



## Weathering of gasification and grate bottom ash in anaerobic conditions

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### ARTICLE INFO

#### Article history:

Received 25 March 2009

Received in revised form 28 August 2009

Accepted 11 September 2009

Available online 19 September 2009

#### Keywords:

Aeration

Anaerobic

Carbonation

Gasification ash

Weathering

### 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> from biodegradation. The results of the aeration study suggest that the role of atmospheric CO<sub>2</sub> 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 processes, in which atmospheric CO<sub>2</sub> 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 ( $20 \pm 2^\circ\text{C}$ ), were used. Two of the lysimeters were filled with  $17.45 \pm 0.15$  kg (wet weight) of gasification ash and two with  $10.35 \pm 0.15$  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 throughout 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 ( $\text{SO}_4$ ), 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 ( $N_{\text{tot}}$ ) using the Tecator application note (Perstor Analytical/Tecator AB 1995).

During the aeration period  $\text{CO}_2$  was measured from the in- and outflows of the aerobic lysimeters.  $\text{CO}_2$  was determined with a gas chromatograph (PerkinElmer Autosystem XL, Varian Select 50 m  $\times$  320  $\mu\text{m}$ , carrier gas helium, Oven  $90^\circ\text{C}$ , injection port  $90^\circ\text{C}$ , thermal conductivity detector  $160^\circ\text{C}$ ).

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).

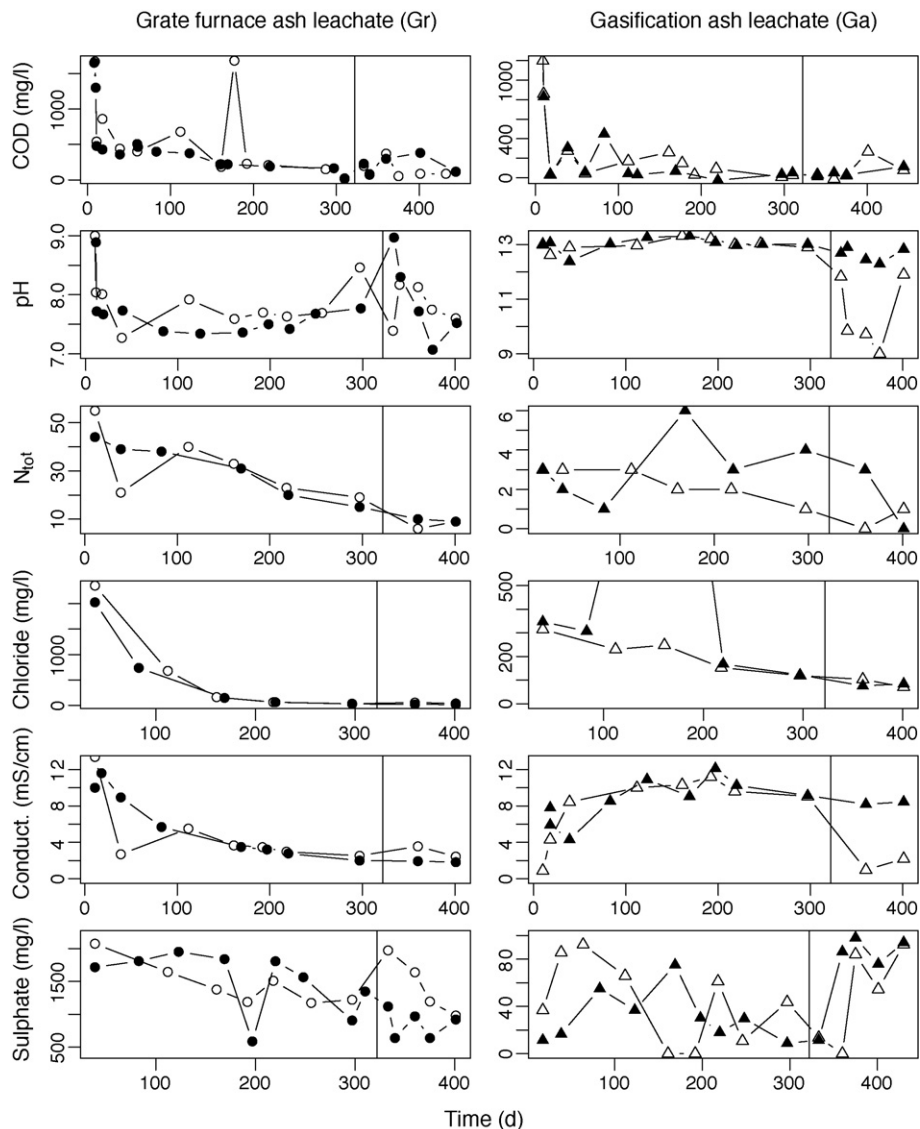
### 3.2. Effect of aeration on leachate quality

