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Characterisation of the main properties and leaching behaviour of bottom ash from different types of waste thermal treatment plants in view of specific reuse or disposal scenarios

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Abstract

I processi di trattamento termico di rifiuti, quali ad es. biomasse, rifiuti solidi urbani indifferenziati o combustibile derivato dai rifiuti, CDR, in appositi impianti di termodistruzione con produzione di energia (quali inceneritori e gassificatori) danno origine ad alcuni residui solidi, tra cui le scorie di fondo (bottom ash, BA) che rappresentano circa il 10-20% in peso dei rifiuti trattati. Il crescente impiego di tali impianti per il trattamento termico di varie tipologie di rifiuti ha suscitato, negli ultimi anni, un forte interesse nell’individuazione di adeguate strategie gestionali per le BA, le quali non solo rappresentano il flusso di residui solidi più abbondante derivante da tali processi ma anche, al tempo stesso, il più idoneo per caratteristiche fisiche (es. densità e granulometria) e proprietà tecniche (es. resistenza a compressione) al riutilizzo come materiale da costruzione in luogo di aggregati naturali. Per tali ragioni, il recupero delle BA in vari settori dell’ingegneria civile (principalmente nella costruzione di sottofondi stradali, terrapieni e barriere antirumore) è comunemente praticato in diversi Paesi Europei, come l’Olanda e la Danimarca. In altri paesi, tra cui l’Italia, invece, non esistono specifiche norme che regolamentino i requisiti tecnici ed ambientali di tali residui ai fini della loro valorizzazione, per cui essi sono prevalentemente smaltiti in discarica per rifiuti non pericolosi.

A tale proposito, bisogna osservare che, generalmente, le BA presentano un maggiore contenuto di componenti potenzialmente tossici per l’ambiente, quali metalli (es. Pb, Cu e Zn), metalloidi (es. Cr, Mo e Sb) e sali (es. cloruri e solfati), rispetto ai materiali naturali impiegati nell’edilizia. Tuttavia, l’aspetto più rilevante da valutare per l’individuazione di idonee strategie gestionali riguardanti il recupero o lo smaltimento di tali residui è il rilascio dei suddetti costituenti in soluzione acquosa (“lisciviazione”), nonché i principali meccanismi geochimici che ne influenzano la solubilità nel breve e nel lungo periodo, piuttosto che il loro contenuto totale. Dunque, un’appropriata analisi dell’impatto ambientale concernente il riuso o lo smaltimento delle BA richiede tali valutazioni.

L’obiettivo della presente tesi di dottorato è stato quello di studiare le principali caratteristiche fisiche, chimiche, mineralogiche e il comportamento alla lisciviazione di BA prodotte da impianti di trattamento termico di rifiuti differenti tra loro sia per la tecnologia utilizzata, sia per la tipologia di rifiuti trattati, al fine di individuare per tali residui le proprietà ambientali in condizioni di recupero o smaltimento. In particolare, sono state analizzate le BA derivanti da: un impianto di incenerimento di CDR (refuse derived fuel incineration, RDF-I); un impianto di gassificazione di CDR (refuse derived fuel gasification, RDF-G); un impianto di incenerimento di rifiuti ospedalieri (hospital waste incineration, HW-I). A tale proposito, bisogna notare che, in letteratura, sono disponibili soltanto alcuni studi riguardanti la caratterizzazione di questi specifici residui, a causa del recente impiego di tecnologie, quali l'incenerimento e la gassificazione, per la valorizzazione energetica del CDR, così come del piuttosto limitato numero di impianti esclusivamente dedicati al trattamento termico dei rifiuti ospedalieri.

L'obiettivo finale di questa ricerca è stato quello di identificare, sulla base di un'attenta caratterizzazione della composizione chimica e mineralogica di tali residui, i principali processi geochimici che controllano la lisciviazione dei maggiori costituenti e dei metalli in traccia dalle BA in esame, nonché di valutarne le strategie gestionali più idonee. A tale scopo, dapprima, sono stati condotti test sperimentali di lisciviazione, i cui risultati sono stati, successivamente, analizzati mediante l'impiego di modelli geochimici predittivi, in accordo con l'approccio utilizzato in studi precedenti riguardanti le BA prodotte da impianti di incenerimento di rifiuti solidi urbani (municipal solid waste incineration, MSWI).

Innanzitutto, nel presente studio, sono stati individuati i principali meccanismi e i componenti (organici ed inorganici) che contribuiscono a determinare gli alti valori della perdita al fuoco (loss on ignition, LOI) a 550 o 1000 °C per le RDF-I BA e le HW-I BA, mediante termogravimetria e spettrometria di massa (TG-MS) (**Chapter 1**). A questo proposito, bisogna osservare che la LOI è considerata quale un parametro di qualità dei residui da incenerimento, essendo tipicamente associata al loro contenuto di sostanza organica. Di conseguenza, alti valori della LOI per le BA sono stati, generalmente, correlati ad una scarsa efficienza del processo di combustione dei rifiuti. Tuttavia, i risultati ottenuti in questo studio per le RDF-I BA hanno indicato che la LOI è associata all'evaporazione di H2O e alla decomposizione di fasi d'idratazione (portlandite, hydrocalumite) e di carbonati di calcio ($CaCO_3$) contenute nei campioni in esame. Per le HW-I BA, invece, i risultati hanno mostrato che gli alti valori della LOI sono attribuibili principalmente alla decomposizione di carbonio elementale (EC) inerte. Pertanto, dal presente studio risulta evidente che la LOI non può essere impiegata come stima indiretta del contenuto di carbonio organico dei residui in esame, tanto più dell'efficienza del processo di combustione dei rifiuti da cui le BA sono prodotte.

In seguito, sono state esaminate le principali caratteristiche chimiche, mineralogiche e il comportamento alla lisciviazione delle HW-I BA (**Chapter 2**). La composizione chimica di tali residui è risultata simile a quella tipicamente osservata per le MSWI BA in studi precedenti. L'analisi mineralogica mediante diffrattometria a raggi X (XRD), invece, ha mostrato la preponderanza di fasi amorfe e vetrose nelle HW-I BA, diversamente da quanto indicato in letteratura per le MSWI BA. Sulla base del confronto delle concentrazioni di metalli misurate negli eluati del test di cessione con i criteri Europei di accettabilità dei rifiuti in discarica e con i limiti della legislazione italiana ed olandese per il riuso di rifiuti non pericolosi in specifiche applicazioni dell’ingegneria civile, le HW-I BA in esame possono essere smaltite in discariche per rifiuti non pericolosi. Inoltre, tali BA hanno mostrato di rispettare i limiti per il riuso, nonostante la legislazione italiana ne obbliga lo smaltimento in discarica per rifiuti pericolosi. Tuttavia, le HW-I BA hanno mostrato una capacità di neutralizzazione acida piuttosto bassa e inferiore ai valori generalmente riportati per le MSWI BA, riconducibile al suo elevato contenuto di fasi vetrose caratterizzate da una scarsa capacità tampone. Ciò implica che il pH dell’ambiente in cui le HW-I BA vengono smaltite o, eventualmente, riutilizzate può essere di cruciale importanza per la valutazione del comportamento ambientale di questi residui poiché il loro pH originario (circa pari a 10) tenderebbe rapidamente a diminuire verso un valore acido con un conseguente aumento della solubilità di alcuni contaminanti (ad es. Cu e Zn). Un ulteriore confronto qualitativo e quantitativo della lisciviazione dei maggiori costituenti e dei metalli in traccia delle HW-I BA con le concentrazioni osservate per le MSWI BA ha indicato che la tecnologia utilizzata per il trattamento termico dei rifiuti (temperatura e configurazione del forno) è il fattore che maggiormente influenza le caratteristiche ambientali di tali residui.

In seguito, il comportamento ambientale delle RDF-I e delle RDF-G BA è stato valutato e confrontato sulla base della composizione chimica, della mineralogia, della capacità di neutralizzazione acida (ANC) e del rilascio dei maggiori componenti di tali residui al variare del pH (**Chapter 3**). Complessivamente, i risultati dell’analisi elementale hanno mostrato che non esistono significative differenze nelle caratteristiche chimiche di queste BA, in parte riconducibili alla simile composizione del rifiuto (RDF) trattato dagli impianti. Tuttavia, differenze nelle proprietà di lisciviazione (di macro-componenti e metalli in traccia) dei residui in esame sono state attribuite alle diverse caratteristiche tecnologiche (es. temperatura, agente ossidante) degli impianti di incenerimento e gassificazione da cui le BA sono prodotte. Inoltre, l’analisi mineralogica ha rivelato la presenza di numerose fasi cristalline nelle RDF-I BA e la preponderanza di fasi amorfe e vetrose nelle RDF-G BA, per effetto delle diverse condizioni operative del trattamento termico dei rifiuti adottate negli impianti considerati. Successivamente, i risultati dell’analisi elementale e mineralogica di tali residui sono stati inclusi in un modello geochimico (mediante il programma LeachXS/Orchestra) per l’individuazione dei principali processi e fasi minerali che controllano l’ANC e il rilascio dei maggiori costituenti dalle BA in esame. In particolare, è stato osservato che la minore ANC e le più basse concentrazioni dei macro-componenti (es. Ca, Mg e Si) misurate per le RDF-G BA sono, sostanzialmente, riconducibili ad un minore contenuto di fasi minerali solubili presenti in tali BA in confronto con le RDF-I BA.

Successivamente, sono stati analizzati i principali meccanismi che controllano le concentrazioni dei metalli in traccia rilasciati dalle RDF-G BA, al variare del pH (2-12.5) e del tempo di contatto (48 ore, 1 settimana e 2 settimane) tra le BA e la soluzione acquosa (**Chapter 4**). L'analisi di quest'ultimo aspetto è stata considerata di rilevante importanza per tali residui che sono caratterizzati da una matrice prevalentemente vetrosa e quindi potrebbero richiedere tempi di contatto maggiori di quelli stabiliti nel test di lisciviazione standard per raggiungere la condizione di equilibrio termodinamico con la soluzione acquosa. Il confronto dei risultati ottenuti in questo studio ha permesso di verificare che, in realtà, le concentrazioni dei metalli rilasciate dalle BA in esame non hanno mostrato significative variazioni per effetto del tempo di contatto tra i residui e la soluzione acquosa al variare dei valori di pH analizzati. Inoltre, il confronto delle concentrazioni lisciviate dalle RDF-G BA con quelle osservate in precedenti studi riguardanti le MSWI BA ha indicato che le concentrazioni di metalli (ad es. Zn, Ni) determinate negli eluati dei test di cessione delle RDF-G BA sono significativamente (da 1 a 3 ordini di grandezza, in dipendenza del pH considerato) inferiori a quelle misurate per le MSWI BA. Infatti, l'elevata temperatura del reattore di gassificazione (> 1200 °C) può aver causato la volatilizzazione di questi elementi dalla matrice solida dei rifiuti con riduzione della loro disponibilità nelle BA e, conseguentemente, del loro rilascio in acqua. Inoltre, le minori concentrazioni di Cu misurate negli eluati delle RDF-G BA in confronto con le MSWI BA sono state attribuite ai più bassi livelli di carbonio organico disciolto (DOC) determinati per i residui da gassificazione. Questi risultati sono in buon accordo con studi precedenti sulle MSWI BA in cui è stato dimostrato che la lisciviazione del Cu può essere quantitativamente correlata alla formazione di complessi solubili Cu-DOC. In seguito, i risultati della modellazione geochimica hanno indicato che per le RDF-G BA la lisciviazione di alcuni metalli (ad es. Pb e Cu) è controllata da processi di precipitazione di minerali, tra cui ossidi contenuti in tali residui. La mobilizzazione di altri componenti (ad es. Ni e Cr), invece, è apparsa fortemente dipendente da meccanismi di assorbimento su superfici amorfe contenenti Al/Fe, il cui contenuto è risultato significativo nella matrice di questa tipologia di BA.

Infine, sono stati valutati gli effetti del processo di invecchiamento naturale (condotto per 6 mesi alla scala di laboratorio) sulla mineralogia e sul rilascio di macroelementi e costituenti in traccia per le RDF-I BA (**Chapter 5**). A questo proposito, bisogna considerare che tale processo avviene naturalmente nelle scorie in condizioni di smaltimento o recupero nell'edilizia, per effetto del contatto con l'aria e le precipitazioni atmosferiche. Per questo motivo, un'attenta valutazione delle proprietà ambientali di tali BA (contenenti numerose fasi cristalline potenzialmente reattive) a seguito dell'invecchiamento è stata ritenuta di significativa importanza. I risultati hanno indicato che la mineralogia, l'ANC ed il comportamento alla lisciviazione di alcuni metalli sono variate in seguito al trattamento d'invecchiamento naturale esaminato. In particolare, sono state misurate minori concentrazioni di metalli (ad es. Pb, Zn) e maggiori concentrazioni di ossianioni (ad es. Mo, Cr) negli eluati dei test di cessione condotti al pH naturale dei campioni invecchiati. Tuttavia, i risultati ottenuti in questo studio hanno indicato che l'invecchiamento (condotto per 6 mesi) non ha influenzato in maniera significativa le proprietà di lisciviazione delle RDF-I BA, al variare del pH. Ciò implica che il contenuto di composti minerali che principalmente determinano il rilascio di macro/micro componenti di questi residui non è variato sostanzialmente a seguito del trattamento in esame. Inoltre, la modellazione geochimica dei risultati sperimentali ha indicato che i meccanismi di precipitazione di fasi minerali idrosside presenti nelle RDF-I BA costituiscono i principali processi che controllano il rilascio di metalli (es. Pb, Zn, Ni) da tali residui, in accordo con quanto osservato in studi precedenti riguardanti le MSWI BA.

Abstract

Thermal treatment of waste materials (e.g. biomass, unsorted municipal solid waste, MSW or selected refuse derived fuel, RDF) in Waste to Energy (WtE) plants, i.e. combustion or gasification facilities generate a number of solid by-products, among which the most abundant is bottom ash (BA), which accounts generally for 10-20 wt.% of the feedstock. This slag-like material is produced worldwide in large quantities. Over the past few decades, in some European countries, BA from MSW incineration (MSWI) is increasingly being reused in construction applications (e.g. in road foundations, embankments or sound barriers) due its suitable physical (e.g. bulk density, particle size) and mechanical properties (e.g. compressive strength). However, BA generally exhibits higher concentrations of toxic constituents of environmental concern compared to natural materials, including metals, oxyanions and salts. To ensure the environmentally safe utilization or disposal of this type of residue, the leaching properties and the major geochemical processes that control contaminant leaching need to be thoroughly investigated. Once the leaching properties are known, an improved understanding of the long term environmental behavior of BA under possible management scenarios can be developed.

The aim of this thesis was to perform an in depth analysis of the main mineralogical, physical and chemical composition and the resulting leaching properties of BA produced in different types of waste thermal treatment plants, in order to gain a proper insight on the environmental behaviour of this material in utilization or disposal applications. In particular, evaluations were performed on BA samples originated from: a refuse derived fuel incineration (RDF-I) plant, a refuse derived fuel gasification (RDF-G) plant and hospital waste incineration (HW-I) plant. These specific types of bottom ash were selected since for these materials there is a lack of knowledge regarding both their main composition and the mechanisms governing their leaching. Specifically, based on the results of characterization analysis, the final objective of this study was to identify the chemical and physical processes responsible for the observed release of major and trace components from each type of residue. In view of that, a combination of experimental leaching tests and a geochemical modelling approach that was established for MSWI BA was employed.

In particular, the main reactions and organic or inorganic species that contribute to the relatively high loss on ignition (LOI) measured for RDF-I BA and HW-I BA were investigated using thermogravimetrical (TG) and mass spectrometry (MS) analysis method (**Chapter 1**). Results for RDF-I BA indicated that the LOI measured at 550 °C was due to moisture evaporation and dehydration of $Ca(OH)_2$ and hydrocalumite. Results for the HW-I BA instead showed that the LOI resulting at 550 °C was related to the high elemental carbon (EC) content of the slag. The results imply that LOI cannot be considered as a generic quality control parameter for the effectiveness of a waste incineration system with respect to the content of unburned organic material in the incineration residues. In addition, reaction mechanisms that can bias the determination of LOI in general and of the EC and $CaCO_3$ contents in particular were identified. The newly found reaction mechanisms quantitatively explain why EC is underestimated while the $CaCO_3$ content of the slag is overestimated if measured by TG analysis. Similar artefacts are expected to occur also in conventional LOI methods and for other types of materials such as e.g. MSW incineration bottom and fly ashes. In addition, it is suggested that the identified mechanisms can also occur during the combustion of the waste and that the formation of calcium carbonate in BA can already take place in the incineration plant. Therefore, these results may also give direction to further optimization of waste incineration technologies with regard to stimulating in-situ carbonation in order to achieve a subsequent quality improvement of bottom ash.

Subsequently, the chemical characteristics, mineralogy and leaching properties of HW-I BA were investigated (**Chapter 2**). The bulk chemical composition of HW-I BA was quite similar to the data typically reported for MSWI BA. On the other hand, mineralogical characterization revealed that the analyzed HW-I BA was predominantly amorphous and therefore exhibited a different mineralogy than that reported in the literature for MSWI BA. Furthermore, leaching test results showed that HW-I BA would meet the European acceptance criteria for non hazardous waste landfills and the limits for reuse in specific application scenarios. However, the acid neutralization capacity was low so that possible implications on the pH dependent release of many constituents should be considered in order to draw further conclusions regarding the expected leaching behaviour of the material in real case applications. The comparison of the leaching properties of fresh and aged HW-I BA with those typically found for MSWI BA suggested that the observed differences may be most likely related to the nature of the input materials and differences in the combustion conditions (such as temperature typically resulting for rotary kiln and grate furnace incineration technologies).

Another part of the study concerned the comparison of the main composition and environmental properties of bottom ash resulting from thermal treatment of RDF applying two different technologies: grate-fired incineration (RDF-I) and gasification (RDF-G) (**Chapter 3**). Mineralogy analysis showed that the RDF-I slag consisted of an assemblage of several crystalline phases, while the RDF-G slag was mainly made up by amorphous glassy phases as a result of the different operating conditions, in particular temperature, employed by the two plants. A new geochemical modelling approach using the LeachXS/Orchestra framework was developed to predict the leaching behaviour of major components and the pH buffering capacity of the samples, based on the combined used of independent mineralogical information and the bulk composition of the slag. It was found that the combined analysis of the mineralogical characteristics and of the buffering capacity of the ash can be used to adequately obtain an independent estimate of both the type and the amount of minerals that contribute to the leaching process. The results suggested that the extremely low buffering capacity and low leaching of major components determined for the RDF-G BA may be explained by the presence of significantly lower amounts of mineral phases available for leaching as compared to the RDF-I BA.

Subsequently, the leaching behavior of trace metals from RDF-G BA as a function of pH and equilibration time was investigated (**Chapter 4**). Given the previous findings, the latter aspect is believed to be particularly important, since the glassy matrix of the BA may limit, to some extent, the availability of metals for leaching depending on the time scale of the performed leaching tests. The leached concentrations and availabilities of elements, such as Zn and Ni obtained for the RDF-G BA were found to be lower than those typically found for MSWI BA, used as a reference material in this study. These results may be ascribed to the strong volatility of these elements at the high formation temperatures of the gasification residue (> 1200 °C). In addition, RDF-G BA exhibited significantly lower leached concentrations of Cu compared to the mean values reported for the MSWI BA, as a result of the low concentration of dissolved organic carbon (DOC) with which copper forms strong complexes. The results of the tests carried out at different equilibration times were quite similar indicating that contact time does not greatly affect the leaching behaviour of this type of BA, suggesting that the glassy matrix of the RDF-G BA is responsible for the reduced availability of metals. Modeling results showed that the relevant processes controlling trace metal leaching were precipitation of (hydr)oxide minerals (e.g. Pb and Cu) and sorption (e.g. Ni and Cr) on Fe/Al based surfaces present in the matrix of the RDF-G BA.

Finally, the effects of natural weathering on the mineralogical composition and leaching properties of RDF-I BA were studied (**Chapter 5**). Weathering is an important process that takes place during disposal or application in construction works and, therefore, it is important to study the effects it exerts on the leaching of trace metals. It was decided to specifically investigate the effects of weathering on RDF-I BA since, based on its main composition, leaching behaviour and mineralogy (alkaline pH and content of hydroxide phases), the weathering treatment was expected to cause significant effects on the properties of this type of slag. Indeed, the results evidenced that the tested treatment was able to modify the mineralogy, acid neutralization behavior and metal leaching of the BA. In particular, a significant decrease in the mobility of metals such as Pb, Zn and Cu, as well as a the mobilization for oxyanions such as Cr and Mo were found due to the reduction of natural pH of the BA upon ageing. However, the main processes controlling the leaching of contaminants were not found to change significantly during the investigated weathering period. Geochemical modelling of the leachates indicated solubility control by a number of (hydr)oxide minerals for most metal cations, similarly to the results reported in literature for MSWI BA.

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Introduction and overview

BACKGROUND

Waste thermal treatment technologies

Over the past decades, thermal treatment of municipal solid waste (MSW) in Waste to Energy (WtE) plants has become an essential component of an integrated waste management system when considered both from an environmental and energetic perspective. This waste management option has the potential to strongly reduce the original mass (by 70-80 %) and volume (by 80-90 %) of the waste to be disposed of in landfills, while converting the energy value of (non recyclable) waste fractions into heat and electricity for utilization in industrial facilities or heating districts (Chandler et al., 1997; Consonni et al., 2005; Münster and Lund, 2010; Arena, 2012). Furthermore, the solid residues generated from the combustion of MSW (mainly bottom ash, BA) are utilized as secondary construction materials (e.g. in road foundations, embankments or sound barriers) in some countries.

Following the current European Union (EU) legislation regarding the management of waste (Council of the European Union, 1999), governments and local authorities have changed their respective national regulations shifting from simplified systems, including e.g. collection of unsorted wastes and subsequent disposal in landfills, to sustainable systems, comprising e.g. material recycling and energy recovery processes from commingled or pre-sorted MSW (Vehlow et al., 2007; Münster and Lund, 2010). In this view, a number of countries have already implemented waste management measures that may contribute to achieve substantial material or energetic valorization of waste fractions by using recycling strategies and thermal waste treatment in state of the art WtE plants. For example, in Germany, The Netherlands and Denmark both recycling and thermal treatment of waste is commonly practiced with the target of reducing the amount of material going to landfills. In addition, waste recycling and the increasing trend of reusing combustion residues, mainly MSW incineration (MSWI) BA in construction works results in savings of primary materials. This strategy, hence, provides a relatively low amount of landfilled waste (less than 5 % of the produced waste) in these countries, as can be seen in Figure 1. On the other hand, recycling and thermal processes only play a subordinate role in waste management practices for many other countries, such as Spain, Portugal and Italy where waste disposal in landfills is still a substantial part of the total waste produced (above 60 % of the produced waste, see Figure 1).

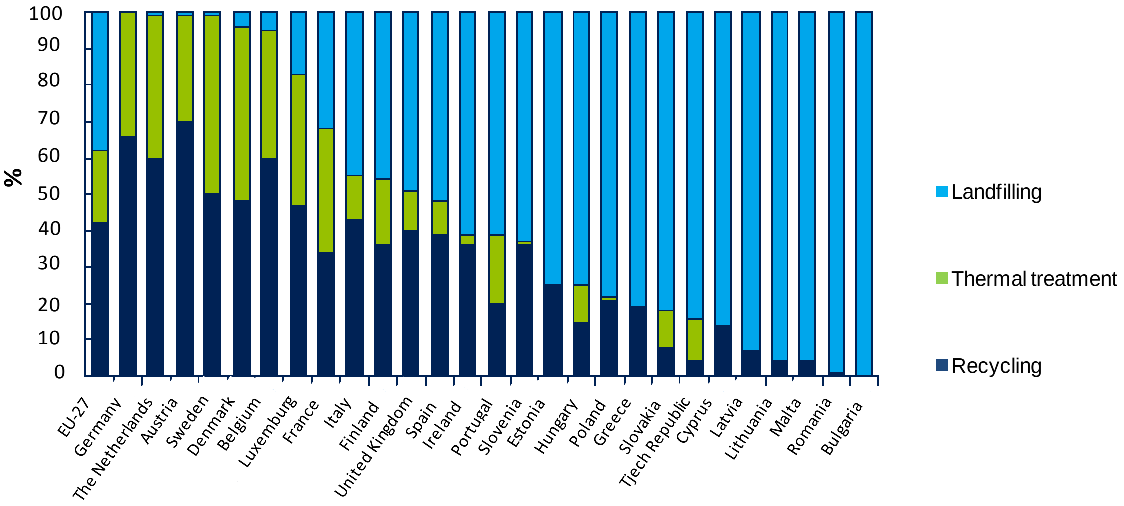

Figure 1. Waste management policies applied in EU-27 Countries (Dutch Waste Management Association, 2010).

Given the advantages that may be provided by the thermal treatment of waste, an important challenge is, therefore, to identify the best WtE strategies, with respect to environmental, energetic and economical points of view. A wide range of possible WtE technologies are currently available, including conventional incineration and advanced gasification systems. These technologies are characterized by different operating conditions, waste thermo-chemical conversion mechanisms, energy efficiency, environmental impacts (i.e. atmospheric emissions of pollutants such as CO_2, CO, NO_x; solid residues production) and costs (i.e. capital and operating costs of the plants).

In particular, waste incineration facilities typically operate under highly oxidizing conditions with excess of air at atmospheric pressure and temperatures averaging from 850 to 1200 °C. The most adopted types of combustion chamber designs in incineration plants are: rotary kiln, grate-fired and fluidized bed systems, depending on the composition of the waste to be treated. For incineration-based WtE technologies, the combustible fractions of the waste are converted to high temperature flue gas, mainly containing CO_2 and H_2O to be used for heat and electricity production (Bébar et al., 2002; Consonni et al., 2005; Arena, 2012).

Alternatively, advanced waste gasification systems operate a partial oxidation of the carbonaceous waste materials under reducing atmosphere (the amount of oxidant, i.e. air or oxygen, is lower than that required by stoichiometric combustion) at high-temperature (1000-1600 °C) and in a pressurized gasification reactor. Possible configurations of the gasification-based WtE systems include: fixed bed, fluidized bed, moving grate, rotary kiln and plasma reactors. The waste gasification process produces a synthesis gas (named syngas) containing large amounts of not completely oxidized products, i.e. CO, H_2 and CH_4 that have a high calorific value and, hence, can be utilized in separate processing equipment for different applications, e.g. energy generation or liquid fuels and chemicals manufacturing processes, even at different times or locations (Arena et al., 2012).

In addition, it must be considered that thermal treatment of MSW specifically processed in order to increase its homogeneity and calorific value and, thus, denominated refuse derived fuel (RDF) is being progressively applied in WtE systems with the aim of increasing energy recovery and employ technologies characterized by a lower environmental impact (Dalai et al., 2009; Bosmans et al., 2010). In particular, RDF is produced by sorting, size and weight-based separation and shredding of commingled MSW in mechanical-biological treatment plants (MBT). It is therefore characterized by a relatively constant size distribution and composition, mainly consisting of high caloric waste fractions like paper and cardboard (50-60% wt.), plastics (20-30% wt.), along with textiles and rubber (10-15% wt.). Consequently, it is believed that thermal treatment of this type of waste in traditional combustion or advanced gasification plants can lead to quite stable operating conditions, treatment temperature, as well as a more homogenous quality of the resulting gas products as compared to MSW, hence allowing to employ more advanced technologies than those in use for thermal treatment of commingled waste (Consonni et al., 2005; Bosmans and Helsen, 2010; Arena et al., 2012). Following the indications of recent EU guidelines to favour technologies that allow to reduce the volumes of waste for final disposal while enhancing material and energy recovery (European Commission, 2005), the treatment capacities of WtE plants employing RDF are expected to increase in the future, in some European countries such as Germany, as indicated by Haker et al. (2010). Incineration in water-cooled grate combustors at temperatures around 850-1000 °C with air, which is the most adopted technology for WtE treatment of MSW, is commonly applied also for the energetic valorisation of RDF (Jannelli and Minutillo, 2007). On the other hand, in recent years, RDF gasification in a high temperature (1200-1400 °C) fluidized bed reactor applying sub-stoichiometric oxygen concentrations, has also gained acceptance due to its higher potential energy recovery efficiency and lower production of NO_x and SO_x emissions compared to incineration (Belgiorno et al., 2003; Bosmans and Helsen, 2010; Castaldi and Themelis, 2010).

Hence, in recent studies significant efforts have been made to assess and compare the merits of the alternative WtE strategies based on well-established combustion technologies vs. new gasification systems by applying detailed energy, environmental and economic analyses (Consonni et al., 2005; 2012; Giugliano et al., 2008; Munster and Lund, 2010). The results showed that gasification of RDF could be the best strategy from an energetic point of view, since it may provide higher electrical conversion efficiencies (Giugliano et al., 2008). Furthermore, gasification technologies generally allow the production of a smaller volume of gas (to be treated in the gas cleaning units), being much easier to control than traditional combustion systems (Consonni et al., 2005). Notwithstanding these important features, RDF gasification does not show significantly lower atmospheric emissions of pollutants (e.g. dioxins, furans and NO_x) compared to those derived from traditional WtE systems and, besides, RDF production (in separate MBT plants) may reduce the net energy recovery of the entire process. In this perspective, it was concluded that the best results, seen from both the energetic and environmental perspectives, were obtained for conventional WtE technologies, particularly when unsorted MSW is used (Consonni et al., 2005; Giugliano et al., 2008). From an economic point of view, gasification-based WtE results the best solution since it may allow to achieve the highest revenues from the sale of energy. However, costs analysis is probably the crucial factor for any gasification configuration, since ranges of both operating and capital costs appeare certainly higher than those of conventional combustion-based WtE systems. Furthermore, the assessment of the potential benefits of gasification vs. incineration is also made difficult by the scarce operating experience and the fragmentary data available. Therefore, it is deemed premature to indicate gasification as the thermal processing strategy of the future or even as a strong competitor for any sized combustion systems (Arena et al., 2012; Consonni et al., 2012).

Bottom ash characterization and management options

Regardless of the type of thermal treatment option adopted in WtE plants, combustion or gasification processes of waste materials (e.g. biomass, unsorted MSW or selected RDF) generate a number of solid by-products, among which the most abundant is bottom ash (BA), generally accounting for 10-20 wt.% of the feedstock (e.g. Chandler et al., 1997; Sabbas et al., 2003). In some European countries, e.g. Denmark, The Netherlands and France, the reuse of BA from MSW incineration (MSWI) facilities is commonly practiced as a substitute aggregate for natural materials in construction applications, due to the suitable physical (e.g. bulk density, particle size) and mechanical properties (e.g. compressive strength) of the material. In some other countries, such as Italy and Spain, BA is generally landfilled as a non hazardous waste, since there is no specific legislation regulating its utilization conditions (Polettini, 2009).

However, given the variation in waste composition, furnace configuration and operating temperature and pressure conditions of incineration/gasification WtE plants, the resulting BA may present significantly different characteristics with respect to natural materials.

Over the past decades, important progress has been made in understanding the main mineralogical and chemical composition of MSWI BA. In particular, it has been found (using X-Ray diffraction) that this residue predominantly consists of amorphous/glassy constituents (> 70 wt.%) and metastable minerals which can transform into secondary minerals. This complex and non-stable mineralogical composition mainly results from the (rapid) quenching in water at the outlet of the combustion chamber of the hot and partly molten BA. Detailed petrographic analyses, which were primarily done on the basis of X-Ray diffraction (XRD) and qualitative/quantitative energy dispersive spectrometry (EDS) analyses, led to the identification of the following mineralogical components in MSWI BA (e.g. Eighmy et al., 1994; Meima and Comans, 1999; Piantone et al., 2004):

- non combusted materials (15-45 %): quartz (SiO_2); feldspars ($(K,Ca,Na)(Al,Si)_4O_8$); piroxene($Ca(Mg,Fe)Si_2O_6$); olivine ($(Mg,Fe)_2(SiO_4)$); metal alloys and organic materials;

- melt products (55-85 %): silicate glasses; crystalline complex silicate minerals (melilite group minerals, e.g. ghelenite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$)); crystalline oxide minerals (e.g. lime (CaO), hematite (Fe_2O_3), magnetite (Fe_3O_4)).

Given the amount of metastable solids in MSWI BA, this type of residue might be highly reactive under atmospheric (pressure and temperature) conditions upon contact with air and rainwater, leading to the occurrence of natural weathering processes. The most important weathering reactions include carbonation, i.e. the absorption of atmospheric CO_2 by reactive mineral species in BA which involve oxidation of some metals (e.g. aluminium, iron, copper), precipitation/dissolution of hydroxides phases and relatively soluble (Ca, Al and Mg) minerals (e.g. calcite; ettringite), neo-formation of reactive sorptive solid substrates (i.e. Fe/Al (hydr)oxides). Weathering, therefore, is capable to significantly change the original mineralogy of BA (Meima and Comans, 1999; Piantone et al., 2004; Polettini and Pomi, 2004).

With regard to its chemical composition, many studies indicated that, as a rough approximation, the major chemical constituents of the MSWI BA are those of the earth’s crust, i.e. Si, Al, Ca, Fe, Mg and Na (each one varying between 100-500 g/kg of BA). However, higher concentrations of toxic constituents compared to natural materials have been found, including: metals, e.g. Pb, Cu, Zn, Ni (1000-10000 mg/kg of BA), oxyanions, e.g. Cr, Mo, Sb (500-5000 mg/kg of BA) and soluble salts, e.g. sulphate and chloride (1000-10000 mg/kg of BA) (e.g. Eighmy et al., 1994; Chandler et al., 1997; Meima and Comans, 1999; Bayuseno and Schmahl, 2010). In addition, the occurrence of (residual) organic matter originating from incomplete combustion of the original waste was identified in MSWI BA (10-100 g/kg) (van Zomeren and Comans, 2007). Given the presence of relatively high amounts of these contaminants in BA, concerns exist whether the reuse of this residue may exert adverse environmental effects.

However, a proper assessment of the environmental impacts related to the beneficial utilization or safe disposal of BA must be based on the evaluation of the leaching of contaminants instead of their total content in the residue. Leaching is defined as the release of components from the solid phase to the water phase with which the BA may be in contact (e.g. percolating rainwater). Numerous studies have addressed quantitative predictions of the leaching of trace contaminants from MSWI BA when reused as a secondary construction material (e.g. Dijkstra et al., 2002; Kosson et al., 2002; Ecke and Aberg, 2006). The results evidenced that no direct correlation exists between the total contents and the leaching of metals from BA. Only for specific components, such as chlorides and Na leached amounts were clearly affected by their bulk contents and availabilities, i.e. maximum leachable concentrations (Meima and Comans, 1999; Rendek et al., 2007; Hyks and Astrup, 2009). In fact, the extent to which major and trace metals of this type of residue are susceptible for leaching depends on the interrelation between different parameters and processes, including:

- chemical speciation, that refers to the different chemical forms into which metals may be present in solution (i.e. leachate BA). Metals speciation is mainly controlled by pH, which depends, in turn, on the dissolution/precipitation of mineral phases or reactive surfaces (e.g. clay minerals, Fe and Al based (hydr)oxides surfaces, particulate and dissolved organic matter) to which these components are chemically bound to the BA;

- availability, that means the maximum concentration at which metals are released in solution from BA. Availability depends on the chemical and mineralogical characteristics of the slag, which are affected by the quality of the waste input and, in particular, the combustion conditions used in the plant from which BA were originated from (Rendek et al., 2007), as well as the particle size of the slag, that affects its specific surface area and partly also its total composition (Chimenos et al., 2003);

- weathering reactions that can strongly influence the mineralogy of BA (transformation of metastable mineral phases into more stable secondary minerals) and hence the solubility of mineral phases, leachate pH and metals leaching;

- time dependent processes, such as dissolution/precipitation kinetics of minerals contained in BA, which can affect the rate of the mass transfer of contaminants from the solid to the liquid phase.

Figure 2 presents the indicative leaching behaviour as a function of pH for a metal cation such as Cu from MSWI BA samples.

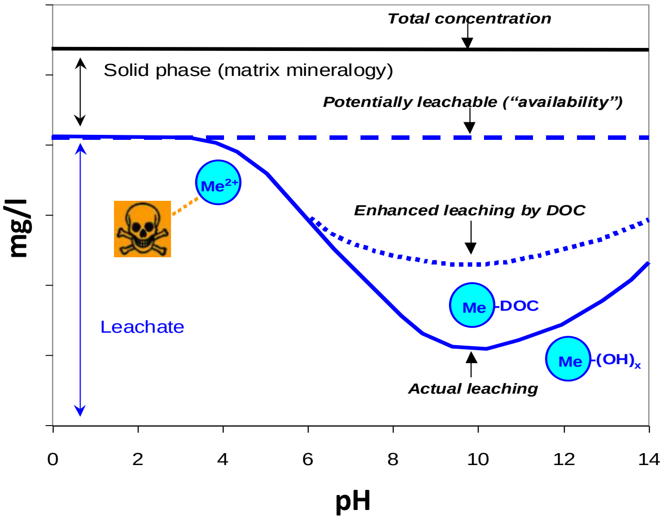

Figure 2. Indicative metals concentrations (mg/l) in BA leachates as a fuction of pH (note that leachate concentrations are presented in logaritmic scale), modified after van der Sloot et al. (1997).

Consequently, the assumption that the total concentration of a contaminant is fully available for leaching at any pH value (dotted straight line in Fig. 2) will lead to a gross (i.e. up to 3-4 orders of magnitude) overestimation of the environmental impacts deriving from the utilization of this type of residue (see the actual leaching curve in Fig. 2). Therefore, in order to properly evaluate the potential reuse of BA in construction, as an alternative option to landfilling, it is important to assess the overall leaching behaviour of the contaminants contained in this type of material for specific application scenarios. The identification of the major processes and binding mechanisms that are responsible for contaminant leaching from various waste materials can be obtained by a combination of laboratory leaching tests and (computerized) geochemical models that have been specifically developed to simulate these processes. In fact, many previous studies showed that lab-scale pH dependent leaching data coupled with geochemical modeling calculations provide valuable short and long term leaching predictions of MSWI BA over a range of relevant conditions, i.e. pH conditions that can be met in field scenarios (e.g. Meima and Comans, 1997, 1998; Dijkstra et al., 2002, 2006; Cornelis et al., 2008; Arickx et al., 2010).

In particular, proposed geochemical processes and binding mechanisms that possibly control the (short and long term) leaching of major and trace components from fresh/weathered MSWI BA include:

- dissolution/precipitation of mineral phases contained in BA, e.g. portlandite ($Ca(OH)_2$), calcite ($CaCO_3$) and gibbsite ($Al(OH)_3$) that mainly govern leachate pH and leaching of major (e.g. Ca and Al) and trace (e.g. Pb, Ni and Cd) components;

- sorption mechanisms on amorphous/crystalline Fe and Al (hydr)oxides (Hydrous ferric and amorphous aluminum (hyr)oxides, namely HFO and AAM) were found to be important for trace metals, e.g. Pb, Ni and Cd, depending on the degree of weathering, which generally led to relevant increases in reactive Fe/Al based surfaces;
- complexation phenomena with dissolved organic carbon (DOC) originating from incomplete combustion of the original waste are known to have a great effect on the leaching of Cu;
- adsorption mechanism on HFO in combination with solid solution formation with minerals containing Ca, e.g. ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3{\cdot}26H_2O$) may control leachate concentrations of oxyanionic metalloids (As, Cr, Mo, Sb and V), depending on their redox state (oxidizing/reducing conditions) in leachates BA.

