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Artificial carbonation for controlling the mobility of critical elements in bottom ash

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Abstract In municipal solid waste incineration (MSWI), bottom ash, generated at a stoker grate type incinerator, the critical elements were identified in terms of EU regulation. The stabilizing effect of moderate carbonation (pH 8.28 ± 0.03) on critical contaminants was studied through availability and diffusion leaching protocols. Data from the performed tests were evaluated with the goal of reusing MSWI bottom ash as secondary construction material. To investigate the mobilizing effect of CO_2 , suspended MSWI bottom ash was severely carbonated (pH 6.40 ± 0.07). The effect of CO_2 and its interaction with other leaching factors, such as liquid/solid (L/S) ratio, leaching time, pH, ultrasound treatment, and leaching temperature, were examined using a reduced 2^{6-1} experimental design. Contaminants identified as critical were Cr, Cu, Mo, Sb, Cl^- , and SO_4^{2-} . Although moderate carbonation decreased the release of Cr, Cu, Mo, and Sb from compacted bottom ash, the main disadvantage remains its inability to demobilize Cl^- and SO_4^{2-} . The hypothesized mobilizing effect of severe carbonation was proven. The treatment enhanced the separation of critical components ($\alpha = 0.05$) (except for Cl^-), i.e., about fivefold for Sb and about twofold for Cr, Cu, and S. Nevertheless, the prospect is good that severe carbonation could substitute the deciding key parameter to facilitate the technical feasibility of a future washing process for MSWI bottom ash.

Key words Bottom ash · MSW · Carbonation · Leaching · Metals

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Introduction

Incineration has been emerging as a waste treatment option in industrialized countries over the past three decades. However, the pollution potential remaining in municipal solid waste incineration (MSWI) residues can be significant.¹ The reuse of incineration residues, e.g., as secondary construction materials, is thus challenged and in some countries it is regulated, with the likelihood of further restrictions in the future. Criteria for the acceptance of waste at landfills have also been stipulated within the EU.² With consideration of the economy and the environment, these developments call for treatment processes that facilitate the safe landfilling or reuse of incineration residues. Nevertheless, no such process has yet gained wide acceptance.^{3,4} Elsewhere,⁴⁻⁶ the carbonation of air pollution control (APC) residues from MSWI has been investigated and judged to be a promising stabilization method. APC residues are highly contaminated, but amount to only about 2%–3% w/w of the incinerator feedstock. For bottom ash, the mass flow is at least tenfold compared to APC residues, but its potential for reuse as a secondary construction material is higher than for APC residues.

The objective of this investigation was to test the impact of carbonation on the mobility of critical components in MSWI bottom ash from a common stoker type incinerator in Umeå, Sweden. The critical components were identified according to regulatory criteria for the acceptance of inert waste at landfills,² followed by the testing of the hypothesis that moderate carbonation stabilizes critical metals. In landfilling or reuse, such stabilization might be followed by solidification; the interaction between solidification and treatment with CO_2 was thus also studied. Whether severe carbonation mobilizes the critical components in question and how this variable interacts with other leaching factors were also tested. Such empirical knowledge might help to develop a washing process for MSWI bottom ash.

Materials and methods

The investigated MSWI bottom ash was sampled from the Dåva kraftvärmeverk incinerator near Umeå, Sweden. The plant uses stoker grate type (SGT) combustion with a capacity of $\sim 150 \times 10^3$ tonnes per year, and is supplied mainly with MSW and minor fractions of light industrial waste such as wood, rubber, and plastics. Approximately 200 kg of magnetically separated MSWI bottom ash (SGT-BA) were sampled in a metal container from a 6-month old heap. In the laboratory, the material was quartered into subsamples and stored in a nitrogen atmosphere. The mobility of regulated components was determined ($n = 5$) according to the two-step compliance leaching test stipulated by the EU for the acceptance of waste at landfills.² Ecke and Åberg⁷ characterized the basic total composition of the SGT-BA (Table 1).

