents 10 separated bottom hoppers in which solid residues produced at each section are collected and then discharged. Each section differs in terms of function, temperature and piping configuration, as reported in Allegrini et al. (**I**), and pipe bundles are equipped with rapping gears for the regular removal of ash deposits. Currently the boiler ash is mixed together with fly ash and APC residues, and disposed of.

Boiler ash samples

Boiler ash was sampled over two separate sampling campaigns: a one-day sampling campaign (2011) and a three-day sampling campaign (2012). The bottom hopper of each section of the boiler (see Figure 1) was opened, and ashes were collected and weighed continuously over a few hours (up to 5½ hours). Secondary samples for each section were obtained by mass-reducing the collected material using a riffle splitter. For each section four samples were obtained corresponding to each sampling day.

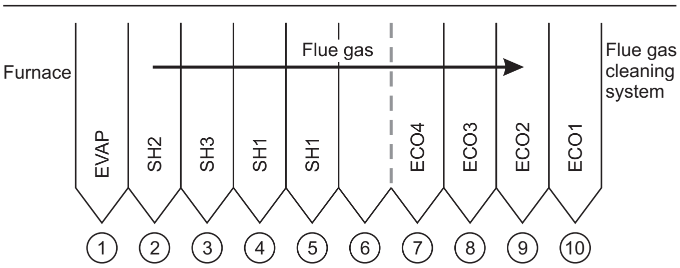

Figure 2: Scheme of the boiler of Line 4 at the AffaldPlus WtE plant. Numbers are relative to each boiler section, while labels in each section denote the function: EVAP, protective evaporator screen; SH, superheater; ECO, economiser.

3 Quantitative assessment of resource potential in MSWI residues

3.1 Scrap metals in BA: content and recovery

3.1.1 Quantification of scrap metal content in BA samples

The quantification of scrap metal content in BA is a simple and common activity within the characterisation of materials such as BA. During sampling preparation for analysis where grain size reduction is required (e.g. leaching testing and total composition analysis), quantification of the amount of unbreakable materials is carried out. Typically, results for total content and leaching tests carried out for compliance purposes by certified laboratories report the minimum crushing dimension and estimate the content of Fe and NFe scrap and other non-breakable, non-metallic objects. This is also similar to what was reviewed in Chandler et al. (1997), where the quantification of scrap metals in BA was achieved through visual observation testing. This characterisation was carried out in two steps: on coarse BA larger than 50 mm, characterised mainly in the field during sampling or the ordinary handling of BA, and on fine fractions below 50 mm, characterised in the laboratory in a dry state down to a maximum of 2 mm, under which it is difficult to visualise metallic pieces. This procedure is followed in most characterisation studies; however, the actual methodology applied is often not reported. The increasing interest in recovering scrap metals from BA has led to the development of more detailed procedures for BA characterisation in this respect. For example, a detailed procedure is reported by Muchova (2010) for the quantification of Fe and NFe for BA fractions 20-40, 6-20, 2-6 and <2 mm in size. Other institutes have developed their own procedures; for example, the Swiss Institute of Environmental and Process Engineering (UMTEC) developed a method for characterising BA from 16 mm down to 0.5 mm and with intermediate cutting sizes of 8 mm and 2 mm. Recently, at the European level, a draft of a standard dedicated to metal content determination in BA was published (prEN 16262:2011). In the European standard, metals are handpicked from BA fractions 32-63, 16-32 and 4-16 mm in size. All of these methods apply a simple combination of screening and crushing steps followed by handpicking and magnetic separation of Fe metals from NFe. Some of these methods complement the procedure with additional analyses aimed at estimating the content of individual metal types (e.g. light NFe from HNFe, copper within the HNFe fraction, etc.). Some of the applicable techniques are density separation, X-ray fluorescence (XRF) analysis and visual and hand-sorting.

Determining BA resource potential in terms of scrap metals (total content of scrap metals in BA which can be possibly recovered) requires a detailed characterisation of the material in its different fractions, including the finest ones. However, there are very few examples in which the resource potential has been estimated thoroughly and reported in detail (e.g. Muchova, 2010; Morf et al., 2013). Moreover, the harmonisation and standardisation of procedures for estimating and reporting scrap metal content in BA is absent, which makes it difficult to compare data on content and recovery efficiencies.

In Allegrini et al. (**II**), the scrap metal content in BA was estimated by following the procedure developed by UMTEC. However, for the actual estimation of resource potential, the results from the abovementioned procedure were integrated with information about material and substance flow in the treatment system (cf. section 2.2.1). This was done in order to take into account fractions of BA discharged at the first screening in the treatment system and then not properly considered in the quantification of scrap content. Moreover, in this way, long data series reporting the amount of metals sold to refiners for a given amount of wet BA could be used. The inclusion of these factors provides robustness and completeness to the results. As a result of the use of historic data based on wet weight, it was decided to treat and report the data in the present study on a wet basis, too.

3.1.2 An integrated procedure for assessing scrap potential in BA

The procedure applied in Allegrini et al. (**II**) consisted of the following steps:

- An analysis of BA samples (cf. 2.2.1) by employing the procedure developed by UMTEC.
- An analysis of material flow in a BA treatment system, including direct measurements taken at the plant and an analysis of long historical data series relating to treated BA and sold metals.
- Elaboration on the results, using material and substance flow analysis (MFA and SFA).

Laboratory procedures

The procedure for analysing BA samples consisted of a sequence of crushing and sieving operations aimed at liberating and separating metal particles dispersed in the material or included in ash chunks. In total, 30 kg of BA was initially dried at 105°C for 24 hours. The dry material was then sieved through 16, 8 and 2 mm screens, and any material retained at each screen was cyclically crushed and sieved until only metallic pieces remained on top of the screen. Metals were handpicked and classified into Fe and NFe metals by means of a manual magnet. In addition, unburned materials were separated during the procedure. Fractions passing through the sieve during this step were crushed in a mill (disc mill), thereby reducing the material grains down to 0.5 mm, and then sieved in 2 and 1 mm sieves. The metals retained on top of the screen were handpicked and magnetically separated between Fe and NFe. Samples of fine BA were analysed directly by the UMTEC Institute (CH). Density separation with sodium polymetatungstate was used for separating light NFe (Al) from HNFe, and HNFe were further divided on a colour basis. These latter analyses were carried out by the Institute of Metallurgy and Metal Forming of the University of Duisburg-Essen (DE) and by the UMTEC Institute.

Material flow measurement campaigns

Material flow within BA treatment system was measured through nine measuring campaigns over one year. During each campaign, 100 Mg of BA was treated and all relevant plant outputs were weighed by means of frontloaders. Moreover, the coarse fraction of the BA (above 50 mm) and the rejected flow from the final upgrading of the Fe scrap were handpicked to quantify the content of different metals and copper coils, respectively. The NFe upgrading section was excluded from the measurements, but historical data on the treatment of NFe sorted from 30 batches of 5,000 Mg of BA were used. The data included the amount of Al, HNFe, SS scrap sold for recycling and residues. All data provided by the facility were reported per “batch” of BA, where “batch” represents approximately 5,000 Mg of wet BA, as required by N.1662:2010 for quality control.

Material and substance flow analysis

The MFA methodology was applied, in order to elaborate on the information gathered in the previous two steps. MFA is a systematic assessment of flows and stocks in a system based on simple material balance (Brunner and Rechberger, 2004), and it has been applied in various fields, including the analysis of waste treatment technologies (e.g. Morf et al., 2013; Tonini et al., 2014). The STAN software package (Cencic and Rechberger, 2008) was used, and the analysis was carried out at two different levels: on a material basis (BA wet mass) and then on a substance basis within the material flow. The substances modelled were Fe, NFe, Al and Cu scrap.

3.1.3 Scrap metal potential in BA and recovery efficiencies

The results of the integrated analysis can be represented in a Sankey diagram, as reported in Figures 3 and 4, for MFA and SFA (only NFe shown).

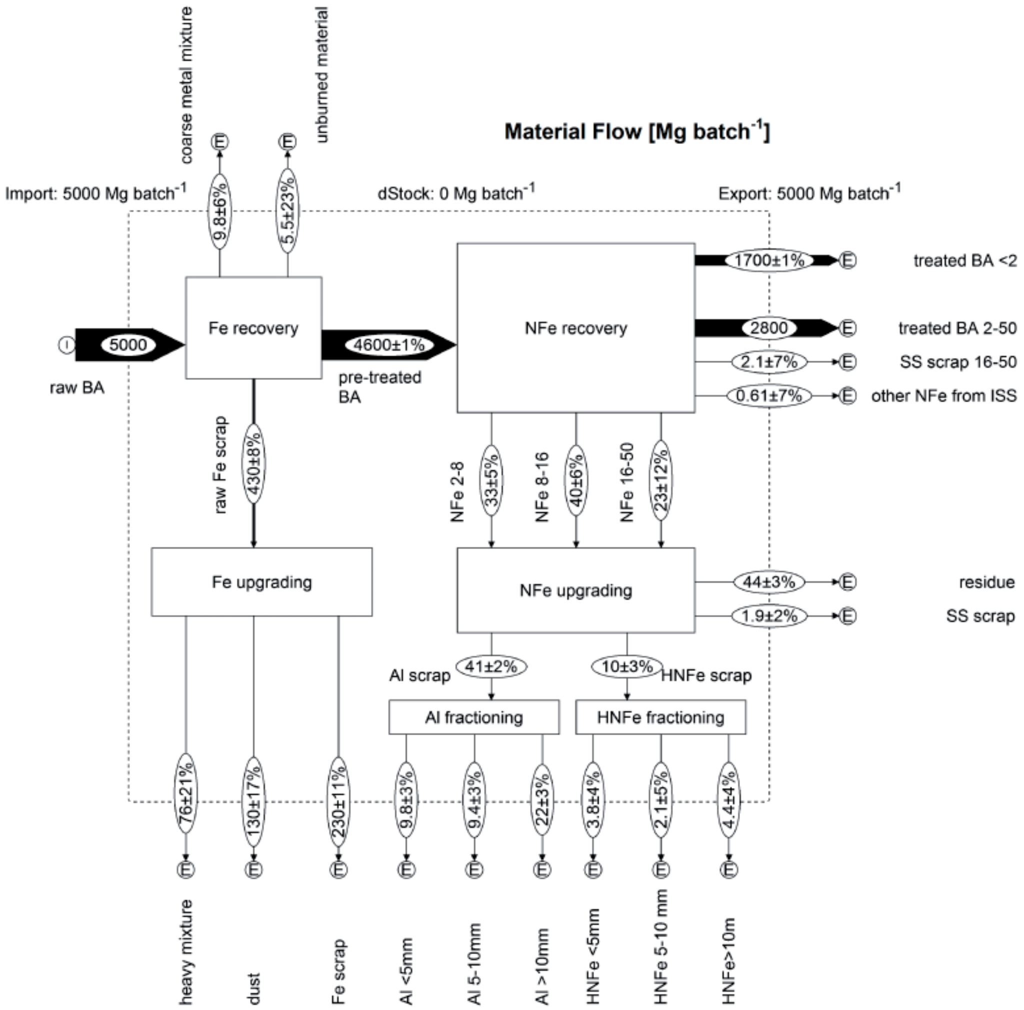

Figure 3 MFA results for the BA treatment system as reported in Allegrini et al. (**II**). Values are given as Mg of material in each flow from the treatment of 5000 Mg of wet BA. (Batch = 5000 Mg BA; BA, bottom ash)

The potential content of scrap metals in wet BA received at the treatment facility was 7.2%ww (wet weight) ±18% for Fe and 2.2%ww±2% for NFe (1.4%ww±2% for Al scrap and 0.24%ww±6% for Cu scrap). Translated on a dry basis, by considering an average moisture content of BA of 12%w/w (as measured on pre-screened BA), the potential for Fe and NFe, respectively, was approximately 8.2% and 2.5%.

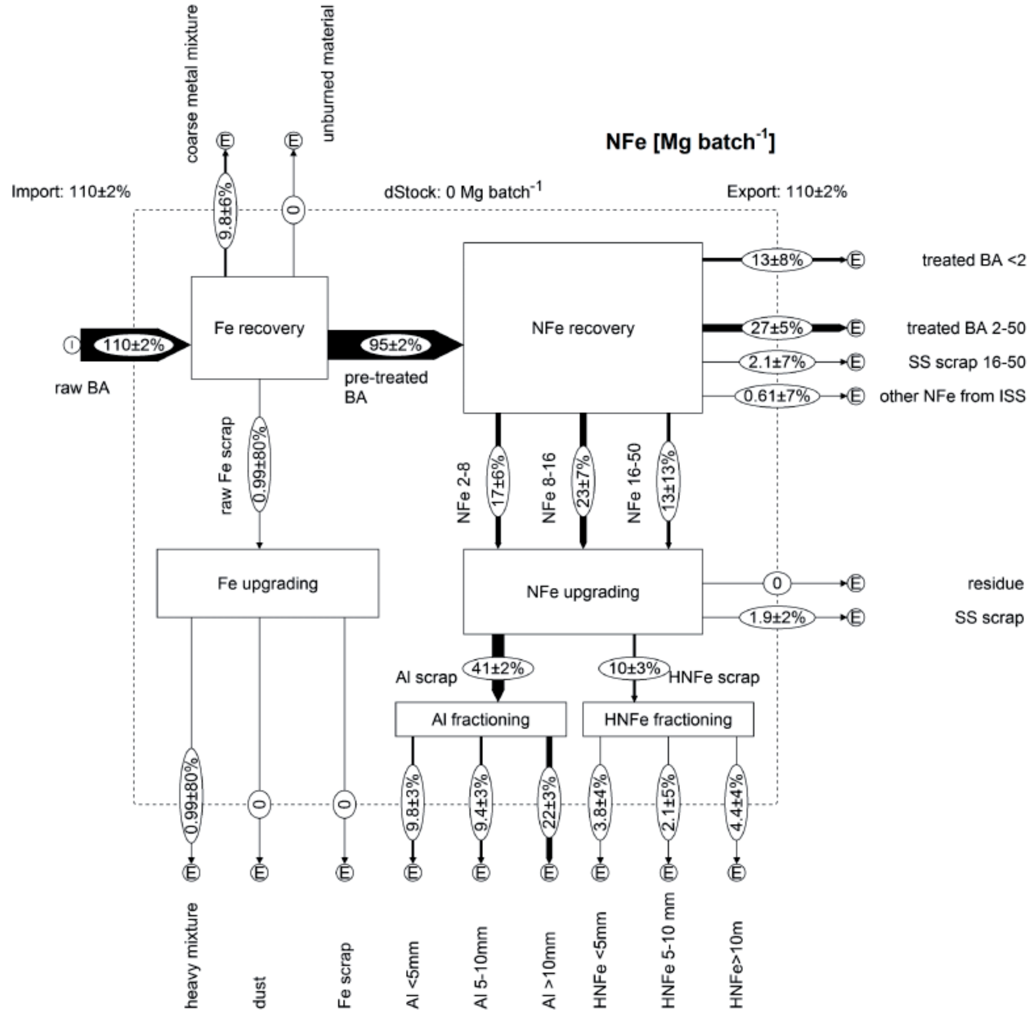

Figure 4 SFA results for NFe scrap as reported in Allegrini et al. (**II**). Values are given as Mg of material in each flow from the treatment of 5,000 Mg of wet BA (Batch = 5,000 Mg BA; BA, bottom ash).

