Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Effect of accelerated carbonation and zero valent iron on metal leaching from bottom ash

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ABSTRACT

About 85% of the ashes produced in Sweden originated from the incineration of municipal solid waste and biofuel. The rest comes from the thermal treatment of recycled wood, peat, charcoal and others. About 68% of all ashes annually produced in Sweden are used for constructions on landfills, mainly slopes, roads and embankments, and only 3% for construction of roads and working surfaces outside the landfills (SCB, 2013). Since waste bottom ash (BA) often has similar properties to crushed bedrock or gravel, it could be used for road constructions to a larger extent. However, the leaching of e.g. Cr, Cu, Mo, Pb and Zn can cause a threat to the surrounding environment if the material is used as it is. Carbonation is a commonly used pre-treatment method, yet it is not always sufficient.

As leaching from aged ash is often controlled by adsorption to iron oxides, increasing the number of Fe oxide sorption sites can be a way to control the leaching of several critical elements. The importance of iron oxides as sorption sites for metals is known from both mineralogical studies of bottom ash and from the remediation of contaminated soil, where iron is used as an amendment.

In this study, zero valent iron (Fe(0)) was added prior to accelerated carbonation in order to increase the number of adsorption sites for metals and thereby reduce leaching. Batch, column and pH_{stat} leaching tests were performed and the leaching behaviour was evaluated with multivariate data analysis. It showed that leaching changed distinctly after the tested treatments, in particular after the combined treatment.

Especially, the leaching of Cr and Cu clearly decreased as a result of accelerated carbonation. The combination of accelerated carbonation with Fe(0) addition reduced the leaching of Cr and Cu even further and reduced also the leaching of Mo, Zn, Pb and Cd compared to untreated BA. Compared with only accelerated carbonation, the Fe(0) addition significantly reduced the leaching of Cr, Cu and Mo. The effects of Fe(0) addition can be related to binding of the studied elements to newly formed iron oxides. The effects of Fe(0) addition were often more distinct at pH values between 7 and 9, which indicates that a single treatment with only Fe addition would be less effective and a combined treatment is recommended. The pH_{stat} results showed that accelerated carbonation in combination with $Fe(0)^0$ addition widens the pH range for low solubility of about one unit for several of the studied elements. This indicates that pre-treating the bottom ash with a combination of accelerated carbonation and Fe(0) addition makes the leaching properties of the ash less sensitive to pH changes that may occur during reuse. All in all, the addition of Fe^0 in combination with carbonation could be an effective pre-treatment method for decreasing the mobility of potentially harmful components in bottom ash.

1. Introduction

Each year about 1 million tons of bottom ashes are produced in Sweden as a result of waste incineration. Bottom ash (BA) has similar properties to virgin ballast material like crushed bedrock and gravel and can therefore replace some of the 40 million tons of virgin material used for road constructions each year. However using wastes such as ash must not harm the environment and must not exceed the guidance levels for emissions from waste that is used as construction material set up by the Swedish EPA (SNV, 2010). Today, the most common areas of application for bottom ash in Sweden are in landfill constructions such as slopes, roads and embankments, since for this type of application the emission limits are less strict than for uses outside of landfills.

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Nevertheless, pre-treatment prior to use on the landfill is anyhow needed in most cases as ashes from waste incineration contain considerable amounts of soluble salts and partly soluble constituents, such as metals. A common method is carbonation that will reduce the pH and thereby decrease the leaching of elements like Cd, Pb, Cu, Zn and Mo (Meima and Comans, 1999). This treatment is, however, not always sufficient and alternative methods are needed. One possibility is to increase the number of adsorption sites for trace elements. The importance of iron oxides as sorption sites for metals is known from both mineralogical studies of bottom ash (Saffarzadeh et al., 2011; Cornelis et al., 2008; Cornell and Schwertmann, 2003) as well as from remediation of contaminated soil, where iron is used as an amendment in order to immobilize metals (Kumpiene et al., 2008).

Fettihydrite is the first iron oxide phase formed during iron oxidation. Ferrihydrite is poorly crystalline and therefore has more sorption sites than more crystalline iron oxides. However, it is thermodynamically unstable, and will transform into other more crystalline iron oxides, most commonly goethite and hematite. A more crystalline iron oxide will have less sorption sites, and can thus retain less metal. However, the rate of transformation can be reduced if foreign species, like metals, are retained within the structure (Cornell and Schwertmann, 2003). Formation of iron oxides in an environment that contains metal ions would possibly enhance the chance of metals to be sorbed to ferrihydrite and thereby decreasing the chance of transformation. Iron oxides can bind ions like Cu, Cr(III) and Zn (Sabbas et al. 2003), oxyanions like Mo and Cr as well as fulvic acids that in turn can bind e.g. Cu (Dijkstra et al., 2006).

