Leena Sivula

Characterisation and Treatment of Waste Incineration Bottom Ash and Leachate

JYVÄSKYLÄN YLIOPISTO

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ABSTRACT

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Waste incineration produces residues including bottom ash that contain metals, sulphate and residual organic material. The major environmental burden of bottom ash is the leachate formed during its disposal. This thesis focuses on the chemical and toxicological characteristics of the bottom ash leachates, anaerobic weathering of bottom ash as well as on the utilisation of microbiological sulphate reduction in the leachate treatment and ash stabilisation. Weathering and leachate characteristics of gasification and grate firing bottom ash were studied with laboratory and landfill lysimeters. In addition, for the grate firing bottom ash, leachate treatment with sulphate reduction and ash stabilisation with sulphide-rich water were studied using laboratory reactors and columns. Three year continuous monitoring of the landfill lysimeters showed that final liquid-solid ratio was 0.4 l/kg (pH 10.8) for the non-quenched gasification ash and 1.0 l/kg (pH 8.4) for the quenched grate ash. Arsenic leaching was higher from the gasification ash than from the grate ash, irrespective of similar concentrations in the fresh ash. Both grate and gasification ash leachates showed a pH dependent toxicity for a period of two and three years after disposal, respectively. Biodegradation of residual organic carbon under anaerobic conditions carbonated the grate ash and decreased the leachate pH from 9 to 7.7, while the pH of gasification ash leachate remained high (> 12). Treatment of grate ash leachate through sulphate reduction removed 65 % of the sulphate and decreased concentrations of Ba, Ca, Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, Sr, and Zn. In the stabilisation experiment, use of sulphide-rich water improved the retention of Ca, Cu, Pb, S, and Zn in the grate ash. In conclusion, the initial moisture content and the amount of residual carbon in the fresh ash are the key parameters, which could be adjusted to decrease the pH and therefore the toxicity of ash and leachates during the initial phase of landfilling. In addition, anaerobic sulphate reduction can be utilised to treat the leachate and to mitigate the metal release from the grate bottom ash.

Keywords: Gasification; landfilling; leachate; monitoring; stabilisation; toxicity.

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LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I–V.

I have planned all the studies with my supervisor and co-authors. I did a major part of the experimental work in the papers II–V and participated in experiments of the paper I. I wrote the first drafts of all the articles, which were then completed with my supervisor and co-authors.

I   Sivula L., Sormunen K. & Rintala J. 2011. Leachate formation and characteristics from gasification and grate firing bottom ash under landfill conditions. *Waste Management*. In press.

II   Sivula L., Oikari A. & Rintala J. 2011. Toxicity of waste gasification bottom ash leachate. *Waste Management*. Accepted.

III   Sivula L., Ilander A., Väisänen A. & Rintala J. 2010. Weathering of gasification and grate bottom ash in anaerobic conditions. *Journal of Hazardous materials* 174: 344–351.

IV   Sivula L., Väisänen A. & Rintala J. 2007. Treatment of leachate from MSWI bottom ash landfilling with anaerobic sulphate-reducing process. *Water Research* 41: 835–841.

V   Sivula L., Väisänen A. & Rintala J. 2008. Stabilisation of MSWI bottom ash with sulphide-rich anaerobic effluent. *Chemosphere* 71: 1–9.

ABBREVIATIONS

APC	air pollution control
BA	bottom ash
BOD	biological oxygen demand
CHP	combined heat and power
COD	chemical oxygen demand
DOC	dissolved organic carbon
d.w.	dry weight
EC	effective concentration
EROD	ethoxyresorufin-o-deethylase
FB	fluid bed
FBC	fluid bed combustion
GA	gasification
GR	grate firing
IC	ineffective concentration
ICP	inductively coupled plasma
LID	lowest ineffective dilution
LS	liquid to solid
MSW	municipal solid waste
MSWI	municipal solid waste incineration
N_{tot}	total nitrogen
OES	optical emission spectrometer
PAH	polyaromatic hydrocarbons
PCB	polychlorinated biphenyls
PCDD	polychlorinated dibenzodioxins
PCDF	polychlorinated dibenzofurans
RDF	refuse derived fuel
SE	sequential extraction
SI	saturation index
SRB	sulphate reducing bacteria
TOC	total organic carbon
TS	total solids
UASB	upflow anaerobic sludge blanket
VS	volatile solids
WTE	waste to energy

1 INTRODUCTION

1.1 Thermal treatment of waste

Utilisation of different waste to energy (WTE) processes is increasing as an alternative to landfill disposal. Globally, capacity of WTE facilities was 170 million tons in the year 2007 with a growth rate of 4 million tons per year (2000–2007) (Castaldi & Themelis 2010). Within the EU area 101 kg/person of municipal solid waste (MSW) was incinerated in 2009 compared to 65 kg/person during 1995 (Eurostat 2011). During the same time period deposit to landfills decreased from 296 kg to 191 kg/person/year (Eurostat 2011). This has been the aim of the EU waste framework directive, which includes the five-step waste hierarchy: prevention, reuse, recycle, recovery and disposal (European Parliament and The Council 2006). Thermal waste treatment can be used to recover the energy content of such waste materials, which cannot otherwise be reused or recycled. In addition, thermal treatment of waste serves other purposes such as hygienisation and volume reduction. Besides heat, thermal treatment produces flue gases and solid residues (Fig. 1).

Grate firing (GR) is the most common thermal waste treatment technology with increasing installation capacity (Castaldi & Themelis 2010). The major advantage of the process is that it can handle heterogeneous waste material both in terms of particle size and energy content. Alongside grate firing, other conversion processes such as fluidised bed combustion (FBC) and gasification for energy recovery are emerging. Advantages of FBC are flexibility with fuel heating value, efficiency of electricity production and reduction of pollutants emitted with flue gas (Ravelli et al. 2008). Utilising fluid bed (FB) for waste gasification has gained interest as the product gas can be utilised in various industrial processes as an energy source or as a raw material (Belgiorno et al. 2003, Malkow 2004, Yassin et al. 2009). Common for FBC and for FB gasification is that waste has to be industrially processed to refuse derived fuel (RDF) before utilisation. Production of RDF includes processes such as separation, drying and particle size reduction (Caputo & Pelagagge 2002). Regardless of the
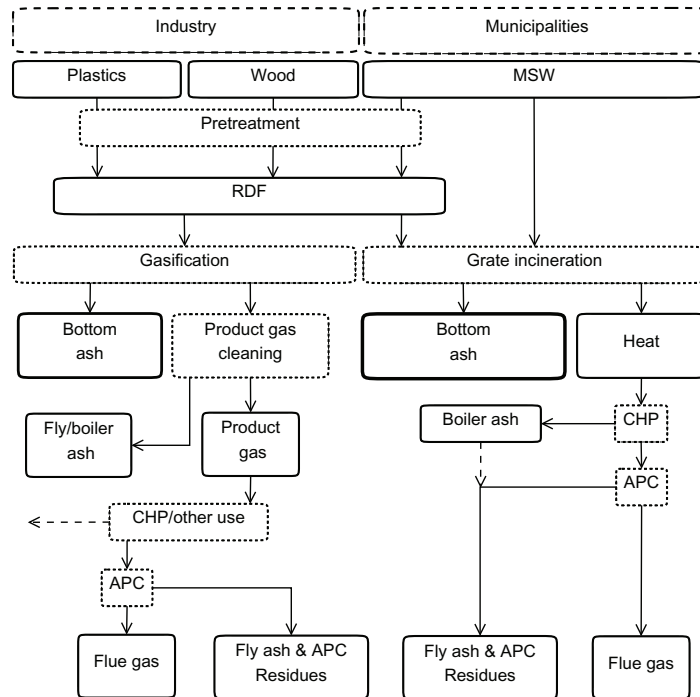
FIGURE 1 Material flows for the waste grate firing and for the waste gasification processes in the present study.

combustion technology residual material is produced in several stages of the thermal process (Fig. 1). The residues consist of inorganic material, residual organic material and materials added to process during combustion or flue gas cleaning.

1.2 Residues from thermal treatment

The residues from thermal treatment can be divided into three main types; bottom ash, fly ash and other air pollution control (APC) residues (Chandler et al. 1997). However, types and quantities of solid residues formed vary according to the waste composition, thermal process, flue gas cleaning technology and residue handling at facility. This thesis focuses on the bottom ash, which is usually considered non-hazardous waste and can be landfilled or utilised as such or with modest pre-treatment. Although, bottom ash is not the most hazardous residue, it is produced in large quantities, which poses challenges for its disposal. In the grate firing, bottom ash typically forms 85–90 % by weight of the incineration residues, which is 25–45 % of the mass of the incinerated municipal solid waste (MSW) and about 10 % of its volume (Hjelmar 1996). Process parameters affecting the quality of the grate bottom ash are furnace configuration, combustion temperature, retention time and

quenching process (Meima & Comans 1997a, Rendek et al. 2007). Fresh grate firing bottom ash has a pH value of 12 or higher. The main factor affecting the final pH is quenching process. The longer the ash is in contact with water the lower the pH becomes (Marchese & Genon 2010). In addition to the combustion process, the major factor affecting composition of residues is the composition of waste fuel used. Composition of the fuel depends on the waste composition, collection system, source separation and pre-treatment methods utilised (Rendek et al. 2007).

In contrast to grate firing, the main residue from FBC is fly ash. For instance, from fluid bed gasification 40–50 % of residues by mass is fly ash, while bottom ash forms 20–36 % (Belgiorno et al. 2003). However, the amount of bottom ash is 2–9 % of the original mass of waste material in the fluid bed gasification (Belgiorno et al. 2003). In fluid bed gasification, a significant share of the bottom ash, is bed materials and additives used to remove impurities already in the boiler (Raskin et al. 2002). In FBC, flue gas goes from the boiler to the pre-cooling chamber, where part of the metals and other impurities are solidified from the flue gas before going to the heat exchangers. In the gasification process, removal of impurities from product gas can be done in the boiler with primary methods or before the turbine with secondary methods such as filtration. The use of primary methods such as use of proper operating parameters, additives or catalysts, has begged the question, whether the removed tars, alkalines and heavy metals are concentrated in increasing amounts in the gasifier bottom ash (Arena et al. 2010).

The partitioning of elements between bottom ash, fly ash and flue gas, depends on combustion processes, temperatures in the different phases of a process and waste composition (Pedersen et al. 2009). In the grate firing, over 80 % of the many main elements (Fe, P, Al, Si, Ca, and Na) and some of the toxic elements (Cr, Co, Mg, Ni, Mo) remain in the bottom ash (Belevi & Moench 2000). Also a high share of arsenic (69–76 %) remains in the bottom ash. In contrast, 90 % of Cd and 100 % of Hg and 88 % of Sb are volatilised and finally concentrated into APC residues (Belevi & Moench 2000). It has been found that the chemical composition of waste can affect partitioning of elements. For example Cl present in waste as HCl is mainly transferred to gaseous phase, while Cl present as salts (e.g. NaCl) mostly remains in the bottom ash (Pedersen et al. 2009). In addition, waste composition can affect partitioning of toxic elements such as Pb and Zn, volatilisation of which have been observed to increase with increasing amount of Cl in the waste (Pedersen et al. 2009).

In FBC, the bulk of solid residues consist of fly ash and APC residues. However, based on the previous research on sludge combustion, low volatility heavy metals such as Ni, Cr, Cu and Zn mainly remain in the bottom ash (Toledo et al. 2005). Similar to grate firing, in FBC, waste composition has been shown to affect partitioning. During waste FBC toxic elements have been found to associate with Ca and Fe, whose concentrations in the cyclone ash correlate with the concentrations of As, Cd, Co and Cu (Karlfeldt Fedje et al. 2010). In

addition, chlorine content of waste has been observed to affect partitioning of Pb during sludge FBC (Toledo et al. 2005).

1.3 Characterisation of residues

The characterisation of waste incineration residues can be done with analyses of chemical composition, with leaching studies and with toxicological assays. The main environmental burden from the waste incineration residues during disposal is the leachate formed as rainwater infiltrates through it (Sabbas et al. 2003). The factors affecting leachate composition include volume of infiltrating water, flow rate, pH and mineral composition of the ash (Kosson et al. 1996, Meima & Comans 1997b).

An assessment of total elemental and mineral composition along with binding mechanisms can be used to evaluate the environmental and human health risks posed by the residues. In addition, sequential extraction can be utilised to determine the type and strength of binding of the elements into ash. In order to ascertain how firmly an element is bound to the matrix, a series of extractions under varying combinations of oxidising/reducing conditions and pH conditions can be used. Sequential extraction provides information on the type of binding and, therefore, on the release potential of elements. Sequential extraction has been criticised as giving information only on present status and not taking into account mineral changes (Chandler et al. 1997). However, sequential extraction can be performed with relative ease in different stages of weathering similarly to the mineralogical characterisation. When performed carefully by taking into account the material heterogeneity (with large enough sample size), sequential extraction gives useful information on total and available amount of elements, as well as relative availabilities of different elements within ash (Bruder-Hubscher et al. 2002).

With sequential extraction five fractions are usually obtained. They are presented here from the most mobile/available fraction to the most resilient fraction (Bruder-Hubscher et al. 2002, Rao et al. 2008).

1. Exchangeable or non-specifically sorbed fraction, where adsorbed elements are retained on the solid surface by relatively weak electrostatic interaction. These elements can be released for example by ion-exchange (pH 7).
2. Carbonate bound fraction, which is soluble under acidic conditions. These elements can be extracted with acetic acid (pH 5).
3. Iron- and manganese-oxides bound fraction. These elements are available under reducing conditions obtained with the addition of hydroxylammonium chloride (pH 2).
4. Organic matter and sulphides bound fraction. Compounds bound to humic and fulvic acids and to sulphide. Elements bound to this

fraction can be extracted under oxidative conditions with e.g hydrogen peroxid combined with heating or microwave oven treatment (pH 2).

5. Residual fraction containing silicates and other minerals which retain elements in their crystalline structure. These can be extracted using strong acids such as mixture of hydrofluoric and perchloric acids.

To assess the release of contaminants from waste materials, a variety of leaching tests have been developed. In the standardised laboratory batch tests, leaching condition such as time and LS-ratio are defined to produce comparable data (SFS-EN 12457-4 2002, SFS-EN 12457-1 2002). The purpose of the batch tests is usually to obtain equilibrium or near-equilibrium conditions by agitating the sample and liquid. The laboratory column tests such as NEN 7343 usually simulate field conditions including flow rate and contact time. The laboratory column tests usually differ from real disposal conditions as they do not take into account changes in flow rate, temperature, or prevailing reducing conditions (van der Sloot et al. 1996). In the landfill-scale lysimeter effects of such parameters as redox-potential, ambient temperature and rainfall on leaching can be studied (Hjelmar 1996, Johnson et al. 1999, Freyssinet et al. 2002).

Broadening of the waste material assessment with biological assays has been encouraged (Moser & Römbke 2009). It has been shown that the chemical characterisation of waste does not necessarily reveal the toxic properties of waste material (Lapa et al. 2002). Therefore, ecotoxicological assessment is needed. The toxicological characteristics can be assessed with a variety of standardised toxicity tests. As the effects on different organisms may vary, a test battery, covering species and function at several trophic levels in the exposed environment, should be selected. The use of aquatic test organisms is justified, because the main environmental exposure pathway is probably the leachate. Toxicity assays with aquatic organisms include inhibition of bioluminescence of bacteria, growth of the green alga, and the decreased mobility of water fleas, among others. In addition, biomarkers on a cellular and molecular level have been used to study toxicity of MSWI bottom ash (Radetski et al. 2004, Feng et al. 2007).

Biomarkers can be used detect the origin of toxicity, when it is specific to certain groups of contaminants. The induced activity of ethoxyresorufin-O-deethylase (EROD) is a specific biomarker indicating exposure to a set of polycyclic aromatic hydrocarbons (PAH) and related planar aromatic compounds such as dioxins (PCDD) and furans (PCDF) (Safe 1990). Therefore, it can be utilised to screen whether organic contaminants are present in an environmental sample. The EROD assay is based on the receptor mediated induction of cytochrome P450 dependent mono-oxygenases, especially of the subfamily CYP1A (Safe 1990). The useful aspect of CYP1A is that, the enzyme concentration increases with increasing concentration of contaminant and it can be used to describe dose-response relation (Safe 1990).

1.4   Chemical and toxicological characteristics of bottom ash

The fresh waste grate firing bottom ash is mainly inorganic material, consisting of oxides, hydroxides and salts of Al, Ca, K and Na (Kosson et al. 1996, Meima & Comans 1999). Solids formed in the high temperature are mineral assemblages, which transform through the weathering process to naturally occurring secondary minerals. Bottom ash particles consist of melt products (55–85 %) and non-combusted material (15–45 %) (Meima & Comans 1997a, Wei et al. 2011). Melt products include glasses, silicate minerals, melilite (rich in Fe, and Ca), scapolite (rich in Ca and Na) and oxide minerals (e.g. lime, Fe-oxides) (Meima & Comans 1997a). Non-combusted material is glass, soil minerals, metals and organic material (Meima & Comans 1997a). The residual organic carbon content is 0.5–4.7 % for the grate firing bottom ash and 0.5 % for the gasification bottom ash (Raskin et al. 2002, Zhang et al. 2004). There seems to be very little extant knowledge on characteristics of fluid bed gasification residues. Raskin et al. (2002) describes on general level bottom ash of fluid bed gasification to contain sand, limestone and only minor amounts (< 1000 ppm) of heavy metals. In addition, bottom ash from a gasification process with ash vitrification has been shown to have an elevated concentration of Cu, Cr and Ni, which can hinder its utilisation (Gori et al. 2011).

When the environmental effects of ash are assessed, the inorganic fraction is interesting as it contains potentially harmful elements including heavy metals (e.g. Cu, Cd), oxyanions (e.g. As and Mo) and soluble salts (e.g. sulphate and chloride) (Meima & Comans 1999, Sabbas et al. 2003, Cornelis et al. 2008). Inorganic contaminants can cause a risk to environment when they are enriched in the ash compared to concentrations found in lithosphere (Chandler et al. 1997). However, the release potential of the elements has to be considered. Release of the elements in the alkaline ash may differ from those of natural mineral assemblages or those of other waste materials such as acidic mining wastes. There are three main models describing the leaching behaviour of the elements: availability limited, concentration limited (kinetic) and equilibrium limited (Kirby & Rimstidt 1994). Availability limited leaching is typical for salts of Na, K, and Cl. In an availability limited system, ash is exhausted from the element and solubility or other factors do not limit the leaching process. In a kinetically limited system, the rate of mass transfer from solid to liquid (dissolution rate) limits the leaching process. Kinetics are important, when the contact time between solid and liquid is shorter than the time needed for equilibrium to be established. In an equilibrium controlled system, dissolution/precipitation equilibrium or sorption equilibrium determines the concentration of an element in leachate.

The bulk of residual organic carbon in the grate bottom ash consists of carbohydrates (0.6 % of ash TS), amino acids (0.6 %) and hexosamines (0.1 %) (Zhang et al. 2004). In addition, grate bottom ash contains low (< 100 µg/kg) concentration of carboxylic acids, steroids, n-alkanes, phthalates and PAH

compounds (Dugenest et al. 1999). Other organic contaminants detected include PCB, PCDD and PCDF (Matsui et al. 2003). When the above mentioned organic contaminants are leached, they can have direct toxic effects in the aquatic environment. In addition, residual organic carbon can affect toxicity indirectly. Hydrophobic organic contaminants like PAH compounds and some elements like Cu are known to be associated with organic carbon (Meima & Comans 1999, Comans & Roskam 2002, Postma et al. 2009). The presence of dissolved organic carbon (DOC) in leachate can lower the bioavailability of the hydrophobic organic contaminants (Haitzer et al. 1998, Akkanen & Kukkonen 2003). Therefore, the total organic carbon (TOC) and DOC content in a leachate can modify its toxicity.

Organic molecules of relatively high molecular weight such as PAH-compounds and polychlorinated biphenyls (PCB) are likely to concentrate in bottom ash rather than to fly ash (Wheatley & Sadhra 2004). In the grate firing bottom ash PAH compounds have been detected in the concentration range of 130–210 µg/g (Dugenest et al. 1999). The most common PAH-compounds in the grate firing bottom ash are phenantere (25.5 %), fluoranthene (21.1 %) and pyrene (16.6 %). The same low molecular weight PAH-compounds (with four rings or less) have been detected from the bottom ash leachate (Liu et al. 2008). On the other hand, dioxins and furans are known to concentrate in fly ash during grate firing (Wang et al. 2010). No information on the PCDD/F content of gasification ash was found. However, some indication of PCDD/F content can give the Cl- concentration of incinerated waste and operating temperature, which have been shown to correlate with the PCDD/F concentration of the residue (Wang et al. 2008).

1.5 Utilisation, pre-treatment and disposal of bottom ash

Globally, the bottom ash is most commonly utilised as an aggregate in the concrete, road basements and as cement clinker (Lam et al. 2010). Applications used on a smaller scale or under investigation include ceramic tiles, zeolite production and use as a binding or stabilizing agent (Reijnders 2005, Lam et al. 2010). Bottom ash is a heterogeneous material containing corrosive and toxic elements, which restrict its utilisation. Pre-treatment such as screening into size classes is often needed before it can be utilised (Wiles 1996, Forteza et al. 2004, Reijnders 2005). Although, bottom ash is not usually considered hazardous the cost of pre-treatment to meet quality needed for utilisation can be high and landfill disposal remains as the only option. However, also the need to reduce the leaching of contaminants from bottom ash landfills has been recognised (Sabbas et al. 2003).

The amount of released contaminants can be affected with pre-treatment before landfilling, with operational and design measures of active landfill operation and with measures carried out during passive phase of landfilling

(Sabbas et al. 2003). The amount of the contaminants released during disposal can be affected in three principle ways (Sabbas et al. 2003):

1. The total amount of the contaminants can be reduced with pre-treatment such as water extraction.
2. The available amount of the contaminants can be affected before, or during, operational landfilling. The immobilisation methods include chemical and thermal treatments, which stabilise ash over long period of time.
3. The release rate of contaminants can be reduced with physical stabilisation methods. Delayed release shares the environmental burden from elements released over a longer period of time.

Pre-treatment methods used to decrease concentration of contaminants can be divided into active and passive. The most commonly used active methods include screening, magnetic or gravity separation of metals, extraction of metals with water or other solvent and screening to size fractions (Astrup 2007). A commonly used passive method is natural weathering. Ash is stored in piles in ambient conditions from 3 to 6 months to decrease leachate pH and leaching of inorganic contaminants (Chimenos et al. 2000, Astrup 2007). Thermal methods, affecting availability, include vitrification, sintering, calcination, co-smelting with glass and artificial stone formation (Reijnders 2005). The physical stabilisation methods include; stabilisation with cement or self-hardening with water. The chemical stabilisation methods published include phosphate, sulphide and thiourea addition (Reijnders 2005). Youcai et al. (2002) used natriumsulphide successfully to stabilise Cd and Pb in fly ash. Alternatively, sulphide from biological anaerobic processes could be used.

1.6 Weathering of bottom ash during disposal

Weathering is a naturally occurring process, which changes the composition of ash and leachate during pre-treatment or disposal. Weathering is a series of geochemical processes caused by atmospheric gases and rain, leading to decreased leaching of contaminants and stabilised pH. Carbon dioxide absorption is the most important weathering process (Meima & Comans 1997b). The carbonation process decreases the initially high pH of ash through changes in the mineral composition of ash, towards the equilibrium of 8.3 (Meima & Comans 1997b). This in turn, stabilises the inorganic contaminants in ash. Carbon dioxide can be atmospheric or derived from the biodegradation of residual carbon in ash. The role of biodegradation is speculated to be significant (Belevi et al. 1992, Zevenbergen & Comans 1994, Meima & Comans 1997a, Rendek et al. 2007). However, the effect of anaerobic conditions on biodegradation and weathering is a less studied topic. It is known that, in a

large ash heap the diffusion of atmospheric gases is limited to the surface layer (Freyssinet et al. 2002).

Bottom ash is composed of metastable solids which transform into naturally occurring secondary minerals due to the weathering process. Three weathering stages for bottom ash have been identified. In the first stage, dry bottom ash contacts water and hydrolysis reactions of major oxides (Ca, Al, Na, K) takes place resulting in a high pH (> 12) of leachate. In the second stage, pH decreases to 10. During the second stage, ash is not yet carbonated and the main minerals present are ettringite ($Ca_6Al_2(SO_4^3(OH)_{12} \cdot 26H_2O)$), gibbsite ($Al(OH)_3$), and gypsum ($CaSO_4 \cdot 2H_2O$). Secondary minerals, such as Fe/Al hydroxides, hydrous aluminosilicates and zeolites, begin to precipitate. Soluble salts leach out rapidly and residual organic matter biodegrades, which may create reducing conditions (Meima & Comans 1997b). At the third stage, the pH of bottom ash further decreases to 8–8.5 due to absorption of CO_2. Neoformation of Fe/Al-hydroxides and -oxides and hydrous aluminosilicates continues. Hydrous aluminosilicates are an intermediate product in the transformation of glasses to clay minerals of which illite has been recognised as the final weathering product of bottom ash (Meima & Comans 1997a).

The main chemical and physical processes of weathering are: complexation, precipitation, dissolution, sorption and redox potential changes (Meima & Comans 1997a). Complexation processes include hydrolysis, complexation with carbonates and complexation with DOC. Hydrolysis is controlled by leachate pH, while absorption of CO_2 can limit cabonate formation (Meima & Comans 1997a). Precipitation and dissolution processes control bottom ash pH, which in turn, control the leaching of major and trace elements. Sorption processes control leaching of Fe and Al-hydroxides and oxides, hydrousaluminosilicate and calcite. Especially, the sorption of trace elements to neoformed Fe/Al-minerals affects leachate composition (Meima & Comans 1997a). In fresh bottom ash, redox conditions are oxidising. However, during disposal, biodegradation or presence of reduced mineral phases can decrease the redox potential. Low redox potentials have been observed in the bottom ash leachates (Johansson & van Bavel 2003, Meima & Comans 1997b). Redox potential affects mobility of trace elements directly by changing the oxidation state, and indirectly by changing the amount of redox sensitive metal surfaces. Decrease of redox potential have been observed to increase the leaching of Fe and to decrease the leaching of Cu, Cr, As, and V (Meima & Comans 1997a).

1.7 Bottom ash and leachate treatment with sulphate reduction

The biological sulphate reduction can be utilised to simultaneously remove sulphate, organic carbon and toxic elements present in the bottom ash leachate. In the sulphate-reducing process under anaerobic conditions, sulphate-reducing bacteria (SRB) use sulphate as an electron acceptor in a process where hydrogen or organic compounds are oxidised and sulphate simultaneously is reduced to

sulphide (Muyzer & Stams 2008). In general form, degradation reaction can be described as a reduction-reaction, wherein organic carbon is the electron donor and sulphate is the terminal elector acceptor (1).

$$2CH_2 + SO_4^{-2} \rightarrow 2HCO_3 + H_2S \qquad (1)$$

Therefore, sulphate reduction produces hydrogen sulphide and bicarbonate ions (Widdel 1988). Sulphide formed in reduction reaction can react with dissolved divalent metal cations and with some metals or metalloids of the other oxidation states (e.g. Ag_2S, As_2S_3, Sb_2S_3) to form sulphide compounds with a low solubility, whereas sulphides of e.g. alkaline earth metals are less stable in the presence of water.

In theory, when the ratio of chemical oxygen demand (COD) and sulphate in waste water is greater than 0.67, all of the sulphate can be reduced to sulphide by SRB (Widdel 1988). Bottom ash leachate contains some organic carbon, but the amount is small compared to the sulphate concentration, and therefore, addition of a source of organic carbon may be necessary in order to remove all the sulphate. SRBs are divided into two groups: heterotrophic and autotrophic, both of which utilise sulphate as an electron acceptor. Heterotrophic SRB use organic compounds as substrate whereas autotrophic SRB use CO_2 as carbon source and oxidise H_2 to obtain electrons (Liamleam & Annachhatre 2007). Heterotrophic SRB oxidise simple organic fermentation products of the anaerobic degradation. The heterotrophic SRB can be divided in to two groups, those which can completely degrade simple organic compounds such as ethanol, formate, lactate and pyruvate to carbon dioxide, and to those which can degrade the same compounds incompletely to acetate (Muyzer & Stams 2008). In addition, SRBs able to grow on the short chain fatty acids (e.g. acetate), on long chain fatty acids and on aromatic compounds (phenols and benzoate) have been found (Muyzer & Stams 2008).

Previously, the treatment of ash leachates has been studied for example by constructed wetlands and by reverse osmosis (Ye et al. 2001, Ushkikoshi et al. 2002). On the other hand, sulphate reduction has been used to remove metals from mining waste waters and groundwater (e.g. Lens & Hulshoff Pol 2000). In contrast to acidic mining waste waters, which have high concentrations (hundreds of milligrams per litre) of a few elements (e.g. Cu, Zn), ash leachates are alkaline and contain relatively low concentrations of many trace elements. In addition, sulphate-reduction has been studied in treatment of landfill leachates, which resemble ash leachates as both contain relatively low concentrations of metals. However, landfill leachates are usually high strength e.g. they contain high amounts of organic biodegradable compounds. The sulphate-reducing process has been shown to remove Cu, Mn, Ni and Zn present in low concentration (> 100 ppm) from landfill leachate (Nedwell & Reynolds 1996). However, the same removal efficiency was obtained with methanogenic reactor, leaving the doubt, whether the actual removal mechanism was precipitation of metal sulphides or sorption to biomass.

In addition to toxic elements, bottom ash leachate contains a high concentration of sulphate. If sulphate is not removed, it can form hydrogen sulphide naturally under anaerobic conditions. On the other hand, surplus sulphide also is produced in the sulphate reducing leachate treatment when the amount of sulphate and organic carbon are high compared to the concentration of precipitating elements. The hydrogen sulphide formed either naturally or during the sulphate reducing process has several harmful characteristics; it is toxic and causes corrosion and odour problems (Widdel 1988, Liamleam & Annachhatre 2007). Therefore, both sulphate and sulphide should be removed. One option is the removal of sulphate with the sulphate reduction process followed by partial oxidation of sulphide to elemental sulphur (Hulshoff Pol et al. 1998). In the present study, possibility to utilise the sulphide, formed in sulphate reduction, to stabilise the toxic elements into ash has been explored. Sulphide could be removed from the effluent and simultaneously heavy metals could be stabilised in the bottom ash by treating ash with the sulphide-rich effluent.

2 OBJECTIVES

The main objective was to study the environmental effects of bottom ash disposal and to develop ash and leachate treatment techniques to mitigate the adverse environmental impacts. The specific objectives were:

- To characterise the chemical composition of bottom ash leachates under landfill conditions (I).
- To characterise the toxic properties of leachates for the aquatic organisms (II).
- To study the effect of anaerobic conditions prevailing in the ash fills on bottom ash weathering (III).
- To evaluate applicability of the sulphate reducing process on treatment of the grate firing bottom ash leachate (IV).
- To evaluate the possibility to use the sulphide containing by-product of sulphate reduction in the stabilisation of the grate firing bottom ash (V).

3   MATERIALS AND METHODS

3.1   Bottom ash (I, II, III, IV, V)

The type of bottom ash used, the experimental setup and the analyses used in each part of this study, are summarised in Table 1. Gasification bottom ash was obtained from a circulating fluidised bed facility (established in 1998, operating temperature 850–900 °C, Lahti, Finland). The facility gasified recycled wood, industrial plastics (glued wood 33 %-w, 16 %-w wood and 8 %-w plastic) and 43 % refuse-derived fuel (RDF) produced from municipal solid waste. The grate bottom ash was obtained from a facility (Turku, Finland) established in 1975 (modernised in 1995) and operating at 1000–1100 °C. It incinerated municipal solid waste (MSW), from which most of the glass, paper, and metal were source separated through the regional waste collection system. The grate ash was quenched, while the gasification ash was not and both were disposed of in a landfill at the time of the study. The total solids (TS) content of the grate ash was 88 % and that of volatile solids (VS) was 5.5 % of TS. The corresponding values for the gasification ash were 99 % and 0.1 %, respectively. The bottom ash from both facilities was transported by lorries to the Mustankorkea landfill (Jyväskylä, Finland), where it was heaped up on an asphalt surface for two weeks before placing into lysimeters.

TABLE 1   Materials, methods and experimental setups used in each study.

Name and number	Material	Setup	Analyses
Characterisation of leachate (I)	GA[a]/GR[b]	Landfill lysim.	LC[c], elements
Toxicity of leachate (II)	GA/GR	Landfill lysim.	LC, tox. assays, elements
Anaerobic weathering (III)	GA/GR	Lab. lysim.	LC, elements, CO_2
Leachate treatment (IV)	GR	Landfill lysim., Lab. UASB	LC, elements, sulphide, SE[d]
BA stabilisation (V)	GR	Lab. UASB, stab. column	elements, sulphide, SE, COD, pH

[a]Gasification bottom ash, [b]Grate bottom ash, [c]Leachate composition (COD, pH, N_{tot}, conductivity), [d] Sequential extraction.

3.2 Laboratory and landfill lysimeters (I, II, III)

The landfill lysimeters (height 3.9 m, width 2.4 m, length 12 m, volume 112 m^3) were made of steel frames (rectangular hollow section (RHS) 60 x 80 mm) and walls (2 mm) and coated with acrylic paint (Hempatex Hi-build 46410) (Fig. 2) and embedded in a 30 year old landfill body in November 2003. The lysimeters were filled with 0.5 m thick layers of ash and compacted using a sheep foot roller (Bomag 105, 1.6 t). The grate ash was filled to a height of 2.4 m and the gasification ash to a height of 2.9 m. The resulting bulk densities were 1.7 and 1.5 t/m^3, respectively. The top of the lysimeters were open, except when they were covered with plywood sheets for the first 104 days, in order to extend the beginning of the experiment until spring (April 1, 2004). In June 2004 (days 165–194) tap water (2 × 500 l) was added to the lysimeters in order to promote leachate formation. The addition of water equalled 70 % of one month's rainfall calculated from the local yearly average for 2004 (1423.2 l/lysimeter/month).

Leachate ran gravimetrically (angle 5 %) through a drainage layer (thickness 30 cm, gravel particle size < 25 mm) and a collection drain (110 mm) to a sampling well. The leachate flow was detected as water level changes in the well with a pressure meter (Keller PR-36W) and a data logger (Campbell Scientific CR10X). The leachate level as well as other continuously measured parameters was recorded every half hour. The temperature and moisture content within the ash was monitored using a soil temperature and moisture station (Davis 6343), temperature probes (Davis 6470) and moisture probes (Watermark 200SS) with a wireless Vantage Pro console (Davis 6310). Ambient air temperature was monitored by a weather station (Davis Vantage Pro 6150) equipped with a data logger (PC-link 6510) at the landfill site. The mean daily rainfall was obtained from the Finnish Meteorological Institute (2004–2007).

Four laboratory lysimeters (diameter 18, height 70 cm) made of PVC were operated at room temperature (20 ± 2 °C) (Fig. 3). Two of the lysimeters were filled with the gasification ash and two with the grate ash. The lysimeters were fed with 100 ml of ion-exchanged water from top, three times per week during the total study period of 486 days. Leachate was collected in a 2-l glass bottle, which was hermetically connected to the bottom of the lysimeter. Two of the
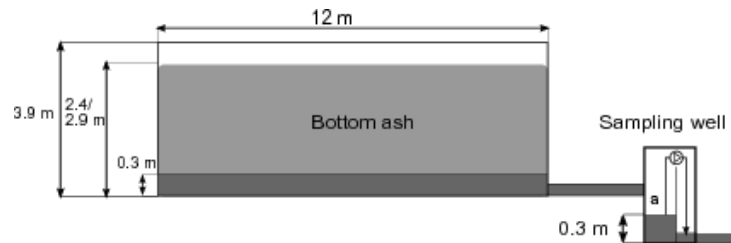

FIGURE 2   Scheme of the landfill lysimeter and the sampling well. Samples were taken and volume detected as water level in the first (a) section of the well.
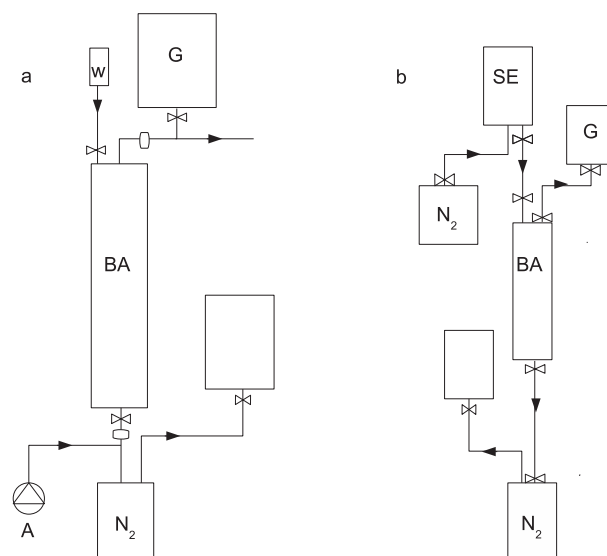
FIGURE 3   The laboratory lysimeter (a) and stabilisation column (b) set-ups (not in scale). Symbols: air pump (A), gas collection (G), bottom ash (BA), water (W) and sulphide-rich leachate (SE).

laboratory lysimeters were filled with the same ash and operated as replicates for the first 322 days. Thereafter, one lysimeter containing gasification ash and one containing grate ash were aerated during days 323–466 (132 d), in order to study the effect of enhanced contact with air on the leaching of contaminants. Air was pumped through the gravel layer at the bottom of the lysimeters. An aquarium pump (Rena Air 100, 3W) was used and the average flow rate was 35.6 l/h (SD = 21.7). The flow rate was measured from the top of the lysimeter with a bubble meter every weekday.

3.3   Chemical analyses (I, II, III, IV, V)

The element concentrations of ash and leachate were determined with a inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 4300 DV, Norwalk, CT, USA) using nebulizer flow 0.5–1.1 l/min, auxiliary gas flow 0.2 l/min, plasma gas flow 15 l/min and plasma power of 1300 or 1400 W (Ilander & Väisänen, 2009). From the leachates, concentrations of Al, As, Ca, Cd, Cr, Cu, Mg, Mo, Ni, Pb, Zn were determined in all five studies (I, II, III, IV, V). In addition, concentrations of Ba, Hg, S, Sb, Se (I, III, IV); B, Co, Cs, Fe, K, Mn, Na, P, Si, U, V (I and III) and Ag, Be, Bi, Ga, In, Li, Rb, Sr,Tl (IV) were determined from the leachate in the selected studies. The samples for elemental analyses were centrifuged (I, III, IV and V), preserved with HNO_3 (pH < 2) and stored at 4 °C until analysed.

The concentrations and binding mechanisms of the selected elements (As, Ca, Cr, Cu, P, Pb, Mo, S, and Zn) into bottom ash (I, III, V) or sludge (IV) were determined with sequential extraction followed by ICP-OES (Väisänen & Kiljunen 2005). Five fractions were obtained from the sequential extraction: (1) elements bound by ion-exchange; pH 7, (2) elements bound to carbonates; pH 5, (3) elements bound to Fe and Mn oxides; pH 2, (4) elements bound to organic matter and sulphides pH 2, and (5) residuals. The solid samples for determination of total element concentrations were extracted with ultrasound in presence of 8 ml aqua regia and 0.5 ml hydrofluoric acid per 0.5 mg of sample (I and II) or the total concentration was calculated as the sum of the five fractions obtained from the sequential extraction (III, IV and V). All the concentrations of the elements were calculated per dry weight (d.w.).

Redox and pH of leachate were measured with a WPA meter (CD70, electrodes: Sensorex ORP 450 and Sensorex pH 450 CD) or with Metrohm 744 (pH). Conductivity was measured with meter of Hanna instruments (Hi9635). N_{tot} and NH_4-N were analysed according to the application note by Tecator (Perstorp Analytical/Tecator AB, 1995). COD, BOD_7, TS, and VS were determined according to Finnish standard methods (SFS 5504 1988, SFS-EN SFS 3008 1990, 1899-2 1998). Sulphide was determined according to the colorimetric method at 670 nm (Hitachi U-1500 UV/VIS) (Trüper & Schlegel, 1964). TOC and DOC were analysed with a total organic carbon analyser (Shimadzu, TOC-5000A, Shimadzu Europe). For the DOC analyses samples were syringe filtered (0.45 µm, polyvinylidene fluoride membrane, Perkin Elmer, USA).

Fifteen PAH-compounds were measured with high performance liquid chromatography (HPLC, Agilent 1100, Agilent Europe), using fluorescent and diode array detectors. The detection limits were 10 ng/l for naphthalene, acenaftene, fluorene, phenanthrene, anthracene, fluoranten, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranten, benzo(k)fluoranten, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene and 1 ng/l for benzo-(a)pyrene. Uncertainty of the measurement was 30 %. The method used was the in-house method (0–5) of the accredited laboratory (SFS-EN ISO/IEC 17025) (Institute of Environmental Research, University of Jyväskylä).