Using the results of the MFA and SFA, recovery efficiencies can be directly calculated: 85% for Fe and 61% for NFe scrap. Recovery efficiencies were found to be in the medium-high range of currently reported recovery efficiencies in Europe, though it should be noted that significant losses were found in the fine BA fraction and also in the treated BA. In Europe, advanced recovery systems for NFe in BA are being implemented, and current recovery efficiencies reach up to 75% (Muchová and Rem, 2006; Heinrichs et al., 2012). The moisture content of BA is one of the major problems in the sorting operation. Particularly, the fine fraction of the material is mainly affected by moisture content, as it limits the screening and sorting of scrap. Moreover, as shown in Allegrini et al. (**II**), the fine fraction has higher water content, though new technologies are being implemented to overcome this drawback, one example of which is the use of innovative classifiers such as the Advanced Dry Recovery technology developed and patented by Berkhout and Rem (2009), which facilitates the separation of fine and moist BA fractions down to 1 mm (De Vries et al., 2012). Alternatively, different handling of BA, by avoiding wet quenching, will lead to a completely dry material, although this would mean the modification of WtE discharge systems. Nonetheless, this has been done in Switzerland, for example, where dry discharged BA is treated for metal recovery down to a grain size of 0.2 mm, reaching recovery efficiencies above 90% for NFe (ZAR, 2014).

3.2 Content of valuable metals in BA and boiler ash

Additionally to the value related to coarse metallic pieces in BA, many metals of economic and environmental interest are found in BA and other MSWI residues. Quantification of the total content of such metals can be carried out using different techniques: non-destructive techniques, where the solid material is directly analysed (e.g. XRF), and digestion methods followed by analysis of the eluate. The latter allows for the quantification of an element once transferred in the solution following material matrix destruction. Various digestion methods exist that use acid attack or fusion techniques based on lithium metaborate or alkaline fusion, as well various procedures for acid digestion using different combinations of acids and digestion conditions. The selection of the most suitable analytical methods depends on the material under investigation and on the elements of interest (Chandler et al., 1997).

Valuable metals of interest in the present study were Cu, Co, Mo, Ni, Pb, Sn and Zn (selected by considering their value on the London Metal Exchange (LME)), platinum group metals (PGM), Au, rare earth metals (REE) and other metals included in the list of critical elements identified by the European Commission (European Commission, 2010). These metals are generally found in BA and boiler ash in trace concentrations (< 1000 mg/kg) except for Cu, Pb and Zn, which can be present at concentrations above 10,000 mg/kg. Apart from the first group of listed elements (from Cu to Zn), which are often analysed because of their potential toxic effects, the other elements have rarely been analysed in BA and boiler ash. To the knowledge of the author, REE (only some of them) and precious metals have been analysed in boiler ash only in one recent study by Morf et al. (2013), while few studies have reported on REE or PGM concentrations in BA (Kida et al., 1996; Zhang et al., 2001; Fujimori et al., 2005; Chung et al., 2007; Jung and Osako, 2007; Zhao et al., 2008; Morf et al., 2013) and other MSWI residues (i.e. fly ash)

(Kida et al., 1996; Fujimori et al., 2005; Jung and Osako, 2007; Zhao et al., 2008; Morf et al., 2013). In Allegrini et al. (**I & II**), concentrations of valuable metals in BA and boiler ash are reported. Particularly, a wide range of elements (as reported in Table 1) was analysed in treated BA and its grain size fractions, as well as in ten boiler ash samples collected along the heat recovery system. Analysis of the samples was carried out by means of microwave-assisted acid digestion with HNO_3, HCl, HF and H_3BO_3, following the procedure set out in EN 13656:2003. The produced eluates were then analysed by ICP-MS. Various digestion methods were initially considered; however, based on previous literature studies and the use of three reference materials (fly ash, sediments and soil), the EN 13656:2003 procedure was found suitable for the materials and elements investigated.

As reported in Table 1 and Figure 5, REE were detected in all samples, with concentrations of the individual elements ranging between 0.09 and 51 mg/kg. REE were slightly enriched in the BA samples compared to boiler ash, though concentrations were nevertheless below typical ore levels. Little enrichment could be observed within the BA and boiler ash samples. For example, REE such as Sc, Ce, Sm, Dy, Ho, Tm, Yb and Lu were found enriched in the coarse BA (16-50 mm), while within the boiler ash, samples from the evaporator section had generally lower concentrations of REE. Metals belonging to the platinum group metals (PGM) (Pt, Pd, Ir, Rh, Ru) were hardly detected. Particularly, Pt, Pd and Ir were mostly found below detection limits. Indium (In) was also not detected in BA or boiler ash, while gold (Au) was detected in all samples at an average level of 0.26 mg/kg, though significant variability was observed in these results (see Figure 5).

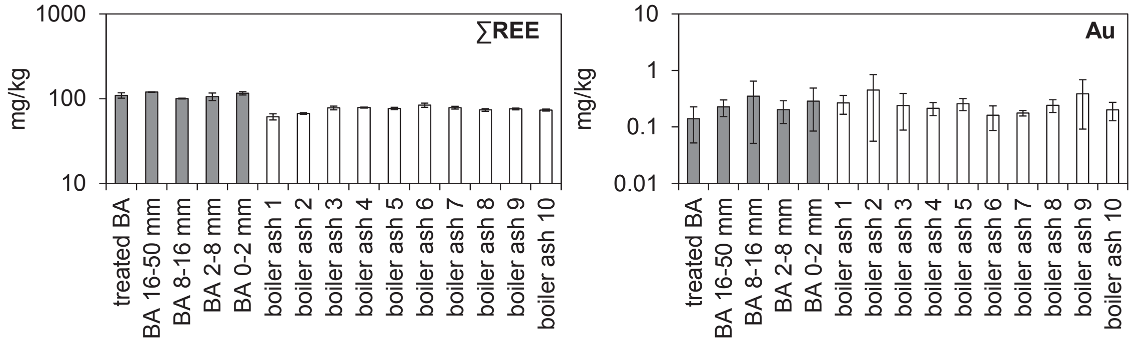

Figure 5 Total content of rare earth elements (REE) and gold (Au) in the BA and boiler ash samples collected at 10 points along the boiler of the WtE plant. Values reported in mg/kg of dry material. Error bars represent standard deviations between analysed samples and grey and white bars indicate respectively BA and boiler ash samples.

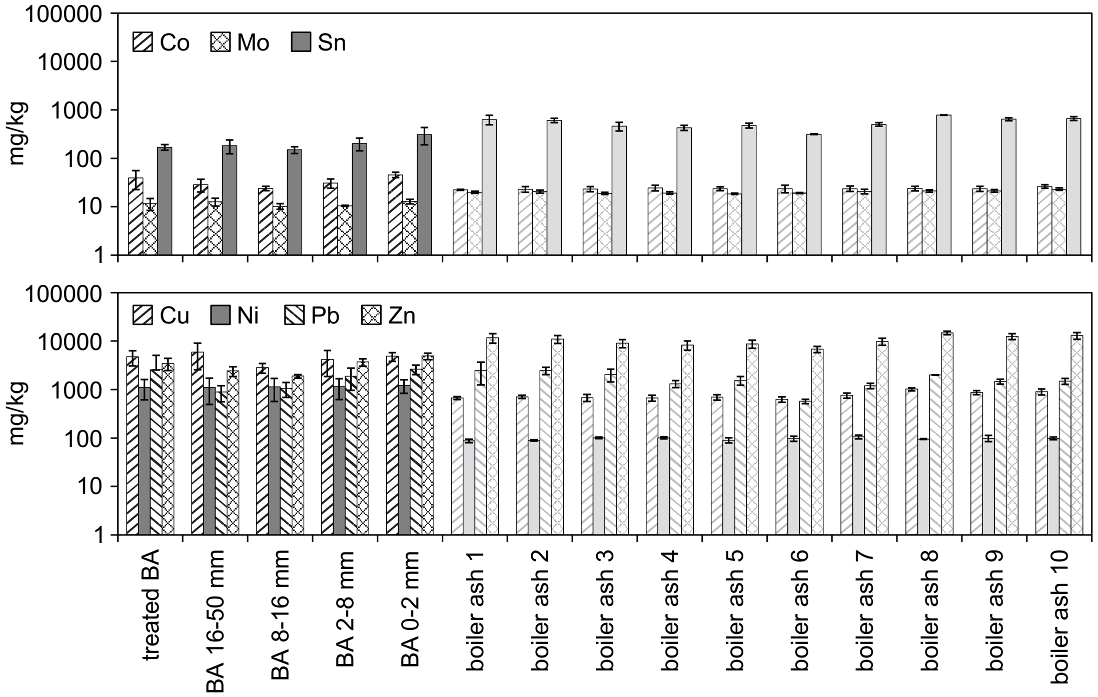

Figure 6 Total content of metals in the BA (Treated BA: total BA after metal recovery; and specific BA grain size fraction) and boiler ash samples collected at 10 points along the boiler of the WtE plant. Values reported in mg/kg of dry BA. Error bars represent standard deviations between analysed samples. Dark and bright patterns indicate BA and boiler ash samples, respectively.

Table 1 Chemical composition of BA after weathering and metal recovery (from Allegrini et al. (**II**)) and of boiler ash (partly from Allegrini et al. (**I**)). Boiler ash composition was calculated as the weighted average of boiler ash samples collected at 10 different points along the heat recovery system of the WtE plant during a three-day sampling period. Values are reported in mg/kg of dry material (and relative standard deviation (RSD) for treated BA), and compared with literature values. (n.d. not detected)

			Literature data	
	Treated BA	**Boiler ash**	**BA [a] min-max**	**Boiler ash [b]**
Rare Earth Elements - REE				
Sc	4.6 ± 18 %	3.8	1.3-22 (6)	4.5
La	21 ± 7 %	19	2-30 (5)	-
Ce	44 ± 9 %	32	11-51 (4)	-
Pr	5.5 ± 7 %	3.3	1.1-10 (4)	3.0
Nd	20 ± 6 %	11	4.0-37 (4)	13
Sm	3.05 ± 27 %	1.9	0.93-5 (4)	-
Eu	0.67 ± 11 %	0.66	0.25-2.6 (4)	-
Gd	2.8 ± 11%	2.0	0.88-5 (4)	1.9
Tb	0.43 ± 6 %	0.35	0.18-3 (4)	-
Dy	2.3 ± 10 %	1.45	0.54-3 (3)	-
Ho	0.43 ± 10 %	0.28	0.11-0.45 (2)	-
Er	1.95 ± 9 %	0.82	0.31-2 (3)	-
Tm	0.18 ± 13 %	0.12	0.01-0.18 (2)	-
Yb	1.25 ± 11 %	0.96	0.31-5 (4)	-
Lu	0.17 ± 10 %	0.12	0.02-0.23 (2)	-

Table 1 Continue

			Literature data	
	Treated BA	**Boiler ash**	**BA [a] min-max**	**Boiler ash [b]**
Platinum Group Metals – PGM				
Pt	<0.009	<0.0099	0.074-0.53 (3)	0.20
Pd	0.01 ± 61 %	<0.0081	0.03-1.8 (2)	-
Ir	<0.0012	<0.0012	0.00072-0.0075 (1)	-
Rh	0.13 ± 98 %	0.096	<0.030 (2)	n.d.
Ru	0.0062 ±75 %	0.0074	<0.0175 (2)	n.d.
Other precious and critical elements				
Au	0.14 ± 63 %	0.27	<3 (5)	0.32
Sb	60 ± 24 %	430	7.6-430 (7)	2200*
Be	1.2 ± 8 %	0.70	1.2-6 (2)	n.d.
Co	39 ± 43 %	25	6-350 (8)	63
Ga	10± 16 %	14	7.8-24 (5)	8.7
Ge	0.53 ± 18 %	0.84	0.78-2.7 (3)	0.87
In	0.04 ± 98 %	<0.0015	<1.7 (3)	1.4
Mg	11000 ± 5 %	18000	400-26000 (5)	14000*
Nb	12 ± 19 %	15	2-14 (2)	13
Ta	6.8 ± 152 %	2.4	2.5-14 (3)	5.5
W	9.7 ± 55 %	12	10-320 (4)	55
Other elements of typical environmental concern				
As	25 ± 26 %	130	0.12-190 (6)	17-295**
Ba	1400 ± 10 %	1300	69-5700 (6)	1200
Cd	8.2 ± 123 %	63	0.3-70 (6)	33
Cu	4700 ± 35 %	800	190-25000 (7)	880
Cr	650 ± 4 %	480	23-3400 (8)	750
Mo	12 ± 27 %	21	2.5-280 (7)	34
Ni	1100 ± 45 %	100	7-4300 (7)	330
Pb	2500 ± 102 %	1700	75-14000 (7)	1400
Se	1.45 ± 28 %	5.7	0.05-10 (2)	1.1
Sn	170 ± 13 %	580	2-470 (5)	310
Tl	0.26 ± 26 %	1.3	0.0077-0.23 (2)	0.031
V	48 ± 11 %	37	16-120 (8)	43
Zn	3400 ± 28 %	11000	460-20000 (7)	14000

[a] The number of literature sources used to define the range in the table is reported in parentheses. The sources for BA were: Bayuseno and Schmahl, 2010; Chandler et al., 1997; Chung et al., 2007; Fujimori et al., 2004 and 2005; Hyks, 2008; Jung and Osako, 2007; Kida et al., 1996; recalculated from Morf et al., 2013; Zhang et al., 2001; Zhao et al., 2008.