Two types of carbonation were performed on the SGT-BA samples, i.e., severe carbonation by applying an excess of CO_2 in suspension and moderate carbonation on the total solids (TS) content as received. For severe carbonation, the SGT-BA was suspended with a stirrer in 100 ml deionized water according to a preset liquid/solid (L/S) ratio (Table 2). Using a gas diffuser, the stirred suspension was treated with technical-grade CO_2 gas for 2.5 h (Fig. 1). As a control, the SGT-BA was treated according to the same protocol with the exception of the addition of CO_2 . The end-point

pH of carbonated and noncarbonated leachate was recorded.

For moderate carbonation, the SGT-BA was placed in a 50-l gas bag (Tecobag for gas analysis, Tesseraux, Germany) equipped with a gas vent. The bag was closed, all the air was sucked out through the vent, and the bag was filled with technical-grade CO_2 gas. No water was added. The bag was shaken manually two to three times per week and carbonation was terminated after 27 days. A sample of the treated material was suspended with a stirrer in deionized water at an L/S ratio of 10 l kg^{-1} . The end-point pH value of the leachate was recorded.

The effect of severe carbonation was investigated together with five other factors (Table 2) that were combined according to a reduced 2^{6-1} experimental design, including six center points at the intermediate level.⁸ Together with carbonation, ultrasound treatment (Branson DTH2510E; Branson Ultrasonics, Danbury, Connecticut K, USA) was carried out at 42 kHz and 100 W as a pretreatment method for suspended SGT-BA (Fig. 1). When the specified treatment with ultrasonic waves was less than 40 min, the suspension was kept at room temperature for the remaining time. The subsequent wet extraction of pretreated SGT-BA was performed using a TIM900 Titration Manager and an ABU901 Autoburette (Radiometer Analytical, Copenhagen, Denmark) running on the software TimTalk 9, LabSoft (Radiometer Analytical, Copenhagen, Denmark) (Fig. 1). The factors investigated were the L/S ratio, the leaching time, the leaching temperature, and the leaching pH (Table 2). To control the latter, the following titration solutions were used depending on the preset pH level: 2 M NaOH, 1 M NaOH, 2 M HNO_3 , 1 M HNO_3 , and 0.5 M HNO_3 .

The effect of moderate carbonation was investigated together with the impact of solidification as per the two-level, full factorial design. For solidification, the SGT-BA was mixed with deionized water at a ratio of 0.11 kg^{-1} . The mixture was placed in plastic beakers (10.5 cm in diameter) and solidified using Proctor compaction, resulting in a specimen height of 5.0–5.5 cm. The specimens were dried at 60°C for 15 days.

Moderately carbonated samples, solidified samples (solidified, as sampled), or both (solidified, moderately carbonated), including the control (as sampled), were studied in triplicate using the Nordic availability test.⁹ This availability test is a two-step leaching test performed on finely grained material (95 wt% > $125 \mu\text{m}$). The first step was performed at an L/S ratio of $100 \text{ l (kg TS)}^{-1}$ at pH 7 for 3 h and the second was performed at an L/S ratio of $100 \text{ l (kg TS)}^{-1}$ at pH 4 for 18 h. Both leachate fractions were combined prior to the analysis. Analysis of variance (ANOVA)¹⁰ was performed on the data from the availability testing.

The Dutch diffusion test NEN 7345¹¹ was performed on solidified moderately carbonated SGT-BA specimens ($n = 3$) and solidified as-sampled specimens ($n = 2$). This test was conducted in eight successive leaching steps of specified duration, giving eight leachate fractions. The test applies a leachant with a pH of 4 ± 0.1 adjusted with nitric acid. pH was not adjusted during the leaching, but was determined

Table 1. Averages with SDs for total solids (TS) ($n = 12$), loss on ignition (LOI) ($n = 12$), oxides ($n = 3$), and abundant elements ($n = 3$) in municipal solid waste stoker grate type incineration bottom ash (SGT-BA) as sampled⁷