In fact, recent studies on fresh or weathered MSWI BA showed the importance of combining geochemical speciation modelling codes containing generic thermodynamic parameters with additional geochemical sub-models that allow to describe specific interactions affecting the leaching of contaminants from this material, such as metals sorption on amorphous and crystalline Al/Fe surfaces and complexation on reactive fractions of dissolved and particulate organic matter, i.e. humic and fulvic acid (Dijkstra et al., 2002; 2006). Hence, it is believed that such a geochemical approach provides an improved understanding of the environmental quality of MSWI BA when reused in construction applications, with the final aim of further optimization of the quality of bottom ash. This approach is applied for several waste materials, such as MSWI bottom ash that is increasingly being recycled as a construction material in The Netherlands and also in other countries like Germany and Denmark. However, there is still a lack of knowledge regarding the leaching behaviour of many other types of BA (e.g. RDF incineration BA).

AIMS AND OUTLINE OF THE THESIS

The aim of this thesis was to perform an in depth analysis of the main mineralogical, physical, chemical composition and leaching properties of bottom ash (BA) originating from different types of waste thermal treatment plants, in order to gain a proper insight on the environmental behaviour of this material in relation to possible (utilization or disposal) management scenarios. Based on a detailed and thorough characterization of the bottom ash, the final objective of the present research was to attain an improved understanding of the most relevant processes and binding mechanisms that are responsible for the observed leaching phenomena involving both the major and trace components of the residue. In view of that, a combination of experimental leaching tests and a geochemical modelling approach established for MSWI BA was applied for different types of slag. Evaluations were performed on BA samples originated from:

- a refuse derived fuel incineration (RDF-I) plant;
- a refuse derived fuel gasification (RDF-G) plant;
- a hospital waste incineration (HW-I) plant.

Up to now, only few studies have specifically investigated the main composition and leaching behaviour of RDF incineration and gasification bottom ash, as a result of the relatively recent development of RDF thermal treatment technologies. In fact, alternative uses of RDF for energy production have become increasingly interesting in recent years, with the target of enhancing the energy efficiency of conventional waste incineration plants. In addition, waste gasification is a quite recent technology in Europe and it is expected that its use will increase in the future, also for the energetic valorisation of RDF due to its potential benefits compared to traditional combustion based WtE facilities (as described above).

Furthermore, it should be noted that there is little information on the fundamental mineralogical and chemical properties that control the leaching behaviour of the BA produced from dedicated hospital waste incineration plants. Anyhow, owing to the increasing employ of incineration as a treatment technology for the destruction of infectious and toxic organic/inorganic substances contained in this special type of waste, an appropriate strategy for the management of this type of BA is becoming an issue of interest.

The experimental approach applied in the present thesis is reflected in the different chapters that have been structured as follows:

in **Chapter 1**, the nature of the relatively high loss on ignition (LOI) measured for RDF incineration bottom ash (RDF-I BA) and hospital waste incineration bottom ash (HW-I BA) was studied in detail using thermogravimetry (TG) coupled with mass spectrometry (MS) analysis (no LOI was measured for RDF-G BA and, hence, this sample was not investigated by TG-MS). In addition, a better understanding of the individual processes that take place during laboratory characterization of the carbon species in heterogeneous (waste) materials such as BA was obtained by combining different analytical techniques, i.e. LOI, TG, MS, total inorganic carbon (TIC) and calcimetry analyses. The TG-MS results obtained from the investigated BA samples were also used to gain new insight on the reaction mechanisms generally occurring during LOI analyses of these types of residues, in order to develop a better interpretation of the results that can be obtained applying such methods. Finally, the results of the laboratory experiments for the quantification of the different carbon species retrieved in the RDF-I and HW-I BA samples were also interpreted in terms of the possible effects occurring during combustion of waste materials in general;

in **Chapter 2**, the bulk chemical composition, mineralogy and leaching properties of HW-I bottom ash were attentively examined. Subsequently, the overall characterization results (i.e. total contents and leaching of major and trace components) obtained for the analysed BA type were compared with observations reported for other HW-I bottom ashes produced by incineration plants under different operating conditions (i.e. waste sources, furnace configurations and combustion temperatures) that were found in the literature, as well as with those generally resulting for MSWI BA. The detailed overview of the bulk chemical composition and leaching results presented in this study contributed to validate our results and, besides, suggested that differences existing between the various HW-I and MSWI BA samples may be most likely ascribed to the adopted thermal treatment technology that showed to greatly affect the chemical and leaching properties of the residues. This type of approach also contributed to achieve an improved understanding of the leaching-controlling mechanisms that different types of waste products, such as HW-I BA and MSWI BA samples from worldwide origin may have in common;

Chapter 3 compares and assesses the environmental properties of the RDF incineration and gasification BA samples on the basis of their total composition, mineralogy, leaching of major components as a function of pH and buffering capacity. It is well known that these properties play an important role in determining the leaching behaviour of a material in specific application scenarios and, hence, should be carefully analysed in order to better understand the impacts associated with the use of these waste materials in the environment. The results of pH dependent leaching tests were subsequently used to develop a new geochemical modelling approach based on independent information obtained from mineralogical analyses, bulk composition and the buffering capacity of the materials. The results derived from the applied modelling approach contributed to extend the knowledge regarding the types and amounts of minerals that control the leaching properties and pH buffering capacity of solid residues, such as RDF incineration and gasification BA;

Chapter 4 describes the leaching behavior of trace metals from RDF gasification bottom ash as a function of pH and equilibration times of the pH dependent leaching tests, in order to investigate the effects of leaching kinetics for this type of residue. The latter aspect is believed particularly important since the predominant glassy matrix of the gasification BA may limit, to some extent, the availability for leaching of certain metals depending on the time scale of the performed leaching tests. Also, a comparison of the pH dependent leaching behavior with literature results obtained for MSWI BA was carried out to validate the results of the present investigation and to better understand the findings reported for this relatively less studied type of thermal treatment residue. Finally, based on the geochemical model assumed for evaluating major components leaching and the buffering capacity of the RDF-G BA (described in Chapter 3), in combination with the modelling approach established for MSWI BA reported in the literature, the most relevant leaching mechanisms involved in the release of trace elements from the same gasification sample were further identified. The results, thus, provided a better insight on the environmental behaviour of this type of BA in possible application scenarios;

Chapter 5 reports the effects of different stages of natural weathering on the mineralogical composition and leaching properties of RDF-I bottom ash. Weathering is an important process that takes place during disposal or application in construction works and the effects on the leaching of trace metals is, therefore, an important subject. Also for this type of BA, starting from the geochemical modelling analysis of major components leaching and the pH buffering capacity in combination with a modelling approach developed for MSWI BA, new insights were provided about the geochemical processes and binding mechanisms that govern trace metals leaching from the fresh and weathered material. Such an approach provided a better interpretation of the long term leaching results that were obtained in the present study. In addition, the modeling predictions contributed to extend the knowledge on possible environmental impacts associated to the utilization or disposal of BA from RDF incineration.

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Chapter 1

Main composition of different types of waste incineration bottom ash and quantification of carbon species by thermal analysis

This chapter has been submitted for publication as:

Stefania Rocca, André van Zomeren, Giulia Costa, Joris J. Dijkstra, Rob N.J. Comans, Francesco Lombardi (2012). Mechanisms contributing to the thermal analysis of waste incineration bottom ash and quantification of different carbon species. *Waste Management*

The focus of this study was to identify the main compounds affecting the weight changes of bottom ash (BA) in conventional loss on ignition (LOI) tests and to obtain a better understanding of the individual processes that take place during laboratory characterization of the carbon species in heterogeneous (waste) materials such as BA, by combining different analytical techniques. Evaluations were performed on BA samples from a refuse derived fuel incineration (RDF-I) plant and a hospital waste incineration (HW-I) plant using thermogravimetric analysis and subsequent mass spectrometry (TG-MS) analysis of the gaseous thermal decomposition products. Results of TG-MS analysis on RDF-I BA indicated that the LOI measured at 550 °C was due to moisture evaporation and dehydration of $Ca(OH)_2$ and hydrocalumite. Results for the HW-I BA showed that LOI at 550 °C was predominantly related to the elemental carbon (EC) content of the sample. Decomposition of $CaCO_3$ around 700 ^oC was identified in both materials. TG-MS analyses of mixtures of BA and $Ca(OH)_2$ demonstrated that artefacts can take place during LOI and TG-MS analyses of these materials. We have identified reaction mechanisms that can bias the determination of LOI in general and of the EC and $CaCO_3$ contents in particular. CaO has been observed to sequester the CO_2 resulting from the combustion of organic Carbon (OC) or EC within the timeframe of the experiment. This reaction determined an underestimation of the OC+EC content of the HW-I BA by LOI, since the formation of $CaCO_3$ caused a weight gain of the sample. In addition, the $CaCO_3$ content of the slag which provides an indication of the weathering/secondary carbonation reactions it is overestimated if measured by TG analysis, since it includes the $CaCO_3$ formed as a consequence of EC combustion in the presence of CaO. These types of errors in the quantification of specific carbon phases are expected to occur also when conventional LOI methods are adopted, in particular for other materials that contain $CaO/Ca(OH)_2$ in combination with EC/OC, such as e.g. municipal solid waste incineration (MSWI) bottom and fly ashes. Hence, the results of this study imply that conventional loss on ignition (LOI) measurements cannot be considered as a generic quality control parameter for the effectiveness of a waste incineration system with respect to the content of unburned organic material in the incineration residues. In addition, the results of the present study may also have implications when considering secondary $CaCO_3$ formation in BA prior to or during utilization. In general, it is believed that the presence and concentration of $CaCO_3$ in BA samples indicates the stage of weathering of the material. We suggest that the same mechanisms that we have found in the TG-MS results can also occur during combustion of the waste and contribute to in-situ carbonation of the bottom ash between 450 and 650 ^oC. This finding indicates that the presence of calcium carbonate in bottom ash is not necessarily indicative only of weathering reactions occurring in the slag during storage, but may be originated also from carbonation occurring during or just after incineration. As such, the carbonation process that is generally believed to improve the environmental quality of bottom ash starts already during incineration. Therefore, these results may also give direction to further optimization of waste incineration technologies with regard to stimulating in-situ carbonation and subsequent quality improvement of bottom ash.

1.1 INTRODUCTION

Loss on ignition (LOI) is one of the most adopted methods to estimate the amount of residual unburned organic carbon of the bottom ash (BA) generated during incineration of waste materials such as (presorted) municipal solid waste (MSW), industrial waste or biomass and, hence, is also generally considered as a quality control parameter of the effectiveness of the combustion process from which the BA were originated from. According to the current Italian legislation regulating waste thermal treatment (Leg. Decree 133/2005), for example, one of the landfill acceptance requirements for waste incineration BA is that LOI values are equal or lower than 5 % by weight.

In general, LOI refers to the mass loss of a sample after it is heated under an air or oxygen atmosphere for a certain period of time. So far, many LOI standard procedures have been developed each one characterized by a specific heating temperature and testing time depending on the type of analysed material and its field of application. If a solid residue such as MSW incineration BA is analysed to determine its unburned carbon content in relation to landfill disposal or reuse in e.g. concrete, a commonly accepted LOI method determines its weight loss at 550 °C for two hours. Therefore, high LOI values have been associated with a poor effectiveness of the combustion process from which BA were originated from (e.g. Chandler et al., 1997; Izquierdo et al., 2002). With regard to the evaluation of organic carbon in coal fly ash (FA) to be reused in cement, LOI has been referred to mass losses in samples heated to temperatures between 750°C and 950°C (Payà et al., 1998; Fan and Brown, 2001; Zhang et al., 2012).

A critical evaluation of the suitability of using LOI as a proxy for the organic carbon content of a combustion residue is particularly important because the residual organic carbon provides not only an indication of the efficiency of the combustion process, but is also an important parameter when evaluating reuse options for BA, e.g. as a material for concrete production. Furthermore, the study of van Zomeren and Comans (2004) indicated that only specific organic carbon species (i.e. humic substances) in the BA matrix may contribute to the leaching of dissolved organic carbon (DOC) and associated contaminants. Hence, detailed information about the different carbon species of BA is needed for assessing the environmental risk related to its reuse in specific application scenarios.

There is evidence that LOI is not always an appropriate measurement of the organic carbon content of ash materials. Based on thermogravimetric (TG) analyses, it was found that the dehydration of portlandite ($Ca(OH)_2$) and the decomposition of carbonates and/or volatile organic compounds may significantly overestimate the unburned carbon content of fly ash (FA) measured adopting conventional LOI methods (Brown and Dykstra, 1995; Fan and Brown, 2001).

Van Zomeren and Comans (2009) observed a large contribution from elemental carbon (EC) to the LOI results obtained for MSWI BA samples using a combination of different carbon-specific analytical techniques. The results demonstrated that only 25% of the LOI consisted of organic carbon. The authors concluded that LOI is not a sufficiently discriminative parameter for quantifying the unburned organic carbon content of BA, which proved to be overestimated on the basis of LOI analysis compared to other methods.

On the other hand, Vandenberghe et al. (2010) showed that oxidation of iron minerals in coal BA and FA samples led to a weight gain at temperatures of about 960 °C. This weight gain may partially compensate the weight loss due to the burning of the residual organic carbon (combustion at around 350 °C) of the sample. Thus, LOI when defined at this temperature range can possibly underestimate the remaining organic content of ash materials.

In the present study, thermogravimetric and mass spectrometry (TG-MS) analysis was performed on BA samples originating from a refuse derived fuel (RDF) incineration plant and from a hospital waste (HW) incinerator. These materials vary substantially in carbon content. The same samples were also used in a previous study on the leaching behaviour of these types of bottom ashes (Rocca et al., 2009; 2012). The aim of this study was to gain insight in the main reactions and organic or inorganic species that contribute to the high LOI values (> 5 wt.% in most samples) that were measured at temperatures of 550 and 1000 °C for both types of BA. Up to now, only few studies have focused on the characterization of the physical, chemical and environmental properties of these special types of BA (e.g. Kougemitrou et al., 2011; Rocca et al. 2009; 2011; 2012) and furthermore to our knowledge there is no comprehensive study regarding the thermal analysis and the carbon speciation of these types of waste materials.

In this study, we have determined the weight loss of the two types of BA samples in relation to controlled temperature variations by TG analysis. We were able to identify the major processes (e.g. water desorption, dehydration of hydrated phases, carbonate decomposition and mineral oxidation) contributing to the weight losses of the BA at different temperatures. Furthermore, the MS analysis of the gaseous products that were released during the heating of the samples allowed us to discriminate between the main carbon species of the BA. The results of this investigation are important for a correct interpretation of LOI measurements for waste incineration residues.

1.2 MATERIALS AND METHODS

1.2.1 Bottom ash sampling and preparation

Approximately 100 kg of freshly quenched BA was sampled from two thermal treatment plants: a refuse derived fuel incineration (RDF-I) plant with a grate combustion chamber operating at temperatures between 850 and 1000 °C and a hospital waste incineration (HW-I) plant equipped with a rotary kiln combustion chamber operating at 1000-1200 °C. Both samples were homogenized by quartering and oven-dried at 60 °C. Next, both materials were sieved to produce two size classes that were separately analysed: a coarse fraction (0.425-12 mm) and a fine fraction (<0.425 mm) which accounted for, respectively, about 90 and 10 % by weight of both BA types. Experiments were performed on both the coarse and fine size fractions of the RDF-I and HW-I BA samples prior to and after 6 months of natural weathering. The weathering treatment was carried out in the laboratory by contacting the samples with air at controlled temperature and humidity and at atmospheric pressure. Detailed characterization analyses of these BA samples in terms of elemental composition, mineralogy and leaching behaviour are reported in the previous study (Rocca et al., 2012).

1.2.2 Loss on ignition (LOI) test methods

Two types of LOI standard methods were employed in this study. The first method was performed according to UNI EN 15169 (2007). By this procedure the weight loss was determined after heating the samples at 550 °C for two hours (LOI 550). The second LOI method was performed in accordance with the ASTM C25 procedure (2011) by heating the samples first at 400 °C for 30 minutes and, subsequently, at 1000 °C for 20 minutes. Only the overall weight losses at 1000 °C were recorded using this method (LOI 1000). Tests were performed with about 5 grams of BA placed in a ceramic crucible and heated in a muffle furnace according to one of the above cited standard procedures. After heating, the samples were placed in a desiccator for about 30 minutes before weighing. LOI was calculated as the relative weight difference between the initial and the heated sample. Difference between LOI 1000 and LOI 550 was assumed to be essentially related to the amount of carbonate phases contained in the BA samples. All measurements were carried out in triplicate.

1.2.3 Thermogravimetric and mass spectrometry (TG-MS) analysis

The TG-MS analysis was performed with a Mettler-Toledo TG system coupled with a Quadrupole mass-spectrometer (Pfeiffer, Thermostar). About 20 mg of BA was heated from 25 to 1100 °C under an oxygen atmosphere at a heating rate of 40 °C/min. A specific temperature program was applied for each BA type in order to obtain a good separation of the individual reactions occurring at different temperatures (Table 1.1). Indeed, preliminary TG-MS experiments indicated that isothermal equilibration time steps of 15 min at the temperatures of 350 and 550 °C were needed to clearly identify the weight losses and associated gaseous products derived from complete thermal decomposition of hydrated compounds or (organic/inorganic) carbon species present in the RDF-I BA and HW-I BA samples, respectively. The weight loss of the samples was recorded by the TG microbalance, while the MS was used to monitor the simultaneously released CO_2 and H_2O. All measurements were carried out in triplicate.

Table 1.1 Temperature programs applied for the RDF-I BA and the HW-I BA samples during the TG-MS analysis.

Step	Temperature range (°C)	Isothermal time (min)
RDF-I BA		
1	25	15
2	25-100	-
3	100	15
4	100-350	-
5	350	15
6	350-1100	-
HW-I BA		
1	25	15
2	25-100	-
3	100	15
4	100-550	-
5	550	15
6	550-1100	-

1.2.4 Carbonate analysis methods

First, the carbonate content of BA samples was analysed with a Shimadzu solid sample module (SSM-5000A). About 100 mg of BA was weighted and total inorganic carbon (TIC) was determined after H_3PO_4 addition at 200 °C under an oxygen atmosphere for carbonate decomposition. The released CO_2 was subsequently quantified using a non-dispersive infrared detector.

Alternatively, the amount of carbonate in the BA samples was also measured using a Dietrich-Früling calcimeter. This analysis involved acidification (HCl) of the sample and subsequent measurement of the total evolved gas volume. Tests were performed with about 1 gram of material that was put into contact with 10 ml of (11.37 M) HCl in a glass bottle. The resulting gaseous volume was then measured in a gas-container connected to the bottle by replacement of water. All measurements were carried out in triplicate.

1.3 RESULTS AND DISCUSSION

1.3.1 Comparison of LOI measurements and TG analysis

The results of the cumulative weight losses determined by the two LOI standard methods for the different coarse and fine fractions of the fresh and aged BA samples showed that the LOI 550 values measured for the HW-I BA (from 9.6 to 23 % on a dry weight basis) were generally higher compared to those obtained for the RDF-I BA (from 3 to 8.4 % on a dry weight basis), indicating a higher content of volatile compounds with low decomposition temperatures in the HW-I BA samples. On the other hand, the LOI 1000 values obtained for specific RDF-I and HW-I BA samples were quite similar for the two types of BA (from 8 to 16 % on a dry weight basis) as a possible result of the significant content of carbonate phases and/or volatile compounds with high decomposition temperatures in the RDF-I samples. The LOI results obtained for the different RDF-I and HW-I BA samples is provided in the Annex A, Supporting Information. In addition, the results of the carbonates content of the two types of BA as determined by LOI analysis are described in the following paragraph 1.3.3.

Figure 1.1 compares the results of the two applied LOI methods (LOI 550 and LOI 1000) to the weight losses determined by TG analysis (total weight loss up to 1100 °C, see Table 1.1) for the two types of BA samples. The RDF-I BA samples are plotted as open (550 ^{o}C) and closed (1000 ^{o}C) dots, while the HW-I BA samples are plotted as open (550 ^{o}C) and closed (1000 ^{o}C) diamonds.

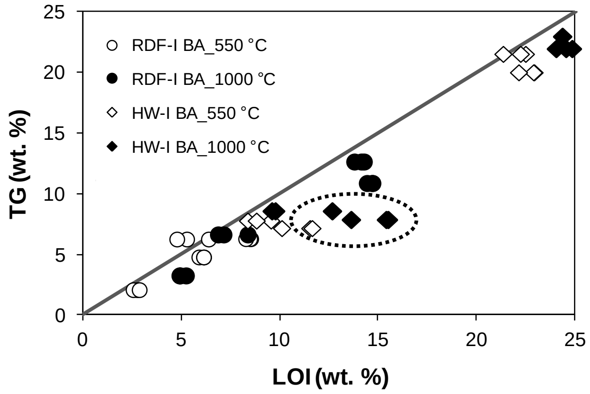

Figure 1.1. Comparison of the weight loss (wt. %) of the RDF-I BA and HW-I BA samples at 550 °C and 1000 °C obtained by the LOI standard methods and TG analysis (up to 1100 ^{o}C, see Table 1.1). The dotted line indicates the samples exhibiting maximum deviation values between LOI and TG results.

The results of the cumulative weight losses determined by the two LOI standard methods for the different coarse and fine fractions of the fresh and aged BA samples showed that the LOI 550

values measured for the HW-I BA (from 9.6 to 23 % on a dry weight basis) were generally higher compared to those obtained for the RDF-I BA (from 3 to 8.4 % on a dry weight basis), indicating a higher content of volatile compounds with low decomposition temperatures in the HW-I BA samples. On the other hand, the LOI 1000 values obtained for specific RDF-I and HW-I BA samples were quite similar for the two types of BA (from 8 to 16 % on a dry weight basis) as a possible result of the significant content of carbonate phases and/or volatile compounds with high decomposition temperatures in the RDF-I samples. The LOI results obtained for the different RDF-I and HW-I BA samples is provided in the Annex A, Supporting Information. In addition, the results of the carbonates content of the two types of BA as determined by LOI analysis are described in the following paragraph 1.3.3.

The results show that the cumulative weight loss determined by LOI and TG analysis are in reasonably good agreement (550 °C: slope= 0.88, R^2= 0.95; 1000 °C: slope= 0.83, R^2= 0.90), although the TG results were consistently lower than the LOI results. Maximum deviation between the cumulative LOI and the TG values was found at 1000 °C for the coarse fraction of the fresh HW-I BA sample, for which the weight loss measured by TG was 7.8 wt. % (as reported in Table 1.3) whereas that determined by LOI analysis was 15.5 wt. % (results evidenced by the dotted line in Fig. 1.1). These differences might be attributed to possible oxidation of (oxidizing) metals (e.g. Si, Zn and Cu) or iron-minerals (e.g. hematite, Fe_2O_3; ferrous and silicon oxides, Fe_2SiO_4) during TG analysis. The results of the previous study on this BA sample corroborates the hypothesized mechanism since the coarse fractions of the ash proved to be enriched in oxidizing metals compared to the fine ones (results shown in Annex A, Supporting Information). Indeed, the use of pure oxygen in the TG experiments is likely to establish stronger oxidizing conditions than during the LOI analysis for which air is used.

1.3.2 TG-MS analysis

1.3.2.1 Quantification of the weight loss determined for the two types of bottom ash

In figure 1.2, examples of the TG-MS results obtained for the coarse fraction of fresh RDF-I BA (graph a) and HW-I BA (graph b) are reported. Similar results, summarized in Table 1.2 (RDF-I BA) and Table 1.3 (HW-I BA), were determined for the other tested samples.

With regard to the RDF-I BA, a relatively large H_2O peak was released from moisture evaporation at 100 °C (0.9 wt. %). In addition, two weight loss steps are visible at 280 °C (1.2 wt. %) and 430 °C (0.1 wt. %) associated with the release of H_2O as detected by the MS. These weight losses may be ascribed to the decomposition of hydrated phases, such as hydrocalumite ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$), which shows a complete dehydration between 260-280 °C (Vieille et al., 2003), and $Ca(OH)_2$ which decomposes at around 400-450 °C (Brown and Dykstra, 1995; Payá et al., 1998). These specific two types of hydrated phases were indicated since they were both identified by X-ray diffraction (XRD) analysis in this type of BA (Rocca et al., 2012). Therefore, it is concluded that the weight loss measured for RDF-I BA at 280 °C and 430 °C is most probably associated with the dehydration of hydrocalumite and $Ca(OH)_2$, respectively. Additional experiments with standard addition of $Ca(OH)_2$ for further confirmation of the processes controlling the weight loss of these BA samples in this temperature range are described in the next paragraph 1.3.2.2. The weight loss measured at around 700 °C (1.0 wt. %) in correspondence with only a CO_2 peak suggested the decomposition of inorganic carbon from carbonate phases ($CaCO_3$), in agreement with the findings of van Zomeren and Comans (2009) and Ferrari et al. (2002). This observation is also consistent with the results of the calcimetry and the XRD analyses obtained for this BA sample (Rocca et al., 2012). Additional experiments with standard additions of $CaCO_3$ for further confirmation of the processes controlling the weight loss of these BA samples around this temperature are described in paragraph 1.3.2.2.

The TG-MS results obtained for the HW-I BA showed a relatively large weight loss (6.2 wt. %) of the sample at 550 °C in combination with a CO_2 peak detected by the MS. Since the CO_2 peak was not associated with a H_2O peak, this weight loss can most probably be ascribed to the release of elemental carbon (EC), according to van Zomeren and Comans (2009). In addition, inorganic carbon from carbonates was probably decomposed (0.7 wt. %) at about 700 °C, also resulting solely in the CO_2 peak detected by the MS. The presence of $CaCO_3$ in this type of BA was also found by both calcimetry and XRD analyses, as reported in Rocca et al. (2012). Finally, only small amounts of water were found to be released from this type of BA at 100 °C (moisture content) and at temperatures between 160-240 °C (crystal water desorption or hydrated phases decomposition, according to Brown and Dykstra, 1995).

Furthermore, the insets of the graphs a and b in Figure 1.2 show that a small weight gain was observed in both types of ashes, from 700-800 °C up to 1000 °C. This weight gain might be related to the oxidation of metals and/or iron-bearing minerals occurring in the ash materials as suggested by Vandenberghe et al. (2010). This observation is consistent with the presence of hematite (Fe_2O_3) but also of iron oxide (FeO) especially in the coarse fractions of both types of BA, as detected by XRD (Rocca et al., 2012 and Annex B, Supporting Information). These results also corroborate our explanation of the lower TG values compared to those of LOI, as shown in Figure 1.1.

1.3.2.2 Reaction mechanisms in bottom ash during thermal analyses

Subsequently, in order to further identify the origin of the H_2O and CO_2 peaks that were primarily released at different combustion temperatures from the two BA samples, additional TG-MS experiments with mixtures of BA and about 2 mg of portlandite ($Ca(OH)_2$) or 1 mg of calcium carbonate ($CaCO_3$) were performed; the amounts of the two additives were calculated such that the expected MS peaks were doubled in area. The results of the cumulative weight losses determined by the two LOI standard methods for the different coarse and fine fractions of the fresh and aged BA samples showed that the LOI 550 values measured for the HW-I BA (from 9.6 to 23 % on a dry weight basis) were generally higher compared to those obtained for the RDF-I BA (from 3 to 8.4 % on a dry weight basis), indicating a higher content of volatile compounds with low decomposition temperatures in the HW-I BA samples. On the other hand, the LOI 1000 values obtained for specific RDF-I and HW-I BA samples were quite similar for the two types of BA (from 8 to 16 % on a dry weight basis) as a possible result of the significant content of carbonate phases and/or volatile compounds with high decomposition temperatures in the RDF-I samples. The LOI results obtained for the different RDF-I and HW-I BA samples is provided in the Annex A, Supporting Information. In addition, the results of the carbonates content of the two types of BA as determined by LOI analysis are described in the following paragraph 1.3.3.

Figure 1.2 shows the TG-MS results for the (coarse fraction of the fresh) RDF-I BA (graphs c and e) and the HW-I BA (graphs d and f) when $Ca(OH)_2$ or, alternatively, $CaCO_3$ were added to the samples. First, the addition of $Ca(OH)_2$ to the RDF-I BA (graph c and Table 1.2) resulted in an increased weight loss and associated H_2O peak at 430 °C relative to the initial samples. These results confirmed the decomposition of $Ca(OH)_2$ at 430 °C in these samples. The same results were obtained with the addition of $Ca(OH)_2$ to the HW-I BA samples (graph d and Table 1.3), although there was no $Ca(OH)_2$ present in the original HW-I BA samples.

The addition of $CaCO_3$ to both BA types resulted in an increased weight loss at 700 °C (Figure 1.2, graphs e and f and Table 1.2 and 1.3) in combination with the formation of solely CO_2, compared to the initial samples. Thus, these results confirm the presence and decomposition of $CaCO_3$ at 700 °C in both bottom ash types.

Furthermore, after the addition of $Ca(OH)_2$ to the HW-I BA (graph d in Figure 1.2 and Table 1.3) TG-MS results show that the sample also exhibited an increased weight loss (from 0.7 to 5.2 wt. %) at 700 °C (temperature at which the decomposition of $CaCO_3$ was identified) in combination with an increased CO_2 peak, compared to the initial sample. It can also be seen that the weight loss at 550 °C (EC decomposition) decreased (from 6.2 to 4.7 wt.%) relative to the initial HW-I BA sample. These results can be explained by the following chain of reactions taking place during the TG-MS experiment. At 430 °C, dehydration of $Ca(OH)_2$ occurred in the sample according to equation 1.

Next, the newly formed CaO reacted with (part of the) CO_2 that was released from combustion of

EC at 550 °C to form $CaCO_3$ (equation 2). Finally, the newly formed $CaCO_3$ subsequently decomposed at 700 °C releasing the CO_2 that originated from the decomposition of EC (equation 3).

$$Ca(OH)_2\ (s) \rightarrow CaO(s) + H_2O\ (g) \qquad (1)$$

$$CaO\ (s) + CO_2(g) \rightarrow CaCO_3\ (s) \qquad (2)$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2\ (g) \qquad (3)$$

The hypothesized mechanisms taking place during the TG-MS analyses with mixtures of HW-I BA and $Ca(OH)_2$ were found for all samples (see Table 1.3) with the highest effects measured for the fine fraction of the fresh BA (EC decrease: from 17.6 to 14.1 wt. % and $CaCO_3$ increase: from 1.9 to 8.5 wt. %). In addition, from the TG-MS results presented in Table 1.3 it can be noted that the weight loss due to the dehydration of $Ca(OH)_2$ at 430 °C was not observed for the fine fractions of the HW-I BA when mixtures of these (fresh/weathered) samples and $Ca(OH)_2$ were analysed. The expected decrease in EC and increase in $CaCO_3$ are clear for these samples, suggesting that the considerably high weight loss measured at 550 °C (about 20 wt. %) due to the decomposition of EC probably masked the weight loss associated to the dehydration of $Ca(OH)_2$. The TG-MS results for RDF-I BA (see Table 1.2) after the addition of $Ca(OH)_2$ did not reveal the same effect on the increase of the $CaCO_3$ weight loss that was observed for the HW-I BA samples. These results confirm that the RDF-I BA did not contain (unburned) carbon species that decompose at 550 °C leading to a relevant CO_2 production. Furthermore, these results are in good agreement with those derived from the analysis of the Total Organic Carbon (TOC) content of the RDF-I BA, which appeared to be formed by only 0.35 % wt. of unburned organic matter (Rocca et al., 2012). As such, the results of this study suggest that the relatively constant size distribution and composition of the RDF feedstock in the incineration plant possibly contributed to the high efficiency of the combustion system, resulting in a negligible content of residual organic carbon in the produced BA. On the other hand, the TG-MS results determined for the HW-I BA imply that a pyrolytic-like process may take place in the rotary kiln combustion system due to an oxygen-deficient atmosphere that limits the complete combustion of the HW feedstock. Consequently, the BA originating from such a thermal treatment process results in a carbonaceous solid residue that is mainly constituted of elemental black carbon with a decomposition temperature of 550 °C that was clearly identified by TG-MS. With regard to these results, it must be pointed out that the elemental carbon content of the HW-I BA was adequately approximated by the TOC value of the sample, which accounted for 8-20 % wt. (results not shown) depending on the size fractions of the analysed material, but did not contribute to the production of the DOC and hence to an enhanced release of metals such as Cu, as indicated by the leaching test results that were obtained in a specific study carried out on the same HW-I BA sample (see Chapter 2). These findings confirmed those obtained by van Zomeren and Comans (2009).

In order to further investigate the observed decrease in EC and increase in $CaCO_3$, TG-MS experiments were also carried out with the coarse and fine fractions of the fresh HW-I BA samples and addition of different amounts of $Ca(OH)_2$. As shown in Figure 1.3, the samples exhibited an increased weight loss of H_2O (graphs a and d) in combination with a decreased weight loss of EC (graphs b and e) and increased weight loss of $CaCO_3$ (graphs c and e) compared to the initial samples, as an effect of the increasing addition of $Ca(OH)_2$. From Figure 1.3 it can also be seen that the measured mass losses of H_2O (from dehydration of $Ca(OH)_2$, graphs a and d) and CO_2 (from decomposition of $CaCO_3$, graphs c and e) were always lower than the theoretical maximum values calculated based on the amounts of $Ca(OH)_2$ that were added to the samples, according to equations 1, 2 and 3. This observation indicates that only a fraction of the added $Ca(OH)_2$ is converted to $CaCO_3$. This effect is particularly noticeable in Figure 1.3 graphs b and e (related to decomposition of EC) which show that the theoretical weight gain that would result at high $Ca(OH)_2$ additions (according to equations 1 and 2) was not observed.

Moreover, a linear correlation was observed between the measured decreases in EC and increases in $CaCO_3$ both for the coarse and fine fractions of the BA, as an effect of the different amounts of $Ca(OH)_2$ added to the samples (slope= -0.34, R^2= 0.98 for the coarse sample; slope= -0.38, R^2= 0.97 for the fine sample). This observation further corroborates the hypothesized chain of reactions represented by equations 1-3. Given the results of the additional TG-MS experiments carried out with the BA samples and increasing amounts of $Ca(OH)_2$, it can also be deduced that the conversion of free lime (CaO) (originated from dehydration of $Ca(OH)_2$) to $CaCO_3$ ranged from 40 to 100 %. In particular, the highest conversion values were determined for the BA samples exhibiting the lowest additional amounts of $Ca(OH)_2$, i.e. 1 or 2 mg. As such, the results suggest that the reaction time might not be sufficient for converting the total amount of CaO to $CaCO_3$ when the highest amounts of $Ca(OH)_2$, i.e. 4 or 8 mg were added to the samples during the (performed) TG-MS analyses. The TG-MS results presented in Tables 1.2 and 1.3 also indicate that the $CaCO_3$ content increased as the particle size fraction of BA decreased. However, this effect was substantially higher for the RDF-I BA (from 1.0 wt. % for the coarse fraction to 9.5 wt. % for the fine fraction of the fresh BA) in comparison to that observed for the HW-I BA samples (from 0.7 wt. % for the coarse fraction to 1.8 wt. % for the fine fraction of the fresh BA). These results are consistent with those reported in previous studies on different size fractions of BA (e.g. Chimenos et al., 2003;

Baciocchi et al., 2010; Onori et al., 2011). In general, the same trend was found when comparing the individual results of the LOI, TG, MS, TIC and calcimetry analyses for both types of BA. Further discussion on the carbonate content of BA as determined by different analytical methods is provided below.

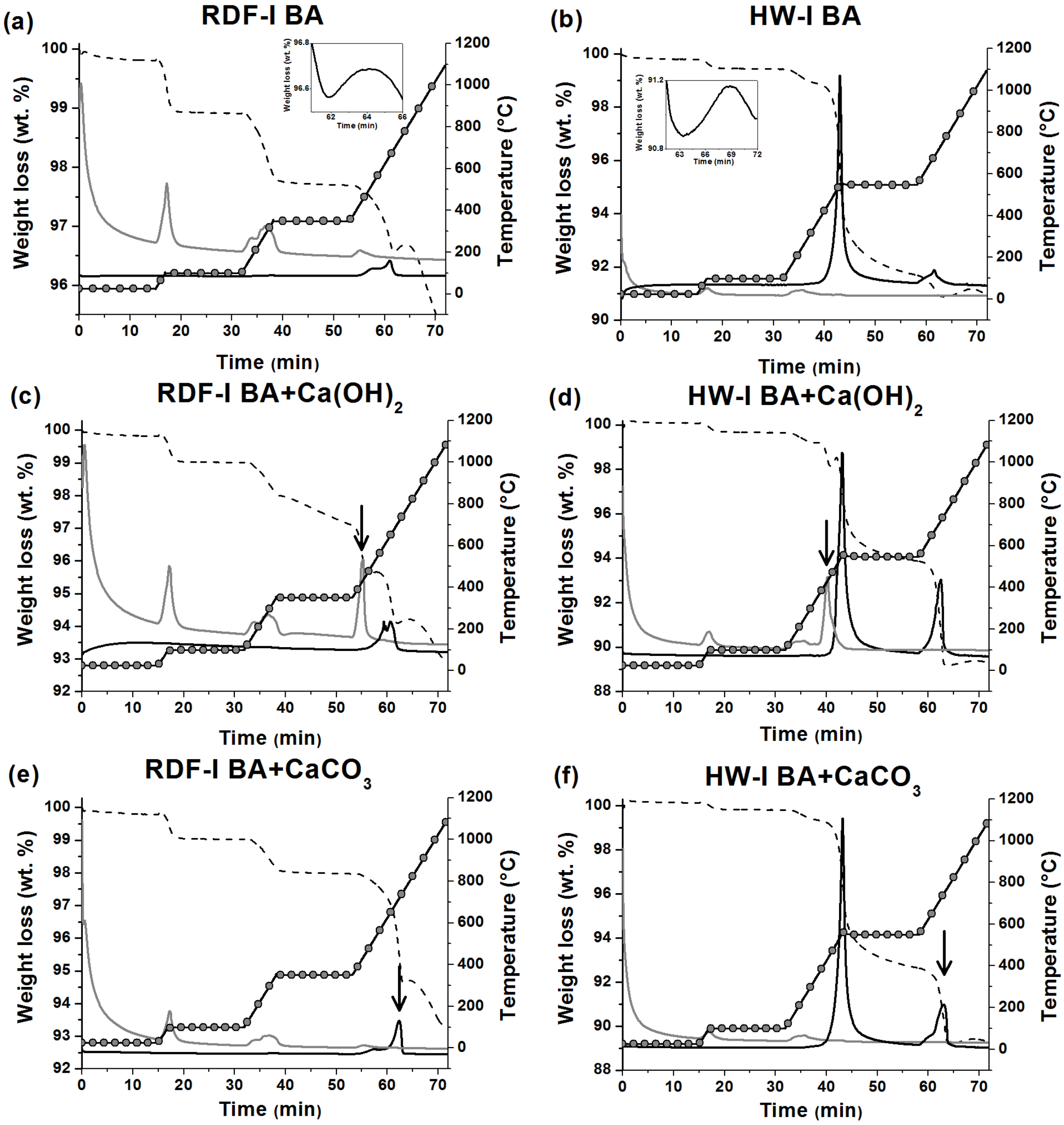

Figure 1.2. Typical examples of TG-MS analysis results obtained for the coarse fraction of the fresh RDF-I BA (graph a) and the HW-I BA (graph b) samples. Results of additional TG-MS experiments with mixtures of BA and $Ca(OH)_2$ (graphs c and d) or $CaCO_3$ (graphs e and f) are shown in the same figure. The dashed line indicates the weight loss recorded by TG, while the line with circles represents the temperature program applied. Black and grey lines show the relative MS signals for evolved CO_2 and H_2O, respectively. The insets of the graphs a and b evidenced the (slight) weight gain of the samples detected from 700-800 °C up to 1000 °C. The arrows included in the graphs indicate the increased mass losses of H_2O and CO_2 during additional TG-MS experiments with mixtures of BA and $Ca(OH)_2$ (graphs) or $CaCO_3$ (graphs e and f).