In the laboratory lysimeter study (III) CO_2 samples were taken with a pressure-locked glass syringe (Supelco, Series A-2, USA) from the in- and outflows of the aerobic lysimeters and determined with a gas chromatograph (Perkin Elmer Autosystem XL, USA; Varian Select 50 m × 320 µm; carrier gas Helium; Oven 90 °C; injection port 90 °C; thermal conductivity detector 160 °C). The amount of absorbed CO_2 was calculated from the cumulative in- and outflows.

3.4 Toxicity assays (II)

The bacterial bioluminescence assay was performed with a kinetic method (Lappalainen et al. 2001) at 15 °C. Freeze-dried bacteria *Vibrio fischeri* (BioTox™, Aboatox, Turku, Finland) were used with an automated luminometer (Sirius, Berthold Detection Systems, Germany). All gasification ash toxicity assays were performed both, with pH adjustment (7.0 ± 0.2) and in the native pH of sample (9.2–12.4).

The growth assay with unicellular green alga *Pseudokirchneriella subcapitata* (SAG 61.81, Culture Collection of Algae, University of Göttingen, Germany) was a standard method (EN 28692, 1993) adapted to 48-well microplate. After the calibration carried out by microscopic counting with a glass chamber (Bürker, Germany), the cell density was measured with a fluorometer (Fluoroscan Ascent, Labsystems, Finland), with an excitation wavelength of 444 nm and an emission of 670 nm. The cell density at the beginning was approximately 10^4/ml and was monitored after 0, 24, 48 and 72 hours.

The water flea (*Daphnia magna*) assay was done according to the standard method (EN ISO 6341, 1996). Six replicates were used in the control treatment and three replicates in each dilution of five exposure concentrations. There were five water fleas per each replicate containing 10 ml of liquid. The mobile individuals were counted after 24 and 48 hours.

Induction of the EROD activity was studied with mouse hepatoma cells. The leachate samples were syringe filtered (0.2 µm polyethersulphone membrane, VWR, USA) and all samples were pH adjusted to 7 ± 0.1. The cells were transferred to a 96-well microplate (Sarsted, USA) one day prior to the exposure. Three parallel wells were used for the samples and six were used for the controls. Positive control was *β*-naphtoflavone (130 µg/l). Cells were exposed for three days, after which the microplates were frozen to –80 °C. The EROD activity was measured on the same or following day. In essence, the cell cultivation and EROD analyses were performed as described by Koistinen et al. (1998).

All of the toxicity assays were conducted as the same series in order to minimise variation due to changes in sensitivity of test organism over time. The samples were taken from the freezer to room temperature on the day before the toxicity assays began. Samples were not pre-treated before chemical analyses or toxicity assays, except for the EROD assay, where filtration (0.2 µm) to sterilise samples was used. Subsamples for metal and PAH analyses were taken from samples that were thawed and then thoroughly mixed.

3.5 UASB-reactors (IV)

Two parallel continuously fed up-flow anaerobic sludge blanket (UASB) reactors were used for sulphate reducing leachate treatment. The reactors (0.5 l, height 345 mm, inner diameter 47 mm, glass) were run at 20 ± 2 °C. The influent and effluent sampling ports were located immediately before the inlet and after the outlet of the reactors. The tubing was made of PVC and aluminium gas bags were used to collect biogas from the top of the reactors. Both the reactors were inoculated with 300 ml of anaerobically digested sludge (TS 17.8 g/l, VS 9.9 g/l) from a municipal waste water treatment plant (Jyväskylä, Finland), after which reactors were flushed with nitrogen and air-sealed.

Preliminary experiments (data not shown) suggested inhibition of sulphate reduction when undiluted leachate was used; hence leachate was diluted with tap water (1:1) for the reactor studies. Concentrations of the elements were under the detection limits in the tap water. The feed (diluted leachate) was pumped to the reactors at a constant flow rate (hydraulic retention time 1 day). Influent COD without ethanol addition was 314 mg/l (SD = 181, n = 57) mg/l and biological oxygen demand (BOD_7) was 15 mg/l. Ethanol (96 %) was added (1 g/l) as an electron donor in the feed of reactor R2 from day 30 onwards.

3.6 Stabilisation columns (V)

Stabilisation of the bottom ash with sulphide-rich effluent was studied in five parallel 50 ml glass-columns (diameter 3 cm, height 11.5 cm) at 20 ± 2 °C (Fig. 3). Two fresh samples (10 l each) of the grate bottom ash were obtained and kept under nitrogen before they were mixed and 60 ± 2 g (wet weight) of the ash was compacted into each stabilisation column. The columns were fed from the top with influents and effluents of the UASB reactors. The types of feed were: leachate (L), leachate with added ethanol (LE), anaerobically treated leachate (TL), sulphide-rich treated leachate (STL), and ion-exchanged water (C). Each column was fed every weekday with 20 ml of liquid and two hours before the next feed, the bottom tap was opened and leachate was slowly released from the columns. Seeping water was collected in glass bottles, which were hermetically connected under each column. From day 90 onwards, all columns were fed with ion-exchanged water in order to remove the dissolved fraction of the elements.

3.7 Calculations (I, II)

The amount of elements released from the landfill lysimeters during the study period (1236 d) was calculated by multiplying the concentration of each element with the volume of leachate between two samples (I). The equilibrium speciation modelling for the landfill lysimeter leachates was performed with Minteqa2 4.03 (US EPA) (I). Ettringite with solubility constant of log $K_{sp} = -56.7$ was added to mineral database of the Minteqa2. Modelling was performed with the batch test results assuming they present equilibrium conditions. All precipitation was suppressed and resulting saturation indexes (SI) were compared.

Statistical software R was used to perform t-test and to determine EC-values (R Development Core Team 2008). A log-logistic model of drc-package was used to calculate the EC-values in regards to all of the toxicological assays (Ritz & Streibig 2005). The possible cell toxicity in EROD analyses were observed by comparing protein amount of the leachate exposed wells and the negative controls. Statistical difference in the protein amount between exposure concentration and negative control was calculated. Bartlett's test was used to study the equality of variances within each sample. Analyses of variance or Kurskal-Wallis tests were used to detect, whether there were differences between the exposure concentrations compared to the negative control or not. Multiple comparisons were made with a pairwise t-test ($p > 0.05$), the p-values were adjusted using the Holm's method. All analyses were made with statistical program R (R Development Core Team 2008). As a result concentrations of 0.5, 1.9, 3.8 and 15 %, in which no cell toxicity was observed, were selected for calculation of the EC-values.

4 RESULTS

4.1 Formation and chemical characteristics of leachate (I)

Formation and chemical composition of the leachates was studied with the landfill lysimeters under ambient conditions. In the grate ash lysimeter 24 % and in the gasification ash lysimeter 17 % of the cumulative flow occurred, when the flow rate was > 200 l/d (Fig. 4). In the case of grate ash lysimeters, this corresponded to 3.4 % (37 d) of the study period (1236 d), and in the gasification ash lysimeter 2 % (22 d). At the end of the study, the LS-ratio of the grate ash was twice that of the gasification ash. The gasification ash was initially dry having LS-ratio of 0.0 l/kg (d.w.) (99 % dry weight), which increased to 0.4 l/kg by the end of the study (day 1236). The LS-ratio of the quenched grate ash increased from an initial 0.54 l/kg (d.w. 82 %) to 1.0 l/kg (Fig. 4). The initial water content of the grate ash was significant and the LS-ratio at the end of the study would have been 0.46 l/kg, if the initial water content is not summed in the LS-ratio (Fig. 4).

The mean pH of the grate ash leachate was 7.0 (SD = 1.6) at the beginning of the experiment (day 139–554) increasing up to 8.4 by the end of the study period (day 1035) (Fig. 5). Initially, the gasification ash leachate had a low pH ($\bar{x}$ = 6.5, day 139–212), after which it increased to a high level ($\bar{x}$ = 13.1, SD 0.94, day 212–1148). During the final 100 days of the study, a decrease in pH of gasification ash leachate to 10.8 (day 1236) was observed. The alkalinity showed a similar trend with an increase during the first 400 days (Fig. 6). In the batch test (LS 10 l/kg (d.w.)) pH of the gasification ash leachate was 13.55 and that of the grate ash leachate was 10.84.

The conductivity of the leachate was measured continuously to determine leaching behaviour of the major salts. The maximum conductivity of the grate ash leachate was 20 times higher than that of the gasification ash (Fig. 5). The grate ash leachate conductivity decreased steadily from high initial values (2500 mS/m, day 104). The conductivity of the gasification ash leachate increased after day 212, and remained at a constant level until the end of the study period
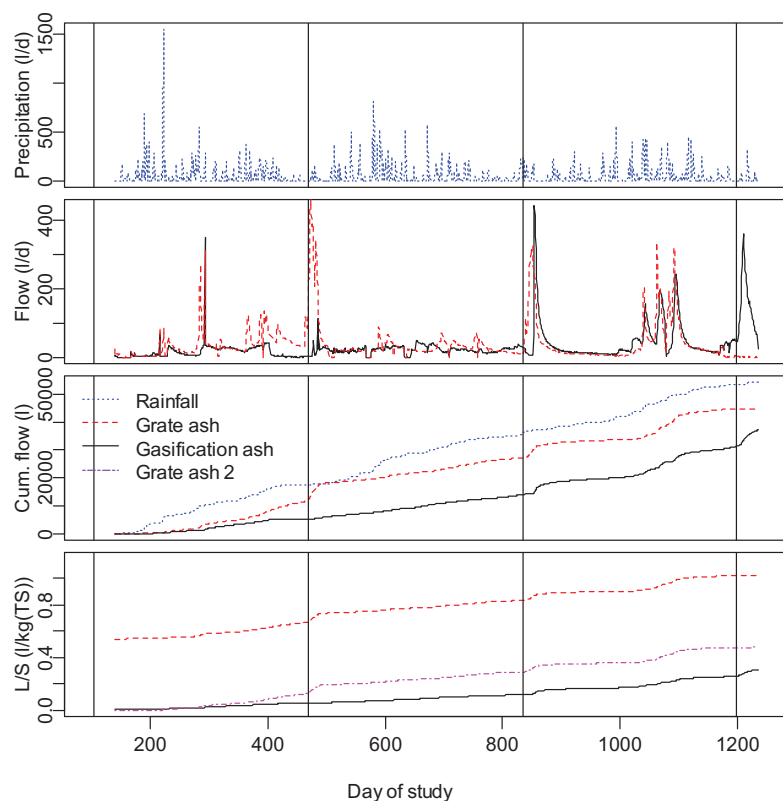
FIGURE 4   Precipitation, leachate flow, cumulative flow and LS-ratio from the landfill lysimeters calculated per lysimeter. Grate ash LS-ratio is given both including the initial water content of ash (Grate ash) and without it (Grate ash 2). Vertical lines show the 1st of April, after which snow melts rapidly.

($\bar{x}$ = 750, SD = 130, day 364–1099), except for the peak from day 320 to day 364 (Fig. 5).

The leachate redox potential was measured to obtain information on gas diffusion and biodegradation. The redox potential of both the ash leachates showed seasonal variation. The lowest values were detected during the warmest months of the year between study days 600 and 900 (Fig. 5, 6).

The grate ash leachate contained some readily biodegradable organic carbon during the first 3–6 months after disposal. The BOD_7 of the grate ash leachate had a maximum of 79 mg/l (day 114) and decreased to 4 mg/l (day 293) (Fig. 6). In the gasification ash leachate the BOD was low (3–8 mg/l) throughout the measurement period. The average TOC content of the grate ash leachate was higher ($\bar{x}$ = 318 mg/l, SD = 130, n = 15) than that of the gasification ash leachate ($\bar{x}$ = 157 mg/l, SD = 137, n = 9) during the first 355 days. The share of the DOC ($\bar{x}$ = 111 mg/l, SD = 54, n = 18) from the TOC was 35 % for the grate
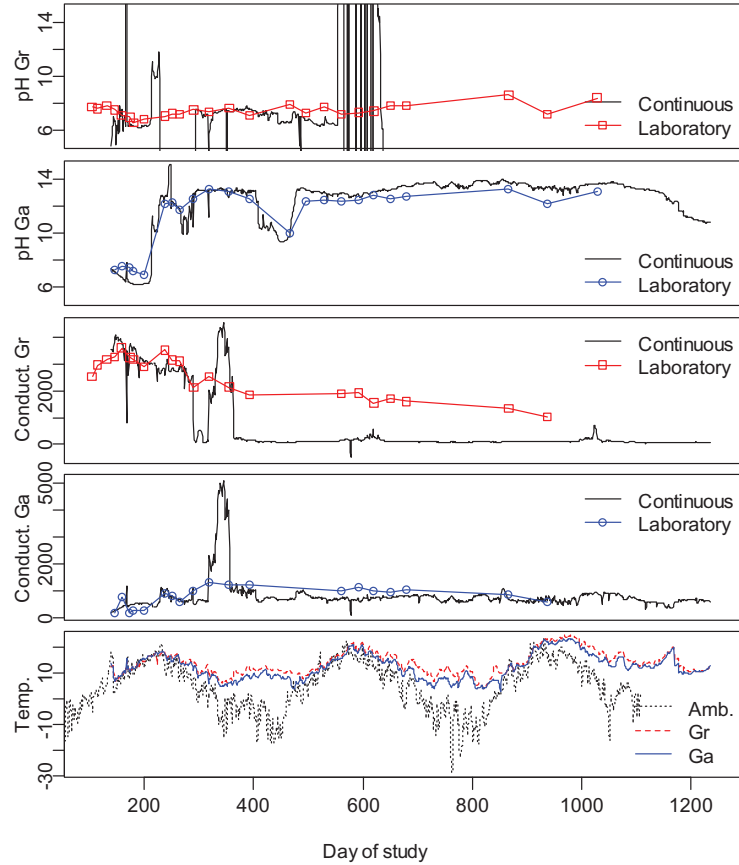
FIGURE 5   Conducitivity (mS/m), pH and temperature (°C) of leachates from landfill
            lysimeters containing grate ash (Gr) and gasification ash (Ga).

ash leachate and 17 % for the gasification ash leachate ($\bar{x}$ = 53 mg/l, SD = 111, n = 14).

In the grate ash leachate, the mean value of total nitrogen concentration was 47 mg/l (SD = 105) and for gasification ash 17 mg/l (SD = 8.3) (Fig. 6). The concentration of ammonium nitrogen in the grate ash leachate was 8 mg/l (SD = 9) and in the gasification ash leachate 2 mg/l (SD = 4).

The released amount of elements during three-year lysimeter study, the released amount in the batch test (LS 10 l/kg (d.m)), and the total amount from the fresh ash were determined (Table 2). For most of the major elements release was lower under landfill conditions than in the laboratory batch test as the LS-ratio under landfill conditions also was lower. For example, 20 % of Ca and 51 % of S were released from the grate ash under landfill conditions compared to the batch test. From the gasification ash the corresponding release was 1.8 % of Ca and 5.3 % of S (Table 2). The released amount of Al and Si were higher
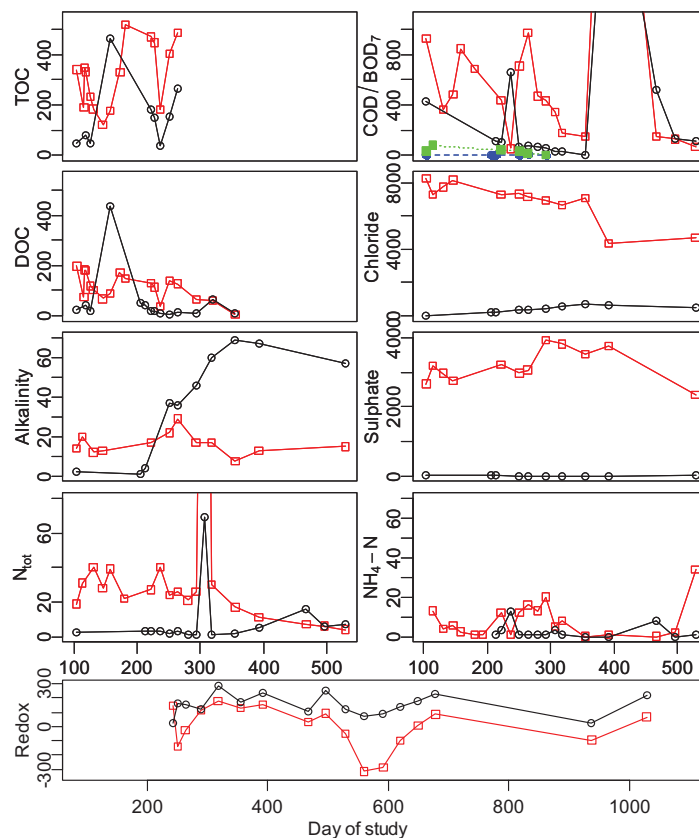
FIGURE 6   TOC (mg/l), DOC (mg/l), alkalinity (mmol/l), N_{tot} (mg/l), and redox potential (mV) of landfill lysimeter leachates. Symbols: grate ash leachate □ and ■; gasification ash leachate ∘ and ●.

from the gasification ash than from the grate ash under landfill conditions. On the other hand, in the batch test more Al was released from the grate ash than from the gasification ash. Noticeable among the toxic elements was the leaching behaviour of As. As leaching was higher from the gasification ash than from the grate ash, both in the batch test and under landfill conditions, although, the total concentration in both types of fresh ash was similar.

The mineral composition of both types of ash was studied based on the pH and main elemental composition of leachate in the batch test. In the grate ash leachate, at the pH of 10.84, the Ca-minerals closest to equilibrium were gypsum (SI –0.806) and anhydride (SI –1.056), however, both were undersaturated. The gasification ash leachate was oversaturated in respect to portlandite (SI 1.324) at pH 13.55. In the batch test the grate ash leachate was oversaturated in respect to minerals potentially controlling Al leaching: diaspore (SI 1.817), boehmite (SI 0.112) and gibbsite (SI 0.399), while the gasification ash leachate was undersaturated with respect to same minerals: diaspore (SI –2.4), boehmite (SI –4.111) and gibbsite (SI –3.823).

TABLE 2 Total concentration (mg/kg (d.w.)) and its recovery percentage (Rec.) in the fresh ash. Leached amount (mg/kg (d.w.)) in the batch test and in the landfill lysimeter detected as the leachate concentration (mg/l) . Detection limits (DL) for the leachates (mg/l).

| | Gasification bottom ash | | | | Grate bottom ash | | | | | |
	Total	Batch	Lysimeter	Conc. Range ($\bar{x}$)	Total	Batch	Lysimeter	Conc. Range ($\bar{x}$)	Rec.	DL
pH		10.84	6.55–8.6 (7.4)			13.55	6.2–14 (12.5)			
Al	N.A.	8	3.81	<DL–68.4 (12.2)	N.A.	220	0.015	<DL–0.4 (0.06)	N.A.	0.02
As	58	15.4	0.015	<DL–1.7 (0.22)	61	2.9	0.004	<DL–2.4 (0.34)	101	0.1
B	N.A.	N.A.	0.11	<DL–4.95 (0.74)	N.A.	N.A.	0.72	<DL–10.8 (2.26)	N.A.	0.2
Ba	N.A.	16.6	0.29	<DL–5.41 (1.14)	N.A.	0.55	0.02	<DL–0.49 (0.08)	N.A.	0.005
Ca	73200	5580	5.36	<DL–500 (55.7)	97300	740	145	62–1570 (590)	47	0.005
Cd	2.86	0.08	0	<DL–0.01 (0.006)	9.9	0.05	0	<DL–0.02 (0.007)	831	0.005
Co	12.9	N.A.	0.013	<DL–0.68 (0.04)	19	N.A.	0.001	<DL–0.06 (0.02)	38	0.02
Cr	100	0.01	0.003	<DL–0.2 (0.03)	128	0.085	0.001	<DL–2.2 (0.09)	15.9	0.02
Cs	N.A.	N.A	0.33	<DL–7.5 (1.34)	N.A.	N.A.	0.012	<DL–0.18 (0.08)	N.A.	0.02
Cu	890	0.68	0.03	<DL–1.35 (0.14)	3180	2	0.013	<DL–0.14 (0.06)	23.8	0.02
Fe	6390	N.A.	0.02	<DL–9.7 (0.51)	26600	N.A.	0.09	<DL–8.5 (0.56)	5.3	0.02
K	1130	N.A.	128	4.2–1398 (516)	5390	N.A.	225	42–1330 (600)	5.5	0.02
Mg	19500	10.5	0.06	<DL–29 (3.3)	10800	5.3	113	6–950 (412)	68	0.01
Mn	220	N.A.	0.002	<DL–3.8 (0.18)	660	N.A.	0.43	<DL–47 (6.8)	18	0.01
Mo	63	0.87	0.01	<DL–0.18 (0.05)	81	N.A.	0.08	<DL–0.99 (0.17)	252	0.05
Na	3860	N.A.	188	6.7–2100 (740)	12600	N.A.	1030	100–5600 (2880)	252	0.05
Ni	64	0.53	0	<DL–0.06 (0.02)	138	0.13	0.012	<DL–0.2 (0.07)	19	0.02
P	74	2.5	0.031	<DL–1.1 (0.24)	1960	0	0.031	<DL–0.67 (0.14)	49	0.1
Pb	22	0.4	0	<DL–0.1 (0.03)	948	0.24	0.006	<DL–0.9 (0.07)	20	0.02
S	154	8.3	0.44	<DL–147 (9.4)	5180	520	270	61–1710 (700)	91	0.1
Si	N.A.	N.A.	1.5	<DL–37.8 (6.27)	N.A.	N.A.	0.64	<DL–73.1 (3.1)	N.A.	0.2
U	N.A.	N.A.	0	<DL–0.25 (0.2)	N.A.	N.A.	0	<DL–0.73 (0.23)	N.A.	0.2
V	17	N.A	0.01	<DL–0.22 (0.06)	37.6	N.A.	0.004	<DL–0.2 (0.11)	27	0.02
Zn	350	0.56	0.0071	<DL–0.92 (0.09)	2660	0.63	0.01	<DL–0.71 (0.06)	12.4	0.02
Sum			327				1778			

4.2 Toxicological characteristics of leachates (II)

Three aquatic toxicity assays on different trophic levels and one protein level biomarker were used to study toxicity of landfill lysimeter leachates. The chemical composition of the three toxicity samples (2004, 2005, and 2007) were similar to those obtained in the leachate monitoring study (I). The maximum concentrations of the elements are given in Table 3. Conductivity and pH of the gasification ash leachate were at the highest level after one year of disposal (in 2005) being 840 mS/m and 12.4, respectively. Conductivity of the grate ash leachate decreased during the study from 2450 mS/m (2004) to 60 mS/m (2007). However, the pH of the grate ash leachate increased slightly from 7.8 (2004) to 8.2 (2007). In both the leachates, the PAH concentrations were below the detection limits (10 ng/l and 1 ng/l for benzo(a)pyrene) in all three samples.

Gasification ash leachate inhibited bioluminescence during the entire study period, both in assays with pH adjustment (pH 7 ± 0.2) and without it (pH 9.2–12.4) (Table 3). The adjustment of the pH decreased the toxicity of the gasification ash leachate; however, it was still clearly toxic. The highest toxicity was observed in the 2004 and 2005 samples. In 2005, even the lowest selected dilution (5 vol-%), caused inhibition at nearly 100 %. Surprisingly, some stimulation was observed in the 2004 sample, assayed without pH adjustment. The difference compared to the control was statistically significant in dilutions of 1 vol-%, 0.2 vol-% and 0.05 vol-% (t-test, $p < 0.05$). Grate ash leachate did not inhibit bioluminescence; instead, stimulation was observed. The stimulation was observed in all of the years; however, statistically significant stimulation was only observed in 2005, in dilutions 5, 9, and 15.5 vol-% of the leachate.

The gasification ash leachate was toxic to algae during the first two years (2004, 2005) of landfilling. The highest toxicity was observed in year 2005 in

TABLE 3   The maximum concentrations and detection limits (DL) in the grate ash (Gr) and gasification ash (Ga) leachates (mg/l) used in toxicity assays (II).

	Ga	Gr	DL
As	0.23	0.39	0.1
Ca	86	737	0.005
Cd	0.01	0.009	0.005
Cr	0.01	0.01	0.02
Cu	0.02	0.02	0.02
Fe	0.8	1.27	0.02
K	795	753	0.02
Mg	0.1	646	0.01
Mo	0.12	0.33	0.05
Na	1304	3990	0.05
Ni	0.01	0.05	0.02
Pb	0.025	0.024	0.02
Zn	0.15	0.02	0.02

assay without pH adjustment (pH 9.2–12.4) (Table 4). In the sample from 2007, a 290 % increase was noted in comparison to algae growth of the control. When pH was adjusted, only the sample from 2005 of gasification ash was inhibitory at the highest concentrations. In addition, adjustment of the pH decreased the maximal stimulation in the 2007 sample. The grate ash leachate was toxic to algae in the two highest concentrations in 2004 (max. inhibition 22 %, in 66 vol-% of leachate, 72 h exposure), and in the highest concentration in 2005. Although, toxicity was detected in the highest concentrations in 2004 and 2005, stimulation of growth was observed in lower concentrations. The highest observed stimulation was 320 %, compared to the control (10 vol-% sample, 2007, 72 h exposure).

The gasification ash leachate was toxic to water fleas throughout the study, when pH was not adjusted and the highest toxicity was observed in 2005 (Table 4). When pH was adjusted, all the water fleas survived even in the undiluted leachate over 24 h. However, extension of the exposure to 48 h reduced survival slightly. In the pH adjusted sample of 2004, the survival at the highest concentration after 48 h was 86 %, whereas in 2005 and 2007 it was 93–100 %. Toxicity of grate ash leachate to *D. magna* decreased over the study period (Table 4). By 2007, no toxicity was observed, as all individuals survived even in the undiluted leachate.

Both the leachates induced EROD activity during the first two years of disposal. In 2004, the EROD activity increased with increasing dose of the gasification ash leachate, resulting in an EC_{50} value of 1.19 % (SE = 0.88). Gasification ash also induced EROD activity in 2005, although no clear increase with dose was observed. The grate ash leachate induced EROD activity in 2004 and 2005, giving EC_{50} values of 12.3 vol-% (SE = 10.41) and 2.3 vol-% (SE = 1.22), respectively.

TABLE 4　　EC-values calculated from bacterial bioluminesence (BL), algae (A), and water flea (WF) assays. Only the assays with observed toxicity are shown.

Ash	sample	assay	x	EC_x(vol-%)	SD	exp.time	pH adj.
Ga	2004	BL	50	4.7	0.66	30 min	no
Ga	2005	BL	50	<5	–	30 min	no
Ga	2007	BL	50	8	0.13	30 min	no
Ga	2004	BL	50	6.4	0.86	30 min	7 ± 0.2
Ga	2005	BL	50	27	1.11	30 min	7 ± 0.2
Ga	2007	BL	50	15.7	0.65	30 min	7 ± 0.2
Ga	2004	A	50	62	7.7	72 h	no
Ga	2005	A	50	7.5	16.6	72 h	no
Ga	2007	A	50	–	–	72 h	no
Ga	2004	WF	50	0.52	0.56	48 h	no
Ga	2005	WF	50	0.09	0.09	48 h	no
Ga	2007	WF	50	0.46	0.15	48 h	no
Gr	2004	WF	50	0.54	1	48 h	no
Gr	2005	WF	20	1.01	0.04	48 h	no
Gr	2007	WF	20	–	–	48 h	no

The protein content and EROD activity (0.19 pmol/min/mg protein) were on same level between the controls in 2004 and 2005 indicating good comparability of the results across these years. In addition, the positive control β-naftophlavon (130 µg/l) induced EROD activity from 0.56 (STD 0.30) to 1.03 (STD 0.255) pmol/min/mg protein in 2004 and 2005, when compared to the control, giving p-values of 0.07 and < 0.01, respectively. In the 2007 sample the protein level and EROD activity (0.06 pmol/min/mg protein) were slightly lower than in the other samples.

4.3 Anaerobic weathering of bottom ash (III)

The effect of anaerobic and aerobic conditions on weathering of the grate and the gasification bottom ash were compared with laboratory lysimeters. Two parallel lysimeters for both types of ash were run anaerobically for 322 days, after which, one of the lysimeters was aerated for the rest of the study period (day 323–464). In order to monitor the weathering processes, COD, pH, N_{tot}, chloride, conductivity and element concentrations of the leachates were determined. In addition, the binding of elements into ash was analysed with sequential extraction at the beginning and at the end of the study.

The clearest change in both leachates under anaerobic conditions was a rapid decrease of COD during the first 40 days of the study period (Fig. 7). The pH of the gasification ash leachate remained above 12 throughout the study period; while for the grate ash, the maximum pH was 9.00 and it decreased towards the end of the study period. The decrease in the concentration of major elements was observed as a decreasing trend in conductivity of grate ash leachate (Fig. 7). Nitrogen, chloride and sulphate concentrations of the grate ash leachate decreased constantly and a similar but not as rapidly decreasing trend was observed in the gasification ash leachate (Fig. 7).

Aeration of laboratory lysimeters after anaerobic study period was used to study the effect of atmospheric gases on weathering processes. The performance of the aerated lysimeters was compared with those obtained from the parallel anaerobic lysimeters during the same period (day 323–466). The effect of aeration was the clearest in the gasification ash leachate, in which pH and conductivity decreased (Table 5, Fig. 7). The decrease in pH of gasification ash leachate was statistically significant (p = 0.02) compared to the leachate of the parallel anaerobic lysimeter during the same period (day 323–466). Leachate conductivity was low ($\bar{x}$ = 1.6 mS/cm) in the aerobic compared to anaerobic gasification ash lysimeter ($\bar{x}$ = 8.3 mS/cm). In the grate ash lysimeter, aeration increased the leaching of sulphate, although, the difference between the aerated and anaerobic lysimeters was not statistically significant (p = 0.07) (Table 5).
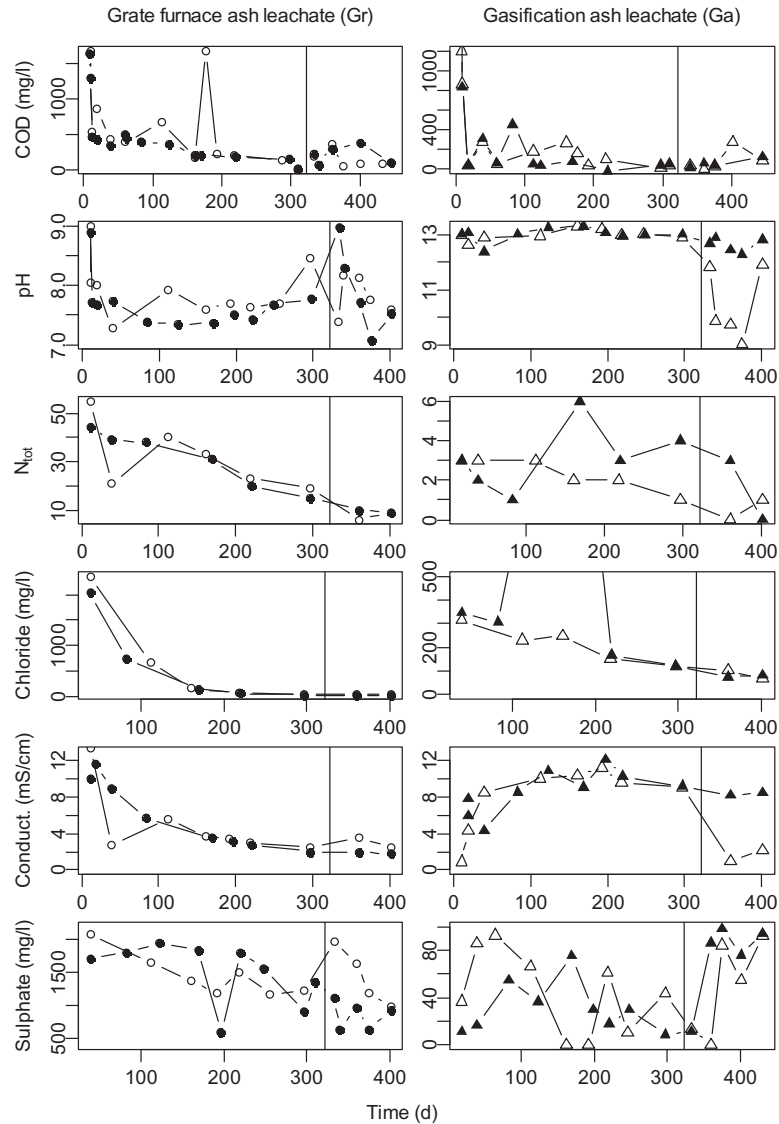
FIGURE 7   Characteristics of the laboratory lysimeter leachates. All the four laboratory
              lysimeters were run anerobically on days 0–322. Two of the lysimeters were
              aerated from study day 323 onwards (marked with a vertical line).

In the gasification ash lysimeter the absorption of CO_2 was observed as a consistently lower concentration in the out-flowing air than in the inflowing air. In the grate ash lysimeter CO_2 absorption was strongest during the first 40 days of the aeration. Absorption declined slowly and by the day 380 no absorption was observed in the grate ash lysimeter. The grate ash absorbed 4.44 mmol/g (d.w.) of CO_2 and the gasification ash 3.94 mmol/g (d.w.).

TABLE 5   The effect of aeration on characteristic of laboratory lysimeter leachate. Minimum (min), maximum (max), mean ($\bar{x}$) standard deviation (SD), number of measurements (n) and result of t-test are presented. Measurements are taken from parallel lysimeters between days 323–466.

| | Grate ash leachate | | | | | | | | | | | Gasification ash leachate | | | | | | | | | | |
| | Anaerobic | | | | | Aerobic | | | | | | Anaerobic | | | | | Aerobic | | | | | |
	min	max	$\bar{x}$	SD	n	min	max	$\bar{x}$	SD	n	t-test	min	max	$\bar{x}$	SD	n	min	max	$\bar{x}$	SD	n	t-test
COD	84	381	222	125	5	54	372	141	112	7	0.28	11.6	115	51.9	45	4	0	268	80	109	5	0.62
pH	7.07	8.97	7.9	0.74	5	7.39	8.17	7.81	0.34	5	0.77	12.29	12.9	12.63	0.25	5	9	11.9	10.5	1.32	5	0.02
N_{tot}	9	10	9.5	0.71	2	6	9	7.5	2.12	2	0.4	0	3	1.5	2.12	2	0	1	0.5	0.71	2	0.73
Cl	15.9	20.2	18.1	3.04	2	37.3	55.2	46.3	12.7	2	0.18	75.6	84	79.8	5.94	2	71	103	87	22.6	2	0.73
Cond.	1.8	1.93	1.87	0.09	2	2.43	3.56	3	0.8	2	0.29	8.19	8.45	8.32	0.18	2	0.97	2.18	1.57	0.86	2	0.048
SO_4	637	1120	857	213	5	981	1974	1447	446	4	0.07	11.45	98.1	73.17	35.53	5	0	92.3	48.9	41.2	5	0.35

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The effect of aeration on elemental composition of leachate was studied by comparing the leachates from the anaerobic and aerobic lysimeters during the aeration period (day 323–466). The aeration significantly (t-test, $p < 0.001$) decreased the concentration of Ca in the gasification ash leachate, compared to the leachate from anaerobic lysimeter during the same period. In the aerated lysimeter the concentration of Ba decreased rapidly in the gasification ash leachate from 30 mg/l to close to the detection limit of 0.005 mg/l (t-test, $p = 0.028$) (Fig. 8). In the grate ash leachate, the concentration of P decreased significantly (t-test, $p = 0.034$) compared to anaerobic conditions. The concentration of S in the grate ash leachate increased (t-test, $p = 0.029$) during the aeration period as did the concentration of Mg (Fig. 8).

The effects of anaerobic conditions on the elemental composition of ash and on the changes in binding were studied with the lysimeters that remained anaerobic throughout the study period. Total concentrations were determined and sequential extraction performed at the beginning and at the end of the study, to reveal the changes in total concentrations and within the fractions (Fig. 9).
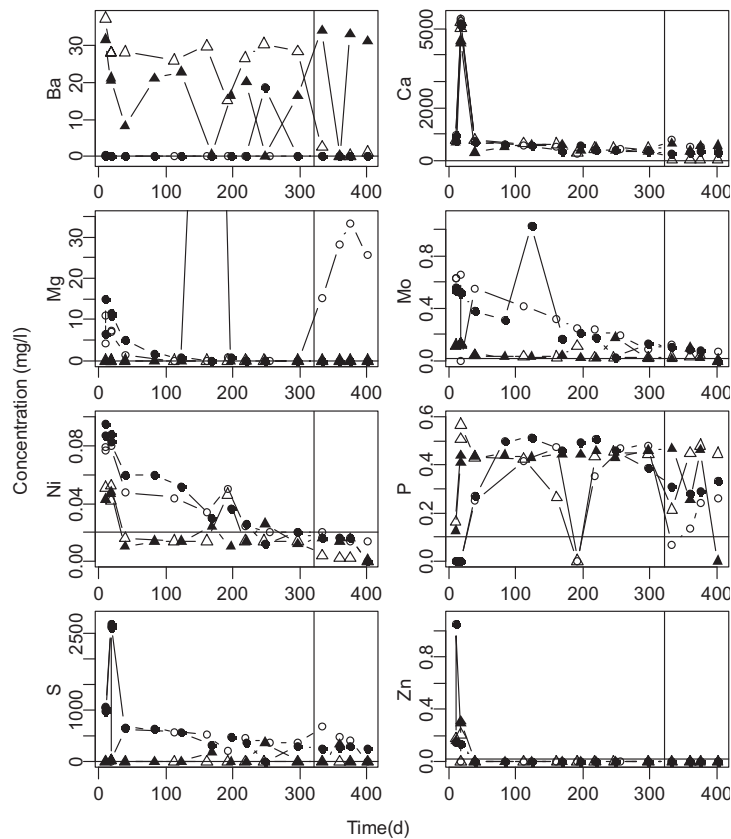

FIGURE 8   Concentrations of selected elements in the laboratory lysimeter leachates. Aeration of the gasification ash lysimeter (Ga1 Δ) and the grate ash lysimeter (Gr1 ○) began on day 323 (vertical line). The horizontal line is detection limit.

Under the anaerobic conditions Ca, Cr and Mo leached from the gasification ash, and As, Ca, Cr, Cu, Mo, Pb and S from the grate ash (Fig. 9). Under anaerobic conditions the major change in binding was observed in oxidisable fraction (4), in which the amount of As increased in the grate ash and the amount of Cr in both types of ash.

In the gasification ash the total concentration of Ca decreased 10 % under anaerobic conditions by the end of the study. Ca leached from exchangeable (1) and reducible (3) fractions. The total concentration of Cr in the gasification ash decreased 52 % during the study period. The decrease was the highest in the exchangeable (1) fraction but was significant also in the residual fraction (5). On the other hand, the concentration of Cr increased by over 100 % in the oxidisable fraction (4), 57 % in carbonate bound fraction (2) and 92 % in the reducible fraction (3). The concentration of Mo decreased by 89 %, mostly from the exchangeable (1) and carbonate-bound (2) fractions.

In the grate ash, the decrease in the total concentration of Ca was 7 % and that of Cr 16 % under anaerobic conditions. Ca decreased in the residual (5) and exchangeable fractions (1) and Cr in the exchangeable (1) and carbonate bound fraction(2). The concentration of Cr increased in fractions 3 (26 %) and 4 (265 %). Cu decreased in all fractions in the grate ash; the total decrease was 75 %. Similarly, total decrease in Mo was 75 % and distributed among all the fractions. The total amount of Pb decreased by 29 % from the carbonate-bound fraction, in which Pb was mostly bound. The concentration of S decreased by 45 % in fractions 1, 2, and 5.

The effect of aeration (day 323–464) on elemental composition of ash was studied by comparing the concentrations of elements in ash from the aerated and anaerobic lysimeters at the end of the study (Fig. 9). These comparisons show that aeration decreased the leaching of Cr, Cu, and Mo in the both types of ash. However, release of Pb increased in the aerated grate ash lysimeter and the total concentration of Pb was 47 % lower in the aerobic lysimeter than in the anaerobic.