A local waste-to-energy plant in Northern Sweden incinerates waste and the BA can possibly be used as construction material. A previous study (Oja, 2012), showed that a number of trace elements (Cr, Cu, Mo, Pb and Zn) exceeded the guideline values of the Swedish EPA for the use of waste as construction material (SNV, 2010), even though the BA had been stored outdoors for more than six months. Additional treatment is therefore necessary before the BA can be used as construction material.

The aim of this study was to reduce the leaching of Cr, Cu, Mo, Pb and Zn by pre-treating the bottom ash using two different methods: accelerated carbonation in a 30 °C humid CO_2 atmosphere and equal accelerated carbonation but with the addition of zero valent iron (Fe(0)), a by-product from the steel industry, in order to increase the number of sorption sites.

The objectives of the study were to investigate (1) how pre-treatment including accelerated aging and accelerated aging with addition of Fe(0) affects the leaching of Cr, Cu, Mo, Pb and Zn and (2) which processes are behind these effects.

2. Material and methods

2.1. Material

BA from a combined heat and power plant in the municipality of Boden in Northern Sweden was tested. The ash was derived from two fired grate stoker boilers burning a mixture of municipal, industrial and wood waste. The ash is collected in one big heap during a whole year and once per year, typically in July and August, the material is treated in a mobile metal separation plant. During this process, the material is also classified into three grain size fractions: 0–10 mm, 10–50 mm and >50 mm. The samples were taken from the 0–10 mm fraction resulting from the metal separation treatment. At the time of sampling the ash in that heap was between 1 and 10 months old. In order to take a representative samples of the whole heap subjected to the separation treatment,

one sample was taken each day during the metal separation process (that had a duration of 32 days).

In a pre-study Nilsson et al. (2013) screened the samples for systematic inhomogeneity with regard to TDS, LOI, electrical conductivity and pH and came to the conclusion that the heterogeneity of the material was evenly distributed. The 32 samples were therefore combined before being employed for the tests described in this paper.

2.2. Pre-treatment

The 32 samples were homogenized using a rotary splitter. After homogenization sub-samples of the BA were pre-treated with accelerated carbonation (BA_A) and accelerated carbonation with addition of 2% zero valent iron (BA_AFe). 15 kg of the 0–10 mm fraction were pre-treated. Non-treated bottom ash (BA) was used as control (note: the ash had been stored outside for 1–10 months prior to sampling, *i.e.* it cannot be considered as "fresh" BA). For accelerated carbonation (with/without Fe(0)) the ash was moistened and placed in a CO_2-filled barrel at 30 °C for two weeks. CO_2 was refilled and the ash was agitated by occasionally rolling the barrel.

The Fe(0) used in this experiment is a by-product from a steel factory in Sweden called SSAB Merox, where it is used as a blasting material. The Fe(0) powder presented the following particle size distribution: 2.5% $d \geqslant 1$ mm; 20.5% $0.5 \leqslant d < 1$ mm; 68% $0.25 \leqslant d < 0.5$ mm and 9% $d < 0.25$ mm. The chemical composition was determined by a laboratory specialised in ore and metal analyses (Nilab AB): 96.50% Fe_{tot}, 0.91% Mn, 0.81% C, 0.76% Si, 0.24% Cr, 0.11% Ni, 0.04 Mo and 0.02% S.

2.3. Chemical composition

Samples of 1.5 kg from fractions of BA, BA_A and BA_AFe were dried at 50 °C for 7 days, comminuted in a jaw crusher to <3 mm and subdivided into samples of 30 g each before milling (disc mill). The total content was analysed in triplicates at ALS Scandinavia AB using ICP–AES (Inductively Coupled Plasma – Atom Emission Spectroscopy) and ICP–SFMS (– Sector Field Mass Spectroscopy). The carbon content was analysed with a TOC analyser (Shimadzu, TOC-V CSH).

2.4. Leaching behaviour

The leaching of bottom ash was evaluated with (1) column tests, CEN/TS 14405, (SIS, 2004), (2) batch test, SS EN 12457-2, (SIS, 2003) and (3) pH-stat test, CEN/TS 14497, (SIS, 2007). The tests all reach a liquid to solid ratio (L/S) of 10, but differ with regard to a number of factors, see Table 1. The pH_{stat} tests were performed at pH 2, 4, 7, 8, 9 and 10 and also with only water in order to uncover possible impacts of the test conditions in comparison to the standard batch test.

Table 1
Characteristics of the leaching tests used.

	Column test[a]	Batch test	pH_{stat} test
Duration	About 30 days	24 h	48 h
L/S ratio	0.1, 0.2, 0.5, 1, 2, 5, 10	10	10
Particle size	<10 mm	Sieved < 4 mm	Crushed < 1 mm
Sample mass (DM)	2.7 kg	90 g	15 g
Separation leachate – solids	0.45 μm filter	0.45 μm filter	0.45 μm filter
pH adjustment	None	None	HNO_3

[a] Up-flow column tests in 40 cm long columns with a diameter of 10 cm. Flow rate: 12 cm/day.