Table 1.2. Weight loss (% dry wt.) measured during TG analysis for all the examined RDF-I BA samples.

RDF-I BA samples	weight loss (wt. %)			
	100 °C (moisture)	280 °C (hydrated phases)	430 °C ($Ca(OH)_2$)	700 °C ($CaCO_3$)
Coarse Fresh	0.9	1.2	0.1	1.0
Coarse Fresh+$Ca(OH)_2$	0.9	1.2	1.7	1.8
Coarse Fresh+$CaCO_3$	0.8	1.1	0.1	3.4
Coarse Weath.	1.8	2.7	0.3	1.8
Coarse Weath.+$Ca(OH)_2$	1.9	2.6	1.9	2.6
Coarse Weath.+$CaCO_3$	1.8	2.5	0.2	4.2
Fine Fresh	1.8	2.5	0.9	9.5
Fine Fresh+$Ca(OH)_2$	2.2	3.3	2.9	7.6
Fine Fresh+$CaCO_3$	1.7	2.5	0.9	12.6
Fine Weath.	2.6	3.6	0.6	4.8
Fine Weath.+$Ca(OH)_2$	2.1	3.4	2.4	6.0
Fine Weath.+$CaCO_3$	2.0	3.4	0.7	8.6

Table 1.3. Weight loss (% dry wt.) measured during TG analysis for all the examined HW-I BA samples.

HW-I BA samples	weight loss (wt. %)				
	100 °C (moisture)	160-240 °C (crystal water/hydrated phases)	430 °C ($Ca(OH)_2$)	550 °C (EC)	700 °C ($CaCO_3$)
Coarse Fresh	0.3	0.6	-	6.2	0.7
Coarse Fresh+$Ca(OH)_2$	0.4	0.5	1.1	4.7	5.2
Coarse Fresh+$CaCO_3$	0.3	0.4	-	6.3	3.6
Coarse Weath.	0.3	0.3	-	7.4	0.8
Coarse Weath.+$Ca(OH)_2$	0.3	0.3	1.7	4.7	4.7
Coarse Weath.+$CaCO_3$	0.2	0.3	-	6.7	3.4
Fine Fresh	0.9	0.3	-	17.6	1.9
Fine Fresh+$Ca(OH)_2$	0.9	0.7	-	14.1	8.5
Fine Fresh+$CaCO_3$	0.8	0.6	-	17.2	5.0
Fine Weath.	0.9	0.3	-	20.2	1.3
Fine Weath.+$Ca(OH)_2$	0.8	0.5	-	16.2	7.6
Fine Weath.+$CaCO_3$	0.7	0.5	-	19.0	5.3

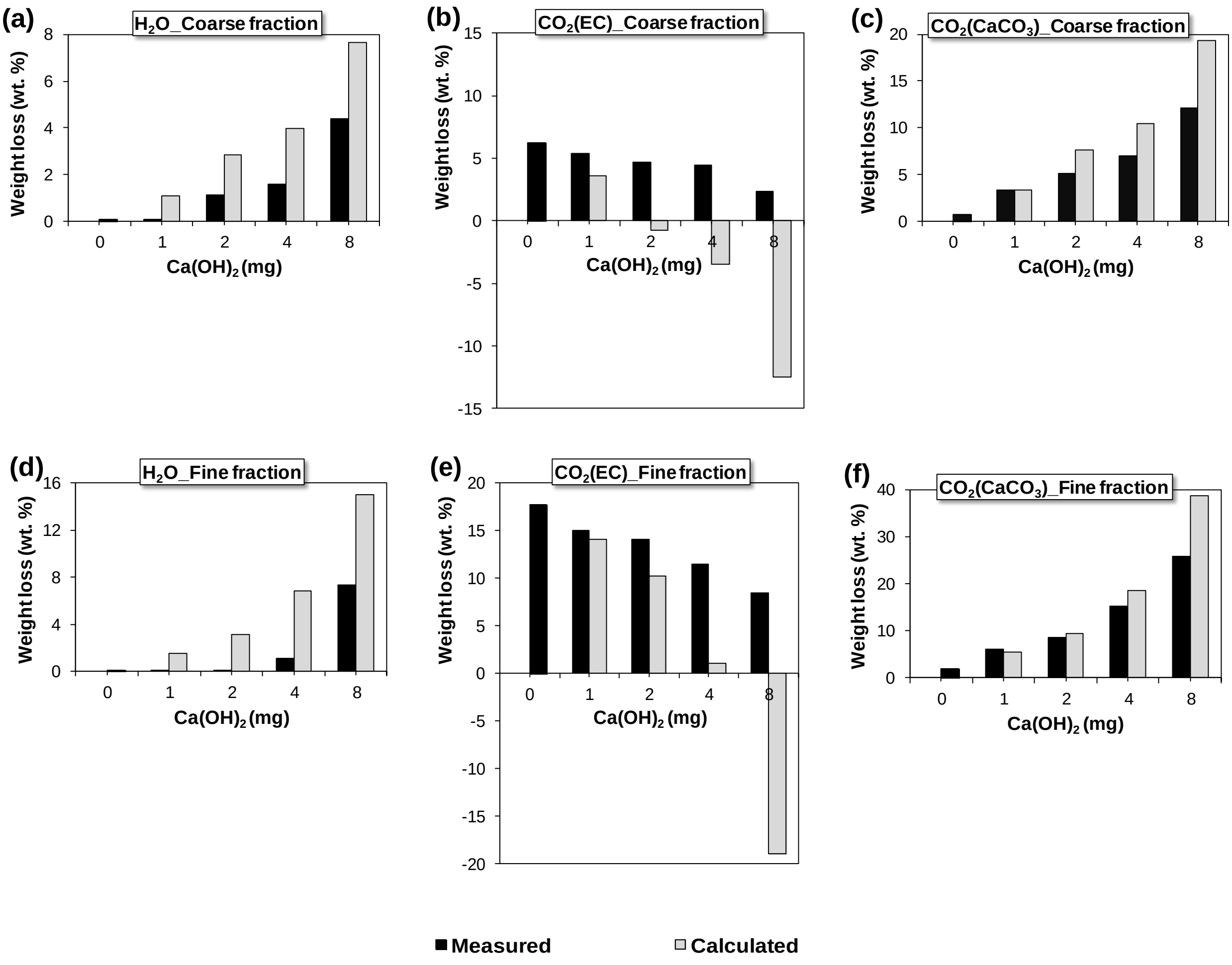

Figure 1.3. Measured and calculated weight losses (wt. %) determined by the TG-MS experiments with mixtures of the coarse (graph a, b and c) and fine (graph d, e and f) fractions of the HW-I BA samples and increasing amounts of $Ca(OH)_2$ (i.e. 1, 2, 4 and 8 mg). The TG-MS results obtained for the initial BA samples (i.e. 0 mg of $Ca(OH)_2$) were included in the graphs for comparison.

1.3.3 Comparison of the carbonate content of bottom ash determined by different methods

First, the amount of $CaCO_3$ in BA was estimated based on the weight losses (wt. %) detected at 700 °C by the TG microbalance. Next, the $CaCO_3$ content of the BA was calculated by integration of the peak areas of the evolved CO_2 at 700 °C monitored by the MS. In addition, the $CaCO_3$ concentrations of BA was determined by LOI (i.e. LOI 1000-LOI 550), TIC and calcimetry analyses. Results obtained for both the RDF-I and HW-I BA samples are shown in Figure 1.4.

With regard to the RDF-I BA (graph a), the results from LOI, TG, MS and TIC were in reasonably good agreement with each other, mainly for the coarse fraction of the fresh/weathered samples. For the fine fractions of the same type of BA, instead, TIC results proved to be higher in comparison with those obtained by TG and MS analyses.

For the HW-I BA, the results reported in Figure 1.4 (graph b) show that TG, MS and TIC methods led to similar $CaCO_3$ concentrations for the coarse fractions of the sample, while LOI appeared to consistently overestimate the carbonate content for the coarse fraction of the fresh sample. On the other hand, also for the fine fractions of this type of BA, the results from TIC measurements were 2 times higher in comparison with the values determined applying the other methods.

These results suggest that the TIC method (heating of the sample at 200 °C after the addition of H_3PO_4) can affect the measurement accuracy of $CaCO_3$ in these ash materials as it might account for additional CO_2 quantities originating from oxidation of (a small part of) EC or decomposition of phases other than carbonates contained in BA. Further investigations should be hence carried out in future research in order to better understand the differences in $CaCO_3$ concentrations measured by TG-MS and TIC analysis.

In addition, Figure 1.4 shows that the $CaCO_3$ content as measured by calcimetry analysis was about 2 times higher in comparison with the other methods for most samples of both types of BA (e.g. the coarse fraction of the fresh/weathered RDF-I BA and the fine fraction of the fresh/weathered HW-I BA). Indeed, calcimetry analyses is based on the estimation of the total gas volume evolved after acidification of the sample. The relatively large overestimation of the $CaCO_3$ content might be related to the release of gaseous products other than the CO_2 released from the decomposition of $CaCO_3$. It is likely that hydrogen gas and/or H_2S were also released from the samples after contact with water and thus have contributed to the measured gas volume in the calcimeter. Hydrogen sulphide was organoleptically detected in eluates at low pH, while the formation of hydrogen gas is known to occur in MSWI bottom ash (e.g. Chandler et al., 1997) and can be substantial (around 50 ml per 500 g of BA, unpublished results).

In addition, Figure 1.4 shows that the $CaCO_3$ concentrations determined by TG analysis were only slightly lower than those derived by LOI, apart from the coarse sample of the fresh HW-I BA. Thus, from these results we can exclude that the oxidation of iron-bearing minerals occurring at 700-1000 °C (as detected in the TG-MS thermograms, see graphs a and b in Figure 1.2) has substantially influenced the carbonate measurements of both the BA types. Given the findings of this study, it should be realized that in the quantification of $CaCO_3$ in heterogeneous materials, such as BA by each of the applied methods, other phases present in BA matrix can contribute to the different measurement principles (weight loss, gas volume or CO_2 release).

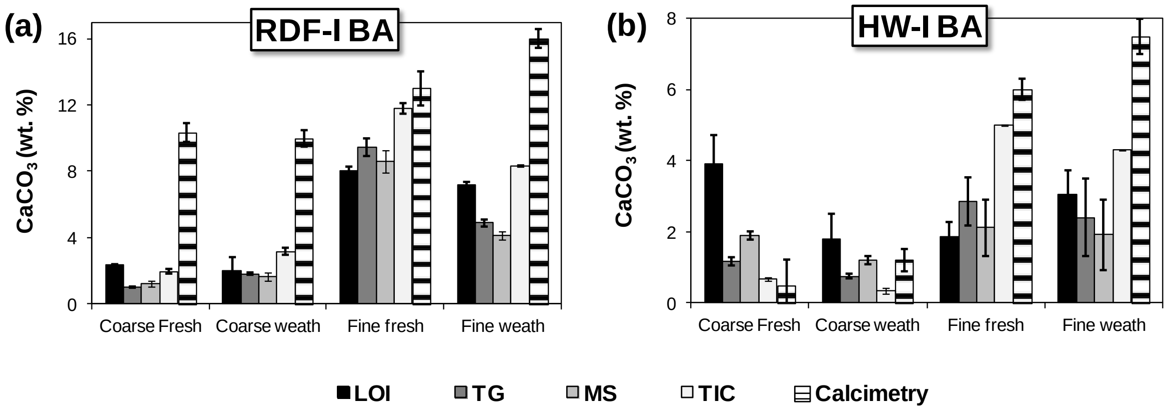

Figure 1.4. Carbonate content ($CaCO_3$, wt. %) in the RDF-I BA (graph a) and the HW-I BA (graph b) samples as determined by LOI (LOI 1000-LOI 550), TG, MS, TIC and calcimetry analysis. The error bars indicate the standard deviation calculated based on the triplicate measurements of each $CaCO_3$ analysis method.

1.4 CONCLUSIONS

In the present study, bottom ash (BA) samples from two different incineration plants treating refuse derived fuel (RDF-I) and hospital waste (HW-I) were analysed by thermogravimetric and mass spectrometry (TG-MS) analysis. The aim of this study was to identify the main compounds affecting the weight changes of BA in conventional LOI tests and to obtain a better understanding of the individual processes that take place during laboratory characterization of the carbon species in heterogeneous waste materials such as BA, by combining different analytical techniques.

The TG-MS experiments performed on RDF-I BA indicated that the LOI measured at 550 °C was mainly due to moisture evaporation and dehydration of hydrated phases. We found that hydrocalumite and $Ca(OH)_2$ are most probably the phases that decompose in RDF-I BA at temperatures below 550 °C and determine the LOI values. Both phases were identified by XRD and the decomposition of $Ca(OH)_2$ was also confirmed by standard addition experiments. Furthermore, the LOI measured at 1000 °C for this type of BA accounted for the decomposition of $CaCO_3$ as was also confirmed by standard addition experiments. TG-MS results obtained for the HW-I BA showed that the total LOI at 550 °C mostly resulted from the decomposition of elemental carbon contained in this material. The results thus indicate that no organic carbon species could be detected in either of the examined types of materials. The decomposition of $CaCO_3$ was found to occur around 700 ^{o}C and was confirmed by standard addition experiments. Furthermore, the TG-MS results with mixtures of BA and $Ca(OH)_2$ have revealed a number of processes that take place during thermal analysis (LOI and TG-MS measurements) of these materials and influence the assignment of observed results to specific carbon species. The results of this study, hence, imply that TG-MS analysis and conventional LOI measurements can overestimate the carbonate content and underestimate the EC content of a combustion residue, as was clearly demonstrated for the HW-I BA. We have identified the reaction mechanisms that influence the determination of the LOI in general and the EC and $CaCO_3$ content in particular. In fact, the results showed that the CO_2 released from the combustion of EC (and possibly OC) is partly reacting directly with the CaO to produce $CaCO_3$. This reaction causes an underestimation of EC because the production of $CaCO_3$ causes a weight gain of the sample. The determination of (originally present) $CaCO_3$ is subsequently overestimated due the $CaCO_3$ that is newly formed during the thermal analysis. Similar phenomena are expected to occur also for other materials that contain $CaO/Ca(OH)_2$ in combination with EC/OC, e.g. MSW incineration bottom and fly ashes. In addition, given the findings of this study, it should be realized that in the quantification of $CaCO_3$ in heterogeneous materials, such as BA by different analytical methods, i.e. LOI, TG, MS, TIC and calcimetry other phases present in BA matrix can contribute to the measurement principles of each of the applied method (weight loss, gas volume or CO_2 release).

Hence, the results of the present study may also have implications when considering the $CaCO_3$ formation in BA. Several authors indicate that carbonates usually form as a result of several interrelated alteration processes, e.g. hydrolysis, dissolution, precipitation and carbonation which start immediately after the production of the bottom ash (e.g. Meima and Comans, 1997; Speiser et al., 2000; Polettini and Pomi, 2004). In general, it is believed that the presence and concentration of $CaCO_3$ in BA samples indicates the stage of weathering of the material. It is likely that the same reactions that we observed to operate in TG-MS analysis do also occur during combustion of the waste in the incinerator. Carbonate can then be formed when the BA reaches a temperature comprised between 450 and 650 ^{o}C. This finding would also explain the considerable carbonate content that has been found in unquenched and freshly quenched incineration ashes (Meima and Comans, 1997), demostrating that the presence of carbonate in bottom ash is not necessarily indicative for weathering. This is important since carbonation is generally believed to improve the environmental quality of bottom ash. Therefore, these results may also provide insight on how to further optimize waste incineration technologies in order to obtain a subsequent improvement of the environmental behaviour of the bottom ash generated during the thermal treatment process, such as for example by enhancing in-situ carbonation reactions.

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Chapter 2

Main composition and leaching behaviour of hospital waste incineration bottom ash

Part of this chapter has been published in similar form as:
Stefania Rocca, André van Zomeren, Giulia Costa, Joris J. Dijkstra, Rob N.J. Comans, Francesco Lombardi, 2012. Scorie di fondo da incenerimento di rifiuti ospedalieri. *Rifiuti Solidi* vol. XXVI n. 3 maggio-giugno, 164-172 (in Italian).

In this study, the chemical characteristics, mineralogy and leaching properties of bottom ash (BA) originated from a hospital waste incineration (HW-I) plant were investigated. Bulk chemical analysis indicated that BA mainly contains Si, Ca and Al, as well as high concentrations of Cu, Ni, Zn and Cr, with concentration values that are quite similar to those typically reported for MSWI BA. On the other hand, mineralogical characterization by X-Ray diffraction analysis revealed that the analyzed HW-I BA was predominantly an amorphous material containing only few crystalline phases, i.e. carbonates and silicates, and therefore exhibited a different mineralogy than that reported in the literature for MSWI BA. Furthermore, results from the EN 12457-2 compliance leaching test showed that HW-I BA would meet the European acceptance criteria for non hazardous waste landfills and the limits for reuse in specific application scenarios. However, the acid neutralization behaviour of this type of BA appeared low so that possible implications on the pH dependency release of many constituents should be considered in order to draw some conclusions on the expected behaviour of the slag under the conditions characteristic of an application scenario. Qualitative and quantitative comparison of the leaching properties of fresh and aged HW-I BA with those typical of MSWI BA suggested that differences existing between the various BA samples may be most likely ascribed to the thermal treatment technology adopted in the plants from which the residues were originated from.

2.1 INTRODUCTION

The waste produced at any medical or veterinary treatment and/or research facility, typically defined medical or hospital waste (HW), is generally considered a hazardous waste due to its potential content of infectious and toxic substances that may pose a threat to human health and the environment. The Italian legislation, in accordance with European guidelines, requires the incineration of HW at high temperature (>1100 °C) in dedicated plants before final disposal.

HW incineration (HW-I) facilities generate a number of solid residues, among which bottom ash (BA) is the one produced in the largest amount accounting for approximately 10% by weight of the original waste. In Italy, BA from HW-I plants is usually disposed of as a hazardous waste, as a precautionary measure given the infectious and toxic characteristics of the feed waste. Furthermore, the disposal of this type of BA at special landfills still remains the most common management practice in many countries (Zhao et al., 2009; Kougemitrou et al., 2011). Anyhow, owing to the increasing adoption of incineration as a treatment technology for HW, an appropriate strategy for the management of the BA generated from these types of plants is becoming an important issue. Recently, considerable progress has been made in understanding the main physical, chemical and mineralogical characteristics of this special type of BA (e.g. Filipponi et al., 2003, Gidarakos et al., 2009). In particular, many references reported the presence of high concentrations of potentially hazardous metals, such as Cu, Ni, Zn, Cr, Cd and Pb in this material (e.g. Idris et al., 2002; Zhao et al., 2009). However, it well known that total composition is not an adequate proxy parameter for the environmental behaviour of BA, as only fractions of the total amount of elements present in this residue are susceptible to leaching processes (e.g. Meima and Comans, 1997; Polettini and Pomi, 2004; Dijkstra et al., 2006). It is therefore remarkable that, so far, considerably less attention has been paid to the leaching behaviour of this special type of BA. Furthermore, it should be considered that the available leaching results were derived from the EN or DIN test types at the material's own pH (9.5-11.5), as well as from the TCLP test which implies leaching at acid pH (5 or 2.8) that would represent a rare case of waste mismanagement in practice. Consequently, there is a lack of information on the leaching behaviour of major and trace components from the HW-I BA under different pH conditions, as well as on the effects of natural weathering on this type of BA. Thus, this paper reports the chemical and the mineralogical composition, as well as the leaching quality (at natural pH) of the same type of HW-I BA that was analysed in Rocca et al. (2012), see Chapter 2, and provides additional data on the pH dependency leaching characteristics of fresh and 6 months naturally weathered BA. The leaching behaviour of the HW-I BA has been analysed as a function of pH because of the important role of this parameter in controlling the release of contaminants from waste materials in specific application scenarios (van der Sloot, 2001). Therefore, it is important to understand the pH dependent leaching mechanisms occurring in HW-I BA with the final aim of identifying suitable management strategies for its safe disposal or reuse. In addition, chemical composition and leaching properties of the HW-I BA were compared with other data regarding BA samples produced by HW incineration plants and with those obtained for municipal solid waste incineration (MSWI) BA, so to identify the main differences or similarities between the two different types of slag.

2.2 MATERIAL AND METHODS

2.2.1 Bottom ash sampling and preparation

The examined BA was sampled from a dedicated hospital waste incineration (HW-I) plant located in central Italy, operating on two independent lines, each one with a treatment capacity of about 50 t/d. The HW incinerator is equipped with a rotary kiln combustion chamber where operational temperatures can range from 1000 to 1200 °C in order to destroy different infectious organisms that may exist in this special type of waste. Approximately 100 kg of freshly quenched BA were collected from the material's storage tank at the outlet of the combustion chamber, during a typical day of operation of the plant. To obtain representative sample for the laboratory testing program, BA was homogenized through a quartering procedure, in accordance with the Italian norm UNI

10802:2004. Coarse metallic and ceramic fragments (5-10 cm), accounting for about 5% by weight of the BA stream, were manually removed. Subsequently, BA was oven dried at 60 °C and sieved to produce the following 5 particle size fractions: class A (9.18-4.76 mm); class B (4.76-2 mm); class C (2-0.425 mm); class D (0.425-0.150 mm) and class E (<0.150 mm). Particles size of the analysed HW-I BA was distributed as follows: 2.95% wt. in the class A, 41.7% wt. in the class B, 49.3% wt. in the class C, 5.1% wt. in the class D and 0.9% wt. in the class E. Each size class was thoroughly characterized in terms of mineralogy, chemical composition and leaching behaviour at the material's own pH, as reported in a previous study (see Annex A and B, Supporting Information). As a matter of fact, the results showed that there were no substantial differences in the main mineralogical and chemical properties, as well as in the leaching behaviour of the different size fractions of the BA. Therefore, in the present study, class C was selected as the representative sample of the HW-I BA, since it corresponds to the most abundant size fraction of the BA stream (approximately 50% wt.). The HW-I BA was subsequently naturally weathered in a controlled humidity environment and after 6 months of this treatment it was sampled, sieved to produce 5 particle size classes and analyzed for mineralogy and leaching behaviour so to gain insight on the major effects of weathering on this type of BA.

2.2.2 Bulk chemical and mineralogical composition

The loss on ignition (LOI) at 1000 °C of BA was determined according to the ASTM C25 procedure. Bulk chemical composition of major (Ca, Si, Mg, Al, Fe, Na and K) and trace elements (Cu, Zn, Pb, Cd, Cr, As, Mn, Ni, Sb, V and Mo) of this material was determined by atomic absorption spectrometry (AAS, equipped with a graphite furnace for the analysis of trace concentrations) following alkaline digestion of the samples with lithium tetraborate at 1050 °C. The total content of chlorides (Cl^-) and acid soluble sulphates (SO_4^{2-}) was measured by titration with $AgNO_3$ and spectrophotometric analysis, respectively, after dissolution of the samples with hot deionised water, according to the Italian standard UNI 8520 method. The carbonate (CO_3^{2-}) content of fresh and weathered BA was measured using a Dietrich-Frülingh calcimeter, which involved acidification (HCl) of the samples and subsequent measurement of the evolved gas volume. All the measurements were carried out in triplicate. Qualitative mineralogical characterization of both the fresh and the weathered BA samples was determined by X-ray diffraction (XRD) using a Philips Expert Pro diffractometer system adopting Cu Kα radiation at an accelerating voltage of 40 kV.

2.2.3 Leaching experiments

First, the batch compliance leaching test EN 12457-2 was carried out to evaluate the release of pollutants from the untreated HW-I BA at the material's own pH. In detail, around 4 g of BA were continuously stirred (3-5 rpm) in 40 ml of distilled water (L/S= 10 l/kg)on a tumbler device. After 24 h, the pH of the eluates was measured and the solutions were subsequently filtered through 0.45 μm pore size filters before chemical analyses. Elemental leaching concentrations were measured by AAS; the leaching of soluble Cl^- and SO_4^{2-} were evaluated by titration with $AgNO_3$ and spectrophotometric analysis, respectively. The dissolved organic carbon (DOC) was measured with a Shimadzu TOC-V CPH analyzer. Leaching results were then compared with the acceptance criteria reported in Annex II of the European Landfill Directive (2003/33/EC). In addition, leachate concentrations were compared with the limits of the Italian legislation for the reuse of non hazardous waste (Italian Environmental Ministry, 1998), although these limits currently do not specifically apply to BA from incineration plants, and the Dutch regulation for the reuse of materials in construction (Dutch Soil Quality Decree). Leaching tests were carried out in duplicate.

Subsequently, to evaluate the leaching behaviour of the fresh and the weathered BA as a function of pH, the CEN/TS 14429 leaching test was performed. The test was carried out on 4 g of BA that were equilibrated for 48 h on a tumbler with 40 ml solutions (L/S= 10 l/kg) of varying acidity, ranging from deionized water to different amounts of 0.1 M HNO_3. In this way, various leachates with end-pH values in regular intervals between the natural pH of BA and pH 2 were analysed. The pH of each leachate was then measured and the different eluates were subsequently filtered through 0.45 μm pore size filters before the analysis of major and trace elements, as well as soluble Cl^- and SO_4^{2-} that were determined with the same methods adopted for the batch compliance leaching tests.

2.3 RESULTS AND DISCUSSIONS

2.3.1 Bulk chemical composition

Table 2.1 presents the results of the global chemical composition of the analysed HW-I BA and provides a comparison with other observations on HW-I bottom ashes from incineration plants adopting different operating conditions (i.e. furnace configuration and combustion temperature). In addition, the results of the chemical composition for the different types of HW-I BA were compared with those reported for MSWI BA by Chandler et al. (1997). Chemical analyses indicated that HW-I BA samples contained high concentrations of Si, Ca, Al, Fe, Mg and K, ranging between 2,000 and 200,000 mg/kg of dry BA. Furthermore, a number of HW-I ashes showed relevant concentrations of Cu, Ni, Zn and Cr (>1,000 mg/kg). The data presented herein also show that the highest concentrations of volatile metals, such as Pb and Zn were found in HW bottom ashes originated from incineration plants operating at lower temperature (around 800 °C) . Considering the differences in the types of incineration plants, in the types of treated waste and in the analytical techniques used to determine the chemical composition of the BA, the variation of the total content of major and trace elements for the different HW-I BA samples is generally around or below one or two orders of magnitude. The results in Table 2.1 provide an overview of the observed range in chemical composition for this type of waste material. Comparing these concentration ranges with those typically observed for MSWI BA, it can be concluded that there are similarities in the composition of the two types of BA as almost all the data related to the HW-I BA samples fall within the range values found for MSWI BA. On the other hand, some HW-I samples showed lower concentrations of Al, Fe, Zn, Pb, Cd and V than the average values reported for MSWI BA. Conversely, only few HW-I bottom ashes contained higher levels of Cu, Cr and Zn compared to MSWI BA. Furthermore, it can be seen that all the HW-I samples presented higher LOI values than MSWI BA range values, as a result of the elemental carbon content of the sample which was found to mainly affect conventional LOI measurements for this type of material, as reported in Chapter 1. Lower contents of SO_4^{2-} were also obtained for HW-I BA compared to MSWI BA, as a possible effect of the different composition of the treated waste (Rendek et al., 2007).

Table 2.1. Bulk chemical composition of HW-I BA and MSWI BA from different studies.

	HW-I BA[a] (n= 3)	HW-I BA[b] (n= 6)	HW-I BA[c] (n= 3)	HW-I BA[d] (n= 3)	HW-I BA[e] (n= 14)	HW-I BA[f] (n= 2)	HW-I BA[g] (n= 3)	HW-I BA[h] (n= 2)	MSWI BA[i]
wt.% d.m.									
LOI	15.5	n.a.	5.55	11	2-15	n.a.	0.1	n.a.	0.1-1.7
Cl^-	n.a.	n.a.	<0.01	n.a.	0.154	n.a.	n.a.	n.a.	0.142-0.751
SO_4^{2-}	n.a.	n.a.	0.09	n.a.	0.147	n.a.	n.a.	n.a.	0.370-1.11
mg/kg d.m.									
Si	221,500	n.a.	n.a.	n.a.	106,300	n.a.	n.a.	n.a.	91,000-308,000
Ca	82,000	n.a.	22,985	n.a.	60,000	97,600	n.a.	n.a.	370-123,000
Al	29,807	n.a.	8,393	80,000	29,520	49,650	n.a.	n.a.	21,900-72,800
Fe	32,219	n.a.	4,659	10,000	15,710	50,150	n.a.	3,000	4,120-150,000
Mg	10,000	n.a.	3,177	n.a.	5,390	17,200	n.a.	n.a.	400-26,000
K	1,916	n.a.	3,264	n.a.	4,970	n.a.	n.a.	n.a.	750-16,000
Cu	4,386	698	1,084	300	11,130	1,250	n.a.	1,000	190-8,240
Ni	2,070	278.4	332	n.a.	1,731	583.5	3,948	600	7-4,280
Zn	1,351	72	201	9,000	472.7	10,550	526	3,800	613-7,770
Hg	n.a.	0.05	n.a.	1	n.a.	n.a.	0.01	n.a.	0.02-7.75
Cr	944	94.6	168	100	5,970	705	n.a.	400	23-3,170
Mn	266	n.a.	72	n.a.	938.2	n.a.	n.a.	n.a.	83-2,400
Pb	<100	15.7	<80	300	8.9	200	82.5	200	98-13,700
Sb	23	n.a.	n.a.	n.a.	63.6	n.a.	50.9	n.a.	10-432
Cd	<2	0.17	<8	30	n.a.	n.a.	0.4	0.012	0.3-70.5
V	0.6	n.a.	n.a.	n.a.	30.0	n.a.	61.0	n.a.	20-122
As	18	6.1	n.a.	n.a.	7.97	11.5	23.9	n.a.	0.12-189
Mo	14	n.a.	n.a.	n.a.	45.2	n.a.	69.0	n.a.	2.5-276

n= number of specimens analysed; LOI= loss on ignition at 1000 °C; d.m.= dry matter; n.a.= not analysed

[a] Data from Rocca et al. (2009), operating temperature formation of BA= 1000-1200 °C; [b] Data from Idris et al. (2002), operating temperature formation of BA= 1200 °C; [c] Data from Filipponi et al. (2003), operating temperature formation of BA= not available; [d] Data from Al-Mutairi et al. (2004), operating temperature formation of BA= 800-1200 °C; [e] Data from Lategano et al. (2007), operating temperature formation of BA= 1000-1200 °C; [f] Data from Zhao et al. (2008), operating temperature formation of BA= 700-800 °C; [g] Data from Kougemitrou et al. (2011), operating temperature formation of BA= >1100°C; [h] Data from Iliopoulos et al. (2008), operating temperature formation of BA= 850°C; [i] Data from Chandler et al. (1997).

2.3.2 Mineralogical characterization

The results of the XRD analysis for the freshly sampled and the weathered HW-I BA are reported in Figure 2.1. The fresh BA primarily contained amorphous phases, which were deduced from the intense hump of the diffractograms in the 2 Theta range from 15 to 40°. On the other hand, the main crystalline phases detected in HW-I BA were calcite (C: $CaCO_3$) and gehlenite (G: $Ca_2Al_2SiO_7$), together with other silicate minerals (A: anorthite= $CaAl_2Si_2O_8$; Q: quartz= SiO_2; O: Fe-silica= Fe-SiO_2) and iron oxide (H: hematite= Fe_2O_3). The crystalline phases identified in this study were also reported in previous works on HW-I BA (e.g. Filipponi et al., 2003; Gidarakos et al., 2009). In addition, we analysed the mineralogy of the BA after 6 months of lab-scale natural weathering. The results indicated only a small increase of calcite (C), gehlenite (G), as well as anorthite (An) upon the aging period. As a matter of fact, the comparison of the different XRD patterns showed that the weathering process did not drastically affect the mineralogy of this type of BA. Furthermore, based on the results of calcimetry analysis, we found just a small increase (about 0.75 wt%) of carbonates (that were assumed to be in the form of $CaCO_3$) in the weathered BA with respect to the fresh one.

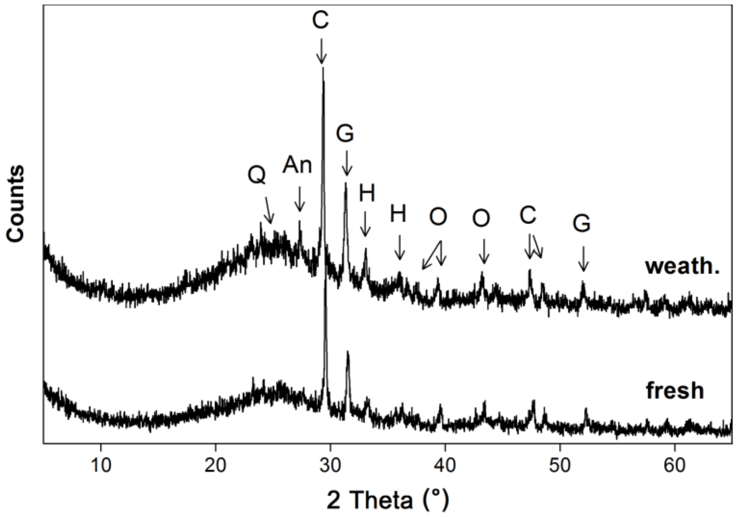

Figure 2.1. XRD patterns for fresh and weathered HW-I BA (Legend: Q= Quartz (SiO_2); An= Anorthite ($CaAl_2Si_2O_8$); C= Calcite ($CaCO_3$); G= Gehlenite ($Ca_2Al_2SiO_7$); H= Hematite (Fe_2O_3); O= Fe-silica (Fe-SiO_2))

2.3.3 Leaching tests at natural pH

The results of the EN 12457-2 leaching test for the examined HW-I BA, together with the leaching data at natural pH (obtained from EN 12457-2 or DIN 38814 leaching tests) for various HW-I samples by previous studies are presented in Table 2.2. In addition, the average values at natural pH resulting from CEN/TS 14429 leaching tests applied to MSWI BA are included in Table 2.2. These latter data are part of a leaching dataset that was compiled by using the LeachXS database/expert system and contains 15 MSWI BA samples of worldwide origin.

Differences in leaching among the various HW-I BA samples were remarkably high (one or two orders of magnitude) for Pb, Ni, Zn, Cu and Cr. In detail, it can be noted that the lowest leaching concentrations of Pb, Zn and Ni were generally observed for BA exhibiting a natural pH around 10, in accordance with previous results for MSWI BA (Meima and Comans, 1997), or originating at high combustion temperature (>1000 °C) as reported by Zhao et al. (2008). Furthermore, the leaching of Cu resulted relatively high for samples exhibiting high levels of DOC. These results are consistent with previous studies on MSWI BA which reported that Cu leaching can be quantitatively explained by its strong complexation with DOC (van Zomeren and Comans, 2004).

The comparison of eluate concentrations with European landfill acceptance criteria and reuse limits showed that some HW-I BA samples may be disposed of at landfills for non hazardous waste and also complied with the Italian and the Dutch regulatory criteria for reuse of waste materials. On the other hand, for other HW-I BA samples the leaching concentrations of Cd, Cr, Pb and Sb exceeded the European acceptance criteria for non hazardous waste landfilling, however complied with those established for hazardous waste landfilling.

Comparing the leaching results obtained for the HW-I samples with the average leaching data reported for MSWI BA, it can be noted that HW-I BA generally presents Cu, DOC, Sb, Cl^- and SO_4^{2-} concentrations 1 or 2 orders of magnitude lower than MSWI BA.

Table 2.2. Leaching test results at natural pH (from EN 12457-2 or DIN 38814 test type) for different HW-I BA samples and MSWI BA in comparison with the European Landfill acceptance criteria (2003/33/EC, EU LFD), the Italian (M.D. 05/02/1998) and the Dutch (Soil Quality Decree) regulation for reuse of waste materials. Results are reported in mg/l.

Component	HW-I BA[a] n= 2	HW-I BA[b] n= 6	HW-I BA[c] n= 7	HW-I BA[d] n= 4	MSWI BA n= 15	EU LFD			Italian Reuse	Dutch Reuse
						inert	non hazardous	hazardous		
pH	9.97	11.4-12.8	9.91	n.a.	11.37	n.a.	n.a.	n.a.	5.5 -12	n.a.
As	0.002	n.a.	0.0006	<0.001	0.004	0.05	0.2	2.5	0.05	0.09
Cd	n.a.	*0.05-0.09*	n.a.	**0.04-0.12**	0.0003	0.004	0.02	0.2	0.005	0.004
Cr	0.038	**0.22**-*1.1*	0.032	0.01-**0.245**	0.01	0.05	1	7	0.05	0.063
Cu	0.02	0.18-**0.91**	0.007	0.162-**0.611**	**0.635**	0.2	5	10	0.05	0.09
Mo	0.024	n.a.	0.024	n.a.	**0.064**	0.05	1	3	n.a.	0.1
Ni	0.002	**0.18-0.27**	0.001	**0.11-0.32**	0.0026	0.04	1	4	0.01	0.044
Pb	0.009	**0.93**-*3.93*	0.0004	<0.002	0.022	0.05	1	5	0.05	0.23
Sb	**0.01**	n.a.	**0.012**	n.a.	**0.024**	0.006	0.07	0.5	n.a.	0.016
V	< 0.04	n.a.	0.003	n.a.	0.0058	n.a.	n.a.	n.a.	0.25	0.18
Zn	0.1	0.23-**2.84**	0.002	0.03-0.07	0.0322	0.4	5	20	3	0.45
Cl-	54.4	n.a.	**501.3**	n.a.	**226.15**	80	1500	2500	200	61.6
SO_4^{2-}	68.4	n.a.	81.0	n.a.	**297**	100	2000	5000	250	173
DOC	0.81	11.7	n.a.	n.a.	*121.5*	50	80	100	30	n.a.

Bold values indicate concentrations above inert waste landfilling; *Italic values* indicate concentrations above non hazardous waste landfilling; Underlined values indicate concentrations above the limits for reuse; n.a.: not available.

[a] Data from Rocca et al. (2009), operating temperature formation of BA= 1000-1200 °C; [b] Data from Ibañez et al. (2000), operating temperature formation of BA= not available; [c] Data from Lategano et al. (2007), operating temperature formation of BA= 1000-1200 °C; [d] Data from Gidarakos et al. (2009), operating temperature formation of BA= 650-800 °C.