The binding of Cr increased in the both aerobic lysimeter in the residual (1) and in the oxidisable fraction (4) and fell close to zero in the residual fraction (5). Cu bound more in the reducible (3) and residual (5) fractions in the aerated lysimeters than in the anaerobic ones. The binding of Mo in the aerobic grate ash was higher in fractions 4 and 5 than in the anaerobic grate ash. In aerobic gasification ash, binding to fraction 4 was especially high (Fig. 9).
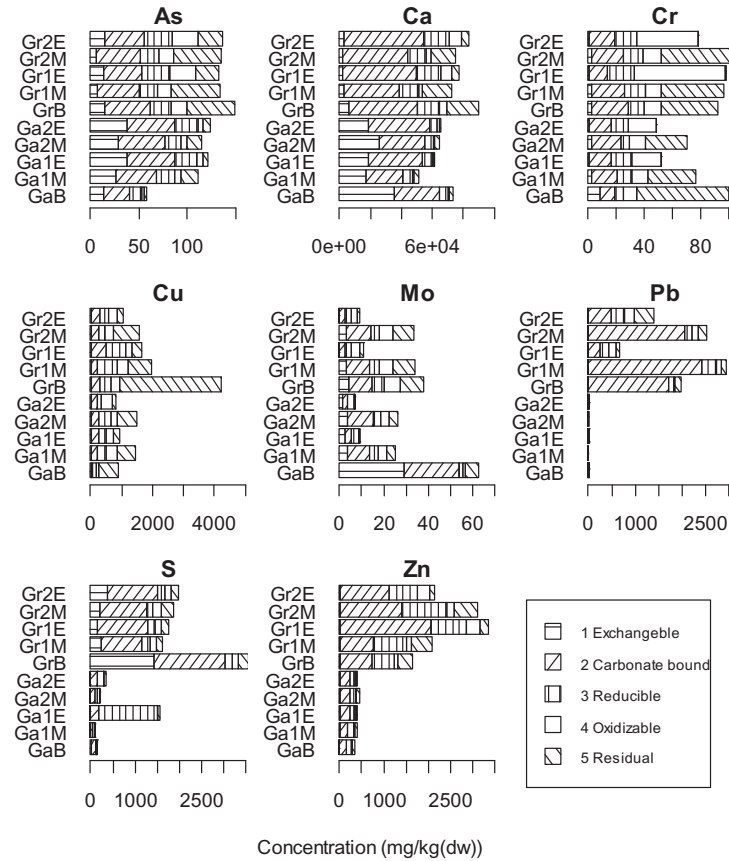
FIGURE 9   Effect of anaerobic conditions (Ga2, Gr2) and aeration (Ga1, Gr1) (day 323–466) on binding of elements in the laboratory lysimeters. Gasification (Ga) and grate ash (Gr) were analysed with sequential extraction at the beginning (B, day 0), before aeration (M, day 309), and at the end (E, day 466) of the study.

4.4   Leachate treatment with sulphate reduction (IV)

The feasibility of the sulphate-reducing process to treat the leachate of the grate bottom ash was studied using two UASB reactors (R1 and R2). Leachate from the landfill lysimeter was diluted with tap water (1:1) and fed to both reactors. To the feed of the reactor R2 ethanol (1 g/l) was added. The reactor with added ethanol (R2) removed 60–70 % of the COD, while R1 without ethanol addition showed varying and negligible COD removal (Fig. 10). The influent pH ranged from 7.45 to 8.46, and the pH of the effluents followed those changes (Fig. 10). At the beginning of the runs the amount of TS was 5.35 and VS 2.97 g/reactor.
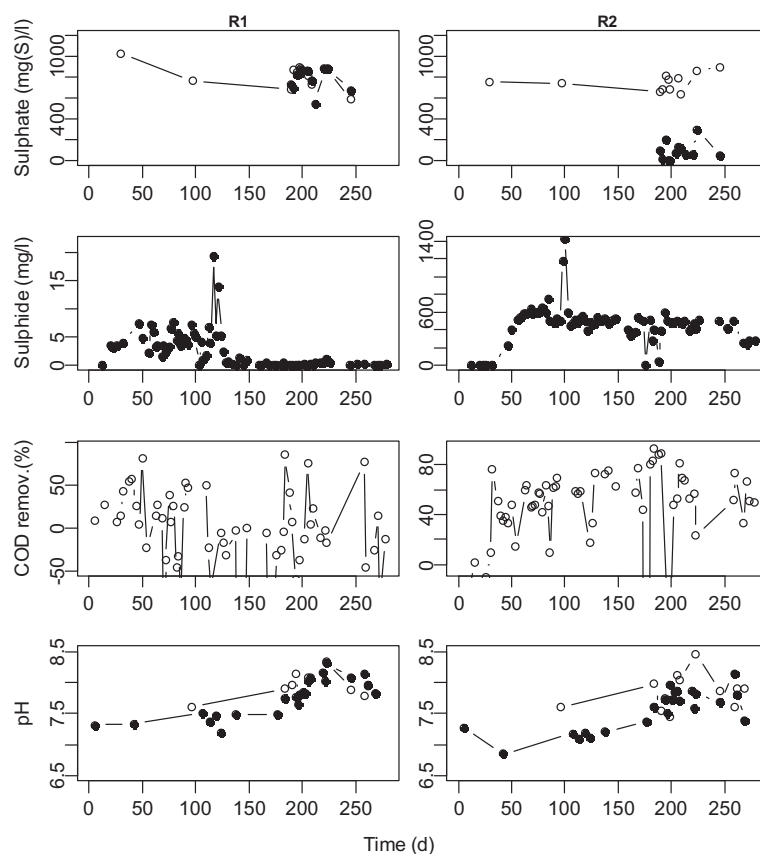
FIGURE 10   Performance of UASB reactors treating grate ash leachate with (R2) and without (R1) ethanol addition. The influents and COD removal denoted by (◦) and the effluents (•).

At the end of the runs TS was 3.62 g/reactor in R1 and 10.0 g/reactor in R2. Sulphide concentration in the effluent of R1 was low (maximum 19 mg/l), while in the effluent of R2 the sulphide concentration rapidly increased after ethanol addition remaining mostly between 400 and 600 mg/l (Fig. 10). According to the sulphate measurements no sulphate was removed in R1 while in R2 over 65 % was removed (Fig. 10).

The ability of the ethanol-supplied reactor (R2) and reference reactor without ethanol addition (R1) to remove the elements was investigated by comparing concentrations in the influents and in the effluents. In the ethanol supplied reactor Ba, Ca, Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, Sr, and Zn were removed totally or partially between days 191–261 (Table 6). At the beginning (days 33, 51) and at the end of the run (days 269, 274) removal was lower or there was no removal. It was not possible to observe the removal of Ag, Al, Be, Bi, Cd, Co, Cr, Cs, Hg, In, Li, P, and Rb, because the concentrations in the influents were under the detection limits. Cd was detected in the influents of R2

four times and never in the effluents, which may suggest that it was removed. Mn and Zn were removed, although Zn was detected in the influent only in the beginning (days 33, 51) of the run (Table 6).

In the reference reactor (R1) only Ba and Cu were removed. Cu was detected in the influent from day 223 onwards and in the effluent only once (day 253). The removal of Cu in R1 was 12–82 %. The highest Ba removal was achieved between days 191–261 (9–31 %) and it was not removed at the beginning or at the end of the run.

The total concentration of nine elements (As, Ca, Cr, Cu, Mo, P, Pb, S, and Zn) in the inoculum was determined at the beginning, while sequential extraction was done at the end of the run, to determine the chemical binding of the elements in the sludge samples. Four of the elements (S, As, Cu, and Mo) were accumulated in the reference reactor (R1) and seven (Ca, S, As, Cr, Cu, Mo, and Zn) in the ethanol supplied reactor (R2). Of the elements which accumulated in both reactors, As, Cu, and Mo accumulated in higher amounts in R2. The amount of S was at the same level in both reactors at the end (Fig. 11).

The highest binding percentage to organic material and sulphides (fraction 4) were for Mo (73 %) and Zn (83 %) in the sludge of the ethanol supplied reactor (R2). Cu was also mainly bound to the organic carbon and sulphide fraction (4) in both reactors (R1 87 % and R2 89%). Ca, which accumulated only in R2, was mainly bound to Fe and Mn oxides (60 %) and to carbonates (30 %). In R1 most of the S (57 %) was dissolved in water (fraction 1), while in R2 the main mechanism was the formation of insoluble metal-sulphides (52 %) (Fig. 11).

TABLE 6   Removal of the elements from the grate ash leachate in the ethanol supplied reactor (R2). Results are presented over days 191–261, when sulphide concentrations of the effluent was high and over whole study period 33–275. Removal percentage was negative when the concentration of effluent was higher than in the influent.

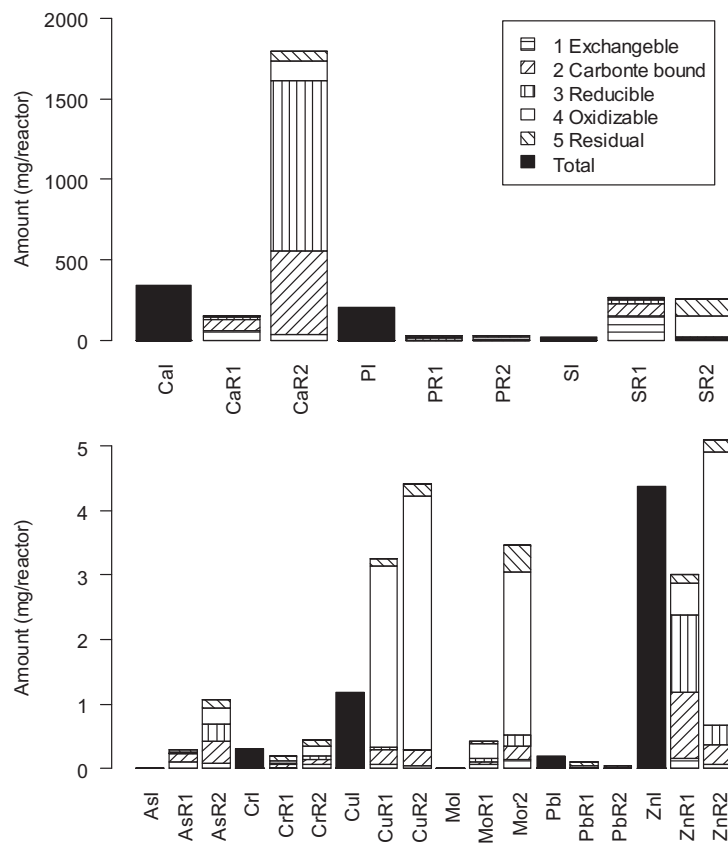| | Removal (%) | | | |
| | Days 191–261 (n = 5) | | Days 33–275 (n = 9) | |
Element	range	$\bar{x} \pm SD$	range	$\bar{x} \pm SD$
Ba	11–62	40 ± 26	(−140)–62	9 ± 62
Ca	38–64	46 ± 11	(−31)–63	25 ± 30
Cu	(>52)–(>87)	70 ± 13	0.0–87	48 ± 37
Mn	63–93	83 ± 12	(−35)–92	53 ± 43
Mo	10–(>90)	57 ± 33	(−38)–90	28 ± 48
Ni	42–(>86)	64 ± 19	(−24)–(>86)	41 ± 39
Pb	0.0–95	45 ± 43	(−71)–95	29 ± 52
Tl	30–(>68)	48 ± 17	(−340)–79	8 ± 130
Sb	0.0–76	28 ± 37	(−27)–77	18 ± 33
Sr	14–50	29 ± 14	4–50	22 ± 16

FIGURE 11   Binding of elements into sludge of the UASB reactors. Concentrations were determined from inoculum (I) as total concentration at the beginning of the run and with sequential extraction method at the end of the run (R1 without ethanol and R2 with ethanol addition).

4.5   Stabilisation of ash with sulphide-rich water (V)

The stabilisation of the grate bottom ash with the sulphide containing effluent was studied with laboratory columns. The effluent used was from the sulphate reducing process (IV) treating the leachate from the landfill lysimeter (I). Stabilisation of elements was studied with concentration measurements from the column leachates and with sequential extraction of ash. In addition, COD and sulphate concentrations in the column effluents were determined along with pH measurements (Fig. 12, Table 7).

Changes in organic carbon content during the stabilisation were studied with leachate COD measurements. A clear decrease in the COD value of the column effluent compared to column influent was observed in the columns fed
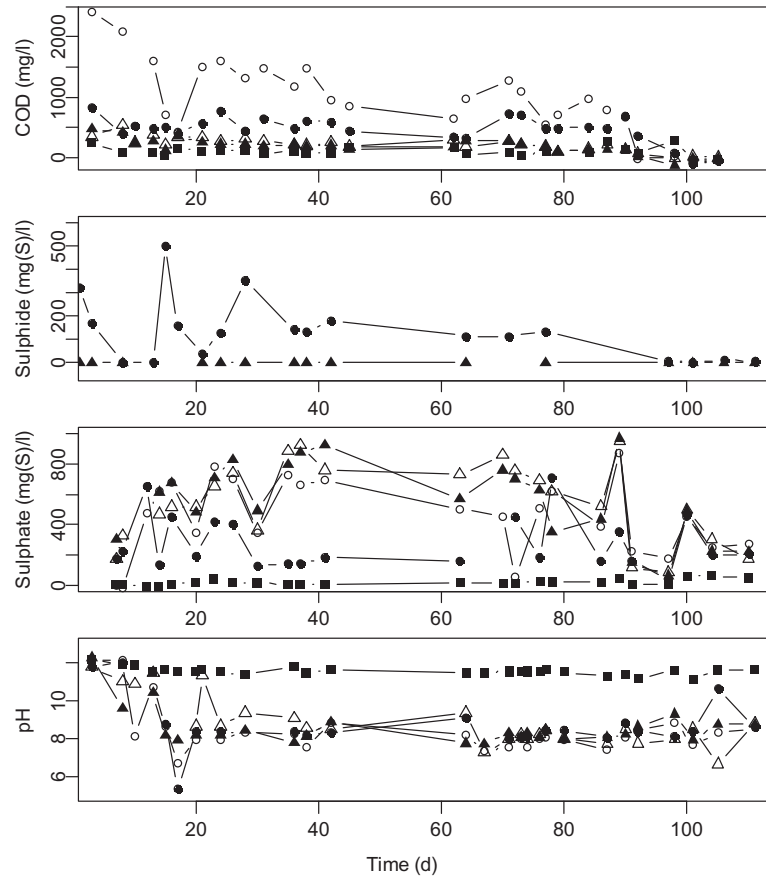
FIGURE 12   COD, sulphide, sulphate and pH of leachates from the grate ash stabilisation columns. The columns were fed with ion-exchanged water (C, ■), with leachate (L, Δ), with treated leachate (TL, ▲), with ethanol added leachate (LE, ○), and with sulphide-rich treated leachate (STL, •).

with the sulphide-rich effluent (STL) and with the untreated leachate with added ethanol (LE) (Table 7). COD in the effluent of the control column (C) (113 mg (O_2)/l), derived entirely from the bottom ash and was lower than in the other columns, as there was no input of COD from the landfill lysimeter or from the added ethanol.

The sum of sulphide and sulphate calculated as S was lower in the effluents of the TL and STL columns than in their feeds showing that S accumulated in the columns. The accumulation was highest in the STL column (Table 7). S in all column effluents was mainly present as sulphate, and the lowest concentration was in the control column. Some sulphide in the STL column went through the column; however, the concentration was low compared to that in the feed. The rapid decrease of pH from 12 to about 8 was observed in all the effluents except that of the control column. In the effluent of the control column pH was about 12 throughout the study (Fig. 12).

TABLE 7   Mean ($\bar{x}$) and standard deviation (SD) of COD (mg/l), sulphide (mg(S)/l), sulphate (mg(S)/l) and pH values from the feeds and the effluents of the stabilisation columns. The feeds of the columns were: leachate (L), leachate with added ethanol (LE), treated leachate (TL), sulphide-rich treated leachate (STL)) and ion-exchanged water (C). The corresponding column effluents were: L-C, LE-C, TL-C, STL-C and C-C. Not-measured values are denoted by – and the number of measurements by n.

	COD		S^{2-}		SO_4^{-2}		pH	
	$\bar{x} \pm SD$	n	$\bar{x} \pm SD$	n	$\bar{x} \pm SD$	n	$\bar{x} \pm SD$	n
L	291 ± 267	15	–		796 ± 108	9	7.94 ± 0.20	12
LE	1700 ± 397	15	–		754 ± 93	9	7.86 ± 0.28	12
TL	168 ± 41	15	0.33 ± 0.29	17	785 ± 105	12	7.95 ± 0.17	15
STL	676 ± 361	15	432 ± 199	22	88 ± 87	12	7.75 ± 0.18	15
L-C	223 ± 123	27	–		548 ± 265	22	8.88 ± 1.35	26
LE-C	969 ± 635	26	–		448 ± 251	24	8.42 ± 1.28	27
TL-C	191 ± 129	27	0.40 ± 0.33	15	557 ± 259	22	8.56 ± 0.98	26
STL-C	478 ± 219	27	133 ± 136	19	275 ± 177	23	8.68 ± 1.36	22
C-C	113 ± 79	25	–		16 ± 19	24	11.58 ± 0.21	28

The comparison of total element concentrations before and after stabilisation shows that the treatment with sulphide-rich effluent (STL) improved the retention and even led to the accumulation of S, Cu, and Zn into the bottom ash from the effluent (Fig. 13). The highest accumulations of Cu and Zn were in the STL column and that of S in the TL column. The total concentration of Cu increased by 145 % in the STL column compared to that in the fresh bottom ash, while in the LE column the increase was 94 %. In the other columns 22–52 % of Cu was leached out. The amount of accumulated Cu in the LE column was one thousand-fold compared to the estimated input from the leachate and was even higher in the STL column (Table 8).

Ca, P, S, Zn, and As were better retained in the columns fed with treated leachates (TL, STL) than in those fed with the corresponding untreated leachates (L, LE), when the total concentrations were compared at the beginning and end of the study (Fig. 13). In addition, Ca, S, Pb, Zn, and Cr were better retained in the column fed with sulphide-rich treated leachate (STL) than in the control column (C) fed with ion-exchanged water. Ca was best retained in the STL column in which the reduction in the total concentration was only 10 % compared to that in the fresh bottom ash. The sequential extraction of the bottom ash at the beginning and at the end of the study showed changes in the binding of the elements. Increases were most often detected in the organic material and sulphide containing fraction (4) and carbonate-bound fraction (2). The highest changes were observed in the binding of S, Cu and Zn in the STL column.

The concentration of Ca increased in the carbonate (2) and sulphide (4) fractions and decreased in the ion-exchanged fraction (1). The concentration of Ca increased in all columns in sulphide fraction (4). The increase was highest in the TL column (52 %) and lowest in the L column (5 %). In addition, there was
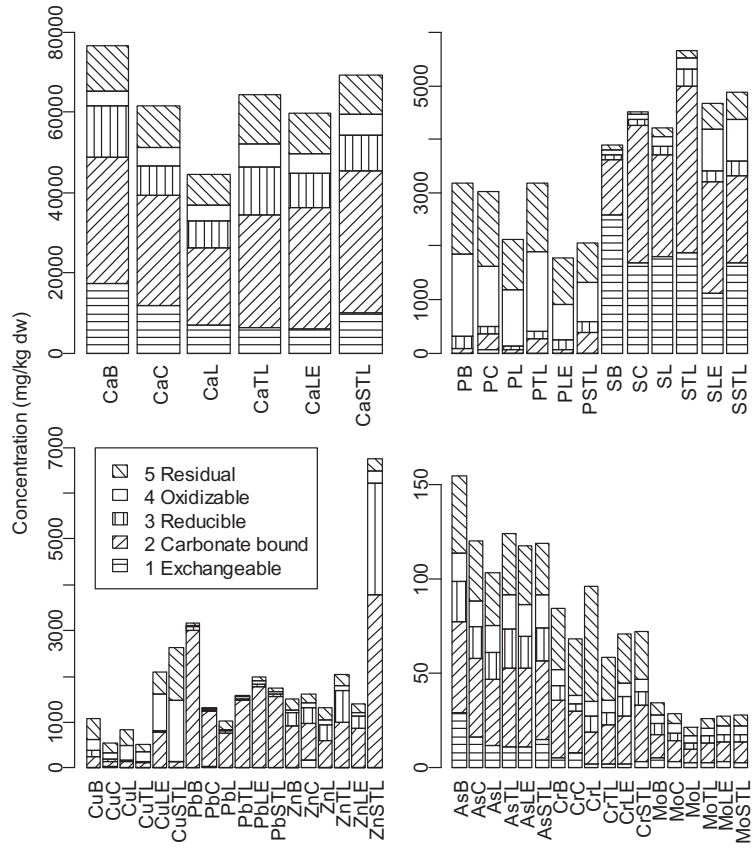
FIGURE 13   Sequential extraction of the grate ash before (B) and after stabilisation treatment. Treatments: ion-exchanged water (C), leachate (L), anaerobically treated leachate(TL), leachate with ethanol addition (LE) and sulphide containing anaerobically treated leachate (STL).

a 12 % increase in the carbonate fraction of the STL column. In the L column Ca leached out mostly from the ion-exchanged (60 % decrease) and carbonate fractions (39 % decrease).

The concentrations of S increased in all the fractions of all the columns during the study, except in the exchangeable fraction and, in the control column, in residual fraction. The highest increase compared to fresh ash (730 % both) was in the sulphide fraction in the LE, and STL columns. The second highest increase was in the residual fraction of the LE and STL columns. However, the highest absolute increases were in the carbonate (609–1050 mg/kg (d.w.)) and sulphide (690 mg/kg (d.w.)) fractions in the LE and STL columns.

TABLE 8   Concentrations (mg/l) of selected elements in the leachates fed to the stabilisation columns (determined 5-6 times during 111-day study). The detection limit (DL), mean concentration ($\bar{x}$), standard deviation (SD) and total input mg/kg(TS) (In) are presented.

	DL	Leachate			Leachate with ethanol			Treated Leachate			Sulphide containing treated leachate		
		$\bar{x}$	SD	In	$\bar{x}$	SD	In	$\bar{x}$	SD	In	$\bar{x}$	SD	In
As	0.1	<0.1	–	–	<0.1	–	–	<0.1	–	–	<0.1	–	–
Ca	0.005	350	41	9800	340	37	11500	350	22	9500	230	60	6500
Cr	0.02	<0.02	–	–	<0.02	–	–	<0.02	–	–	<0.02	–	–
Cu	0.02	0.062	0.028	1.72	0.05	0.037	1.79	0.025	0.014	0.68	<0.02	–	–
Mo	0.02	0.87	0.15	24	0.87	0.095	29	0.91	0.11	24	0.59	0.21	16
P	0.1	<0.1	–	–	<0.1	–	–	<0.1	–	–	<0.1	–	–
Pb	0.05	1.4	0.51	39	1.6	0.67	56	1.6	0.23	43	1.2	0.5	31
S	0.1	650	90	18000	690	169	23000	690	130	18500	4800	3300	136000
Zn	0.02	<0.02	–	–	<0.02	–	–	<0.02	–	–	<0.02	–	–

Cu accumulated in three columns with the highest increase in sulphide fraction (4). In the LE column, the increase was 250 % and in STL column 590 %. In addition, Cu increased by 212 % in the carbonate fraction of the LE column and 158 % in the residual fraction of the STL column. Pb was mainly bound in the carbonate fraction in all columns (74–93 %). Concentrations of Pb increased in residual fraction of the L column (340 %), LE column (55 %), and STL column (55 %). In the LE column Pb increased by 82 % in sulphide fraction. The concentration of Zn increased in all columns in sulphide fraction (38–313 %). The highest increase of Zn (740 %) was found in the Fe and Mn oxides bound fraction (3) in the STL column. In the same column relative increases in the carbonate and sulphide fractions were also high: 310 % and 313 %, respectively. In the control column a high increase of Zn in ion-exchanged fraction (1500 %) was observed.

The concentration of As increased in sulphide fraction of the TL column (19 %), LE column (11 %), and STL column (14 %). In the L column As leached more in the carbonate fraction (27 %) than in the other columns (12–14 %). The most obvious difference between As and Mo was the higher relative binding of As to residual fraction. Cr behaved similarly except in the L-column where it was accumulated in a residual fraction.

5 DISCUSSION

5.1 Main findings of the thesis

Under landfill conditions gasification bottom ash leachate had lower LS-ratio, higher leachate pH, and lower leachate DOC content than the grate ash leachate. In the laboratory lysimeter study the anaerobic weathering of gasification ash was shown to be slower than that of the grate ash due to lower residual organic carbon and moisture content. The main Ca-minerals in the fresh grate ash were gypsum and anhydride, while portlandite prevailed in the gasification ash according to modelling of batch leaching test results. Under landfill conditions the most obvious difference between the ash types was the higher pH of gasification ash leachate, which in turn affected chemical and toxicological characteristics. For example As leaching was higher from the gasification ash than from the grate ash, although, the total concentration in both ash types was the same.

The toxicity assays showed that both the gasification and the grate ash leachate can have adverse environmental effects, when assessment is based on the leachate as such without pH adjustment. Overall, it seems that the gasification ash leachate was more toxic than the grate ash leachate, which was probably related to a combined effect of inorganic contaminants, higher pH, lower DOC content and the presence of organic contaminants.

The present study shows that sulphate reducing process has the potential to remove 65 % of sulphate and some trace elements (Mn, Mo, Ni, Pb, Tl, Sb, Se, Zn) from the grate bottom ash leachate when an external source of carbon is provided. In addition, utilisation of sulphide-rich water in grate ash stabilisation was able to improve retention and accumulation of the elements. Stabilisation was not only a result of increased amount of low solubility sulphide compounds, but also due to weathering induced by organic carbon.

5.2 Leachate formation and characteristics

5.2.1 Leachate formation and LS-ration development in ash

The formation of bottom ash leachate from the grate firing ash and from the gasification ash was studied during initial phase of landfilling (1236 days). The leachate formation rate showed variation due to changing climatic conditions. The peaks in leachate flow rates coincided with the melting of snow layer in the beginning of April. Seasonal heavy rain has been observed to cause similar variation in leachate formation (Ishii et al. 2009).

The bottom ash LS-ratio development was dependent on the moisture content of the ash before disposal. Therefore, the initially dry gasification ash reached LS-ratio of 0.4 l/kg (d.w.) and LS-ratio of quenched grate ash increased from an initial 0.54 l/kg to 1.0 l/kg during the study period. The LS-ratio of the grate ash was as high as the values (from 0.6 to > 1 l/kg) obtained in 20-year full-scale studies (Kosson et al. 1996, Hjelmar 1996). If the initial moisture content would not be considered the LS-ratio of grate ash at the end of the study would be 0.46 l/kg. Regarding the LS-ratio the setup of the landfill lysimeter experiment can be considered as a worst case scenario of the initial phase of landfilling as there was no covering and the ash fill was quite shallow. On the other hand, the LS-ratios could represent some 20 years of landfilling in the case of covering shortly after filling. However, comparison with full scale conditions is challenging as only few full-scale studies exist and information from them is incomplete (Table 9).

TABLE 9   Bottom ash (BA) leachate pH and LS-ration obtained or calculated from landfill scale studies compared to information obtained in this study.

Material	Leach ate pH	LS-ratio	Weathering stage	Period	Assay	Reference
Gasification BA	13.6	10	Fresh	–	Batch	This study
Gasification BA	10	0.4	Intermediate	3	Landfill lysimeter	This study
Grate BA	10	10	Fresh	–	Batch	This study
Grate BA	7	1	Intermediate	3 y	Landfill lysimeter	This study
MSWI BA	8	0.2	Intermediate /weathered	1.5 y	Heap (375 t)	Freyssinet et al. (2002)
MSWI BA and fly ash (15 %)	8.7–10.5	0.017–0.615	Intermediate /weathered	20 y	Full scale	Hjelmar (1996)
Combined ash	5.1–7.5	–	–	5 y	Full scale	Hjelmar (1996)
MSWI BA	8.7–11.3	0.007/y	–	1 y	Full scale	Johnson et al (1999)
MSWI BA	11.5–12	0.2–0.3	Fresh	129 d	Heap	Marchese & Genon (2009)

5.2.2 Chemical characteristics of leachate

In the present study, chemical characteristics of leachates were studied with the landfill lysimeters, with the laboratory lysimeters and in the batch tests. In general the gasification ash had lower elemental concentrations, lower carbon content and higher pH in all studies (I, III). As an exception, Arsenic leaching was higher from the gasification ash (I). The gasification ash pH was at the same level in all studies, while the pH of the grate ash leachate was significantly lower in the landfill (I) and laboratory (III) lysimeters than in the batch test (I). The changes in grate ash leachate composition (I, III) were related to biodegradation of residual organic carbon. Indirect evidence such as a decrease in the COD and BOD level of the grate ash leachate and changes in the leachate redox potential along with temperature, support this. The role of the organic carbon in the grate ash weathering has also been reported previously (Rendek et al. 2006, Belevi et al. 1992). Belevi et al. (1992) estimated that biodegradation can produce 1 mol/kg of weak acid and that the neutralisation capacity of grate bottom ash is 2 mol/kg (pH 7).

Leachate TOC and DOC were higher in the grate ash than in the gasification ash leachate during the first 355 days of landfill lysimeter study. This reflects the amount of VS: 5.5 %of TS in the grate ash and 0.1 % of TS in the gasification ash. The levels of the DOC in the grate ash leachate were within the same range (90–290 mg/l) as previously reported for leachate of fresh grate bottom ash in laboratory studies (Meima & Comans 1999, van Zomeren & Comans 2009). Weathering is known to rapidly decrease the concentration of the DOC and values of 10–100 mg/l are typically reported for leachate of weathered grate bottom ash (Dijkstra et al. 2006, Meima & Comans 1999, van Zomeren & Comans 2009).

The concentrations of trace elements in the both of studied leachates were low in comparison with those determined in previous studies of grate bottom ash (Ferrari et al. 1999, Chou et al., 2009, Römbke et al. 2009). For example, the present concentrations of Cr, Cu, Pb and Zn were among the lowest reported by Römbke et al. (2009), who determined the trace elements from water eluates of twelve different samples of MSWI grate bottom ash. Studies on the bottom ash of MSW-gasification are scarce: only the elemental composition of ash (not leachates) and mass balance of the trace elements between different residues have been published (Raskin et al. 2002, Cioni & Riccardi 2002).

The leachate concentrations of all elements in the grate ash batch test (LS 10 l/kg) were higher than the leached amounts under landfill conditions (LS 1 l/kg (d.m)), as was expected based on LS-ratios. In general, the difference in leaching behaviour of the two ash types were more pronounced under landfill conditions than at laboratory batch test. For example: under landfill conditions from the grate ash 20 % Ca and 51 % of S were released, compared to the batch test; while from the gasification ash 1.8 % of Ca and 5.3 % of S were mobilised compared to the batch test. This is probably related to lower LS-ratio (0.46 l/kg (d.m)) of the gasification ash under landfill conditions. However, from a

longitudinal perspective this can mean a longer release period and therefore longer aftercare period for the gasification ash.

Leaching of As from the gasification ash was higher than from the grate ash both in the batch test and under landfill conditions, although the total concentration in the both types of ash was the same. This was probably due to higher pH of the gasification ash, the arsenic solubility is known to increase with increasing pH and oxidation state (Cornelis et al. 2008). Arsenic was the only element in both ash types that exceeded the EU landfill limit-values for non-hazardous waste (European Council 2003). In batch tests, the released amount of As was 10 times higher than from the gasification ash and 1.5 times higher from the grate ash than the limit value (2 mg/kg (d.w.)) (European Council 2003). In both landfill lysimeter leachates, the maximum As concentration observed exceeded the limit value for percolation test (0.3 mg/l) (European Council 2003). Based on the LS-ratio observed in the landfill lysimeters, it can be estimated that it will take from 60 to 75 years to reach the same LS-ratios and released amounts than in the batch test. However, release time and amount of As can differ from the estimated values as weathering decreases pH and increases the oxidation state.

5.2.3 Leachate toxicity

The three aquatic toxicity assays showed that both the gasification and the grate ash leachates can have adverse effects on different trophic levels when assessment is based on leachate as such without pH adjustment. Overall, it seems that the gasification ash leachate was more toxic than the grate ash leachate. To the author's knowledge there are no previous studies on the gasification bottom ash toxicity. However, the present results of moderate and decreasing toxicity of the grate ash leachate were parallel to those found in the other grate bottom ash toxicity studies confirming that the methodology used was reliable (Table 10). For the gasification ash leachate the maximum toxicity was observed after two years, while the grate ash leachate showed a decreasing trend in toxicity during the three-year follow-up period. Gasification ash had toxic properties even three years after disposal, while the grate ash leachate showed no toxicity in any of the assays at the end of study.

The higher toxicity of the gasification ash leachate compared to the grate ash leachate in the water flea and algae assays were probably mainly related to higher pH. In addition, pH independent toxicity of gasification ash leachate in the bioluminescence assay and the grate ash leachate in the water flea assay was observed. The high pH can cause toxicity directly as a high concentration (pH > 10) of OH- ions are known to be toxic for example to *Daphnia Magna* (Seco & Vale 2003). The indirect effects of pH are related to the solubility and speciation of elements. In weathered bottom ash, reactive sorbet minerals such as

TABLE 10   Toxicity of bottom ash from grate firing (GR), fluidised bed combustion (FBC) and gasification (GA) of waste.

Process	Solvent	LS-ratio (l/kg)	pH	Organism	Dilution (%)	End point	Reference
GA	water	0.02–0.31	9–12.4	Algae (DS[a] or PS[b])	75–NT	EC$_{50}$	This study
				water flea (DM[c])	0.09–0.52		
				Luminescent bacteria (VF[d])	4.7–8		
GR	water	0.56–1	6–8.5	Algae (DS or PS)	NT[e]	EC$_{50}$	This study
				water flea (DM)	0.54–NT		
				Luminescent bacteria (VF)	NT		
GR	water	10	≥12	Algae (DS or PS)	12.5–25	LID[f]	Römbke et al. (2009)
				water flea (DM)	6.25–50		
				Luminescent bacteria (VF)	33–100		
GR	water	10	10–12	Algae(DS or PS)	12.5–100	LID	Römbke et al. (2009)
				water flea (DM)	512–100		
				Luminescent bacteria (VF)	16.7–100		
GR	water	10	8.7–10	Algae(DS or PS)	50–100	LID	Römbke et al. (2009)
				water flea (DM)	25–100		
				Luminescent bacteria (VF)	100		
FBC	acetic acid	20	8.3	Luminescent bacteria (VF)	29–60	Inhibition%	Chou et al. (2009)
			11.7	Luminescent bacteria (VF)	>3		
GR	water	10	8.9–12.5	Algae (PS)	0.4–8.7	EC$_{50}$	Lapa et al. (2007)
				water flea (DM)	<0.5–95		
				Luminescent bacteria (VF)	1–(>99)		
GR	water	0.5–1.5	8±0.5	Algae(PS)	< 1.6–34.6	IC$_{50}$	Triffault- Bouchet et al. (2005)
				water flea (DM)	NT	EC$_{50}$	
				Luminescent bacteria (VF)	14–20	IC$_{50}$	
GR	water	10	>11	Algae(PS)	1	EC$_{50}$	Ferrari et al. (1999)
			8	Luminescent bacteria (VF)	25–45		Ferrari et al. (1999)

[a]*Desmodesmus Subspicatus*, [b]*Pseudokirchneriella subcapitata*, [c]*Daphnia Magna*, [d]*Vibrio Fischeri*, [e]not toxic, [f]Lowest ineffective dilution

Fe/Al-hydroxides are present and elements such as Cd, Pb, Zn, Cu and Mo have a high affinity for them (Meima & Comans, 1999). However, under strongly alkaline conditions (pH > 10) Me-hydrolysis can take place and increase the amount of dissolved metals (Meima & Comans, 1999). Therefore, highly alkaline conditions can potentially increase toxicity. The present results show that concentrations of Al, Ca, Mo and Na increased with increasing pH in the gasification ash leachate (I). Lapa et al. (2007) observed that toxicity of grate ash leachate increased with an increase in the leachate pH. As Seco & Vale (2003) point out, the pH in the exposed environment plays an important role in regards to toxicity of metals and, therefore, the toxicity assays should be performed in the native pH of leachate. Due to high buffering capacity of ash leachates, dilution needs to be significant to remove toxic characteristics. This can be seen for example in the EC_{50} values (< 1 %) obtained in the water flea assay for the gasification ash leachate.

The observed trends of toxicity within the both leachates seemed to follow conductivity. However, conductivity and element concentrations were lower in the gasification ash leachate than in the grate ash leachate throughout the study. Therefore, concentrations of the toxic elements gave no explanation for the higher toxicity of the gasification ash leachate. Although, no conclusion can be drawn about the leachate toxicity based on single element toxicity, the potential causes of leachate toxicity were screened based on the EC_{50} database and limit value comparisons. Based on the EU-limit values for the landfilling of non-hazardous waste As in both leachates and Mo in the grate ash leachate were identified to be present in elevated concentrations compared to percolation test limit values (European Council 2003). In addition, in the database survey As, Ca, Cd, and Cu were identified as having a maximum concentration in both leachates, which could potentially have toxic effects in either water flea or algae assays (US EPA 2011).

The lower TOC and DOC of the gasification ash leachate could explain the higher toxicity compared to the grate ash leachate. The presence of dissolved organic carbon can lower the bioavailability of the hydrophobic organic contaminants (Haitzer et al. 1998, Akkanen & Kukkonen 2003). Therefore, the lower TOC content and the lower proportion of DOC from TOC in the gasification ash leachate could have increased bioavailability of contaminants compared to the grate ash leachate. The presence of DOC is known to control the availability of certain heavy metals in bottom ash, of which Cu is the best known example. Dissolved Cu is known to be mainly (95–100 %) bound to DOC and its leaching is controlled by strong organic ligands and in weathered ash also by Fe/Al-hydroxides (Meima et al. 1999). High pH can also increase the dissolution of contaminants sorbed to inorganic surfaces such as Fe/Al hydroxides, which release cations under highly alkaline conditions (pH > 10) (Meima et al. 1999). Therefore, high pH can increase dissolution of Cu by several mechanisms.

In the present study, the fact that both leachates induced EROD-activity suggests that organic contaminants could have partially caused the toxicity.

Based on an EROD assay, Osaki et al. (2006) also concluded that the toxicity they observed for the ash landfill leachate was not related to elemental ions. In addition, the present result of gasification ash toxicity in the bacteria assay is similar to observation of Chou et al. (2009) that grate ash leachate was toxic to luminating bacteria, regardless of the pH level. However, the concentrations of PAH-compounds in the present study were below the detection limit of 10 ng/l, which is less than Liu et al. (2008b) observed for the grate bottom ash leachate under static leaching conditions.

5.3 Bottom ash composition and weathering

5.3.1 Mineral composition of fresh ash

The mineral composition of both ash types were studied based on the pH and main element composition of leachate in the batch test. The equilibrium modelling showed that the grate ash leachate pH was likely controlled by gypsum, while gasification ash leachate was controlled by portlandite. The leaching of the calcium and sulphate are controlled by the same mineral phases such as anhydrite, gypsum and ettringite depending on the weathering stage of ash (Table 11). In the dry grate ash calcium and sulphate are known to be present mainly as anhydrite ($CaSO_4$), which forms gypsum ($CaSO_4*H_2O$), when it comes into permanent contact with water (Kirby & Rimstidt 1994). The present results for the grate ash show that in the batch test pH of 10.84 the Ca-mineral closest to equilibrium were gypsum (SI −0.806) and anhydride (SI −1.056), however, both were under-saturated. The gasification ash leachate was oversaturated with respect to portlandite ($CA(OH)_2$) (SI 1.324) in the batch test (pH 13.55). This is similar to previous studies showing that portlandite prevails at the high pH-range (Hampson & Bailey 1982, Meima & Comans 1997a).

TABLE 11   Calcium minerals prevailing in bottom ash of different age/weathering stage.

Processes	pH	Age	Ca-Minerals	Reference
MSW GA	13.6	fresh	portlandite	This study
MSWI	10.8	fresh	anhydride, gypsum	This study
MSWI	12.3	fresh	portlandite, andhydride	Meima & Comans (1997b)
MSWI	10-10.5	6 wk	ettringite, gypsum, anhydride	Meima & Comans (1997b)
MSWI	8.5	12 y	calcite	Meima & Comans (1997b)
MSWI	11–11.5	4 y	ettringite, Ca-zeolites	Zevenbergen et al. (1994)
MSWI	8.2–8.5	12 y	calcite, gypsum, 2:1 clays	Zevenbergen et al. (1994)
MSWI	9.0	14 y	hydrocalumite, ettringite, amphibole	Bayseno & Schmal (2010)

In the gasification ash, the total amount of sulphur was low compared to that of calcium, and in batch test, a large share of the Ca was released, while in the landfill lysimeter only a small fraction was actually released. The Ca concentration in the gasification ash leachate showed an increase along with decreasing pH in the lysimeter. This indicates that release of the Ca could further increase as the weathering of the gasification ash proceeds.