2.4.1. Leachate analyses

Column and batch test leachates were analysed with regard to pH, electrical conductivity (EC) and redox potential (Eh) as well as elemental concentrations (ICP–AES and ICP–SFMS), Cl^- and SO_4^{2-} concentrations (QuATTro Bran + LUEBBE), ANC (only column test; L/S 2, 5 and 10; SS-EN ISO 9963-1 (SIS, 1996) using an automatic TitroWico titration unit) and dissolved organic matter (DOC) using a TOC analyser (Shimadzu, TOC-V CSH). The leachates from the pH$_{stat}$ tests were only analysed with regard to pH, EC, Eh and elemental concentrations.

2.4.2. Comparison to limit and guideline values

In order to assess the suitability of using the ash as construction material, the results were compared with Swedish guideline levels for reuse of waste as construction material (WCM) above a landfill cover liner (SNV, 2010; values for total content and leaching), and with the leaching criteria for waste acceptance (WAC) at landfills for inert waste (EC, 2003). Meeting these criteria indicates that water coming into contact with the ash does not need to be treated but can be released to the environment.

2.5. Statistical evaluation

The leaching data were evaluated with multivariate data analysis (MVDA) using the program Simca (Umetrics AB, 2013). Using MVDA, large amounts of data can be evaluated taking into account the influence of all variables at the same time. Information from complex data sets can be extracted and visualised. Dominant patterns and latent structures within the data matrix can be uncovered. In the present study principal component analyses (PCA) were performed to evaluate the effect of the two pre-treatment methods on the leaching of BA and to compare the results from three different leaching tests. PCA is used to find a transformation that contracts a given set of correlated variables to a new set of uncorrelated variables (called principal components, PC), which represent the main variation in the data. PCA can also be seen as an attempt to reveal approximate linear dependencies among variables. The results are displayed in plots that illustrate variables, observations, correlations and importance. For each model two plots are presented that are to be interpreted together: The score plot and the loading plot. The numbers on the axes are coordinates of data points on the respective PC. The score plot is a map of the observations and displays how they are situated with respect to each other, based on the variables in the loading plot. It shows possible outliers, groups, similarities and other patterns in the data. Outliers are located outside the confidence ellipse based on Hotelling's T2 with 5% significance level. The loading plot projects the correlation structure of the analysed variables. Observations located in a certain part of the score plot (e g upper left) are often correlated to variables located in the corresponding part of the loading plot. A large distance from the origin represents a strong influence of a variable. Variables close to each other are positively correlated and variables opposite to each other, *i.e.* on opposite sides of the origin, are negatively correlated (Eriksson et al., 2013; Jackson, 1991).

3. Results and discussion

3.1. Composition of the ash

The content of major and minor elements in the ash before and after treatment is shown in Fig. 1. The element concentrations vary for the different treatments but stay within the standard deviations for almost all treatments and can, hence, be related to sample heterogenities. Only Mo was significantly higher after accelerated carbonation combined with Fe(0) addition but no explanation for this could be found. The content of Fe was not significanlty higher after Fe(0) addition. As expected, the accelerated carbonation treatment, both with and without Fe(0), caused an increase of the inorganic carbon (IC) content of the slag (see Table 2) The difference in IC seen between BA_A and BA_AFe cannot be explained, however the total alkalinity of the material was similar (Table 2). Cu content is high compared to literature values for MSWI bottom ashes but also compared to earlier analyses of BA from the same plant (Oja, 2012). Compared to Swedish guidelines for the use as construction material on landfills above the cover liner (SNV, 2010), the average concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn exceed the target values 4, 3, 8, 150, 3, 5 and 20 times, respectively. For environmental risk assessments, however, the mobility under the expected conditions of the reuse scenario, and not the total content, is the crucial factor and will be discussed further down.

3.2. Leaching behaviour

3.2.1. General leaching trends

The effects of the two treatments and the overall leaching trends can be seen in Figs. 2 and 3. Fig. 2 illustrates the results from the column tests in form of a PCA based on the composition of the leachates at seven different L/S ratios (concentrations per dry mass of ash). Explaining 83% of the total data variance, two distinct patterns become visible in the score plot: the difference between the treated and untreated ashes and the shifting of concentrations due to the progress of leaching in the column test. The distant location of the dots for the treated ashes from the ones for the untreated BA illustrate that the column leaching behaviour of the treated ashes clearly differs from that of the untreated BA, which is in accordance with other carbonation studies. The distance is biggest for BA_AFe, showing that the effect of the combined treatment was bigger than the effect of only accelerated carbonation.

The elongated distribution of the dots of each group from lower left to upper right is caused by decreasing electric conductivity (EC), chloride and ANC due to the washing out at lower L/S ratios.