[a] The sources for boiler ash were: recalculated from Morf et al., 2013; *Yang et al., 2008;** De Boom and Degrez, 2012

Valuable metals, found in higher concentrations than precious and REE, did not show significant enrichment in the different material samples (as shown in Figure 6). However, generally, the fine BA fraction (below 2 mm) was slightly enriched, especially in Zn, but also in Pb, Sn and Co. Similar results were reported previously (Chandler et al., 1997; Chimenos et al., 2003), and the enrichment of metals in the fine fraction is probably related to melting phenomena in the furnace which lead to particles that are small in size. Within the boiler ash these metals tended to enrich at the beginning of the boiler (evaporator) and at the end (economiser), while central sections presented generally lower concentrations. This was attributable to condensation mechanisms within the boiler as well as the grain size of the boiler ash. For example, boiler ash collected at section 6 of the boiler presented the lowest share of fine particles below 0.125 mm while simultaneously the lowest concentrations of metals such as As, Cd, Cu, Pb, Sb, Sn and Zn.

Even though an enrichment trend could be observed for individual fractions of BA and boiler ash, the significance of enrichment was too low to justify the diversion of selected fractions for optimised processing aiming at metal recovery. However, boiler ash as a whole has the potential for metal recovery based, for example, on acid leaching processing (cf. Schlumberger, 2010). During sampling at the WtE plant, boiler ash production was estimated to range between 0.2 and 0.3% by weight of the input waste, which was within the range reported by Hjelmar (1996). Thus, based on the yearly incinerated waste in Denmark, which in 2011 was 2,605,000 Mg (Miljøstyrelsen, 2013), 73 Mg of Zn, 11 Mg of Pb, 5.2 Mg of Cu and 3.8 Mg of Sn accumulates in boiler ash on a yearly basis.

Based on the same statistics, and assuming for BA production equal to 30% of the input waste, approximately 781,500 Mg of BA is produced yearly in Denmark. Considering an average 12% (w/w) moisture content of BA after treatment (see Table 1), 2,900 Mg of Cu and 86 kg of Au are lost and deposited in road sub-bases annually.

4 MSWI residues as resources for the construction sector: environmental aspects

4.1 Release of contaminants into the environment

MSWI residues can be utilised in the construction sector instead of natural aggregates such as gravel and sand, as well as additives in various building products. However, apart from the possible technical problems involved in the use of these residues (Müller and Rübner, 2006; Sorlini et al., 2011,), environmental concerns and strict regulations have often limited the reuse of MSWI residues for these purposes.

MSWI residues may represent a threat to the environment and human health because of the potential release of toxic substances from the material while in contact with water (i.e. leaching). Substances of concern are mainly inorganic, such as metals, while other potentially harmful organic compounds, such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF), polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH), are of less concern because of their low solubility in water (Chandler et al., 1997; Badreddine and Francois, 2009). However, the release of low molecular weight organic acids and humic and fulvic compounds is significant in BA, and it affects the leaching behaviour of other elements, too (e.g. Cu) (Van Zomeren and Comans, 2004).

4.1.1 Leaching behaviour

The leaching behaviour of MSWI residues has been extensively investigated in the last 20 years (Chandler et al., 1997; Dijkstra et al., 2006; Hyks et al., 2009; Rocca et al., 2012), and leaching testing procedures have been developed (Kosson et al., 2002) to address the influence of important parameters on leaching behaviour, while the standardisation process towards a harmonised use of leaching tests in Europe is ongoing.

Leaching tests are experimental procedures in which a liquid (i.e. leachant) is put into contact with the tested material in different modalities, following which the resulting leachate (also called eluate) is collected and analysed. Depending on the leachant used, the type of contact with the material, the material's form and the contact time, various aspects of the leaching behaviour can be investigated. The simplest leaching tests are batch tests, with distilled water used as leachant and where the material is stirred for a given time (e.g. 24 hours) at a fixed ratio between the leachant and the material (i.e. a liquid-to-solid ratio, L/S). These types of test are applied in many countries for compliance purposes; for example, they are used at the European level to define the acceptance of waste materials into landfill (European Commission, 2003). Batch tests can be also used to assess the influence of pH conditions or L/S ratios on the release of different substances, by using acid or basic leachant or by varying the amount of leachant in contact with the material. Moreover, the release of substances as a function of L/S can also be assessed by means of percolation tests (i.e. column leaching tests) in which the material is compacted into a column and new leachant is continuously pumped through it until the desired L/S value is reached. Release as a function of pH or L/S ratio provides more information than a simple batch test, thereby providing insights into substance solubility and material geochemistry determining release mechanisms. For example, as shown in Figure 7, inorganic elements can be classified in three groups, depending on their release curves (Hykš et al., 2009):

- Availability-controlled elements (e.g. Na, Cl, K), which are present in the material in the form of readily soluble species. They are characterised by pH-independent release and significant release in the first steps of a percolation test, followed by a fast decrease in solution concentration.
- Solubility-controlled elements (e.g. Ca, S, Si), whose release is limited by the solubility of the species bearing the element. In this case the eluate concentration as a function of L/S tends to be constant, as it is controlled by mineral solubility, while the pH-dependent behaviour depends on specific mineral solubility as a function of pH.
- Sorption-/complexation-controlled elements, which are mainly controlled by mechanisms other than the ones mentioned above. Typical metals belonging to this group are metal cations (e.g. Cu^{2+}) and oxyanion-forming elements (e.g. CrO_4^{2-}). Mechanisms controlling release are complexation by organic substances (Van Zomeren and Comans, 2004), sorption on iron and aluminium oxide surfaces (Meima and Comans, 1998) or on other mineral phases and solid solution formation along with metal incorporation (Cornelis et al., 2008).

Data resulting from percolation and pH-dependent leaching tests are suitable input data for geochemical modelling, which has been largely applied in this field to help describe leaching mechanisms (Astrup et al., 2006; Dijkstra et al., 2008; Hyks et al., 2009). Minteq, PHREEQC and Orchestra (Meeussen, 2003) are examples of software employed for the chemical equilibrium models applicable in this context. Specifically, Orchestra is today embedded in the leaching framework database expert system LeachXS (Van der Sloot et al., 2008).

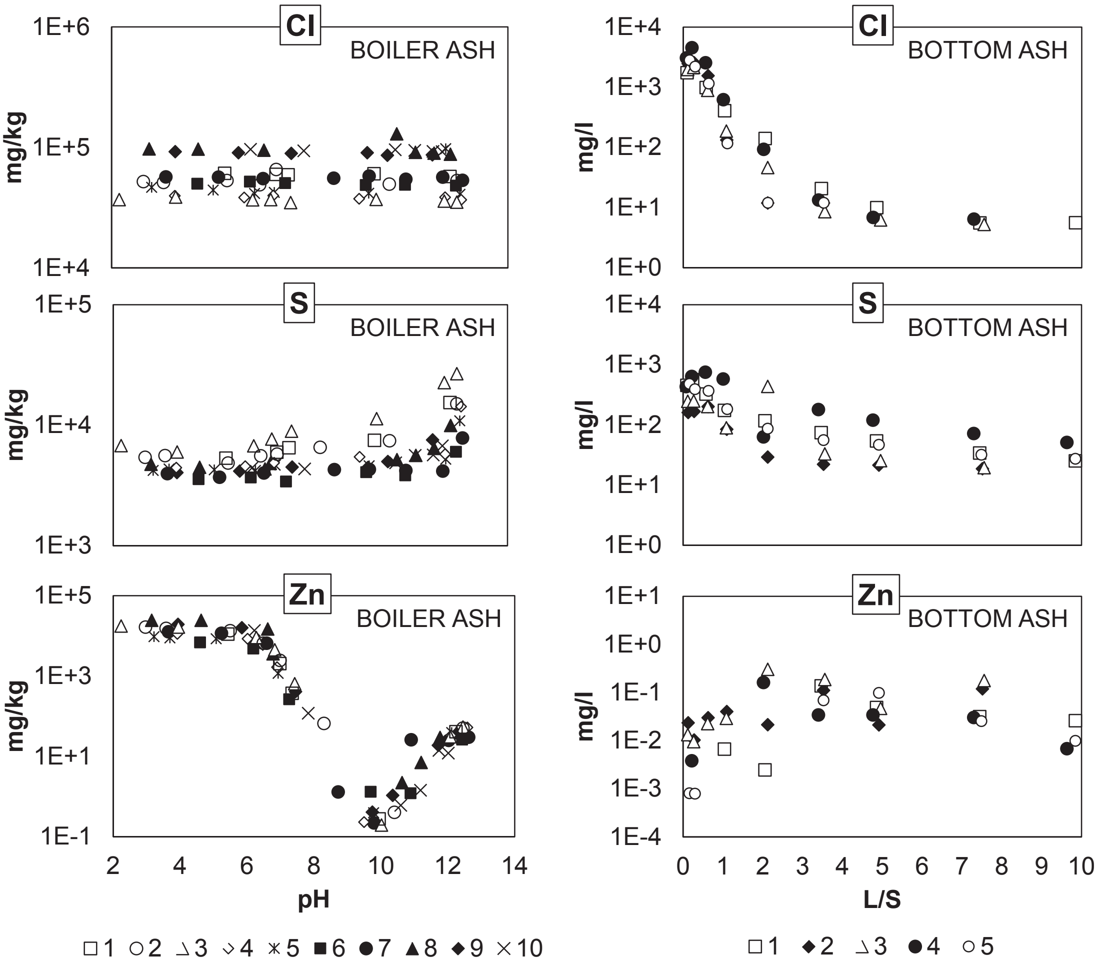

Figure 7 Examples of leaching behaviour as a function of pH and L/S: availability-controlled release (Cl); solubility-controlled release (S); sorption-/complexation-controlled release (Zn). pH-dependent data (on the left) are based on the leaching test prEN 14429:2014 carried out on ten boiler ash samples collected along the boiler, as reported in Allegrini et al. (**I**). L/S-dependent data (on the right) are based on percolation leaching tests prEN 14405:2014 on five BA samples, as reported in Astrup et al. (2010).

4.1.2 Elements of environmental concern and material hazardousness

Elements of environmental concern are routinely analysed for compliance purposes. As an example, in Table 2 a list of elements is given in relation to Danish limits on the reuse of residues in construction, as well as European limits pertaining to the acceptance of waste into landfill.

Table 2 Regulatory limits (restricted list) for elements' released through leaching for acceptance into landfill (European Commission, 2003) and for reuse in construction works in Denmark (N. 1662:2010), as well as release values obtained in BA and boiler ash samples. Limits and release values are based on the leaching procedure EN 12457-1:2002 (RSD, relative standard deviation; n.d. not detected; n.m. not measured).

	2003/33/CE			N.1662:2010[a]	BA[b]	boiler ash[e]	
	Type of waste accepted in landfill:						
	inert	non-hazardous	hazardous		average±RSD	min	max
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
As	0.1	0.4	6	0.1	0.017±20%	n.d.	0.35
Ba	7	30	100	8	0.23±138%	0.082	2.5
Cd	0.03	0.6	3	0.08	n.d.	0.0044	0.023
Cr	0.2	4	25	1	0.16±38%	9.1	25
Cl	550	10000	17000	6000	1800±49%[c]	32000	86000
Cu	0.9	25	50	4	1.1±71%	n.d.	0.15
Hg	0.003	0.05	0.5	0.002	n.d.[c]	n.m.	n.m.
Mn				2	0.0018±131%	0.0082	0.070
Mo	0.3	5	20		0.44±46%	0.27	6.4
Na				3000	1400±25%	14000	49000
Ni	0.2	5	20	0.14	0.0037±110%	n.d.	0.049
Pb	0.2	5	25	0.2	0.023±64%	6.5	96
S	560	10000	25000	8000	160±36%	1500	28000
Sb	0.02	0.2	2		0.042±0%[d]	n.d.	0.35
Se	0.06	0.3	4	0.06	n.d.	0.20	1.7
Zn	2	25	90	3	0.16±52%	5.9	20
pH					11.5±2.7%	12.2	12.9

[a] limit values for restricted use of residual materials in construction works
[b] average based on leaching tests on three samples of treated BA collected at the treatment plant
[c] values based on 60 batches of BA analysed for compliance reasons
[d] all values below the quantification limit
[e] maximum and minimum release values between samples collected at ten points along the boiler of the WtE plant during a three-day sampling campaign and as reported in Allegrini et al. (**I**)

As shown in Table 2, treated BA (which has undergone a mild weathering process) complies with limits for reuse in construction work (relatively to Danish legislation), and, despite significant variability in the leaching results, leachate concentrations are within established limits for acceptance into landfill for non-hazardous materials. On the other hand, boiler ash exceeds limits for acceptance in landfill for hazardous waste because of the excessive release of Cr, Cl, Pb and S. Furthermore, Danish limits for reuse are exceeded because of the release of Na, Se, Zn and As, albeit to a lesser extent. Boiler ash samples were then analysed individually at each section of the heat recovery system. Goal was to identify fractions with lower release of harmful compounds and which could be managed differently increasing material recovery from MSWI residues. As shown in Figure 8, changes in release behaviour between boiler ash samples were observed. However, variations between the sections were significant only for S, where a clear difference between evaporator/superheater ash and economiser ash was found. The release of critical elements from boiler ash collected at section 6 was generally lower, probably due to the physical properties (e.g. grain size distribution) of the ashes collected in the only section of the boiler without pipe bundles.