In the grate ash batch test (pH 10.84), the concentration of dissolved Al (22.2 mg/l) was high, while in the gasification ash leachate it was low (0.79 mg/l, pH 13.55). However, under landfill conditions Al leaching was higher from the gasification ash than from the grate ash. The modelling of batch test results show that the grate ash leachate was oversaturated with respect to diaspore (SI 1.817), boehmite (SI 0.112) and gibbsite (SI 0.399). This suggests that aluminium hydroxides control the pH of the fresh grate ash. Under landfill conditions the low leaching of Al from the grate ash could be due to low solubility of clay minerals like aluminosilicates, which are formed during weathering (Meima & Comans 1997b). This is further supported by the lower leaching of Si from the grate ash than from the gasification ash. Quenching is known to cause clay formation from glass minerals formed during incineration and weathering increases clay formation (Zevenbergen et al. 1996). In the gasification ash the high amount of Si leached could better fit the assumption that gibbsite $Al(OH)_3$ was controlling Al leaching under landfill conditions (Johnson et al. 1999, Meima & Comans 1997b). The hydrolysis of gibbsite could also partly explains the high pH observed in the gasification ash leachate (Meima & Comans 1997b). However, in batch test pH (13.55), the gasification ash leachate was undersaturated with respect to both diaspore (SI –2.4) and gibbsite (SI –3.823).

In the future modeling of the lysimeter leachate results in combination with mineralogical analyses could give better insight into weathering processes under landfill conditions. However, considering the flow rate results it is questionable, whether model based on the equilibrium assumption is applicable.

5.3.2 Weathering under anaerobic conditions

The weathering of both types of ash under anaerobic conditions was studied with laboratory lysimeters (III) and compared to parallel aerobic lysimeters in order to show the differences between these conditions. The weathering of both types of ash was observed as a rapid change in leachate composition during the first 30 days of the study. In the grate ash leachate the pH and conductivity decreased under anaerobic conditions similar to those in previous large scale experiments (Johnson et al. 1999, Freyssinet et al. 2002). It is assumed that, information on weathering mechanisms from large scale experiments are actually obtained under anaerobic conditions.

The effect of anaerobic conditions was compared to those of aerobic by aerating one of the parallel laboratory lysimeters from day 323 onwards.

Aeration increased leaching of Ca and SO_4 from the grate ash, similar to previous carbonation experiments with air and pure CO_2 (Meima et al. 2002, Todorovic & Ecke 2006). This could be due to a decrease of pH which increases solubility of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) and therefore concentrations of Ca and SO_4 in the leachate (Meima & Comans 1997b). Chloride is easily soluble in both types of ash. Aeration did not affect chloride leaching, which is known to be independent on pH (Todorovic & Ecke 2006, Freyssinet et al. 2002). Also in the gasification ash, aeration decreased the leaching of Ca. However, the results of sequential extraction were unable to confirm the phenomenon observed in the leachate concentrations, which implies that pore water and precipitation/dissolution of Ca-compounds in it play a central role in the chemical changes induced by aeration. Aeration probably induces formation of calcite ($CaCO_3$) and other carbonates, which have lower solubility than the hydroxides formed when dry ash gets into contact with water (Meima & Comans 1997b).

Aeration decreased the leaching of Mo and Cu in both types of ash and Ba in the gasification ash. The sequential extraction results show that leaching of Mo and Cu was hindered in the aerated lysimeters. Natural weathering has been previously shown to decrease Cu and Mo leaching (Arickx et al. 2006, Meima et al. 2002). Meima et al. (2002) found that artificial carbonation does not have a similar effect. This implies that other processes in addition to carbonation are involved (Meima et al. 2002). Also, complex formation with organic carbon is known to affect the leaching of Cu (Olsson et al. 2009).The present results show that, aeration decreased the initial high concentrations of Ba in the gasification ash leachate. This result is similar to that of Arickx et al. (2006), who found that aging decreased Ba concentrations.

Aeration increased the leaching of Cr from both ash types and Mg and Pb from the grate ash according to the sequential extraction results. Aeration increased solubility of Cr slightly more than the anaerobic conditions. This is similar to the previous results showing that aging and aeration increased leaching of Cr (Arickx et al. 2006, Cai et al. 2003). Cai et al. (2003) propose that metallic aluminium reduces Cr (VI) to Cr (III) under anaerobic conditions, which decreases solubility. The sequential extraction shows the highest increases were in oxidisable fraction, which supports reduction-hypothesis. Leaching of Pb from the grate ash increased during aeration. Todorovic & Ecke (2006) argue that artificial carbonation increased cumulative leaching of Pb and Zn. Pb is known to bind to carbonates and newly formed silicate minerals can also retain it (Piantone et al. 2004). The present sequential extraction results show that aeration reduced Pb from carbonate fraction and from residual fraction. The increased leaching of carbonates can result from changes in pH. The reduction in the residual fraction indicates that aeration corrodes silicate minerals and releases Pb bound into them.

In the gasification ash, low residual organic carbon content measured as low VS content could not support biodegradation. Therefore, carbonation was slower in the gasification ash than in the grate ash, which can be seen in the CO_2

absorption pattern during the laboratory lysimeter study (III). Both types of ash absorbed about the same amount of CO_2 during the aeration period; however, the pattern of absorption was different. In the grate ash, the absorption of CO_2 decreased almost to zero towards end of the study period, while in the gasification ash a similar decrease was not observed and saturation was not reached.

It seems that compared to biodegradation, other pH decreasing processes such as the diffusion of the atmospheric gases and dissolution of them to pore water are slow. Totally dry ash reacts very slowly with CO_2; the CO_2 must first dissolve into pore water (Rendek et al. 2006). Therefore, the initially dry gasification ash is not very reactive until rainwater seeps in to the ash heap. In dense gasification ash the diffusion of atmospheric CO_2 can be slow and limited to surface layers. This has been shown on the pilot-scale for conventional bottom ash (Freyssinet et al. 2002). In addition, there is also some evidence that the carbonation itself is slow, taking almost a week under pressure (0.1–0.2 bar) (Rendek et al. 2006).

5.4 Sulphate reduction for leachate treatment and ash stabilistation

5.4.1 Removal of COD in sulphate reducing UASB

The sulphate reducing UASB was able to remove 60–70 % of the total COD. Based on the comparison with the reference reactor (R1), the added ethanol was not totally degraded. Undegraded ethanol was 30–50 % of the residual COD and the rest was originally present in the leachate. Ethanol is effectively used by SRB when a surplus of sulphate is available (Nagpal et al., 2000). Therefore, incomplete removal of the COD could be due to inhibition by toxic substances. The negligible removal of the COD in the reactor without ethanol addition (R1) implies that SRB or other micro-organisms were unable to use the leachates own COD (ca. 300 mg/l) as a source of carbon. The low BOD_7 value (15 mg/l) of the influent, without the ethanol addition, indicates that only a small fraction of the leachate COD originated from readily bioavailable organic matter. According to Zhang et al. (2004), only 1.2 % of the organic carbon content of bottom ash was found to consist of amino acids, hexoamines and carbohydrates, which form the "labile" or easily biodegradable portion of organic compounds. When the COD originating from the leachate is subtracted from the total COD of the influent of the ethanol supplied reactor (R2), the actual COD:SO_4-ratio was 0.49 and thus, there was not enough easily bioavailable carbon to reduce all of the sulphate.

A possible cause for the incomplete removal of the COD could have been a high concentration of cations such as Na and Ca, which can inhibit anaerobic processes. When concentrations of Ca are about 400 mg/l, calcium precipitates

($CaCO_3$, $Ca_3(PO_4)^2$) may entrap biomass and limit the transport of substrates (Hulshoff Pol et al. 1998, Widdel 1988, Dries et al. 1998). When calcium is precipitated as phosphates, it can also cause phosphate deficiency (Widdel 1988). The calcium concentration fluctuated between 200–470 mg/l in the influent and was consistently lower (< 280 mg/l) in the effluent of the ethanol-supplied reactor (R2), which indicates that calcium was precipitated in the reactor.

5.4.2 Element removal in sulphate reducing UASB

Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, and Zn, which were effectively removed in the ethanol-supplied reactor (R2), are known to precipitate as non-water soluble sulphides (Widdel 1988). In addition, Ba, Ca, and Sr, which form water-soluble sulphides, were removed in R2. Increase in the carbonate fraction of R2 suggested that bicarbonate formed as the end product of the sulphate reduction was mainly precipitated as $CaCO_3$. Ba and Cu were also removed in R1, which suggests that their removal mechanism was other than precipitation as sulphides. The inhibitory effect of calcium carbonate precipitation in R2 could explain the decrease, both in sulphate reduction and in removal of the elements at the end of the run.

The sequential extraction confirmed that precipitation as sulphides was the main mechanism in the removal of trace elements from leachate, and that Cu, Mo and Zn in particular were effectively bound to organic matter and/or sulphides (fraction 4). This is supported by the result that in the ethanol supplied reactor (R2) over half of S was found in fraction 4. However, in the case of Cu the fraction containing organic matter and sulphides was equally important in the both reactors, which implies that organic matter probably absorbed most of removed Cu. In the MSW landfill leachate, formation of organic complexes can decrease amount of the free metal ions below 10–30 % and, therefore, decrease efficiency of heavy metal removal by sulphide precipitation (Baun & Christensen 2004). Formation of colloids and organic complexes could explain why the extraction results of the reference reactor (R1) showed a removal of 75 % for Cu.

Higher removal of As and Mo in the ethanol-supplied reactor (R2) compared to control reactor (R1) could have been, in addition to sulphide formation, due to precipitation as carbonates or sorption to biomass. In the reference reactor (R1) the elements were removed probably mainly due to sorption to biomass. In fact, it has been shown in the recent study of Villa-Gomez et al. (2012) that excess sulphide needs to be present in order to favour the precipitation of metals as sulphides. When the metal to sulphide ratio is below that of calculated from the stoichiometric equation, metals are more likely to sorb into organic material or precipitate with macronutrients such as phosphate (Villa-Gomez et al 2012).

5.4.3 Stabilisation of grate ash with sulphide

The sulphide-rich effluent of the UASB-reactor (R2) was able to stabilize elements (Ca, Cu, Pb, S, and Zn) in to the grate bottom ash and to remove sulphide from the effluent of the UASB-reactor. Besides formation of insoluble sulphides the stabilisation was probably due to organic carbon and CO_2 from biodegradation. Improved retention of Ca was the result of an increased concentration of Ca in the sulphide (4) and carbonate (2) fractions. The bottom ash was kept under anaerobic conditions and showed an increase in carbonate fraction i.e. carbonation was the result of CO_2 originating from the degradation of organic carbon in the ash or added ethanol. Considering the rapid pH drop in all the leachate fed columns and the fact that COD decreased in all the columns, some microbial activity might have caused rapid carbonation of the bottom ash both when the treated and untreated leachates were used.

Up to 10 % of the estimated input of S was accumulated and its binding changed, as expected, towards low solubility compounds (fractions 4 and 5). The increase of S in fraction 4 (LE and STL columns) indicated the reduction of sulphate to sulphide or an increased binding to organic carbon. The COD measurements of the column feeds and effluents suggest that COD was retained partly in the STL column. However, both the input and the retained amount of COD were lower in the sulphide fed column (STL) than in the corresponding non-sulphide fed column (LE); while the increase in the organic carbon and sulphide fraction (4) was the same in both the columns, indicating that the increase in the STL column was at least partly due to an increase in sulphides. In the sulphur cycle, metal sulphides are long-term natural sulphur storage (Lens & Kuenen 2001) and in sequential extraction, an extreme condition such as pH 2 has to be used to dissolve elements bound to sulphides. Therefore, the changes in binding show that it is possible not only to enhance naturally occurring mineral changes, but also to affect end-products so as to favour the low solubility compounds such as sulphides.

Cu was mainly accumulated in the sulphide (4) and residual (5) fractions in the column fed with sulphide-rich effluent (STL). The increase in fraction 4 was higher when ash was treated with sulphide-rich effluent compared to the effluent with low sulphide content (LE), indicating that Cu stabilisation was at least partly a result of sulphide formation. The increase in the LE column can also be due to complexation of Cu with organic carbon (Meima & Comans 1999). In the LE column Cu was increased in fraction 4 and to some extent in the carbonate-bound fraction (2). An increase in the carbonate-fraction can indicate the formation of minerals like malachite ($Cu_2(OH)_2CO_3$) (Meima et al., 2002)

The carbonate fraction had a major role in stabilisation of Pb and Zn indicating that the observed stabilisation was result of increased carbonation due to CO_2 from biodegradation. Pb is known to be controlled by carbonate precipitation (Johnson et al. 1996) and in this study also, it was mainly bound to the carbonate fraction. The concentration of carbonate-bound Pb decreased in

all columns compared to fresh bottom ash. Also Zn accumulated mainly in the carbonate and in the Fe- and Mn- oxides fraction in the STL column.

The stabilisation columns were flushed with ion-exchanged water for 21 days at the end of the experiment to ensure that the changes observed were of a permanent nature. The present results show that the overall changes in binding were such that most of the elements studied were better retained or even accumulated in the bottom ash in equilibrium pH, which was reached during the study. Meima and Comans (1997b) showed that long-term leaching of elements is determined by the pH of the bottom ash, which in turn is the result of mineral composition and is about 8.3 in equilibrium.

6 CONCLUSIONS

The gasification ash leachate had a higher pH, but lower DOC and element concentrations than the grate ash leachate under landfill conditions. The observed differences were mainly due to lower initial moisture and carbon content of the gasification bottom ash. LS-ratio of the non-quenched gasification ash was 0.4 l/kg (d.w.) compared to 1 l/kg (d.w.) of grate ash after three years of landfill disposal. As a result, the release of major elements from the gasification bottom ash was delayed compared to the grate ash, which could mean longer after-care period for the gasification ash. In addition, the high pH (> 13) of the gasification ash increased As leaching compared to the grate ash both in the laboratory batch test and under landfill conditions.

Both bottom ash leachates showed toxic properties. The conductivity corresponds to observed toxicity changes within the both leachates indicating the role of inorganic contaminants in the toxicity. EROD assays showed that the presence of the organic contaminants may also contribute to toxicity of both the leachates. The waste gasification ash leachate appears to be more toxic and the toxicity lasted longer than that of the grate ash leachate. The higher toxicity of the gasification ash leachate probably was due to direct and indirect effects of high pH. However, pH independent toxicity of gasification ash leachate was observed with the bioluminescent bacteria. The higher toxicity of the gasification ash leachate could not be explained with the element concentrations as they all were constantly lower in the gasification ash leachate than in the grate ash leachate. However, the lower TOC and DOC content of gasification ash could affect the availability of contaminants and therefore explain the higher toxicity of the gasification ash leachate in combination with the high pH. As the EC_{50}-values were even below 1 % in the gasification ash leachate significant dilution of the leachate is required to remove the toxicity.

Anaerobic conditions did not change known weathering behaviour of the grate bottom ash indicating that biodegradation and therefore residual carbon content of the ash has key role in the weathering during landfill disposal. The addition of aeration did not result in changes that would induce changes of the same magnitude. No further decrease in the concentrations of toxic elements

was detected in the leachates during aeration. Therefore, the role of atmospheric carbon dioxide in short-term weathering of both ash-types is questionable. As the gasification ash contains very little residual carbon it seems that during anaerobic weathering; salts, organic carbon, and toxic elements are merely leached out. In grate ash the biodegradation of organic carbon probably produces enough carbon dioxide to carbonate the ash, but other chemical weathering processes and leaching are also involved.

Sulphate reduction can be utilised to treat grate ash leachate. However, the process requires an external supply of organic carbon. The sulphate-reducing process decreased concentrations of potentially harmful elements such as Cu, Mo, Ni, and Sb in the grate ash leachate. The removed elements precipitated as insoluble sulphides also when the initial concentrations were low.

Sulphide-rich effluent from sulphate reducing processes can be used to stabilise bottom ash. When the sulphide-rich effluent was added the retention of Ca, Cu, Pb, S, and Zn in the grate bottom ash was improved. The stabilisation was due to increase of low solubility metal sulphides and increased weathering induced by organic carbon. The elements stabilised as metal sulphides are not likely to leach out even at low pH conditions. In addition, utilisation of sulphide-rich effluent for stabilisation was able to remove most of the sulphide from the anaerobic effluent. Utilisation of sulphate reduction in leachate treatment and stabilisation of MSWI bottom ash could reduce contaminant release from landfills, treatment/storage sites and utilisation sites. Furthermore, sulphide from treated leachate can be removed, diminishing the need to use other post-treatments. However, more knowledge from larger scale experiments is needed before practical solutions can be designed.

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Acknowledgements

YHTEENVETO (RÉSUMÉ IN FINNISH)

Jätteenpolton ja -kaasutuksen pohjatuhkien ja niistä muodostuvien suoto-vesien ominaisuudet ja käsittely

Laitospoltto jätteenkäsittelymenetelmänä on lisääntynyt sekä Euroopassa että globaalisti tarkasteltuna viimeisten vuosikymmenien aikana. Tämä johtuu toi-saalta kasvavista jätemääristä ja toisaalta tarpeesta hyödyntää jätteen sisältämä energia. Jätemäärien kasvaessa on etsitty uusia tehokkaita, hygieenisiä ja vähän ympäristöä kuormittavia jätteenkäsittelymenetelmiä. Jätteenpoltto vastaa aina-kin osittain näihin haasteisiin. Jätteen energiasisällön hyödyntämisellä tavoitel-laan kasvihuonekaasupäästöjen vähentämistä verrattuna kaatopaikkasijoittami-seen. Jätteenpoltto kuitenkin tuottaa kiinteitä sivujakeita sekä kaasumaisia päästöjä, joista on huolehdittava tavalla, joka minimoi mahdolliset haittavaiku-tukset ympäristölle ja ihmisille. Tämän työn tavoite oli tutkia yhdyskuntajätteen polton pohjatuhkien ja niistä kaatopaikalla muodostuvien suotovesien ominai-suuksia, suotovesien ympäristövaikutuksia sekä tuhkien ja suotovesien käsitte-lymenetelmiä, joilla ympäristöhaittoja voitaisiin pienentää.

Yhdyskuntajätteen polton pohjatuhkan laatu ja määrä riippuvat poltto-prosessista. Tässä työssä tutkittiin yleisesti käytössä olevan arinapolton sekä kiertoleijupetikaasutuksen pohjatuhkaa. Jätteen arinapoltossa pohjatuhkaa muodostuu 24 – 45 % poltetun jätteen massasta, joka puolestaan on 85 – 90 % kiinteiden jäännösjakeiden massasta. Vastaavasti kaasutuksessa pohjatuhkaa muodostuu 2 – 9 % poltettavan jätteen massasta ja se on 20 – 36 % kaasutukses-sa muodostuvien kiinteiden jäännösjakeiden massasta. Pohjatuhkat täyttävät useimmiten tavanomaiselle kaatopaikkajätteelle EU:n kaatopaikkadirektiivissä annetut kriteerit ja ne eivät siten ole ongelmajätteitä. Pohjatuhkaa voidaan hyö-tykäyttää, mutta useimmiten tarvitaan esikäsittelyä, joka vähentää haitta-ainepitoisuuksia tai parantaa tuhkan geoteknisiä ominaisuuksia. Tavallisimmat käsittelymenetelmät ovat tuhkan vanhentaminen varastoimalla ja seulominen haluttuun raekokoon. Hyötykäyttö ei kuitenkaan käytännössä ole aina mahdol-lista esimerkiksi korkeiden kustannusten, riittävän lähellä sijaitsevien kohteiden puutteen tai tuhkan ominaisuuksien vuoksi. Kun hyötykäyttö ei ole mahdollis-ta, pohjatuhka sijoitetaan kaatopaikalle. Tällöin on varmistuttava, että tietylle alueelle kerätyt suuret tuhkamassat eivät vuosikymmenien tai -satojen saatossa aiheuta sellaisia päästöjä, joista voisi olla haittaa ihmiselle tai ympäristölle.

Suotovettä muodostuu sadeveden kulkeutuessa tuhkan lävitse. Tässä tut-kimuksessa havaittiin, että kaatopaikalla muodostuvien suotovesien laatuun vaikuttivat etenkin tuhkassa olevan jäännöshiilen määrä sekä tuhkan kosteuspi-toisuus kaatopaikalle sijoitettaessa. Jäännöshiili ja kosteuspitoisuus vaikuttavat tuhkassa tapahtuviin mineraalikoostumuksen muutoksiin, joita kutsutaan van-henemiseksi (eng. weathering). Tuhkan vanhenemisen etenemistä voidaan seu-rata suotoveden pH:n muutosten avulla. Tuoreen tuhkan ja sen suotoveden korkea pH ($\geq$ 12) laskee tuhkan vanhetessa kohti kalsiittimineraalille tyypillistä tasapaino-pH:ta 8,3. Tuhkan pH-muutos on toisaalta seurausta mineraalikoos-

tumuksen muutoksesta ja toisaalta sillä on merkittävä vaikutus haitta-aineiden, kuten raskasmetallien, liukenemiseen. Kaatopaikkaolosuhteissa pH:n laskun havaittiin olevan nopeampaa enemmän jäännöshiiltä sisältävän arinatuhkan suotovedessä kuin kaasutustuhkan suotovedessä.

Suotovesi sisältää raskasmetalleja, sulfaattia ja pieniä määriä orgaanista hiiltä. Kaasutustuhkasta muodostuva suotovesi poikkesi ominaisuuksiltaan arinatuhkan suotovedestä. Erityisesti arseenin liukoisuuden todettiin olevan suurempi kaasutustuhkasta sekä kenttä- että laboratorio-olosuhteissa. Kaasutuspohjatuhkan korkeampi pH luultavasti lisäsi arseenin liukoisuutta. Kummastakin tuhkasta kaatopaikkaolosuhteissa muodostuvalla suotovedellä todettiin oleva toksista vaikutuksia vesikirpulle, valoa tuottavalle bakteerille ja viherlevälle. Kaasutusarinatuhkan suotovesi oli haitallisempaa ja sen haitalliset ominaisuudet jatkuivat pidempään kuin arinatuhkan suotoveden. Kaasutuspohjatuhkan suotovesi olivat toksista vielä 3 vuotta tuhkan kaatopaikkasijoittamisen jälkeen seurantajakson päättyessä, kun taas arinatuhkan suotoveden toksisuus kesti noin kaksi vuotta kaatopaikalle sijoittamisesta.

Tuhkien vanhenemisen tutkiminen hapettomissa olosuhteissa oli yksi tämän työn tavoitteista. Kaatopaikkaolosuhteissa ilmakehän kaasujen tunkeutuminen tuhkaan on hidasta ja rajoittuu pinta-osiin, jonka vuoksi tuhkatäytössä vallitsevat hapettomat olosuhteet. Laboratorio-mittakaavan lysimetrikokeissa todettiin, että palamatonta orgaanista hiiltä sisältävä arinatuhka vanheni hapettomissa olosuhteissa samoin kuin aiemmissa tutkimuksissa on havaittu kaatopaikkaolosuhteissa. Tämä johtui ilmeisesti arinatuhkan sisältämän orgaanisen hiilen biohajoamisessa muodostuvasta hiilidioksidista. Sen sijaan vähän hiiltä sisältävän kaasutustuhkan vanheneminen oli hidasta hapettomissa olosuhteissa.

Tässä työssä tutkittiin myös sulfaattia pelkistävän mikrobiologisen prosessin hyödyntämistä arinapolton pohjatuhkan päästöjen hallitsemisessa. Prosessissa mikrobit pelkistävät sulfaattia sulfidiksi käyttäen energianlähteenä orgaanista hiiltä. Sulfaattia pelkistävien bakteerien avulla pystyttiin poistamaan haitallisia alkuaineita kuten kuparia, molybdeenia, nikkeliä ja lyijyä arinatuhkan suotovedestä. Lisäksi suotovedestä pystyttiin poistamaan 65 % sulfaatista. Prosessin toimiminen edellyttää orgaanisen hiilen lisäämistä energian lähteeksi, sillä suotoveden orgaanisen hiilen pitoisuus oli vähäinen verrattuna sulfaattipitoisuuteen. Sulfaattia pelkistävästä suotoveden-käsittelyprosessista muodostuvassa vedessä on korkeita pitoisuuksia sulfidia, joka on haitallinen yhdiste. Tämän vuoksi prosessissa muodostuva vesi tulee käsitellä edelleen. Yleisesti käytetään esimerkiksi sulfidin hapetusta alkuaineriksiksi vähähappisissa olosuhteissa. Tässä työssä tukittiin mahdollisuutta käyttää sulfidia sisältävää vettä edelleen tuhkien stabilointiin.

Sulfidipitoinen vesi stabiloi arinapolton pohjatuhkaa muodostamalla tuhka sisältämien metallien kanssa niukkaliukoisia metallisulfideja. Laboratoriomittakaavan stabilointikokeissa todettiin, että kalsiumin, kuparin, lyijyn, rikin ja sinkin liukeneminen arinapohjatuhkasta väheni sulfidipitoisella vedellä käsiteltäessä verrattuna kontrollikäsittelyyn tislatulla vedellä. Lisäksi kaikki haital-

linen sulfidi pystyttiin poistamaan. Tulokset osoittavat, että sulfaatinpelkistys-
prosessia on mahdollista hyödyntää sekä suotovesien käsittelyssä että tuhkan
stabiloinnissa ja siten vähentää haitallisten alkuaineiden päästöjä. Saatujen tu-
losten soveltaminen käytännössä vaatii kuitenkin lisää tutkimusta ja suurem-
man mittakaavan koejärjestelyjä.

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ORIGINAL PAPERS

I

LEACHATE FORMATION AND CHARACTERISTICS FROM GASIFICATION AND GRATE FIRING BOTTOM ASH UNDER LANDFILL CONDITIONS

by

Leachate formation and characteristics from gasification and grate incineration bottom ash under landfill conditions

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ABSTRACT

Characteristics and formation of leachates from waste gasification and grate firing bottom ash were studied using continuous field measurements from 112 m³ lysimeters embedded into landfill body for three years. In addition, the total element concentrations of the fresh ash were analysed and laboratory batch tests were performed to study leachate composition. The three-year continuous flow measurement showed that about one fifth of the leachates were formed, when the flow rate was >200 l/d, covering <3.5% of the study time. After three years, the liquid/solid-ratio for the quenched grate ash was 1 (l/kg (d.m.)) and for the initially dry gasification ash 0.4 (l/kg (d.m.)). The low initial water and residual carbon content of the gasification ash kept the leachate pH at a high level (>13) major part of the study. In the grate ash leachate pH was lower (<8) due to the presence of organic carbon and biodegradation indicated by biological oxygen demand and redox potential measurements. In the gasification ash the high pH probably delayed leaching of major elements such as Ca, therefore, raising the need for a longer after-care period. The high pH also explains the higher leaching of As from the gasification ash compared to the grate ash both in the batch test and under landfill conditions.

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1. Introduction

Waste incineration produces residues that need proper utilisation or disposal in order to prevent potentially harmful effects to the environment and human health. The chemical composition and amount of the residues depends on type, quality and pre-treatment of the waste material as well as on incineration technology. Moving grate incineration is a commonly used technology, but technologies like fluidised bed combustion are emerging. Application of the fluidised bed for gasification is among the new technologies. Advances in fluidised bed gasification compared to other incineration technologies include improved energy efficiency and the ability to integrate it with industrial processes (Belgiorno et al., 2003). Irrespective of the technology used waste incineration produces residues such as bottom ash which are usually not considered hazardous waste, but cannot always be utilised. For instance, when the quality of bottom ash is inappropriate or the cost of pre-treatment or transport are too high, landfill remains the only feasible option for disposal.

Fresh bottom ash is an inorganic material, consisting mainly of oxides, hydroxides and salts of Al, Ca, K and Na (Kosson et al., 1996; Meima and Comans, 1999). Immediately after incineration, bottom ash is chemically unstable and when it reacts with atmospheric gases and water the mineralogical changes begin. These geochemical processes cause changes in mineral composition of ash and consequently in leachate composition. The absorption of carbon dioxide is one of the most important processes decreasing the initially high pH of ash towards the equilibrium pH of calcite 8.3 (Meima and Comans, 1997a). This in turn stabilises the inorganic contaminants in ash. It is known that in a large ash heap the diffusion of atmospheric gases is limited to the surface layers (Freyssinet et al., 2002). Therefore, it has been speculated that the role of biodegradation is significant (Belevi et al., 1992; Meima and Comans, 1997b; Rendek et al., 2007; Zevenbergen and Comans, 1994). Characterisation of leachates by such analyses as biological oxygen demand (BOD), chemical oxygen demand, total organic carbon (TOC), and dissolved organic carbon (DOC) can be used to acquire indirect information on the rate and degree of biodegradation within ash fill. In addition, these analyses give valuable information, when possibilities of leachate treatment are studied.

The main environmental burden from landfill disposal is the leachate formed as rainwater seeps through bottom ash. Leachate contains potentially harmful contaminants like sulphate, chloride and toxic elements (Meima and Comans, 1999). The factors affecting leachate composition include volume of seeping water, flow rate, pH, redox potential and mineral composition of the ash (Kosson et al., 1996). It is usually assumed that the leaching of

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contaminants from ash is predominantly dependent on the share of seeping water compared to the amount of ash, which is called the liquid-to-solid (LS) ratio. Therefore, it has been suggested that future leachate composition can be predicted based on the LS-ratio, when the amount of leached contaminants (per dry mass) are presented as a function of LS-ratio instead of as a time-scale (Grat-hwohl and Susset, 2009; Hjelmar, 1996). However, presenting data on LS-scale can give misleading impression of those processes depending on time e.g. biodegradation or slow reaction kinetics (Dijkstra et al., 2006; Hyks et al., 2009). In addition, determination of LS-ratio under landfill condition poses a challenge.

The leaching properties of an ash can be studied with laboratory batch or column tests according to standardized methods, in order to control testing condition and produce comparable data (van der Sloot, 1996). The purpose of the batch tests is usually to obtain equilibrium or near-equilibrium conditions by agitating the sample and liquid. The column tests usually simulate field conditions including flow rate and contact time. The laboratory column tests usually differ from real disposal conditions as they do not take into account changes in flow rate, temperature, or prevailing reducing conditions (van der Sloot, 1996). In previous landfill-scale studies concentrations of different elements in the leachates have been determined (Freyssinet et al., 2002; Hjelmar, 1996) as well as the effects of variation in the flow rate on leachate concentrations (Johnson et al., 1999). However, there is a dearth of studies combining the leachate composition and quantity in order to determine the cumulative leaching of elements under landfill conditions. This requires the ability to monitor leachate flow and composition as well as knowledge about the initial ash composition. The objective of this study was to assess formation rate and the chemical composition of leachates from waste gasification and grate incineration bottom ash under landfill conditions for three years. In addition, the composition of the leachates and both type of ash were studied using the laboratory batch tests and with elemental analyses of the fresh ash. The obtained result can be used to verify information obtained from laboratory test as well as to design leachate treatment.

2. Materials and methods

2.1. Bottom ash

Bottom ash from waste gasification and moving grate incineration (hereafter referred to as grate incineration) was studied. The gasification bottom ash was obtained from a circulating fluidised bed facility (established 1998, operating temperature 850–900 °C, Lahti, Finland). Recycled wood, industrial plastics (glued wood 33%, 16% wood and 8% plastic) and 43% by weight of refuse-derived fuel (RDF) manufactured from municipal solid waste were gasified at the time of ash sampling. The grate incineration facility (Turku, Finland) was established 1975 (modernised 1995), and was operating at 1000–1100 °C. It incinerated municipal solid waste (MSW), from which most of the glass, paper, and metal have been separated through the regional waste collection system. The grate ash was quenched, while the gasification ash was not, and both were disposed of in a landfill. The total solid (TS) matter content of the grate ash was 88% and that of volatile solids (VS) 5.5%/TS. The corresponding values for the gasification ash were 99% and 0.1%/TS, respectively. The bottom ash from both facilities was transported by lorries to Mustankorkea landfill (Jyväskylä, Finland), where they were heaped up on an asphalt surface for two weeks before being placed into lysimeters. Fifteen random ash samples (10 l) were taken from the both ash heaps at day of arrival. For the batch tests and analyses a composite sample was mixed manually. In order to retain comparability with landfill lysimeter, the only pre-treat-

ment of the grate ash composite sample was the manual removal of pieces over 30 mm in diameter. As the gasification ash had no such particles it was not pre-treated.

2.2. Landfill lysimeters

The ash was placed in landfill lysimeters (height 3.9 m, width 2.4 m, length 12 m, volume 112 m³), which were monitored throughout the study period of 1236 days. The lysimeters were made of steel frames (rectangular hollow section (RHS) 60×80 mm) and walls (2 mm) and coated with acrylic paint (Hempatex Hi-build 46410) (Fig. 1). The lysimeters were embedded in a 30 year old landfill body in November 2003. They were filled in with 0.5 m thick layers and compacted using a sheepfoot roller (Bomag 105, 1.6 t). The grate ash was filled to a height of 2.4 m and the gasification ash to a height of 2.9 m. The resulting bulk densities were 1.7 and 1.5 t/m³, respectively. The top of the lysimeters were open, except when they were covered with plywood sheets for the first 104 days in order to extend the beginning of the experiment until spring (1.4.2004). In June 2004 (days 165–194) tap water (2×500 l) was added to the lysimeters in order to promote leachate formation. The addition of water equalled 70% of one months rainfall calculated on the basis of the local yearly average for 2004 (1423.2 l/lysimeter/month).

Leachate ran gravimetrically (angle 5%) through a drainage layer (thickness 30 cm, gravel particle size <25 mm) and a collection drain (110 mm) to a sampling well. The leachate flow was detected as water level changes in the well with a pressure meter (Keller PR-36W) and a data logger (Campbell Scientific CR10X). The leachate level as well as other continuously measured parameters were recorded every half hour. The temperature and moisture content within the ash was monitored using a soil temperature and moisture station (Davis 6343), temperature probes (Davis 6470), moisture probes (Watermark 200SS) and wireless Vantage Pro console (Davis 6310). The setup is described in detail by Sormunen et al. (2008). Ambient air temperature was monitored by a weather station (Davis Vantage Pro 6150) equipped with a datalogger (PC-link 6510) at landfill site. The mean daily rainfall was obtained from the Finnish Meteorological Institute (2004–2007).

2.3. Analysis and calculations

To obtain more information on leachate composition and to validate the continuously measured parameters additional laboratory analyses were performed during the first 600 days of the study. The concentrations of the elements were determined from the leachates of the landfill lysimeters, which were sampled 35 times (study days: 105, 111, 116, 119, 126, 158, 206, 213, 222, 228, 237, 249, 264, 280, 293, 318, 343, 355, 392, 467, 528, 560, 592, 620, 650, 679, 804, 867, 938 and 1029) from the flow-meter wells. From these cumulative leached amount (mg/kg (dry matter (d.m.))) of each element was calculated. The leachate samples for elemental
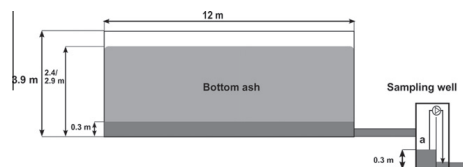

Fig. 1. Scheme of a landfill lysimeters and a sampling well. Samples were taken and volume detected as water level in the first (a) section of the well.

analyses were preserved with HNO_3 (pH < 2), stored at 4 °C and centrifuged before analyses to remove particles. Concentrations of Al, As, B, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, U, V and Zn were determined with ICP-OES (Perkin–Elmer Optima 4300 DV). The default parameters of the instrument (nebuliser flow 0.8 l/min, plasma power 1300 W, auxiliary gas flow 15 l/min) were used (Ilander and Väisänen, 2009). Total amount of the elements in fresh ash were determined and reference material (SRM 1633b) was used to determine the recovery percentages. In addition, the laboratory batch leaching test was performed according to EN 12457-2, in two-litre scale with a LS-ratio of 1:10.

Cl and SO_4 were analysed according to SFS-EN ISO 10304-1 (2007) and APHA (1998). During the first 500 days of the study the TOC, COD, BOD, DOC, chloride, alkalinity, sulphate, total nitrogen and ammonium–nitrogen concentrations were analysed from lysimeter leachate samples at laboratory. In addition, oxidation reduction (redox) potential was studied for the first 1100 days. N_{tot} and NH_4-N were analysed by Kjeldal-method, where in the presence of H_2SO_4 and catalyst nitrogen is converted to ammonium. After the addition of NaOH, the ammonia is distilled from an alkaline medium and absorbed in boric acid (Perstorp Analytical/Tecator AB, 1995). Redox, pH and conductivity were measured with a WPA (CD70) meter (Sensorex ORP 450, Sensorex pH 450 CD electrodes) and with a conductivity meter (Hanna Instruments, Hi9635). The pH measurements of leachate samples in the laboratory closely followed those obtained from the continuous measurement. Laboratory measurements were used when continuous results were not available due to sensor failure (from day 546 onward). The pH and temperature correction for the redox potential was made (pH 7, 25 °C) (Zhang and Pang, 1999). TOC was determined using a Total Organic Carbon Analyser (Shimadzu, TOC-5000A, Shimadzu Europe), (SFS-EN:1484, 1997). DOC, COD, BOD_7, TS, and VS were determined according to the Finnish standard methods (SFS 5504, 1988; SFS-EN 1899-2, 1998; SFS 3008, 1990). For the DOC analyses samples were filtered (0.45 μm).

The cumulative released amount of elements from the landfill lysimeters during study period was calculated by multiplying the concentration of each element with the volume of leachate between two samples. The equilibrium speciation modelling was performed with Minteqa2 4.03 (US EPA). Ettringite with solubility constant of log $K_{sp} = -56.7$ was added to Minteqa2 mineral database. Modelling was performed with the batch test results assuming they present equilibrium conditions. All precipitation was suppressed and resulting saturation indexes (SI) compared.

3. Results and discussion

3.1. Leachate flow and LS-ratio

Continuous flow measurement of leachate from landfill lysimeters was used to detect the dynamics of flow rate and to determine LS-ratios. The cold climate appeared to be the cause of the high variation in flow rate. In winter time the freezing of top layer and in spring time the snow layer melting probably effected leachate formation (Figs. 2 and 3). The mean precipitation during the study period (days 139–1236) was 50 l/lysimeter/d, the mean flow rate of the grate ash leachate was 40.6 l/d, and that of gasification ash leachate was 33.7 l/d (Fig. 2). During high flow rate periods (flow rate >200 l/d) 24% of the grate ash leachate volume and 17% of the gasification ash leachate volume was formed. In the case of grate ash lysimeter this corresponded 3.4% (37 d) of the study period and in the gasification ash 2% (22 d) of the study period. Therefore, a significant share of the leachate was formed during short periods of time. Most of the peaks in the flow rate seems to coincide with the beginning of April (Fig. 2), indicating that the

melting snow layer caused the high variation in leachate flow. Other climatic conditions such as seasonal heavy rain can cause similar variation in leachate formation (Ishii et al., 2009).

The development of LS-ratio and moisture content of the both ash types were monitored (Figs. 2 and 3). LS-ratio of ash was calculated based on flow measurements and the initial moisture content of the ash. At the end of the study the LS-ratio of the grate ash leachate was twice that of the gasification ash. The gasification ash was initially dry having 99% dry matter content. The moisture measurements from different depths in the gasification ash lysimeter show that it took 217 days before any moisture reached the lowest measurement depth of 2.1 m from surface (Fig. 3). The LS-ratio of the gasification ash reached 0.3 l/kg (d.m.) by the end of the study (day 1236). Based on previous gasification ash studies by the authors (unpublished) the water holding capacity was estimated to be 0.12 kg/kg (d.m.) resulting in a final LS-ratio of 0.42 l/kg (see Section 2.4). The LS-ratio of the quenched grate ash increased from an initial 0.54 l/kg (d.m. 82%) to 1.0 l/kg (Fig. 2). The LS-ratio of the grate ash was high as it was on same level as those values (from 0.6 to >1 l/kg) obtained in 20-year full-scale studies (Hjelmar, 1996; Kosson et al., 1996). From the studies just mentioned it was not clear if the initial water content of the ash had been included in the sum of total liquid amount as has been done in this study. The initial water content was significant and if not taken into account the LS-ratio of grate ash at the end of the study would be 0.46 l/kg (Fig. 2). Regarding the LS-ratio, the present landfill lysimeter setup can be considered a worst case scenario of the initial phase of ash landfilling, as there was no covering and the ash fill was quite shallow. On the other hand, when results are presented relative to LS-ratio this experiment could represent some 20 years of landfilling in the case of covering shortly after filling.