2.3.4 Leaching tests as a function of pH

The Acid neutralization behaviour of a waste material is an important parameter for evaluating its reuse or disposal options. From its the Acid Neutralization Capacity (ANC), an estimate can be made on how fast the pH of the material, and subsequently pH dependent leaching processes, will vary upon ageing processes and modifications in environmental conditions. Figure 2.2 provides information on the ANC of the fresh and the weathered HW-I BA. Results show that both samples exhibited a rapid decline in pH (from the initial pH value of 10 to 7) upon addition of 0.2 equivalents of nitric acid per kg of dry BA. This behavior can possibly be attributed to the limited quantity in the HW-I BA of rapidly soluble Ca based hydroxides/silicates species and carbonates which are typically reported to determine the ANC of MSWI BA (e.g. Johnson et al., 1995). These results are consistent with those of the XRD analysis (Figure 2.1). On the other hand, a relatively extensive plateau in the ANC at the pH interval 5-3 was found for this type of BA which might be related to the presence of amorphous glassy phases in the material that are generally characterized by a buffering capacity at pH 4. In addition, as may be observed in Figure 2.2, both the “natural” pH and the titration curves of the fresh and the weathered HW-I bottom ashes did not differ significantly. This result reasonably means that the amount of alkaline phases that primarily control the ANC for this type of BA did not vary upon 6 months of aging.

Figures 2.3 and 2.4 present the leaching results of major (Ca, Si, Mg, Fe, Al and SO_4^{2-}) and trace components (Pb, Cu, Zn, Cr, Mo and Sb) for the fresh and the weathered HW-I BA, under different pH conditions. Leached concentrations from HW-I BA observed in previous studies (results from EN 12457-2, DIN 38814 and TCLP tests) were also included in the Figures for comparison (Ref. 1-7). In addition, the leaching results for the HW-I BA were compared to a MSWI BA leaching dataset (containing 15 MSWI BA samples) that was compiled by means of the LeachXS database/expert system. In fact, the graphical comparison shown in Figure 2.3 might be important to evaluate whether the leaching of major and trace components for special HW bottom ashes presents similarities or differences with respect to typical MSWI BA that are commonly disposed of as non hazardous waste or reused in many countries. Furthermore, MSWI BA can be considered as a valuable reference material for a better understanding of the leaching behaviour of HW-I BA, since many studies have been extensively focused on the leaching properties of this type of BA (e.g. Dijkstra et al., 2006 and references therein).

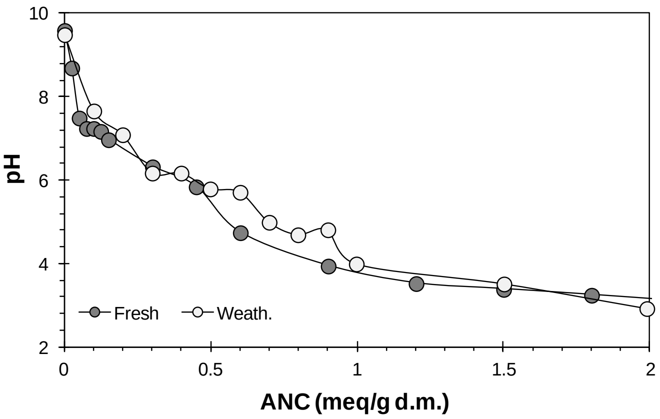

Figure 2.2. Acid neutralization capacity (ANC) for the fresh and the weathered HW-I BA.

In many cases, the leaching concentrations that were found in previous studies on HW-I BA at alkaline or acidic pH conditions, showed to be in quite good agreement with those derived in this work by applying the pH dependent leaching test, see Figure 2.3. This result implies that for a given pH condition the different EN, DIN and TCLP test types lead to similar results as the pH dependence test. On the other hand, higher concentrations of Zn, Cr, Mo and Sb can be noted for specific HW-I BA samples (Ref.4, Ref.6) compared to those derived from the pH dependent leaching test (Figure 2.4).

The leached concentrations of Ca, Si and SO_4^{2-} were generally found in lower amounts in the HW-I BA than in MSWI BA over the whole pH range examined. As a matter of fact, the leaching of Ca and Si in the HW-I BA may have been largely controlled by the amorphous glassy phases present in the material (see XRD results in Figure 2.1) that may have limited the amounts potentially available for leaching. The lower release of SO_4^{2-} for the HW-I BA compared to the MSWI BA, instead, might be related to its lower bulk content in the former type of BA (see Table 2.1).

Regarding trace elements, the results showed a relatively lower leachability of Pb and Zn for the HW-I BA compared to the MSWI BA, from neutral to acidic pH values. The lower release of these elements in the HW-I BA compared to MSWI BA might be related to their lower total content in the original product (see Table 2.1 and associated comments). Furthermore, the differences in leaching between the two types of BA possibly imply that different chemical mechanisms (e.g. minerals dissolution, adsorption processes) are responsible for the release of these contaminants from the solid matrix. In addition, Figure 2.4 shows that lower Cu concentrations were leached from HW-I BA than MSWI BA under alkaline pH conditions. This result is consistent with the lower DOC level that was found (at a natural pH value of 10) for HW-I BA compared to MSWI BA (see Table 2.2). In fact, previous studies on MSWI BA suggest that the leaching of Cu mainly results from the mobilization of Cu-DOC complexes at pH 7-12 (e.g. Van Zomeren and Comans, 2004). Finally, the leaching curves of the fresh and the weathered HW-I BA indicated that the differences existing between the two samples are quite limited, both for the major and the trace components. This result confirmed the low degree of ageing of the main solubility controlling phases of the BA, in agreement with the experimental results retrieved for other parameters (i.e.: XRD, ANC curves).

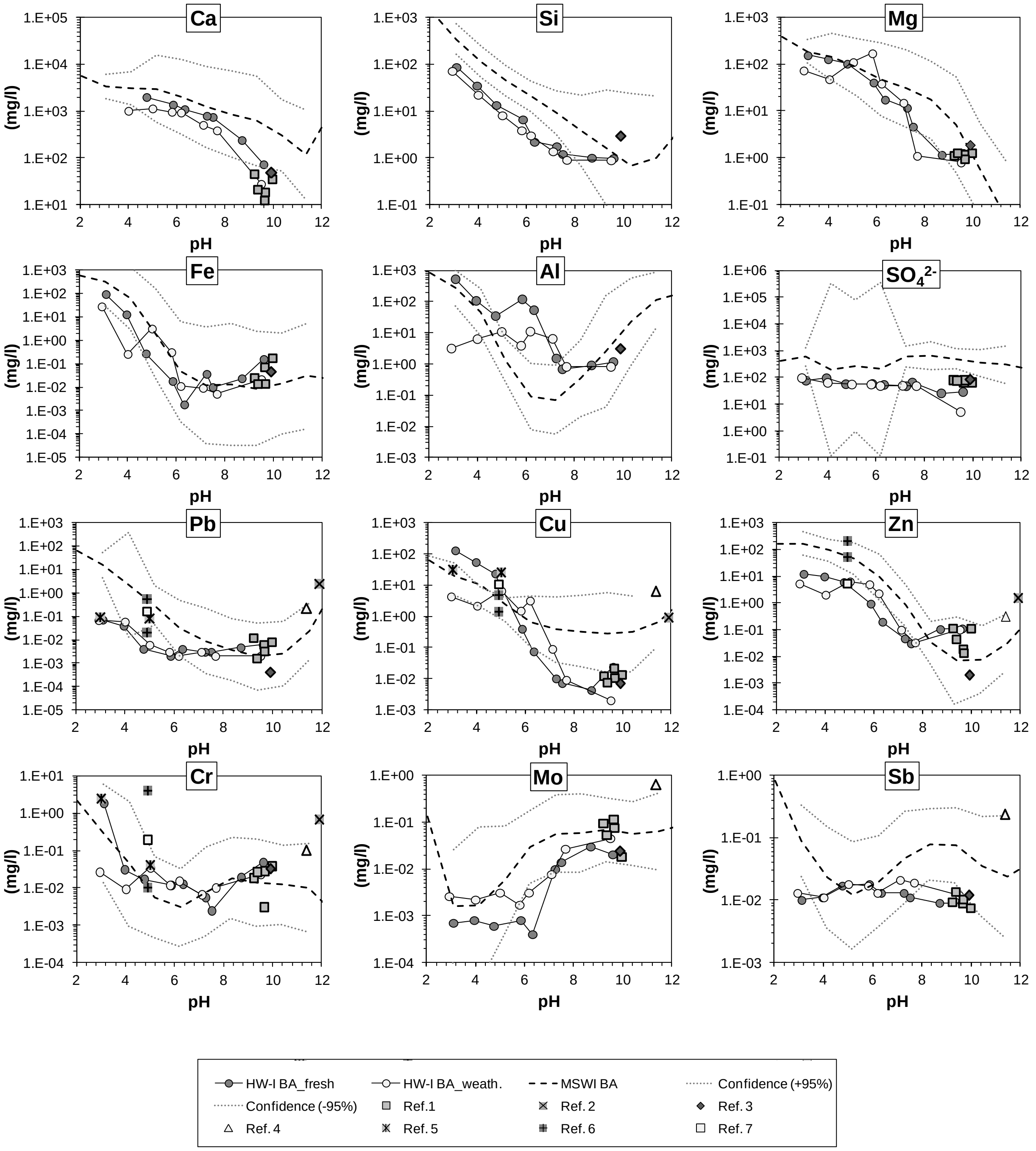

Figure 2.3. Leaching concentrations of major and trace components as a function of pH from the fresh and weathered HW-I BA, in comparison to MSWI BA data (mean values and (±) 95% confidence interval are shown). The leaching concentrations at natural pH reported in prior studies (Ref. 1= Rocca et al., 2009; Ref. 2= Ibàñez et al., 2000; Ref. 3= Lategano et al., 2007; Ref. 4= Gidarakos et al., 2009), as well as the results found at acidic pH applying the TCLP test (Ref. 5= Idris et al., 2002; Ref. 6= Zhao et al., 2009; Ref. 7= Kougemitrou et al., 2011) for different HW-I BA samples are also included in the graphs.

2.4 CONCLUSIONS

In this study, the chemical characteristics, mineralogy and leaching properties of bottom ash (BA) collected from a hospital waste incineration (HW-I) plant operating at high temperature (1000-1200 °C) in a rotary kiln combustion system were investigated. Bulk chemical analysis indicated that HW-I BA mainly contains Si, Ca, Al and Fe, as well as high concentrations of Cu, Ni, Zn and Cr, in quite similar amounts to typical MSWI BA. On the other hand, qualitative mineralogical characterization by XRD revealed that the HW-I BA was predominantly amorphous and contained only few crystalline compounds, i.e. carbonates and silicates, indicating notable differences with MSWI BA.

Although Italian regulations prescribe that HW BA should be landfilled as a hazardous waste, the results of the compliance leaching test EN 12457-2 indicated that the leaching of contaminants would meet the European acceptance criteria for non hazardous waste landfills, as well as the Italian and the Dutch limits for reuse of waste materials in specific applications. However, it should be noted that the parameters specified in the landfill directive or in reuse regulations taken into account in the present study might not cover all the relevant pollutants that can be present in this special type of waste (Kougemitrou et al., 2011).

The acid neutralization behaviour of the HW-I BA showed not to be very significant and possibly lower than that normally reported for MSWI BA. This result implies that the pH of the environment in specific disposal or reuse scenarios might be of crucial importance for this type of BA, as “natural” pH (around 10) of the BA may rapidly drop to acidic values with possible implications on the release of many constituents. The qualitative and quantitative comparison of the HW-I BA pH dependency leaching properties with the leaching results at alkaline or acid pH of many HW-I samples from previous studies showed to fit quite adequately. These observations suggested that for a specific pH value, different test types such as EN 12457 and TCLP can lead to similar result as the CEN/TS 14429 pH dependence test. Further evaluation on the pH dependency of major and trace components release, supported by the database/expert system LeachXS, contributed to evaluate the main differences and similarities of the leaching behaviour of HW-I BA and typical MSWI BA. The reduced leaching of major constituents (Ca, Si and SO_4^{2-}) from the HW BA compared to MSWI BA is expected to be mainly controlled by amorphous glassy phases present in this material. Furthermore, we found lower potentially leachable amounts of Pb and Zn in HW-I BA than in MSWI BA, that may be related to their lower total content in the raw material which is generated at high temperature in a rotary kiln combustion system. On the other hand, the lower leaching of Cu in HW-I BA compared to MSWI BA seems to be correlated to the lower DOC concentrations typically measured in the eluates of the former type of slag. The detailed overview of the bulk chemical and leaching results presented in the present study suggested that differences existing between the various HW-I and MSWI BA samples may be most likely ascribed to the the type of thermal treatment technology applied (i.e. temperature) that showed to greatly affect the chemical and leaching properties of the residues.

In addition, mineralogical observations together with the results of leaching tests indicated that the tested ageing process seemed not to have considerably modified the main characteristics of the HW-I BA, differently from previous observations on MSWI BA (e.g. Meima and Comans, 1997), probably owing to the differences in the mineralogical composition of the two types of slag.

Based on the results of the present study, it may be concluded that the analyzed HW-I BA could be predominantly disposed of as non hazardous waste. On the other hand, it is recommended in future works to investigate the technical and environmental implications of reusing HW-I BA as a fine aggregate in concrete mixtures or as a filler material, e.g. in landfill cover constructions, as this type of BA did not evidence pozzolonic characteristics (Filipponi et al., 2003) and is primarily made up composed by fine fractions (0.5-150 mm).

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Chapter 3

Major component leaching and buffering capacity of RDF incineration and gasification bottom ash

This chapter has been published in similar form as:

Stefania Rocca, André van Zomeren, Giulia Costa, Joris J. Dijkstra, Rob N.J. Comans, Francesco Lombardi. Characterisation of major component leaching and buffering capacity of RDF incineration and gasification bottom ash in relation to reuse or disposal scenarios. *Waste Management* 12 (2012), 759-768.

Thermal treatment of refuse derived fuel (RDF) in waste-to-energy (WtE) plants is considered a promising solution to reduce waste volumes for disposal while improving material and energy recovery from waste. Incineration is commonly applied for the energetic valorization of RDF, although RDF gasification has also gained acceptance in recent years. In this study we focused on the environmental properties of bottom ash (BA) from an RDF incineration (RDF-I, operating temperature 850-1000 °C) and a RDF gasification plant (RDF-G, operating temperature 1200-1400 °C), by evaluating the total composition, mineralogy, buffering capacity, leaching behaviour (both at the material's own pH and as a function of pH) of both types of slag. In addition, buffering capacity results and pH-dependence leaching concentrations of major components obtained for both types of BA were analysed by geochemical modeling. Experimental results showed that the total content of major components for the two types of BA was fairly similar and possibly related to the characteristics of the RDF feedstock. However, significant differences in the contents of trace metals and salts were observed for the two BA samples, as a result of the different operating conditions (i.e. temperature) adopted by the two RDF thermal treatment plants. Mineralogy analysis showed in fact that the RDF-I slag consisted of an assemblage of several crystalline phases while the RDF-G slag was mainly made up by amorphous glassy phases. The leached concentrations of major components (e.g. Ca, Si) at the natural pH of each type of slag did not reflect their total contents, as a result of the partial solubility of the minerals in which these components were chemically bound. In addition, comparison of total contents with leached concentrations of minor elements (e.g. Pb, Cu) showed no obvious relationship for the two types of BA. According to the compliance leaching test results, the RDF-G BA would meet the limits of the Italian legislation for re-use and the European acceptance criteria for inert waste landfilling. RDF-I BA instead would meet the European acceptance criteria for non hazardous waste landfilling. In addition, a new geochemical modelling approach was followed in order to predict the leaching behaviour of major components and the pH buffering capacity of the two types of slags, on the basis of independent mineralogical information obtained by XRD analysis and the bulk composition of the slag. It was found that the combined use of data regarding the mineralogical characterization and the buffering capacity of the slag material can provide an independent estimate of both the identity and the amount of minerals that contribute to the leaching process. This new modeling approach suggests that only a limited amount of the mineral phases that control the pH, buffering capacity and major component leaching from the solid samples is available for leaching, at least on the time scale of the applied standard leaching tests. As such, the presented approach can contribute to gain insight for the identification of the types and amounts of minerals that control the leaching properties and pH buffering capacity of solid residues such as RDF incineration and gasification bottom ash.

3.1 INTRODUCTION

Thermal treatment of municipal solid waste (MSW) in waste-to-energy (WtE) plants is one of the essential components of the integrated waste management strategies currently adopted by most developed countries. In this context, thermal treatment of specifically processed MSW in order to increase its homogeneity and calorific value and thus denominated refuse derived fuel (RDF), is being progressively applied with the aim of increasing energy recovery and employ technologies characterized by a lower environmental impact (Dalai et al., 2009; Bosmans et al., 2010). RDF is produced by sorting, size and weight-based separation and shredding of commingled MSW. It is therefore characterized by a relatively constant size distribution and composition , mainly consisting of high caloric waste fractions like paper and cardboard (50-60% wt.), plastics (20-30% wt.), along with textiles and rubber (10-15% wt.). Therefore, thermal treatment of this type of waste can lead to quite stable operating conditions, treatment temperature in particular, as well as a more homogenous quality of the resulting gas products as compared to MSW (Consonni et al., 2005; Bosmans et al., 2010) and hence may allow to employ more advanced technologies than those employed for WtE treatment of commingled waste Currently, thermal treatment of RDF in dedicated plants, or together with MSW in co-combustion facilities, is applied in 17 of the 53 thermal treatment plants in operation in Italy (ISPRA, 2009). Following the indications of recent environmental legislation to favour technologies that allow to reduce the volumes of waste for final disposal while enhancing material and energy recovery, the treatment capacities of WtE plants employing RDF are expected to increase in the future, especially in Italy and in other European countries such as Germany, as indicated by Haker et al. (2010). Incineration in water-cooled grate combustors at temperatures around 850-1000 °C with air, which is the most adopted technology for WtE treatment of MSW, is commonly applied also for the energetic valorization of RDF (Jannelli and Minutillo, 2007). On the other hand, in recent years, RDF gasification in a high temperature (1200-1400 °C) fluidized bed reactor applying sub-stoichiometric oxygen concentrations, has also gained acceptance due to its higher potential energy recovery efficiency and lower production of NOx and SOx emissions compared to incineration (Belgiorno et al., 2003; Bosmans et al., 2010; Castaldi and Themelis, 2010). However, higher operating costs must be considered for this advanced waste management technology, as reported by Giugliano et al. (2008).

Regardless of the type of thermal treatment technology adopted, WtE plants generate a number of solid by-products, among which the most abundant is bottom ash (BA), which accounts generally for 10-20% wt. of the feedstock (e.g. Polettini, 2009). In many European countries (e.g. Denmark, The Netherlands and France) the reuse of BA from MSW incineration (MSWI) plants as an aggregate substitute for natural materials in construction applications is commonly practiced if the residues present suitable technical properties. In other countries BA is generally landfilled as a non hazardous waste as there is no specific legislation regulating its utilization conditions. More information on the current status of BA management practices in the EU may be found in the literature (see e.g. Polettini, 2009).

However, given the non negligible content of potentially toxic components, such as for example metals, in this type of material, concerns exist whether the reuse of BA may exert adverse environmental effects. Therefore, several studies have extensively addressed the leaching behavior of contaminants from MSWI BA when reused as a secondary construction material, for both short and long term scenarios (e.g. Dijkstra et al., 2002; Kosson et al., 2002; Ecke and Aberg, 2006).

As a result of the quite recent development of RDF thermal treatment technologies, relatively few studies have focused up to now on the technical and environmental properties of RDF incineration and gasification BA. Beneficial utilization of RDF incineration BA as a fine aggregate in concrete, cement blends or in landfill cover constructions seems to be feasible from a technical point of view, as high compressive strength has been observed for this residue in specific application scenarios (Chang et al. 1999; Onori et al., 2011). Although there is no comprehensive study on the leaching behavior of these types of BA, Travar et al. (2009) have indicated relatively high leaching concentrations of soluble salts (Cl^- and SO_4^{2-}) from RDF incineration bottom ash, while Baciocchi et al. (2010) indicated Pb, Cr and Cu as the most critical contaminants leached from freshly quenched RDF incineration BA. The physical and geotechnical characteristics of RDF gasification BA have been also indicated as suitable for reuse in specific applications, as e.g. in road constructions. However recent studies regarding the leaching behavior of fresh and weathered gasification BA showed that Cu, Cr, Mo and Ni concentrations may hinder the reuse of this type of thermal treatment residues (Sivula et al., 2010; Gori et al., 2011). Anyhow, it should be noted that there is little information on the fundamental physical and chemical mechanisms that control the leaching behavior of the BA produced from either type of RDF thermal treatment technology.

The purpose of this study is to assess and compare the environmental properties of RDF incineration and gasification BA on the basis of their total composition, mineralogy, leaching of major components as a function of pH and buffering capacity. It is well known in fact, that these properties play an important role in determining the leaching behaviour of a material in a specific application scenario and should, hence, be attentively examined before focusing on the leaching concentrations of trace contaminants (Meima and Comans, 1997). The long-term pH development of BA in a specific scenario depends in fact on the buffering capacity of the slag matrix, which is in turn determined by its mineralogy (Johnson et al., 1995). In addition to major components, the leaching of trace elements at the natural pH of the slags was also analyzed and the results were compared with regulatory limits for disposal or reuse, as a first indication for evaluating the reusability of the two types of BA. The leaching mechanisms involved in the release of minor elements will be addressed instead in following Chapters 4 and 5. It is believed in fact that a fundamental study on the environmental properties of bottom ash generated from specific RDF thermal treatment technologies is necessary for establishing environmentally and economically sound management practices.

3.2 MATERIALS AND METHODS

3.2.1 Bottom ash sample preparation

About 100 kg of freshly quenched BA were sampled from two thermal treatment plants: 1) a RDF incinerator (RDF-I) equipped with a grate-type combustion chamber and 2) a RDF gasification plant (RDF-G) equipped with a high temperature gasifying and direct melting reactor. The two types of BA were homogenized through a quartering procedure, according to a standardized methodology (Italian norm UNI 10802:2004) in order to obtain representative samples for the experimental analyses. Coarse metallic and ceramic fragments (d > 5 cm) were manually removed. The BA was oven-dried at 60 °C to constant weight and sieved in order to analyze its grain size distribution. From this analysis, the fraction presenting a grain size ranging from 0.425 to 12 mm, making up more than 90% wt. of both types of slags, was selected as the most representative in terms of grain size and employed for the subsequent analysis. In addition, characterization analysis performed on the fraction with d<0.425 mm (results not shown) indicated that there were no substantial differences in the main properties and specifically in the leaching behaviour of these samples compared to the 0.425-12-mm size fraction.

3.2.2 Composition analysis

The characterization of the main composition of the two types of BA included the determination of the loss on ignition, total organic carbon content, bulk concentration of major and trace components, carbonate content and mineralogical composition of each material.

The Loss On Ignition (LOI) at 1000 °C was evaluated following the ASTM C25 procedure. The Total Organic Carbon (TOC) content of the BA samples was measured with a TOC-5000A Shimadzu analyzer. The bulk chemical composition of each type of BA was obtained after lithium tetraborate digestion of the slag samples at 1050 °C and dissolution of the molten material in a 10% HNO_3 solution. The total content of major (Ca, Si, Al, Mg, Na, Fe, K and Mn) and trace elements, including metals(Zn, Cu, Pb, Ni and Cd) and oxyanion-forming metalloids (Cr, Mo, Sb, As and V) were determined by atomic absorption spectroscopy (AAS), employing a Perkin Elmer AAS equipped with a graphite furnace and a hydride generation system, or alternatively by inductively coupled plasma atomic emission spectroscopy(ICP-AES). The BA contents of chlorides (Cl^-) and acid soluble sulphates (SO_4^{2-}) were measured respectively by dissolution of the samples with hot deionized water and titration of the resulting solutions with $AgNO_3$ and by dissolution of the samples with 3% HCl solutions followed by spectrophotometric analysis of the produced solutions. The carbonate (CO_3^{2-}) content of the slag was investigated using a Dietrich-Frülingh calcimeter, which involved acidification (HCl) of the samples and subsequent measurement of the evolved gas volume. All the measurements were carried out in triplicate.

The qualitative mineralogical characterization of the two types of BA was determined by X-ray powder diffraction (XRD) analysis using a Philips Expert Pro diffractometer equipped with a copper tube operated at 40 kV and 40 mA. Diffraction patterns were collected over a 2 Theta range from 5 to 85°, employing an angular step of 0.02° and a count time of 2 s.

3.2.3 Leaching experiments

To evaluate the potential release of main and trace components from the two types of BA, related to disposal or secondary material reuse scenarios, a combination of different characterisation and compliance leaching tests were employed. A batch compliance leaching test at the material's own pH was carried out according to the European standard EN-12457-2. In short, BA with a particle size reduced to below 4 mm was leached with distilled water at a liquid to solid (L/S) ratio of 10 l/kg, under continuous stirring for 24 h. After measuring the pH of the solutions, these were filtered through 0.45 μm pore size filters and eluate concentrations of different inorganic contaminants were determined by AAS and ICP-AES. In addition, leachate concentrations of Cl^- and SO_4^{2-} were analysed by titration with $AgNO_3$ and spectrophotometric analysis, respectively. The dissolved organic carbon (DOC) content of the obtained solutions was measured with a Shimadzu TOC-V CPH analyzer. Eluate concentrations of specific elements were compared with the limit values established for inert waste landfilling reported in Annex II of the European Landfill Directive (2003/33/EC). In addition, leachate concentrations were compared with the limits set by the Italian legislation for the reuse of non hazardous waste (Italian Environmental Ministry, 1998), although these limits currently do not specifically apply to BA from WtE plants. Leaching tests were carried out in duplicate.

The pH dependence leaching test was performed according to the CEN/TS 14429 standard procedure on the two types of BA for pH values ranging from 2 to 12.5. In short, analytical-grade nitric acid (HNO_3) or sodium hydroxide (NaOH) was used to adjust the pH in parallel batch leaching tests. Each suspension was equilibrated at a final L/S ratio of 10 l/kg for 48 h and after measuring its final pH value, was filtered through 0.45 μm pore size filters and subsequently analysed by AAS and ICP-AES, of which only the concentrations of major elements are reported and discussed in this study. Cl^- and SO_4^{2-} concentrations were also analysed using the same methods adopted for the batch compliance leaching tests.

3.2.4 Geochemical modeling of major components

In this work we focused on understanding the leaching behaviour of the major components (Ca, Si, Mg, Al, Fe, SO_4^{2-} and CO_3^{2-}) of both types of BA. Previous studies on MSWI BA have demonstrated in fact that these substances play a major role in governing leachate pH (e.g., Meima and Comans, 1997; Dijkstra et al., 2008). The modeling approach is largely similar to that described in Dijkstra et al. (2008) to which the reader is referred for details. In short, the measured total contents of major components were used as initial estimates for the reactive amounts of elements needed as input for the speciation modeling framework ORCHESTRA (Meeussen, 2003), included in the LeachXS database/expert system (http://www.leachxs.com/lxsdll.html). The XRD results obtained in the present study were used as a starting point to select the set of mineral phases to take into account in the modeling approach. Where considered appropriate, based on the modeling results of previous studies regarding MSWI BA (e.g. Dijkstra et al., 2006), other mineral phases were also considered as indicated below. Unless noted otherwise, equilibrium mineral solubility and solution speciation was calculated using thermodynamic data from the MINTEQA2 3.11 database and subsequent additions/corrections made in previous publications (Allison et al., 1991; Dijkstra et al, 2008 and references therein).

3.3 RESULTS AND DISCUSSIONS

3.3.1 Bottom ash composition

Table 3.1 shows the results of the total chemical composition for the RDF-I and the RDF-G bottom ashes. The LOI at 1000 °C measured for the RDF-I BA corresponded to about 5% wt., which was mainly associated to inorganic phases, since TOC analysis showed that only 0.35% wt. of the samples could be associated to unburned organic matter. No LOI or TOC was detected instead for the RDF-G BA, due to the type of thermal treatment the material undergoes in the plant (melting at 1600 °C). Regarding the elemental composition of the two types of BA, the results exhibited in Table 3.1 show that the total content of major components such as Ca, Si, Al and Mg was fairly similar, indicating that the concentration of these elements in the slag depends chiefly on the characteristics of the waste fed to the plant, which in both cases was RDF. These results are in good agreement with those of Rendek et al. (2007) that demonstrated that the quality of the waste input to MSW incineration plants significantly affected the bulk content of major elements in the resulting BA. Significant differences in the elemental composition of the two types of BA were however observed for: inorganic carbon, salts-forming components (Na, K, Cl^- and SO_4^{2-}), metals (mainly Zn and Pb), as well as oxyanion forming metalloids (Sb and Mo). The RDF-I BA showed to be relatively enriched in the above mentioned phases compared to the RDF-G BA with concentration values of at least 1 or 2 orders of magnitude higher, probably owing to the operating temperature adopted in the second type of plant that possibly increased the volatilization of elements such as e.g. Zn, Pb and Sb. In this perspective, the process technology applied for the thermal treatment of RDF appeared to exert a great influence on BA quality. A significantly (about a factor of 5) higher concentration of Cr was measured instead in the RDF-G BA compared to the RDF-I BA. This result might be correlated to the partial deterioration of the refractory material coating the gasification reactor walls which, as reported by gasification plant personnel, contains chromium oxides. Overall, the bulk chemical composition of major components (Ca, Si and Mg) and trace contaminants (Pb, Cu and Zn) for the two samples showed a good agreement with the data reported in previous studies regarding bottom ash originated from RDF incineration (Travar et al., 2009, Baciocchi et al., 2010) and gasification plants (Gori et al., 2011).

Table 3.1. Bulk chemical composition for the RDF-I BA and the RDF-G BA. Data are presented as mean values ± standard deviation.

	RDF-I BA	**RDF-G BA**
Values (%) ± s.d. (abs. v.)		
LOI	5.1 ± 0.2	<0.01
TOC	0.35 ± 0	0.02 ± 0
Major Components: Concentration (g/kg d.m.) ± s.d. (abs. v.)		
Ca	258.4 ± 6.1	227.9 ± 21.5
Si	205.4 ± 6.6	154.2 ± 26.4
Al	63.5 ± 3	137.6 ± 5.9
Mg	19.1 ± 0.8	12.9 ± 1.2
Na	54.2 ± 0.9	4.6 ± 0.1
Fe	26.8 ± 1.2	6.7 ± 1.6
K	4.2 ± 0	0.5 ± 0.02
Cl^-	48.7 ± 2.6	0.6 ± 0.1
SO_4^{2-}	2.4 ± 0.1	0.4 ± 0.03
CO_3^{2-}	103.3 ± 5.8	<0.5
Trace Elements: Concentration (mg/kg d.m.) ± s.d. (abs. v.)		
Zn	4209.6 ± 121.2	44.4 ± 11.3
Cu	3848.2 ± 417.9	1158.6 ± 237.4
Pb	986.9 ± 111.7	21.4 ± 3.8
Mn	530.1 ± 37.6	322.4 ± 7.2
Cr	326 ± 14.4	1441.9 ± 38.7
Ni	141.8 ± 16.5	162.9 ± 62.2
Sb	133.6 ± 6	1.3 ± 0.3
Mo	26.6 ± 2.8	<0.5
As	4.6 ± 0.5	1.2 ± 0.2
V	2.2 ± 0.6	<1.5
Cd	<0.02	<0.02

s.d.= standard deviation; abs. v.= absolute value; d.m.= dry matter

Qualitative mineralogical characterization of the BA by XRD analysis revealed that the RDF-I BA contained a variety of crystalline phases (Figure 3.1, a). The most intense diffraction peaks corresponded to gehlenite (G: $Ca_2Al_2SiO_7$) and calcite (C: $CaCO_3$). The presence of the latter component is consistent with the direct measurement of CO_3^{2-} (see Table 3.1) and could have been originated from the partial natural carbonation of the hydrated Ca-bearing phases during the storage of this type of BA; the following hydrated phases were in fact detected in RDF-I BA: hydrocalumite (H: $Ca_4Al_2Cl_2O_6 \cdot 10H_2O$) and portlandite (Ca: $Ca(OH)_2$). A significant content of several silica-containing phases, namely: quartz (Q: SiO_2), anorthite (An: $CaAl_2Si_2O_8$) and akermanite (Ak: $Ca_2MgSi_2O_7$), as well as hematite (He: Fe_2O_3) were also identified by XRD analysis. The main crystalline phases detected in this study were also reported by Baciocchi et al. (2010) for different size fractions of the same type of BA. The XRD diffractogram for RDF-G BA showed a consistent amorphous glassy matrix which was deduced from the evident hump in the diffractogram measured in the 2 Theta range from 10 to 40 (Figure 3.1, b). Therefore, only a few crystalline phases were identified in this type of BA, namely akermanite and magnetite (M: Fe_3O_4). These results are consistent with those of Gori et al. (2011) which also indicated the prevalence of glassy phases in gasification BA.

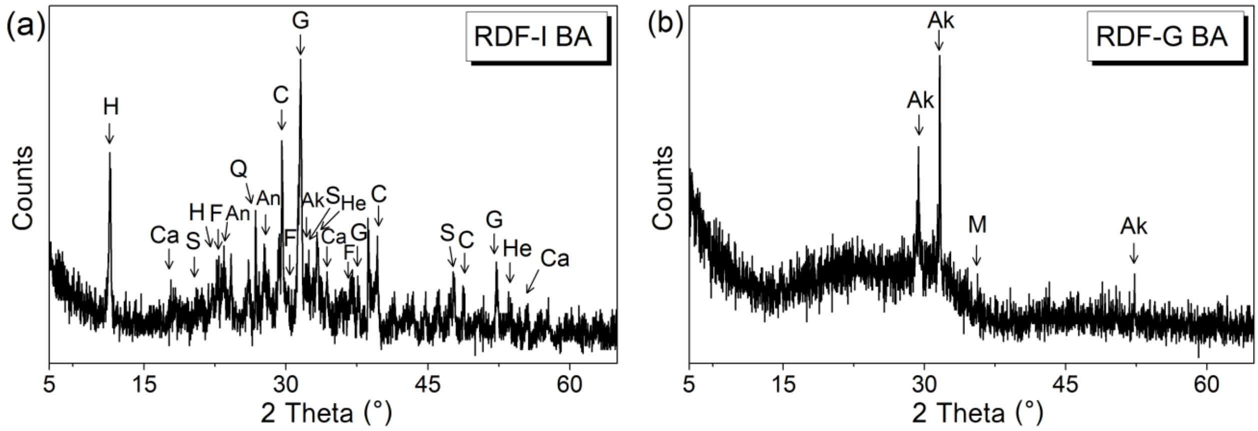

Figure 3.1. XRD pattern for RDF-I BA (a) and tRDF-G BA (b) (Legend: H= Hydrocalumite ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$); Ca= Portlandite ($Ca(OH)_2$); S= di-calcium Silicate (Ca_2SiO_4); F= Forsterite (Mg_2SiO_4); An= Anorthite ($CaAl_2Si_2O_8$); Q= Quartz (SiO_2); G= Gehlenite ($Ca_2Al_2SiO_7$); C= Calcite ($CaCO_3$); Ak= Akermanite ($Ca_2MgSi_2O_7$); He= Hematite (Fe_2O_3); M= Magnetite (Fe_3O_4)).

3.3.2 Leaching characterisation at natural pH

The pH values of the two types of BA determined from the batch compliance leaching test were significantly different: 12.4 for RDF-I BA and 10.3 for RDF-G BA. The alkaline pH resulting for RDF-I BA was correlated to its higher Ca-leaching (about 2 orders of magnitude) compared to RDF-G BA (Figure 3.2, graph a), which might indicate (near) equilibrium dissolution of portlandite ($Ca(OH)_2$) at pH>12 (Meima and Comans, 1997; Polettini and Pomi, 2004). Hence, although, as shown in Table 3.1, the total Ca content of the two types of BA was similar, Ca leaching concentrations varied considerably, owing to the different mineralogy of the two types of slag.

In addition, higher concentrations of salts-forming components (Na, K, Cl^-), metals (mostly Pb, Cu and Zn), as well as oxyanionic metalloids (mainly Sb and Mo) were measured in the eluates of RDF-I BA compared to those of RDF-G BA. The higher leaching of salts-forming components was directly correlated to their total content in the first type of BA (see Table 3.1), as also indicated (for Cl^- in particular) in previous studies on MSWI BA (Rendek et al., 2007; Hyks and Astrup, 2009). In the case of more reactive elements, e.g. Pb, Cu and Zn, comparison of total contents (exhibited in Table 3.1) with leaching concentrations showed no obvious correlations for the two types of BA. As will be investigated further below, differences in the leaching concentrations of these metals for the two types of slag were probably also due to the different natural pH of the samples, since the solubility of these elements is strongly dependent on the pH value, as indicated in previous studies regarding MSWI BA (e.g. Meima and Comans, 1997). The leached concentrations of Pb, Cu and Zn reported by Travar et al. (2009) for RDF-I BA were at least 1 order of magnitude lower compared to our results for the same type of BA. These differences can possibly be related to the lower pH (10.2) of the slag tested in the previous study, which was partly aged upon 1 year exposure to the atmosphere. In general, in fact, ageing and reduction of a very alkaline pH value result in a lower leaching of the above mentioned contaminants that present an amphoteric behavior (e.g. Chimenos et al., 2003; Dijkstra et al., 2006; Hyks and Astrup, 2009). However, to confirm this hypothesis, pH-dependent leaching analysis of these relatively less studied materials is required.

The leaching results determined at the natural pH of the two types of BA were compared with the European acceptance criteria for inert waste landfilling (2003/33/EC) and the Italian limits for the reuse of non hazardous waste (Italian Environmental Ministry, 1998). From this comparison it emerged that RDF-G BA would meet both the Italian legislation requirements for re use and the European acceptance criteria for inert waste landfilling. RDF-I BA instead would meet the requirements for non hazardous waste landfilling, since eluate concentrations of Cl^-, Zn, Pb, Cu, and Sb exceeded the European acceptance criteria for inert waste landfilling (Figure 3.2).

Furthermore, for RDF-I BA samples eluate concentrations of Cl^-, Pb and Cu resulted above the Italian limits for reuse.

It should be noted however, that compliance leaching tests are not able to reproduce the complete picture of the emissions related to a real landfill or reuse scenario, as released concentrations vary over time and are influenced by key factors such as the L/S ratio and pH. To assess the long-term environmental emissions of these types of materials in any type of application, pH development is an important parameter to investigate because it may exert important consequences in terms of emissions of contaminants. In addition, as previously mentioned, the solubility of the major mineral phases involved in the leaching process is linked to the acid neutralization capacity of the material. For these reasons, pH dependent leaching tests and associated geochemical modeling of major component chemistry was also performed to provide a more fundamental characterization of the slag materials.