Material hazardousness

The assessment of waste material hazardousness in Europe is based on the Framework Waste Directive (European Commission, 2008a) and on the list of waste defined by the European Commission (2000), which is currently being revised with the aim of harmonising waste legislation with product legislation (UK EPA, 2011). Specifically, criteria for the hazard assessment of products are defined by regulation N. 1271:2008 for the classification, labelling and packaging of substances and mixtures (CLP) (European Commission, 2008b).

Based on the CLP regulation, boiler ash exceeds pH limits defined for hazard categories H4 and H8 (irritant and corrosive), so they are classified as hazardous materials. Moreover, boiler ash exceeds concentration limits for Pb (only in section 1) and Zn (in all sections) for chronic ecotoxicity. However, while limits for Pb are given as a generic entry, Zn speciation needs to be specified for ecotoxic assessment. On the other hand, based on these concentration limits for chronic ecotoxicity properties, BA is also defined as hazardous, since content limits for Pb, Cu and Zn (the two latter metals requiring further assessment) are exceeded.

According to the CLP regulation, the hazardousness of a material is related to the form in which an element is present in the product – and not to its total elemental or leachable content. Differences between elements' release as a function of pH reflect differences in their geochemistry within the ash and thus different forms in which the element is present in the material, or different release mechanisms controlling the material release. Hence, pH-dependent leaching data can provide information on the form in which an element is present in the material. More specifically, comparing the pH-dependent releases of different samples materials can help in identifying geochemical differences between the materials, eventually leading (after further investigation) to a different classification in terms of material hazardousness. In this respect, the boiler ash samples were analysed as a function of pH. As shown in Figure 9, the pH-dependent release of elements, previously identified as of concern (Figure 8), was not significantly different between sections, apart from a few exceptions. Thus, a separate classification and management of boiler ash collected at different points within the heat recovery system of the WtE appeared not to be a realistic option.

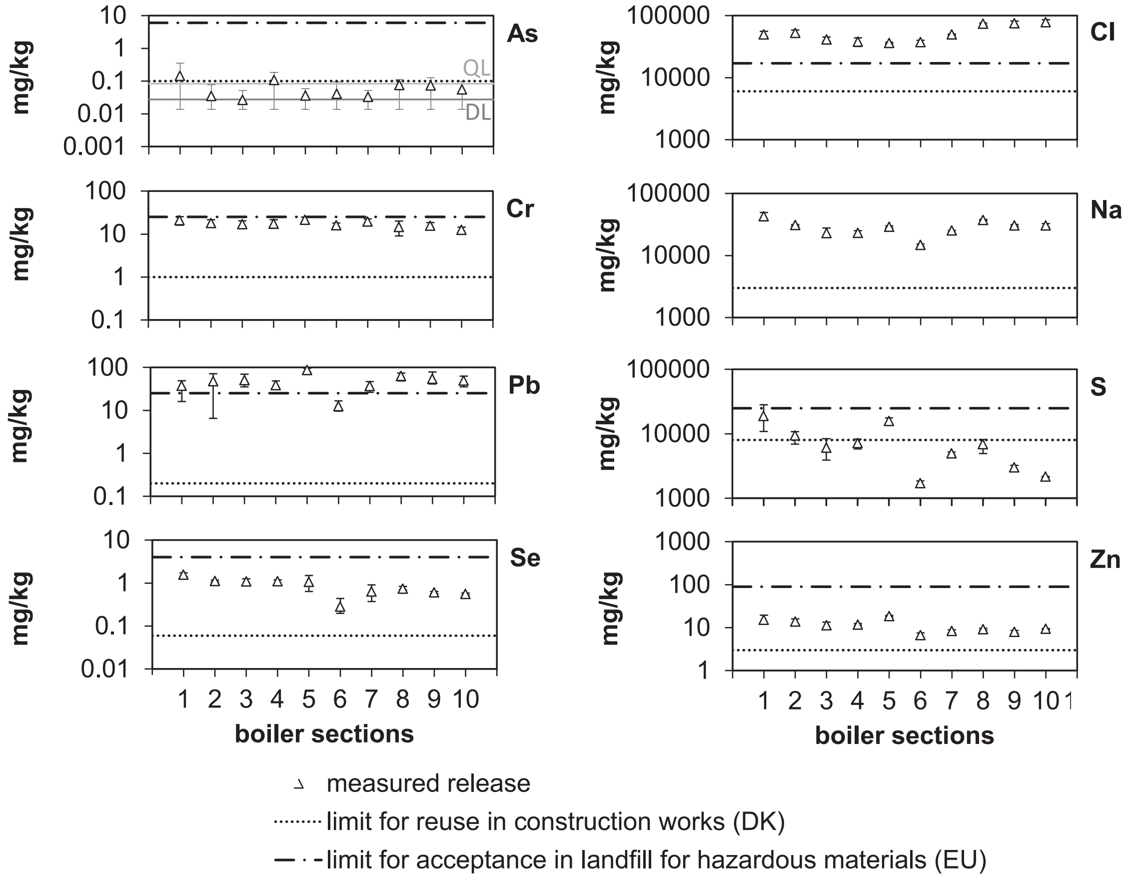

Figure 8 Release of elements from boiler ash samples collected at ten points along the boiler of the WtE plant. Triangles represent average values from the three samples collected over three days, while error bars represent the maximum and minimum values detected. Results are based on the compliance leaching test EN 12457-1:2002 and are compared with Danish limit values for utilising residues in construction works, as well as European limits for acceptance into landfill for hazardous waste. For As, values below detection limits are included as half of the detection limit, and the detection limit (DL) and the quantification limit (QL) are reported. Data are based on Allegrini et al. (**I**).

Assessment of the hazardousness of both BA and boiler ash is currently a hotly debated subject. No clear procedures have been indicated for waste characterisation with respect to limits within the CLP regulation, and judgments are currently being based on information about the waste source in terms of technology and raw materials. However, assessment procedures are in the processes of being proposed and tested (Van der Sloot and Kosson, 2012; Hjelmar et al., 2013a; Hennebert et al., 2014), while new insights into ash toxicity are being generated (Stiernström et al., 2013 and 2014).

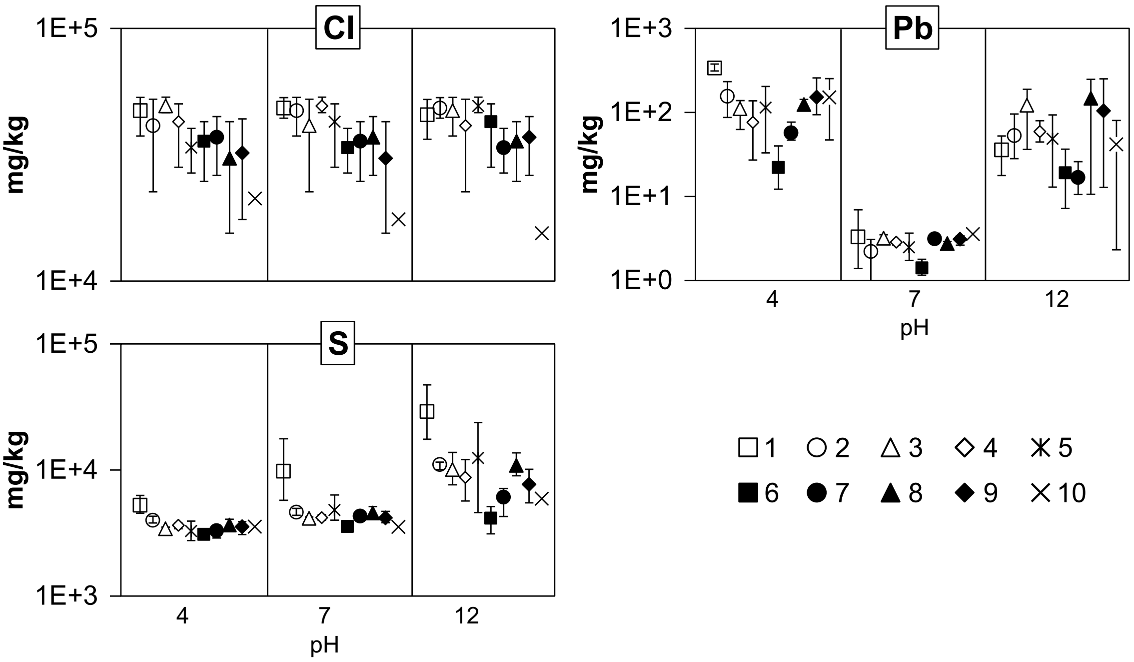

Figure 9 Release of problematic elements from boiler ash as a function of pH (pH 4, 7 and 12) resulting from the leaching test procedure prEN 14997:2014. Data are reported as average results of tests carried out on three samples for each section of the WtE boiler. Error bars represent minimum and maximum values. Data based on Allegrini et al. (**I**).

4.2 MSWI BA utilisation and release scenarios

Due to its technical properties and low release of potentially toxic elements, BA is often reused as aggregate in embankments and road sub-bases and as aggregate in concrete. The release of elements into the environment during material utilisation can be estimated on the basis of leaching test results and the characteristics of the utilisation scenario (Kosson et al., 1996). Scenario utilisation is divided between percolation- and diffusion-dominated scenarios, depending on the type of contact between BA and water.

4.2.1 Percolation-dominated scenario

In a percolation-dominated scenario, water passes through the bulk material, entering in contact with the individual grains of the material. Estimating the L/S ratio is carried out by dividing the amount of water infiltrating through the material over a given time frame and the amount of material within a parallelepiped of a defined height and 1 m^2 base. This approach is commonly applied (Kosson et al., 1996; Hjelmar, 2003; Astrup, 2004; Birgisdóttir, 2005; Allegrini et al., (**III**) and (**IV**)), and it can be related to L/S values used in laboratory leaching tests. This approach can be used to describe the contact between water and BA aggregates used in road sub-bases, even though diffusion processes are likely to occur if infiltration is obstructed by an intact asphalt layer (Kosson et al., 1996).

Taking Denmark as an example, and by considering annual precipitation in Denmark from 1874 to 2011 (DMI, 2012) and not specifying the location of the road in the country, precipitation can be assumed to be normally distributed with average 700 mm/year. For infiltration, Danish statutory order N.1662:2010 states that residual materials complying with limits for restricted applications (i.e. MSWI BA) have to be utilised in construction works where the possibility of water infiltration stands at a maximum 10%. However, an intact asphalt layer can maintain the infiltration rate below 4%, as measured by Ramier et al. (2004) and Hjelmar et al. (2007) and reported in Dawson (2009), while the edge effect (infiltration of water through the shoulder of the road structure) and fractures and joints in the asphalt layer can significantly increase infiltration (Taylor, 2004; Apul et al., 2007; Hjelmar et al., 2007; Dawson, 2009; Dabo et al., 2009; Ramier et al., 2011). Based on the experience of previous authors, and on technical guidelines, the infiltration rate can be described by a lognormal distribution with a median of 7% and a geometric standard deviation of 2. In this way, low infiltration values are more frequent, but high values due to cracks or edge effects are also possible. Concerning the BA layer, the dry density of the material ranges between 1,500 and 2,100 kg/m^3 (Hjelmar et al., 2010; Danish Road Directorate, 2012), while the height of the BA layer can range between 0.2 and 1 m. The last two parameters are assumed uniformly distributed. Combining these parameters through a MonteCarlo simulation, a lognormally distributed range of possible L/S values reached at the road site after a given time frame is obtained and reported in Table 3.

Table 3 Liquid-to-solid ratio (L/S) values as calculated over given time frames and by considering a percolation-dominated scenario. The values in the table resulted from a MonteCarlo analysis as reported in Allegrini et al. (**III**).

Percentiles	5th	25th	50th	75th	95th
Time frame	l/kg	l/kg	l/kg	l/kg	l/kg
10 years	0.13	0.28	0.49	0.86	2.0
20 years	0.26	0.56	0.98	1.7	4.0
50 years	0.66	1.4	2.4	4.3	9.9
100 years	1.3	2.8	4.9	8.6	20

The cumulative release of metals into the environment can be approximated by results from column leaching tests. Batch leaching tests can be also used, if the appropriate L/S is applied. For example, in Figure 10, the release of two metals (Cr and Zn) over a 100-year time frame is reported, including the 5th, 50th and 95th percentiles of the L/S values, and additionally L/S 2 and 10 l/kg with release estimates based on both batch and column leaching tests. As shown in Figure 10, Cr release is independent of the L/S and the type of leaching test applied, while Zn cumulative release increases proportionally with the L/S ratio. Also in this case, differences between the application of column and batch leaching data are not significant, due to the significant variability of release values within each testing procedure. However, using the same set of data, some of the metals (e.g. Ni, As, Cu) show releases significantly higher after batch leaching testing (Allegrini et al. **III**).