3.2. Leachate pH and alkalinity

The pH of the grate ash leachate remained near neutral throughout the lysimeter study, while the gasification ash leachate had a pH of over 13 during a major part of study (Fig. 4). The pH of the gasification ash was consistent with the pH (13.55) obtained at batch test. However, the grate ash leachate had a significantly lower pH under landfill condition than in the batch test (10.84). The observed difference between the lysimeter and the batch test of the grate ash as well as between the two ash-types can be explained with higher organic carbon content of the grate ash. The beginning of formation of leachate from the landfill lysimeter took almost half a year, during which biodegradation producing CO_2 and organic acids could have caused lowering of the grate ash leachate pH. Belevi et al. (1992) estimated that biodegradation can produce 1 mol/kg of weak acid and that the neutralisation capacity of grate bottom ash is 2 mol/kg (pH 7). The biodegradation hypothesis is supported by the fact that the pH increased shortly after (day 473) COD decrease (<150 mg/l, day 467) to low level (Fig. 5), indicating the end of rapid biodegradation in the grate ash. Initially the amount of organic carbon and the rate of biodegradation was high enough to lower the pH of the grate ash leachate. The amount of easily biodegradable organic carbon decreases with time due to degradation and leaching, meanwhile the hydrolysis and dissolution process producing OH^- continues (Meima and Comans, 1997a), causing the pH of the leachate to increase. This is observed in the grate ash leachate as an increase of pH towards the final value of 8.4 (day 1035). The final pH is close to calcite equilibrium pH of 8.3, which is expected for weathered bottom ash (Meima and Comans, 1997a).

Under landfill conditions the gasification ash leachate initially had low pH (mean 6.5, SD 0.38, day 139–212), after which it increased to a high level (mean 13.1, SD 0.94, day 212–1148)
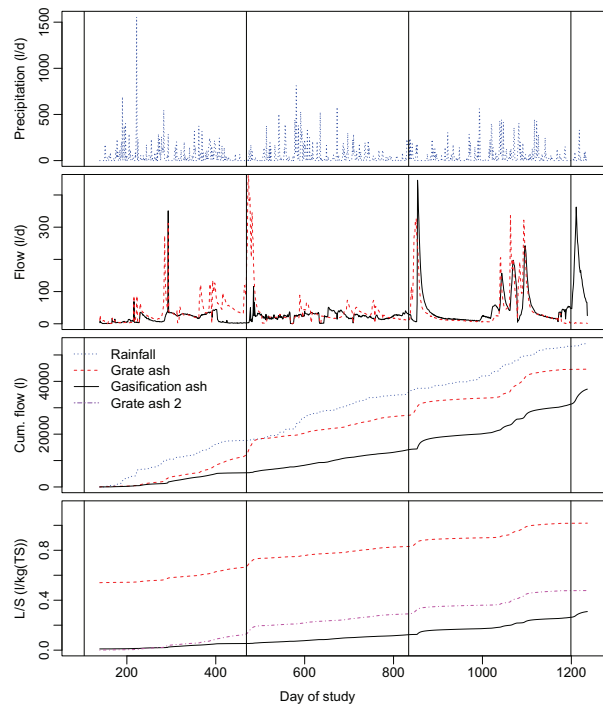
Fig. 2. Precipitation, leachate flow, cumulative flow and LS-ratio under landfill conditions. LS-ratio of the grate ash is given both including the initial water content of ash (Grate ash) and without it (Grate ash 2). Vertical lines indicate 1st of April.

(Fig. 4). The alkalinity showed a similar trend with an increase during the first 400 days (Fig. 5). The increase was probably related to chemical processes, which began as water infiltrated into the initially dry ash. Leaching water causes hydrolysis of oxides of Ca, Al, Na and K, therefore, increase in the pH (Meima and Comans, 1997a). During the final 100 days of the study, a decrease to 10.8 (day 1236) was observed. The decrease observed towards the end of continuous measurements could indicate the beginning of the acidifying processes such as carbonation and oxidation reactions (Johnson and Furrer, 2002). The high pH and alkalinity of the gasification ash were due to large amounts of calcium added to the process (Raskin et al., 2002). In addition, the absence of quenching is known to retard and even completely halt the decrease of pH due to a weathering reaction in the grate ash (Belevi et al., 1992). The slow weathering of the gasification ash can be due to the slow diffusion of the atmospheric gases and dissolution of them into pore water, which are the rate-limiting steps in the grate ash carbonation (Freyssinet et al., 2002; Rendek et al., 2006). In addition, the low organic carbon content (VS 0.1%) in the gasification ash cannot support biodegradation, which can be a significant carbonation mechanism in grate bottom ash.

3.3. Conductivity and redox potential of leachate

The conductivity of the leachate was measured continuously to determine leaching behaviour of the major salts. The maximum conductivity of the grate ash leachate was 20 times higher than

that of the gasification ash (Fig. 4). Its conductivity decreased steadily from high initial values (2500 mS/m, day 104) indicating that the highest concentrations of major elements occur within the first 400 days of disposal. The conductivity of the grate ash leachate was 100 times higher than that found in the laboratory for unweathered grate bottom ash (160–270 mS/m) (Belevi et al., 1992) and 1000 times higher than that (5–15 mS/m) reported for weathered grate bottom ash leachate in a full-scale study (Johnson et al., 1999). Biodegradation could explain this as it produces organic acids which increase conductivity. The simultaneous decrease of COD and conductivity around day 400 supports this hypothesis (Fig. 5). The gasification ash leachate had a conductivity of 150 mS/m on day 146. The conductivity increased after day 212 remaining at a constant level until end of the study period (mean 750, SD 130, days 364–1099), except for the peak between days 320–364 (Fig. 4).

The leachate redox potential was measured to obtain information on gas diffusion and biodegradation. The redox potential of the both ash leachates showed seasonal variation, in which the lowest values were detected during the warmest months between days 600 and 900 (Figs. 5 and 4). This was assumed to be an indication of an increase in the microbiological activity or in the chemical oxygen consuming reactions in ash during periods with higher temperature. The redox potentials in the grate ash (−300 to 200 mV) remained at same level as previously detected in landfill-scale studies (Kosson et al., 1996). From previous studies it is also known that reducing conditions can prevail for over
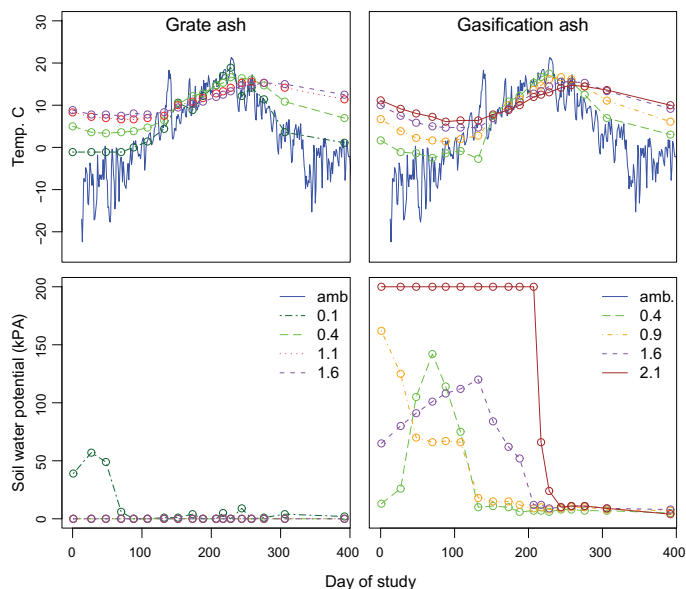
Fig. 3. Temperature and soil water potential in the different depths (expressed as meters (m) from the surface) of the landfill lysimeters.

twenty-year periods (Hjelmar, 1996). In the weathered bottom ash samples, however, positive redox potentials have been observed (Meima and Comans, 1997a). Therefore, it seems that redox potential can be used as an indicator for the state of ash weathering. However, the redox potential for gasification ash was at a high level throughout the redox observation period (1029 d). The low moisture content and high pH may have prevented the oxygen consuming weathering reactions.

3.4. Ash and leachate temperature

The ash temperature inside the lysimeter and the leachate temperature in the sampling well were measured to observe the effects of ambient temperature and exothermic weathering reactions (Figs. 3 and 4). The temperature inside the lysimeters followed the same trends as the ambient temperature; however, they remained above 0 °C except at the top layer. No warming due to exothermic reactions was observed. The temperature of the leachate measured from the sampling well also followed ambient temperature. However, as the wells were placed under the landfill cover layer, which provided insulation, large variation in temperature was not observed and wells did not freeze during winter (Fig. 4). In the lysimeters only the very top layer was frozen during the winter (Fig. 3). The high temperatures observed in full-scale landfills corresponded to the surface-to-volume ratio of the ash fill and were near the surface close to the ambient temperature (Klein et al., 2001). Therefore, the relatively small size (112 m³) of the landfill lysimeters probably explains why a temperature increase was not observed even in the initially dry gasification ash, where exothermic hydroxylation reactions were expected to result in an increase in the temperature.

3.5. Leaching of organic carbon and nitrogen compounds

The leaching pattern and composition of organic carbon was monitored with TOC, DOC, COD and BOD₇. In addition, total nitrogen and ammonium nitrogen amounts were studied. The grate ash leachate contained readily biodegradable organic carbon during the first 3–6 months after disposal (Fig. 5). The BOD₇ of the grate ash leachate had a maximum of 79 mg/l (day 114) which decreased to 4 mg/L (day 293) (Fig. 5). This supports the assumption that during the rapid weathering phase immediately following the disposal biodegradation can have a significant role in the grate ash weathering (Belevi et al., 1992; Rendek et al., 2006; Sivula et al., 2010). However, in the gasification ash leachate the BOD₇ concentration was very low (3–8 mg/l).

Leachate total organic carbon (TOC) was higher in the grate ash (mean 317 mg/l, SD 130) than in the gasification ash leachate (mean 157 mg/l, SD 137) (Figs. 5). This reflects the amount of volatile solids: 0.1%/TS in the gasification ash and 5.5%/TS in the grate ash. Furthermore the share of DOC compared to TOC was higher in the grate ash leachate (35%, $\bar{x} = 111$ mg/l, SD = 54, $n = 18$) than in the gasification ash leachate (17%, $\bar{x} = 53$ mg/l, SD = 111, $n = 14$). The amount of the DOC is known to effect toxicity of the leachate as it can bind both organic and some inorganic contaminants like Cu. The levels of the DOC in the grate ash leachate were within the same range (90–290) as previously reported for fresh grate bottom ash leachate in laboratory studies (Meima and Comans, 1999; van Zomeren and Comans, 2009). The DOC concentration showed less variation compared to TOC suggesting that high flow periods may flush the particles out of the ash and increase variation in TOC.

In the grate ash the mean value of total nitrogen concentration was 47 mg/l (SD 105) and for gasification ash 17 mg/l (SD 8.3) (Fig. 5). The ammonium nitrogen in the grate ash leachate was
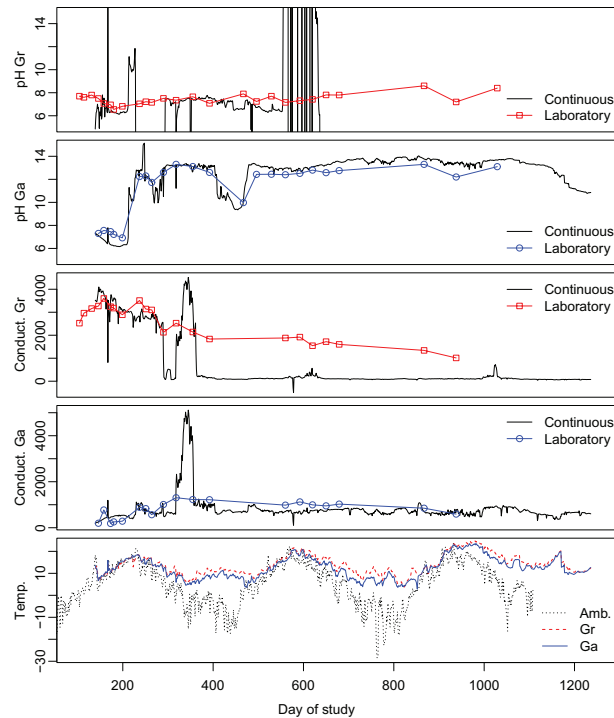
Fig. 4. Daily means of continuous pH, conductivity (mS/m), leachate temperature and ambient temperature. Laboratory analyses for the grate ash leachate (□), and gasification ash (○).

8 mg/l (SD 9). In the gasification ash the ammonium concentration was 2 mg/l (SD 4). The ammonium concentrations are high enough to cause toxic effects for example in fish and high pH of leachate further increases ammonia toxicity. For example threshold concentration 3.48 mg/l (total ammonia) at pH 6.5 and 0.25 mg/l at pH 9 have been announced by the US EPA for fresh water and for salt water even lower values are used (Ip et al., 2001).

3.6. Leaching of inorganic compounds

The element concentrations and volume of leachates were monitored to obtain information on release of elements under landfill conditions over the three years study period. The release of elements under landfill conditions was compared to the released amount at the batch test representing equilibrium conditions (LS 10 l/kg (d.m)) and to the total amount determined from the fresh ash (Table 1). As expected for the grate ash the total concentration in the fresh ash was the highest and released amount under landfill condition (LS 1 l/kg (d.m)) the lowest. However, in the gasification ash more Mo and Mg were released under landfill conditions than in the batch test. The difference in leaching behaviour of the two ash-types were more pronounced under landfill conditions than at laboratory batch test. For example: under landfill conditions from the grate ash 19.6% of Ca and 51% of S was released, compared to batch test results; while under landfill conditions from the gas-

ification ash only 1.8% of Ca and 5.3% of S was mobilised compared to the batch test (Table 1). This is probably related to lower LS-ratio (0.46 l/kg (d.m)) of the gasification ash under landfill conditions. However, from a longitudinal perspective this can mean a longer release period and therefore longer aftercare period for the gasification ash.

The mineral composition of ash was studied based on the pH and main element composition of leachate. The leaching of the calcium and sulphate are controlled by the same mineral phases such as anhydrite, gypsum and ettringite, which explains the similar behaviour. In the dry grate ash calcium and sulphate are known to be present mainly as anhydrite ($CaSO_4$), which forms gypsum ($CaSO_4 \cdot H_2O$), when it comes into permanent contact with water (Kirby and Rimstidt, 1994). The present results show that at the batch test pH of 10.84 the Ca-mineral closest to equilibrium were gypsum (SI −0.806) and anhydrite (Si −1.056), however, both were under-saturated. The gasification ash leachate was over-saturated in respect to portlandite (SI 1.324) in the batch test (pH 13.55). This is similar to previous studies showing that in the high pH range portlandite prevails (Hampson and Bailey, 1982; Meima and Comans, 1997a). In the gasification ash the total amount of sulphur was low compared to that of calcium and in batch test a large share of the Ca was released, while in the landfill lysimeter only a small fraction was actually released (Table 1). The Ca concentration in the gasification ash leachate showed an increase along with
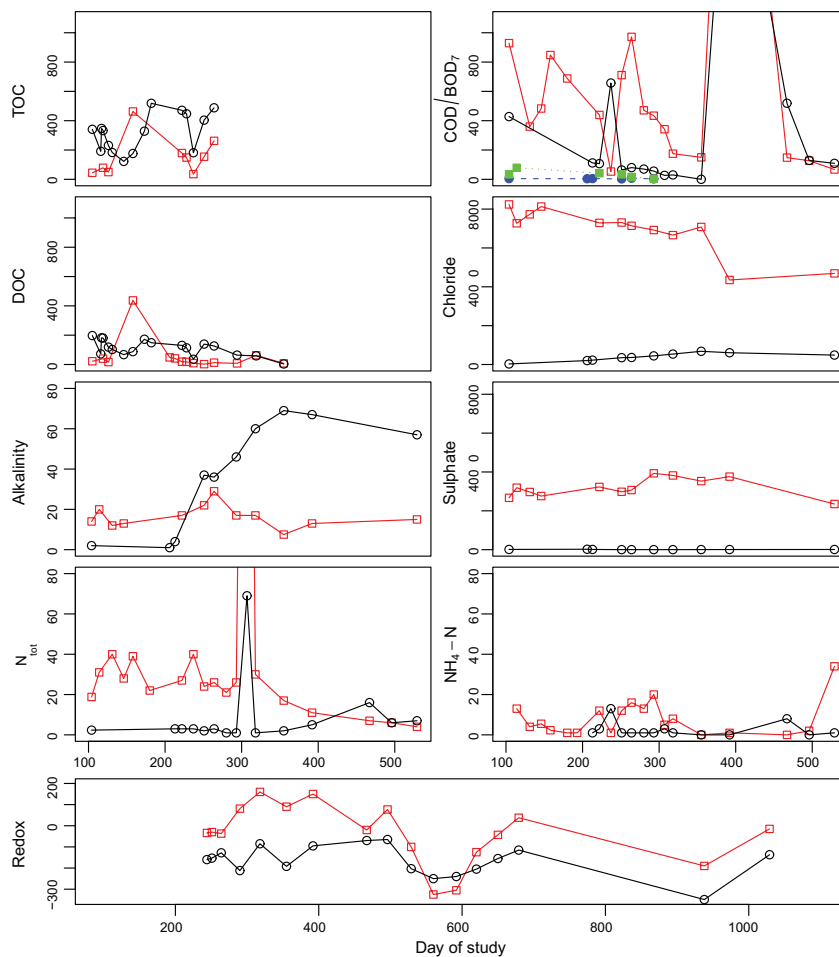
Fig. 5. Organic carbon, nitrogen compounds and redox potential of the gasification (○) and the grate ash (□) leachates (concentrations in mg/l, alkalinity in mmol/l, Redox in mV).

decreasing pH in the lysimeter. This indicates that release of the Ca could further increase, as the weathering of the gasification ash proceeds.

In the grate ash batch test at pH of 10.84 the concentration of dissolved Al (22.2 mg/l) was high, while in the gasification ash leachate it was low (0.79 mg/l) at pH 13.55. The modelling results show that the grate ash leachate was over-saturated in respect to diaspore (SI 1.817), boehmite (SI 0.112) and gibbsite (SI 0.399). This suggests that aluminium hydroxides control the pH of the fresh grate ash. On the contrary, Al leaching was higher from the gasification ash than from the grate ash under landfill condition. The low leaching of Al from the grate ash has been suggested to be due to low solubility of clay minerals like aluminosilicates, which form during weathering (Meima and Comans, 1997a). This

is supported by the lower leaching of Si from the grate ash than from the gasification ash. Quenching is known to cause clay formation from glass minerals formed during incineration and weathering increases clay formation (Zevenbergen et al., 1996). In the gasification ash the high amount of Si leached could better fit the assumption that gibbsite $Al(OH)_3$ was controlling Al leaching (Johnson et al., 1999; Meima and Comans, 1997a). The hydrolysis of gibbsite could also partly explain the observed high pH in the gasification ash leachate (Meima and Comans, 1997a). However, at batch test pH (13.55) the gasification ash leachate was undersaturated in respect to both diaspore (SI −2.4) and gibbsite (SI −3.823).

From the gasification ash over 100% of Mo and Mg were released under landfill conditions compared to the released amount

Table 1
Total concentration (mg/kg (d.m.)) and recovery percentages of elements in the fresh ash. Released amounts from the batch test and from the landfill lysimeter (mg/kg (d.m.)). Range and mean (x̄) of pH and element concentration in leachates and corresponding detection limits (DL) (mg/l).

	Gasification bottom ash				Grate bottom ash				Rec.	DL
	Total	Batch	Cum. Lysim.	Range (x̄)	Total	Batch	Cum. Lysim.	Range (x̄)		
pH		10.84	6.55–8.6(7.4)			13.55	6.2–14(12.5)			
Al	N.A.	8.0	3.81	<DL-68.4 (12.2)	220	0.015		<DL-0.4(0.06)	N.A.	0.02
As	58	15.4	0.015	<DL-1.7 (0.22)	61	2.9	0.004	<DL-2.4(0.34)	101	0.1
B	N.A.	N.A.	0.11	<DL-4.95 (0.74)	N.A.	N.A.	0.72	<DL-10.8(2.26)	N.A.	0.2
Ba	N.A.	16.6	0.29	<DL-5.41 (1.14)	N.A.	0.55	0.020	<DL-0.49(0.08)	N.A.	0.005
Ca	73,200	5580	5.36	<DL-500 (55.7)	97,300	740	145	62–1570(590)	47	0.005
Cd	2.86	0.08	0.00	<DL-0.01 (0.006)	9.9	0.05	0.00	<DL-0.02(0.007)	831	0.005
Co	12.9	N.A.	0.013	<DL-0.68 (0.04)	19	N.A.	0.001	<DL-0.06(0.02)	38	0.02
Cr	100	0.01	0.003	<DL-0.2 (0.03)	128	0.085	0.001	<DL-2.2(0.09)	15.9	0.02
Cs	N.A.	N.A	0.33	<DL-7.5 (1.34)	N.A.	N.A.	0.012	<DL-0.18(0.08)	N.A.	0.02
Cu	890	0.68	0.03	<DL-1.35 (0.14)	3180	2.0	0.013	<DL-0.14(0.06)	23.8	0.02
Fe	6390	N.A.	0.02	<DL-9.7 (0.51)	26,600	N.A.	0.09	<DL-8.5(0.56)	5.3	0.02
K	1130	N.A.	128	4.2–1398 (516)	5390	N.A.	225	42–1330(600)	5.5	0.02
Mg	19,500	10.5	0.06	<DL-29 (3.3)	10,800	5.3	113	6–950(412)	68	0.01
Mn	220	N.A.	0.002	<DL-3.8 (0.18)	660	N.A.	0.43	<DL-47(6.8)	18	0.01
Mo	63	0.87	0.01	<DL-0.18 (0.05)	81	N.A.	1030	<DL-0.99(0.17)	252	0.05
Na	3860	N.A.	188	6.7–2100 (740)	12,600	N.A.	1030	100–5600(2880)	252	0.05
Ni	64	0.53	0.00	<DL-0.06 (0.02)	138	0.13	0.012	<DL-0.2(0.07)	19	0.02
P	74	2.5	0.031	<DL-1.1 (0.24)	1960	0.00	0.031	<DL-0.67(0.14)	49	0.1
Pb	22	0.4	0.00	<DL-0.1(0.03)	948	0.24	0.006	<DL-0.9(0.07)	20	0.02
S	154	8.3	0.44	<DL-147 (9.4)	5180	520	270	61–1710(700)	91	0.1
Si	N.A.	N.A.	1.5	<DL-37.8 (6.27)	N.A.	N.A.	0.64	<DL-73.1(3.1)	N.A.	0.2
U	N.A.	N.A.	0.00	<DL-0.25 (0.2)	N.A.	N.A.	0.00	<DL-0.73(0.23)	N.A.	0.2
V	17	N.A	0.01	<DL-0.22 (0.06)	37.6	N.A.	0.004	<DL-0.2(0.11)	27	0.02
Zn	350	0.56	0.0071	<DL-0.92 (0.09)	2660	0.63	0.01	<DL-0.71(0.06)	12.4	0.02
Sum			327				1778			

determined in the batch test (Table 1). The underestimation of release of Cu, Ni, and Mo under equilibrium conditions compared to non-equilibrium conditions was predicted by Hyks et al. (2009), who found that flow interruptions in the column test increased their concentrations in the leachate. They assumed that increased leaching in non-equilibrium conditions was related to an increase in the leaching of DOC. However, as the gasification ash contains only little DOC this seems unlikely explanation in the present study. Further research is required on this topic.

Arsenic was the only element in both ash types that exceeded the EU landfill limit-values for non-hazardous waste. In batch tests, the released amount of As was 10 times higher from the gasification ash and 1.5 times higher from the grate ash than the limit value (2 mg/kg (d.m.)) (European Council, 2003). In both landfill lysimeter leachates, the maximum As concentration observed exceeded the limit value for percolation test (0.3 mg/l) (European Council, 2003). The release of As was higher from the gasification ash than from the grate ash both in the batch test and under landfill conditions despite the fact that the total concentrations in the both ash types were same (Table 1). This was probably due to the higher pH of the gasification ash, as the arsenic solubility is known to increase with increasing pH and oxidation state (Cornelis et al., 2008). Based on the LS-ratio observed in the landfill lysimeters, it can be estimated that it will take from 60 to 75 years to reach the same LS-ratios and released amounts than in the batch test. However, release time and amount of As can differ from the estimated values as weathering decreases pH and increases oxidation state.

4. Conclusions

One fifth of the leachates from the gasification and the grate incineration bottom ash under landfill conditions were formed when the flow rates were high (>200 l/d) mainly due to the melting of snow in the spring. Pre-treatment of the ash e.g. quenching and residual carbon content have significant effect on behaviour of the ash under landfill conditions. The LS-ratio of the non-quenched gasification ash was 0.4 (l/kg (d.m.)) compared to 1 (l/kg (d.m.)) of grate ash after three years of landfill disposal. The low initial moisture and carbon content slowed down the weathering of the gasification ash. As a result release of major elements is delayed compared to the grate ash, which could mean longer after care period for the gasification ash. In addition, the high pH (>13) of the gasification ash increased As leaching compared to the grate ash both in laboratory batch test and under landfill conditions.

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II

TOXICITY OF WASTE GASIFICATION BOTTOM ASH LEACHATE

by

Leena Sivula, Aimo Oikari & Jukka Rintala 2011

Toxicity of waste gasification bottom ash leachate

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Abstract

Toxicity of waste gasification bottom ash leachate from landfill lysimeters ($112 \ \mathrm{m}^3$) was studied over three years. The leachate of grate incineration bottom ash from a parallel setup was used as reference material. Three aquatic organisms (bioluminescent bacteria, green algae and water flea) were used to study acute toxicity. In addition, an ethoxyresorufin-O-deethylase (EROD) assay was performed with mouse hepatoma cells to indicate the presence of organic contaminants. Concentrations of 14 elements and 15 PAH compounds were determined to characterise leachate. Gasification ash leachate had a high pH (9.2–12.4) and assays with and without pH adjustment to neutral were used. Gasification ash leachate was acutely toxic (EC_{50} 0.09–62 vol-%) in all assays except in the algae assay with pH adjustment. The gasification ash toxicity lasted the entire study period and was at maximum after two years of disposal both in water flea (EC_{50} 0.09 vol -%) and in algae assays (EC_{50} 7.5 vol -%). The grate ash leachate showed decreasing toxicity during the first two years of disposal in water flea and algae assays, which then tapered off. Both in the grate ash and gasification ash leachates EROD-activity increased during the first two years of disposal and then tapered off, the highest inductions were observed with the gasification ash leachate. The higher toxicity of the gasification ash leachate was probably related to direct and indirect effects of high pH and to lower levels of TOC and DOC compared to the grate ash leachate. The grate ash leachate toxicity was similar to that previously reported in literature, therefore, confirming that used setup was both comparable and reliable.

Keywords: EROD, PAH, grate ash, toxic elements,

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1. Introduction

Relatively little information is available on toxicological properties of the waste incineration ash leachates in general, but especially about residues produced by emerging technologies like waste gasification. Waste gasification produces several residues of which bottom ash forms 20–40 % by mass. The amount of bottom ash in waste gasification is usually less than 9% of the original waste material including the sand and lime added in the process (Belgiorno et al., 2003). Bottom ash is the main residue in waste grate incineration as well. In municipal solid waste (MSW) grate incineration, approximately 30% of the original waste mass is converted to bottom ash, which, in turn, is 60% of the formed residues (Sabbas et al., 2003). Bottom ashes are usually classified as non-hazardous waste based on their elemental composition.

Fresh bottom ash is an inorganic material, consisting mainly of oxides, hydroxides and Al, Ca, K and Na salts, which causes a high pH value of 12 or higher (Meima and Comans, 1997). Fresh bottom ash may also contain organic compounds originating from incomplete combustion (Dugenest et al., 1999). Therefore, bottom ash can have toxic properties related to trace elements, organic contaminants and alkalinity, or a combination of these factors.

The composition of the bottom ash changes over time. During disposal seeping water, atmospheric gases and biodegradation change the chemical composition of ash. The quality of leachate is believed to improve during the time due to the weathering processes, which decreases the pH and the release of toxic elements (heavy metals and oxyanions) (Chimenos et al., 2000). However, only a few studies on the effects of weathering on toxicity exist, and they have produced contradictory conclusions (Ore et al., 2007; Römbke et al., 2009).

The composition of ash leachates can be assessed with batch, column and lysimeter studies. In the standardised laboratory batch tests, the leaching condition such as contact time and liquid to solid (LS) ratio are controlled in order to produce comparable data. In the column tests also the flow rate of leachate can be controlled. However, the laboratory column tests usually differ from real disposal conditions as they do not take into account: changes in flow rate, changes in temperature or reducing conditions (van der Sloot,

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1996). With landfill lysimeter the evolution of the leachate composition can be studied in realistic conditions. Landfill lysimeters have been previously used to study the effects of ambient conditions such as redox-potential, temperature and rainfall on leachate composition (Freyssinet et al., 2002; Hjelmar, 1996; Johnson et al., 1999).

Broadening the assessment of waste materials with biological assays has been encouraged (Moser and Römbke, 2009). Combining the ecotoxicological assay with leaching test could be used to characterise ecotoxicological properties of waste materials (Postma et al., 2009). It has been shown that the chemical characterisation of ash does not necessarily reveal the toxic properties (Lapa et al., 2002). Therefore, ecotoxicological assessment is needed. Leachates of municipal solid waste landfills have been previously studied with similar methods (Bernard et al., 1997). As the effects on different organisms may vary, a test battery, covering species and function at several trophic levels in the exposed environment, should be selected (Wilke et al., 2008). Toxicity assays with aquatic organisms can include: standardised protocols for the inhibition of bioluminescence of bacteria, the growth of the green alga, and the decreased mobility of water fleas among other assays.

The characterisation of the origin of toxicity can be done with specific biomarkers reacting to certain groups of contaminants. The activity of ethoxyresorufin-O-deethylase (EROD) is a biomarker induced by planar aromatic molecules such as PAH, dioxins and planar PCBs. The EROD assay is based on the receptor mediated induction of cytochrome P450 dependent mono-oxygenases, especially of the subfamily CYP1A, by planar PAH or similar compounds (Safe, 1990). The aspect of CYP1A that is useful is the increasing enzyme concentration with increasing concentration of xenobiotics (Safe, 1990). With an EROD assay, it is possible to conclude whether planar organic contaminants are present, as the toxic elements should not induce EROD-activity. However, when interpreting results one should consider speculations about heavy metal inhibition on EROD activity (Korashy and El-Kadi, 2004).

The objective of this study was to assess toxicity of gasification bottom ash leachate under landfill conditions over a disposal period of 1265 days. In order to assure validity of results a parallel study with the grate bottom ash leachate of which more knowledge exists was performed. The possible causes for the observed toxic effects were characterised with pH-adjusted assays and with the EROD assay. Leachate was characterised by determination of element and PAH concentrations.

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2. Materials and Methods

2.1. Landfill lysimeters and leachate samples

Gasification bottom ash was obtained from a gasification facility (established in 1998, operating at temperatures between 850–900 °C, in Lahti, Finland) which used refuse-derived fuel (RDF), recycled wood and plastics from industry. Grate bottom ash was from an incinerator with a moving grate furnace (established in 1975, modernised in 1995, in Turku, Finland) operating in 1000–1100 °C. The incinerator used municipal solid waste (MSW) from which glass, paper, and metal were separated by regional collection system. Grate bottom ash was quenched, while gasification bottom ash was not and both ashes were disposed of separately in landfill.

Two landfill lysimeters (height 3.9 m, width 2.4 m, length 12 m) made of steel frames (RHS 60*80 mm, walls 2 mm) and coated with acryl paint (Hempatex Hi-build 46410) were placed in a 30 year old landfill body. The top of the lysimeters was left open. The lysimeters were filled with ash in 0.5 m horizontal layers, which were compacted with a sheepfoot roller (Bomag 105, 1.6 t). The gasification ash was filled to height of 2.9 m and to a density of 1.5 t/m^3. For the grate ash, the height was 2.4 m and the density was 1.7 t/m^3. Leachate ran gravimetrically (angle 5%) through a drainage layer (thickness 30 cm, gravel particle size <25 mm) and a collection drain (110 mm) to a sampling well (Sormunen et al., 2007; Sivula et al., 2011). The drainage layer was designed to prevent the formation of a saturated zone at the bottom of the lysimeter. However, it was not monitored to determine whether saturated zone was formed or not. Leachate samples for the toxicity assays were taken from sampling wells. The total duration of the lysimeter study was 1265 days and leachate began to form from day 139 onwards.

Leachate characteristics including pH and conductivity were continuously measured every half hour between study days 139 and 1236. In addition, element concentrations were determined from leachate samples 35 times during the study (Sivula et al., 2011). The leachates for this study were sampled on September 24th 2004 (sample 2004), December 1st 2005 (sample 2005) and June 6th 2007 (sample 2007), which were study days 280, 713 and 1265, respectively. The volume of leachate was measured continuously and liquid to solid (LS) ratios were calculated based on the cumulative volumes (l/kg total solids (TS)). LS-ratios for grate ash were 0.56 (2004), 0.79 (2005) and 1 (2007), and for gasification ash 0.02 (2004), 0.1 (2005) and 0.31 (2007). Leachate samples were collected in 2-litre glass bottles and frozen to -22 °C

on the same day. All of the toxicity assays were conducted as the same series in the autumn of 2007 in order to minimise variation due to changes in sensitivity of test organism over time. It is known from the sediment studies that effect of freezing on the PAH concentrations and sample toxicity are minor (Carr and Chapman, 1995; Rost et al., 2002). The samples were taken from the freezer to room temperature on the day before the toxicity assays began. Samples were not pre-treated before chemical analyses or toxicity assays, except for the EROD assay, where filtration (0.2 um) to sterilise samples was used. Subsamples for metal and PAH analyses were taken from samples that were thawed and then thoroughly mixed.

2.2. Chemical analyses

The major elements (Ca, K, Mg, Na, S) and trace elements (As, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Zn) were determined from each leachate sample without pre-treatment. The measurements were performed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 4300 DV, Norwalk, CT, USA). The instrument's default parameters were used (nebuliser flow 0.6 l/min, auxiliary gas flow 0.2 l/min, plasma gas flow 15 l/min and plasma power of 1400 W) (Ilander and Väisänen, 2009). Fifteen PAH compounds were determined with high performance liquid chromatography (HPLC, Agilent 1100, Agilent Europe), using fluorescent and diode array detectors. The detection limits were 10 ng/l for naphthalene, acenaftene, fluorene, phenanthrene, anthracene, fluoranten, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranten, benzo(k)fluoranten, dibenzo(a, h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene and 1 ng/l for benzo(a)pyrene. Uncertainty of the measurement was 30%. The method used was the in-house method (0-5) of the accredited laboratory (SFS-EN ISO/IEC 17025) (Institute of Environmental Research, University of Jyväskylä). Total and dissolved organic carbon (TOC/DOC) were analysed with a total organic carbon analyser (Shimadzu, TOC-5000A, Shimadsu Europe,) (SFS-EN:1484, 1997). For the DOC analyses samples were syringe filtered (0.45 µm, polyvinylidene fluoride membrane, Perkin Elmer, USA).

2.3. Bioluminescence inhibition assay

The bioluminescence assay was performed by a kinetic method (Lappalainen et al., 2001) at 15 °C. Freeze-dried bacteria (*Vibrio fischeri*) from a BioTox^{TM}(Aboatox, Turku, Finland) test kit were used with an automated luminometer (Sirius, Berthold Detection Systems, Germany). In each run,

three replicates and five dilutions were used. Gasification ash assays were performed both with a pH adjustment (7.0±0.2) and in the native pH of the sample (9.2–12.4). The grate ash leachate pH (7.4–8.2) was within the acceptable range (6–8.5) given in the standard, and therefore the pH adjusted assay was not performed (ISO11348-3, 1998). The samples were not filtered and, hence, contained some particles. Therefore, the results are expressed as a ratio of luminescence at the point of measurement (5, 15, and 30 minutes), normalised with the peak value (Lappalainen et al., 2001). Statistical software R and a drc-package were used to calculate the EC-values with a log-logistic model in regards to all of the assays (Ritz and Streibig, 2005; R Development Core Team, 2008).

2.4. Growth inhibition assay with green alga

The growth assay with unicellular green alga *Pseudokirchneriella subcapitata* (SAG 61.81, Culture Collection of Algae, University of Göttingen, Germany) was a standard method (EN 28692, 1993) adapted to a 48-well microplate. There were five dilutions, each with four replicates. A parallel plate without algae was used to measure the background in each dilution. Two series with and without pH adjustment to 8.3±0.2 were performed. After the calibration carried out by microscopic counting with a glass chamber (Bürke, Germany), the cell density was measured with a fluorometer (Fluoroscan Ascent, Labsystems, Finland), with an excitation wavelength of 444 nm and an emission of 670 nm. The cell density at the beginning was approximately 10^4/ml and was monitored after 0, 24, 48 and 78 hours. The results were calculated by comparing the cell densities in each dilution with the control at the same time point.

2.5. Water flea immobility assay

The water flea (*Daphnia magna*) assay was done according to the standard method (EN ISO 6341, 1996). There were five individuals per each test flask containing 10 ml of liquid. In the control treatment six replicates were used and in each dilution of five exposure concentrations there were three replicate flasks. The mobile individuals were counted after 24 and 48 hours. The grate ash leachate had a pH within the range of the standard (6–9) and therefore was not adjusted. The gasification ash leachate was distinctly alkaline and the assays were conducted both with the pH adjusted to 7.8 ±0.2 and without the pH adjustment.

2.6. Activity of ethoxyresorufin-O-deethylase

Induction of the EROD activity was studied with mouse hepatoma cells. The hepa-1 cell line was obtained from the Institute of Applied Biotechnology, University of Kuopio, Finland. In carrying out the EROD analyses, the leachate samples were syringe filtered (0.2 µm polyethersulphone membrane, VWR, USA) and pH adjusted to 7±0.1. The cells were transferred to a 96-well microplate (Sarsted, USA) one day prior to the exposure. Three parallel wells were used for the samples and six were used for the controls. β-naphtoflavone (130 µg/l) was used as the positive control. Cells were exposed for three days, after which the microplates were frozen to −80 °C. The EROD activity was measured within 48 h. In essence, the cell cultivation and EROD analyses were performed as described by Koistinen et al. (1998).

The possible cell toxicity was observed by comparing protein amount of the leachate exposed wells and the negative controls. Those exposure concentrations, in which the amount of protein was significantly different ($p < 0.05$) from the negative control in t-test were removed. Therefore, concentrations of 0.5, 1.9, 3.8 and 15% were selected for calculation of the EC values. Bartlett's test was used to study the equality of variances within each sample and the p-value of 0.05 was used to indicate a statistically significant difference between the means. Analyses of variance or Kurskal-Wallis tests were used to detect, whether there were differences between the exposure concentrations compared and the the control treatments. Multiple comparisons were made with a pair-wise t-test, the p-values of which were adjusted using Holm's method. All analyses were made with statistical program R (R Development Core Team, 2008).

3. Results

3.1. Chemical characterisation of leachates

When assessed visually, the gasification ash leachate was clear, colourless and contained some fine particles, while the grate ash leachate was light brown and contained more particulate material. Conductivity and pH of the gasification ash leachate were at the highest level in the 2005 sample. The conductivity in 2004 was 600 mS/m, in 2005 840 mS/m, and in 2007 370 mS/m. Gasification ash leachate pH was 9.2, 12.4, and 10.7, respectively. Conductivity of the grate ash leachate decreased during the study being 2450 mS/m in 2004, 100 mS/m in 2005 and 60 mS/m in 2007. Conversely, the grate ash leachate pH increased slightly and was 7.8 in 2004, 7.7 in 2005 and

8.2 in 2007. The average TOC content of the grate ash leachate was higher ($\bar{x}$=318 mg/l, SD=130, n=15) than that of the gasification ash leachate ($\bar{x}$=157 mg/l, SD=137, n=9) during the first 355 days (Sivula et al., 2011). The share of the DOC from the TOC was 35 % ($\bar{x}$=111 mg/l, SD=54, n=18) for the grate ash leachate and 17% for the gasification ash leachate($\bar{x}$=53 mg/l, SD=111, n=14).

In the gasification ash leachate the concentrations of As, Ca, Mo, Ni and Zn decreased during the study period and concentrations of Cd, Cr, Cu, Fe and Mg remained constant. The concentrations of As, Ca and Cu in the leachate samples used for toxicity assays and in the samples taken during the entire lysimeter experiment are presented in Fig. 1. Concentration data for all the other elements is presented in the supplement (Supplement Figs. 1 and 2). The maximum for K and Na in the gasification ash leachate was observed in year 2005. In the grate ash leachate a decreasing trend was observed for all elements other than Cd, Cr, Pb and Zn, whose concentrations remained steadily near detection limits. The element concentrations in the samples for toxicity assays closely followed those observed in the leachate monitoring study (Fig. 1) (Sivula et al., 2011). The maximum concentration of elements in the leachates samples are given in the Table 1. In both leachates, the PAH concentrations were below the detection limits (10 ng/l and 1 ng/l for benzo(a)pyrene) in all three samples.