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 anaerobically 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.

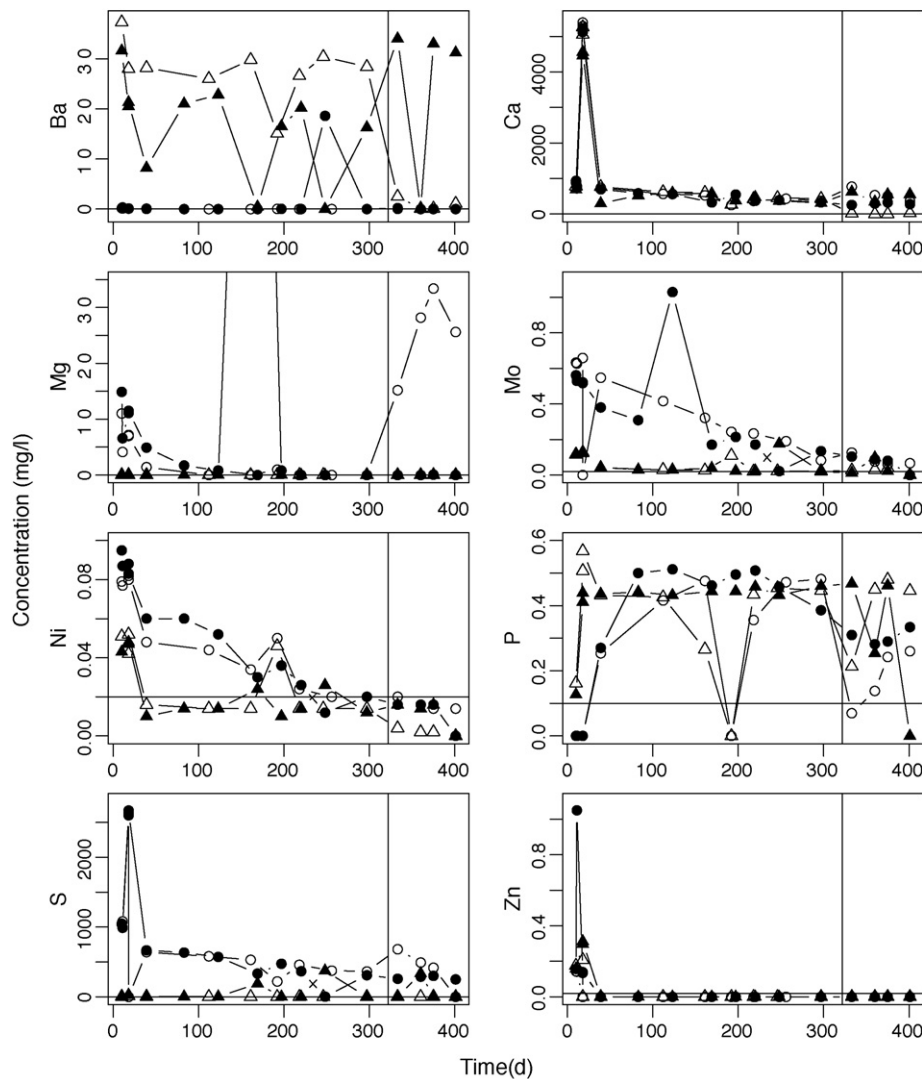
### 3.4. Effect of aeration on leaching of elements

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.