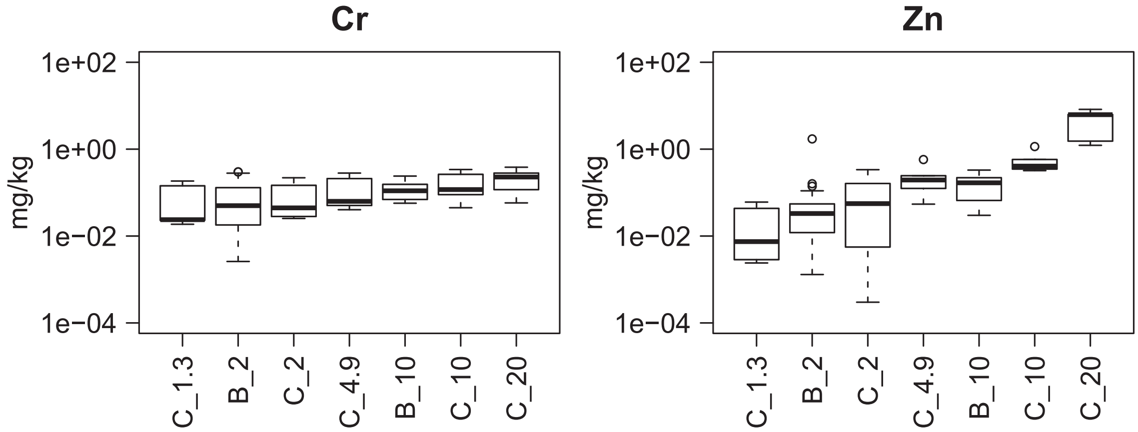

Figure 10 Box plots of the cumulative release of Cr and Zn over a 100-year BA utilisation in a road sub-base as estimated using column (C) and batch (B) leaching tests at various L/S values (1.3, 2, 4.9, 10, 20), as reported in Allegrini et al. (**III**). Data are based on five column leaching tests on BA published in Astrup et al. (2010) and 60 batch leaching tests at L/S 2 l/kg, and 7 at L/S 10 l/kg carried out on BA for compliance purposes.

4.2.2 Diffusion-dominated scenario

In the case of diffusion-dominated scenarios, water does not come into contact with all grains in the material; rather, it flows around the surface of the compacted bulk materials or monolithic specimens, including BA. In these circumstances, the release of metals is not limited by the species' solubility or by other leaching mechanisms, as described in section 4.1.1; instead, mass transfer through diffusion is the limiting mechanism. Dedicated leaching tests for monolithic materials exist (e.g. NEN 7375:2005), in which material specimens are merged in distilled water for a certain period during which the leachant is renewed seven times. Figure 11 shows the output of such tests carried out on concrete specimens with 100% BA aggregates and 100% natural aggregates (Allegrini et al. **IV**).

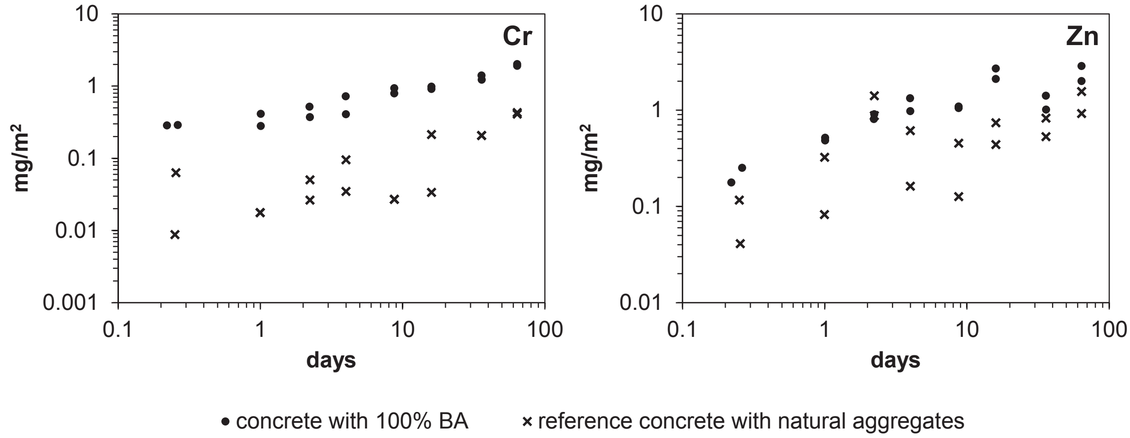

Figure 11 Cumulative release of Cr and Zn from concrete specimens with BA as aggregate (circles) and with natural aggregate (crosses). The values are based on a tank leaching test NEN 7375:2005 performed on a plastic concrete specimen of type 1, as reported in Allegrini et al. (**IV**).

Based on the cumulative release shown in Figure 11, the release mechanisms can be judged accordingly. Whether the release is diffusion-controlled or not, following the standard procedure NEN 7375:2005 the diffusion coefficients (D_e) can be calculated. D_e is calculated using the following formula (Kosson et al., 1996):

$$D_e[m^2/s] = \frac{\pi \cdot M_t^2}{4 \cdot t \cdot (\rho \cdot C_o)^2} \qquad \text{Eq. 1}$$

where M_t is the cumulative release of the metal during the leaching test, ρ is the dry density, C_o is the availability of the metal (as measured by means of the leaching test procedure NEN 7371:2004) and t is the time of the test. Once D_e is calculated, cumulative release over a time horizon in a specific utilisation scenario can be estimated. This can be done by inverting Eq. 1 and then by including site-specific parameters (e.g. surface available for leaching and the amount of time for which the material is wet). For example, assuming that the analysed concrete is utilised for tile production (tile dimensions 0.30x0.30x0.05 m), and the tile is utilised for 50 years in an outdoor pavement that is wet for 30% of the time, the release of Cr and Zn is on average 0.15 and 0.305 mg/kg of BA in the concrete tile and 0.00925 and 0.0535 mg/kg of natural gravel in the concrete tiles. Emissions were calculated by considering that the only surface available for leaching was the base of the tile.

Based on the study by Kosson et al. (1996), this modelling approach is a conservative approach. In their study, in which Cl and Pb were analysed in a laboratory-based lysimeter experiment, Cl release was in close agreement with modelling results, while Pb could not be detected in the lysimeter. Thus, the modelling results for Pb were considered as conservative estimates.

5 Environmental assessment of resource recovery from MSWI BA

5.1 The Life Cycle Approach

As described in the previous chapters, the recovery of resources from MSWI residues – specifically BA – includes sorting and recycling scrap metals and re-using BA as a construction material. From an environmental perspective this represents a variety of potential impacts, from emissions through the leaching of harmful compounds to savings of mineral resources. Hence, to be able to assess comprehensively such a system, a life cycle approach is needed, which means studying the system in all its parts including externally affected systems and activities during its service life.

A life cycle assessment (LCA) is a standardised methodology (EN ISO 14044 and 14040:2006) designed to assess holistically the environmental impacts of products and systems. An LCA study consists of four phases:

- The ***goal and scope definition*** phase, in which the goal of the study, the system boundary, the functional unit (FU), the main assumptions and the methodological choices are defined. The FU is a distinctive feature of an LCA (Sleeswijk et al., 2003), and it quantifies the functions (performance characteristics) of the product or system, thereby providing a reference for all input and output flows and thus assuring comparability of the LCA results (EN ISO 14040:2006).
- The ***life cycle inventory (LCI)*** phase, in which relevant inputs into and outputs from the system into the natural environment are quantified.
- The ***life cycle impact assessment (LCIA)*** phase, in which LCI results are characterised with respect to selected relevant impact categories (e.g. global warming potential, acidification, human toxicity), thus converting from physical emissions to potential impacts.
- The ***interpretation*** phase, where LCI and LCIA results are interpreted consistently with the goal of the study, in order to deliver conclusions and to provide recommendations.

An LCA is an iterative process, so the results of one of the four phases, for instance, could require the revision of the other phases. This is a consequence of the complexity of many systems' life cycles, whose assessment involves a substantial learning process for the LCA practitioner. Important LCA definitions which will help in the coming paragraphs are reported in Box 1.

Box 1 Important definitions in LCA.

Attributional modelling: a *descriptive* LCI modelling principle identifying potential environmental impacts attributable to the system over its life cycle in a status quo situation. The system and the background are modelled as they are on the basis of *historical and measurable data* (EC-JRC, 2010).

Consequential modelling: a *change-oriented* LCI modelling principle which aims at identifying the consequences induced by a decision in the foreground system in the foreground and background systems. In such modelling the supply chain (the response from other systems to the change) is generic and based on market mechanisms as well as political and social constraints (EC-JRC, 2010).

Marginal technology: a technology or process responding to small changes in demand in consequential modelling. The selection of marginal technologies depends on the magnitude of the change imposed by the system, and it is based on market trends and the existence of political constraints. A procedure for marginal identification is reported in Weidema et al. (1999).

Multifunctional process: a "process or system that performs more than one function" (EC-JRC, 2010). A main issue linked to multifunctional processes is the procedure for distributing the consumption of resources and emissions into the environment for individual products in the process.

Allocation: an approach used for solving multifunctional problems, in which exchanges in the multifunctional process (e.g. resource consumed, emissions) are distributed over its co-products on the basis of a certain criterion (e.g. economic allocation, physical allocation).

System expansion: a recommended solution for solving multifunctional problems (EC-JRC ,2010), in which exchanges in the multifunctional process are ascribed to the main product (related to the functional unit of the study), while credits for the production of the co-products are accounted for by subtracting the equivalent production of the co-product in an alternative system (i.e. displaced production). For more details see Weidema (2001).

5.1.1 LCA and waste management systems

The LCA methodology has been mainly applied in the waste management sector since the mid-1990s as a valuable decision-support tool to identify environmentally-sound solutions for managing solid waste (Laurent et al., 2014a). For this reason, the life cycle approach was also proposed by the European Waste Framework Directive (European Commission, 2008a) as a tool for justifying departing from the *waste hierarchy (i.e. prevention, re-use, recycling, recovery and disposal)* for some waste streams.

5.1.2 Recycling of metals in a waste LCA

Recycling processes are multifunctional processes (see Box 1). In an LCA, with FU as the "treatment of a certain amount of a specific waste stream at a given plant, time and location", the existence of co-products (e.g. scrap metals) as a result of fulfilling the function described in the FU creates a multifunctional problem (see Box 1). To solve multifunctionality, allocation should be generally avoided (EN ISO 14044:2006), and alternatively the division of the process (not always possible) or system expansion should be applied. This is valid in both attributional and consequential LCI modelling (Weidema, 2001), even though the data used change depending on the LCI modelling principle applied (Finnveden et al., 2009).

Using system expansion, all exchanges related to the mechanical sorting process, scrap metal transportation, pre-treatment and recycling are ascribed to the treatment of the waste (reference flow), as well as the displaced production of primary metals (with a negative sign). This is an approach equivalent to the "recyclability substitution approach" (also known as the "end-of-life" recycling approach) utilised in generic LCAs (EC-JRC, 2010) and recommended by the metal industry for the environmental modelling of systems involving metal recycling (Atherton, 2007). In a waste LCA, system boundaries are often set from the waste collection to the final disposal/recycling, meaning that the burdens related to a product before its end-of-life (i.e. production and use) are neglected in what is called the "zero-burden assumption". This setting of the system boundary implies an ad hoc application of the recycling substitution approach, which is not applied to a product, as described in the ILCD handbook (EC-JRC, 2010), but to a waste treatment. In a product LCA, the impact of a product which undergoes recycling during its life cycle includes the impact of production and the impact of any material lost during recycling (as not displacing an equivalent amount of primary product). In a waste LCA, what is recycled as part of a waste treatment is credited to the treatment as much as the displaced production of primary material.

System expansion or the recyclability substitution approach can be utilised in closed- and open-loop recycling. The difference between the two types of recycling is how the inherent property of the material is maintained (Dubreuil et al., 2010): in closed-loop recycling the material maintains the inherent properties and can still provide the same function, while in open-loop recycling the material loses its inherent properties and is recycled in a different product system. Metals have excellent chemical/physical properties for recycling (Von Gleich et al., 2007), and they can virtually be recycled an infinite number of times in a closed loop. However, phenomena such as corrosion, oxidation and the inefficient collection of end-of-life scrap compromise recycling rates and quality, thereby leading to downcycling (the use of the material in lower degree applications). For metals such as steel and aluminium, which are often used in alloy form (i.e. mixed with other metals), the presence in the scrap metals of alloying elements which cannot be separated during the melting process (Nakajima et al., 2011) leads to a situation whereby the scrap cannot be used in a range of metal-based products. This quality issue is nowadays being addressed by means of diluting old scrap with primary metals or high-quality scrap, or by cascade recycling into metal products with low-quality requirements (Paraskevas et al., 2013). Downcycling can be described as open-loop recycling in an LCA. Using a “recyclability substitution approach”, the benefits of recycling scrap metals are included by partially discounting any avoided primary metal production – this is done proportionally to the value of the obtained final product and to the amount of primary or high-quality metals used for the dilution. Conversely, if secondary production serves a different function than the primary metal, the recycling process is credited by avoiding the production of the alternative product serving that particular function.

In a waste LCA, the production of secondary metals after recycling is a co-product resulting from the treatment of the waste. Thus, aspects that need to be considered, in order to account properly for recycling processes, are:

- Potential: content of scrap metals in the waste stream.
- Recovery efficiency: efficiency in collection, sorting and upgrading.

- Quality of the scrap metals: chemical composition, corrosion and oxidation levels, combined with the efficiency of the recycling process (metal yield of the plant) where metal losses during the process are accounted for.

- Substitution: which product is substituted and to what extent.

While the first two aspects and the losses of metals in the recycling process have been included in waste LCAs, to a certain extent, substitution and the quality of scrap sent for recycling have not been addressed consistently. Allegrini et al. (**IV**) was the first LCA study to assess metal recovery in a waste LCA, by addressing the four points above. Particularly, none of the existing LCAs assessing metal recovery from MSWI BA has considered the quality and actual substitution of recovered scrap metals (Georgeson, 2006; Muchova, 2010; Kuusiola et al., 2012; Boesch et al., 2014; Meylan and Spoerri, 2014).