3.2. Effects on bioluminescence

Gasification ash leachate inhibited bioluminescence during the whole study period, both in assays with pH adjustment (pH 7±0.2) and without (pH 9.2–12.4)(Table 2, Fig. 2). The adjustment of the pH decreased the toxicity of the gasification ash leachate; however, it was still clearly toxic. The highest toxicities were observed both in the 2004 and in the 2005 samples. In 2005, even the lowest selected dilution (5 vol-%), caused inhibition at nearly 100 %. Surprisingly, some stimulation was observed in the 2004 sample, assayed without pH adjustment. The difference compared to the control was statistically significant in dilutions of 1 vol-%, 0.2 vol-% and 0.05 vol-% (t-test, p<0.05) (Fig. 2). Grate ash leachate did not inhibit bioluminescence; instead, stimulation was observed. The stimulation was observed in all of the years; however, statistically significant stimulation was only observed in 2005, in dilutions of 5, 9, and 15.5 vol-% of the leachate.

3.3. Effects on the growth of algae

The gasification ash leachate was toxic to algae during the first two years (2004, 2005) of landfilling. The highest toxicity was observed in the 2005 assay without pH adjustment (pH 9.2–12.4) (Table 2). No adverse effect on growth was observed in the sample from 2007; instead, even and increase up to 290% was noted in comparison to the control with the standard substrate. When the pH was adjusted, only the 2005 sample of the gasification ash leachate was inhibitive at the highest concentrations. Adjustment of the pH decreased the maximal stimulation of the 2007 sample (Fig. 3). For the grate ash leachate toxicity was observed in the two highest concentrations in 2004 (max. inhibition 22%, in 66 vol-% of leachate, with a 72 h exposure), and in the highest concentration in 2005. While toxicity was detected in the highest concentrations of the samples in 2004 and 2005, the stimulation of growth was observed in lower concentrations. The highest observed stimulation was 320% (10 vol-% sample, 2007, with a 72 h exposure) compared to the control.

3.4. Toxicity to Daphnia magna

The gasification ash leachate was toxic throughout the study, when the pH was not adjusted and the highest toxicity was observed in 2005 (Table 2). When the pH was adjusted all water fleas survived even in the undiluted leachate over 24 h. However, extension of the exposure to 48 h reduced survival slightly. In the pH adjusted sample of 2004, the survival at the highest concentration after 48 h was 86%, whereas in 2005 and 2007 it was 93–100%.

Toxicity of grate ash leachate to *D. magna* decreased over the study period (Table 2). The highest toxicity was detected in the 2004 sample, whereas the toxicity was reduced in 2005, and only the EC_{20} values could be calculated reliably (Table 2). By 2007, no toxicity was observed, as all individuals survived even in the undiluted leachate.

3.5. Induction of EROD activity

Both leachates induced EROD activity during the first two years of disposal. In 2004, the EROD activity increased when the gasification ash leachate dose increased, resulting in an EC_{50} value of 1.19 % (SE=0.88). Gasification ash also induced EROD activity in 2005, although no clear increase with dose was observed. In 2005, the second highest dilution of 3.8 % induced the greatest EROD activity in both leachates during the study (See supplementary data: Fig. 3). It is possible that the highest concentration

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actually inhibited the EROD activity, thus showing lower inductions. The grate ash leachate induced EROD activity in 2004 and 2005, giving EC_{50} values of 12.3 vol-% (SE=10.41) and 2.3 vol-% (SE=1.22), respectively. The protein content and EROD activity (0.19 pmol/min/mg protein) were stable between the controls in 2004 and 2005 indicating good comparability of the results across these years. In addition, the positive control β-naftophlavon (130 µg/l) induced EROD activity from 0.56 (SD=0.30) to 1.03 (SD=0.255) pmol/min/mg protein in 2004 and 2005, when compared to the control, giving p-values of 0.07 and < 0.01, respectively. In the 2007 sample the protein and EROD (0.06 pmol/min/mg protein) levels were slightly lower than in the other samples. After removing outliers the EROD induction in the positive control of 2007 was 2.8 pmol/min/mg prot (SD=4.34) and not statistically different from the negative control.

4. Discussion

The three toxicity assays showed that both the gasification and the grate ash leachates can have adverse effects on different trophic levels when assessment is based on leachate as such without pH adjustment. Overall, it seems that the gasification ash leachate was more toxic than the grate ash leachate. To our knowledge there are no previous studies on the gasification bottom ash toxicity. However, the present results of moderate and decreasing toxicity of the grate ash leachate were parallel to those found in the other grate bottom ash toxicity studies confirming that the methodology used was reliable (Moser and Römbke, 2009; Römbke et al., 2009; Chou et al., 2009; Lapa et al., 2007; Triffault-Bouchet et al., 2005; Lapa et al., 2002; Ferrari et al., 1999). For the gasification ash leachate the maximum toxicity was observed after two years, while the grate ash leachate showed a decreasing trend in toxicity during the three-year follow-up period. Gasification ash had toxic properties even after three years of disposal, while the grate ash leachate showed no toxicity in any of the assays at the end of study.

The higher toxicity of the gasification ash leachate compared to the grate ash leachate in the water flea and in the algae assays was probably related to the higher pH in the former. In addition, pH independent toxicity of the gasification ash leachate in the bioluminescence assay and the grate ash leachate in the water flea assay were observed. The high pH can cause toxicity directly as high concentration (pH > 10) of OH$^-$ -ions is known to be toxic for example to *Daphnia magna* (Seco and Vale, 2003). The indirect effects

of pH are related to solubility and speciation of elements. In weathered bottom ash, reactive sorbet minerals such as Fe/Al-hydroxides are present and elements such as Cd, Pb, Zn, Cu and Mo have high affinity for them (Meima and Comans, 1999). However, under strongly alkaline conditions (pH >10) Me-hydrolysis can take place and increase the amount of dissolved metals (Meima and Comans, 1999). Therefore, highly alkaline condition can potentially increase toxicity. In a previous study,the authors observed that concentrations of Al, Ca, Mo and Na increased with increasing pH in the gasification ash leachate (Sivula et al., 2011). Lapa et al. (2007) observed that toxicity of grate ash leachate increased with an increase in the leachate pH. As Seco and Vale (2003) point out, the pH in the exposed environment plays an important role in regards to toxicity of metals and, therefore, the toxicity assays should be performed in native pH of leachate.

The observed trends in the leachate toxicities seemed to follow conductivity. Similarly, the highest concentrations of most of the elements for gasification ash leachate were observed in 2005, while concentrations of grate ash leachate decreased steadily. Although no conclusion can be drawn about the leachate toxicity based on single element toxicity, the potential causes of leachate toxicity were screened based on the EC_{50} database and limit value comparisons. Based on the EU-limit values for the landfilling of non-hazardous waste As in both leachates and Mo in the grate ash leachate were identified to be present in elevated concentrations compared to percolation test limit values (European Council, 2003). In addition, based on database survey (US EPA ECOTOX database, accessed 3.11.2011) the As, Ca, Cd, and Cu were identified to have maximum concentration in both leachates, which could potentially have toxic effects in either water flea or algae assays.

The present maximum concentrations of trace elements in both of the studied leachates were low in comparison with those determined in previous studies of grate bottom ash (Ferrari et al., 1999; Chou et al., 2009; Römbke et al., 2009). For example, the present concentrations of Cr, Cu, Pb and Zn were among the lowest reported by Römbke et al. (2009), who determined the trace elements from water eluates of twelve different MSWI grate bottom ashes. Studies on the bottom ash of MSW-gasification are, to our knowledge, scarce: only the element composition of ash (not leachates) and mass balance of the trace elements between different residues have been published (Raskin et al., 2002; Cioni and Riccardi, 2002). Although, the determined elements probably contributed to toxicity of both leachates they do not explain the higher toxicity of the gasification ash leachate as, throughout the study, the

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concentrations of all determined elements were lower in the gasification ash leachate than in the grate ash leachate.

The pH independent toxicity of gasification ash leachate in the bacteria assay could be due to lower TOC and DOC concentrations, higher Al concentration or due to organic contaminants. Al is potential element causing the higher toxicity of the gasification ash leachate as its leaching from gasification ash increased with an increase in pH, and Al leached more from the gasification bottom ash than from the grate bottom ash (Sivula et al., 2011). In addition, the lower TOC and DOC of the gasification ash leachate could explain the higher toxicity compared to grate ash leachate. The presence of DOC is known to control availability of certain heavy metals in bottom ash of which Cu is the best known example. Dissolved Cu is know to be mainly (95–100%) bound to DOC and it's leaching is controlled by strong organic ligands and in weathered ash also by Fe/Al hydroxides (Meima et al., 1999). Fe/Al hydroxides dissolve under highly alkaline conditions (pH > 10) and high pH can therefore increase dissolution of Cu (Meima et al., 1999). On the contrary, leaching of DOC from the MSWI bottom ash is not dependent on pH, but rather on the amount of available organic carbon which decreases as the ash weathers (Meima and Comans, 1997).

Hydrophobic organic contaminants like PAH compounds are also known to be associated with organic carbon (Comans and Roskam, 2002). The presence of dissolved organ carbon can lower the bioavailability of the hydrophobic organic contaminants (Haitzer et al., 1998; Akkanen and Kukkonen, 2003). Therefore, the lower TOC content and the lower share of DOC from TOC in the gasification ash leachate could have increased bioavailability of contaminants compared to the grate ash leachate. Postma et al. (2009) also points out that increased salt and Ca levels can increase, due to salting out effect, bioavailability e.g. "free" unbound concentration of the toxic elements such as Cu and organic contaminants. However, the Ca-levels as well as conductivity, which reflects the salt content of the leachates were lower in the gasification ash leachate than in the grate ash leachate. Thus the salt content gives no explanation for the higher toxicity of gasification ash leachate.

The concentrations of PAH compounds in the present study were below the detection limit of 10 ng/l, which is less than observed by Liu et al. (2008) under static leaching conditions for the grate bottom ash. They detected that solubility for PAHs having four or less rings were <1.8–2.5 µg/l and for the high molecular weight PAH with five or more rings 100–300 ng/l

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(Liu et al., 2008). However, the fact that in the present study both leachates induced EROD-activity suggests that organic contaminants could have partially caused the toxicity. Based on an EROD assay, Osaki et al. (2006) also concluded that the toxicity they observed for the ash landfill leachate was not related to elemental ions. In addition, the present result of gasification ash toxicity in the bacteria assay is similar to Chou et al. (2009)'s, observation that grate ash leachate was toxic to luminating bacteria, regardless of the pH level. However, considering the complexity of the samples a detailed conclusive mechanism of observed toxicity is probably not possible with present data.

Differences in the sensitivities of aquatic species indicate that the cause of toxicity and its mechanism are not similar in the studied leachates. The gasification ash leachate was most toxic in the bioluminescence assay, which gave the lowest EC-values both with and without pH adjustment. Instead, the grate ash leachate was most toxic in the water flea assay. The present result was parallel to previous single species and microcosm studies showing that the water flea *D. magna*(Cladoceran, Crustacea) is the most sensitive species for grate ash leachate (Triffault-Bouchet et al., 2005; Römbke et al., 2009). The EROD activity proved to be a very sensitive indication of potentially adverse properties, as it gave the lowest EC values for both of the leachates.

Stimulation observed in the bacteria and in the algae assays can be an indication of toxic properties. While studying the effects of leachate on a microcosm, Triffault-Bouchet et al. (2005) found that bottom ash leachate can promote eutrophication. They were especially concerned about the increased algal growth combined with toxicity to daphnids grazing on green algae, which could further enhance eutrophication. Stimulation can be an indication of an organism's attempt to adapt to an environmental stressor, which subsequently leads to over-compensation (Calabrese and Baldwin, 2002). Stimulation of bioluminescence was observed in the present study in both leachates. Metals (Cr, Cu, and Zn) are known to cause stimulation of luminescence in *V. fischeri* (Christofi et al., 2002). As stimulation can be a weak indication of toxicity, which can have adverse long term effects, the chronic toxicity of leachates should be studied.

Conclusions

In the present study the waste gasification bottom ash leachate appear to be more toxic and toxicity lasted longer than that of the grate incineration bottom ash leachate. The higher toxicity was observed in all three assays presenting different trophic levels. In addition to the direct effects of the high pH (9.2-12.4), the higher toxicity of the gasification ash leachate probably was due to indirect effects of pH such as changes in the solubility of elements. EROD assay suggested that organic contaminants may contribute to toxicity. The higher pH independent toxicity of gasification ash leachate in the bioluminescent bacteria assay could be related to lower TOC and DOC content compared to the grate ash leachate. The higher toxicity of the gasification ash leachate could not be explained with the element concentrations as they all were constantly lower in the gasification ash leachate than in the grate ash leachate. However, the element concentrations and conductivity correspond to observed toxicity changes within both leachates. The bioluminescent bacteria were the most sensitive for the gasification ash leachate and water fleas for the grate ash leachate.

Acknowledgements

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Table 1: The maximum concentrations and detection limits of the grate ash (Gr) and the gasification ash (Ga) leachates (mg/l).

	Ga	Gr	DL
As	0.23	0.39	0.1
Ca	86	737	0.005
Cd	0.01	0.009	0.005
Cr	0.01	0.01	0.02
Cu	0.02	0.02	0.02
Fe	0.8	1.27	0.02
K	795	753	0.02
Mg	0.1	646	0.01
Mo	0.12	0.33	0.05
Na	1304	3990	0.05
Ni	0.01	0.05	0.02
Pb	0.025	0.024	0.02
Zn	0.15	0.02	0.02

Table 2: EC-values of the gasification ash leachate (GA) and the grate ash leachate (GR) calculated from Bioluminescence (BL), algae (A), and water flea (WF) assays. No toxicity is denoted with -. Only the assays with observed toxicity are shown.

Ash	sample	assay	x	EC_x(vol-%)	SD	exp.time	pH adj.
Ga	2004	BL	50	4.7	0.66	30 min	no
Ga	2005	BL	50	<5	-	30 min	no
Ga	2007	BL	50	8	0.13	30 min	no
Ga	2004	BL	50	6.4	0.86	30 min	7±0.2
Ga	2005	BL	50	27	1.11	30 min	7±0.2
Ga	2007	BL	50	15.7	0.65	30 min	7±0.2
Ga	2004	A	50	62	7.7	72 h	no
Ga	2005	A	50	7.5	16.6	72 h	no
Ga	2007	A	50	-	-	72 h	no
Ga	2004	WF	50	0.52	0.56	48 h	no
Ga	2005	WF	50	0.09	0.09	48 h	no
Ga	2007	WF	50	0.46	0.15	48 h	no
Gr	2004	WF	50	0.54	1.00	48 h	no
Gr	2005	WF	20	1.01	0.04	48 h	no
Gr	2007	WF	20	-	-	48 h	no
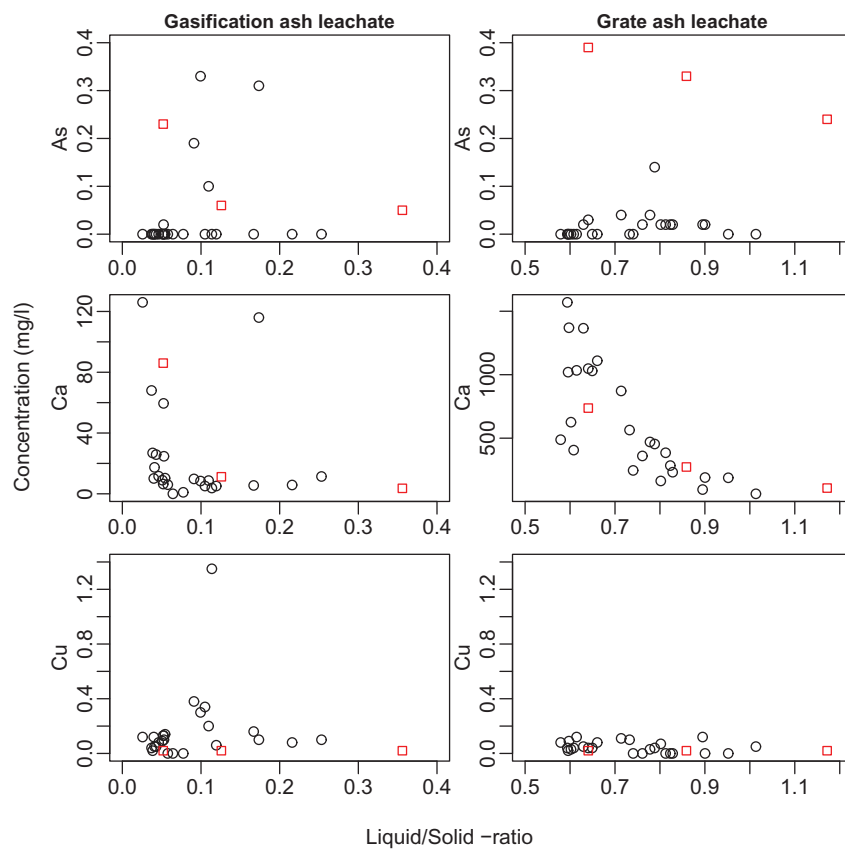
Figure 1: The concentrations of selected elements in relation to LS-ratio in the leachates measured in the monitoring study (○) and in the samples used for toxicity analyses (□).
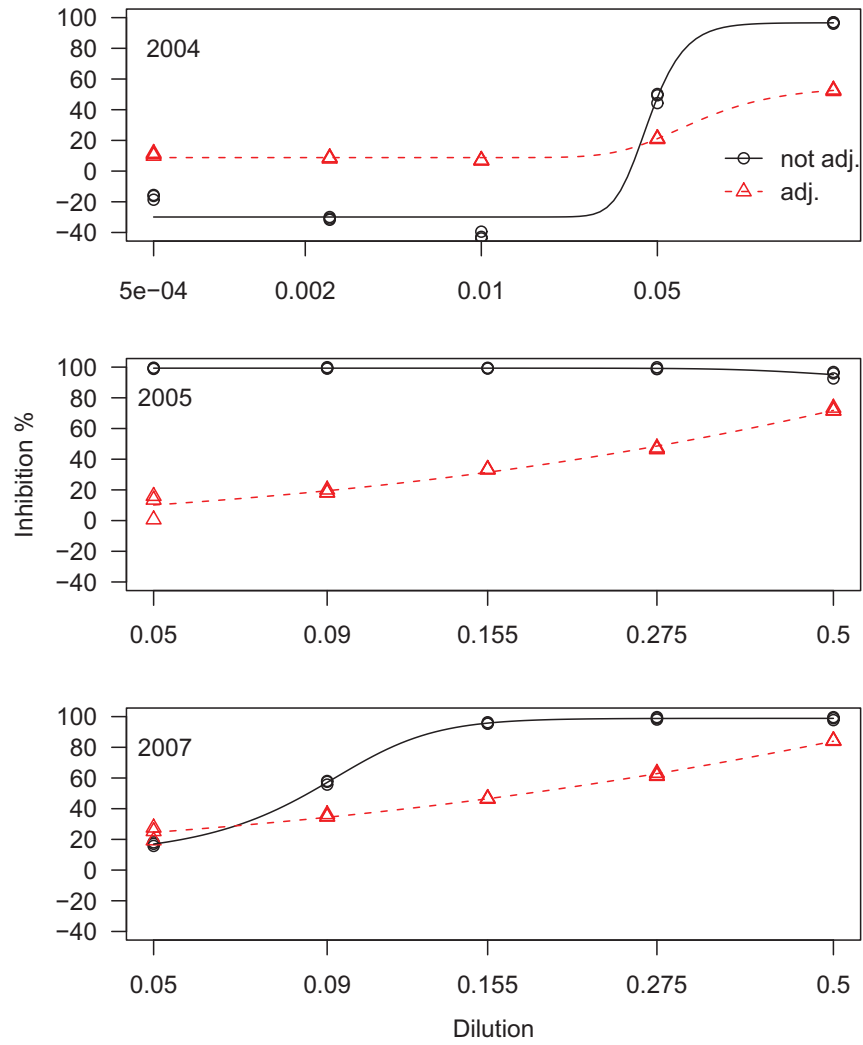
Figure 2: Inhibition of bioluminescence of *V. fischeri* by gasification ash leachate. Results from two parallel assays with and without pH adjustment and with exposure time of 30 minutes are shown.

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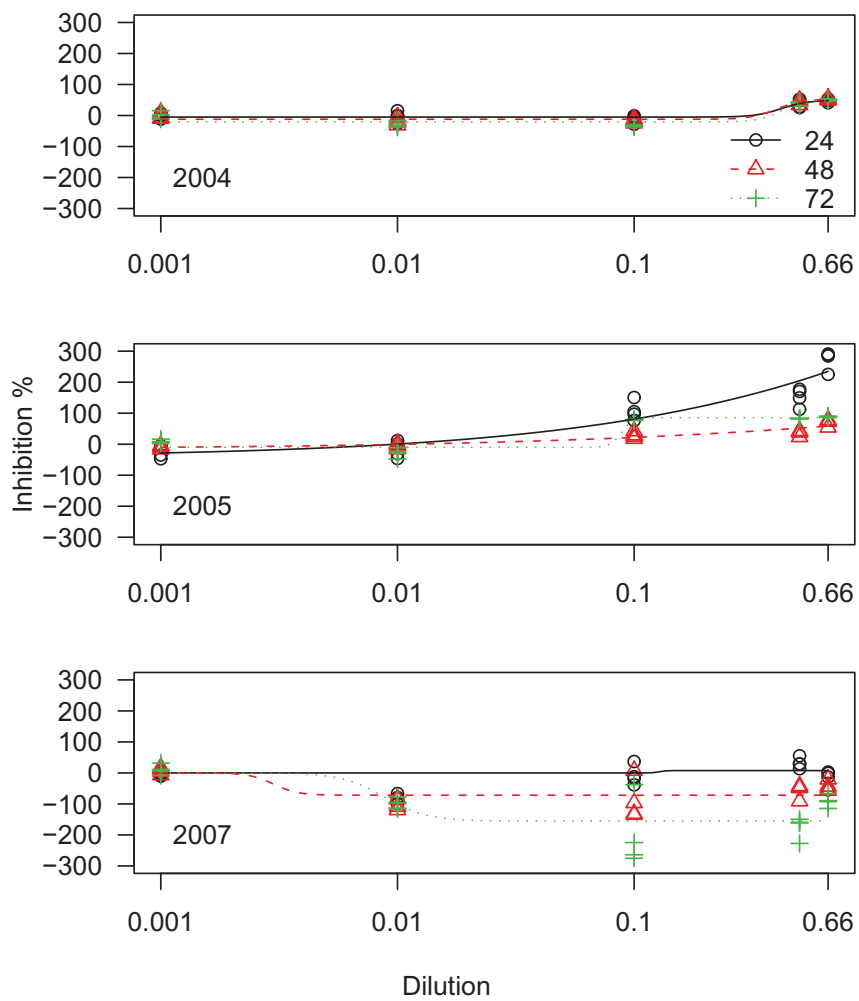
Figure 3: Development of gasification ash leachate toxicity without pH adjustment for green algae (*Pseudokirchneriella subcapitata*). Growth was measured after 24, 48 and 72 hours from the beginning of exposure.

Supplement
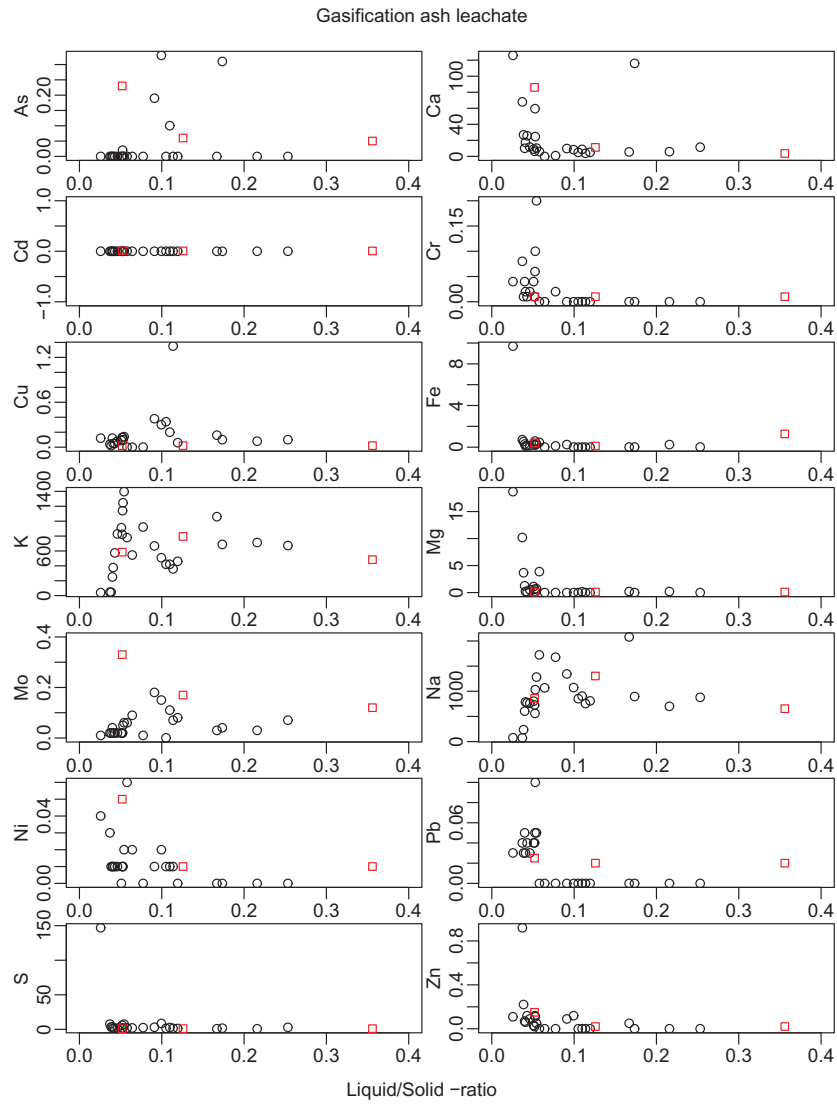
Figure 1: The concentrations (mg/l) of elements in relation to L/S ratio (mg/kg (dw)) in the gasification ash leachate measured in the monitoring study (○) and in the samples used for toxicity analyses (□).

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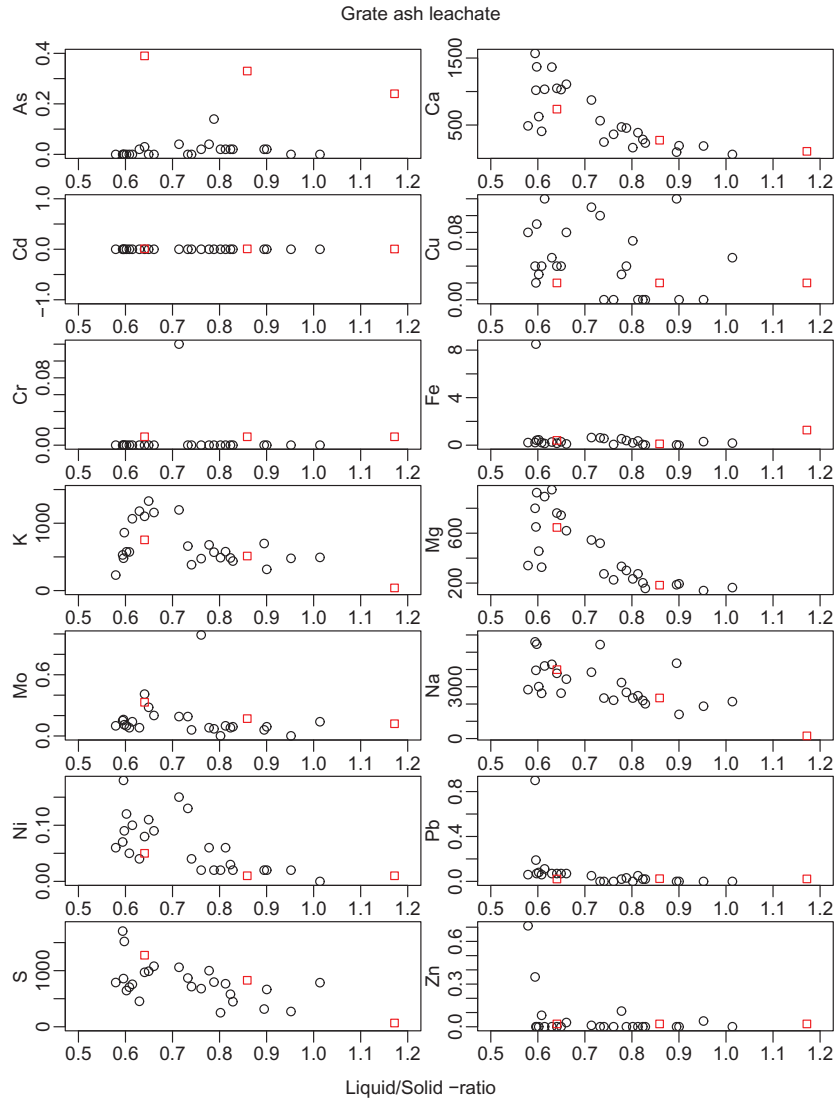
Figure 2: The concentrations of elements (mg/l) in relation to L/S-ratio in the grate ash leachate measured in the monitoring study (○) and in the samples used for toxicity analyses (□).
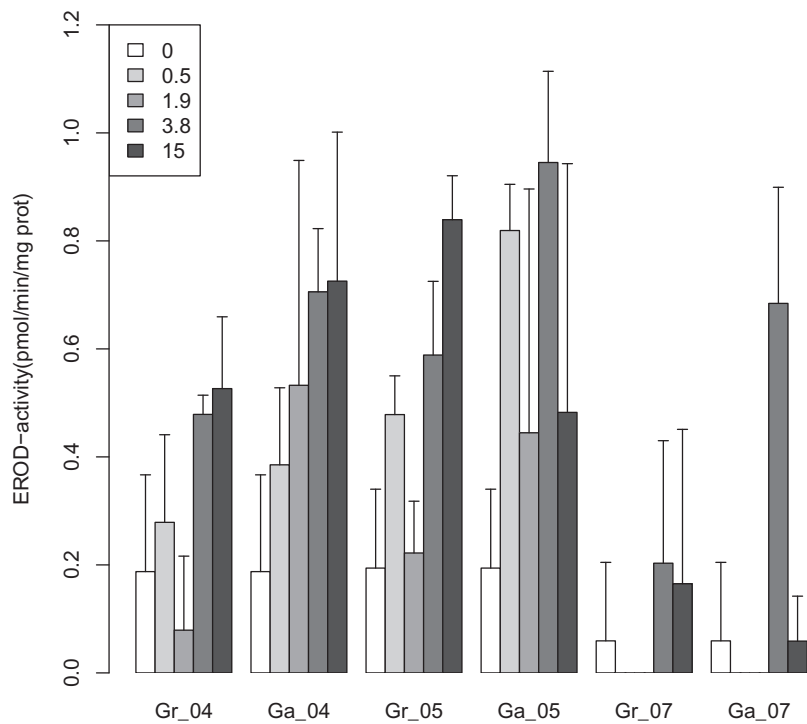
Figure 3: Erod-activity (and standard deviation) measured from mouse hepatoma cells (Hepa- 1) exposed to grate ash (Gr) and gasification ash(Ga)leachates. Five concentrations ranging from 0.5 to 5 % were used.

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III

WEATHERING OF GASIFICATION AND GRATE BOTTOM ASH IN ANAEROBIC CONDITIONS

by

Leena Sivula, Aki Ilander, Ari Väisänen & Jukka Rintala 2010

Weathering of gasification and grate bottom ash in anaerobic conditions

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ABSTRACT

The effect of anaerobic conditions on weathering of gasification and grate bottom ash were studied in laboratory lysimeters. The two parallel lysimeters containing the same ash were run in anaerobic conditions for 322 days, after which one was aerated for 132 days. The lysimeters were watered throughout the study and the quality of leachates and changes in the binding of elements into ash were observed. The results show that organic carbon content and initial moisture of ashes are the key parameters affecting the weathering of ashes. In the grate ash the biodegradation of organic carbon produced enough CO_2 to regulate pH. In contrast the dry gasification ash, containing little organic carbon, was not carbonated under anaerobic conditions and the pH decreased only after aeration was started. During the aeration the CO_2 absorption capacity was not reached, indicating that intense aeration would be needed to fully carbonate gasification ash. The results indicate that in common weathering practice the main emissions-reducing processes are leaching and carbonation due to CO_2 from biodegradation. The results of the aeration study suggest that the role of atmospheric CO_2 in the weathering process was insignificant.

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1. Introduction

It is common practice to weather ashes for few months before utilisation or disposal as this decreases the leaching of contaminants [1]. During weathering, atmospheric gases and rain induce a series of geochemical processes, which leads to decreased leaching of contaminants and stabilised pH. Carbonation is one of the important weathering process, in which atmospheric CO_2 is absorbed to ash [2]. The carbonation process decreases the initially high pH of ash, through change in the mineral composition of ash, toward the equilibrium of 8.3 [2]. This in turn stabilises the inorganic contaminants in ash.

Emission of bottom ash disposal and utilisation and the processes involved in these have been widely researched. However, the effect of anaerobic conditions on the formation of emissions is a relatively little studied topic. Anaerobic conditions may prevail inside the ash heap, in the landfill, or when ash is utilised for example in road foundations. It is known that in a large ash heap the diffusion of atmospheric gases is limited to the surface layers [3].

The objective was to study weathering processes under anaerobic conditions and effect of ash characteristics on it. In addition, role of atmospheric gases on weathering process was studied by aerating ashes. Two different kind of bottom ash, grate bottom ash

and gasification bottom ash, were used. The effect of weathering on leachate quality was studied as well as changes in the release of elements from ash.

2. Materials and methods

2.1. Bottom ashes

Bottom ashes were obtained from two facilities, one waste gasification unit and another MSWI incineration installation with a moving grate. The circulating fluidised bed gasification facility (established 1998, operating temperature 850–900 °C, Lahti, Finland) uses recycled wood from industry, plastics and refuse-derived fuel (RDF). The process is based on the production of gas which is then utilised in a boiler. In the combustion chamber the fuel dries and volatile material is released to form the product gas. After the combustion chamber, solids are separated from the product gas in a cyclone from which they are returned to the combustion chamber. From the bottom of the combustion chamber bottom ash is removed with screw conveyors. Bottom ash comprises unburned material and the solids, sand and limestone, added to the process. Bottom ash is cooled down and landfilled without pretreatment.

The moving grate incineration facility (established 1975, modernised 1995, operating temperature 1000–1100 °C, Turku, Finland) incinerates MSW, from which the most of glass, paper, and metal have been separated through the regional waste collection system. Bottom ash is quenched and landfilled.

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The bottom ashes from both facilities were transported with trucks to Mustankorkea landfill (Jyväskylä, Finland), where they were placed as heaps on an asphalt surface. Ashes were sampled with a shovel from about 20 different points on the heap. The mixed samples for the element analyses performed as sequential extraction were placed in 1-l plastic bags from which air was removed. The mixed samples for the laboratory lysimeters were placed in 10-l plastic buckets, which were air-tightly sealed with lids.

2.2. Laboratory lysimeters

Four laboratory lysimeters (diameter 18, height 70 cm) made of PVC and situated at room temperature ($20 \pm 2\,^\circ$C), were used. Two of the lysimeters were filled with 17.45 ± 0.15 kg (wet weight) of gasification ash and two with 10.35 ± 0.15 kg of grate ash. The lysimeters were air-tightly sealed, and the air-space purged with nitrogen after sealing. The lysimeters were fed with 100 ml of ion-exchanged water three times per week during the total study period of 486 days. This corresponds to 4.5 years of rainfall in local conditions (assuming that 50% of the precipitation infiltrates). There were two taps on the top, one to feed water and another one connected to an aluminium bag for the collection of possible gas emissions. Leachates were collected in a 2-l glass bottle, which was air-tightly attached to the bottom of the lysimeter. The bottle was filled with nitrogen to avoid contact with air during collecting and changed as it filled. Leachate pH was measured and samples taken for sulphate, conductivity, nitrogen, total chemical oxygen demand (COD), chloride and element analyses.

The two lysimeters filled with the same ash were operated as replicates for the first 322 days. Thereafter, one lysimeter containing gasification ash and one containing grate ash were aerated during days 323–466 (132 days), in order to study the effect of enhanced contact with air on the leaching of contaminants from the ashes. Air was pumped through the gravel layer at the bottom of the aerobic lysimeters. An aquarium pump (Rena Air 100, 3 W) was used and the average flow rate was 35.6 l/h (SD 21.7). The flow rate was measured from the top of the lysimeter with a bubble meter every weekday. The corresponding anaerobic lysimeters were run without aeration through the study.

The ash in the top layer of lysimeters were sampled once before the aeration period (study day 309). At the end samples were taken from the top, middle and bottom layers and mixed before analyses.

2.3. Analyses and calculations

From the leachates the concentrations of Al, As, Ba, Ca, Cd, Cr, Cu, Hg, Mg, Mo, Ni, Pb, S, Sb, Se, and Zn were determined with ICP-OES (PerkinElmer Optima 4300 DV, nebuliser flow 0.8 l/min, plasma power 1300 W, auxiliary gas flow 15 l/min). In addition, the concentration and binding of As, Ca, Cr, Cu, Mo, Pb, S, and Zn in the ashes were studied with sequential extraction followed by ICP-OES [4,5]. Chemical oxygen demand (COD), sulphate (SO_4), and pH were determined as previously described in [5]. Used conductivity meter was CDM210 (Radiometer analytical). Chloride was measured with the Dr Lange cuvette test (LCS 311, Dr. Bruno Lange GmbH) and total nitrogen (N_{tot}) using the Tecator application note (Perstor Analytical/Tecator AB 1995).

During the aeration period CO_2 was measured from the in- and outflows of the aerobic lysimeters. CO_2 was determined with a gas chromatograph (PerkinElmer Autosystem XL ,Varian Select 50 m $\times$320 μm, carrier gas helium, Oven 90 $^\circ$C, injection port 90 $^\circ$C, thermal conductivity detector 160 $^\circ$C).

Student's *t*-test was used to compare the results of the different treatments, *p*-value of 0.05 was used throughout the study.

3. Results

3.1. Leachate quality

The changes in leachate quality under the anaerobic disposal conditions were studied by measuring COD, pH, total nitrogen, chloride, and conductivity in the lysimeter leachates. The replicability of the grate ash lysimeters were fairly good in all parameters (Fig. 1). In the gasification ash lysimeters some variation occurred, especially in the sulphate and nitrogen; however, the concentrations were low. The clearest changes in the grate ash leachate were a rapid decrease of COD from 1650 mg/l (day 9) to 360 mg/l (day 39), and in pH, from 8.9 (day 11) to 7.7 (day 40). The decrease in the nitrogen, chloride, and sulphide concentrations was constant. The decrease in the major elements was also visible as a decreasing trend in conductivity (Fig. 1).In the grate ash all the measured parameters decreased, while in the gasification ash conductivity and concentration of sulphate in the leachate increased in the initial phase. In the gasification ash leachate the most noticeable change was a rapid decrease in COD during the first 30 days (Fig. 1).

The pH of the gasification ash leachate remained above 12 throughout the study period, while in the grate ash leachate pH at its highest was 9.00. The sulphate concentration in the grate ash leachate was 2000 mg/l at the beginning and 1000 mg/l at the end, while in the gasification ash, the sulphate concentration in the leachate was 92 mg/l at its highest (days 64, 430) (Fig. 1). The chloride concentration was 2350 mg/l at the beginning in the grate ash leachate and had fallen to below 100 mg/l by day 218. In the gasification ash leachate the initial chloride concentration was 300 mg/l and falling slowly to slightly under 100 mg/l by the end of the experiment (Fig. 1).

3.2. Effect of aeration on leachate quality

The effect of aeration on ash leaching behaviour was observed by comparing the quality of leachate in the aerated lysimeter to that in the anaerobic lysimeter during the same period (days 323–466). The effect of aeration was the clearest in the gasification ash leachate, in which pH and conductivity decreased (Table 1, Fig. 1). The decrease in pH was statistically significant ($p = 0.02$) compared to that of the leachate in the anaerobic lysimeter during the same period (days 323–466). Leachate conductivity was low (mean 1.6 mS/cm) in the aerobic compared to anaerobic lysimeter (mean 8.3 mS/cm); however, only two samples were taken during the aeration period. Aeration of the grate ash increased the leaching of sulphate, although the difference between the aerated and anaerobic lysimeters was not statistically significant ($p = 0.07$) (Table 1).

3.3. Leaching of elements

The leaching of elements under anaerobic conditions (days 0–322) was studied by measuring the concentrations of major and minor elements in the lysimeter leachates. Ca leached out in high concentrations from both ashes: leachate concentrations up to 5.2 g/l were measured in the gasification leachate and concentrations up to 5.3 g/l in the grate ash leachate. From the grate ash S also leached out in high concentrations (2600 mg(S)/l) while in gasification ash leachate it remained under 15 mg(S)/l throughout the study. In the grate ash the trend in the leaching S and Ca was similar. The concentration of P was around 0.4 mg/l in both leachates (Fig. 2).