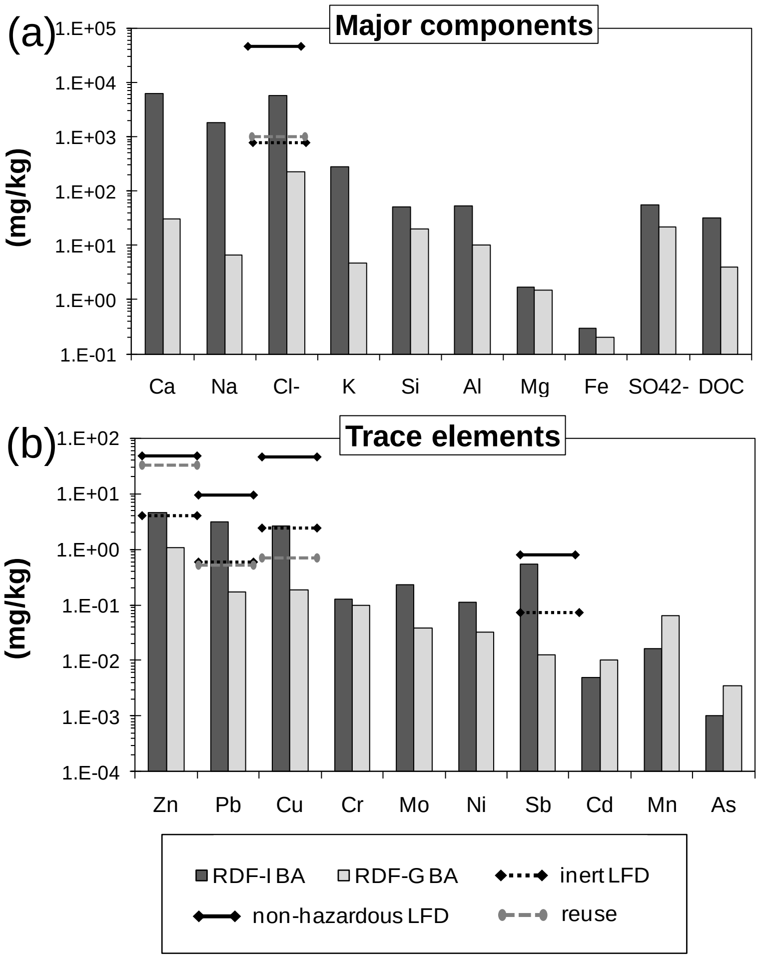

Figure 3.2. Leaching test (EN 12457-2) results for major components (a) and trace elements (b) for RDF-I BA (pH = 12.4) and RDF-G BA (pH = 10.3). The acceptance criteria for inert waste (inert LFD) and non-hazardous waste (non-hazardous LFD), as well as Italian requirements for reuse (reuse) are also reported when relevant.

3.3.3 pH-DEPENDENCE LEACHING CHARACTERISATION

3.3.3.1 Acid/base neutralization capacity

The ANC/BNC curves derived from the pH-dependence leaching test are shown in Figure 3.3. The two types of BA displayed a remarkable difference in the acid neutralization capacity below pH 12, which may be attributed to their different mineralogical composition, as indicated by the results of XRD analysis (see Figure 3.1).

An increase in acid addition corresponded to a gradual decrease in the pH of the eluates of RDF-I BA from values above 12 to 4, with a total acid buffering capacity of about 6 meq H^+/g d.m. These results were ascribed to the significant content of hydrated phases, such as calcium hydroxide and hydrocalumite, calcium silicate-containing phases, as well as of calcium carbonate/bicarbonate detected for this type of slag by XRD analysis. A similar ANC behavior was found in a previous study on the same type of RDF incineration BA (Baciocchi et al., 2010).

For the RDF-G BA instead, the addition of a small amount of nitric acid (<0.01 meq H^+/g d.m.) resulted in a rapid drop of the pH of the eluates (from 12 to 5) followed by an extensive buffering capacity at pH values between 3 and 4.5. This behavior was correlated to the mineralogy of the slag, characterized by a lack of rapidly soluble alkaline crystalline phases and a predominance of amorphous glassy phases that are typically characterized by a buffering capacity at pH 4. These results proved consistent with those reported by Gori et al. (2011).

This finding is highly relevant as the pH of MSWI BA has generally been indicated to be buffered at alkaline pH field-site conditions due to its content of mineralogical phases such as ettringite and calcite (Meima and Comans, 1997). From the above discussed results, however, RDF-G BA, may be expected to exhibit a different behaviour due to its negligible acid buffering capacity, resulting in a decrease of pH to values of 7 or lower, induced by the conditions imposed by the local environment (e.g.: for rainwater pH 5-6; for soils pH 3 to 8; Lindsay, 1979), with possible consequences on the leaching behaviour of the slag. The solubility of many contaminants, such as amphoteric metals for example, increases considerably at pH values below 6; hence, to evaluate the leaching behaviour of RDF-G BA in an application scenario, it may be more correct to consider the eluate concentrations obtained at acidic pH values instead of those resulting at the natural pH of the material.

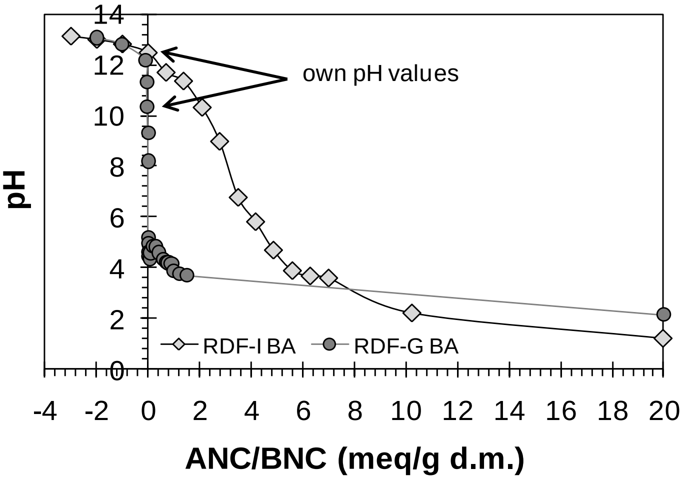

Figure 3.3. Acid/base neutralization capacity (ANC/BNC) curves for RDF-I BA and RDF-G BA samples.

3.3.3.2 pH-dependent leaching properties of major components

As a possible result of the different mineralogical composition and ANC of the two types of BA, differences were observed in the pH-dependent leaching curves of Ca, Si, Mg, Al, Fe and SO_4^{2-} , reported in Figure 3.4. As a reference, in Figure 3.4 also the mean, upper and lower 95% confidence interval limits obtained from a compiled dataset contained in the LeachXS database/expert system based on leaching concentrations of 15 samples of MSWI BA of worldwide origin are reported. MSWI bottom ash is an important reference material since extensive information is currently available on the leaching behavior of this type of ash (e.g. Dijkstra et al., 2006). The graphical comparison reported in Figure 3.4 is believed to provide a valuable way to evaluate whether the leaching properties of RDF BA are similar or differ significantly from those of MSWI BA.

The results of the compliance leaching test at the natural pH of the two samples are also included in the graphs as single points, in order to evaluate if these concentrations match those derived from the pH dependent leaching test.

The differences between the leaching behaviour of RDF-I and RDF-G BA are evident for Ca, Mg, Si, Fe and to a lesser extent for Al and SO_4^{2-}. In particular, RDF-I BA exhibited significantly higher leaching concentrations of Ca and Mg compared to the average values obtained for MSWI BA, whereas RDF-G BA showed a much lower release of these elements. The leaching curves of Si, Fe and Al obtained for RDF-I BA were quite similar to those determined for MSWI BA, while lower concentrations were measured for RDF-G BA. SO_4^{2-} concentrations for both RDF incineration and gasification BA samples were roughly 1 order of magnitude lower than those of average MSWI BA samples in the entire pH range considered.

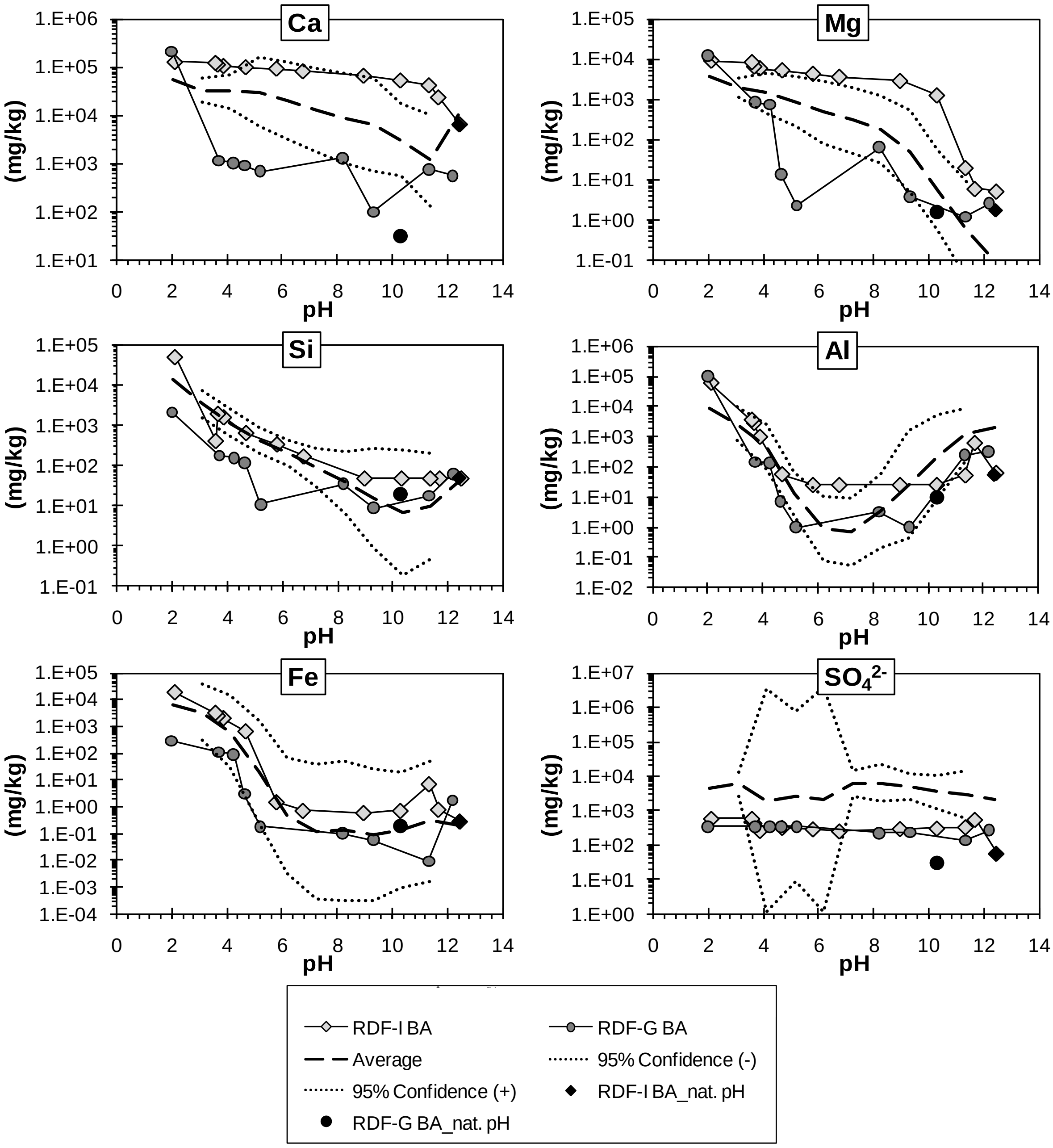

Figure 3.4. Leachate concentrations of Ca, Mg, Si, Al, Fe and SO_4^{2-} as a function of pH for RDF-I, RDF-G and MSWI BA. Note that for RDF-I BA Si and Al concentrations were below detection limits in the pH range 9-11.7 and 6.7-10, respectively.

In general, leaching results obtained with the EN 12457-2 test at the natural pH for the two BA samples showed a good agreement with those derived from the pH dependence leaching tests at a corresponding pH value, although lower Ca and SO_4^{2-} concentrations were measured for the RDF-G BA in the batch test at natural pH. These differences are probably related to the slower leaching kinetics of these particular components from the glassy RDF-G samples, since for the pH dependence leaching tests a longer equilibration time was applied (48 h instead of 24 h).

3.3.4 Geochemical modelling of major components

Based on the above discussed results, it can be hypothesized that the noteworthy differences in the leaching behaviour of RDF-I and RDF-G BA is either of a chemical origin, i.e. due to different mineral composition and solubility, and/or physical origin, i.e. kinetically hindered dissolution of mainly amorphous glassy phases. Equilibrium geochemical modeling was hence performed to further investigate the factors that lead to the lower leaching concentrations in the eluates of RDF-G BA as compared to those of RDF-I BA.

As a first start, a geochemical model was set-up independently from the measured leaching data. To this end, a limited set of minerals indicated in Table 3.2 as Dataset 1, based solely on the mineralogical composition of the BA from XRD analysis (Figure 1), was selected. In this list of phases also halite (NaCl) and anhydrite ($CaSO_4$) were included, since they were assumed as plausible solubility controlling phases for Na and SO_4^{2-} for both types of BA on the basis of the findings of previous studies on MSWI BA (Mahieux et al., 2010; Bayuseno et al., 2010). Amorphous Al and silica were also taken into account in the model prediction for RDF-G BA, based on the results of a previous study on MSW pyrolisis/melting slag (Saffarzadeh et al., 2006). The amounts of each mineral phase, reported in Table 3.2 in mol/kg dry BA, were estimated so that the resulting concentrations of major components (reported in Table 3.3), calculated from the chemical formulas of the minerals, matched or were just below the respective measured total concentrations reported in Table 3.1. The calcite content was independently estimated from the carbonate content of the samples.

Table 3.2. Estimated amounts of mineral phases considered as a starting point for the modeling approaches (Datasets 1 and 2) applied for RDF-I BA and RDF-G BA. Results are reported in g/kg of dry bottom ash.

		RDF-I BA		**RDF-G BA**	
Minerals	Chemical formula	**DATASET 1**	**DATASET 2**	**DATASET 1**	**DATASET 2**
Calcite	$CaCO_3$	167.2	167.2	–	–
Portlandite	$Ca(OH)_2$	33.3	16.7	–	–
Hydrocalumite	$Ca_4Al_2Cl_2O_6\ 10H_2O$	5.6	5.6	–	–
Quartz/Silica	SiO_2	168.3	16.8	264.4	26.4
Gehlenite	$Ca_2Al_2SiO_7$	219.4	109.7	–	–
Akermanite	$Ca_2MgSi_2O_7$	54.5	27.3	136.4	68.2
Anorthite	$CaAl_2Si_2O_8$	27.8	13.9	–	–
Amorphous $Al(OH)_3$	$Al(OH)_3$	–	–	390	390
Di-calcium silicate	Ca_2SiO_4	155.1	77.5	–	–
Forsterite	Mg_2SiO_4	40.8	20.4	–	–
Hematite	Fe_2O_3	36.7	–	–	–
Magnetite	Fe_3O_4	–	–	9.3	–
Ferrihydrite	$Fe(OH)_3$	–	24.6	–	4.3
Anhydrite	$CaSO_4$	3.3	3.3	0.5	0.5
Halite	NaCl	79	79	0.9	0.9
	Total	991	559	801.5	490

Table 3.3. Total amounts of major components for RDF-I BA and RDF-G BA in the modeling approaches (Datasets1 and 2) resulting from the estimated amounts of minerals given in Table 2). Results are reported in g/kg of dry bottom ash.

	RDF-I BA		**RDF-G BA**	
Components	**DATASET 1**	**DATASET2**	**DATASET 1**	**DATASET 2**
Ca	244	156.8	40.3	20.2
Mg	19	9.7	12.2	6.9
Si	151.5	44.4	151.7	26.4
Al	49.1	24.8	135	135
Fe	25.7	12.8	6.7	2.2
SO_4^{2-}	2.3	2.3	0.4	0.4
CO_3^{2-}	100.2	100.2	0	0
Cl^-	48.6	48.6	0.5	0.5
Na	31.1	31.1	0.3	0.3

Using the assumed set of minerals and the estimated total concentrations of major components, geochemical modeling was performed to predict the experimental leaching data of the BA samples. Measured concentrations and model predictions for these components are shown in Figure 3.5 (Dataset 1).The modelled leaching curves obtained for Ca, Mg and Al for RDF-I BA showed an adequate match with measured leaching data. However, the predicted ANC/BNC curve for this type of BA increasingly overestimated the experimental behaviour for pH values below 11. In the case of the RDF-G BA, Dataset 1 led to inadequate model predictions for Ca, Mg, Si and Fe concentrations. Furthermore, the predicted ANC/BNC proved also in this case higher than the measured curve. Based on this important finding, it is plausible to infer that a lower amount of pH buffering mineral phases than those assumed in Dataset 1 was active in the leaching processes of both types of slag.

Consequently, a second set of mineralogical data (Dataset 2) was hypothesized, as shown in Table 3.2, and analyzed by geochemical modelling to try to obtain an optimal description of the buffering capacity and the leachate composition of the two types of BA. In this dataset, the effect of a lower content of mineral phases presenting pH buffering capacity on the predicted ANC and leached concentrations was investigated. In addition, for some elements such as Fe and Mg, different mineral phases were considered (as illustrated in Table 3.2). For RDF-I BA, half of the amount of the main pH buffering minerals considered in Dataset 1 (portlandite, gehlenite, akermanite, forsterite and dicalcium silicate) excluding calcite, the amount of which was independently measured, and hydrocalumite, which was found to play only a minor role in the pH buffering capacity, was considered. Amorphous silica was considered as a more soluble surrogate mineral for quartz and its content was reduced by a factor of 10.

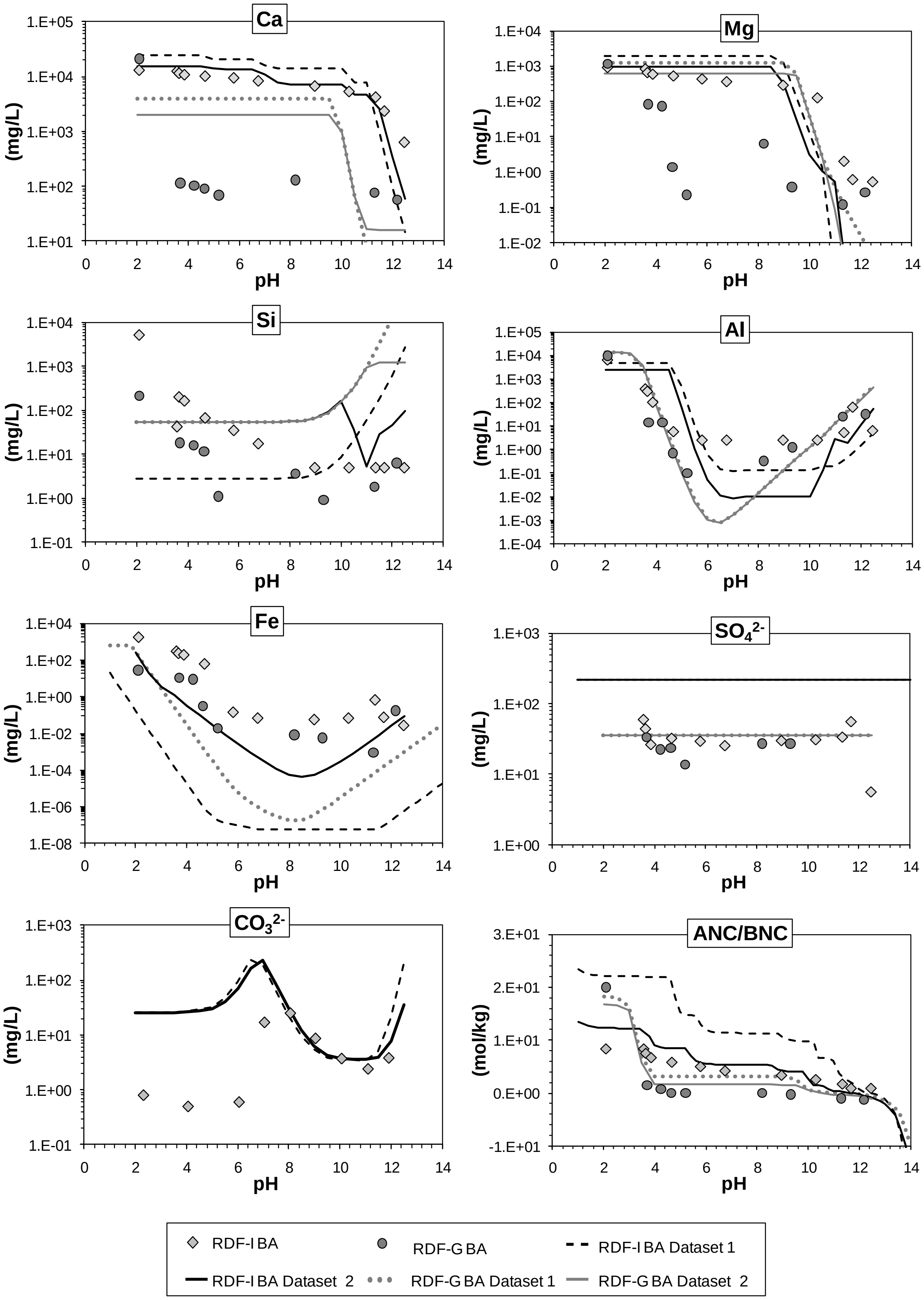

Figure 3.5. Leached concentrations and model predictions as a function of pH for Ca, Mg, Si, Al, Fe, SO_4^{2-}, CO_3^{2-} and ANC/BNC from RDF-I BA and RDF-G BA

In the case of RDF-G BA, the amounts of akermanite and silica were similarly reduced by a factor of 2 and 10, respectively in Dataset 2, since only a small portion of the available concentrations of Ca, Al, Mg and Si seemed to be reactive in the leaching processes. Additional choices with respect to the mineral assemblages were also made in Dataset 2 for both types of BA to achieve a better description of leachate composition. For both samples, brucite ($Mg(OH)_2$) was allowed to precipitate as it was indicated as a solubility controlling phase for Mg leaching from MSWI BA (Dijkstra et al., 2006). The leaching of Fe was assumed to be controlled by the precipitation of ferrydrite ($Fe(OH)_3$) instead of that of relatively insoluble phases such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), following the work of Dijkstra et al. (2006). Modelling results obtained considering Dataset 2 are also shown in Figure 3.5 while Figure 3.6 gives an overview of the amount of the mineralogical phases that were allowed to precipitate in Datasets 1 and 2 for both types of BA.

The reduced amounts of pH buffering minerals, as well as the estimated availabilities of cations and anions assumed in Dataset 2 allowed a better fitting of the measured ANC/BNC curve for both types of slags. For RDF-I BA, improved model descriptions were also obtained for Ca, Mg, Al and Fe based on the input parameters selected in Dataset 2. In addition, the leaching of CO_3^{2-}, for which data were taken from Dijkstra et al. (2008), since a similar concentration at the natural pH was found (26 mg/kg at pH 12.3), was likely consistent with precipitation of calcite at pH>7.

For RDF-G BA, the leachate concentrations of Fe and Al were adequately predicted by the minerals selected in the second dataset. In both RDF-I and RDF-G, predicted concentrations of SO_4^{2-} were undersaturated with respect to anhydrite ($CaSO_4$).

The inadequate match between the model curves and the experimental data for Si, for the two types of BA in both model scenarios, suggests that the precipitation/dissolution of different silicate phases than those considered in this work may occur in BA leachates (Meima and Comans, 1997). Previously adequate model fits were found for phases such as laumontite and wairakite (Dijkstra et al., 2006, 2008) but the presence of these minerals in the RDF-I and RDF-G BA could not be independently confirmed. It is, however, clear that Si showed a different pH dependent leaching behavior than (amorphous) glass that is abundantly present in both types of BA samples. Even though the virtual absence of acid neutralizing capacity of the RDF-G BA sample was well matched by the model, the modelling predictions of Ca and Mg concentrations were still well above the measured data for this type of BA. Equilibrium with the selected mineral phases could not adequately explain in fact the exceptionally low leaching concentrations determined for these elements. It must be noted that modeled mineral assemblages and mineral amounts, in particular those that have been inferred from the same measured data that were being modeled (e.g.:

ANC/BNC in Dataset 2), may suffer to some extent from non-uniqueness, i.e. different choices in mineral assemblages may provide similar model results as indicated also e.g. by Oreskes et al.(1994). Notwithstanding this intrinsic model uncertainty, it is reasonable to conclude that the extremely low buffering capacity and low leaching of major components determined for the RDF-G BA may be explained by the presence of significantly lower amounts of mineral phases available for leaching as compared to the other type of BA. In addition, it must be pointed out that, as previously mentioned, leaching test results can be influenced by kinetic effects related to the time interval for which these tests are carried out (e.g., Dijkstra et al., 2006), and this may be particularly true in the case of the glassy RDF-G BA matrix. Apparently, a large part of the major components was virtually fixed in the glass phases formed at high temperature.

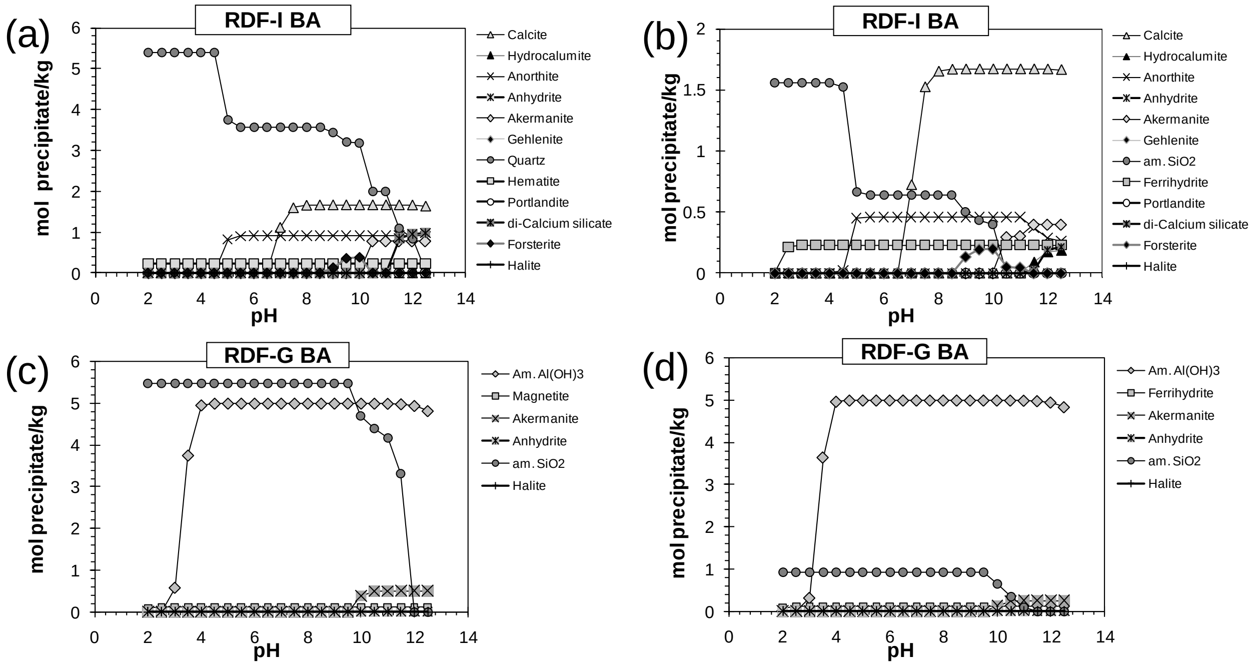

Figure 3.6. Amount of the mineral phases that precipitated/dissolved in the modeling prediction based on Dataset 1 (a, c) and Dataset 2 (b, d) as a function of pH for the RDF-I and the RDF-G BA samples. Results are expressed as mol/kg BA.

3.4 CONCLUSIONS AND IMPLICATIONS FOR FURTHER RESEARCH

The environmental properties of two specific types of bottom ash were investigated in this study: RDF incineration (RDF-I, operating temperature 850-1000 °C) and RDF gasification (RDF-G, operating temperature 1200-1400 °C) BA. The experimental results showed that the total content of major components was fairly similar for both types of bottom ash and possibly related to the characteristics of the RDF feedstock. However, significant differences in the contents of trace metals and salts were observed for the two BA samples, probably as a result of the different operating conditions (i.e. temperature) of the RDF thermal treatment technologies from which the BA originated from. Consequently, the mineralogy of the RDF-I ash consisted of an assemblage of several crystalline phases while the RDF-G ash was mainly characterized by amorphous glassy phases.

Given the similar total Ca concentrations, differences in the pH values of the RDF-I BA (12.4) and the RDF-G BA (10.3) were related to the different Ca concentration values determined from the batch leaching tests (EN 12457-2). These results indicate that there was no direct correlation between the total content of elements such as Ca and their leaching concentrations which are mainly controlled by the solubility of the mineral phases to which these components are chemically bound in the slag matrix. On the other hand, a clear correlation between the bulk contents of non-reactive salts-forming components mainly Cl^- and their leaching concentrations was found for both samples. The leaching of some metals (e.g. Pb, Zn and Cu) from the RDF-I BA at the native pH proved higher in comparison to RDF-G BA due to the different pH and mineralogy of the samples. In general, a more alkaline pH lead to higher solubility of these contaminants. Furthermore, differences in leaching of contaminants between the two types of slag may also be partly related to kinetic effects since the leaching availability of major components from the glassy matrix of the gasification BA proved limited compared to that of the incineration slag, at least within the timeframe of the performed tests. According to the compliance leaching test results, the RDF-G BA would abide the limits of the Italian legislation for reuse and the European acceptance criteria for inert waste landfilling. On the other hand, for RDF-I BA, leaching concentrations of Zn, Pb, Cu, Cl^- and Sb exceeded the European acceptance criteria for inert waste landfilling, while complied with those set for non hazardous waste landfilling. However, the RDF-G BA presented a significantly lower acid buffering capacity compared to the RDF-I sample. This finding is relevant as it is expected that the pH of RDF-G BA could be relatively quickly neutralized as a function of the conditions of the local environment pertaining to the selected disposal or reuse scenario. Different pH conditions could hence potentially lead to different conclusions regarding the environmental impact of the RDF-G BA for a specific management option.

In this study a new geochemical modeling approach was followed using independent mineralogical information from XRD analysis and the measured total contents of the major components to predict the leaching behavior, as well as the pH buffering capacity of the two types of slag. It was found that the combined analysis of the mineralogical characteristics and of the buffering capacity of the ash can be used to adequately obtain an independent estimate of both the type and the amount of minerals that contribute to the leaching process. This new modeling approach suggests that only a limited fraction of the minerals that control pH, buffering capacity and major component leaching from the samples are available for leaching, at least on the time scale of the applied standard leaching tests. As such, the presented approach can contribute to extend knowledge regarding the types and amounts of minerals that control the leaching properties and pH buffering capacity of solid residues such as RDF incineration and gasification bottom ash.

Given the results of this study, it is deemed important to investigate the pH development and the subsequent emission of contaminants from BA under field conditions (i.e. in contact with rainwater and atmospheric CO_2) to further assess the environmental properties of these materials under specific application scenarios. In addition, leaching kinetics needs to be investigated in more detail, particularly for RDF-G BA, as the glassy matrix of this material may limit the availability of metals for leaching.

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Chapter 4

Trace component leaching from RDF gasification bottom ash

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Stefania Rocca, André van Zomeren, Giulia Costa, Joris J. Dijkstra, Rob N.J. Comans, Francesco Lombardi (2012). Leaching characterization of trace metals from refuse derived fuel gasification bottom ash. *Waste Management*

In this study, we focused on understanding the pH dependent leaching behaviour of the following trace metals Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb from bottom ash (BA) originating from a refuse derived fuel gasification plant (RDF-G, operating temperature 1200-1400 °C) for a proper assessment of the environmental impact related to its reuse and disposal options. Leaching experiments were performed in a pH-static system with pH values ranging between 2 and 12.5. Given the presumed glassy nature of the RDF-G BA, accordingly to what indicated by the previous study on this type of residue (Rocca et al., 2012), see Chapter 3, kinetic effects on the release of these metals were also investigated by performing the leaching tests upon different equilibration times, i.e. 48 hours, 1 week and 2 weeks. Additional interpretation of the leaching test results was done using the speciation modelling framework ORCHESTRA included in the LeachXS database/expert system, which was used for subsequent modelling of the processes potentially controlling the leaching behaviour of trace components from the analysed RDF-G BA. In general, the leached concentrations of elements such as Cu, Zn, Ni, Cd, Mo and Sb were found to be lower compared than those typically found for municipal solid waste incineration BA (MSWI BA), used as a reference material, almost over the entire analysed pH range (2-12.5). In particular, the examined RDF-G BA exhibited significantly lower leaching concentrations of Cu in the pH range from 8 to 12 compared to the mean values obtained for the MSWI BA as a result of the low concentrations of dissolved organic carbon (DOC) with which copper forms strong complexes. In addition, the lower availabilities (at pH 2) of Pb, Zn and Ni for the RDF-G BA with respect to MSWI BA were attributed to the strong volatility of these elements at the high formation temperatures of the gasification residue (> 1200 °C). In addition, the results of the tests carried out at different equilibration times indicated that kinetics did not greatly affect the leaching behaviour of this type of BA for most of the elements under consideration. As such, these findings suggest that the glassy matrix of the RDF-G BA is responsible for the reduced availability of (volatile) metals for leaching over time compared to MSWI BA. In fact, modeling results showed that the relevant processes controlling the generally low release of trace elements within the investigated pH domain were found to be the precipitation of (hydr)oxides minerals (e.g. Pb and Cu) and, especially, the sorption (e.g. Ni and Cr) on Fe/Al based surfaces present in the matrix of the RDF-G BA.

4.1 INTRODUCTION

The use of waste-to-energy (WtE) plants for the treatment of different types of unprocessed or presorted municipal solid waste (MSW) has been recognized as a viable option in integrated waste management systems, intending to strongly reduce the mass (about 70-80%) and volume (about 80-90%) of waste while achieving efficient energy recovery in the form of heat and electricity (Consonni et al., 2005; Castaldi and Themelis, 2010; Münster and Lund, 2010).

As an alternative to traditional WtE technologies where MSW is fully oxidized in a combustion system, advanced gasification processes of refuse derived fuel (RDF) appears to be promising technology as it has the potential to improve the energy production from the highest calorific fractions of specifically sorted MSW, i.e. paper, cardboard, plastics and wood waste obtaining a efficiently combustible fuel gas, mainly containing mainly CO, H_2 and CH_4, termed syngas, under reducing atmosphere (Münster and Meibom, 2011; Arena et al., 2012). Thorough previous studies also indicated that RDF gasification leads to lower emissions of pollutants, such as dioxins, furans, NO_X and SO_X in comparison to traditional MSW combustion technologies such as grate-fired incineration (Belgiorno et al., 2003; Castaldi and Themelis, 2010; Arena et al., 2012). In addition, it is expected that most of the solid by-products from gasification-based WtE facilities are collected as inert and vitrified ash materials at the bottom of the reactor, since they are originated at operational temperatures between 1000 and 1600 °C, above the melting point of the slag (Castaldi and Themelis, 2010; Arena et al., 2012; Consonni and Viganò, 2012). Hence, some researchers have indicated that molten gasification bottom ash (BA) has much higher potential for reuse e.g. as an aggregate for concretes or in road construction because of its amorphous, glassy and non-leachable matrix rather than typical combustion BA (Ferraris et al., 2009; Gori et al., 2011). However, the beneficial reuse potential of the BA originating from RDF gasification (RDF-G) technologies has not been thoroughly investigated up to now, especially from the standpoint of its environmental behaviour in disposal or reuse scenarios. So far, only a few studies have focused on the chemical characterization of RDF-G BA indicating Ca, Si, Al, Fe and Mg as the major components of the granular matrix of the slag (making up more than 50 % by weight of the bulk material). From previous experimental analyses (Gori et al., 2011; Rocca et al., 2012), it was also learnt that gasification BA contains several metals of environmental concern, including in particular Cr, Cu and Ni,accounting for more than 1 g/kg of dry material each).

On the other hand, it has long been recognized that the potential release (and not the total content) of toxic metals from BA is the most important factor for assessing the environmental impact of this residue in view of its final disposal or reuse (e.g. Johnson et al., 1995; van der Sloot et al., 2001). The little information that is now available on the leachate quality of RDF-G BA indicates that the leaching of contaminants present in the amorphous slag is not of great concern, considering the released concentrations at the material’s own pH value, which generally varies from 8.7 to 10.3 (Sivula et al., 2010; Gori et al., 2011; Rocca et al., 2012). In fact, from the results of the EN 12457-2 leaching test conducted in the previously mentioned studies, it can be seen that the leaching concentrations of RDF-G BA would meet both the Italian legislation requirements for reuse of non hazardous waste (Italian Environmental Ministry, 1998) and the European acceptance criteria for inert waste landfilling (2003/33/EC) (Gori et al., 2011; Rocca et al., 2012). However, Sivula et al. (2012) indicated that the long term release of pollutants, i.e. Mo, Ni, Pb and Zn may significantly increase under landfill field conditions as an effect of the increase in the pH of the leachates of this type of BA (from 9.2 to 10.7). Furthermore, the evaluation of the major component leaching behaviour of the RDF-G BA provided in Rocca et al. (2012), (see Chapter 3),suggested that the initial pH value of the vitrified slag can rapidly decrease after contact e.g. with rainwater (pH 5-6) as an effect of its extremely low buffering capacity. Consequently, it is believed that a great deal of attention has to be given to the investigation of the pH dependent release of contaminants from RDF-G BA so to properly assess the environmental behaviour of this material under possible application scenarios.

Based on these considerations, the focus of this paper is the analysis of the pH dependent leaching behaviour of the main trace metals contained in the RDF-G BA that was already tested in a previous study (Rocca et al., 2012), see Chapter 3. BA from traditional MSW incineration (MSWI BA) was used as a reference material since extensive information is currently available on the leaching behaviour of metals from this residue, for both the short and long term scenarios (e.g. Meima and Comans, 1999; Dijkstra et al., 2002). In this study, we also focused on understanding the kinetic effects on the pH dependent leaching characteristics of the RDF-G BA, as the glassy matrix of this slag may reduce to some extent the availability of metals in solution upon the different equilibration time scales of the applied leaching tests. Furthermore, the most important release processes that potentially control the leaching behaviour of the trace metals from RDF-G BA were investigated by geochemical modelling.

4.2 MATERIALS AND METHODS

4.2.1 RDF gasification bottom ash sample

Freshly quenched gasification bottom ash (BA) was collected from a refuse derived fuel gasification plant (RDF-G) equipped with a gasifying and melting reactor operating at high temperatures (1200-1400 °C). The same type of bottom ash was also tested in a previous study concerning the characterization of major component leaching from this type of BA (Rocca et al., 2012), see Chapter 3. The analyzed RDF-G BA sample presented a grain size ranging from 0.425 to 4.76 mm mainly consisting of amorphous glassy phases, as indicated by the mineralogical composition of the sample obtained through XRD analysis. As previously mentioned, the detailed characterization results obtained for this BA sample in terms of bulk chemical composition, mineralogy and major component leaching behaviour are provided in Chapter 3.

4.2.2 pH-static leaching experiments

The leaching behaviour of trace metals (Cd, Cu, Cr, Mo, Ni, Sb, and Zn) from the RDF-G BA was investigated by performing pH-static leaching tests at pH values between 2 and 12.5. The kinetic effects on the release of the above mentioned elements from RDF-G BA were also evaluated as a the equilibration contact time of the liquid solution with the slag over the entire pH range considered. First, the pH-static leaching experiments were carried out on the BA adopting an equilibration time of 48 h as prescribed by the European standard CEN/TS 14429 (2005). In detail, 20 g of oven dried BA samples with a grain size below 4 mm were equilibrated in teflon vessels with 200 ml of solution (L/S ratio of 10 l/kg). Each solution was brought to a specific pH value ranging from 2 to 12.5 which was kept constant for the total duration of the test using a computerized pH-stat system. Analytical grade (0.1 M) HNO_3 and NaOH were used to adjust the pH of the suspensions under continuous stirring conditions. Each solution was then filtered through 0.45 μm pore size filters and the eluate concentrations of the inorganic metals under consideration were determined by ICP-OES. Subsequently, the same pH-static leaching experiments were performed on the RDF-G BA samples with a longer equilibration times of 1 and 2 weeks.