The position of the untreated BA in the lower part to the right is correlated to – compared to the treated ashes – higher levels of leachate constituents at corresponding positions in the loading plot, e.g. pH, Cr, Cu, Cd, Al, DOC and lower levels of constituents located in the upper left part of the loading plot, e.g. Ca, Mg, Mn, Zn and Eh.

Leaching from the BA treated with accelerated carbonation was characterized by an opposite pattern for the above named constituents (clearest at higher L/S ratios) including higher sulphate leaching and increased ANC compared to the untreated BA. SO_4^{2-} leaching increased during treatment; from 0.4 to 1.7 times the recommended maximum level.

The increased solubility of sulphates can be related to the destabilization and dissolution of sulphate bearing phases such as ettringite and anhydrite, caused by carbonation and the connected pH decrease. E.g., ettringite dissolves at pH below 10. According to the results from the column test, washing bottom ash in order to reduce sulphate leaching below guideline values would require a liquid to solid ratio of 2.

A PCA model of the results from all leaching tests is shown in Fig. 3. Chloride and sulphate were excluded due to insufficient number of analyses. The model is based on concentrations at L/S 10 in mg/kg (cumulative in column tests apart from pH, EC and Eh for which the average of all column fractions was used). It explains 85% of the data variation.

The treated and untreated ashes can be clearly distinguished also in this model. The positioning of the BA_AFe samples is again further away from the BA samples than the BA_A due to lower concentrations of most of the elements located on the left side.
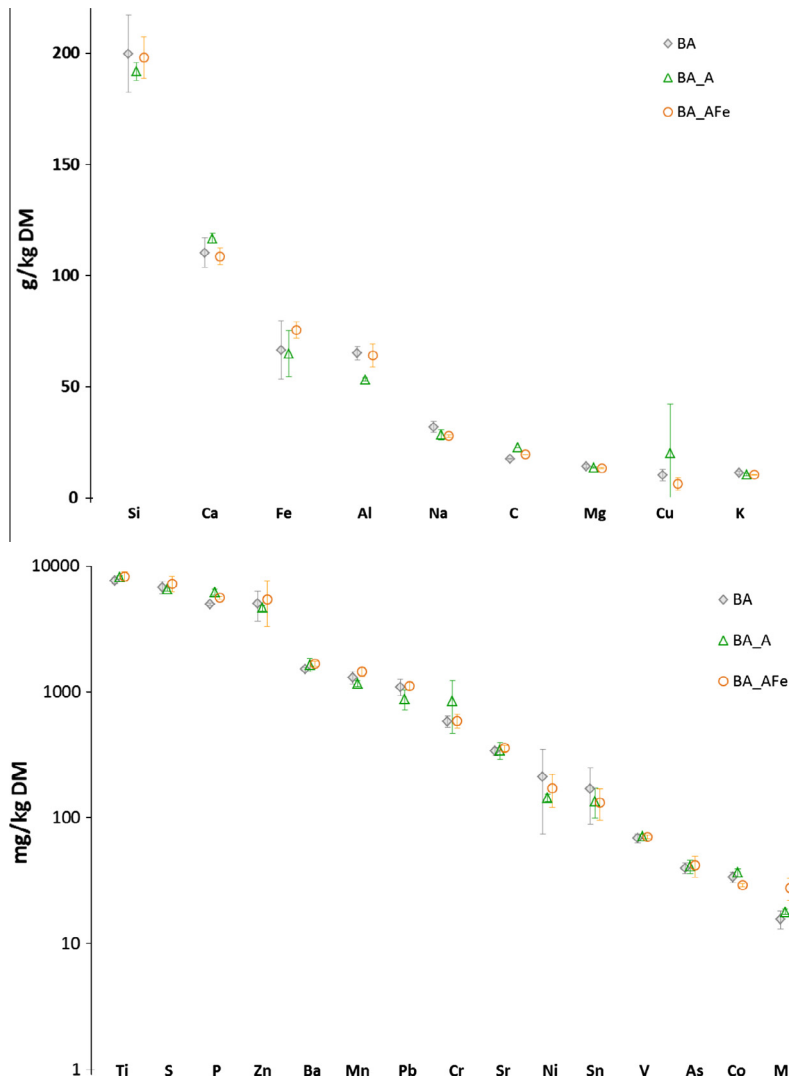
Fig. 1. Elemental composition of the bottom ash before and after treatment. Upper chart > 10 g/kg and lower chart < 10 g/kg.

Table 2
TOC, TIC and total alkalinity of the tested bottom ashes.

	TOC (g/kg DS)	stdev	TIC (g/kg DS)	stdev	Total alkalinity (mmol/g)	stdev
BA	10.98	1.26	6.66	1.32	1.67	0.18
BA_A	10.90	0.42	11.83	0.50	2.09	0.21
BA_AFe	10.72	0.15	8.81	0.14	2.10	0.22

However, the largest variation is caused by the different pH conditions (1st PC, horizontal, explains 71% of the data variation). High concentrations of most elements at pH 2 are the main reason for the location of these elements in the left part of the loading plot. Since also the redox potential was highest at pH 2, Eh is located at the left side together with the majority of elements.