Ba, Mg, Mo, and Ni were detected in significant concentrations in the leachates (Fig. 2). Ba concentrations up to 34 mg/l were determined in the gasification ash leachate. In the grate ash leachate Ba concentrations were around the detection limit (0.005 mg/l). In
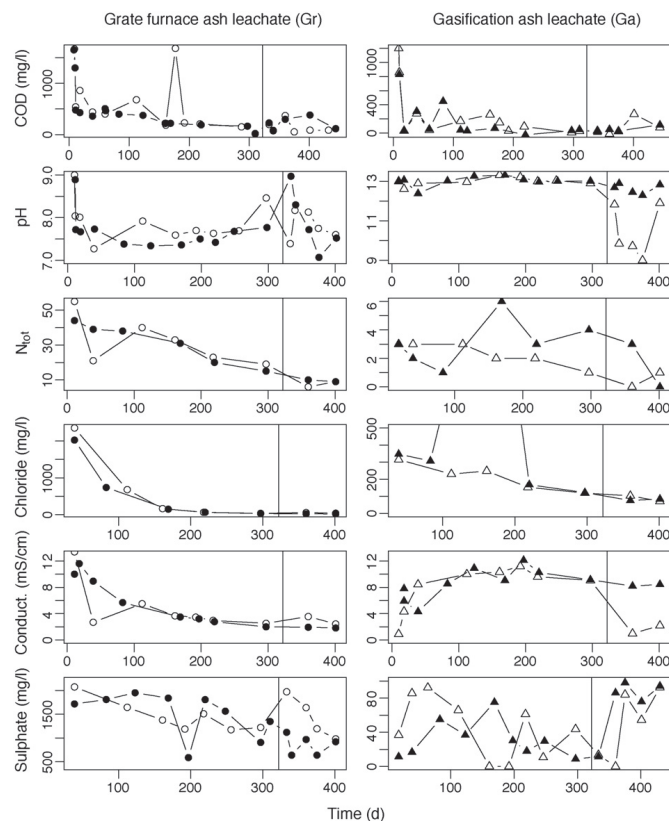
Fig. 1. Leachate quality. All lysimeters were run anerobically on days 0–322. Beginning of aeration (day 323) in the grate ash lysimeters (Gr1 ○) and of gasification ash lysimeters (Ga1 △) is marked with vertical line.

the beginning Mg concentrations up to 15 mg/l were determined in the grate ash leachate. In the gasification ash leachate Mg was not detected (except on outlier day 169). In the grate ash the highest Mo concentration was 1.03 mg/l. In the gasification ash leachate Mo concentrations were lower (0.18 mg/l). In the first measurements the Ni concentration in the gasification ash leachate was 0.05 mg/l, decreasing thereafter below the detection limit (0.02 mg/l). In the grate ash leachate Ni concentrations decreased from 0.1 mg/l to below detection limit by day 248.

Al, Cu, Pb, and Zn were only detected at the beginning decreasing rapidly thereafter to below the detection limits in both leachates, Zn is given as an example in Fig. 2. Cd, Cr, Hg, Sb, and Se remained below the detection limits throughout the study in the anaerobic leachates. The concentration of As remained close to the detection limit (0.1 mg/l) during the study.

3.4. Effect of aeration on leaching of elements

The effect of aeration was studied by comparing elements in the leachates from the anaerobic and aerobic lysimeters during the aeration period (days 323–466). Aeration decreased the leaching of

Ca and Ba from the gasification ash and P from the grate ash. The aeration significantly (t-test < 0.01) decreased the concentration of Ca in the gasification ash leachate compared the corresponding value in leachate of the anaerobic lysimeter during the same period. The concentration of Ba decreased rapidly in the gasification ash leachate from 30 mg/l close to the detection limit of 0.005 mg/l (t-test, 0.028) (Fig. 2). In the grate ash leachate, the concentration of P decreased significantly (t-test 0.034) during the aeration period. The concentration of S in the grate ash leachate increased (t-test 0.029) during the aeration period as did the concentration of Mg up to 30 mg/l (Fig. 2).

3.5. Binding of elements in ashes

The concentrations and binding of elements in the ashes were studied with sequential extraction at the beginning, before aeration (day 309), and at the end of the study (day 466). Based on the changes in the total concentration and concentrations within each fraction the leaching of elements and changes in chemical binding were observed. Comparison have been made only between the samples taken at the begin and at the end of the study as the sam-
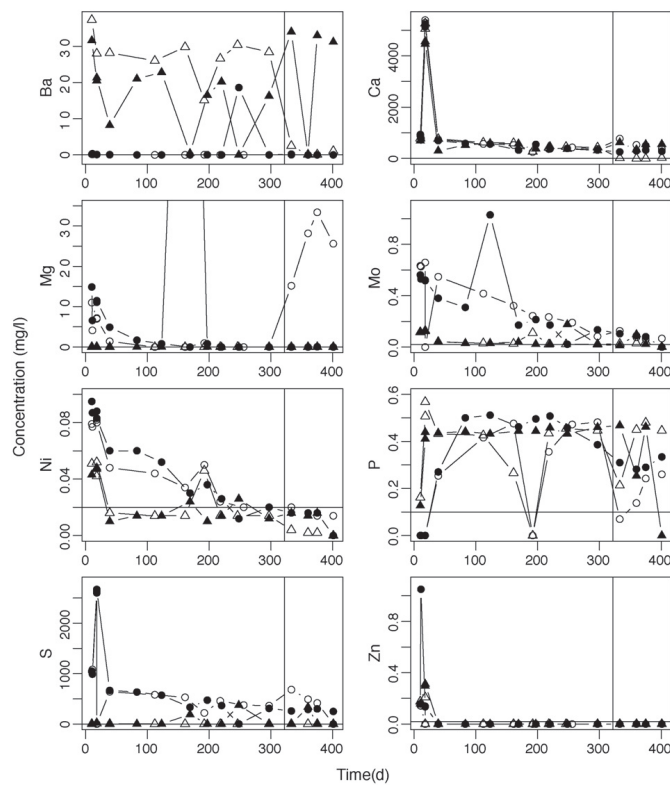
Fig. 2. Concentrations of selected elements in the lysimeter leachates. Beginning of aeration in Gr1 of the grate ash lysimeters (Gr1 ○, Gr2 ●) and Ga1 of gasification ash lysimeters (Ga1 △ and Ga2 ▲) is marked with vertical line. Horizontal line is detection limit.

ples taken only from the top of the lysimeters at the middle (day 309) were not reliable for all elements. Under the anaerobic conditions Ca, Cr, and Mo leached out from the gasification ash and As, Ca, Cr, Cu, Mo, Pb, and S from the grate ash (Fig. 3). The major change in binding was an increase in As to an oxidizable fraction (4) in the grate ash and Cr in both ashes.

In the gasification ash the total concentration of Ca had decreased 10% by the end of the study. Ca leached from exchangeable (1) and reducible (3) fractions. There was increase in the carbonate-bound (2) and in the oxidizable (4) fractions. The total concentration of Cr decreased 52% during the study period. The decrease was the highest in the exchangeable (1) fraction but was significant also in the residual fraction (5). However, the Cr concentration in the oxidizable fraction (4) increased by over 100% compared to the initial concentration, while high increases were also observed in fractions 2 (57%) and 3 (92%). The concentration of Mo decreased by 89%, mostly from the exchangeable (1) and carbonate-bound fractions.

In the grate ash the concentration of As decreased by 10% compared to the initial values. The decrease was mainly in the residual fraction (5). As increased in fractions 3 and 4. The decrease in the concentration Ca was 7% and that of Cr 16%. Ca decreased in the residual (5) and exchangeable fractions (1) and Cr in the exchange-

able (1) and carbonate-bound fractions (2). The concentration of Cr increased in fractions 3 (26%) and 4 (265%). Cu decreased in all fractions; the total decrease was 75%. Total decrease in Mo was 75% and distributed among all the fractions. The total amount of Pb decreased by 29% from the carbonate-bound fraction, in which Pb was mostly bound. However, there were high increases (100%) in Pb in fractions 2, 3, and 4. The concentration of S decreased by 45% in fractions 1, 2, and 5.

The gasification ash proved to be a difficult matrix as the analyses of As, Cu, S, and Zn were unreliable. In addition, concentration of Pb was low preventing reliable comparison of different treatments. The total concentrations of As and Zn seemed to increase, while the concentrations of Cu and S varied strongly during the study. Therefore, no conclusions were drawn about these elements. No such problems were observed with the grate ash, except for Zn, the concentration of which increased during the study.

3.6. Effect of aeration on binding of elements

The effect of aeration was observed by comparing the concentrations in the ashes from the aerated and anaerobic lysimeters at the end of the study. These comparisons show that aeration decreased
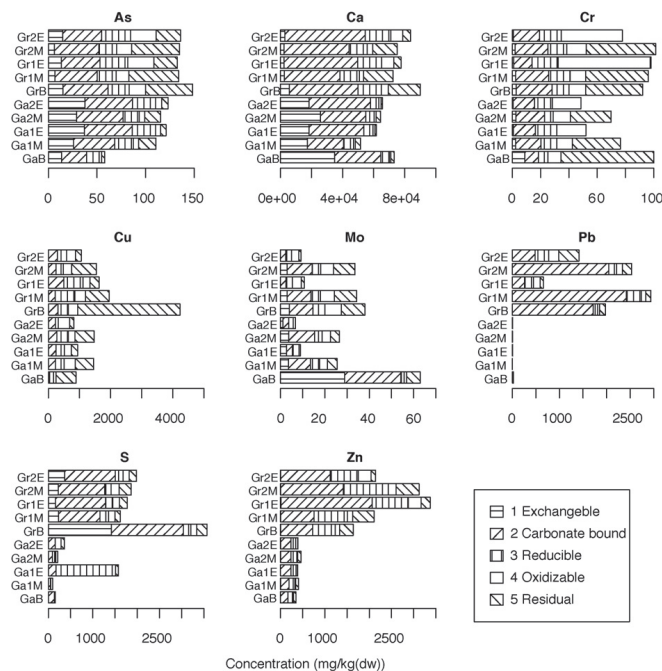
Fig. 3. Binding of elements. Gasification (Ga) and grate ash (Gr) were analysed with sequential extraction at the beginning (B, day 0), before aeration (M, day 309), and at the end (E, day 466) of the study. Gr1 of the grate ash lysimeters and Ga1 of gasification ash lysimeters were aerated between days 323 and 466.

the leaching of Cr, Cu, and Mo in both ashes. For As and Ca the variation in the total concentration between the different treatments remained under ±10% in both ashes. In the grate ash the total concentration of Pb was 47% lower in the aerobic lysimeter at the end of the study than in the anaerobic lysimeter.

The binding of Cr increased in the aerobic lysimeter in the exchangeable oxidizable fractions (4) and fell close to zero in the residual fraction (5) in both ashes. Cu bound more in the reducible (3) and residual (5) fractions in the aerated lysimeter than in the anaerobic. The binding of Mo in the aerobic grate ash lysimeter was higher in fractions 4 and 5, and in the gasification ash lysimeter it was especially high in fraction 4 but was also high in fraction 1. Under anaerobic conditions the binding of Pb was higher in all fractions, especially fractions 2 and 5.

3.7. CO$_2$ absorption

In the gasification ash lysimeter the absorption of CO$_2$ was observed as a consistently lower concentration in the outflowing air than in the inflowing air (Fig. 4). The average CO$_2$ concentration of the air pumped in was 358 ppm (SD 112, $n = 36$) and the average CO$_2$ concentration of the outflowing air was 169 (SD 376, $n = 36$). In the grate ash lysimeter CO$_2$ absorption was strongest during the first 40 days of aeration (Fig. 4). During the first 40 days of aeration the mean CO$_2$ of the inflowing air was 640 ppm (SD 837, $n = 19$) and that of the outflowing air 360 (SD 623, $n = 18$ (outlier day 343 removed)). Absorption declined slowly and by the day 380 no absorption was observed. The amount of absorbed CO$_2$ was calculated from the cumulative in- and outflows. The grate ash absorbed

4.44 mmol/g(dm) (99.5 l/kg(dm)) of CO$_2$ and the gasification ash 3.94 mmol/g(dm) (88 l/kg(dm)).

4. Discussion

The present results show that under anaerobic conditions the leaching of inorganic substances and carbonation due to biodegradation are the main processes of weathering. The aeration experiments show that it is doubtful whether atmospheric CO$_2$ is
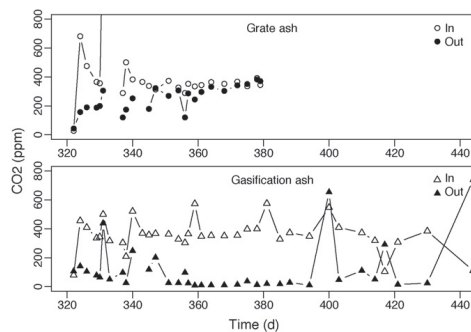

Fig. 4. CO$_2$ absorption. CO$_2$ was measured from air flowing in (○, △) and out (●, ▲) of the lysimeters during the aeration period, days 323–466.

Table 1

The effect of aeration on leachate quality. Minimum (min), maximum (max), mean ($\bar{x}$), standard deviation (SD), number of measurements (n) and result of t-test are presented. Measurements are taken from parallel lysimeters between days 323 and 466. COD, N_{tot}, Cl, and SO_4 are given as mg/l and conductivity as μS/cm. In t-test bold figures are statistically significant $p < 0.05$.

| | Grate ash leachate | | | | | | | | | | | Gasification ash leachate | | | | | | | | | | | |
| | Anaerobic | | | | | Aerobic | | | | | t-test | Anaerobic | | | | | Aerobic | | | | | t-test |
	min	max	$\bar{x}$	SD	n	min	max	$\bar{x}$	SD	n		min	max	$\bar{x}$	SD	n	min	max	$\bar{x}$	SD	n	
COD	84	381	222	125	5	54	372	141	112	7	0.28	11.6	115	51.9	45	4	0	268	80	109	5	0.62
pH	7.07	8.97	7.9	0.74	2	7.39	8.17	7.81	0.34	5	0.77	12.29	12.9	12.63	0.25	5	9	11.9	10.5	1.32	5	**0.02**
N_{tot}	9	10	9.5	0.71	2	6	9	7.5	2.12	2	0.40	0	3	1.5	2.12	2	0	1	0.5	0.71	2	0.73
Cl	15.9	20.2	18.1	3.04	2	37.3	55.2	46.3	12.7	2	0.18	75.6	84	79.8	5.94	2	71	103	87	22.6	2	0.73
Cond.	1.8	1.93	1.87	0.09	2	2.43	3.56	3.0	0.80	2	0.29	8.19	8.45	8.32	0.18	2	0.97	2.18	1.57	0.86	2	**0.048**
SO_4	637	1120	857	213	5	981	1974	1447	446	4	0.07	11.45	98.1	73.17	35.53	5	0	92.3	48.9	41.2	5	0.35

significantly able to carbonate a large heap of ash. Two different types of bottom ashes were studied and their comparison shows that the organic carbon content and moisture of the ashes are the main characteristics influencing the rate of weathering.

The weathering of both types of ashes was observed as a rapid change in leachate quality during the first 30 days of the study. In the grate ash leachate the quality parameters decreased under anaerobic conditions similar to those in previous large scale experiments [6,3]. It is assumed that information on weathering mechanisms from large scale experiments are actually obtained under anaerobic conditions. It can be concluded that, when grate ash is landfilled the filling phase causes significant part of emissions. In the gasification ash, which was not quenched, there is an initial phase during which conductivity and sulphate concentration increase. In the gasification ash the change in leachate quality was not as dramatic and the level of the measured parameters was lower than in grate ash, except to pH and conductivity.

The change in the grate ash pH was rapid and implies that also under anaerobic conditions there are mechanisms that regulate pH. Absorption of CO_2 is known to be the main process regulating the pH of ashes [2]. Under anaerobic conditions the degradation of organic carbon can produce enough CO_2 to fully carbonate the ash [7,8]. The COD measurements from the grate ash leachate show that relatively high amounts of carbon were present in the initial phase. Our previous studies have shown that the carbon is also partially biodegradable in an anaerobic system [5]. Decreased leaching of COD can follow from biodegradation of organic carbon. However, leaching of carbon correlates with pH [9], which could also explain simultaneous decrease in pH and COD. The aeration period caused some fluctuation in the pH of the grate ash leachate, which could have been due to further carbonation.

In the gasification ash, under the anaerobic conditions pH was consistently high until aeration began, when it decreased. Lack of organic carbon can prevent carbonation of the gasification ash under anaerobic conditions. Low level of the organic carbon was observed as rapid decrease in COD below detection limit (30 mg/l), in the gasification ash leachate. Also, the initial pH of unquenched gasification ash is so high (about 13) that it probably hinders any biological activity.

High concentrations of the constituents of inorganic salts (Cl, SO_4, and Ca) were detected in the leachates during the initial phase of the study. Aeration increased leaching of Ca and SO_4 from the grate ash, similar to previous carbonation experiments with air and pure CO_2[10,11]. This could be due to decrease of pH which increases solubility of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) [2] and therefore concentrations of Ca and SO_4 in the leachate. Chloride is easily soluble in both ashes. Aeration did not affect chloride leaching, which is know to be independent on pH [11,3].

Aeration decreased the leaching of Ca from the gasification ash. However, the results of sequential extraction were unable to confirm the phenomenon observed in the leachate concentrations, which implies that pore water and precipitation/dissolution of Ca-compounds in it play a central role in the chemical changes induced by aeration. Aeration probably induces formation of calcite ($CaCO_3$) and other carbonates whose solubility is lower than those of hydroxides formed when dry ash gets into contact with water [2]. The sequential extraction results at the beginning and at the end were compared to find out changes in binding of the elements. Results obtained at the middle of the study (day 309) were excluded as for some elements the total concentration were lower than those taken at the end of the study. At the middle the samples were taken only from the top of the lysimeter and for example Ca probably washed out first from top layer, therefore producing gradient in the lysimeter in which the highest concentration was at the bottom.

Aeration decreased the leaching of Mo and Cu in both ashes and Ba in the gasification ash. The sequential extraction results show that leaching of Mo and Cu was hindered in the aerated lysimeters. Natural weathering has been previously shown to decrease Cu and Mo leaching [12,10]. Meima et al. [10] found that artificial carbonation does not have a similar effect. This implies that other processes in addition to carbonation are involved [10]. Also, complex formation with organic carbon is known to affect the leaching of Cu [13].The present results show that, aeration decreased initially high concentration of Ba in the gasification ash leachate. This result is similar to that of Arickx et al. [12], who found that aging decreased Ba concentrations.

Aeration decreased the leaching of Cr from both ashes according to the sequential extraction results. Aeration decreased solubility of Cr slightly more than the anaerobic conditions. Contrary to the previous results showing that aging and aeration increased leaching of Cr [12,14]. Cai et al. [14] propose that metallic aluminium reduces Cr(VI) to Cr(III) under anaerobic conditions, which decreases solubility. The sequential extraction shows the highest increases were in oxidizable fraction, which supports reduction-hypothesis.

Leaching of Pb and Mg from the grate ash increased during aeration. Todorovic and Ecke [11] found out that artificial carbonation increased cumulative leaching of Pb and Zn. Pb is know to bind to carbonates and newly formed silicate minerals can also retain it [15]. The present sequential extraction results show that aeration reduced Pb from carbonate fraction and from residual fraction. The increased leaching of carbonates can results from changes in pH. The reduction in the residual fraction indicates that aeration corrodes silicate minerals and releases Pb bound into them. Aeration could have increased the leaching of Zn [11]; however, the variation in the measurements of Zn was high. Similar difficulties in the measurement of Zn from bottom ash have also been observed in previous studies [16]. According to the leachate measurements the aeration increased leaching of Mg from the grate ash. Aeration could have released Mg from silicate minerals similar to Pb. Mg is known to be present in the form of MgO and in silicate minerals [17].

Despite the fact that, the direct comparison of ashes from the gasification and conventional grate incineration processes is not possible as the incinerated materials were different, the comparison of the ashes revealed some characteristics that may generally explain the different behaviour under the anaerobic conditions. The ashes differed in their concentration of leaching organic carbon, measured as COD, and initial moisture content. The initial moisture content is dependent on the ash treatment in the incinerator phase. Quenched ash is not only wetter but its pH and buffering capacity are also lower. Dry, alkaline gasification ash, containing little organic carbon is a hostile environment for any microbial activity able to enhance the weathering process.

Both ashes absorbed about the same amount of CO_2 during the aeration period; however, the results reveal differences in the pattern of absorption. In the grate ash the absorption of CO_2 decreased while in the gasification ash a similar decrease was not observed and saturation was not reached. The ashes were aerated with the same power but air more easily penetrated and produced higher outflow in the coarse grate ash than in the gasification ash. At the end of the study the cumulative CO_2 absorption was similar in both ashes. The absorption capacity of the grate ash was reduced owing to CO_2 from biodegradation before the aeration period.

Compared to previous studies (max. 24 l/kg(dm)) the absorption capacity found in this study was high (90–100 l/kg(dm)) [10,18]. Standard deviation of the flow measurements was high, which weakens the reliability of the present results. It is also of note that many carbonation studies have been performed on a small scale (from a few grams to few hundred grams of ash) [10,18,12]. Also, the drying and crushing of ash for the analyses is common practice

[12,10]. During drying, crushing, and other preparation the ash may have already reacted with atmospheric CO_2 and smaller samples sizes facilitate contact with air. Thus, sample preparation as commonly practiced may cause systematic error that underestimates the absorption capacity of the ash.

Gasification ash is resilient to carbonation whether induced by biodegradation or atmospheric CO_2. Totally dry ash reacts very slowly with CO_2; the CO_2 must first dissolve into pore water [18]. Therefore, the initially dry gasification ash is not very reactive until rainwater seeps in to the ash heap. In dense gasification ash the diffusion of atmospheric CO_2 can be slow and limited to surface layers. This has been shown on the pilot-scale for conventional bottom ash[3]. In addition, there is also some evidence that the carbonation itself is slow, taking almost a week under pressure (0.1–0.2 bar) [18].

5. Conclusions

Significant changes in ash and leachate quality take place under anaerobic conditions. The addition of aeration does not result in changes that would induce further changes of the same magnitude. The measurements of trace elements in the ashes showed some effects of aeration, although whether these changes in the binding of the trace elements are large enough to improve the quality of the leachate is questionable. In addition, aeration enhanced, at least, the leaching of Pb. No reduction in the toxic elements was detected in the leachates during aeration, implying that the slightly forced or natural aeration of ashes is not able to appreciably reduce the leaching of trace elements.

The present results question the role of atmospheric carbon dioxide in short-term weathering. On the basis of these results it seems that in gasification ash during anaerobic weathering, salts, organic carbon, and trace elements are leached out. Therefore, during weathering emissions are simply transferred to the water phase instead binding more firmly to the ashes. In grate ash the biodegradation of organic carbon probably produces enough carbon dioxide to carbonate the ash, but other chemical weathering processes and leaching are involved also. In this study forced aeration was not able to fully carbonate the gasification ash. Although the flow rate used was slow, it can be doubted whether the passive diffusion of atmospheric carbon dioxide in a large ash heap or in fill is possible to the extent, required for full carbonation.

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IV

TREATMENT OF LEACHATE FROM MSWI BOTTOM ASH LANDFILLING WITH ANAEROBIC SULPHATE-REDUCING PROCESS

by

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Treatment of leachate from MSWI bottom ash landfilling with anaerobic sulphate-reducing process

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ABSTRACT

Removal of sulphate and toxic elements from the leachate of a field landfill lysimeter ($112\,m^3$), containing municipal solid waste incineration (MSWI) bottom ash, was studied. The leachate was treated in two parallel laboratory upflow anaerobic sludge blanket (UASB) reactors without and with ethanol as additional carbon source. With ethanol more than 65% of sulphate was removed, while without ethanol removal was negligible. The treatment removed Ba, Ca, Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, Sr, and Zn of the studied 35 trace and other elements. The sequential extraction of the reactor sludge at the end of runs confirmed that with a few exceptions (Ba, Ca, and Cu) the main mechanism by which the elements were removed was precipitation as sulphides.

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1. Introduction

Municipal solid waste incineration (MSWI) is an increasingly used method of solid waste pre-treatment. However, incineration produces residues which need to be properly managed. Bottom ash typically forms 85–90% by weight of the incineration residues, which is 25–45% of the mass of the incinerated municipal solid waste (MSW) and about 10% of its volume (Hjelmar, 1996).

Bottom ash can be utilised for example in road bases and as concrete aggregate, but with a number of restrictions. Bottom ash contains corrosive compounds and as a heterogeneous material it may require homogenisation or screening into size classes (Wiles, 1996; Forteza et al., 2004). In addition, for the economic and logistical reasons site of utilisation must be within reasonable proximity to the incinerator. Bottom ash will be landfilled, whenever safe utilisation is not possible, at least in countries where solutions such as placement in salt mines are not available (Hjelmar, 1996).

Emissions from bottom ash landfilling should be assessed and landfills designed such that the environmental burden and period of active management of landfills are minimised. Leachate is the major emission from bottom ash landfilling both in quality and quantity. Bottom ash leachate differs markedly from MSW landfill leachates, which are rich in organic material and nitrogen compounds; instead, it contains trace elements and inorganic salts such as chlorides and sulphates of calcium, potassium, and sodium (Sabbas et al., 2003).

Treatment of ash leachates has been previously studied e.g. in constructed wetlands and by reverse osmosis. Constructed wetland removed trace elements from coal ash leachate effectively over a long period (Ye et al., 2001). Salts and dioxins have been successfully removed by reverse osmosis from leachate of incineration residues (Ushikoshi et al., 2002). However, the presence of sulphate and trace elements in the leachate makes biological sulphate-reduction a potential technology following on from its application to the removal of metals from mining waste waters and groundwater (Lens

and Hulshoff Pol, 2000). Contrary to acidic mining waste waters, which have high concentrations (hundreds of milligrams per litre) of few elements (e.g. Cu, Zn) ash leachates are alkaline and they contain relatively low concentrations of many trace elements.

In the sulphate-reducing process, sulphate-reducing bacteria (SRB) use sulphate as an electron acceptor in a process where hydrogen or organic compounds are oxidised and sulphate simultaneously is reduced to sulphide. Sulphide reacts with divalent metal cations and with some metals or metalloids of the other oxidation states (e.g. Ag_2S, As_2S_3, Sb_2S_3) to form sulphide compounds with a low solubility, whereas sulphides of e.g. alkaline earth metals are less stable in the presence of water. When the ratio of the chemical oxygen demand (COD) and sulphate in waste water is greater than 0.67, which is calculated using a stoichiometric equation, all of the sulphate can be reduced to sulphide by SRB (Widdel, 1988). Bottom ash leachate contains some organic carbon, but the amount is small compared to the sulphate concentration, and therefore the addition of a source of organic carbon may be necessary in order to remove all the sulphate.

The objective of this study was to assess feasibility of a sulphate-reducing process in the treatment of bottom ash leachate. The chemical properties of leachate from a landfill lysimeter containing MSWI bottom ash were studied over a period of 280 days after landfilling. The ability of the sulphate-reducing upflow anaerobic sludge blanket (UASB) reactors to remove COD, sulphate, trace elements, and other elements as well as the concentration and binding mechanism of the elements in the sludges of the reactors were studied.

2. Materials and methods

2.1. Leachate

Bottom ash was obtained from an incinerator using fixed bed technology (31 years old, modernised 1995, Turku, Finland). The incinerated MSW from which glass, paper, and metal were source-separated was from Turku region. Bottom ash was transported immediately after quenching with trucks to Mustankorkea landfill in Jyväskylä (Finland) where it was placed in a field landfill lysimeter (height 3.9 m, width 2.4 m, length 12 m). The ash was compacted with a sheep foot roller and was exposed to ambient weather conditions. Leachate was collected from the drainage system into the well by gravity, from which samples were taken. Preliminary experiments (data not shown) suggested inhibition of sulphate reduction when undiluted leachate was used, hence leachate was diluted with tap water (1:1) before feeding to the reactors. Concentrations of the elements were all under the detection limits in the tap water. Ethanol (96%) was added (1 g/l) as an electron donor in the feed of reactor R2 from day 30 onwards. Influent COD without ethanol addition was 314 (SD 181, $n = 57$) mg/l and biological oxygen demand (BOD$_7$) 15 mg/l (1 sample).

2.2. Reactor experiments

Two parallel continuously fed UASB reactors (0.5 l, height 345 mm, inner diameter 47 mm, glass) were run at $20 \pm 2\,^{\circ}C$.

Reactors were fed with diluted leachate, reference reactor R1 without added ethanol and R2 with the ethanol addition. The feed was prepared twice a week and was stored in 2 l glass bottles in the refrigerator (4 °C) under nitrogen. The feed was pumped to the reactors with constant flow rate (hydraulic retention time 1 day). Both reactors were inoculated with 300 ml of anaerobically digested sludge (total solids (TS) 17.8 g/l, volatile solids (VS) 9.9 g/l) from a local municipal waste water treatment plant (Jyväskylä, Finland), after which reactors were flushed with nitrogen and air-sealed. The tubing was made of PVC and the influent and effluent sampling sites were located immediately in front of and behind the reactors. Aluminium gas bags were used to collect biogas from the top of the reactors.

2.3. Analyses

COD, BOD$_7$, TS, and VS were determined according to Finnish standard methods (SFS 5504, 1998; SFS-EN 1899-2, 1998; SFS 3008, 1990). Sulphate was determined according to the Standard Methods (APHA, 1998). pH was measured immediately after sampling with a Metrohm 744 pH meter. Sulphide was determined according to the colorimetric method (Trüper and Schlegel , 1964), the absorbance was measured at 670 nm (Hitachi U-1500 UV/VIS).

Concentrations of Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Si, Sr, Tl, U, V, and Zn were determined from both the influents and effluents. Samples were preserved by making them acidic (pH 2) with HNO$_3$ and stored at 4 °C before the measurements. Concentrations of the elements were determined with a Perkin–Elmer Optima 4300 DV ICP-OES using the default parameters of the instrument (nebuliser flow 0.8 l/min, plasma power 1300 W, auxiliary gas flow 15 l/min). The concentrations of As, Ca, Cr, Cu, Mo, P, Pb, S, and Zn in the inoculum were determined with an ultrasound assisted extraction method followed by ICP-OES at the beginning of the runs and the binding mechanisms of the same elements were evaluated with the sequential extraction method at the end of the runs. Five fractions were obtained from the sequential extraction: (1) elements bound by ion exchange pH 7, (2) elements bound to carbonates pH 5, (3) elements bound to Fe and Mn oxides pH 2, (4) elements bound to organic matter and sulphides pH 2, and (5) the residual phase. The method used is described in detail by Väisänen and Kiljunen (2005).

3. Results

The feasibility of the sulphate-reducing process to treat the bottom ash leachate was studied using two UASB reactors (R1 and R2). In reactor R1, which was fed with the diluted leachate COD removal varied and was negligible, while in reactor R2 60–70% of the COD was removed after ethanol addition (Fig. 1). The influent pHs ranged from 7.45 to 8.46, and the pH of the effluents followed those changes (Fig 1). At the beginning of the runs the amount of TS was 5.35 g/reactor and VS 2.97 g/reactor. At the end of the runs TS was 3.62 g/reactor in R1 and 10.0 g/reactor in R2. Sulphide concentration
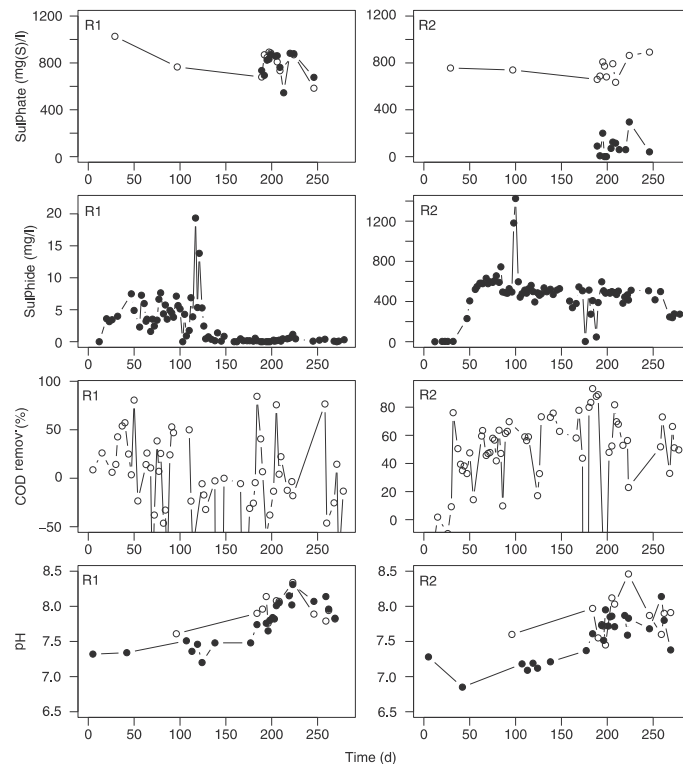
Fig. 1 – Sulphate and sulphide concentrations were determined and pH measured from the influents and effluents of reactors R1 without and R2 with ethanol addition. Removal of COD was calculated from the influent and effluent concentrations. The influents and COD removal are denoted by (○) and the effluents (●).

in the effluent of R1 was low (maximum 19 mg/l), while in the effluent of R2 the sulphide concentration rapidly increased after ethanol addition remaining mostly between 400 and 600 mg/l (Fig. 1). According to the sulphate measurements no sulphate was removed in R1 while in R2 over 65% was removed (Fig. 1).

The concentrations of the 35 elements were determined from the influents and effluents nine times during the 280-days runs (Table 1): twice during the beginning of the runs (days 35, 51), and then seven times during the last third of the runs (191, 197, 223, 253, 261, 269 and 274). The landfill lysimeter from which leachate was obtained was exposed to ambient weather conditions, which could explain the observed variation in the influent concentrations. The elements were divided into 5 groups according to their concentrations in the influents. The concentrations of group 1 (Ag, Bi, Cr, Hg, and In) were below the limits of detection in all samples. The detection limit for most of the elements was 0.02 mg/l, except 0.005 mg/l for Ba, Ca, Cd, and Sr; 0.01 mg/l for Be, Mg, and Mn;

0.05 mg/l for Ga, Na, and Pb and 0.2 mg/l for B, Cs, Hg, Si, Tl, U, and V. The elements in group 2 (Al, Be, Cd, Co, Cs, Li, P and Rb) were detected from 1 to 4 samples of influents, but no trend in their occurrence was observed. The highest concentrations of the elements in group 3 (As, Ga, Fe, Mn, U, V and Zn) were determined during the beginning of the runs. As, Ga, U, and Zn in group 3 were not detected at all after day 197. The elements in group 4 (B, Mo, Ni, Pb, Sb, Se, Si, and Tl) were not detected or their concentrations were low during the beginning of the run (until day 191) but increased towards the end of the run. The concentrations of the elements in group 5 (Ca, K, Mg, and Sr) all increased during first four measurements (35–197), but after day 197 the concentrations started to decrease. The concentrations of Ba, Cu, and Na showed pattern of variation unlike those of each other or any of the other elements.

The ability of the ethanol-supplied reactor (R2) and reference reactor without ethanol addition (R1) to remove the elements was investigated by comparing concentrations

Table 1 – Detection limits (DL), range, mean and standard deviation (SD) of the concentrations of the selected elements determined from the influents

Element	DL (mg/l)	Range (mg/l)	Mean±SD (mg/l)
Al	0.02	<0.02−0.83	0.05 ± 0.19
As	0.1	<0.1−2.4	0.41 ± 0.77
B	0.2	<0.2−15	3.2 ± 4.4
Ba	0.005	0.02−0.07	0.05 ± 0.02
Ca	0.005	200−470	350 ± 82
Cd	0.005	<0.005−0.02	0.005 ± 0.009
Co	0.02	<0.02−0.07	0.02 ± 0.03
Cr	0.02	<0.02	–
Cu	0.02	<0.02−0.38	0.086 ± 0.087
Fe	0.02	<0.02−4.20	0.3 ± 1.0
K	0.02	170−690	450 ± 170
Li	0.02	<0.02−18	0.03 ± 0.03
Mg	0.01	190−320	250 ± 45
Mn	0.01	0.46−8.60	2.0 ± 2.6
Mo	0.02	0.15−1.10	0.58 ± 0.35
Na	0.05	1300−2500	1700 ± 370
Ni	0.02	<0.02−0.33	0.16 ± 0.09
P	0.1	0.18	0.03 ± 0.03
Pb	0.05	<0.005−2.4	0.91 ± 0.83
Sb	0.1	<0.1−1.9	0.89 ± 0.73
Se	0.1	<0.1−1.7	0.63 ± 0.64
Sr	0.005	0.63−1.1	0.87 ± 0.21
T1	0.2	<0.2−4.4	1.8 ± 1.4
V	0.2	<0.02−1.2	0.15 ± 0.36
Zn	0.02	<0.02−1.2	0.13 ± 0.34

The concentrations were measured from both influents 9 times ($n = 18$) during 280 days experiment.

Table 2 – Removal of the elements calculated from influent and effluent concentrations in the ethanol supplied reactor (R2)

	Removal(%)			
	Days 191–261 ($n = 5$)		Days 33–375 ($n = 9$)	
Element	Range	Mean±SD	Range	Mean±SD
Ba	11–62	40 ± 26	(−140)–62	9 ± 62
Ca	38–64	46 ± 11	(−31)–63	25 ± 30
Cu	(>52)–(>87)	70 ± 13	0.0–87	48 ± 37
Mn	63–93	83 ± 12	(−35)–92	53 ± 43
Mo	10–(>90)	57 ± 33	(−38)–90	28 ± 48
Ni	43–(>86)	64 ± 19	(−24)–(>86)	41 ± 39
Pb	0.0–95	45 ± 43	(−71)–95	29 ± 52
T1	30–(>68)	48 ± 17	(−340)–79	8 ± 130
Sb	0.0–76	28 ± 37	(−27)–77	18 ± 33
Se	0.0–(>94)	26 ± 40	(−4)–(>94)	−25 ± 140
Sr	14–50	29 ± 14	4–50	22 ± 16
Zn	–	–	0.0–(>97)	21 ± 42

Measurement days were 33, 51 ,191, 197, 223, 253, 261, 269 and 274. Between days 191 and 261 sulphide concentrations of the effluent were higher compared to the beginning (33, 51) and end of the experiment (269, 274) and also removal percentages of the elements were higher. Removal percentage was negative when the concentration of effluent was greater than that of the influent. When concentration of the elements in the effluent was below the detection limit, removal was calculated using the detection limit. Not detected from the influent (–).

in the influents and effluents. In the ethanol supplied reactor Ba, Ca, Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, Sr, and Zn were removed totally or partially at least between days 191 and 261 (Table 2). During the beginning (days 33, 51) and end of the run (days 269, 274) removal was lower or there was no removal. It was not possible to observe the removal of the elements belonging to groups 1 and 2 (Ag, Al, Be, Bi, Cd, Co, Cr, Cs, Hg, In, Li, P, and Rb), because the concentrations in the influents were under the detection limits. Cd was detected in the influents of R2 four times and never in the effluents, which may suggest that it was removed. Mn and Zn in group 3 were removed, although Zn was detected only during the beginning (days 33, 51) of the run (Table 2).

The concentrations of B, K, Mg, Na, and Si in the effluents closely followed those of the influents in both reactors and no removal was observed (data not shown). The concentrations of Mg during the beginning were higher in the effluents than influents, which suggests that some of Mg in the effluents originated from the inoculum.

In the reference reactor (R1) only Ba and Cu were removed. Cu was detected in the influent from day 223 onwards and in the effluent only once (day 253). The removal of Cu in R1 was 12 – (>82%). The highest Ba removal was achieved between days 191 and 261 (9–31%) and it was not removed during the beginning or end of the run.

The total concentrations of nine elements (As, Ca, Cr, Cu, Mo, P, Pb, S, and Zn) in the inoculum were determined at the beginning, while sequential extraction was done at the end of the run, to determine the chemical binding of the elements in the sludges. Four of the elements (S, As, Cu, and Mo) were accumulated in the reference reactor (R1) and seven (Ca, S, As, Cr, Cu, Mo, and Zn) in ethanol supplied reactor (R2). Of the elements, which accumulated in both reactors, As, Cu, and Mo were accumulated in higher amounts in R2. The amount of S was at the same level in both reactors (Fig. 2).

The highest binding percentage to organic material and sulphides (fraction 4) were for Mo (73%) and Zn (83%) in the sludge of the ethanol supplied reactor (R2). Cu was also mainly bound to the organic carbon and sulphide fraction in both reactors (R1 87% and R2 89%). Ca, which accumulated only in R2, was mainly bound to Fe and Mn oxides (60%) and to carbonates (30%). In R1 most of (57%) S was dissolved in water while in R2 the main mechanism was the formation of insoluble metal-sulphides (52%) (Fig. 2).