4.2.3 Geochemical modelling

Starting from the set of minerals that was assumed for evaluating the major component leaching behaviour from the RDF-G BA described in Rocca et al. (2012), a geochemical modelling approach was developed to predict the experimental pH dependence leaching data of the trace metals contained in the same BA sample. The modelling process was conducted by means of the speciation modelling framework ORCHESTRA (Meeussen, 2003) included in the LeachXS database/expert system. The total availability (i.e. leaching at pH 2) of the trace metals that were determined by performing the pH-static leaching tests were included as input data in the modelling approach. In order to further identify the most important mechanisms governing the release of the metals from RDF-G BA, a number of potentially solubility controlling mineral phases (that are listed below in paragraph 4.3.3) were selected for the modelling prediction on the basis of the results obtained in previous studies on MSWI BA (e.g. Meima and Comans, 1997; Dijkstra et al., 2002; 2008).

In addition, specific sorption processes of the trace elements onto reactive iron and aluminum (hydr)oxides typically present in BA, namely hydrous ferric oxides (HFO) and amorphous aluminum hydroxides (AAM), were taken into account in the modelling approach. The amount of crystalline HFO contained in the RDF-G BA was determined by dithionite extraction, while the amorphous part of the HFO was estimated by ascorbate extraction (Kostka and Luther, 1994). The content of AAM was evaluated by oxalate extraction (Blakemore et al., 1987). In accordance with previous studies on MSWI BA (e.g. Dijkstra et al., 2006; Engelsen et al., 2009), the total HFO content (expressed as kg sorbent per kg of dry BA) included as input for the geochemical modelling prediction was calculated by summing the individual amounts of HFO and AAM. This approach is generally the most applied since a complete and systematic database for sorption reactions of metals on AAM surfaces is currently missing. A specific surface area of 600 m^2/g was used for amorphous Fe and Al- (hydr)oxides (Dzombak and Morel, 1990) while for the crystalline portion, a lower specific surface area of 100 m^2/g was considered (Hiemstra et al., 1989). Phosphate (PO_4^{3-}) concentrations in the eluates of the RDF-G BA samples were not were not analysed, however, to take into account the competition of sorbates with PO_4^{3-}, a constant concentration of $1.0 \cdot 10^{-6}$ M of PO_4^{3-} in the eluates for pH values between 4 and12 was implemented in the model. This concentration value was assumed based on average values reported for MSWI BA, as indicated by Dijkstra et al. (2008).

4.3. RESULTS AND DISCUSSION

4.3.1 pH dependent leaching behaviour

The pH dependent leaching curves of Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb after an equilibration time of 48 h are shown in Fig. 4.1. As a reference, also the mean, upper and lower 95% confidence interval limits from a compiled dataset of 15 MSWI BA samples of worldwide origin contained in LeachXS are reported. In addition, literature data from pH dependent leaching of RDF-G BA samples (Gori et al., 2011) are included in Fig. 4.1 (after digitizing the graphs).

In general, the shapes of the pH dependent leaching curves for Pb, Zn, Cu, Ni and Cr were similar to those determined for the MSWI BA (Fig. 4.1). In fact, from an alkaline pH of around 12 to pH between 8 and 10, a decrease in the leached concentrations of these metals can be seen for both types of BA. After that, the released amounts of the metals under consideration significantly increased (from 1 to 3 orders of magnitude) as the pH decreased from 7 to 2, approaching the maximum available contents for leaching in the most acidic pH region (Fig. 4.1).

In Fig. 4.1, the significantly lower (from 2 to 3 orders of magnitude) Cu concentrations leached at pH values higher than 8 from the RDF-G BA compared to the MSWI BA can also be noted. This result is consistent with the much lower DOC level that was determined for the RDF-G BA (0.4 mg/l) at the material's own pH (10) compared to the one obtained for the MSWI BA (100 mg/l). In fact, previous studies on MSWI BA showed that the leaching of Cu is mainly related to the mobilization of Cu-DOC complexes at alkaline pH values (e.g. Van Zomeren and Comans, 2004; Dijkstra et al., 2006; Arickx et al., 2007).

In addition at pH 2 the RDF-G BA exhibited considerably lower available quantities of Pb, Zn and Ni (from 1 to 3 orders of magnitude) with respect to the mean values obtained for MSWI BA (Fig. 4.1). These differences can be probably ascribed to the higher formation temperature of the (molten) gasification BA (1200-1400 °C) compared to incineration BA (850-1000 °C). Pb, Zn and Ni are relatively volatile elements and are hence should be predominantly retrieved in syngas cleaning residues rather than in bottom ash. The comparison of the chemical composition results of the RDF-G BA presented in Rocca et al. (2012) (i.e. Zn= 44.4 mg/kg; Pb= 21.4 mg/kg; Ni= 162 mg/kg) with those obtained for the MSWI BA e.g. in Dijkstra et al., (2002) (i.e. Zn= 3550 mg/kg; Pb= 1950 mg/kg; Ni= 650 mg/kg) supports these results.

Furthermore, it must be noted that the concentrations of Cd, Mo and Sb leached from the RDF-G BA samples were very low, often under the detection limits, for almost the entire pH range investigated (as shown in Figure 4.1). These results confirm that BA from RDF gasification contains remarkably lower contents of (volatile) leachable metals compared to BA from MSW incineration as a result of the high formation temperature of the glassy RDF-G material.

On the other hand, the amounts of Cr that were released from the RDF-G BA proved to be higher than those obtained for the MSWI BA at pH below 6 (see Figure 4.1). This result might be explained by a strong desorption of this metal from the amorphous RDF-G BA at low pH values.

The pH dependent leaching trends obtained by Gori et al. (2011) for two RDF-G BA samples were overall in good agreement with our results (Fig. 4.1). However, the leached concentrations determined in this study were generally lower compared to those reported by Gori et al. (2011) for all the analysed metals, especially for Ni (at pH values above 6) for which the differences between the samples varied from 1 to 3 orders of magnitude. The observed differences in metals leaching might be attributed to the different characteristics of the waste fed to the plants and operating conditions (i.e. oxidizing agent) of the RDF thermal treatment technologies from which the BA originated from.

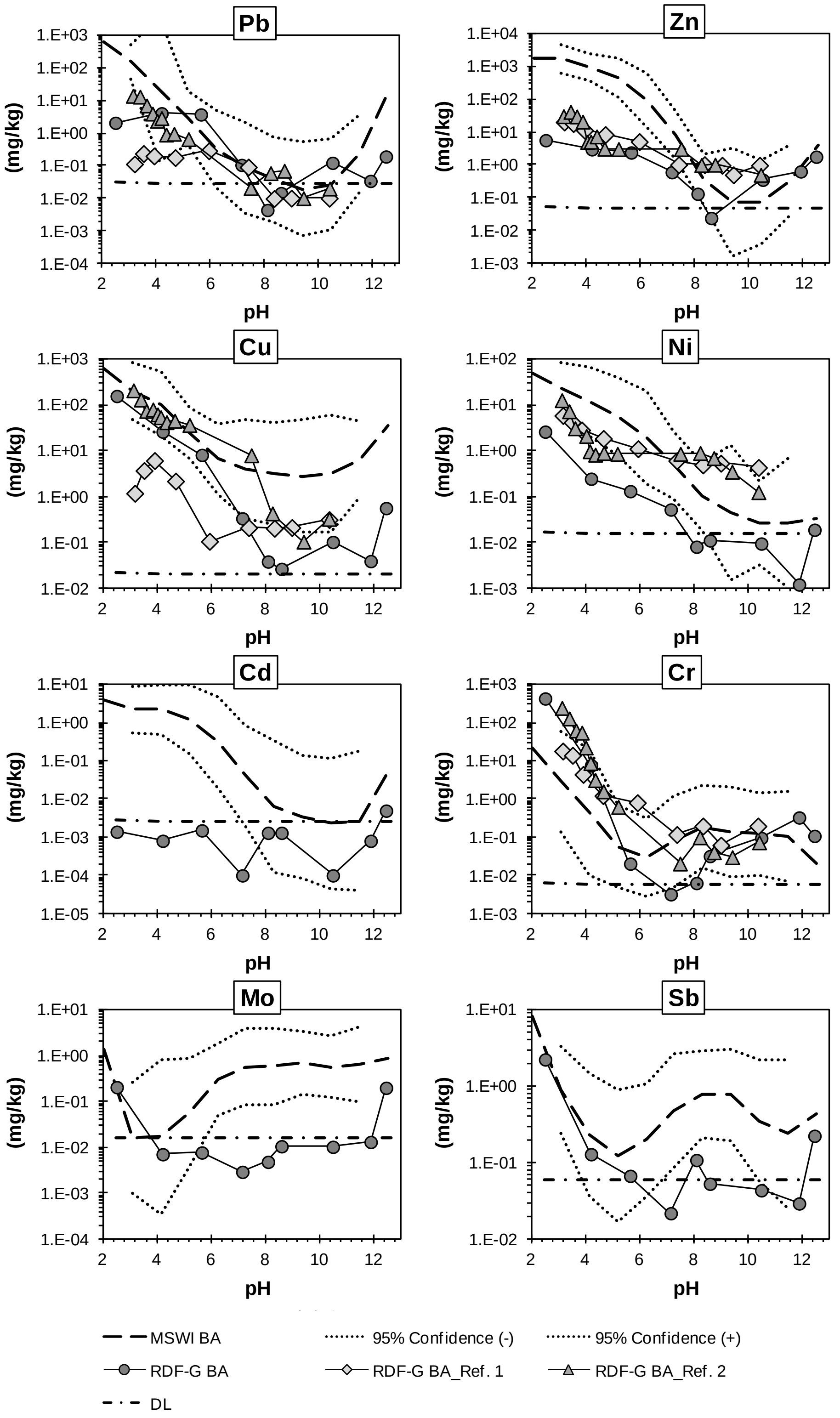

Figure 4.1. Leached concentrations of Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb as a function of pH for the RDF-G BA sample (equilibrated for 48 h) in comparison with the mean, upper and lower 95% confidence interval limits of a MSWI BA dataset. The pH dependent leaching concentrations of the trace metals reported in a previous study (Ref. 1= Sample A, Gori et al., 2011; Ref. 2= Sample B, Gori et al., 2011) for two different RDF-G BA samples are also included in the graphs. The horizontal lines represent analytical detection limits (DL).

4.3.2 Kinetic effects on leaching behaviour

Given the presumed glassy matrix of the RDF-G BA, which may possibly reduce trace metals leaching depending on the time scale of the applied leaching test, the effects of leaching kinetics were also investigated.

In Fig. 4.2 the pH dependent release of Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb is shown at the different equilibration times of the performed pH-static leaching tests, i.e. 48 hours, 1 week and 2 weeks. The results indicated that the leaching trends of the trace metals from the BA samples were rather similar over the different time scales of the pH-static experiments.

Fig. 4.2 also indicates that a consistent and systematic increase of the leaching concentrations with time was not observed, except for Cu, Ni and Cr at specific pH values. In fact, the release of Cu and Ni seemed to increase with time in the leachates with pH below 6, whereas for leaching concentrations increased with contact time at pH values below 6 and above 8. The increasing concentrations of these metals might be explained by kinetically controlled dissolution of low soluble (glassy) phases contained in this type of BA.

On the other hand, the time dependent leaching behaviour of the RDF-G BA samples in Fig. 4.2 shows that the leaching of Zn significantly decreased (about 1 order of magnitude) with time at pH >10. This effect may be related to precipitation mechanisms reducing the solubility of this metal over time, as reported in a previous study on MSWI BA (Dijkstra et al., 2006).

In addition, Fig. 4.2 shows that the released concentrations of Cd, Mo and Sb still remained below the detection limit (DL) of the analytical method that was used. The release of these (volatile) elements, hence, proved to be quite independent of the equilibration time scales used for the leaching tests.

The results of this study, thus, indicate that the measured leaching concentrations after 1 and 2 weeks are rather close to those obtained after 48 h, despite the fact that RDF-G BA mainly consists of glassy phases that may possibly limit the availability of metals for leaching in the short term. As such, the present findings suggest that the glassy matrix of this type of BA causes a reduced availability of metals for leaching over time, e.g. in the case of Zn, Ni, Cd, Mo and Sb if compared to typical values obtained for MSWI BA (see comparison of the results in Fig. 4.1).

On the other hand, it seems that proper equilibrium conditions might not be reached for all the elements within the time scales of the leaching experiments of this complex waste product, e.g. in the case of Cr. Therefore, it cannot be completely excluded that the concentrations of these metals may gradually increase, to some extent, for longer contact times.

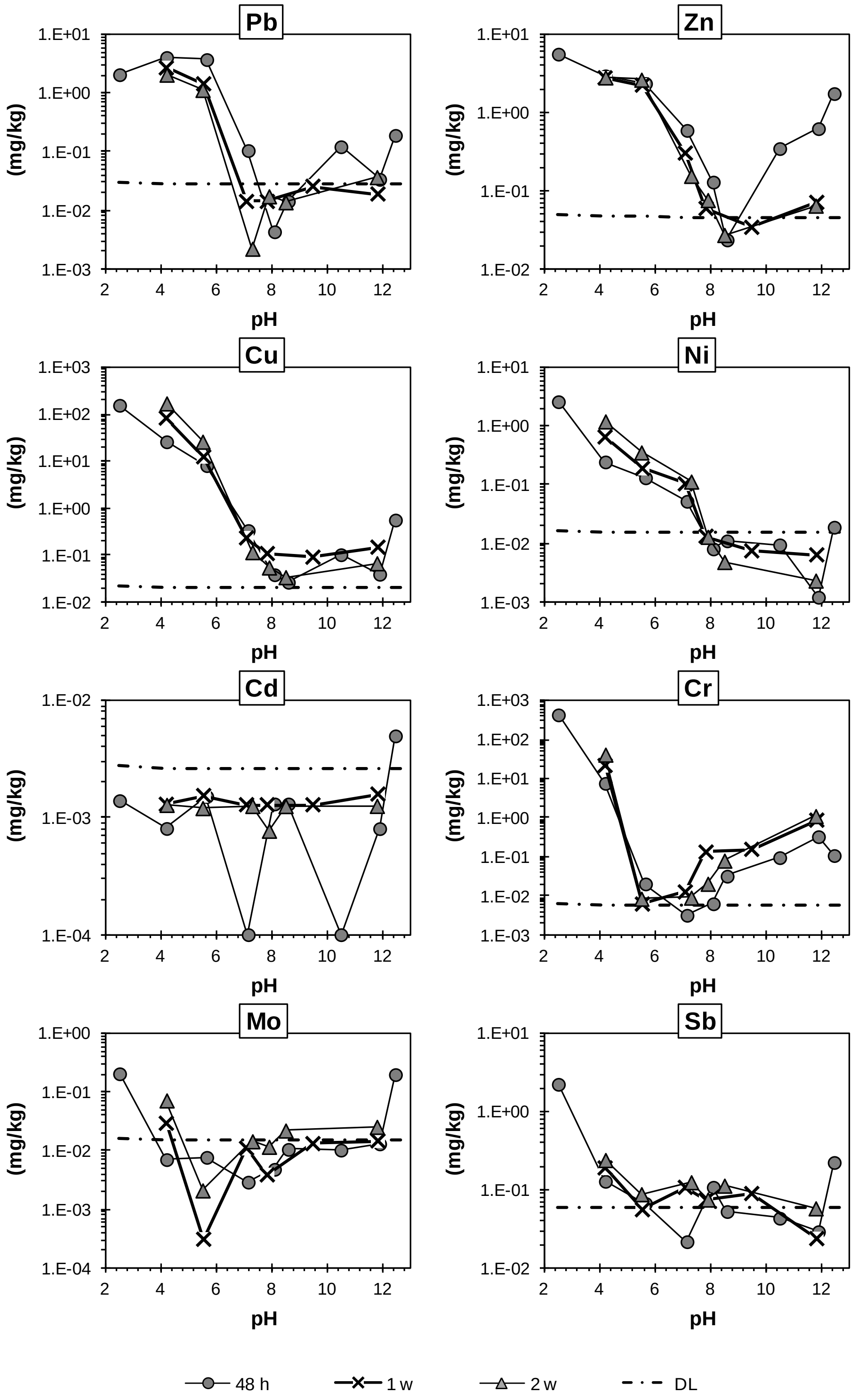

Figure 4.2. pH dependent leaching of trace metals (Cu, Pb, Zn, Ni, Cd, Cr, Mo and Sb) from RDF-G BA as a function of different equilibration times of the pH-static leaching test (i.e. 48 hours, 1 week and 2 weeks). The horizontal lines represent analytical detection limits (DL).

4.3.3 Analysis of the processes controlling the leaching of trace metals

The equilibrium modelling predictions along with the measured pH dependent leaching concentrations of trace metals from the RDF-G BA are presented in Fig. 4.3. For clarity, only the concentration trends obtained for the samples equilibrated for 2 weeks are shown in Fig. 4.3 as it may be assumed that these results are the closest to chemical equilibrium conditions of the system (on which the geochemical modelling calculations are in principle based).

For an adequate assessment of the influence of sorption processes and solubility control on the leaching of trace metals, two different modelling prediction cases were implemented in LeachXS: 1) a number of potentially solubility controlling minerals was selected without considering the estimated quantity of reactive HFO in the slag; 2) a number of potentially solubility controlling minerals was selected, including the estimated amount of HFO sorption sites contained in the slag (i.e. 0.0615 kg HFO/kg BA).

The results reported in Fig. 4.4 indicate that the first modelling simulation based only on the solubility of selected mineral phases in the BA (without HFO) provided an adequate description of the leaching behaviours of Pb and Cu. In particular, the precipitation of lead hydroxide ($Pb(OH)_2$) and tenorite (CuO) was found to potentially control the pH dependent leached concentrations of Pb and Cu, respectively, in agreement with previous results reported for MSWI BA (e.g. Dijkstra et al., 2006 and references therein). On the other hand, when the interaction of Pb and Cu on the reactive HFO surfaces was considered during the second modelling prediction, a less adequate description of the measured data was obtained at pH values below 8. In particular, geochemical modelling strongly underestimated Pb leaching. A possible reason for this finding could be that the combination of the low dissolved concentrations of Pb (below or close to the DL) that were measured for the RDF-G BA sample versus the modelling of reactive amounts of HFO that is typically used for MSWI BA is not well predictable. In this particular case, it appeared that we are looking at the conditions to which the model is sensitive to the prediction of Pb leachate concentrations at 99,99% of sorption. These processes involving the gasification BA deserve considerably more attention in future research.

In the case of Cu, instead, modelling results implied that sorption mechanisms do not exert a great influence on the concentrations of this metal in solution since the predicted leachate concentrations seemed to underestimate the measured results. This finding is in good agreement with the indications reported in previous studies (e.g. Dijkstra et al., 2006; Dijkstra et al., 2008).

Fig. 4.3 also shows that the leaching of Ni and Cr between pH 10 and 12 can be explained on the basis of the precipitation of hydroxide minerals, namely $Ni(OH)_2(s)$ and $Cr(OH)_3(A)$ that have been selected in LeachXS according to previous results retrieved for MSWI BA of Dijkstra et al. (2006).

Below pH 8, instead, the correlation between the simulated and the measured leaching concentrations of Ni and possibly also Cr, appeared adequate when the contribution of HFO was considered in the modelling prediction case (Fig. 4.3). Therefore, the sorption of Ni and Cr to Fe and Al based surfaces may be the dominant reaction mechanism in this type of BA, leading to a strong reduction of their leaching in solution in a certain pH range (pH 6-10 for Ni; pH 6-8 for Cr).

On the basis of the leaching mechanisms identified in previous studies on MSWI BA (e.g. Meima and Comans, 1997, Dijkstra et al., 2006), we expected Zn to precipitate mainly in (hydr)oxide form. On the other hand, the modeling results indicated that the leachate composition only approaches equilibrium with willemite (Zn_2SiO_4). However, it must be considered that although the presence of willemite has been observed in spectroscopic studies in bottom and fly ash materials (Piantone et al., 2004; Struis et al. 2004), it is known that silicates can only slowly dissolve/precipitate and could not be formed in the laboratory (Meima and Comans, 1998).

With regard to Mo and Sb, it was difficult to identify mineral phases potentially controlling their release in solution since the measured leached concentrations were lower or close to the detection limit, almost over the entire pH range analysed. Nevertheless, the overall leaching trends of the simulated and measured curves for Mo were quite similar to each other when the solubility curve of wulfenite ($PbMO_4$) was considered in the modeling prediction. Furthermore, from the modeling results of this study it seems that the leached concentrations of both these oxyanionic metals were underestimated by the model at pH below 6 assuming precipitation of HFO (Fig. 4.3). However, a great factor of uncertainty must be considered in the predictions of these components as their release resulted lower or close to the analytical detection limits.

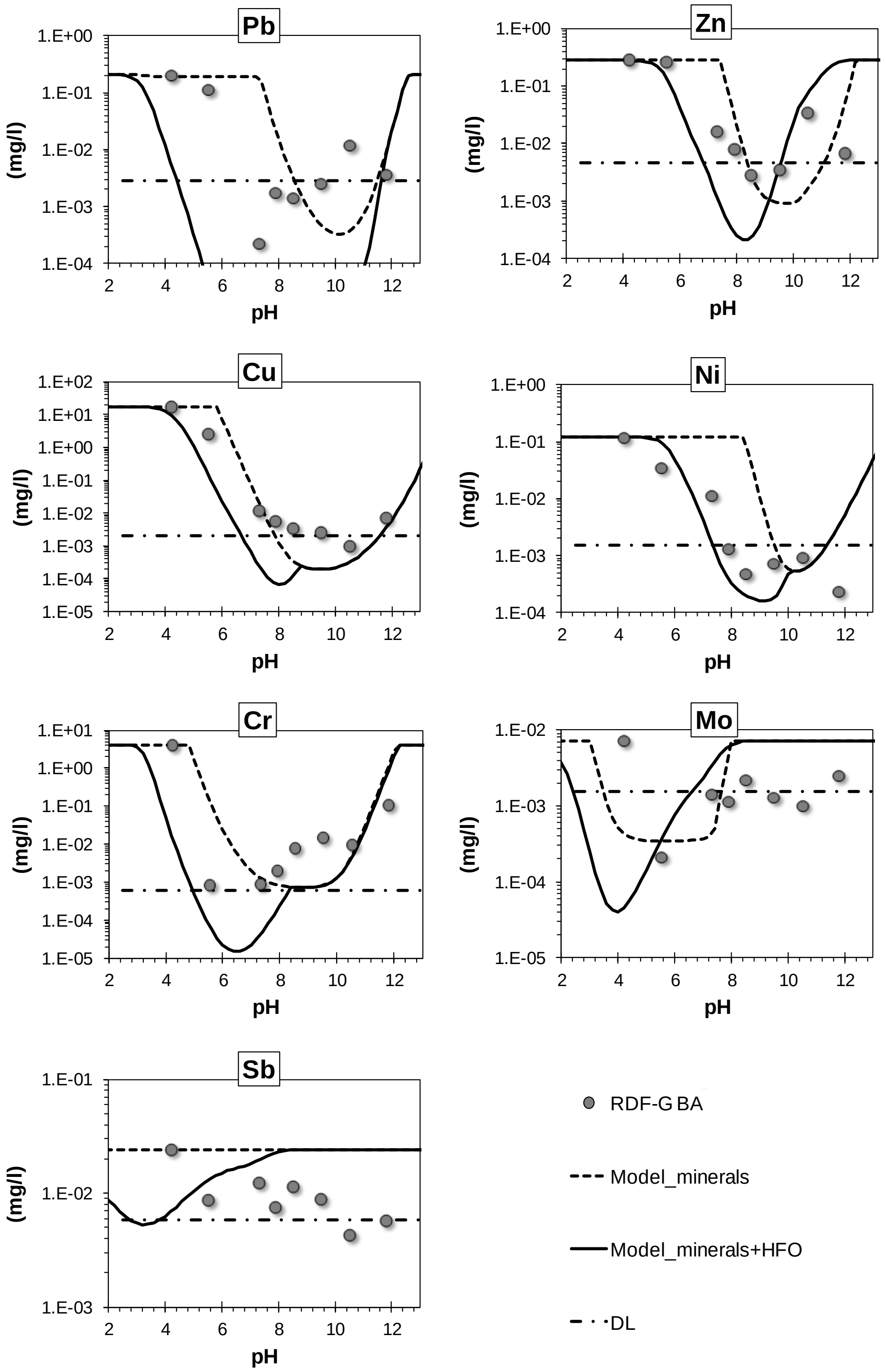

Figure 4.4. Measured and predicted pH dependent leaching concentrations of Pb, Zn, Cu, Ni and Cr in RDF-G BA after an equilibration time of 2 w. The dashed curves represent the first modeling prediction case without metals sorption onto HFO (Model_minerals); the continuous curves represent the second modeling prediction case including metals sorption onto HFO (Model_minerals+HFO). The horizontal lines indicate analytical detection limits (DL).

4.4. CONCLUSIONS

In the present study, the leaching behaviour of trace metals (Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb) from refuse derived fuel gasification (RDF-G) BA was specifically addressed using pH-static characterization leaching tests under different equilibration time conditions, i.e. 48 hours, 1 week and 2 weeks. Geochemical modelling was applied to proper assess the possible mechanisms involved in the release of the analyzed metals.

The comparison of the pH dependent leaching trends obtained for each trace metal for the RDF-G BA with those reported for MSWI BA revealed that important similarities exist between the leaching behaviour of these two types of waste materials. On the other hand, the BA from RDF gasification contained remarkably lower amounts (from 1 to 3 orders of magnitude) of leachable volatile metals of environmental concern, such as Cd, Mo and Sb compared to the BA from MSW incineration as a result of the high formation temperature of the glassy RDF-G slag.

The results of this study also indicated that the leaching concentrations measured after long equilibration times (1 and 2 weeks) were rather close to those obtained after a short equilibration time (48 hours). Thus, these findings suggest that the release of trace metals in this type of BA was not greatly affected by kinetically controlled processes that might occur in the slag, except for Cr for which the leached amount proved to increase, to some extent, as the timeframe of the leaching test increased.

The modelling predictions conducted in this study allowed to identify the precipitation of (hydr)oxides minerals as the main process controlling the leaching of trace metals, such as Pb and Cu from the RDF-G BA. Similar types of minerals are believed to control the leaching of these elements from MSWI BA (e.g. Meima and Comans, 1999; Dijkstra et al., 2002; Dijkstra et al., 2006). In addition, modelling results showed that the sorption mechanism on HFO is a likely solubility controlling process for Ni and Cr in this type of BA.

The findings of the present study proved the importance of considering key parameters (i.e. pH and time) and processes (i.e. precipitation, dissolution and sorption) for a proper characterization of the environmental behaviour of this type of BA. With a particular focus on metals leaching, it appeared that the release of most contaminants, e.g. Cu, Ni and Cr is mostly affected by pH, exhibiting changes in concentrations of orders of magnitude over the whole pH range analysed. Given the low buffering capacity of this material (results shown in Chapter 3), in further research, an in depth characterization of the evolution of the original pH (i.e. 9-10) of the RDF-G BA sample and subsequent metals leaching pertaining to specific application scenarios is required. In fact, it may be expected that pH of this type of BA could relatively quickly adapt to the pH conditions of the local environment and contaminants leaching could hence rapidly change leading to an increased availability of elements such as e.g. Cr for leaching, particularly toward low pH values (below 5). For this reason, other types of leaching tests such as percolation or monolithic tests should be performed in order to gain additional insight on both chemical (e.g. weathering) and physical (transport, diffusion, gas exchange) processes that this material may undergo during possible beneficial utilization or disposal conditions, to attain an adequate assessment of the most suitable management practices, both from environmental and economical points of view, that could be applied for specific type of waste treatment by-product.

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Chapter 5

Effects of weathering on the environmental properties of RDF incineration bottom ash

Part of this chapter has been published as:
Stefania Rocca, Giulia Costa, Francesco Lombardi, 2010. Composition and environmental properties of RDF gasification and grate-fired incineration bottom ash. Proceedings of Venice 2010, Third International Symposium on Energy from Biomass and Waste. Venice, Italy 8-11/11/2010. Pubblicazione su CD-ROM.

This study regards the analysis of the environmental properties of Refuse Derived Fuel incineration (RDF-I) bottom ash (BA) with the final aim of identifying the most suitable disposal or reuse options for this type of waste material. Specifically, the leaching behavior, which has been recognized as one of the most critical aspects for BA management, was examined and related to the mineralogical and chemical characteristics of the slag. In addition, the effects of mineralogical and chemical transformations on the leaching of major and trace components, after set periods of laboratory scale natural weathering, were evaluated for this type of BA. The results evidenced that natural weathering was able to modify some important properties of the slag, including mineralogy, acid neutralization behavior and metal leaching, due to the absorption of atmospheric CO_2 by the reactive compounds present in the residue. In particular, the effects of weathering on trace elements leaching involved a significant decrease in the mobility of Pb, Zn, Cu and Ni, as well as the mobilization for Cr and Mo due to the reduction of the natural pH (from 12.4 to 11.7) of the BA upon ageing. Eluate concentrations of the aged BA showed to exceed the limits for reuse and the European acceptance criteria for inert waste landfilling, while they complied with those established for non hazardous waste landifilling. However, the main processes controlling the leaching behaviour of the this type of slag did not significantly change during a weathering period of 6 months, since the pH dependent leaching curves for most elements of the fresh and aged BA samples resulted rather similar. Geochemical modelling of the leachates indicated solubility control by a number of (hydr)oxide minerals for most metal cations, similarly to what reported in the literature for MSWI BA. Metal binding to sorptive surfaces present in the RDF-I BA was clearly suggested for Pb by modelling results.

5.1 INTRODUCTION

Currently, in Italy, after at source separation a significant part of residual Municipal Solid Waste (MSW) is treated in Mechanical Biological Treatment (MBT) plants which produce a selected material, Refuse Derived Fuel (RDF), that is enriched in waste factions characterized by a high calorific value. Thermal treatment of this selected waste fraction in devoted waste to energy (WtE) plants is a strategy that is being increasingly adopted particularly in Central Italy with the aim of maximizing the energy recovery from non recyclable waste. Following the indications of recent environmental legislation to favour technologies that allow to reduce the volumes of waste for final disposal while enhancing material and energy recovery, the treatment capacities of WtE plants employing RDF are expected to increase in the future, especially in Italy and in other European countries such as Germany, as indicated by Haker et al. (2010).

The most adopted WtE technology for the treatment of RDF is incineration, typically carried out in water-cooled grate combustors at temperatures around 850-1000 °C with air (Jannelli and Minutillo, 2007). Regardless of the specific thermal treatment technology used, WtE plants generate a number of solid by-products, among which the most abundant is bottom ash (BA), accounting for approximately 90% by weight of the total amounts of solid residues generated from the WtE process. In some European countries, such as Denmark, France and The Netherlands, a significant amount of BA from MSW incineration (MSWI) plants is currently reused, mainly as an aggregate substitute in construction of road sub-bases (Astrup, 2007; Polettini 2009). In Italy, instead, there is no specific legislation that regulates the reuse and valorisation of the BA generated by thermal treatment of waste, which is generally disposed of in landfills for non hazardous waste, although, in recent years, there is a growing interest to identify and promote suitable reuse practices for this material in specific civil engineering applications. However, given the non negligible content of potentially toxic components, such as metals and metalloids, in this type of material, concerns exist whether the reuse of BA may exert adverse environmental effects. Specifically, the leaching behavior, which has been recognized as one of the most critical aspects for BA management, has been addressed in many previous studies (e.g. Meima and Comans, 1997, 1998, 1999; Polettini and Pomi, 2004), aiming to identify and predict possible mechanisms governing the release of critical contaminants over time under different environmental conditions.

Another important aspect that has been extensively investigated in previous studies involves natural weathering of MSWI BA, which is commonly used to treat the ash prior to its reuse or final disposal due its the chemical reactivity under atmospheric conditions particularly in alkaline and oxidizing environments (e.g. Meima and Comans, 1999; Chimenos et al., 2003). In fact, the weathering process is expected to result in important mineralogical modifications of this type of material, including: oxidation of some metals (e.g. aluminium, iron, copper), precipitation/dissolution of hydroxide phases and relatively soluble minerals (e.g. calcite; ettringite) and neoformation of reactive sorptive solid substrates (i.e. Fe/Al (hydr)oxides). As a result, weathering reactions proved to affect the evolution of the pH of BA over time and, hence, metals leaching. In particular, a decrease in the release of metals such as Pb and Zn, and an increase in the mobility of oxyanion forming species, such as Cr and Mo, have been indicated to occur for MSWI BA upon weathering by previous studies (e.g. Meima and Comans, 1999; Chimenos et al., 2003; Polettini and Pomi, 2004).

Given the quite recent development of RDF thermal treatment technologies for energy production, there is, however, a lack of systematic studies regarding the characteristics of the fresh/weathered BA originated by RDF incineration plants, which have been briefly summarized in the previous study on this type of BA (Rocca et al., 2012b), see Chapter 3. Thus, the primary focus of the present study was to assess the main mineralogical and chemical weathering processes and their effects on the environmental properties, in terms of buffering capacity and (major/trace) components leaching as a function of pH from RDF incineration bottom ash (RDF-I BA). In addition, in this study, possible mechanisms involved in the release of trace metals from fresh/weathered RDF-I BA were investigated by geochemical modelling in order to derive a suitable description of the overall characteristics and expected long term leaching behavior of this type of material, under possible environmental conditions.

5.2. MATERIALS AND METHODS

5.2.1 Bottom ash samples

About 100 kg of freshly quenched BA was collected from a refuse derived fuel incineration (RDF-I) plant equipped with a grate system combustion chamber operating at temperatures ranging between 850 and 1000 °C. The same RDF-I BA sample was also tested in the previous studies regarding the characterization of inorganic/organic carbon species and major components leaching behaviour (Rocca et al., 2012a ; 2012b), see Chapters 1 and 3. After homogenization (according to the Italian norm UNI 10802:2004) and oven drying at 60 °C to constant weight, the BA samples were sieved to produce two different grain size classes, namely the coarse (0.425-12 mm) and the fine fractions (< 0.425 mm) that were separately analysed to determine their main mineralogical, physical and chemical characteristics, as well as their leaching properties. As already mentioned in the previous studies (Rocca et al., 2012a; 2012b), the coarse fraction (approximately 92% wt. of the BA) was by far quantitatively more abundant than the fine fraction (approximately 8% wt. of the BA) and therefore it was selected as the most representative of the raw material in terms of grain size (see the Annex B, Supporting Information). To this regard, it must be also considered that prior results obtained by thermogravimetric and mass spectrometry (TG-MS) analysis and X-Ray diffraction (XRD) testing evidenced similar characteristics of the two size classes of this type of BA (see the Annex A and Annex B, Supporting Information). Furthermore, no significant variation in pH and subsequent leaching at the material’s own pH of major and trace components was detected between the coarse and fine fractions of the slag (see the Annex B, Supporting Information). Therefore, the following characterization analysis results will be only shown for the coarse size class of the RDF-I BA sample.

5.2.2 Weathering experiments

Approximately half of the amount of the initially sampled RDF-I BA, i.e. about 50 kg, was naturally weathered in the laboratory without initial grain size separation upon contact with air at controlled temperature and humidity and at atmospheric pressure. The aim of this study was to simulate the weathering conditions generally occurring over time during the storage of this type of material at the outlet of the combustion chamber in the incineration plant prior to its final disposal or reuse. To this aim, after set durations of the laboratory scale weathering treatment, i.e. 3, 6, 9 and 12 months, the BA was sampled, oven dried and sieved to be divided into the coarse and fine fractions that were independently investigated to analyse their main mineralogical, physical and chemical characteristics and leaching properties.

5.2.3 Effects of weathering on bottom ash

In the present study, the effects of natural weathering on the mineralogy and pH, as well as on the leaching behaviour of the major and trace components of the RDF-I BA were investigated.

The mineralogy of the fresh and weathered material was determined by X-ray powder diffraction (XRD) analysis using a Philips Expert Pro diffractometer equipped with a copper tube operated at 40 kV and 40 mA.

The leaching behaviour at the material's own pH of the fresh and weathered samples (after 3, 6, 9 and 12 months of treatment) was investigated by performing the batch compliance leaching test EN 12457-2 for evaluating the variations in the pH and mobility of the major (Ca, Mg, Si, Al, Fe, SO_4^{2-}, Cl^-, Na, K and DOC) and trace (Pb, Zn, Cu, Cr, Sb, Mo, Ni and Cd) components from the samples. Subsequently, eluate concentrations of specific contaminants contained in the fresh/aged BA were compared with the acceptance criteria for inert waste landfilling reported in Annex II of the European Landfill Directive (2003/33/EC) and the limits established by the Italian legislation for reuse of non hazardous waste (Italian Environmental Ministry, 1998), although these limits currently do not specifically apply to BA from waste incineration plants.

The leaching behaviour was also investigated, prior to and after 6 months of weathering, using the CEN/TS 14429 pH dependence leaching test (pH range 2-12.5) for evaluating the acid/base neutralization capacity (ANC/BNC) and metals leaching from the fresh and weathered BA samples.

Further description of the analytical methods employed to derive the experimental results of this study is provided in Rocca et al. (2012b).

5.2.4 Geochemical modelling of trace components

The speciation modeling framework ORCHESTRA (Meeussen, 2003) included in the LeachXS database/expert system (http://www.leachxs.com/lxsdll.html) was used to calculate the leached concentrations of trace metals from the fresh and weathered BA samples. The measured pH dependent released amounts and availabilities (i.e. leaching at pH 2) of these components were included as input data in the modelling approach. Next, the analytical leaching data were compared to geochemical modelling predictions that were conducted based on the solubility of a number of minerals (mainly selecting those that have been reported in the literature for MSWI BA); sorption to reactive Fe and Al based amorphous surfaces (i.e. HFO/AAM) contained in the (fresh/weathered) BA and sorption to specific organic carbon fractions (i.e. fulvic and humic acids, FA/HA) present in the solid and solution phases of the (fresh/weathered) BA. The amounts of HFO/AAM was estimated by selective chemical extractions, i.e. dithionite, ascorbate and oxalate extractions that were described in the previous study (Rocca et al., 2012c), see Chapter 4. Independent estimates of the solid and dissolved FA and HA fractions in the BA samples were derived by performing rapid batch procedures that have been developed by van Zomeren and Comans (2004) starting from the conventional method recommended by the International Humic Substances Society, to which the reader is referred for a detailed description of the methods. In order to take into account the competition of sorbates with phosphate (PO_4^{3-}), a constant solution concentration of $1.0\cdot10^{-6}$ M for pH values ranging from 4 to 12 was implemented in the model, based on the concentrations indicated by Dijkstra et al. (2008) for MSWI BA, since PO_4^{3-} concentrations were not analysed for the RDF-I BA sample.

5.3 RESULTS AND DISCUSSION

5.3.1 Effects of weathering on the mineralogy of bottom ash

Fig. 5.1 reports the comparison of the mineralogical characterization of the fresh and (6 months) weathered RDF-I BA samples detected by XRD analysis. A detailed description of the various (crystalline) mineral phases contained in the fresh sample is provided in the previous study (Rocca et al., 2012b), see Chapter 3.