The different types of tests gave similar results when the pH level was similar as can be seen from the nearby location of $pH_{st\_8}|BT\_8.2|CT\_8.1$ for BA_A and $pH_{st\_8}|BT\_7.9|CT\_7.9$ for BA_AFe. The leachate composition differs more for untreated BA, mainly due to different pH ($pH_{st\_10}|pH_{wa\_10.4}|BT\_11.6|CT\_11.8$). pH_{stat} tests were not performed at pH 11.

The variation in vertical direction (2nd PC, only 13% of the data variation) describes mainly the behaviour of the column and batch

test results from the untreated BA (CT_11.6 and BT_11.8). These leachates had highest pH and lowest Eh, low concentrations of Ca, Co, Mg, Mn, Zn and high concentrations of Al, Cr, Cu, K, V. Also, the negative correlation between Eh and pH ($R^2 = 0.7$) is reflected as well as weaker negative correlations (0.3–0.4) between Eh and As, Hg, K, Mo, V for the tests with pH above 2.

3.2.2. pH dependent leaching of critical elements
The effects of accelerated carbonation and Fe(0) addition on the leaching properties at different pH and test conditions are illustrated in Fig. 4. The total content of the respective element in the untreated BA as well as relevant guideline and limit values are included in each chart. Out of the elements exceeding the guideline values for total content, only Cr, Cu and Zn leached at levels that would compromise reuse of the ash in foreseen applications; Cr and Cu before treatment and Zn after treatment. Mo is not included in the guideline values, but based on its high mobility at typical bottom ash pH ranges and the observed effect of the Fe(0) treatment, it is included in the discussion. Despite high total contents, the leaching of Pb, As, Cd and Ni was low. They are included in Fig. 4 but the focus of the discussion below is on the leaching of Cu, Cr, Mo and Zn.
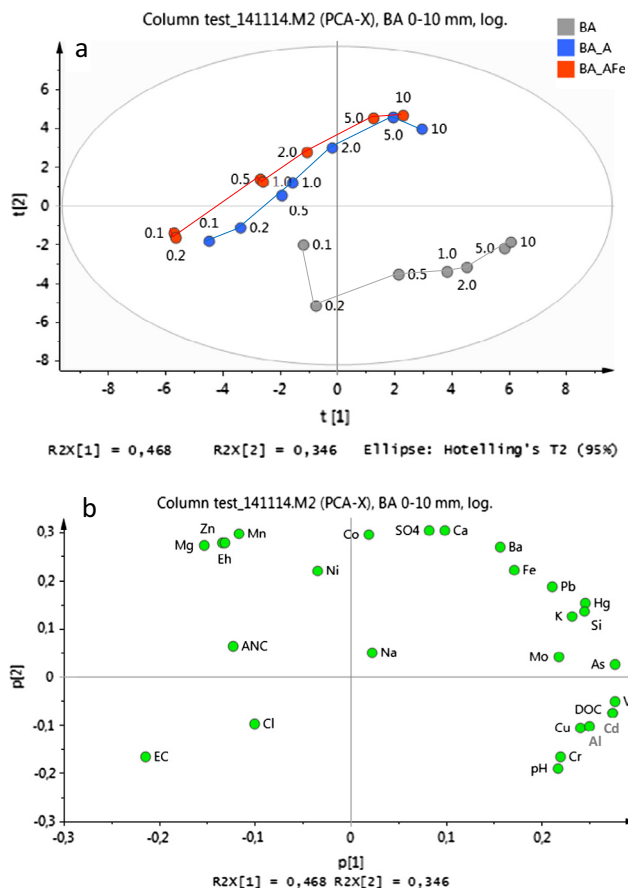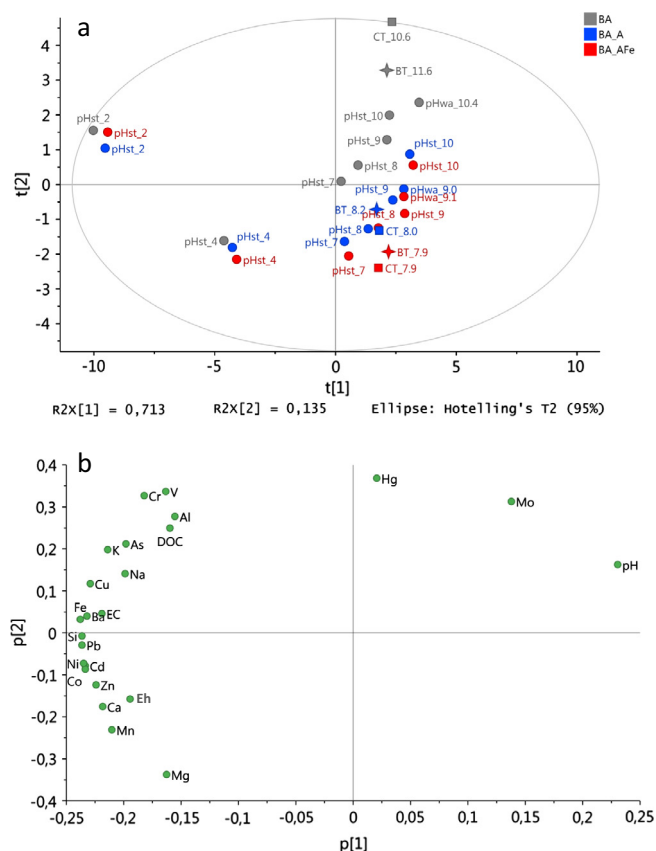
Fig. 2. PCA score plot (a) and loading plot (b) for the results from column test: concentrations at each L/S ratio in mg/kg. The samples are marked with the cumulative L/S-ratio (0.1, 0.2, 0.5, 1, 2, 5 and 10) and coloured according to treatment (BA, BA_A, BA_AFe).