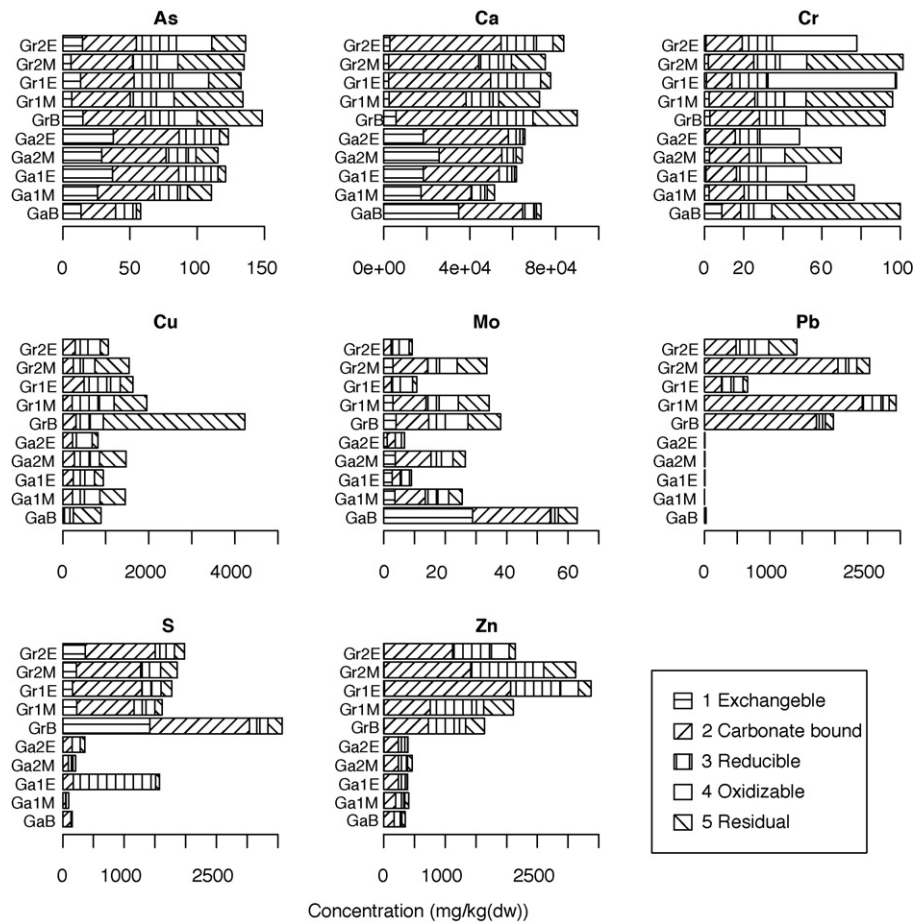
In the grate ash the concentration of As decreased by 10% compared to the initial values. The decrease was mainly in the residual fraction (5). As increased in fractions 3 and 4. The decrease in the concentration Ca was 7% and that of Cr 16%. Ca decreased in the residual (5) and exchangeable fractions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

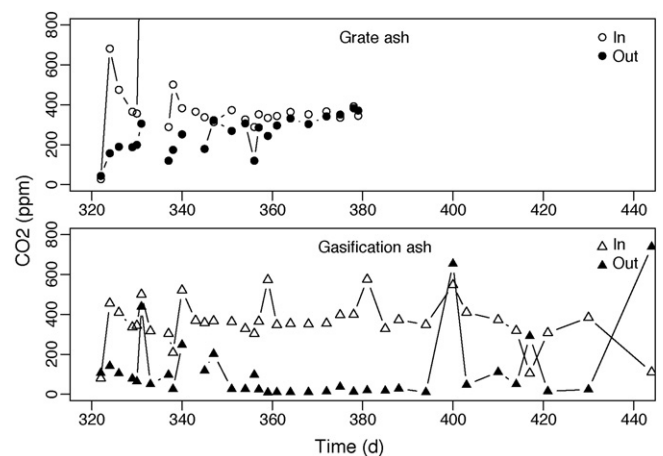
### 3.7. CO<sub>2</sub> absorption

In the gasification ash lysimeter the absorption of CO<sub>2</sub> was observed as a consistently lower concentration in the outflowing air than in the inflowing air (Fig. 4). The average CO<sub>2</sub> concentration of the air pumped in was 358 ppm (SD 112,  $n = 36$ ) and the average CO<sub>2</sub> concentration of the outflowing air was 169 (SD 376,  $n = 36$ ). In the grate ash lysimeter CO<sub>2</sub> absorption was strongest during the first 40 days of aeration (Fig. 4). During the first 40 days of aeration the mean CO<sub>2</sub> 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<sub>2</sub> was calculated from the cumulative in- and outflows. The grate ash absorbed