As shown in Fig. 5.1, mineralogical transformations induced by weathering reactions evidenced the increase in peak intensity for hydrocalumite (H= $Ca_4Al_2Cl_2O_6\cdot10H_2O$), which has been recognized as an aging product under atmospheric conditions in alkaline ashes (pH 10-11) containing high levels of chlorides (Bayuseno and Schmahl, 2010). Furthermore, the comparison of the XRD patterns in Fig. 1 shows the disappearance of the peaks associated to portlandite (Ca= $Ca(OH)_2$) and the increase in peak intensities for calcite (C= $CaCO_3$) by absorption of CO_2 upon weathering of

BA. In fact, calcite formation was identified as the most important weathering process affecting the mineralogy of MSWI BA in prior studies (e.g. Meima and Comans, 1997; Chimenos et al., 2003; Piantone et al., 2004). The increase of the carbonates content induced by the weathering treatment has also been detected by TG-MS, TIC and calcimetry analyses, as reported in the previous study on this type of BA (Rocca et al., 2012a), see Chapter 1.

In addition, a relevant increase in peak intensity was observed for quartz (Q= SiO_2), gehlenite (G= $Ca_2Al_2SiO_7$) and anorthite (A= $CaAl_2Si_2O_8$) during the course of the aging treatment. These results proved consistent with those obtained by Piantone et al. (2004), revealing the presence of newly formed silicate minerals in the weathered MSWI BA.

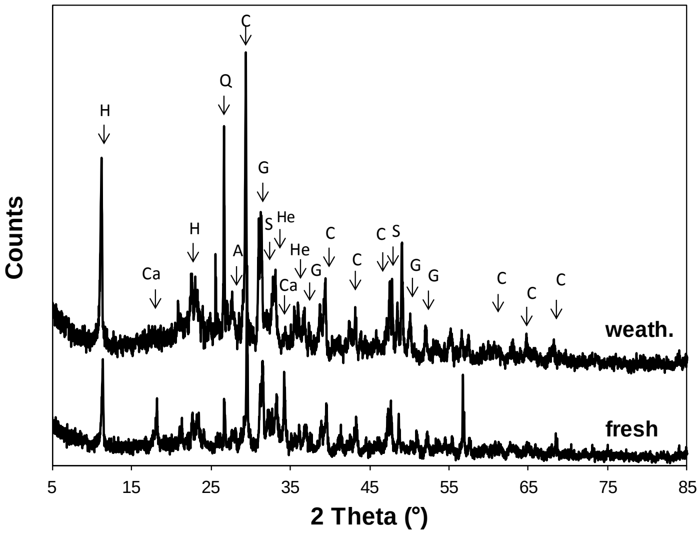

Figure 5.1. XRD patterns of the fresh and (6 months) weathered (weath.) RDF-I BA (Legend: H: hydrocalumite ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$); Ca= Portlandite ($Ca(OH)_2$); S= di calcium Silicate (Ca_2SiO_4); A= Anorthite ($CaAl_2Si_2O_8$); Q= Quartz (SiO_2); G= Gehlenite ($Ca_2Al_2SiO_7$); C= Calcite ($CaCO_3$); He= Hematite (Fe_2O_3)).

5.3.2 Effects of weathering on the leaching behaviour of bottom ash

The results from the EN 12457-2 compliance leaching test reported in Fig. 5.2 indicated that the natural pH of the RDF-I BA decreased from 12.4 to 11.7 after 6 months of natural weathering, as an effect of the absorption of CO_2 and subsequent precipitation of calcite ($CaCO_3$) in the aged BA (Meima and Comans, 1997).This finding is in good agreement with the results obtained by TG-MS, TIC and calcimetry analyses, evidencing the increase of the carbonates content of this type of BA after weathering (Rocca et al., 2012a).

Subsequently, after longer weathering treatment times (9 and 12 months) the pH value of the leachate of the BA samples remained rather constant around 11.5, hence suggesting that the alkalinity of the material (mainly due to free Ca in solution) was not consumed during the investigated aging periods.

Among the major components (Fig. 5.2, b), Ca and Si leaching were reduced for all the weathered BA samples with respect to the fresh slag, as a result of the precipitation of poorly soluble newly formed carbonates and silicates minerals, such as calcite, quartz and gehlenite, in accordance to the results of XRD analysis (see Fig. 5.1).

In addition, a relevant immobilization effect (by one to three orders of magnitude) was observed for most trace contaminants (Fig. 5.2, c), i.e. Pb, Zn, Cu and Ni upon weathering, in good agreement with the results of prior investigations on RDF-I BA (Baciocchi et al., 2010) and MSWI BA (e.g. Meima and Comans 1999; Chimenos et al., 2003). On the other hand, natural weathering also produced a slight increase (up to one order of magnitude) in the release of oxyanion-forming metalloids (Fig. 5.2, c), i.e. Cr and Mo from the BA, which proved in agreement with the findings of previous studies (e.g. Meima and Comans, 1999; Polettini and Pomi, 2004; Baciocchi et al., 2010).

Comparing the results of the compliance leaching tests with the European landfill acceptance criteria (2003/33/EC), it can be observed that the weathered BA would meet the requirements for non hazardous waste landfilling, since eluate concentrations of Cl^- and Pb exceeded the acceptance criteria for inert waste landfilling (Fig. 5.2). In addition, the concentrations of Cr and Mo in the eluates of weathered BA resulted above inert waste acceptance criteria. In Fig. 5.2 it can also be observed that the release of Cl^-, Pb and Cr from at least some of the weathered samples proved above the Italian limits for reuse.

The ANC/BNC curves derived from the pH dependence leaching test of the fresh and weathered BA samples are shown in Fig. 5.3. The following results are referred to the 6 months weathered sample that was selected as the most representative of the behaviour of the aged BA, since no further reduction in the material's own pH was observed after 9 and 12 months of the weathering treatment (see Fig. 5.2, a). For this reason, we assumed that no relevant differences exist between the ANC/BNC and leaching characteristics of the 6, 9 and 12 months weathered slag. In fact, modifications in the leaching behaviour of this type of residue are expected to occur mainly as a result of the changes in pH, according to the results of prior investigations on MSWI BA reported in the literature (e.g. van der Sloot et al., 1996; Chandler et al., 1997; Meima and Comans, 1999). However, it should be noted that, as may be observed in Figure 5.2, for some elements (i.e. Pb, Zn, Cu and Cr) variations in leaching concentrations were observed upon an increase of the duration of the weathering treatment.

In Fig. 5.3 it can be observed that the fresh and aged BA samples clearly displayed a different ANC from pH below 12 to pH 4. In particular, for the fresh BA an increase in acid addition corresponded to a gradual decrease of the pH of the eluates (from 12 to pH 4). These results can be ascribed to the buffering capacity of the hydrated phases (i.e. calcium hydroxide and hydrocalumite), calcium carbonate, (Ca/Al) silicate (i.e. quartz, anorthite and akermanite), as well as iron oxide minerals (i.e. hematite) that were detected in the slag by XRD. A detailed description of the amounts of precipitated/dissolved pH buffering mineral phases retrieved for the freshly sampled BA is provided in the previous study (Rocca et al., 2012b), see Chapter 3.

For the weathered BA, instead, a more rapid drop of the eluates pH can be observed from the initial value of 11.7 up to 7 compared to the fresh sample. These results suggest that a lower amount of alkalinity (due to the dissolution of hydroxides and silicates phases) was available for buffering acid additions at that pH range in the weathered material compared to the fresh one, since part of it had been already consumed by reaction of the slag with CO_2 during aging.

In addition, the acid titration curve obtained for the weathered BA revealed the presence of a plateau that was likely consistent with the complete dissolution of calcite occurring down to pH 7 (Johnson et al., 1995). Indeed, such a behaviour suggested an increased amount of carbonate species in the BA sample after weathering, confirming the results derived from the previous analyses (Rocca et al. 2012a).

In Fig. 5.3 it can also be seen that the fresh and aged BA samples exhibited remarkably similar ANC curves below pH 5, as a result of the slow dissolution of comparable amounts of (Fe/Al) oxides and (Ca/Al) silicate minerals that are responsible for the buffering capacity of the two materials at strongly acidic pH values (Rocca et al., 2012b).

The release of major (Ca, Mg, Si, Al, Fe, Cl^-, SO_4^{2-}, Na and K) and trace (Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb) components measured in the eluates of the pH dependence leaching tests are reported in Figs. 5.4 and 5.5 for the fresh and weathered BA samples. Figs. 5.4 and 5.5 also display the released concentrations determined from the batch leaching tests (EN 12457-2) of the untreated and treated slag for comparison.

Although quite different in their acid neutralization behaviour at pH 6-12 (see Fig. 5.3), the fresh and weathered BA samples showed rather similar pH dependent leaching trends with respect to the shape of the curves and leachate amounts of both major and trace compounds over the whole pH range investigated. Given these similarities, it seems that the mineralogical and chemical changes occurring in the BA upon the analysed weathering period did not significantly affect the solubility of the minerals which mainly controlled the release of such components from this type of residue.

In addition, the leaching results obtained from the EN 12457-2 test at the natural pH of the BA showed a good match with those derived from the pH dependence leaching tests at a corresponding pH value, hence suggesting that the amounts of these components released from the fresh or aged material was not influenced by the equilibration time of the applied leaching test (24 or 48 h).

On the basis of these findings, it is reasonable to assume that similar types and amounts of minerals may contribute to the leaching processes of major and trace components from this type of slag, irrespective of the tested degree of weathering. An extensive geochemical modelling analysis of the leaching behaviour of the major components and pH buffering capacity conducted on the fresh material was addressed in the previous study (Rocca et al., 2012b) to which the reader is referred, see Chapter 3. Therefore, in this study we focused on understanding the most important mechanisms that influence the release of trace elements from RDF-I BA by geochemical modelling.

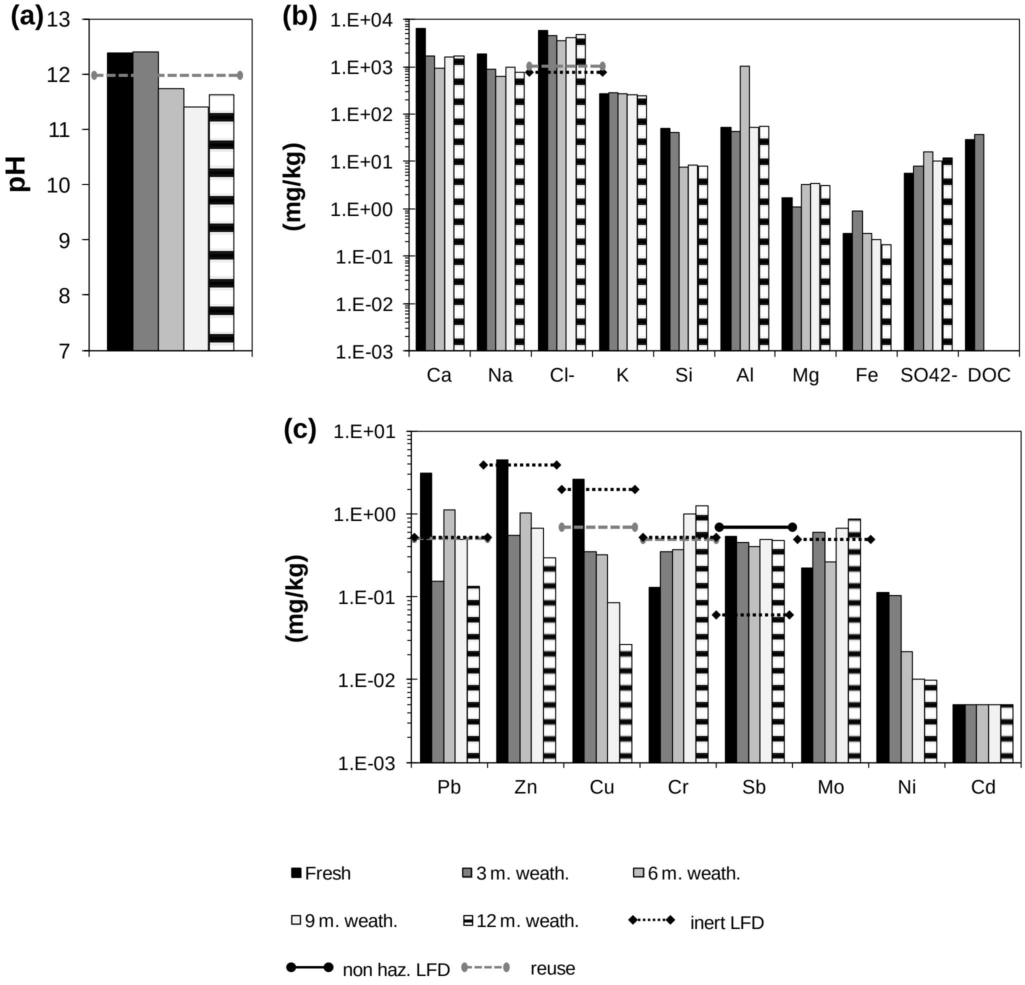

Figure 5.2. pH values (graph a) and leaching test (EN 12457-2) results of major (Ca, Na, Cl^-, K, Si, Al, Fe, SO_4^{2-} and DOC) (graph b) and trace components (Pb, Zn, Cu, Cr, Sb, Mo, Ni and Cd) (graph c) for fresh and (3, 6, 9 and 12 months) weathered RDF-I BA. The acceptance criteria for inert waste landfilling (inert LFD) and non hazardous waste landfilling (non haz. LFD), together with the Italian requirements for reuse (reuse) are reported in the graphs when relevant.

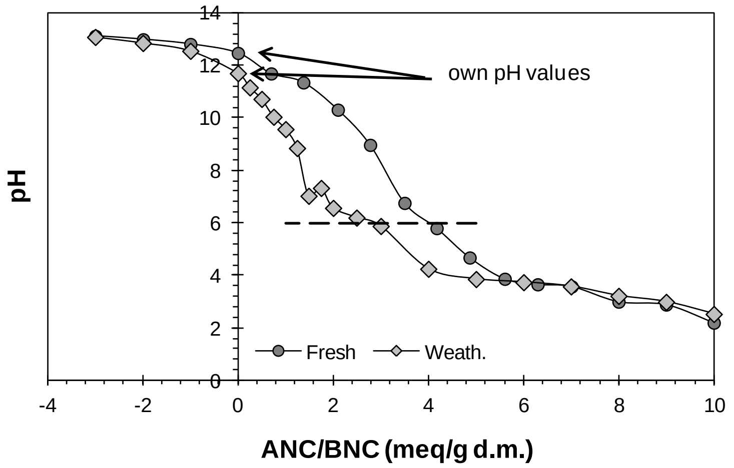

Figure 5.3. Acid/base neutralization capacity (ANC/BNC) curves for fresh and (6 months) weathered RDF-I BA samples (dashed horizontal line indicates the expected titration end points for calcite).

5.3.3 Identification of processes controlling the leaching of trace metals

The release of the trace metals measured in the eluates as a function of pH together with the geochemical modelling predictions are reported in Fig. 5.6. The modelling approach is the same to that described in the previous study on the metals leaching from the RDF-G BA sample (Rocca et al., 2012c), see Chapter 4. In short, in this study, the influence of sorption in controlling the leaching mechanisms of trace metals from this type of BA was evaluated by performing two independent modelling predictions by means of the geochemical speciation code ORCHESTRA (included in LeachXS database) as follows: 1) the program was run selecting a number of potentially solubility controlling minerals in BA (that are listed below) without considering the estimated quantity of reactive HFO in the slag (i.e. the adsorption model of the metals to HFO was turned off); 2) the program was run selecting a number of potentially solubility controlling minerals in BA and including the estimated amount of the HFO sorption sites contained in the slag (i.e. 0.028 kg HFO/kg BA). In addition, the two modelling predictions included the evaluation of the effects of possible metals adsorption to dissolved organic (FA and HA) fractions in leachates, since the results from previous studies on MSWI BA led to the identification of this type of processes in governing contaminants leaching (e.g. van Zomeren and Comans, 2004; Dijkstra et al., 2006; Arickx et al., 2007).

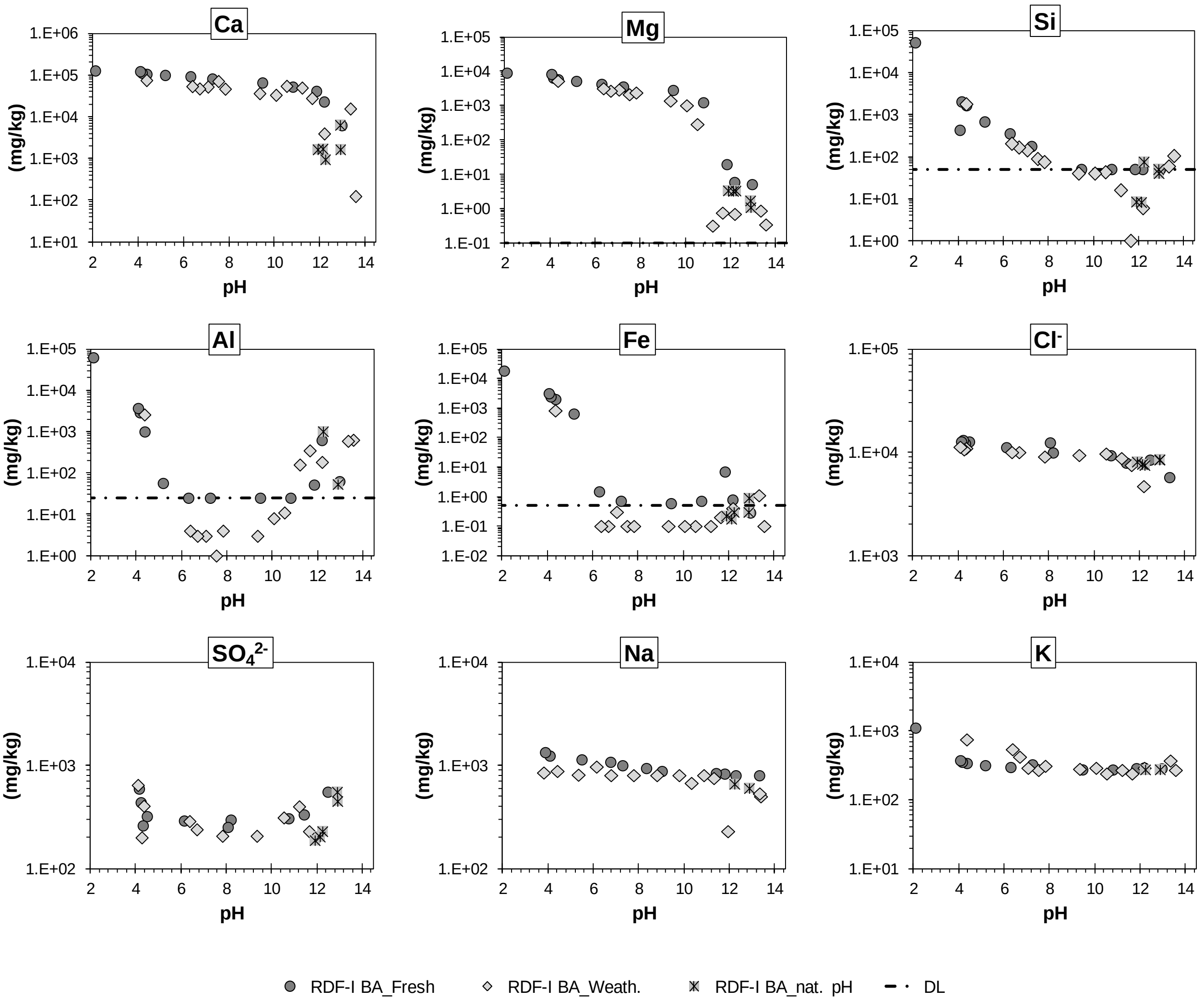

Figure 5.4. Leachate concentrations of major components (Ca, Mg, Si, Al, Fe, Cl$^-$, SO_4^{2-}, Na and K) as a function of pH for fresh and (6 months) weathered RDF-I BA samples. Leachate amounts of trace metals at the natural pH obtained (from the EN 12457-2 leaching test) for fresh and (3, 6, 9 and 12 months) weathered BA samples were also included in the graphs.

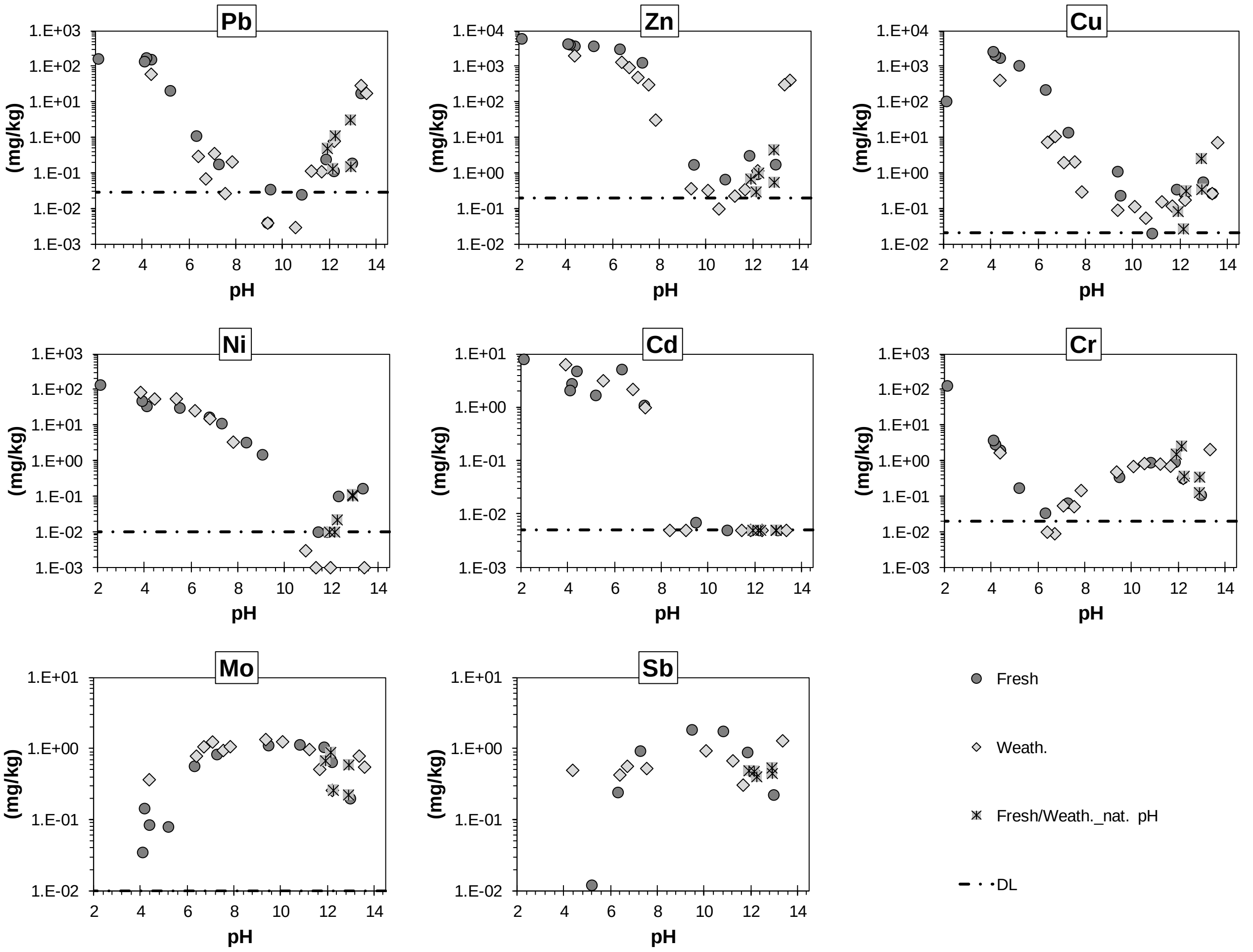

Figure 5.5. Leachate concentrations of trace metals (Pb, Cu, Zn, Ni, Cd, Cr, Mo and Sb) as a function of pH for fresh and (6 months) weathered RDF-I BA samples. Leachate amounts of trace metals at the natural pH obtained (from the EN 12457-2 leaching test) for fresh and (3, 6, 9 and 12 months) weathered BA samples were also included in the graphs.

According to the geochemical modelling calculations derived from the first modelling simulation, the measured leaching of Pb can be adequately explained by the precipitation of hydroxide mineral, i.e. $Pb(OH)_2$ in the strongly alkaline pH >10 (see Fig. 5.6). The measured released amounts of Pb, instead, proved to be largely overestimated by solubility of $Pb(OH)_2$ at pH 2-10. On the other hand, control of Pb leaching in the pH range 2-10 could be ascribed to sorption mechanism on HFO, giving the best fitting of the measured data in the second modelling prediction. These results are in good agreement with those reported in the literature for MSWI BA (Meima and Comans, 1998). The releases of Zn and Ni appeared to be well predicted by solubility curves of (hydr)oxides mineral phases, i.e. ZnO and $Ni(OH)_2$, respectively. Hence, the leaching of these metals from the investigated BA sample can be mainly attributed to the presence of free Zn^{+2} and Ni^{+2} forms which were identified as the dominants species in solution, exhibiting the typical V-shaped pH dependent releases (with orders of magnitude changes in concentrations) over the whole pH range analysed.

These results are consistent with those reported in previous studies on MSWI BA (Meima and Comans, 1999; Dijkstra et al., 2006). The geochemical modelling results derived from the second prediction case (calculating the metals sorption to HFO) were basically overlapped to those obtained from the first modelling scenario, thus suggesting that sorption mechanisms do not govern solution concentrations of Zn and Ni for the tested RDF-I slag.

Tenorite (CuO) was identified as a possible solubility controlling phase for Cu, showing a good fitting of the experimental leaching data over the entire pH range. The release of Cu appeared to be bound to DOC at pH range 8-10, according to what indicated by previous investigations (e.g. van Zomeren and Comans, 2004; Arickx et al., 2007). Furthermore, it was observed that the HFO sorption-based modelling calculations were practically the same as those obtained if HFO was not included in the modelling prediction, proving that this type of process did not exert a great influence on Cu leaching from the analysed RDF-I BA.

The amounts of Cd in leachates were found to be overestimated by 2-3 orders of magnitude at pH >10 with respect to the precipitation of hydroxides ($Cd(OH)_2$) or carbonates (otavite, $CdCO_3$), which have been selected in the first modelling scenario as possible mineral phases for leaching control of this metal, according to the results obtained in previous studies (Meima and Comans, 1999; Dijkstra et al., 2006). In fact, the low releases of Cd toward alkaline pH resulted not well predicted by precipitation/dissolution of any known Cd mineral selected in LeachXS database for this type of BA. Although, in such a case, sorption processes are expected to play a role in controlling metal leaching, again Cd leachates were found to be overestimated by the modelling calculations based on metal sorption on HFO. Further investigations are needed to explain these results.

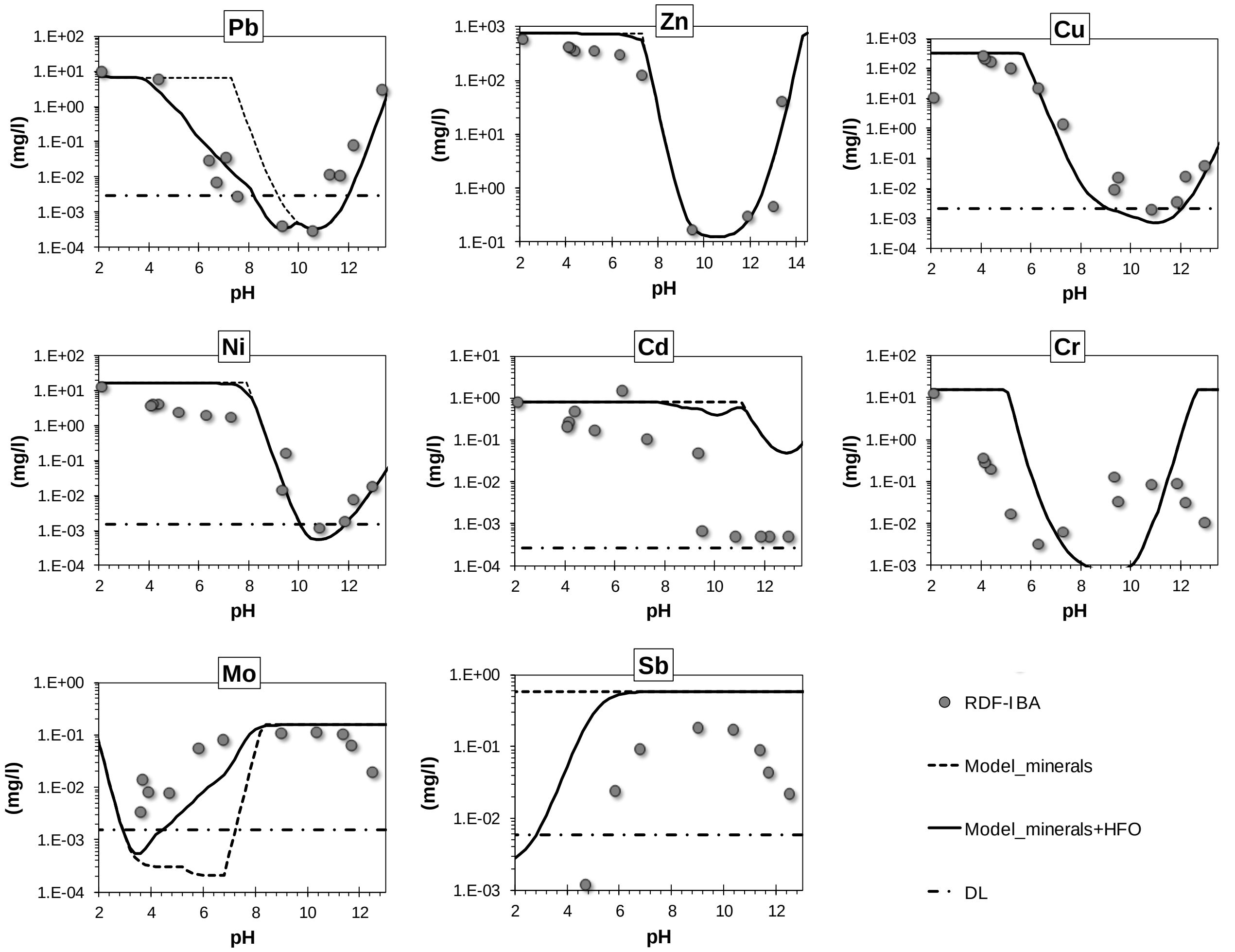

Figure 5.6. Measured and predicted pH dependent leaching concentrations of Pb, Zn, Cu, Ni, Cd, Cr, Mo and Sb from the RDF-I BA sample. The dashed curves represent the first modeling prediction case without the metals sorption to HFO (Model_minerals); the continuous curves represent the second modeling prediction case including the metals sorption to HFO (Model_minerals+HFO). The horizontal lines indicate detection limits (DL).

With reference to Cornelis et al. (2008), solubility prediction of Cr (present in the most soluble hexavalent form in BA leachates) was accomplished using Ca or Fe-containing minerals, including Cr-ettringite ($Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$) or $FeCr_2O_4$.

According to the results obtained by Dijkstra et al. (2006), the modelling calculations regarding Mo leaching were carried out with $Fe_2(MO_4)_3$, Pb MO_4 and $CaMO_4$, that are thought to be the solubility controlling minerals for this oxyanionic metalloid from MSWI BA.

In case of Sb, geochemical modelling predictions were conducted based on the solubility of Sb hydroxide ($Sb(OH)_3$) and calcium antimonate ($Ca(Sb(OH)_6)_2$) that were implemented in the (first) case scenario, according to the results of previous studies (Cornelis et al., 2012). However, the predicted leaching curves derived from the first modeling scenario did not show an adequate fitting of the experimental leaching data for any investigated oxyanions. In addition, model calculations estimating the sorption process of the oxyanion forming species to HFO indicated that this type of mechanism did not appear to largely influence Cr leaching. On the other hand, the sorption model results in Fig. 6 showed that the reduction in Mo and Sb leached concentrations at pH values below 6 may be possibly attributed to adsorption to HFO, in agreement with previous observations on MSWI BA (Cornelis et al., 2006; 2012; Dijkstra et al., 2006).

5.4 CONCLUSIONS

This study focused on the main mineralogical and chemical weathering processes and their effects on the pH dependent leaching properties of major and trace components from RDF incineration bottom ash (RDF-I BA), for a proper assessment of the potential environmental impact related to its disposal and reuse. In addition, in this study, possible mechanisms involved in the release of trace metals from fresh/weathered BA were investigated by geochemical modelling in order to gain insights into the expected long term leaching behaviour of this type of material.

The findings of this study evidenced that natural weathering, carried out at laboratory scale after set periods of time, i.e. 3, 6, 9 and 12 months, was able to affect some important properties of the RDF-I BA, including mineralogy, acid neutralization behavior and metal leaching, mainly resulting from the absorption process of CO_2 by the reactive compounds present in this type of residue. In particular, the weathering treatment proved to be effective in reducing the natural pH of the material, which shifted from 12.4 for the fresh BA to 11.7 after 6 months of natural weathering. Since the natural pH of the aged BA sample almost coincided with the minima of the V-shaped leaching curves of most metal cations, weathering resulted in a relevant immobilization effect, in particular for Pb, Zn, Cu and Ni. In addition, the decrease in natural pH for the weathered BA led to a mobilization effect of oxyanionic metals such as Cr and Mo, with leached concentrations exceeding the acceptance criteria for inert waste landfilling, while complying with those established for non hazardous waste landfilling (2003/33/EC). Furthermore, eluate concentrations of some components such as chorides resulted above the Italian limits for reuse also after the weathering treatment.

Nevertheless, from the results of this study it may be expected that the main processes controlling the released amounts of both major and trace components from fresh and (6 months) weathered RDF-I BA samples were rather similar since the leaching curves relative to the two (fresh or aged) materials did not show significantly different shapes. To this regard, geochemical modelling of leachate concentrations indicated that possible processes governing the main contaminants leaching from the RDF-I BA may be dissolution/precipitation of the following minerals: lead hydroxide

($Pb(OH)_2$); zinc oxide (ZnO); tenorite (CuO) and nickel hydroxide ($Ni(OH)_2$). Solubility control by hese mineral phases was suggested by the results of previous studies on MSWI BA, hence indicating that similar release mechanisms can be identified also in waste materials of different origin. As for oxyanionic metalloids, experimental leaching data were not adequately explained by geochemical modelling and, hence, further investigations are needed to improve the modelling prediction of the experimental results obtained for the fresh/aged RDF-I BA samples. Finally, sorption was likely to be an important mechanisms controlling the release of Pb and possibly also of Mo and Sb, as indicated by the results of the modeling scenario in which interactions of metal leaching with reactive sorption sites (HFO) were taken into account.

As far as the interactions of the RDF-I BA with CO_2 are concerned, the results of this study evidenced the potential of the weathering treatment to neutralize bottom ash pH, leading to a reduction of the release of specific contaminants. However, further investigations are needed to derive information on the overall effects that long term weathering mechanisms, i.e. longer weathering periods, may have in reducing/enhancing metals leaching and increasing metal binding to sorptive surfaces so to obtain a more complete description of the environmental behaviour pertaining to various application scenarios for this type of BA.

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Conclusions and final remarks

In this study the chemical composition, mineralogy and leaching characteristics of several thermal treatment residues (i.e. bottom ash samples from refuse derived fuel incineration or gasification and bottom ash from hospital waste incineration) was assessed. In addition, geochemical modelling was applied in order to identify the chemical and physical processes that determine the release of contaminants from each type of residue.

First, the nature of the relatively high LOI content of RDF-I BA and HW-I BA was investigated by thermogravimetry (TG) and mass spectrometry (MS) analysis (Chapter 1). Results for RDF-I BA indicated that the LOI measured at 550 °C was due to moisture evaporation and dehydration of $Ca(OH)_2$ and hydrocalumite contained in the residue. Results for the HW-I BA showed that LOI at 550 °C was predominantly related to the elemental carbon (EC) content of the sample. These results showed that RDF-I BA did not contain unburned carbon species that decompose at 550 °C leading to CO_2 production. The results suggest that the relatively constant size distribution and composition of the RDF feedstock in the incineration plant possibly contributed to the high efficiency of the combustion process, resulting in a negligible content of residual organic carbon in the BA. On the other hand, the TG-MS results for the HW-I BA imply that a pyrolytic-like process may take place in the rotary kiln combustion system due to an oxygen-deficient atmosphere that limits the complete combustion of the HW feedstock. Consequently, the BA originating from such a thermal treatment process results in a carbonaceous solid residue that is mainly constituted of elemental black carbon with a decomposition temperature of 550 °C that was clearly identified by TG-MS. These results imply that LOI cannot be considered as a generic quality control parameter for the effectiveness of a waste incineration system with respect to the content of unburned organic material in the incineration residues. In addition, reaction mechanisms were identified that can bias the determination of LOI in general and of the EC and $CaCO_3$ content in particular. Within the timeframe of the experiment, CaO has been observed to sequester the CO_2 resulting from the combustion of organic Carbon (OC) or EC. This reaction causes an underestimation of the OC+EC content of the HW-I BA by LOI, since the formation of $CaCO_3$ caused a weight gain of the sample. In addition, the $CaCO_3$ content of the slag, which provides an indication of weathering/secondary carbonation reactions, may be overestimated if measured by TG analysis, since it includes the $CaCO_3$ formed as a consequence of EC combustion in the presence of CaO. These types of artefacts in the quantification of specific carbon phases are expected to occur also when conventional LOI methods are adopted for other materials that contain $CaO/Ca(OH)_2$ in combination with EC/OC, such as e.g. MSWI bottom and fly ashes. It is suggested that the same mechanisms that were found in the TG-MS results can also occur during combustion of the waste and contribute to in-situ carbonation of the bottom ash between 450 and 650 ^{o}C. This finding indicates that the presence of calcium carbonate in bottom ash is not necessarily indicative only of weathering reactions occurring in the slag during storage, but may be originated also from carbonation occurring during or just after incineration. The results may also give direction to further optimization of waste incineration technologies with regard to stimulating in-situ carbonation and subsequent quality improvement of bottom ash.

Subsequently, the chemical characteristics, mineralogy and leaching properties of HW-I BA were investigated (Chapter 2). Bulk chemical analysis indicated that the composition of this BA is quite similar to that typically reported for MSWI BA. On the other hand, mineralogical characterization by X-Ray diffraction (XRD) analysis revealed that the analyzed HW-I BA was predominantly amorphous containing only few crystalline phases, i.e. carbonates and silicates, and therefore exhibited a different mineralogy than that reported in the literature for MSWI BA. Furthermore, results from the EN 12457-2 compliance leaching test showed that HW-I BA would meet the European acceptance criteria for non hazardous waste landfills and the limits for reuse in specific application scenarios. However, the acid neutralization behaviour of this type of BA appeared low so that possible implications on the pH dependent release of many constituents should be considered in order to draw some conclusions on the expected behaviour of the slag under the conditions characteristic of an application scenario. The comparison of the leaching properties of HW-I BA as a function of pH with literature data showed an adequate match. These observations suggest that different test types such as the CEN/TS 14429 pH dependence test, EN 12457, DIN 38814 and TCLP test provide similar results which are easily related to each other using a leaching test covering a broad range of pH values (pH dependence test). Qualitative and quantitative comparison of the leaching properties of fresh and aged HW-I BA with those typical for MSWI BA suggested that differences existing between the various BA samples may be most likely ascribed to the thermal treatment technology adopted in the plants from which the residues were originated from.