Component	Amount		SD
	Average		
Content of total solids [g (kg ash) ⁻¹]			
TS	830	±	3
Major constituents [g (kg TS) ⁻¹]			
LOI	12	±	0.8
SiO ₂	370	±	9
Al ₂ O ₃	130	±	3
CaO	150	±	2
Fe ₂ O ₃	150	±	5
K ₂ O	14	±	0.2
MgO	25	±	1
MnO ₂	3	±	0.2
Na ₂ O	28	±	1
P ₂ O ₅	10	±	1
TiO ₂	16	±	1
Minor constituents [mg (kg TS) ⁻¹]			
As	33	±	3.2
Cd	6	±	1.1
Co	34	±	6.0
Cr	568	±	435
Cu	11570	±	3261
Mo	24	±	2.6
Ni	567	±	446
Pb	2260	±	983
S	5103	±	38
Zn	9117	±	1198

Fig. 1. Experimental setup to investigate the effect of severe carbonation on the release of components.²⁸ Treatment factors (Table 2) were combined according to the reduced 2^{6-1} factorial design with six center points

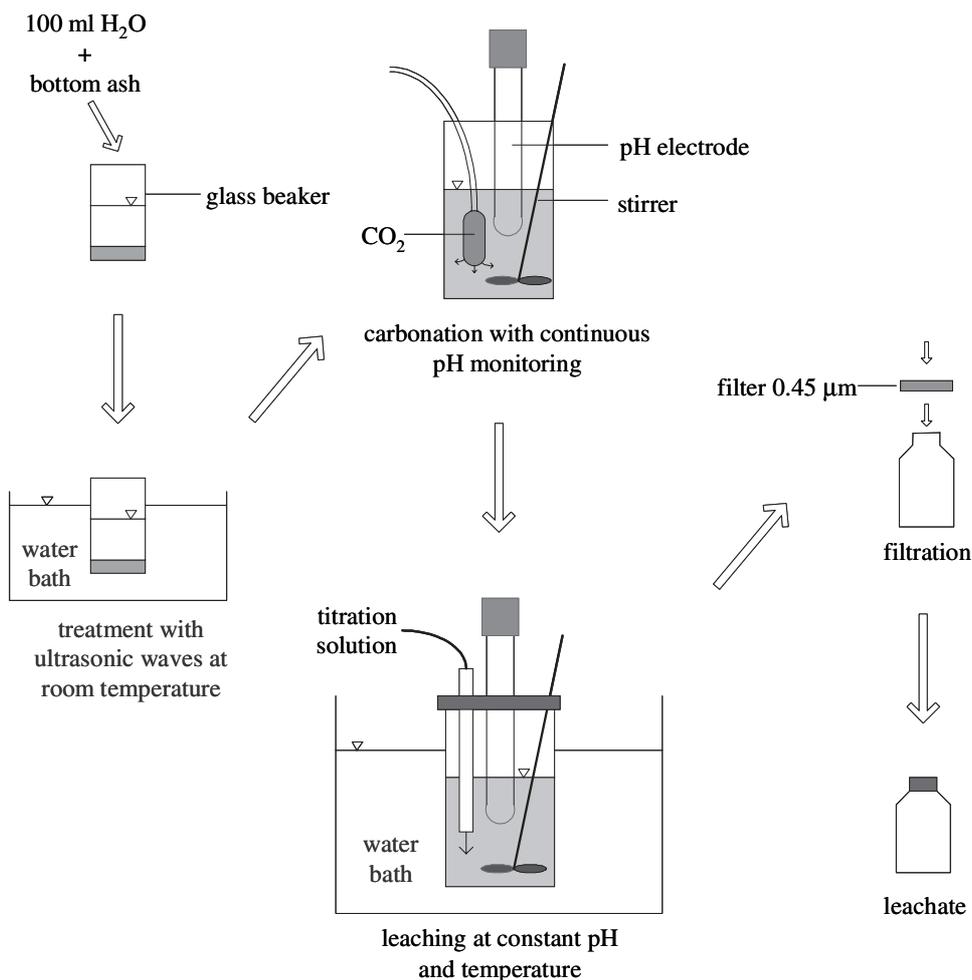


Table 2. Factors used for the reduced 2^{6-1} experimental design with six center points applied in the investigation of severe carbonation