4. Discussion

The present results suggest that the sulphate-reducing process has the potential to remove sulphate and some trace elements from bottom ash leachate, when an external source of carbon is provided. Over 65% of the sulphate was reduced when ethanol was added as the carbon source (R2). In theory, complete reduction of sulphate to sulphide should have been achieved with the applied COD:SO_4-ratio (on average 0.67). The process reduced the total COD of the effluent in the
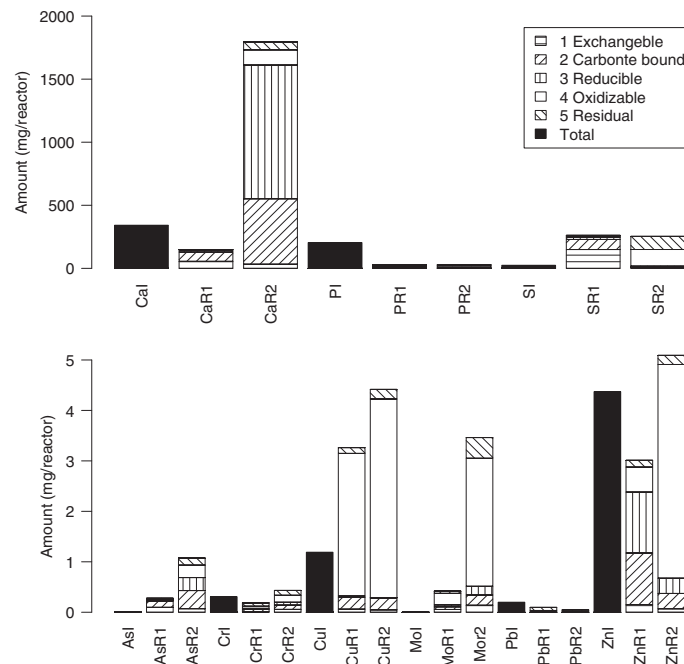
Fig. 2 – Concentrations of Ca, P, S, As, Cr, Cu, Mo, Pb, and Zn were determined from inoculum (I) as total concentration at the beginning of the run and with sequential extraction method at the end of the runs (R1 without ethanol and R2 with ethanol addition). The results are calculated as total amount per reactor.

ethanol-supplied reactor (R2) to 450–600 mg/l, of which 150–300 mg/l was apparently from the ethanol addition and the rest was originally present in the leachate. Ethanol is effectively used by SRB when a surplus of sulphate is available (Nagpal et al., 2000). Therefore, incomplete removal of the sulphate and the COD originating from the ethanol addition, could be due to variation in the COD:SO$_4$-ratio, composition of COD, and possibly inhibition by toxic substances.

The negligible removal of the COD in the reactor without ethanol addition (R1) implies that SRB or other micro-organisms were unable to use the leachate's own COD (ca. 300 mg/l) as a source of carbon. The low BOD$_7$ value (15 mg/l) of the influent, without the ethanol addition, indicates that only a small fraction of the leachate COD originated from readily bioavailable organic matter. According to Zhang et al. (2004), only 1.2% of organic carbon content of bottom ash was found to consist of amino acids, hexoamines and carbohy-drates, which form the "labile" or easily biodegradable portion of organic compounds. When the COD originating from leachate is subtracted from the total COD of the influent of the ethanol-supplied reactor (R2), the actual COD:SO$_4$-ratio was 0.49 and thus there was not enough easily bioavailable carbon to reduce all of the sulphate.

The concentrations of Al, Cd, Cr, Hg, Mo, Na, Pb, and Zn in the diluted leachate (or influent) were in the same range as previously measured in MSWI bottom ash leachates. The concentrations of As, Mg, Mn, Ni, Sb, Se, Si, and V were in the same range or higher and the concentrations of Ca, B, Cu, Fe and K were same range or lower than those presented in the literature (Hjelmar, 1996; Kersten et al., 1997; Johnson et al., 1999; Freyssinet et al., 2002; Øygard et al., 2005). Sulphate concentrations in the literature vary from 500 mg/l up to 10 g/l (Hjelmar, 1996; Øygard et al., 2005) compared to 1700–3000 mg/l determined from diluted leachate in this study. To our knowledge concentrations of Ag, Ba, Be, Bi, Co, Cs, Ga, In, Li, P, Rb, Sr, Tl, and U in bottom ash leachate have not previously been published.

Cu, Mn, Mo, Ni, Pb, Tl, Sb, Se, and Zn, which were effectively removed in the ethanol-supplied reactor (R2), are known to precipitate as nonwater-soluble sulphides. In addition, Ba, Ca, and Sr, which form water-soluble sulphides, were removed in R2. Ba and Cu were removed also in R1, which suggests that their removal mechanism was other than precipitation as sulphides. Non-metallic B and Si, which were detected, but not removed in the process, are anions in water solutions and therefore do not precipitate as sulphides.

In waste water containing a high concentration of sulphate, cations such as Na and Ca can inhibit anaerobic processes. When concentrations of Ca are about 400 mg/l, calcium precipitates ($CaCO_3$, $Ca_3(PO_4)_2$) may entrap biomass and limit the transport of substrates (Hulshoff Pol et al., 1998). When calcium is precipitated as phosphates it can also cause phosphate deficiency. The calcium concentration fluctuated between 200 and 470 mg/l in the influent and was consistently lower (<280 mg/l) in the effluent of ethanol-supplied reactor (R2), which suggests that calcium was precipitated in the reactor. The inhibitory effect of calcium precipitation in R2 could explain decrease both in sulphate reduction and removal of the elements during the end of the run.

The sequential extraction confirmed that precipitation as sulphides was the main mechanism in the removal of trace elements, and that Cu, Mo and Zn in particular were effectively bound to organic matter and/or sulphides (fraction 4). This is supported by the result that in ethanol supplied reactor (R2) over half of S was found in fraction 4. However, in the case of Cu the fraction containing organic matter and sulphides was equally important in the both reactors, which implies that organic matter probably absorbed most of removed Cu. In the MSW landfill leachate formation of organic complexes can decrease amount of free metal ions below 10–30% and therefore efficiency of heavy metal removal by sulphide precipitation (Baun and Christensen, 2004). Formation of colloids and organic complexes could explain why reference reactor (R1) was according to the extraction results able to remove 75% of the amount of Cu compared the ethanol supplied reactor (R2). On the other hand, only 25% of As and 12% of Mo were removed in the reference reactor, which implies that sulphate reduction was the main mechanism in their removal. Ca was precipitated in the ethanol-supplied reactor (R2) as carbonates and with Fe and Mn oxides. It is known from studies of calcium precipitation in sediments, that sulphate reduction enhances calcium carbonate precipitation (Castanier et al., 1999).

The sulphate-reducing process reduced the concentrations of several trace elements. However, in order to function the process needs a supply of organic carbon. Ca accumulation may inhibit sulphate reduction. Inhibition can be prevented, for example, by replacing sludge regularly. In addition, effluent contains sulphide that must be removed, as well as residual COD that possibly also must be removed. Overall, the sulphate-reducing process has potential as an effective method treating leachate from bottom ash landfilling, but the above-mentioned issues related to the process must be resolved before it can be applied in practice. Further research is needed to show long term efficiency of the process in pilot scale as well as properties and replacement need of the sludge.

5. Conclusions

(1) The sulphate-reducing process effectively reduces concentrations of the elements, which precipitate as insoluble sulphides also when initial concentrations are low as in the MSWI bottom ash leachate.
(2) In order to function the process needs a supply of organic carbon.

(3) Precipitation as sulphides was the main removal mechanism. However, Cu was effectively removed by absorption to organic material.
(4) Bottom ash leachate contains Ca, the precipitation and accumulation of which may inhibit sulphate reduction; this must be taken into account when reactors are designed and managed.

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V

STABILISATION OF MSWI BOTTOM ASH WITH SULPHIDE-RICH ANAEROBIC EFFLUENT.

by

Leena Sivula, Ari Väisänen & Jukka Rintala 2008

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Stabilisation of MSWI bottom ash with sulphide-rich anaerobic effluent

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Abstract

Effluent of an anaerobic sulphate-reducing wastewater treatment process was used to stabilise bottom ash. The effect of stabilisation on the concentration and binding of Ca, P, S, Cu, Pb, Zn, As, Cr, and Mo were studied by comparing results of sequential extraction from fresh and stabilised bottom ash. The stabilisation treatment improved the retention of Ca, Cu, Pb, S, and Zn in bottom ash compared to a treatment with ion-exchanged water. In addition to retention, Cu, S, and Zn were accumulated from the anaerobic effluent in the bottom ash. Concentrations of As, Cr, and Mo remained on the same level, whereas leaching of P increased compared to control treatment with ion-exchanged water. Improved retention and accumulation were the result of increased binding to less soluble fractions. The highest increases were in the sulphide and organic carbon bound fraction and in the carbonate fraction. Enhanced carbonation was probably due to CO_2 deriving from the degradation of organic carbon. Flushing of stabilised bottom ash with ion-exchanged water ensured that the observed changes were not easily reversed. Most of the sulphide in the anaerobic effluent was removed when it was passed through bottom ash. The objective was to study the feasibility of sulphide-rich anaerobic effluent in bottom ash stabilisation and changes in the binding of the elements during stabilisation. In addition, the ability of the process to remove sulphide from the effluent was observed.

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Keywords: Incineration; Landfilling; Utilisation; Sulphate reduction; Heavy metals

1. Introduction

The need to reduce long-term leachate emission from municipal solid waste incineration (MSWI) landfills has been recognised (Sabbas et al., 2003). In addition to landfilling bottom ash utilisation e.g. in road foundation has also been a cause of concern (Åberg et al., 2006). The major emissions from bottom ash are inorganic contaminants such as heavy metals. Treating leachate is to treat the symptoms not the cause, therefore, many methods of stabilising contaminants in bottom ash have been studied

and implemented. Because the contaminants tend to be inorganic, the methods are mainly chemical or physical such as stabilisation with cement, vitrification, and natural weathering (Reijnders, 2005).

The stabilisation of trace elements in bottom ash as low solubility sulphides has been shown to be possible. Youcai et al. (2002) used natriumsulphide successfully to stabilise Cd and Pb in fly ash. Alternatively, sulphide from biological anaerobic processes could be used. Biological sulphate reduction has been used in waste water treatment to transform sulphate to sulphide and, additionally, to precipitate metals as sulphides (Hulshoff Pol et al., 1998). Sulphate-reducing leachate treatment has been shown to remove heavy metals like Cu, Mo, Pb, and Zn from bottom ash leachate (Sivula et al., 2007). When the concentration of sulphate in the influent of anaerobic process is high compared to the concentration of heavy metals, there is surplus of sulphide in the effluent. Sulphide could be removed from

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the effluent and simultaneously heavy metals stabilised in bottom ash by treating ash with the sulphide-rich effluent.

The stabilisation of bottom ash with sulphide-rich effluent at MSWI landfills could reduce emissions from landfills and shorten their active care-taking period. Stabilisation with anaerobic effluent could also be used as a pre-treatment method before the utilisation of bottom ash. Common pre-treating methods of bottom ash include such stages as size-separation and natural weathering. In natural weathering bottom ash is exposed in heaps to ambient conditions (e.g. atmospheric carbon dioxide and precipitation) for several months before utilisation. Precipitation decreases the concentrations of soluble elements in ash through leaching. On the other hand, atmospheric CO_2 decreases leaching as result of carbonation (Meima and Comans, 1997). Anaerobic effluent also contains dissolved CO_2 from degraded organic material, which can enhance carbonation. Therefore, the use of anaerobic effluent in pre-treatment sites could stabilise bottom ash through two mechanisms and reduce emissions both from pre-treatment and utilisation sites.

The objective of the present study was to assess the feasibility of sulphide-rich effluent to stabilise selected elements in MSWI bottom ash. The concentrations and binding of nine elements in bottom ash were studied. Ca, S, and P were selected because of their importance in the biological and chemical processes involved. Cu, Pb, Zn, As, Mo and Cr were selected on basis of their potential leaching and toxicity. Leachate was obtained from a landfill lysimeter containing MSWI bottom ash and was treated anaerobically. Bottom ash was stabilised with sulphide-rich anaerobically treated leachate and results were compared to stabilisation with untreated leachate with and without added ethanol and to anaerobically treated leachate without sulphide. In the anaerobic leachate treatment ethanol was added to enhance sulphate reduction as the organic carbon content of the lysimeter leachate was originally low. In addition, the ability of the method to remove sulphide from anaerobic effluent was studied.

2. Materials and methods

2.1. Bottom ash and leachate

The bottom ash used in this study was obtained from a municipal solid waste (MSW) incinerator (32 years old, modernised 1995, Turku, Finland) after quenching. Regional collection places were used to separate glass, paper, and metal from the MSW. The leachate used in this study was obtained during the 11th–14th months of operation of a landfill lysimeter (height 3.9 m, width 2.4 m, length 12 m: structure similar to that described by Sormunen et al. (2007)) filled with bottom ash compacted to 1.5 t m^{-3}. Leachate sample for anaerobic treatment was obtained once a month from landfill lysimeter.

Anaerobically treated leachate was obtained from two parallel upflow anaerobic sludge blanket (UASB) reactors (0.5 l) treating diluted (1:1 with tap water) landfill lysimeter leachate as such or with ethanol addition (96%, 1.05 g l^{-1}) at 20($\pm$2) °C for 280 d (Sivula et al., 2007). The main parameters determined both from the influents and corresponding effluents of the reactors were chemical oxygen demand (COD), pH, and sulphate concentration (Table 1). In addition, the sulphide concentrations of the effluents were determined (Table 1).

2.2. Stabilisation treatment

Stabilisation of the bottom ash was studied in five parallel 50 ml glass-columns (diameter 3 cm, height 11.5 cm) at 20 °C (Fig. 1). The columns simulated condition inside an ash landfill. Two fresh samples (10 l each) of the bottom ash were obtained and kept under nitrogen before they were mixed and 60 g ($\pm$2 g (wet weight)) of the ash was compacted in each stabilisation column. The columns were then flushed with nitrogen and sealed with silicone plugs. The columns were fed with influents and corresponding effluents from the above described UASB reactors and with ion-exchanged water to study the effects of sulphide, pH

Table 1
Mean and standard deviation (SD) of COD (mg l^{-1}), sulphide (mg (S) l^{-1}), sulphate (mg (S) l^{-1}) and pH values from the feeds and effluents of the stabilisation columns

	COD		S^{2-}		SO$_4^{2-}$		pH	
	Mean $\pm$ SD	*n*	Mean $\pm$ SD	*n*	Mean $\pm$ SD	*n*	Mean $\pm$ SD	*n*
L	291 $\pm$ 267	15	–		796 $\pm$ 108	9	7.94 $\pm$ 0.20	12
LE	1700 $\pm$ 397	15	–		754 $\pm$ 93	9	7.86 $\pm$ 0.28	12
TL	168 $\pm$ 41	15	0.33 $\pm$ 0.29	17	785 $\pm$ 105	12	7.95 $\pm$ 0.17	15
STL	676 $\pm$ 361	15	432 $\pm$ 199	22	88 $\pm$ 87	12	7.75 $\pm$ 0.18	15
L-C	223 $\pm$ 123	27	–		548 $\pm$ 265	22	8.88 $\pm$ 1.35	26
LE-C	969 $\pm$ 635	26	–		448 $\pm$ 251	24	8.42 $\pm$ 1.28	27
TL-C	191 $\pm$ 129	27	0.40 $\pm$ 0.33	15	557 $\pm$ 259	22	8.56 $\pm$ 0.98	26
STL-C	478 $\pm$ 219	27	133 $\pm$ 136	19	275 $\pm$ 177	23	8.68 $\pm$ 1.36	22
C-C	113 $\pm$ 79	25	–		16 $\pm$ 19	24	11.58 $\pm$ 0.21	28

The samples from the UASB reactors used as the feeds of the columns were leachate (L), leachate with added ethanol (LE), treated leachate (TL), and sulphide-rich treated leachate (STL) and the corresponding column effluents (L-C, LE-C, TL-C, STL-C, C-C (control with ion-exchanged water)). Not-measured values denoted by – and number of measurements by *n*.
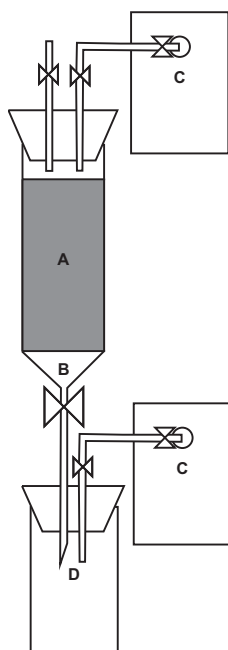
Fig. 1. Schematic illustration of a stabilisation column: (A) bottom ash, (B) fiberglass, (C) aluminium gas bag and (D) glass bottle for leachate collection.

and COD on stabilisation. The feeds were leachate (L), leachate with added ethanol (LE), treated leachate (TL), sulphide-rich treated leachate (STL), and ion-exchanged water (C). L was the influent of the UASB-reactor without ethanol addition and TL was the effluent of the same reactor. Similarly LE was the influent of the UASB-reactor with ethanol addition and STL the corresponding effluent. The L-C, LE-C, TL-C, and STL-C were the effluents of the stabilisation columns.

The columns were run semi-continuously for 111 d. Each column was fed every weekday with 20 ml of liquid, and 2 h before the next feed the bottom tap was opened and leachate slowly released from the columns. From day 90 onwards all columns were fed with ion-exchanged water to remove the dissolved fraction of the elements. Feeding was done with a syringe through the tap on top of the column. There was also a gas removal tube on the top, which was attached to an aluminium gas bag, to avoid pressure forming inside the column. All tubes were made of PVC. Seeping water was collected in glass bottles, which were air-tightly connected under each column. The bottles were changed every week-day, the pH of the seeping water was measured, and samples taken for subsequent analyses.

2.3. Sequential extraction, analyses, and calculations

Sequential extraction followed by inductively coupled plasma-optical emission spectrometer (ICP-OES) was used for the ash samples to study binding of the selected elements (As, Ca, Cr, Cu, P, Pb, Mo, S, and Zn). All the measurements were performed with a radially viewed plasma. The default parameters of the Perkin–Elmer Optima 4300 DV ICP-OES were used (nebuliser flow $0.8 \, l \, min^{-1}$, plasma power 1300 W, auxiliary gas flow $15 \, l \, min^{-1}$). The accuracy of the method has been determined with the analysis of SRM 1633b (Coal fly ash). The determination of analyte concentrations resulted in recovery rates from 85% to 105% (Ilander and Väisänen, 2007). Uncertainties in the ash analyses were about 6% in sampling, 3% in extraction, and 2% in measurement (total 7%). In the analysis of liquid samples, the errors in sampling were about 4% and in sample pre-treatment 2%, and measurement error was 2%, leading to total uncertainty of 5%. Five fractions were obtained from the sequential extraction: (1) elements bound by ion exchange; pH 7, (2) elements bound to carbonates; pH 5, (3) elements bound to Fe and Mn oxides; pH 2, (4) elements bound to organic matter and sulphides; pH 2, and (5) residuals. Sequential extraction method is described in detail by Väisänen and Kiljunen (2005). All the concentrations of the elements were calculated per dry weight (dw).

The concentrations of the elements in the column feeds and effluents were determined with ICP-OES after samples had been made acidic with HNO_3 (pH < 2) and centrifuged. Sulphate, sulphide, COD, total solids (TS) and volatile solids (VS) were determined and their pH measured as described in Sivula et al. (2007). The total inputs of the elements in the columns were calculated according to their concentrations in the leachates (Table 2). The concentrations of As, Cr, P, and Zn were below detection limits in several of the measurements, and therefore it was not possible to determine their inputs reliably.

The total concentrations of the elements in the ash samples were calculated as the sum of the five fractions obtained from the sequential extraction. Change in the total concentration of an element during the column run was calculated by subtracting the initial concentration in the ash from the concentration at the end. Thus, if the resulting value was positive then the element was accumulated in column during the study. When the total concentration in a column at the end of the run was higher than in the control column the element had been retained and, if lower, the treatment had enhanced leaching of the element. Inputs of As, Cr, Cu, P, Pb, and Zn according to their concentrations in the untreated leachate (L) were <1.3% of the initial concentration in ash and thus they were not taken into account, when interpreting the results of sequential extraction. However, the input of Ca, Mo, and S from untreated leachate were 13%, 69%, and 464%, respectively, of the initial concentration in the bottom ash and they should be considered when interpreting the results.

Table 2
Concentrations (mg l^{-1}) of selected elements in the leachates fed to the stabilisation columns (determined 5–6 times during 111-day study)

	DL	Leachate with ethanol			Leachate			Treated leachate			Sulphide containing treated leachate		
		MC	SD	In	MC	SD	In	MC	SD	In	MC	SD	In
As	0.1	<0.1	–	–	<0.1	–	–	<0.1	–	–	<0.1	–	–
Ca	0.005	350	41	9800	340	37	11500	350	22	9500	230	60	6500
Cr	0.02	<0.02	–	–	<0.02	–	–	<0.02	–	–	<0.02	–	–
Cu	0.02	0.062	0.028	1.72	0.05	0.037	1.79	0.025	0.014	0.68	<0.02	–	–
Mo	0.02	0.87	0.15	24	0.87	0.095	29	0.91	0.11	24	0.59	0.21	16
P	0.1	<0.1	–	–	<0.1	–	–	<0.1	–	–	<0.1	–	–
Pb	0.05	1.4	0.51	39	1.6	0.67	56	1.6	0.23	43	1.2	0.5	31
S	0.1	650	90	18,000	690	169	23,000	690	130	18,500	4800	3300	136,000
Zn	0.02	<0.02	–	–	<0.02	–	–	<0.02	–	–	<0.02	–	–

Detection limit (DL), mean concentration (MC) and standard deviation (SD) are presented. Total inputs (In) to the columns (mg kg^{-1} (dry weight)) were calculated from mean concentration and total feed flow (1.28 l). If concentration was below detection limit, SD and inputs were not calculated (denoted by –).

3. Results

3.1. Concentrations of elements in fresh bottom ash

The total concentrations determined with the sequential extraction were for Ca 77000 mg kg^{-1}, for P 3200 mg kg^{-1}, and for S 3900 mg kg^{-1}. Total concentrations of Cu (1070 mg kg^{-1}), Pb (3180 mg kg^{-1}), and Zn (1500 mg kg^{-1}) were in the same range. The concentrations of As, Cr, and Mo were 159 mg kg^{-1}, 85 mg kg^{-1}, and 35 mg kg^{-1}, respectively (Fig. 3). At the beginning of the study the TS of fresh ash was 701 mg g^{-1} and VS 42.5 mg g^{-1}. At the end of the study TS was determined after the columns were emptied of leachate. In all the columns TS was lower at the end of the study than at the beginning of the study (L 604 mg g^{-1}, LE 656 mg g^{-1}, TL 654 mg g^{-1}, STL 611 mg g^{-1}, and C 658 mg g^{-1}). The share of VS increased slightly in all the columns (L 59 mg g^{-1}, LE 44 mg g^{-1}, TL 52 mg g^{-1}, STL 55 mg g^{-1}, and C 61 mg g^{-1}).

3.2. Quality of stabilisation-column effluents

COD and sulphate concentrations were determined and pH measured in the column effluents (Fig. 2, Table 1). The COD of the column effluents reflected the feeds of the columns. A clear decrease in COD values, was observed in the LE and STL columns. Effluent COD in the TL column (191 mg l^{-1}) was lower than effluent COD in the L column (223 mg l^{-1}), which indicates that the anaerobic leachate treatment without ethanol addition is able to reduce the amount of leaching COD. COD in the control column (C) effluent (113 mg l^{-1}) derives wholly from the bottom ash in the column and is lower that in the other columns as there is no input COD from the landfill lysimeter or added ethanol.

Sulphate was measured in all feeds and effluents of the columns and sulphide in the feeds and effluents of the TL and STL columns. In the L, LE, and TL columns the sulphate concentrations of the effluents were lower than those in the feeds (Table 1). Also, the sum of sulphate

and sulphate calculated as S was lower in the effluents of the TL and STL columns than in their feeds. The sum of sulphate and sulphide was lowest in the effluent of the STL column compared to other leachate fed columns (Table 1). S in all column effluents was mainly sulphate, and the lowest concentration was in the control column. Some sulphide in the STL column went through the column; however, the concentration was low compared to that in the feed. The sulphide concentration in both the feed and effluent of the TL column was low (<19 mg l^{-1}). The rapid decrease from 12 to about 8 was observed in the pH of all the effluents except that in the control column. In the control column effluent pH was about 12 through out the study (Fig. 2). The variation in results of Fig. 2 originates mainly from the variation in landfill lysimeter leachate quality.

3.3. Accumulation of elements from leachates in bottom ash

Treatment with sulphide-rich effluent (STL) improved the retention compared to the control column and even led to the accumulation of S, Cu, and Zn into the bottom ash from the feed (Fig. 3). The highest accumulations of Cu and Zn were in the STL column and that of S in the TL column.

The determined concentration of S was higher in all columns at the end of the study than at the beginning. At the end the concentration of S in the TL column was 45% higher than in the fresh bottom ash. This means that, 10% of the input had accumulated in the TL column (Table 2). In the STL column, the concentration of S increased by 26% compared to that in the fresh ash, while the corresponding concentration increase in the in LE column was 21%, in the L column 9%, and in the control column 16%.

The total concentration of Cu increased in the STL column by 145% compared to that in the fresh bottom ash, while in the LE column the increase was 94%. In the other columns 22–52% of Cu was leached out. The amount of accumulated Cu in the LE column was 1000-fold compared to the estimated input from the leachate and was even higher in the STL column (Table 2).
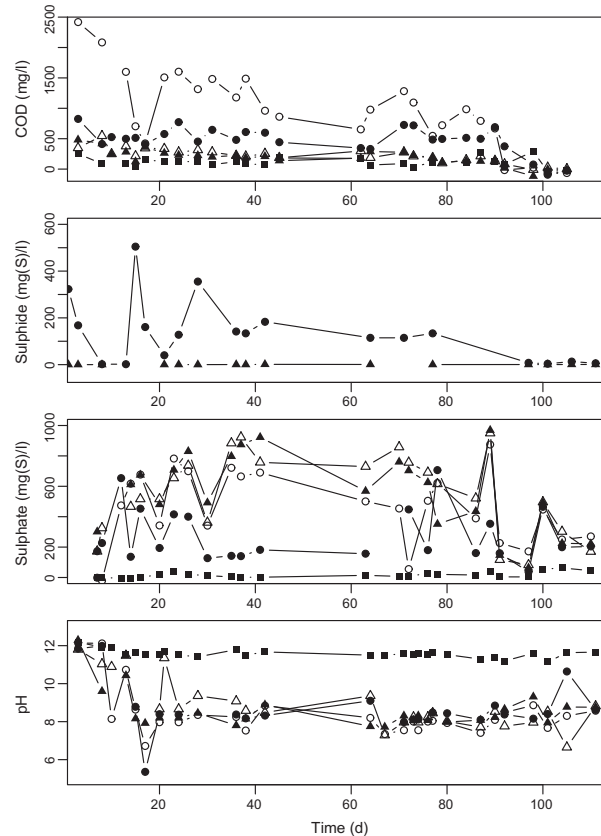
Fig. 2. COD, sulphide, sulphate and pH of stabilisation column effluents. The columns were fed with ion-exchanged water (C, ■), with leachate (L, △), with treated leachate (TL, ▲), with ethanol added leachate (LE, ○), and with sulphide-rich treated leachate (STL, ●).

The total concentration of Zn increased by 348% in the STL column. In the TL column the increase was 36% and in the control column 7%. In the columns fed with untreated leachates 7–13% of Zn was leached out. The accumulation of Zn in the STL column was very high (5250 mg kg^{-1}) compared to the input (0.56 mg kg^{-1}), estimated on the basis of the detection limit (0.02 mg l^{-1}) in the leachate measurements.

3.4. Retention of elements in bottom ash

Ca, P, S, Zn, and As were better retained in the columns fed with treated leachates (TL, STL) than in those fed with the corresponding untreated leachates (L, LE), when the total concentrations were compared at the beginning and end of the study (Fig. 3). In addition, Ca, S, Pb, Zn, and Cr were better retained in the column fed with sulphide-rich treated leachate (STL) than in the control column (C) fed with ion-exchanged water.

Ca was best retained in the STL column in which the reduction in the total concentration was 10% compared to that in the fresh bottom ash. In the control column 19% of Ca leached out, which was more than in the TL column (16%). In the columns fed with untreated leachates leaching was higher (22–42%) than in control column. P was retained best in the TL column, in which it was on same level as in the fresh bottom ash. Also in the control column only 5% leached out, while in the other columns 33–44% leached out. Pb was best retained in the LE column where the decrease was 38%. In the control column 59% of Pb leached out and in other columns 45–67%.

Treatment with sulphide-rich leachate did not affect total concentration of As, Mo and Cr compared to those in the control column (Fig. 3). As was on the same level
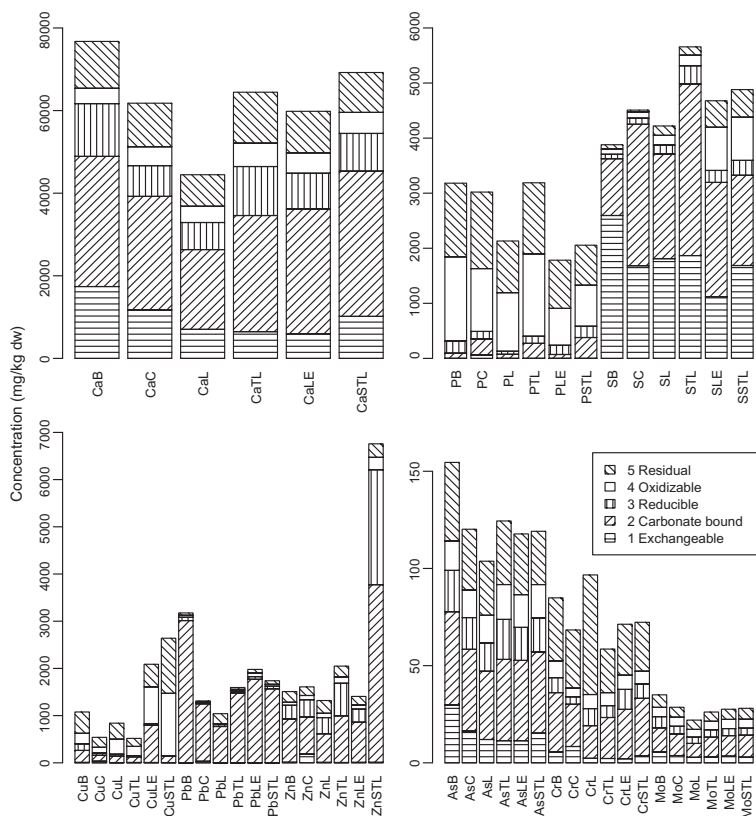
Fig. 3. Results of sequential extraction. At the beginning of the run (B) extraction was performed from the fresh bottom ash. At the end of the run extraction was performed from ashes treated with: ion-exchanged water (C), leachate (L), anaerobically treated leachate (TL), leachate with ethanol addition (LE) and with sulphide containing anaerobically treated leachate (STL).

in the control column (22% leached out) and in the STL, TL, and LE columns (19–24%) compared to fresh ash, whereas in the L column decrease was 33%. In the control column 18% Mo leached out, in the STL column 20%, in the LE column 21%, in the TL column 25% and in the L column 37%. Cr increased by 14% in the L the column compared to fresh ash. In the other columns 15–31% of Cr leached out.

3.5. Changes in element binding

The sequential extraction of the bottom ash at the beginning and at the end of the study showed changes in the binding of the elements. Increases were most often detected in the organic material and sulphide containing fraction (4) and carbonate-bound fraction (2). The highest changes

were observed in the binding of S, Cu, and Zn in the STL column.

The concentration of Ca was increased in the sulphide fraction (4) and decreased in the ion-exchanged fraction (1) of all columns. The concentration of Ca increased in all columns in sulphide fraction (5–52%). The increase was highest in the TL column (52%) and lowest in the L column (5%). In addition, there was a 9% increase in the residual fraction (5) of the TL column and a 12% increase in the carbonate fraction of the STL column. In the L column Ca leached out most from the ion-exchanged (60% decrease) and carbonate fractions (39% decrease). The decreases in ion-exchanged fraction were on the same level as in the LE and TL columns. The concentration of P increased in three fractions in the control column: in the ion-exchanged (520%), in the carbonate fraction (205%), and in the residual fraction (4%). There was a substantial

increase of P in the carbonate fraction in both the TL column (187%) and STL column (297%).

The concentrations of S increased in all the fractions of all the columns during the study, except in the exchangeable fraction and, in the control column, in residual fraction. The highest relative increase compared to fresh ash (730% both) was in the sulphide fraction in the LE, and STL columns. The second highest relative increase was in the residual fraction of the LE and STL columns. However, the highest absolute increases were in the carbonate fraction of the TL (2090 mg kg^{-1}), the C (1540 mg kg^{-1}), and the LE columns (1050 mg kg^{-1}). The absolute increases were high also in the sulphide fraction of the LE and STL columns (both 690 mg kg^{-1}).

Cu accumulated in two columns with the highest increase in sulphide fraction. In the LE column increase was 250% and in STL column 590%. In addition, Cu increased by 212% in the carbonate fraction of the LE column and 158% in the residual fraction of the STL column.

Pb was mainly bound in the carbonate fraction in all columns (74–93%). Concentrations of Pb increased in residual fraction of the L column (340%), LE column (55%), and STL column (55%). In the LE column Pb increased by 82% in sulphide fraction.

The concentration of Zn increased in all columns in sulphide fraction (38–313%). The highest increase of Zn (740%) was found in the Fe and Mn oxides bound fraction (3) in the STL column. In the same column relative increases in the carbonate and sulphide fractions were also high: 310% and 313%, respectively. In the control column there was high increase in ion-exchanged fraction (1500%).

The concentration of As increased in sulphide fraction of the TL column (19%), LE column (11%), and STL column (14%). In the L column As leached more in the carbonate fraction (27%) than in the other columns (12–14%). Most obvious difference between As and Mo was higher relative binding of As to residual fraction. Cr behaved similarly except in L-column where it was accumulated in residual fraction.

4. Discussion

The total concentrations of six elements in the present study were in the same range as those presented in the literature for fresh bottom ash (mg kg^{-1}(dw)): Ca (51 000–10 100), P (2990–4100), S (1800–5750), Cu (600–9700), Zn (197–5620), and Mo (31–33) (Meima and Comans, 1997; Crannell et al., 2000; Kim et al., 2003; Song et al., 2004; Zhang et al., 2004). The present concentrations of Pb (3180) and As (159) were higher than previously determined (Pb 888–1908 and As 26) and the concentration of Cr (85) was low compared to the values found in the literature (208–1335). The differences between studies may be the result of variation in the quality of the incinerated material, incineration techniques, sample pre-treatment, extraction methods and analytical techniques.

The present results show that improved retention and accumulation of the elements in bottom ash were the consequence of changes in their chemical binding. Sulphide-rich effluent improved the retention of Ca, S, Cu, Zn, and Pb compared to the control column, and the highest increases were observed in the organic carbon and sulphide (4) and carbonate-bound (2) fractions. These facts indicate that the observed stabilisation was due to the formation of sulphide compounds and/or direct and indirect effects of organic material. Direct effect of the addition of organic carbon would be increased binding of elements to organic material and an indirect effect increased binding to carbonates due to CO_2 originating from degradation.

Improved retention of Ca in the column fed with sulphide-rich effluent (STL) compared to the control column was the result of an increased concentration of Ca in the sulphide (4) and carbonate (2) fractions. The increase in the carbonate fraction (2) in the STL column was the consequence of precipitation of Ca. In the natural weathering of bottom ash carbonation i.e. reaction of Ca and CO_2 to form calcite ($CaCO_3$), is an important process (Meima et al., 2002). The CO_2 required for the reaction can originate from the atmosphere or from the degradation of organic material (Belevi et al., 1992; Rendek et al., 2006). In this study bottom ash was kept in anaerobic conditions and carbonation was the result of CO_2 originating from the degradation of organic carbon in the ash or added ethanol. Considering the rapid pH drop in all the leachate fed columns and the fact that COD decreased in all the columns, some microbial activity might have caused rapid carbonation of the bottom ash both when the treated and untreated leachates were used.

The changes in the binding of P were similar to those of Ca. The increase of P in the carbonate fraction (2) was highest in the STL column. However, the concentration of P bound to the carbonate fraction was low, and hence it had little effect on the final amount of P in the different treatments.

Up to 10% of the estimated input of S was accumulated and its binding changed, as expected, towards low solubility compounds (fractions 4 and 5). The increase of S in fraction 4 (LE and STL columns) indicated the reduction of sulphate to sulphide or an increased binding to organic carbon. The COD measurements of the column feeds and effluents suggest that COD was retained partly in the STL column. However, both the input and retained amount of COD were lower in the sulphide fed column (STL) than in the corresponding non-sulphide fed column (LE), while the increase in the organic carbon and sulphide fraction (4) was the same in the both columns, indicating that the increase in the STL column was at least partly due to an increase in sulphides.

Cu was mainly accumulated in the sulphide (4) and residual (5) fractions in the STL column. The increase in fraction 4 was higher in the STL column than in LE, indicating that it was at least partly the result of sulphide formation. The increase in the LE column can also be due to

complexation of Cu with organic carbon (Meima et al., 1999). In the LE column Cu was increased in fraction 4 and to same extent in the carbonate-bound fraction (2). An increase in the carbonate-fraction can indicate the formation of minerals like malachite ($Cu_2(OH)_2CO_3$) (Meima et al., 2002).

Pb is known to be controlled by carbonate precipitation (Johnson et al., 1996) and also in this study it was mainly bound to the carbonate fraction. The concentration of carbonate-bound Pb decreased in all columns compared to fresh bottom ash. Zn accumulated mainly in the carbonate and in the Fe and Mn oxides fractions in the STL column. The accumulation of Zn was high compared to the concentration in leachate, which was under the detection limit. As, Mo, and Cr were not better retained when sulphide-rich effluent was used. The differences between columns were mainly consequence of changes in the carbonate-bound fraction (2).

The inputs of the elements in the columns were estimated on the basis of their leachate concentrations. Concentrations were determined from the leachates after centrifugation; therefore elements ad/bsorbed to particles were not taken into account. However, particles were not removed from the leachate before feeding to the stabilisation columns. It is known that significant amount of metals in MSW landfill leachate can be absorbed to particulate material (Baun and Christensen, 2004). In future studies it would be advisable also to digest liquid samples to obtain accurate measurement of total element concentrations in leachates.

The changes in binding show that it is possible not only to enhance naturally occurring mineral changes, but to affect end-products so as to favour low solubility compounds such as sulphides. The elements stabilised as metal sulphides are not likely to leach out even in conditions with extremely low pH values. In the sulphur cycle, metal sulphides are long-term natural sulphur storage (Lens and Kuenen, 2001). In sequential extraction, an extreme condition such as pH 2 has to be used to dissolve elements bound to sulphides.

Besides binding to sulphides some of the observed improvement in element retention was due to increased binding to carbonates and Fe and Mn oxides. The stabilisation columns were flushed with ion-exchanged water for 21 days at the end of the experiment to ensure that the changes observed were of a permanent nature. In addition, the pH of the leachate from the stabilisation columns reached the equilibrium level. Meima and Comans (1997) showed that long-term leaching of elements is determined by the pH of the bottom ash, which in turn is the result of mineral composition and is about 8.3 in equilibrium. The present results show that the overall changes in binding were such that most of the elements studied were better retained or even accumulated in the bottom ash in equilibrium pH.

Leachate treatment and stabilisation of MSWI bottom ash with sulphide-rich anaerobic effluent could reduce emission from landfills and, if applied to treatment/storage sites, it could also reduce emissions from them and from utilisation sites. Furthermore, sulphide from treated leachate was removed, diminishing the need to use other post-treatments. However, more knowledge about chemical changes is needed from larger scale experiments before practical solutions can be designed.

5. Conclusions

Sulphide-rich effluent was able to improve retention of Ca, Cu, Pb, S, and Zn compared to the control column in MSWI bottom ash. Treatment had no effect on As, Cr, and Mo and leaching of P was enhanced. Sequential extraction showed that observed stabilisation of the elements in bottom ash was due to increased binding to the sulphide and organic material fraction and to the carbonate fraction. Flushing of the stabilised ash with ion-exchanged water confirmed that the changes observed in the binding of the elements were lasting and were not easily reversible. The method described in this study can be used to stabilise bottom ash in storage sites before utilisation or in landfills to enhance carbonation and to increase the amount of low solubility metal sulphides. In addition, the method was able to remove most of the sulphide from anaerobic effluent.

Acknowledgements

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