Fig. 3. PCA score plot (a) and loading plot (b) for the results from all leaching tests: concentrations at L/S 10 in mg/kg (cumulative for column tests). The samples are marked according to the test method ($\bigcirc$ pH$_{stat}$, $\square$ column, $\bigstar$ batch test), and coloured according to the treatment (BA, BA_A, BA_AFe). The numbers are the pH at the end of the test; apart from the column tests where it is the non-weighted average of all seven fractions. pH$_{wa}$ stands for pH$_{stat}$ test at the materials' own pH.

A less distinct effect of accelerated aging with Fe(0) addition for pH-stat can be seen for several elements compared with results from column or batch. The BA used for the pHstat test was crushed after the pre-treatment opening up new surfaces that were not exposed to Fe(0). This possibly lead to a reduced effect of the treatment.

3.2.2.1. Leaching of Cr.

Fig. 4a shows the effect of accelerated carbonation and Fe(0) addition on Cr leaching. From pH > 4 the pre-treated ashes leached in all tests considerably less than the untreated BA.

Accelerated carbonation has proven to be an efficient method for reducing Cr leaching (e.g. Ecke, 2001; van Gerven et al., 2005). Carbonation will lead to formation of new adsorption sites where Cr(III) and Cr(VI) can bind (Cornelis et al., 2008). The carbonation process is the main reason for the reduced leaching of Cr.

The added iron lowered the leaching even further; the difference between BA_A and BA_AFe was statistically significant in all tests within the pH range from 7 to 9. A reason for this can be that Fe(0) in the process of oxidation donates electrons, mainly to H_2O or OH^-, but also to Cr(IV), thereby reducing Cr(VI) to Cr(III). The oxidized Fe i.e. Fe^{3+} can then possibly form iron oxides that can bind additional Cr. Adsorption to iron oxides has been reported both for Cr(VI), at pH < 9 (Cornelis et al., 2006), and for Cr(III) (Sabbas et al., 2003; Crawford et al., 1993; Cornell and Schwertmann, 2003; Saffarzadeh et al., 2011). Iron(II)salts are commonly used to reduce Cr(VI) to Cr(III) (C.E. Barrera-Diaz et al., 2012). Reduction of Cr(VI) to Cr(III) can possibly take place

if divalent iron was formed from the added Fe(0). The long-term behaviour of the added Fe(0) has not been studied. However it is most likely that after the oxidation of the Fe(0) on the surface of the iron-grains, the iron still within the grain cannot be oxidized. This would means that the effect of Fe(0) as an electron donor and the process of iron oxides formation will decrease over time.

3.2.2.2. Leaching of Cu.

Fig. 4b shows the effect of accelerated carbonation and accelerated carbonation with addition of Fe(0) on Cu leaching. Despite high total content the leaching is moderate and decreases below the guideline level after accelerated carbonation at pH > 8. For pH values lower than 8 leaching of Cu would become critical again. However, when Fe(0) was added the leached concentration remained below the requirement for reuse until pH 7, suggesting that ash treated also with Fe(0) may present low leaching in a wider pH interval compared to untreated BA or BA submitted to only accelerated carbonation. Then leaching of Cu would become critical again. However when Fe(0) was added it widens the pH range for low leaching with one whole unit (until 7) which means that the treated ash is more robust towards pH changes during reuse. The differences seen in the pH-stat results (Fig. 4b) for BA, BA_A and BA_AFe were statistically significant within the pH range from 7 to 9.