Factor	Unit	Level		
		Low (-)	Intermediate (0)	High (+)
CO ₂ pretreatment	-	No	-	Yes
L/S ratio	l kg ⁻¹	5	12	20
Time	h	2	15	24
pH	-	7	10	12
Ultrasound treatment ¹	min	0	10	40
Temperature	°C	20	40	60

L/S, liquid to solid

¹ Energy output of equipment was 100 W at 42 kHz

by the material itself. The only modification from the original test protocol was that leaching was performed in the beakers used as moulds for the compaction.

Plastic apparatus and glassware were acid washed before use. Before analysis, all leachates were filtered with 0.45-µm-membrane filters (Minisart, nonpyrogenic, Epsom, UK) and stored at 4°C. Major elements in the leachates were analyzed with inductively coupled plasma atomic emission spectrometry (ICP-AES) according to EPA 200.7

(modified). Depending on the concentrations, trace metals were analyzed with ICP-AES (see above) or inductively coupled plasma sector mass spectrometry (ICP-SMS) according to EPA 200.8.

Cl⁻ concentration levels were determined by titration using AgNO₃ according to the Swedish standard SS 02 81 20¹² and SO₄²⁻ was analyzed according to the standard SSEN-ISO 10304. Dissolved organic carbon (DOC) was analyzed using TOC-VCPH/CPN (Shimadzu, Kyoto,

Table 3. Comparison of compliance leaching test results for SGT-BA, as sampled, presented as averages and SDs ($n = 5$) and the limit values stipulated by The Council of the European Union² for acceptance of waste to landfills for inert waste

	SGT-BA				Limit values	
	L/S 2		L/S 10		L/S 2	L/S 10
	Average	SD	Average	SD		
pH	11.5	0.1	11.5	0.1		
Redox (mV)	53.2	11.4	60.7	25.9		
Component [mg (kg TS) ⁻¹]						
Al	123	29	467	46		
As	>0.016		>0.024		0.1	0.5
Ba	0.25	0.02	1.08	0.07	7	20
Ca	154	6	858	29		
Cd	0.0022	0.0003			0.03	0.04
Chloride	3402	71	4597	95	550	800
Co	0.0016	0.0001	>0.003			
Cr total	0.38	0.02	0.78	0.03	0.2	0.5
Cu	1.603	0.051	2.70	0.06	0.9	2
Fluoride					4	10
Fe	>0.01		>0.02			
Hg	>0.00005		>0.00021		0.003	0.01
Mg	>0.4		>2			
Mn	0.003	0.001	>0.01			
Mo	1.06	0.02	1.83	0.06	0.3	0.5
Ni	0.006	0.001	0.012	0.001	0.2	0.4
Pb	0.006	0.004	0.08	0.06	0.2	0.5
Sb	0.06	0.02	0.33	0.08	0.02	0.06
Se	0.0106	0.0008	0.023	0.001	0.06	0.1
Zn	0.06	0.02	0.3	0.1	2	4
Sulphate	640	280	1470	360	560	1000
DOC	79	2	150	8	240	500

Redox was measured in unfiltered leachate

Bold indicates components whose leaching exceeded limit values

DOC, dissolved organic carbon

Japan). Experimental data from both carbonation experiments were evaluated using multiple linear regression ($\alpha = 0.05$).