The environmental properties of the RDF-I and RDF-G BA samples were assessed and compared on the basis of their total composition, mineralogy, leaching of major components as a function of pH and buffering capacity (Chapter 3). Results showed that the total content of major components for the two types of BA was fairly similar and possibly related to the characteristics of the relatively homogeneous RDF feedstock. However, significant differences in the contents of trace metals and salts were observed for the two BA samples, as a result of the different operating conditions (i.e. temperature) adopted by the two RDF thermal treatment plants. Mineralogy analysis showed that the RDF-I slag consisted of an assemblage of several crystalline phases while the RDF-G slag was mainly made up by amorphous glassy phases. The leached concentrations of major components (e.g. Ca, Si) at the natural pH of each type of slag did not reflect their total contents, as a result of the partial solubility of the minerals in which these components were chemically bound. In addition, comparison of total contents with leached concentrations of minor elements (e.g. Pb, Cu) showed no obvious correlations for the two types of BA. According to the compliance leaching test results, the RDF-G BA would meet the limits of the Italian legislation for re-use and the European acceptance criteria for inert waste landfilling. RDF-I BA instead would meet the European acceptance criteria for non hazardous waste landfilling (due to non-compliance of chloride, lead and antimony). A new geochemical modelling approach was developed to predict the leaching behaviour of major components and the pH buffering capacity of the two types of BA, on the basis of independent mineralogical information and the bulk composition of the slag. It was found that the combined use of data regarding the mineralogical characterization and the buffering capacity of the slag material can provide an independent estimate of both the identity and the amount of minerals that contribute to the leaching process. This new modeling approach suggests that only a limited amount of the mineral phases that control the pH, buffering capacity and major component leaching from the solid samples is available for leaching, at least on the time scale of the applied standard leaching tests.

Next, the leaching behavior of trace metals from RDF-G BA as a function of pH and equilibration times of the (pH dependent) leaching tests was investigated (Chapter 4). The latter aspect is believed particularly important since the predominant glassy matrix of the gasification BA may limit, to some extent, the availability of metals for leaching depending on the time scale of the performed leaching tests. The leached concentrations and availabilities of elements such as Zn and Ni obtained for the RDF-G BA were found to be lower than those typically found for MSWI BA, used as a reference material in this study. These results may be ascribed to the strong volatility of these elements at the high formation temperatures of the gasification residue (> 1200 °C). In addition, RDF-G BA exhibited significantly lower leaching concentrations of Cu compared to the mean values obtained for the MSWI BA, as a result of the low concentrations of dissolved organic carbon (DOC) with which copper forms strong complexes. The results of the tests carried out at different equilibration times indicated that kinetics did not greatly affect the leaching behaviour of RDF-G BA. As such, these findings suggest that the glassy matrix of the RDF-G BA is responsible for the reduced availability of (volatile) metals for leaching over time compared to MSWI BA. In fact, modeling results showed that the relevant processes controlling the generally low release of trace elements within the investigated pH domain were found to be the precipitation of (hydr)oxides minerals (e.g. for Pb and Cu) and adsorption (e.g. for Ni and Cr) on Fe/Al based surfaces present in the RDF-G BA matrix. Given the low buffering capacity of this material, it may be expected that the pH of this type of BA, in application or disposal scenarios, could relatively quickly adapt to the pH conditions of the local environment and contaminants leaching could hence change.

Finally, the effects of (different stages of) natural weathering on the mineralogical composition and leaching properties of RDF-I bottom ash were investigated (Chapter 5). Weathering is an important process that takes place during disposal or application in construction works and the effects on the leaching of trace metals is, therefore, an important subject. The results evidenced that natural weathering was able to modify some important properties of the RDF-I BA, including mineralogy, acid neutralization behavior and metal leaching, resulting from the absorption of CO_2 by the reactive compounds present in the residue. In particular, the effects of weathering on trace elements leaching involved a significant decrease in mobility for Pb, Zn, Cu and Ni, as well as the mobilization of Cr and Mo due to the reduction of the natural pH (from 12.4 to 11.7) of the BA upon ageing. Eluate concentrations of the aged BA showed to exceed the limits for reuse and the European acceptance criteria for inert waste landfilling for these elements, while complying with those established for non hazardous waste landifilling. However, the main processes controlling the leaching behaviour of this type of slag did not significantly change during the investigated weathering period, since the pH dependent leaching patterns of the fresh and aged BA samples were rather similar. Geochemical modelling of the leachates indicated solubility control by a number of (hydr)oxide minerals for most metal cations, similarly to what is reported in the literature for MSWI BA. Modelling results showed that adsorption onto Fe/Al based surfaces present in the RDF-I BA was the main process controlling leaching of Pb.

Comparing the results obtained for the three types of analyzed bottom ash samples, it may be concluded that more than the characteristics of the feed waste treated in waste to energy plants, the type of thermal treatment technology adopted is the factor that mostly affects the main properties and the environmental behaviour of the slag by-product. In particular, from an environmental perspective, the residues that appeared to pose the lowest impacts in terms of contaminant release and hence may potentially be the most fit for reuse applications are the RDF-G BA, although as mentioned dynamic leaching tests should be performed in order to verify that the leaching of some contaminants, such as chromium for example, would not be enhanced under field conditions. Based on the results of the physical and chemical characterization tests, a possible reuse option for these residues may be as aggregates for road base construction, since the material presented a quite homogeneous grain size distribution, however specific testing must be carried out to assess whether the material possesses suitable technical properties for this or other engineering applications. As for the two types of tested waste incineration BA, significant differences in their composition, mineralogy and hence in their overall leaching behaviour were found to be possibly correlated more to the differences in the types of combustion systems adopted in the plants than of the type of treated waste material. Therefore, notwithstanding its origin, the results of this study indicate that also HW-I BA could be potentially reused for some specific applications (e.g. as a filler material) in view of its limited release of contaminants. However, the relevant amount of (residual) EC in this type of residue reduces its potential for reutilization in specific civil engineering applications, e.g. as a material for concrete production. Also for this type of BA, hence, further testing would be required to verify the environmental behaviour of the slag under field conditions. Finally, regarding RDF-I BA, the results of this study indicate that differently from the other two types of tested BA samples, owing to its composition and mineralogy, the analysed RDF-I BA showed a potential significant reactivity with CO_2, hence suggesting that by accelerating weathering processes, e.g. contacting the material with pure or diluted CO_2 gas flows (such as incineration flue gas), a further improvement of the leaching behaviour of the material already observed upon natural weathering in terms of Pb, Cu and Zn release may be achieved. However, special attention should be paid to the effects of the treatment on the mobility of oxyanion forming metals.

Annex A

Supporting Information

Contents (Figures A1-A5):

- Experimental TG-MS analysis results for the coarse fraction of the weathered RDF-I BA and HW-I BA samples
- Experimental TG-MS analysis results for the fine fraction of the fresh RDF-I BA and HW-I BA samples
- Experimental TG-MS analysis results for the fine fraction of the weathered RDF-I BA and HW-I BA samples
- Cumulative weight losses (wt. %) of coarse and fine fractions of the fresh and weathered RDF-I BA samples obtained by Loss on Ignition (LOI) standard methods at 550 °C (LOI 550) and at 1000 °C (LOI 1000)
- Cumulative weight losses (wt. %) of coarse and fine fractions of the fresh and weathered HW-I BA samples obtained by Loss on Ignition (LOI) standard methods at 550 °C (LOI 550) and at 1000 °C (LOI 1000)

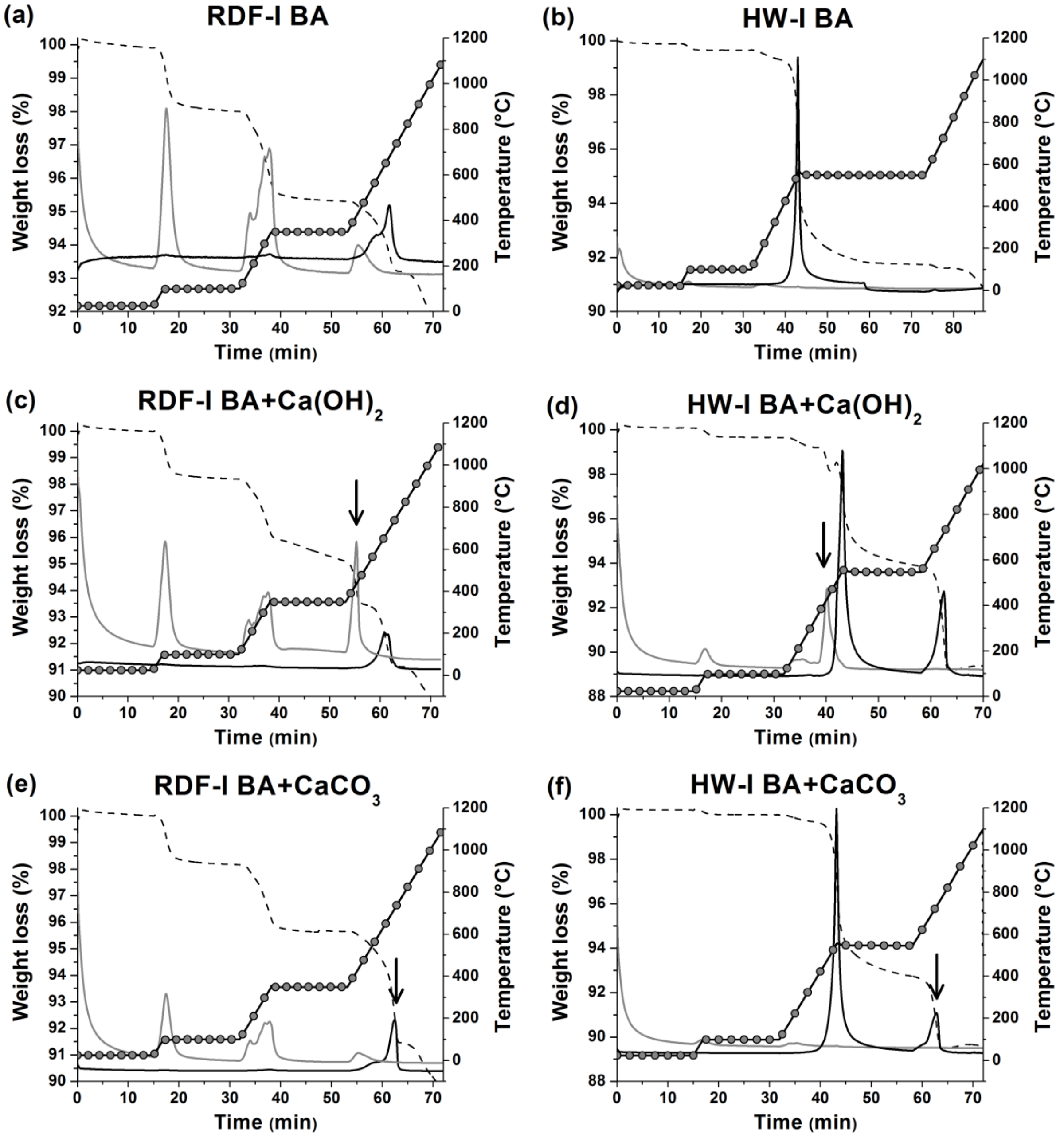

Figure A1. Typical examples of TG-MS analysis results observed for the coarse fraction of the weathered RDF-I BA (graph a) and the HW-I BA (graph b) samples. Results of additional TG-MS experiments with mixtures of BA and Ca(OH)$_2$ (graph c and d) or CaCO$_3$ (graph e and f) are shown in the same figure. The dashed line indicates the weight loss recorded by TG, while the line with circles represents the temperature program applied. Black and grey lines show the relative MS signals for evolved CO$_2$ and H$_2$O, respectively. The arrows included in the graphs indicate the increased mass losses of H$_2$O and CO$_2$ during additional TG-MS experiments with mixtures of BA and Ca(OH)$_2$ (graphs) or CaCO$_3$ (graphs e and f).

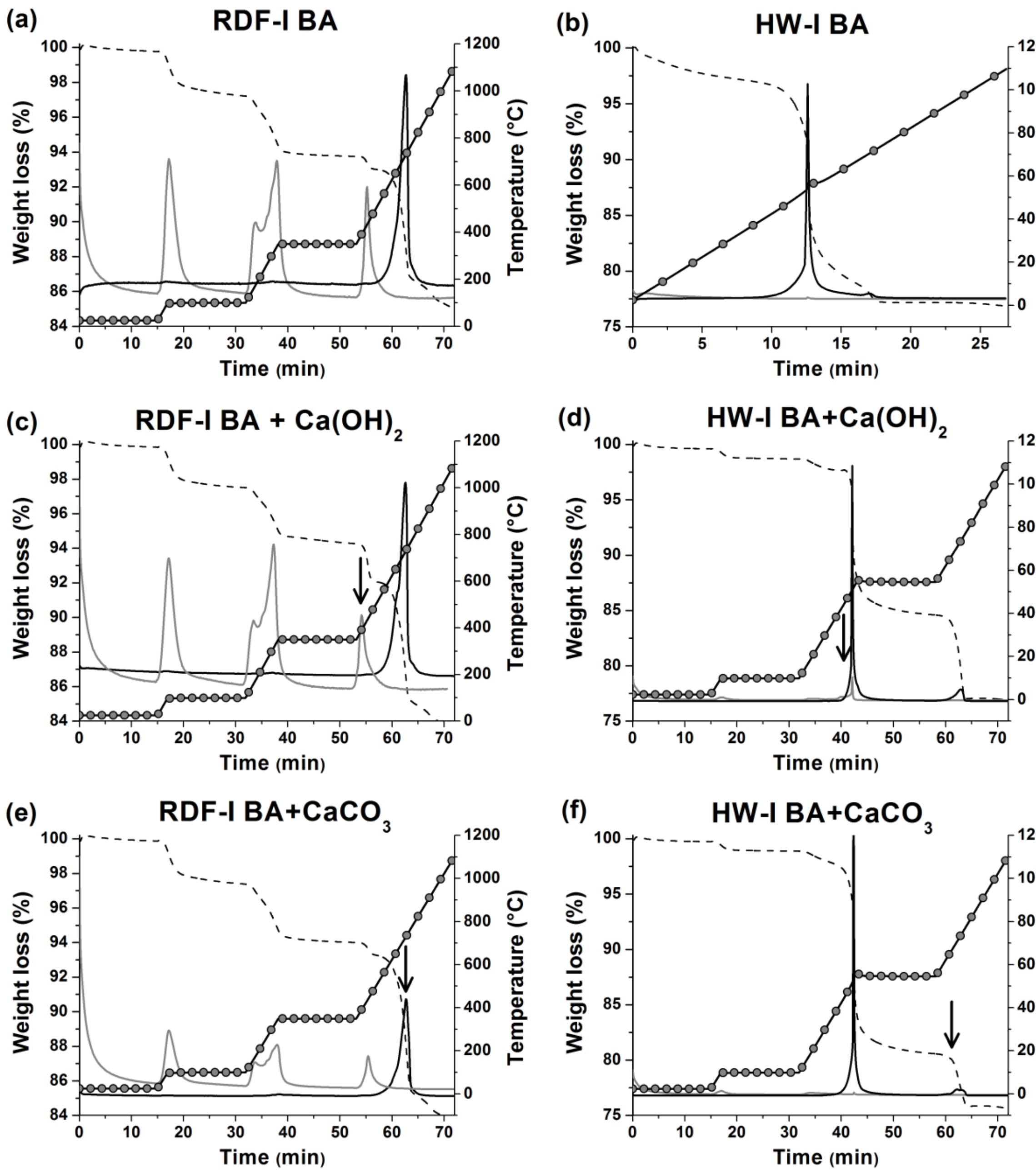

Figure A2. Typical examples of TG-MS analysis results observed for the fine fraction of the fresh RDF-I BA (graph a) and the HW-I BA (graph b) samples. Results of additional TG-MS experiments with mixtures of BA and $Ca(OH)_2$ (graph c and d) or $CaCO_3$ (graph e and f) are shown in the same figure. The dashed line indicates the weight loss recorded by TG, while the line with circles represents the temperature program applied. Black and grey lines show the relative MS signals for evolved CO_2 and H_2O, respectively. The arrows included in the graphs indicate the increased mass losses of H_2O and CO_2 during additional TG-MS experiments with mixtures of BA and $Ca(OH)_2$ (graphs) or $CaCO_3$ (graphs e and f).

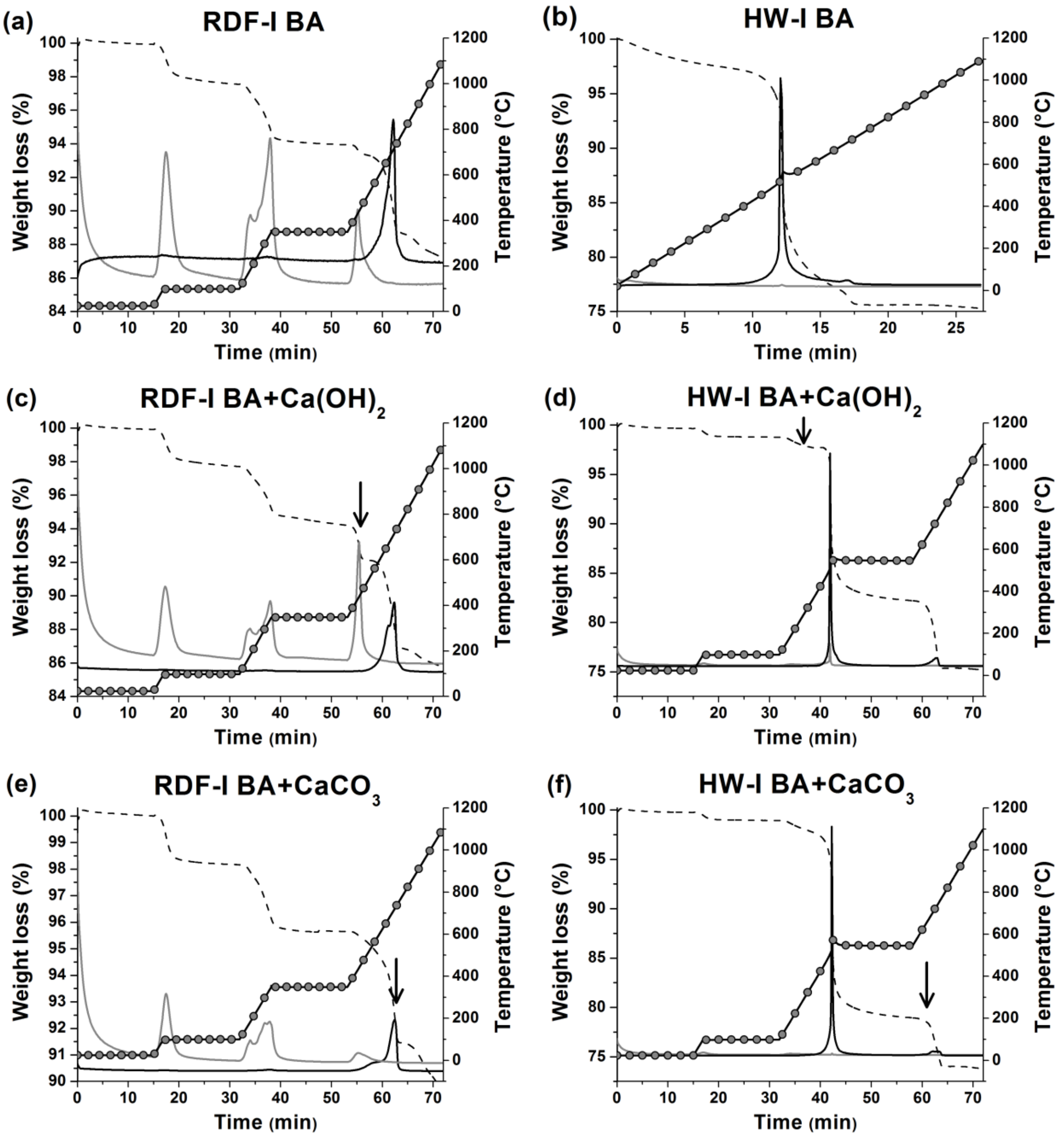

Figure A3. Typical examples of TG-MS analysis results observed for the fine fraction of the weathered RDF-I BA (graph a) and the HW-I BA (graph b) samples. Results of additional TG-MS experiments with mixtures of BA and Ca(OH)$_2$ (graph c and d) or CaCO$_3$ (graph e and f) are shown in the same figure. The dashed line indicates the weight loss recorded by TG, while the line with circles represents the temperature program applied. Black and grey lines show the relative MS signals for evolved CO$_2$ and H$_2$O, respectively. The arrows included in the graphs indicate the increased mass losses of H$_2$O and CO$_2$ during additional TG-MS experiments with mixtures of BA and Ca(OH)$_2$ (graphs) or CaCO$_3$ (graphs e and f).

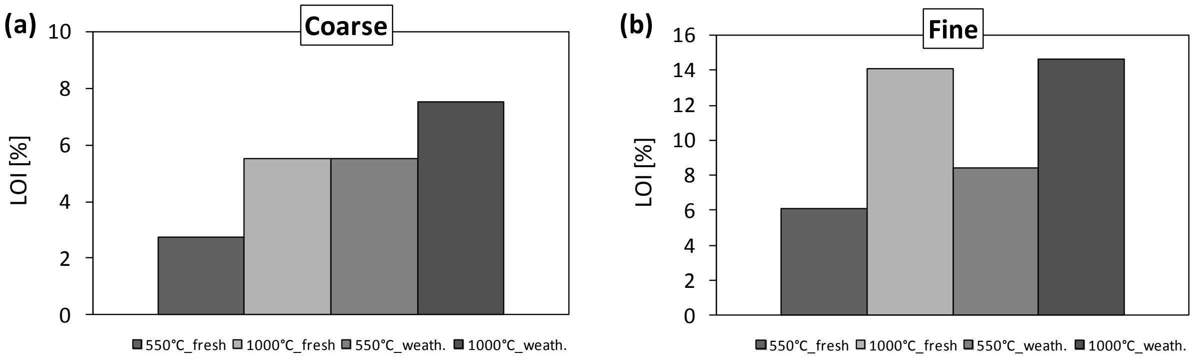

Figure A4. Cumulative weight losses (wt. %) of coarse and fine fractions of the fresh and weathered RDF-I BA samples obtained by Loss on Ignition (LOI) standard methods at 550 °C (LOI 550) and at 1000 °C (LOI 1000)

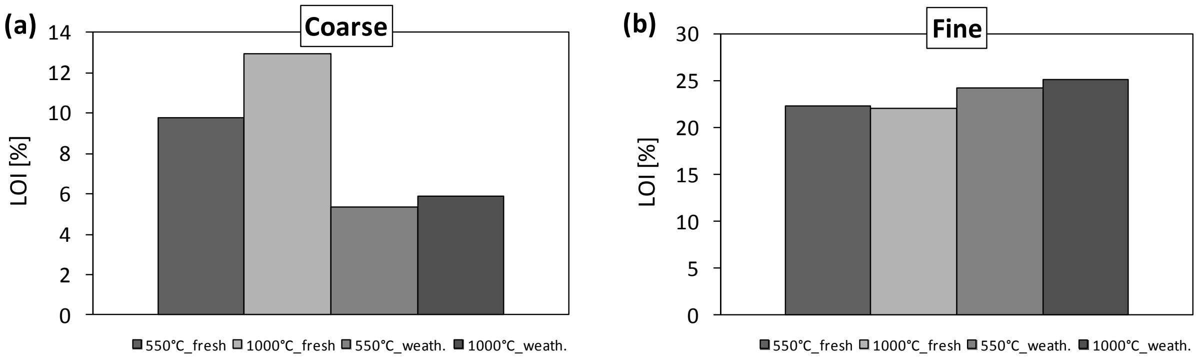

Figure A5. Cumulative weight losses (wt. %) of coarse and fine fractions of the fresh and weathered HW-I BA samples obtained by Loss on Ignition (LOI) standard methods at 550 °C (LOI 550) and at 1000 °C (LOI 1000)

Annex B

Supporting Information

Contents (Figures B1-B7):

- Grain size distribution of the bottom ash (BA) produced in the RDF incineration (RDF-I) and gasification (RDF-G) plants;
- Particle size fractions, i.e. coarse and fine of the RDF-I and RDF-G BA samples;
- XRD patterns for the coarse and fine fractions of the RDF-I BA sample;
- XRD patterns for the coarse and fine fractions of the RDF-G BA sample;
- Leaching test (EN 12457-2) results of major components and trace elements for the coarse and fine fractions of RDF-I BA;
- Leaching test (EN 12457-2) results of major components and trace elements for the coarse and fine fractions of RDF-G BA;

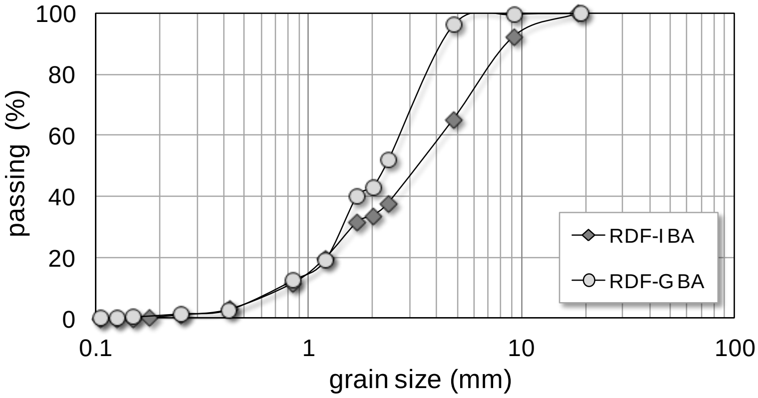

Figure B1. Grain size distribution of the bottom ash (BA) produced in the RDF incineration (RDF-I) and gasification (RDF-G) plants.

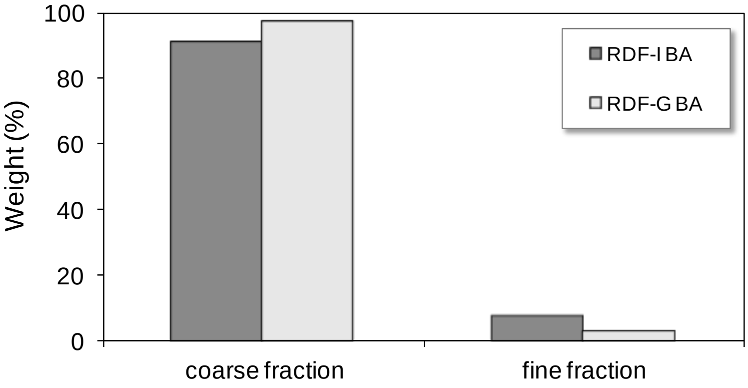

Figure B2. Weight percentages of the coarse (12-0.425 mm) and fine (<0.425 mm) size classes into which the RDF-I and RDF-G BA samples were divided.

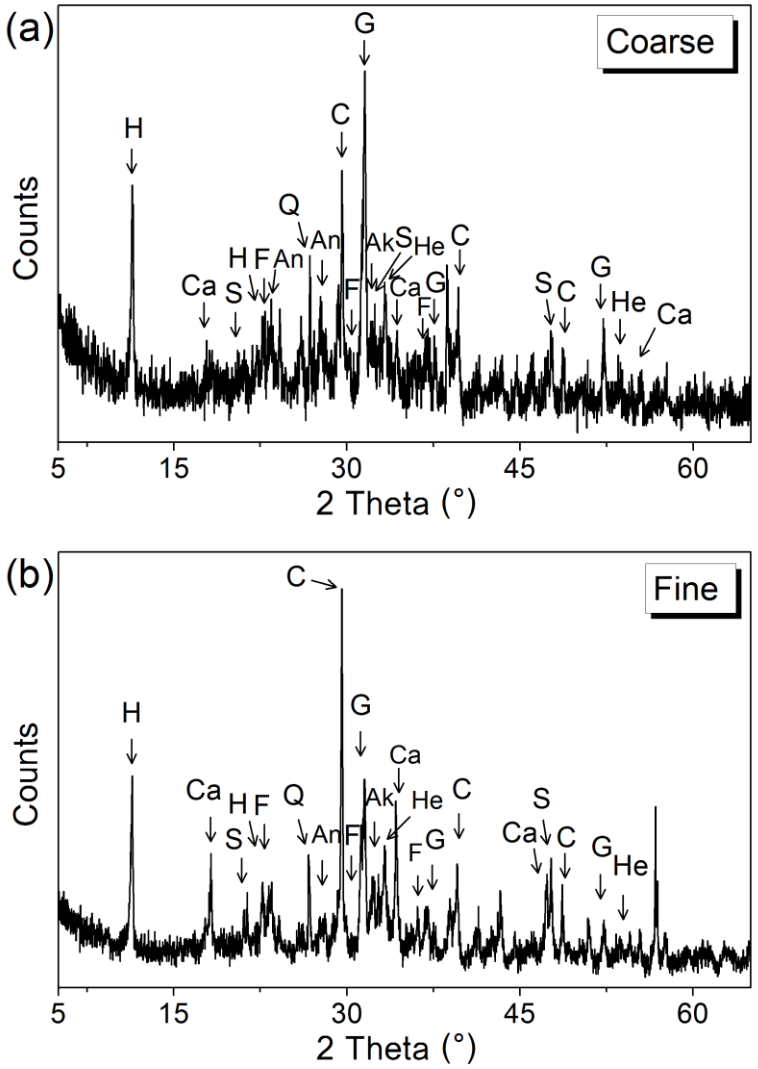

Figure B3. XRD pattern for the coarse (a) and fine (b) fractions of the RDF-I BA sample (H = Hydrocalumite ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$); Ca = Portlandite ($Ca(OH)_2$); S = Di-calcium Silicate (Ca_2SiO_4); F = Forsterite (Mg_2SiO_4); An = Anorthite ($CaAl_2Si_2O_8$); Q = Quartz (SiO_2); G = Gehlenite ($Ca_2Al_2SiO_7$); C = Calcite ($CaCO_3$); Ak = Akermanite ($Ca_2MgSi_2O_7$); He = Hematite (Fe_2O_3)Legend: Ak = Akermanite ($Ca_2MgSi_2O_7$); M = Magnetite (Fe_3O_4)).

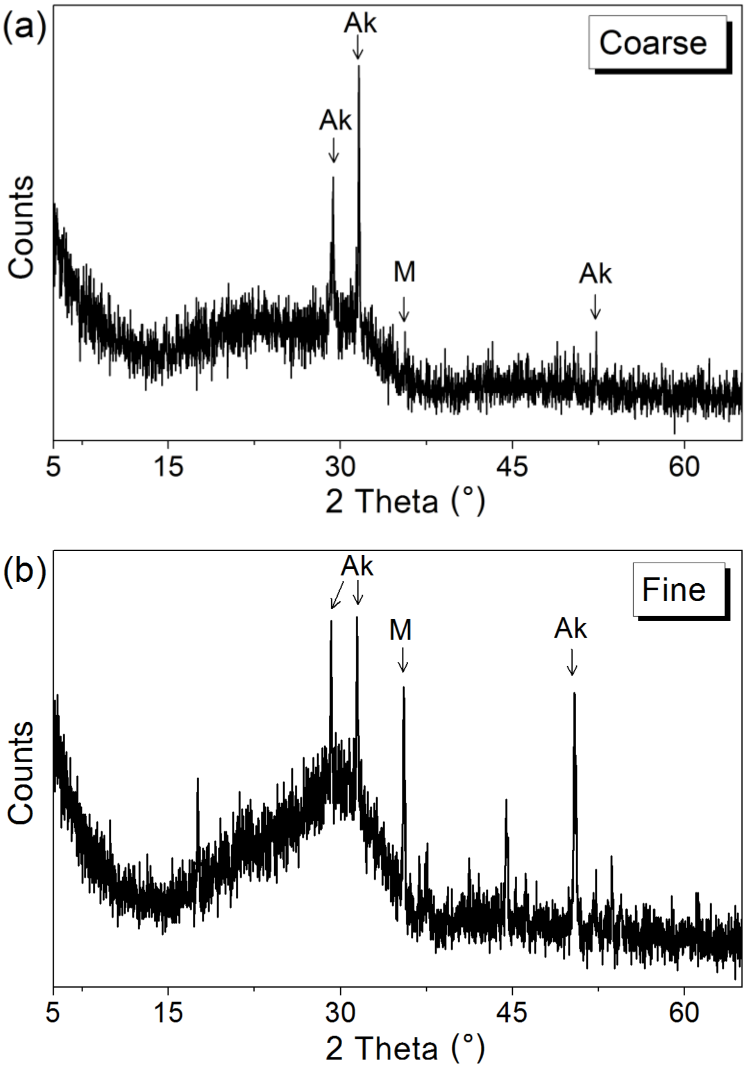

Figure B4. XRD pattern for the coarse (a) and fine (b) fractions of the RDF-G BA sample (Legend: Ak = Akermanite ($Ca_2MgSi_2O_7$); M = Magnetite (Fe_3O_4)).

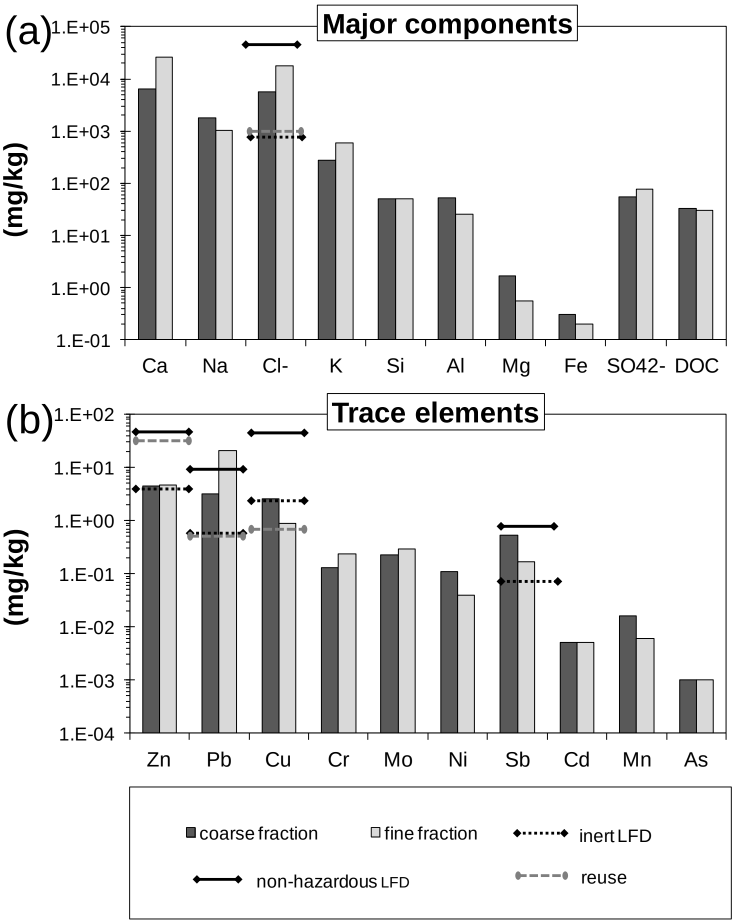

Figure B5. Leaching test (EN 12457-2) results of major components (a) and trace elements (b) for the coarse (pH = 12.4) and fine (pH = 12.6) fractions of RDF-I BA. The acceptance criteria for inert waste landfilling (inert LFD) and non-hazardous waste landfilling (non hazardous LFD), as well as Italian requirements for reuse (reuse) are also reported when relevant.

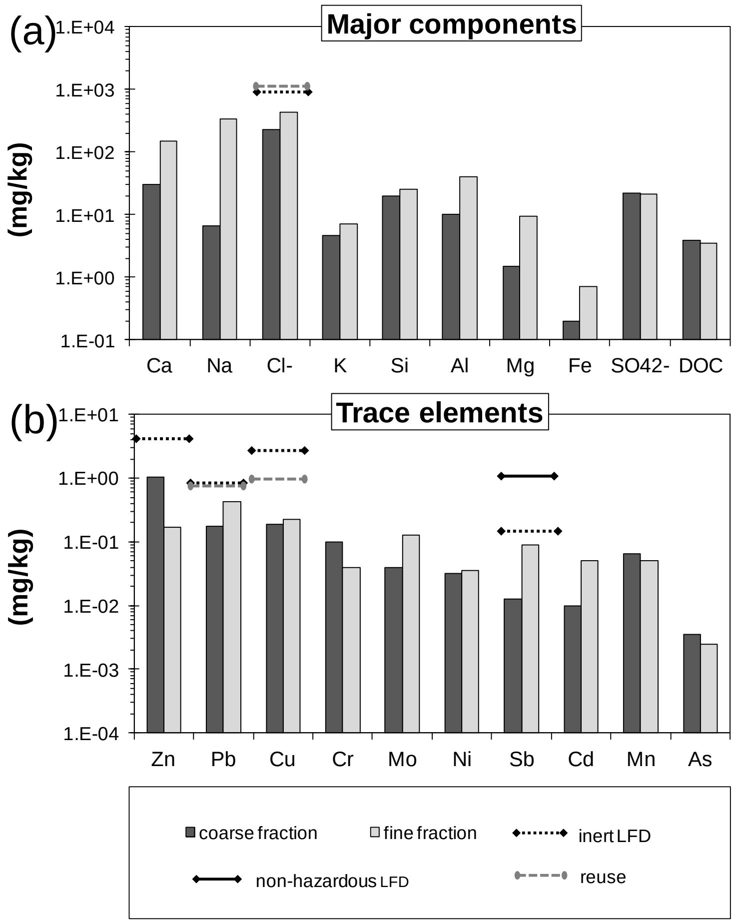

Figure B6. Leaching test (EN 12457-2) results of major components (a) and trace elements (b) for the coarse (pH = 10.3) and fine (pH = 10.4) fractions of RDF-G BA. The acceptance criteria for inert waste landfilling (inert LFD) and non-hazardous waste landfilling (non hazardous LFD), as well as Italian requirements for reuse (reuse) are also reported when relevant.

List of publications

International journals

Rocca, S., van Zomeren, A., Costa, G., Dijkstra, J.J., Comans, R.N.J., Lombardi, F., 2012. Characterisation of major component leaching and buffering capacity of RDF incineration and gasification bottom ash in relation to reuse or disposal scenarios. *Waste Management* 32, pp. 759-768.

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Italian journals

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Rocca, S., Lategano, E., Lombardi, F., 2010. Evaluation and comparison of the energy efficiency of different waste thermal treatment plants. Proceedings of Venice 2010 Third International Symposium on Energy from Biomass and Waste. Venice, Italy 8-11/11/2010. Pubblicazione su CD-ROM.

Rocca, S., van Zomeren, A., Costa, G., Dijkstra, J.J., Comans, R.N.J., Lombardi, F., 2011. Interpretation of loss on ignition measurements of waste incineration bottom ash by thermogravimetry and mass spectrometry of evolved gasses. In: Proceedings of Sardinia 2011 Thirteenth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari (Italy) 3-7 October 2011. Cisa, vol. 1, ISBN/ISSN: 978-88-6265-000-7

Rocca, S., van Zomeren, A., Costa, G., Dijkstra, J.J., Comans, R.N.J., Lombardi, F., 2011. Leaching properties of hospital waste incineration bottom ash in relation to disposal or reuse options. In: Proceedings of Sardinia 2011 Thirteenth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari (Italy) 3-7 October 2011. Cisa, vol. 1, ISBN/ISSN: 978-88-6265-000-7

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