Carbonation and adsorption to iron oxides (Meima and Comans, 1999) such as ferrihydrite and goethite (Sabbas et al., 2003) can explain the reduced leaching. Iron was available in the BA but the surface and availability was increased by the addition of Fe^0, which can account for the difference between BA_A and BA_AFe. Cu also
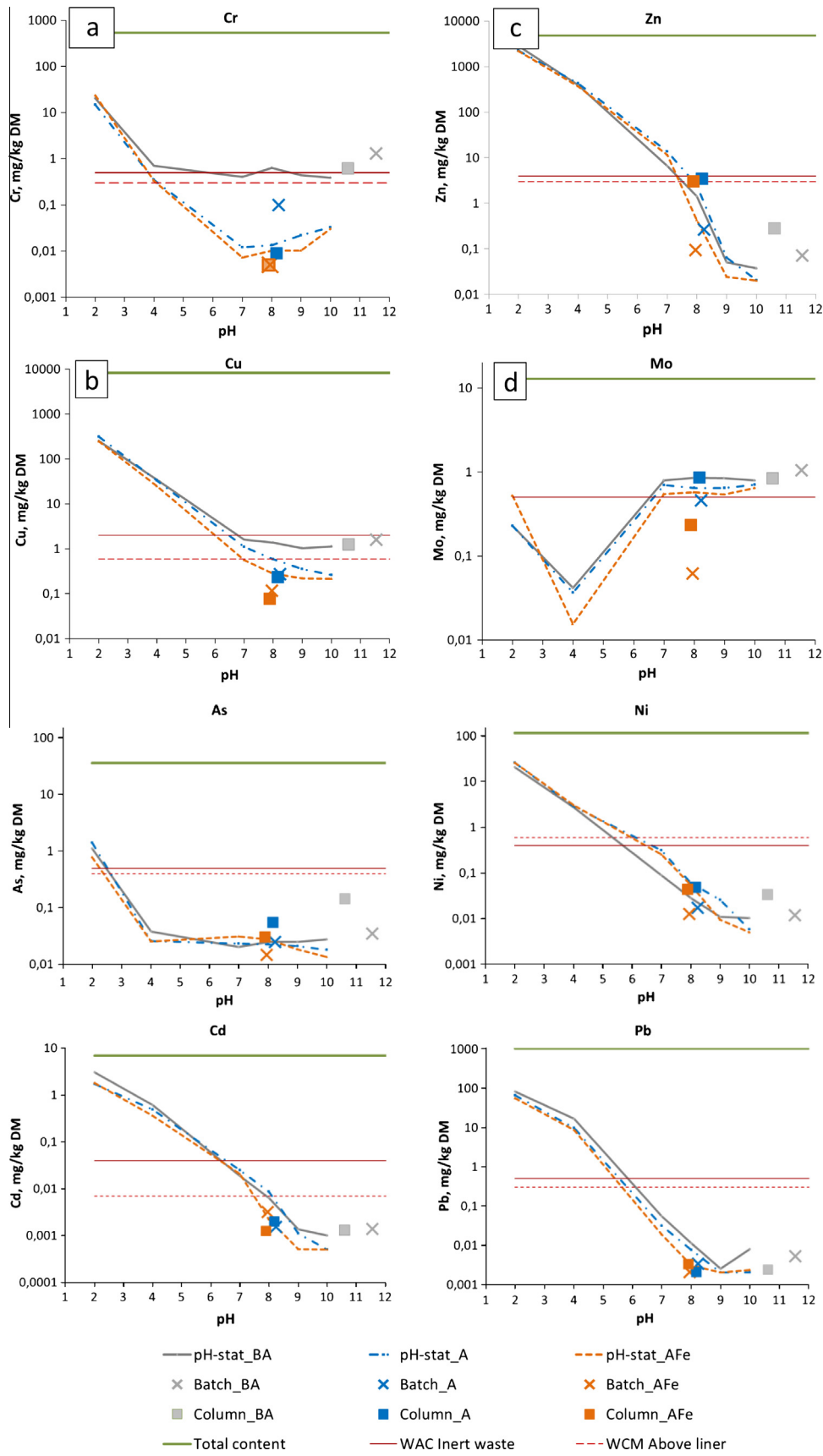
Fig. 4. Leaching of Cr, Cu, Zn, Mo, As, Ni, Cd and Pb in pH-stat, batch and column test cumulative at L/S 10 as a function of pH. Total content in untreated BA. Swedish leaching guideline levels for reuse of waste as construction material (WCM) above the cover liner and the criteria for waste acceptance (WAC) at landfills for inert waste (EC, 2003).

has a high affinity for Al-hydroxides (McBride, 1982), and a correlation between Cu and Al leaching is indicated by the nearby placing of these two elements in the loading plot for the column test leaching results (Fig. 2).

Cu is known to bind to organic matter; as much as 95–100% of the Cu can be bound to organic matter (Meima et al., 1999; Arickx et al., 2006). The DOC–Cu complexes formed can further bind to Al–minerals (Meima et al., 2002) and thereby reduce the leaching. DOC as well can be found close to Cu and Al in the loading plot (Fig. 2).