4.44 mmol/g(dm) (99.5 l/kg(dm)) of CO<sub>2</sub> 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<sub>2</sub> is



**Fig. 4.** CO<sub>2</sub> absorption. CO<sub>2</sub> 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,  $N_{\text{tot}}$ , Cl, and  $SO_4$  are given as mg/l and conductivity as  $\mu\text{S}/\text{cm}$ . In t-test bold figures are statistically significant  $p < 0.05$ .

|                  | Grate ash leachate |      |           |         |   |        | Gasification ash leachate |      |           |         |   |        | t-test |      |      |      |      |   |              |
|------------------|--------------------|------|-----------|---------|---|--------|---------------------------|------|-----------|---------|---|--------|--------|------|------|------|------|---|--------------|
|                  | Anaerobic          |      |           | Aerobic |   |        | Anaerobic                 |      |           | Aerobic |   |        |        |      |      |      |      |   |              |
|                  | min                | max  | $\bar{x}$ | SD      | n | t-test | min                       | max  | $\bar{x}$ | SD      | n | t-test |        |      |      |      |      |   |              |
| COD              | 84                 | 381  | 222       | 125     | 5 | 0.74   | 54                        | 372  | 141       | 112     | 7 | 0.28   | 4      | 0    | 268  | 80   | 109  | 5 | 0.62         |
| pH               | 7.07               | 8.97 | 7.9       | 0.74    | 5 | 0.77   | 7.39                      | 8.17 | 7.81      | 0.34    | 5 | 0.77   | 12.29  | 12.9 | 11.9 | 10.5 | 1.32 | 5 | <b>0.02</b>  |
| $N_{\text{tot}}$ | 9                  | 10   | 9.5       | 0.71    | 2 | 0.40   | 6                         | 9    | 7.5       | 2.12    | 2 | 0.40   | 0      | 3    | 1    | 0.5  | 0.71 | 2 | 0.73         |
| Cl               | 15.9               | 20.2 | 18.1      | 3.04    | 2 | 0.18   | 37.3                      | 55.2 | 46.3      | 12.7    | 2 | 0.18   | 75.6   | 84   | 103  | 87   | 22.6 | 2 | 0.73         |
| Cond.            | 1.8                | 1.93 | 1.87      | 0.09    | 2 | 0.29   | 2.43                      | 3.56 | 3.0       | 0.80    | 2 | 0.29   | 8.19   | 8.45 | 2.18 | 1.57 | 0.86 | 2 | <b>0.048</b> |
| $SO_4$           | 637                | 1120 | 857       | 213     | 5 | 0.07   | 981                       | 1974 | 1447      | 446     | 4 | 0.07   | 11.45  | 98.1 | 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 known 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 known 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 result 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<sub>2</sub> during the aeration period; however, the results reveal differences in the pattern of absorption. In the grate ash the absorption of CO<sub>2</sub> 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<sub>2</sub> absorption was similar in both ashes. The absorption capacity of the grate ash was reduced owing to CO<sub>2</sub> from biodegradation before the aeration period.

Compared to previous studies (max. 241/kg(dm)) the absorption capacity found in this study was high (90–1001/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<sub>2</sub> and smaller sample 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<sub>2</sub>. Totally dry ash reacts very slowly with CO<sub>2</sub>; the CO<sub>2</sub> 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<sub>2</sub> 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 of 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.

## Acknowledgements

This study was supported by the Maj and Tor Nessling Foundation (grant nos. 2005232, 2006118, 2007096), the Stream technology program of the National Technology Agency of Finland (TEKES, grant no. 40449/03), and EU FP5 (ICA2-CT-2001-10001). We are grateful to Nipa Manosuk, Anu Kettunen-Knuutila, and Saija Rasi, for technical assistance and help with the analyses.

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