Results

According to the acceptance criteria of inert waste at landfills,² the following critical components were identified in SGT-BA as sampled: Cr, Cu, Mo, Sb, Cl⁻, and SO₄²⁻ (Table 3). SGT-BA established an end-point pH of 6.40 ± 0.07 ($n = 8$) during severe carbonation and an end-point pH of 8.28 ± 0.03 ($n = 3$) during moderate carbonation compared to a pH of 11.25 ± 0.16 ($n = 8$) for SGT-BA as sampled. The effect of moderate carbonation and solidification of SGT-BA on the availability of components was quantified (Fig. 2). With the exception of Cl⁻, moderate carbonation affected the availability of all components ($\alpha = 0.05$). Moderate carbonation decreased ($\alpha = 0.05$) the availability of Cr, Mo, Sb, and SO₄²⁻, whereas the availability of Cu, Pb, and Zn was increased. The interaction of carbonation and solidification positively affected ($\alpha = 0.05$) the availability of Ca. Solidification demobilized ($\alpha = 0.05$) Ca, Pb, Zn, and SO₄²⁻.

During the diffusion test of solidified SGT-BA, the leachate pH developed differently for solidified moderately carbonated specimens compared to solidified as-sampled specimens (Fig. 3). While acidic leachant was replenished frequently at the beginning of the test, the pH of both leachates was almost neutral. While increasing the intervals between the replenishments, the increase in leachate pH was more pronounced for solidified as-sampled SGT-BA than for solidified moderately carbonated SGT-BA. At the end of the test, the pH of the solidified moderately carbonated SGT-BA was 8.21 ± 0.06 ($n = 3$), whereas the solidified as-sampled SGT-BA had a pH of 11.10 ± 0.14 ($n = 2$).

From solidified SGT-BA, the release of components varied over a wide range (Table 4 and Table 5). Cl⁻ showed the highest mobility with a negative logarithm of the mean effective diffusion coefficient¹¹ of $pD_e = 9.4 \pm 0.1$. Throughout the test, the cumulative release of Cl⁻ approached the content of Cl⁻ available in the matrix. For Cu, Pb, and Zn in solidified as-sampled SGT-BA, the pD_e was calculated at greater than 12.5 (Table 5). The tortuosity¹ was calculated at 25.05 ± 5.95 in solidified as-sampled specimens and at 20.28 ± 1.32 in solidified moderately carbonated specimens. Except for Pb and Sb, moderate carbonation did not greatly affect the diffusivity of the investigated components (Table 5).

Fig. 2. Effect of moderate carbonation and solidification on the availability⁹ of components [mg (kg total solids)⁻¹], illustrated as averages with SDs ($n = 3$). *As sampled*, untreated bottom ash or bottom ash as sampled; *mod carb*, moderately carbonated; *circles*, specimens that were not solidified; *squares*, solidified specimens