Substitution rate

In relation to waste LCAs, most studies in the literature disregard the quality aspect of collected scrap metals. The system has been generally credited for avoiding the production of primary metals with a substitution ratio between secondary and primary products equal to 1 (Muñoz et al., 2004; Damgaard et al., 2009; Rigamonti et al., 2009; Laurent et al., 2014b). However, direction on how to modify the substitution ratio as a function of scrap/secondary product quality exists. As an example, the European Aluminium Association (EAA) recommends defining the substitution ratio as the market price ratio between secondary and primary aluminium (EAA, 2013a), which is equivalent to the “value correction” described in the ILCD handbook (EC-JRC, 2010). Other authors propose instead a correction to the EAA approach by defining the substitution ratio as the market price ratio between scrap metal before refining and primary aluminium (Koffler and Florin, 2013). An additional example of metal quality inclusion in an LCA assessment is found in the recent work by Paraskevas et al. (2013), whose LCA study focuses on the production of secondary aluminium alloys from old scrap (so not on the treatment of waste) and takes into consideration the chemical composition of each scrap type, in order to reflect the quality of the scrap in the LCA result.

Substituted product

The discussion above has been limited to answering the question “To what extent is primary metal substituted?”, but two additional questions are of crucial importance for the LCA results: which material is actually substituted? And where does the production of the substituted material take place? Answering the first question requires knowing the quality and the type of application of the secondary metal produced. In this way the alternative product serving the function of the secondary metal is designed as the “substituted material”. In attributional modelling the selection is based on historical information about the product utilised for serving a given function. In consequential modelling, the substituted material is the marginal technology (see Box 1), which requires an analysis of the market trend in order to be identified (Weidema et al., 1999). Once the substituted material is identified, the geographical location of the production process for the substituted material is also defined, and consequently the technological level of the region and the mix of energy sources (average in the attributional case and marginal in the consequential modelling) used for energy provision are reflected in the LCI. An example of an LCA in which the location of the displaced production was included is a recent study on aluminium recycling from old scrap by Sevigné-Itoiz et al. (2014). An extensive analysis, with the consequential approach defining the marginal primary production of aluminium, is also reported by Schmidt and Thrane (2009).

5.1.3 Leaching of toxic compounds in a waste LCA

Leaching of substances from MSWI BA can be modelled in an LCA and its impact on toxic impact categories and eutrophication (if a significant amount of phosphate is released) can be quantified. Several LCA studies have addressed the impact of leaching from BA and waste disposed in landfill sites (e.g. Finnveden et al., 1995; Hellweg, 2000; Doka and Hischier 2005; Birgisdóttir et al., 2007; Obersteiner et al., 2007; Doka, 2009; Manfredi, 2009), while LCA studies considering BA utilisation in construction works are limited (Birgisdóttir et al., 2006; Birgisdóttir et al., 2007; Toller et al., 2009). Other studies have addressed the utilisation of BA as a construction material, albeit disregarding leaching (Barberio et al., 2010; Margallo et al., 2014).

Leaching modelling in LCAs

Results from laboratory leaching tests and field data (in the landfill case) are applied when modelling leaching in an LCA (Obersteiner et al., 2007; Toller, 2008). Leaching data are input into the LCI as the cumulative release of the individual element over the defined time horizon of the LCA study, and the approach described in section 4.2.1 is generally applied (Birgisdóttir, 2005; Manfredi, 2009). While most studies apply a time horizon limited to 100 years, the disposal of residues is likely to represent a continuous source of metal release into the environment for a much longer-term perspective. Even though long-term emissions have been largely addressed in the literature (e.g. Hellweg et al., 2003; Hauschild et al., 2008; Pettersen and Hertwich, 2008; Doka, 2009), there is no consensus yet on how to model such emissions. Consequently, most authors limit the assessment to within 100 years (Laner, 2009; Laurent et al., 2014b).

Relevant parameters affecting leaching impacts in an LCA

Parameters influencing the cumulative release of an element from a BA deposit into the natural environment are related to the conditions in a given utilisation scenario. Climate conditions, deposit type and geometry influence the amount of water infiltrating BA deposits (the L/S value). Conditions within the BA deposit, such as pH, redox conditions and the presence of organic matter, influence release mechanisms of the different elements. The type of material underneath the BA layer (e.g. subsoil) affects the migration of released contaminants in and into natural compartments (e.g. soil, surface water). These aspects were addressed in Allegrini et al. (**III**), by using leaching datasets based on batch and column leaching tests (the results are summarised in Figure 12). While the origin of the data (whether from a batch or a column leaching test) appears not to affect the results, the LCA results appear more sensitive to the L/S parameter. By testing various L/S values, the toxic impact categories carcinogenic (HTc), non-carcinogenic human toxicity (HTnc) and ecotoxicity to freshwater (ET) (using the LCIA methodology USEtox (Rosenbaum et al., 2008)) resulted sensitive to accuracy of the L/S estimate below 5 l/kg (within the tested range from 1.3 to 22 l/kg).

The migration of pollutants into subsoil below a BA application was modelled over a 100year time frame by using the reactive transport multisurface model described in Dijkstra et al. (2004 and 2009), which is implemented in Orchestra and embedded in LeachXS. The same model has also been used for setting emission limit values in the Dutch Soil Quality Decree (Verschoor et al., 2008). By applying this model to emissions from BA tested with the column leaching test, and by assuming three types of soil (clay, peat and sand), it was estimated that most metals remain within the first metre of soil after 100 years. The most mobile metal was Sb, 63% of which was released into the pore water of the soil at one metre below the BA deposit. Based on these results transfer coefficients (TCs) were estimated, in order to divide leaching emissions between the soil and the water compartment.

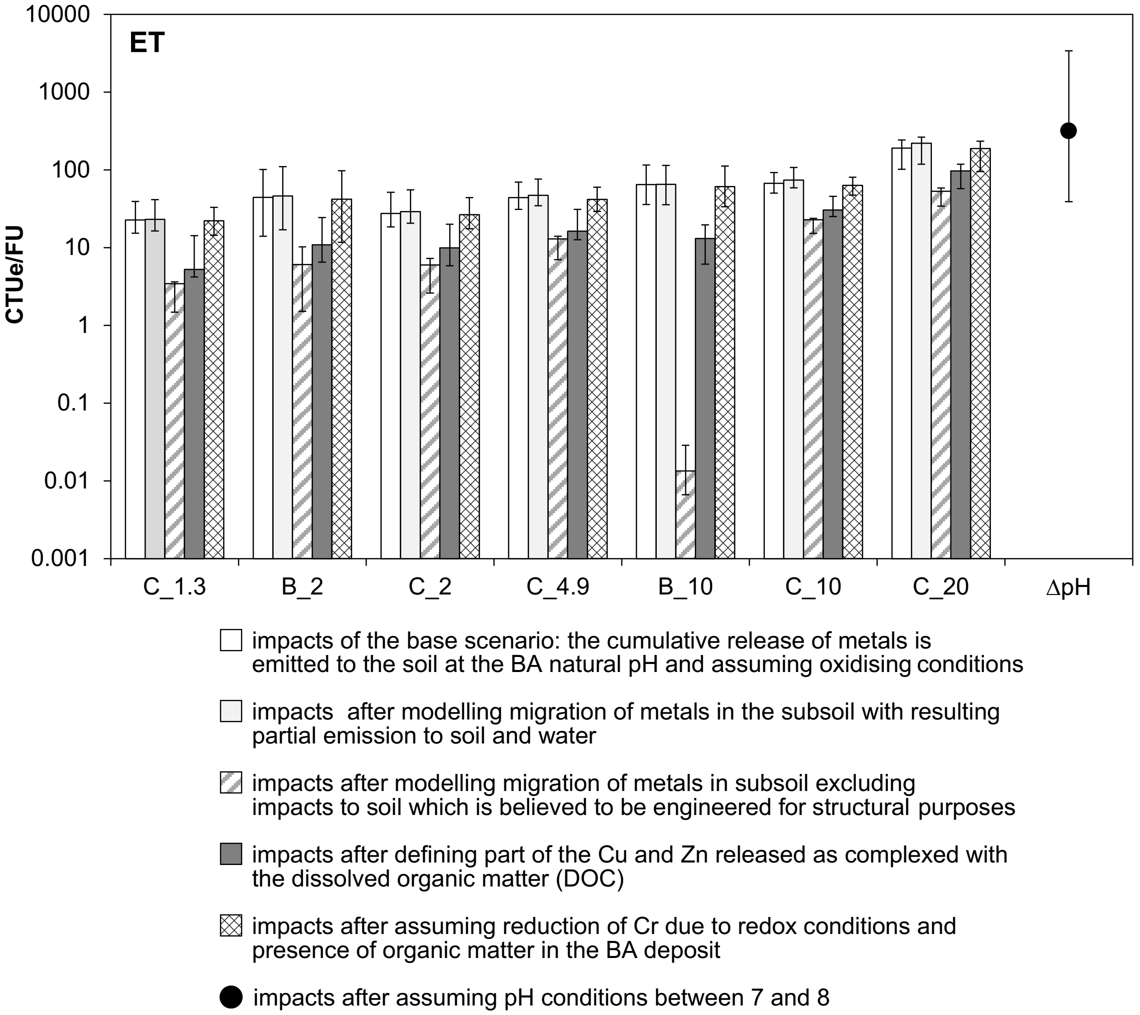

Figure 12 Potential impacts on ecotoxicity to freshwater (ET) from metal released over a 100-year utilisation of 1 Mg of MSWI BA in a road sub-base in Denmark, as analysed in Allegrini et al. (**III**). The results were obtained using different leaching datasets with data from batch (B) or column leaching tests (C) at various L/S ratios (i.e. 1.3, 2, 4.9, 10, and 20). For each leaching dataset, the results of varying different parameters (i.e. metal partitioning into the environment, DOC complexation, Cr oxidation state, pH) are compared with baseline assumptions (i.e. white bars). Error bars represent the 90% confidence interval and the maximum and minimum values in the assessment of the pH parameter. The results are given as comparative toxic units (CTUs), as defined in the USEtox model.

The calculated TCs were applied and the characterisation factors (CFs) for emissions into soil and water were assigned respectively to the portion of metals remaining in the soil and reaching shallow groundwater. However, due to the small amount of release into the shallow groundwater, estimated through the TCs, toxic impacts after this change were comparable with those obtained by considering 100% of emissions into the soil. Nonetheless, emissions of metals into the soil underneath the BA layer in the road could be considered not to contribute to toxic impacts, because 1) this soil might be-long to the technosphere, as it is often engineered in order to assure the structure of the road and 2) being under the road, it is not exposed to atmospheric agents (e.g. wind) and is not in contact with plant roots. Thus, the only exposure or fate path occurring is the leaching of contaminant from the soil and into shallow groundwater which refills surface water bodies. However, if the assessment is limited to 100 years, and within this timeframe most metals remain in the first metre of soil, then the only emission with any reasonable impact is the one reaching the shallow groundwater one metre down. This was tested in Allegrini et al. (**III**), following which, as shown in Figure 12 for ET, the scores for HTc, HTnc and ET reduced considerably.

In Allegrini et al. (**III**) the geochemical modelling of pH-dependent leaching data was carried out by means of Orchestra embedded in LeachXS. Based on these results, sensitivity analyses were carried out on the release of Cu and Zn, which were both assumed to be partially complexed with dissolved organic matter (DOC), which lowers the bioavailability of such metals and thus their potential toxic effect (Boyd et al., 2005; Steenbergen et al., 2005; Cooper et al., 2014). The ET score was reduced on average by 66% with respect to the baseline scenario. A large proportion of the released Cr was found DOC-bound – and thus as Cr(III) – and the change affected the HTc score to the same extent as the imposed variation. Lastly, pH was found to affect toxic impact potentials, in agreement with the highly pH-dependent behaviour of most metals (e.g. Cu, Zn). Only the HTc score was not affected by the change, as the main metal determining HTc is Cr(VI) and its leaching behaviour is only marginally influenced by pH conditions.

Uncertainty and limits for toxic emissions and impact assessment

In LCA studies addressing waste incineration, MSWI BA management and leaching issues have often been disregarded (Astrup et al., 2014), a main reason being that toxic impact categories were not included in the assessment (Laurent et al., 2014b). In most studies, such a choice is justified by mentioning the large amount of uncertainty related to the quantification and characterisation of toxic emissions. However, as shown in Allegrini et al. (**III**) (Figure 13), leaching-related impacts from BA utilisation cannot be disregarded in a waste LCA irrespective of the way leaching is quantified. In Allegrini et al. (**III**), impacts from leaching emissions as the result of utilising BA in roads were compared to the overall impact of three scenarios with increasingly large system boundaries. In the first scenario only transportation and BA use in roads were included, and in this case leaching emissions dominated the overall toxic impact. In the second and the third scenarios, though, the WtE system and the whole WMS were included, respectively. In these scenarios impacts related to energy production and substitution had the largest impact. However, due to the significant uncertainty surrounding the LCI of background processes, such as energy production and related processes, impacts from leaching emissions should not be disregarded. Moreover, considering the importance of toxic categories in the overall LCA outcomes, together with the increasing efforts of the LCA community in reducing uncertainty in the toxic characterisation (Rosenbaum et al., 2008; Hauschild et al., 2013), increased effort by the LCA practitioner is required, in order to include such an aspect and to increase the quality of related LCI data.