3.2.2.3. Leaching of Zn. Fig. 4c shows the effect of accelerated carbonation and Fe^0 addition on Zn leaching. As other amphoteric elements, Zn leaching increases both at low and high pH; in alkaline conditions due to the formation of anionic hydroxide complexes (Chandler et al., 1997).

Zn leaching is strongly pH-dependent (van der Sloot et al., 2001), i.e. small changes in pH affect the leaching distinctly (Chandler et al., 1997), which also can be seen from Fig. 4c. The concentrations in the different tests follow the u-shaped pH-stat curves closely but different from Cr and Cu, the u-shape is steeper and narrower. The pH-stat curve reveals why Zn leaching in the column tests increased after carbonation: the optimum pH range had been passed.

Zn has an affinity for calcite (Comans and Middelburg, 1987) and can be carbonated (Freyssinet et al., 2002). However, varying results with regard to decreased or increased leaching following carbonation are reported (Arickx et al., 2006; Costa et al., 2007). These deviating results can possibly be related to the amphoteric leaching, strong pH dependency and the different pH-values that were achieved after carbonation.

Leaching of Zn in bottom ash aged to pH 8–8.5 is controlled by sorption, whereas Zn leaching at pH > 10–10.5 is solubility controlled (Meima and Comans, 1999). The leaching is pH-dependent regardless if the bottom ash is carbonated or not. The pH dependency superimposes the effects of carbonation which can be seen by the marginal difference between the BA and the BA_A leaching at comparable pH values for pH-stat. Iron admixture, however, decreased leaching additionally and, again, widened the pH range for low leaching though to a lesser extent than for Cu (Fig. 4b). This can be explained by the affinity of Zn for iron oxides and binding to e.g. goethite and ferrihydrite (Meima and Comans, 1999; Sabbas et al., 2003).

3.2.2.4. Leaching of Mo. Fig. 4d shows the effect of accelerated carbonation and Fe^0 addition on Mo leaching. The decrease of pH due to only accelerated carbonation had little effect on the leaching but the addition of Fe^0 lowered the leaching significantly in both column and batch test. The leaching in the pH-stat tests was only marginally affected by the treatments, at least at pH > 7.

Mo, present as molybdate in bottom ash is reported to be very soluble (Kashiwabara et al., 2011; Huang et al., 2012). Leaching of it is therefore difficult to control. Powellite ($CaMoO_4$) has been reported to control Mo leaching at high pH (van Gerven et al., 2005; Meima et al., 2002) but also to be too soluble to have a noticeable effect on the leaching (Hyks et al., 2011).

Another controlling mechanism can be binding to iron oxides like goethite and ferrihydrite (Sabbas et al., 2003; Meima and Comans, 1998). The complexation is pH dependent (Gustafsson, 2003) and higher at lower pH (Meima and Comans, 1999), which also can be seen in Fig. 4d. The pH ranges reported in the literature are, however, higher than observed here; between 4 and 11 (Nilsson, 2014).

The low effect of Fe(0) addition for pH-stat compared with batch and column seen in Fig. 4d at pH > 7can be due to the size reduction of the material. The observed decrease of Mo at pH < 7 can be due to the increased affinity for the available iron oxide at lower pH.

4. Conclusions

The study shows that both accelerated carbonation and accelerated carbonation combined with Fe(0) addition reduce the leaching of elements like Cr and Cu, and that the addition of Fe(0) significantly reduced the leaching of Cr, Cu and Mo compared with just accelerated carbonation. Multivariate data analysis (PCA) showed that the overall leaching behaviour (looking at all analysed components and all three tests performed) changed distinctly due to the treatments and most for the combined treatment.

Even though common practice at many Swedish MSWI plants, the natural carbonation process in large heaps is often not sufficient to achieve leaching properties that allow a safe reuse as construction material, despite long storage times. Leaching from aged ash is often controlled by adsorption to iron and aluminium oxides, and increasing the number of Fe oxide and Al-hydroxide sorption sites can be a way to control the leaching of several critical elements. The effects of Fe(0) addition seen in this study can be related to binding of the studied elements to newly formed iron oxides The addition of Fe(0) to accelerated carbonation widens the pH range for low leaching with about one pH unit for several of the studied elements compared to the leaching from bottom ash submitted to just accelerated carbonation. This means that the bottom ash pre-treated with Fe(0) addition is more robust towards pH changes when reused as a construction material.

With the benefit of hindsight, pre-treatment with only Fe(0) addition should have been tested as well. However, the effects of Fe(0) addition in combination with accelerated carbonation, in most cases led to lowest leaching at pH values between 7 and 9, which indicates that a single treatment with only Fe addition would have been less effective and a combined treatment is recommended.

Sulphate leaching from the bottom ash exceeds the guideline values and increased due to the treatments. The leaching of sulphate thus needs to be reduced using other methods in order to reuse the bottom ash as a construction material.

All of this indicates that the addition of Fe^0 could be an effective pre-treatment method for decreasing the mobility of potentially harmful components in bottom ash.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2015.12.028.

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