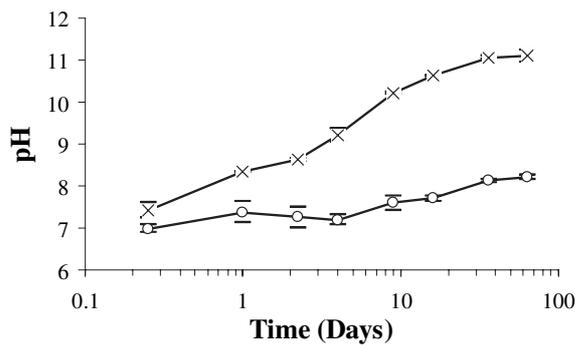
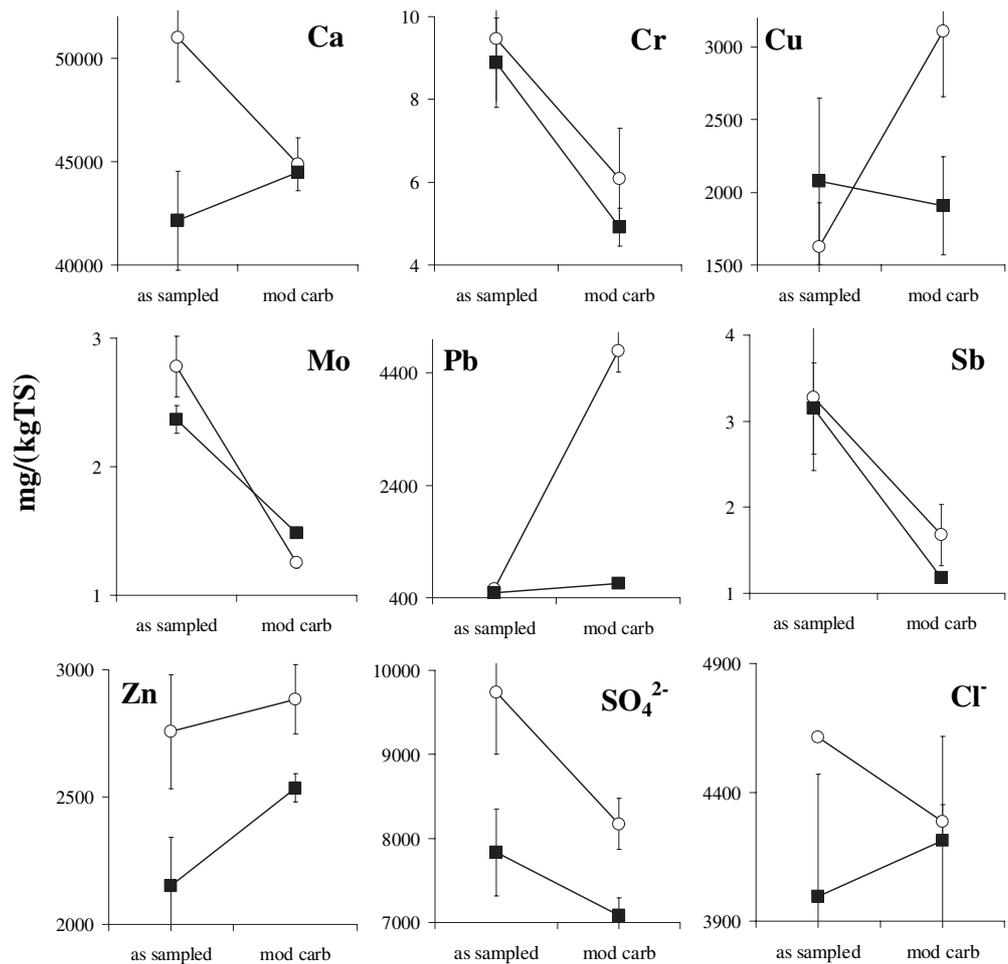


Fig. 3. Trend of leachate pH during the diffusion leaching test for solidified moderately carbonated municipal solid waste stoker grate type incineration bottom ash (SGT-BA) (*circles*, $n = 3$) and solidified SGT-BA as sampled (*crosses*, $n = 2$)

Severe carbonation did not affect the leaching of the elements Pb, Zn, and Cl⁻ whatsoever (Table 6) ($\alpha = 0.05$), with Pb and Zn being the typical carbonate formers. Only for the carbonate former Ca did an excess of CO₂ cause demobilization by a factor of about seven (Fig. 4). Cl⁻ was the only unaffected critical component, whereas Cr, Cu, Mo, S, and Sb were mobilized (Fig. 4), i.e., Sb about five times; Cr, Cu,

Table 4. The cumulative release during m steps of diffusion leaching from solidified as-sampled SGT-BA [presented as averages and SDs, mg (kg TS)⁻¹, $n = 2$] and the increase in cumulative release resulting from moderate carbonation (%)

Component	Solidified, as sampled		Increase (%)	m
	Average	SD		
Ca	275	9	222	8
Cr	0.19	0.01	-97	8
Cu	0.86	0.09	-63	8
Mo	0.39	0.03	-39	6
Pb	0.0165	0.0006	159	8
SO ₄ ²⁻	392	48	320	8
Sb	0.104	0.008	-45	8
Zn	0.040	0.004	583	4
Cl ⁻	2894	31	22	8

The increases presented are higher than the variability between replicates and are considered significant¹⁹

and S about twice; and Mo about 27%. DOC was mobilized almost three times as a result of severe carbonation.