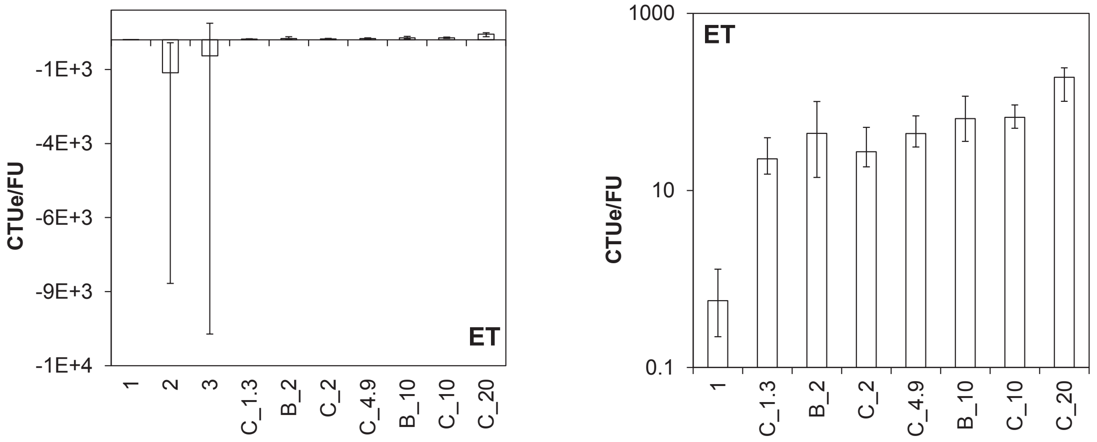

Figure 13 Importance of ecotoxic impacts related to leaching emissions in LCA studies of WMS, as reported in Allegrini et al. (**III**). In the left chart, the bars with labels “1, 2 and 3” represent ecotoxic impacts related to the utilisation of 1 Mg of BA in road (1), incineration of waste and utilisation in road of the resulting 1 Mg of BA (2), waste management, incineration of the residual waste and utilisation in road of the resulting 1 Mg of BA (3). Leaching emissions from BA utilisation are excluded in “1, 2 and 3”, and they are shown separately with the bars labelled from “C_1.3” to “C_20”. “C” indicates leaching data based on column leaching tests, “B” on batch leaching tests and the numbers indicate the L/S values. Error bars represent the 90% confidence interval of the results relative to uncertainties in the LCI.

As shown in Figure 13, uncertainty for the toxic results (e.g. ecotoxicity, ET) is significant, meaning that, when such uncertainty is included in modelling, conclusions are not robust. However, considering the great uncertainty in Figure 13, it is clear how improvements in the data collection of emissions of toxic relevance are of primary importance in increasing the quality of toxic results in LCA studies.

The confidence interval shown in Figure 13 does not include uncertainty associated with the characterisation method (LCIA method); rather, it only relates to uncertainty connected with the quantification of toxic emissions in the LCI. In fact, even though the uncertainty of the CFs for organic substances reduced significantly (down to two or three orders of magnitude) with the development of the consensus model USEtox (Rosenbaum et al., 2008), uncertainty related to the CF for inorganic elements (i.e. metals) remained significant.

5.2 Case study: resource recovery from Danish MSWI BA

In Allegrini et al. (**IV**), quantitative data on the resource potential and recovery efficiencies for BA (cf. 3.1), metal leaching (cf. 4) and qualitative aspects of the recovered resource (cf. 5.1.2) were combined in an LCA study. Figure 14 shows characterised results corresponding to the treatment of one Mg of BA produced by a Danish WtE plant. Ten scenarios were included in the assessment, including various configurations of the metal recovery system (from zero recovery of NFe scrap in scenario A to maximum recovery efficiency for Fe and NFe scrap in scenario K, as well as the current situation in C) and management options for the treated BA.

5.2.1 Scrap metal recovery

The sorting, upgrading, transportation and recycling of scrap metals extracted from BA resulted in net savings for the environment (negative score) for non-toxic categories. Conversely, toxic impacts were generally positive, mainly because of Cr(VI) leaching from the disposal of slags from secondary steel production, though increasing metal recovery resulted in decreasing toxic impacts due to benefits related to Cu recycling.

Increasing the recovery of NFe metals increases savings for the global warming potential (GWP) impact category, while the opposite trend was observed for the depletion of mineral abiotic resources (ADm). Benefits for GWP were the result of the large difference in energy demand between primary and secondary production. This is particularly valid for aluminium recycling (which in the baseline assessment was assumed to substitute for primary aluminium at a substitution rate of 1), as the energy required for refining or remelting Al scrap requires only 5% of the energy needed to produce primary aluminium.

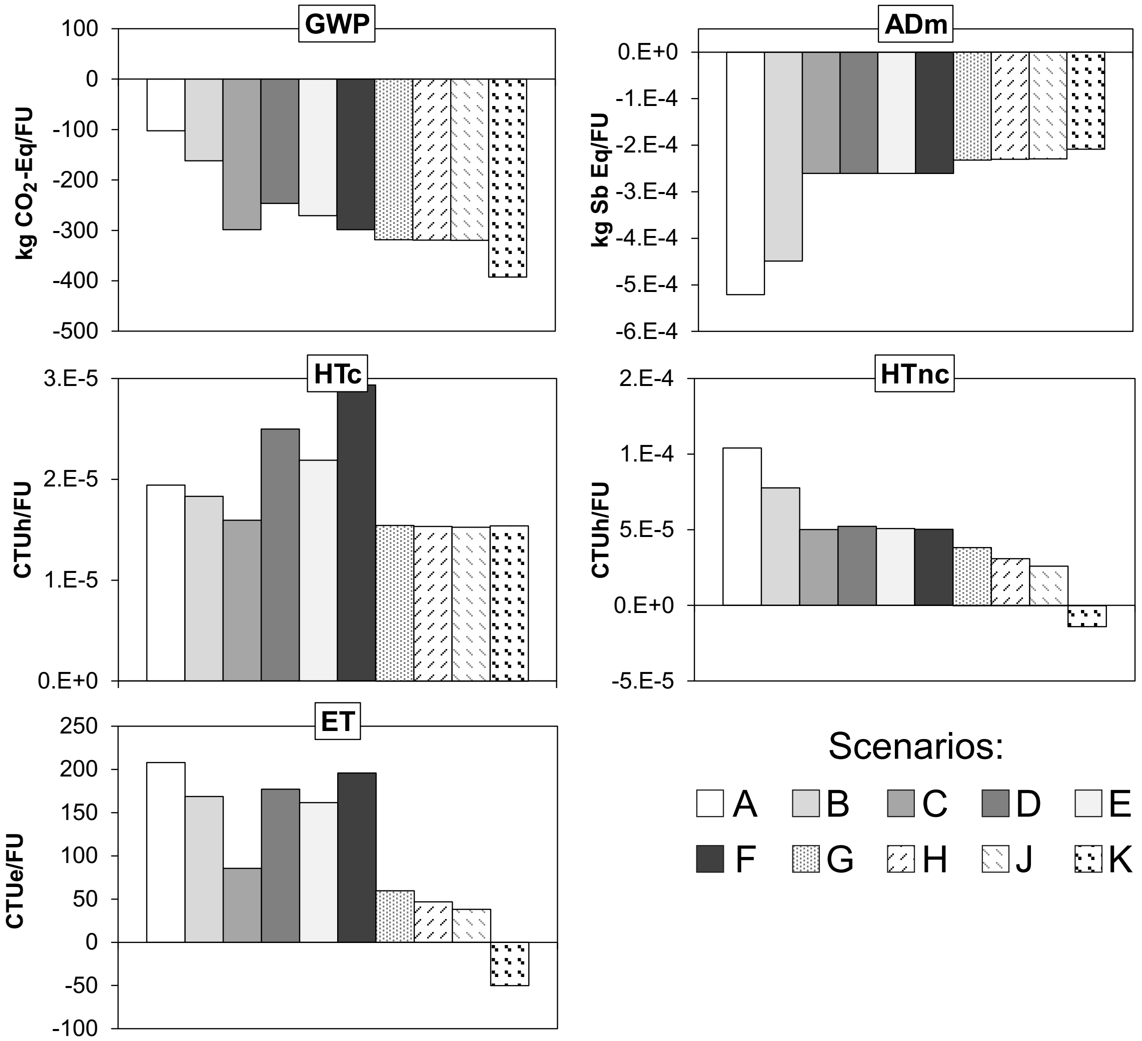

Figure 14 LCA results related to the management of 1 Mg of BA (i.e. transportation, metal recovery, and utilisation in construction works), as reported in Allegrini et al. (**IV**). Scenarios (represented by bars from A to K) include increasing recovery of scrap metals from the BA, from zero NFe recovery (in scenario A) to maximum recovery (in scenario K). In scenario A the treated BA is landfilled, in B, C, G, H, J and K the treated BA is utilised in road construction and in D, E and F the treated BA is used as aggregate in three types of concrete. Impact categories: GWP, global warming potential, IPCC 2007; ADm, abiotic depletion of mineral resource, CML 2013 v.4.2; HTc and HTnc, carcinogenic and non-carcinogenic human toxicity, USEtox; ET, ecotoxicity, USEtox. [CTU, comparative toxic unit]

Burdens associated with the increased energy spent on sorting and upgrading scrap from BA were negligible with respect to the benefits from displacing primary production. The recovery of Al scrap was beneficial, even though losses of aluminium, due to oxidation (e.g. Biganzoli et al., 2013) and to the efficiency of the refining process at the plant, were included.

ADm savings decreased as a result of increasing aluminium recycling, which gave an indication of an issue related to how recycling mixed old scrap is modelled in LCA. The major burden in ADm was represented by the need to add alloying elements (i.e. Zn) to the melt aluminium at the refinery in order to obtain the targeted *cast aluminium alloy*. This impact is negligible in the production of primary aluminium, where the final product is mainly a *wrought alloy*, characterised by tight limits on the content of alloying elements. Thus, this clearly showed that secondary aluminium is a different product from the assumed avoided primary aluminium, and hence complete substitution between the two products is not realistic. Moreover, even though the result in Figure 14 is based on a generic aluminium refining process for old scrap (from the Ecoinvent LCI database), this result shows how alloying element losses, as a result of recycling highly heterogeneous mixtures of aluminium scrap alloys, actually outbalance the savings made by avoiding aluminium from ore. As also shown also by Paraskevas et al. (2013), the practice of recycling old scrap metals (post-consumer or post-incineration) leads to the downcycling of materials, and especially to losses or the unwanted accumulation (as tramp element) of valuable alloying elements.

5.2.2 Substituted marginal technology and substitution rate

In the case study, whose results are shown in Figure 14, the marginal process for each recycled metal was the production of the respective primary metal in China in relation to the significant growth in production in that region in the last decade (Blomberg, 2007; EAA, 2013b; IAI, 2013; ICSG, 2013; ISSF, 2013; World steel association, 2013). However, looking at trends in the production of primary metals, especially aluminium, other regions in the world have seen a significant increase in production capacity and could be selected as marginal candidates for aluminium recycling. For example, the composite marginal, including primary production in China, Russia and the Middle East as proposed by Schmidt and Thrane (2009), was applied to the scenario analysis, while 100% primary aluminium production in the Middle East was based on 100% natural gas. Moreover, a fourth marginal technology was considered, based on the assumption that aluminium recycling from old scrap in Europe affects the European market only, meaning that the additional amount of secondary aluminium produced displaces an alternative product within Europe. In Europe, most of the secondary aluminium from old scrap is used in the automotive industry (Modaresi and Müller, 2012), whose market volume has shown signs of stagnation in the last few years (ICCT, 2013; OICA, 2014). Following the approach of Weidema et al. (1999), in such a market situation marginal technology should be the least competitive one, which in the automotive industry might be represented, for example, by cast iron. Figure 15 shows the results for the GWP category by varying the marginal technology. GWP savings resulted from 16 to 57% lower than in the baseline scenario.

In the analysed system, aluminium and steel recycling played a central role in the LCA results, due to the amount recycled (i.e. steel) and the large credits obtained by displacing primary production (i.e. aluminium). However, aluminium and steel are more prone to downcycling because of the accumulation of alloying elements in the materials, which cannot be separated during the melting process (Nakajima et al., 2010, 2011; Nakamura et al., 2012).

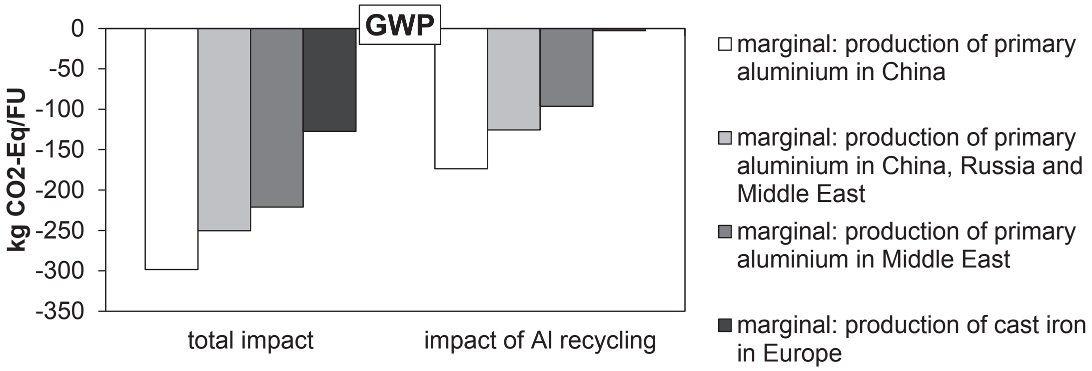

Figure 15 Net impact on global warming potential for the current BA management in Denmark (scenario C) as a function of the selected marginal technology producing the product dismissed by the production of secondary aluminium from Al scrap from BA (Allegrini et al. **IV**). Total net impacts for the entire BA treatment system are reported on the left side of the chart (total impact) while impacts for the sole aluminium recycling activity (secondary and primary aluminium production) are reported on the right side of the chart (impact of Al recycling).

Accumulated alloying elements become tramp elements, thus limiting the application of the material or requiring the addition of high-quality scrap metals up to pure primary metals. Stainless steel is also sensitive to downcycling; however, due to the small amount recovered from BA, variations in the SS substitution rate and marginal technology were found not to affect the results. The recycling of copper made significant contribution to the LCA results, although differently from the other recovered metals the quality of the recovered scrap affects the final yield of Cu after recycling, but not the quality of the produced secondary copper. The application of electrorefining processes effectively removes other metals present in HNFe scrap sold to copper smelters. Hence, the substitution rates for copper and stainless steel recycling remained equal at 1, while the substitution rates for aluminium and steel varied between 0 and 1. With the current metal recovery efficiency, for substitution values below 0.17 and 0.21 for aluminium and steel, points at which burdens related to sorting, transportation and scrap remelting outbalanced the benefits of recycling (i.e. breakeven points) were found. Additionally, the impact of sorting activities was varied (by multiplying it by a factor >1), in order to assess the position of the breakeven point in varying conditions.

In Figure 16 the resulting plane of possible breakeven points (i.e. points respecting the condition GWP=0) is reported for the current scenario (C) and for the case of maximum metal recovery (K). No breakeven point was found (i.e. GWP was always below zero) for scenario K with the assumed energy demand of the recovery system. To reach the breakeven points with the lowest quality of the recovered aluminium and steel, the impact of the recovery system should be 50 times the value found with the baseline scenario. In scenario C, assuming the maximum quality of the scrap (a substitution rate equal to 1), impacts as a consequence of the sorting, upgrading and transportation of scrap should be 70 times the current value, in order to reach the breakeven point. However, by defining the substitution rate for aluminium as the ratio between the price of the secondary aluminium alloy and the primary aluminium, and using prices for the most abundant secondary alloy produced from low-quality scrap, the substitution values came in at approximately 0.05. This means that by employing current recycling practices for post-incineration scrap, the breakeven point might actually be achieved.

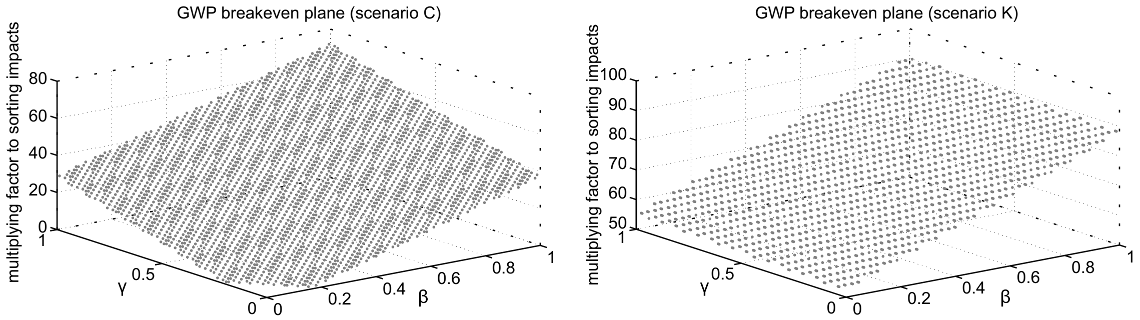

Figure 16 Plane of points representing different combinations of β (substitution rate for secondary aluminium), γ (substitution rate for secondary steel), and impact of sorting activities (vertical axis) resulting in null global warming potential (i.e. GWP=0). Figure from Allegrini et al. (**IV**). The results for the current BA treatment system (scenario C) are shown on the left side, and the results for a future configuration of the system with high recovery efficiencies for scrap metals (scenario K) on the right side.

5.2.3 Utilisation of the treated BA

In the case study, three options were considered in relation to the fate of the treated BA: disposal in a landfill site for non-hazardous materials (scenario A), utilisation as a gravel surrogate in a road sub-base (scenarios B, C, G, H, J, K) and utilisation as aggregate in concrete (scenarios D, E, and F). The concrete specimens used for the assessment were produced with BA completely substituting for natural aggregates. Hence, in order to maintain the required structural characteristics, cement was added to the mixture in far greater amounts than in the normal mix for the reference concrete (i.e. with natural aggregates). As shown in Figure 14, this resulted in potentially lower savings for GWP with respect to a scenario with the same level of metal recovery, albeit where BA was utilised in road (scenario C). Conversely, utilising BA in road sub-bases results in benefits to GWP due to the displaced excavation of gravel – as shown in previous studies (Birgisdóttir et al., 2006).

However, the main impact of utilising or disposing of BA is seen in the toxic categories, particularly for HTc and ET. The leaching of metals from BA in landfills and roads was modelled by following a percolation-dominated approach, as described in section 4.2.1, and using column leaching data published by Astrup et al. (2010). For the application of BA in concrete, it was assumed that concrete tiles for outdoor pavements are produced and then utilised for 50 years. When their useful service life comes to an end, the concrete tiles are demolished, crushed and stored in outdoor heaps for natural weathering, before reutilisation as aggregate in a road sub-base. The leaching of metals was experimentally evaluated using three types of concrete specimens containing 100% BA aggregates, and the reference tiles were provided by the Danish Technological Institute (DTI). Monolithic specimens were tested in the laboratory and analysed by means of tank leaching tests (NEN 7375:2005) and an availability leaching test (NEN 7371:2004), while release under diffusion conditions was estimated as detailed in section 4.2.2. Concrete specimens were also crushed and aged in the laboratory until stable pH conditions were met, in order to simulate the demolition and storage phases. The resulting material was then tested with a batch leaching test to assess compliance with the Danish regulatory limits for residual material utilisation in construction works, even though construction and demolition waste are generally not subject to this regulation. Based on the results from the batch leaching tests, the material was not compliant with Danish regulatory limits due to the excessive release of Cr and Se. In a case of non-compliance, the utilisation of the material is still possible, but further site-specific assessments should be carried out to assure safe use of the material. In the modelling phase, the material was assumed to be used in roads and the results of the batch leaching test were used. Figure 17 presents a detailed overview of toxic impacts as a result of BA utilisation or disposal. The results suggest that the utilisation of BA in concrete production (scenarios D, E and F) is not the best option from an environmental perspective.

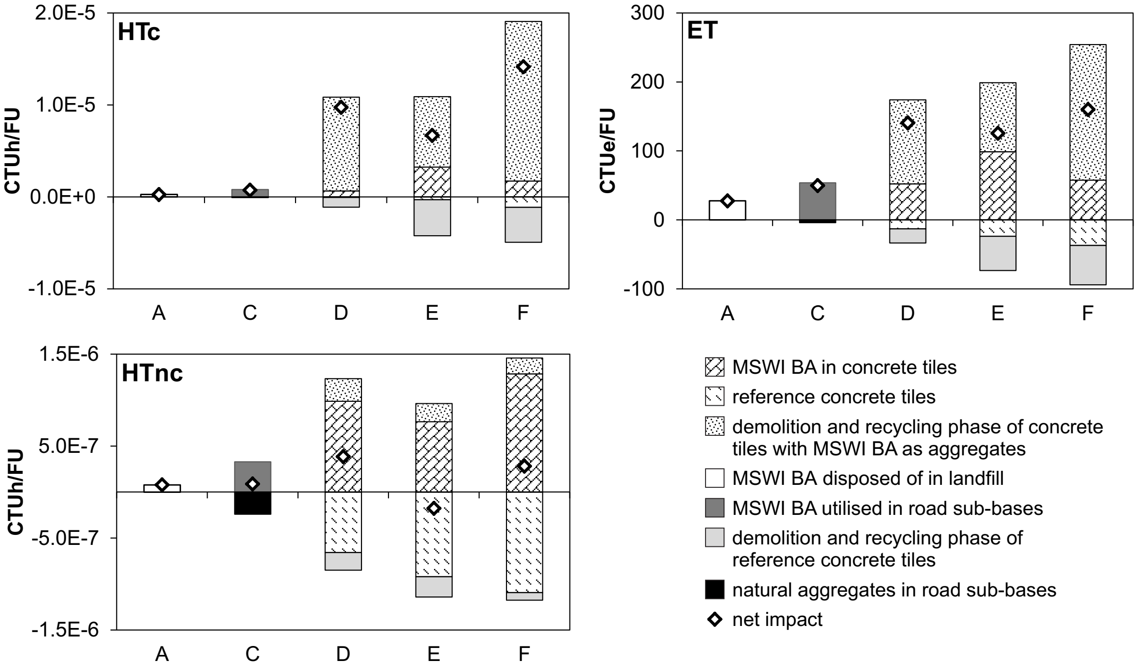

Figure 17 Potential toxic impacts due to leaching of metals from the disposal of or utilisation of BA, as reported in Allegrini et al. (**IV**). BA are disposed of in landfill (in scenario A), utilised as aggregate in road (scenario C) and in three types of concrete specimens (scenarios D, E and F). The results are reported as comparative toxic unit (CTU) based on the USEtox impact methodology. Impacts related to leaching from BA utilisation or disposal (positive impacts) are reported together with the avoided leaching impacts related to the displaced use of natural aggregate in road and concrete (negative impacts). Diamonds represent the net results.

The release of Cr was the most damaging emission, followed by Sb and Cu, and most emissions were accredited to the recycling phase of the concrete. The release of metals into the environment during the “monolithic” phase of the concrete scenario was also significant. However, the modelling used in this phase is conservative, especially for elements released in minor to trace concentrations during the laboratory leaching test, furthermore 100% substitution of natural aggregate with BA is not applicable in practice. Moreover, the service life of concrete tiles used for non-structural applications is generally shorter than 50 years, most probably ranging between 5 to 20 years. Hence, the recycling phase is the dominant phase in the 100-year life cycle of the concrete tile, and the release of metals (particularly Cr) from utilising crushed and aged concrete in construction works significantly affects toxic category results.

6 Conclusions

The aim of this PhD was to provide a quantitative basis for assessing resource recovery from MSWI BA and boiler ash. The main conclusions are summarised as follows.

Using an integrated approach involving BA sample characterisation, full-scale treatment facility analysis, MFA and SFA, the potential contents of valuable scrap metals in BA, as discharged from the WtE plant, were quantified as 7.2, 1.4 and 0.24%ww, respectively, for ferrous, aluminium and copper scrap. Based on this potential, recovery efficiencies at the gate of the recycling facility (e.g. an aluminium refinery) were respectively 85, 62, and 61%. Concentrations of precious (i.e. PGM) and critical elements (i.e. REE) were detected in the treated BA and in the boiler ash; however, concentrations were below a level of interest for recovery. An analysis of these metals was carried out on individual BA grain size fractions and on boiler ash samples collected along the boiler of a WtE plant. The results showed no significant enrichment in specific fractions. Hence, based on these results, separate management of BA or boiler ash fractions for the recovery of precious and critical elements is not justified.

The release of elements of environmental concern from BA and boiler ash was quantified in view of their utilisation. The application of compliance batch leaching tests showed that BA fulfilled limits for utilisation in construction works in Denmark, while none of the ten boiler ash samples collected along the WtE boiler was compliant. The release of readily soluble Cl and Na salts, and the release of Cr, Pb, Se and Zn, was determined to be critical. The leaching behaviour of the boiler samples was further tested as a function of pH, to identify differences in the release mechanisms of critical elements which could have reflected differences in the geochemistry of the ash within the boiler. Except for a few elements (e.g. S), the release of elements was found to be consistent throughout the boiler, so, also from a hazardousness perspective, the separate management of specific fractions of boiler ash was not supported.

Information and experimental data collected during the PhD were applied to analyse the recovery of resources from one Mg of BA from a life cycle perspective. The resources included were scrap metals and aggregates (i.e. treated BA) to be used in road construction or in concrete production. The recovery of metals was found increasingly beneficial to GWP in line with the increasing sorting of metal scrap from BA. Scrap sorting, upgrading and transportation impacts were negligible with respect to the benefits obtained by displacing primary metal production. However, these benefits significantly decreased by varying the marginal technology and substitution rates in metal recycling. Particularly, by varying the substitution rates of secondary steel and aluminium, a breakeven point (GWP=0) for the current BA recovery system was found for values of substitution below 0.21 and 0.17, respectively. The substitution value, for example, of 0.17 for aluminium is far away from the factor of 1 generally adopted in a waste LCA, meaning that even the recycling of low-quality material leads to substantial environmental benefits. However, when defining the substitution ratio based on the metal price ratio between secondary and primary products, and using the price for secondary aluminium as produced by one refiner in Europe, the substitution rate was estimated at approximately 0.05. This shows that with current waste LCA practice, the benefits of metal recycling might be significantly overestimated.

The impact of utilising BA as a construction material was analysed, and the importance of toxic emissions through leaching during BA utilisation was especially assessed. The importance of such emissions in a waste LCA was tested by analysing their impacts in LCA studies with different types and numbers of processes included in the system boundary. The results showed that even in LCA studies where energy substitution (e.g. WtE) plays a prominent role, leaching emissions cannot be disregarded due to significant uncertainties in the inventory data of background processes. In LCA scenarios with system boundaries, including the sole utilisation scenario, leaching emissions dominate toxicity impacts, and thus an accurate choice of parameters for determining release in the utilisation scenario is necessary. In the case study LCA, comparing the use of BA as aggregate in road and in concrete, it was found that impacts following on from the release of toxic elements in the concrete scenario were generally higher than for the road case. Particularly, the main impacts were caused by the release of Cr in the recycling phase of the concrete tiles after finishing their service life, thereby indicating the importance of including leaching over the entire life cycle of the material.

7 Future Research

Based on the experience gained in the course of the present research work, some objectives for future activities could be suggested.

Considering the importance that substitution (marginal technology and rate) has on LCA results in relation to metal recycling, it would be interesting to investigate this aspect further, especially pertaining to the recycling of aluminium and ferrous scrap. In this regard, considering the difficulties encountered during this thesis in accessing information about the secondary metal industry, it is necessary to have an active involvement of the industry. For example, the analysis of historical data on melt composition would enable the determination of more robust quality indicators when estimating substitution factors. Moreover, such historical data based on scrap of different qualities/sources (e.g. old scrap from households and post-incineration old scrap) may be necessary, in order to compare fairly different waste management systems.

The comparative analysis of emerging recovery systems including, for example, dry discharge technology, or metallurgical systems applied for the recovery of non-scrap metals should be considered. Such analyses may in fact helpfully support the technological development of WtE systems and residue treatment. Moreover, a life cycle costing could be coupled with LCA results, in order to evaluate the economic feasibility of existing or hypothetical alternatives for metal recovery.

Concerning leaching emissions in relation to an LCA, efforts should be made to implement existing knowledge about leaching mechanisms in LCA studies. Moreover, with regards to the impact assessment phase, consensus characterisation methods, including toxic impacts on groundwater, and the impacts of availability controlled elements such as Cl and K, should be developed further.

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In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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