CO₂ treatment was the dominating factor in the mobilizations of Cr, Cu, S, and Sb. In all cases, severe carbonation interacted with the other factors, i.e., leaching pH, leaching time, leaching temperature, or a combination

Fig. 4. Modeled effect of severe carbonation on the mobility of elements [mg (kg total solids)⁻¹]. Averages (circles and crosses) are illustrated with 95% confidence intervals ($n = 38$). Except for CO₂, all other factors were set at intermediate levels. As *sampled*, bottom ash extracted as sampled; *severe carb*, bottom ash that was severely carbonated before extraction

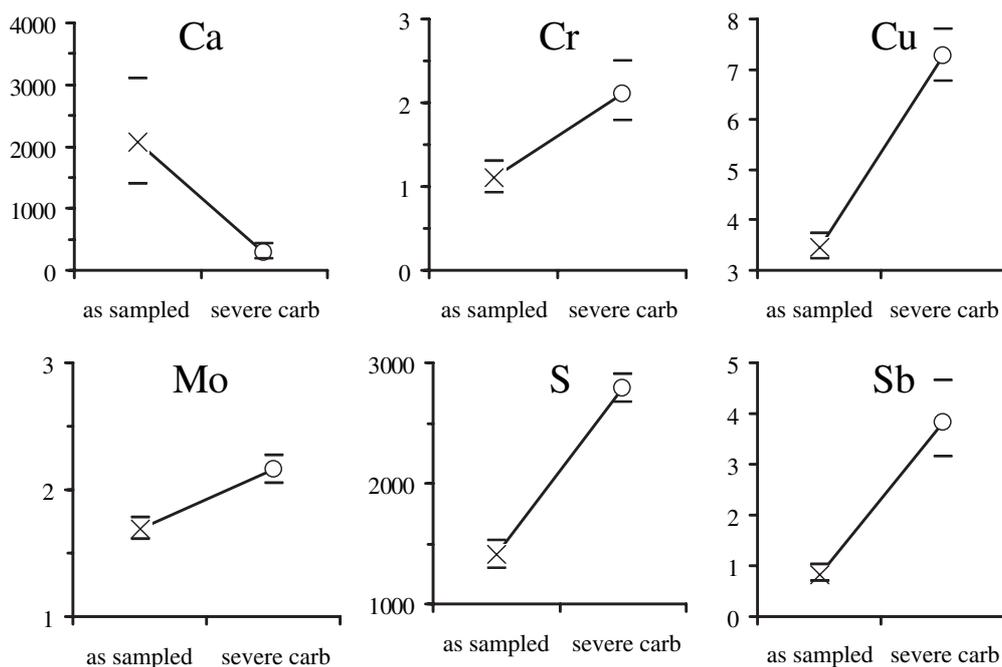


Table 5. Effect of moderate carbonation on the negative logarithm of the mean effective diffusion coefficients (pDe)¹¹ for solidified moderately carbonated or as-sampled SGT-BA

Component	Solidified, as sampled	Solidified, moderately carbonated
Ca	NDL	NDL
Cr	12.06	CTL
Cu	16.3 ± 0.1	NDL
Mo	10.5 ± 0.1	10.5 ± 0.1
Pb	18.77	18.2
SO ₄ ²⁻	NDL	10.4 ± 0.3
Sb	12.2 ± 0.0	12.0 ± 0.0
Zn	19.2	NDL
Cl ⁻	9.4 ± 0.1	9.3 ± 0.1

The average ± SD is given if diffusion-controlled release was observed for two or three specimens

NDL, no diffusion-controlled leaching; CTL, concentration too low to measure

Table 6. Significance ($\alpha = 0.05$) of the effect of severe carbonation and its interactions with other leaching factors on the mobilization of critical elements (Cr, Cu, Mo, S, Sb), carbonate formers (Ca, Pb, Zn), and chloride (Cl⁻)

Factor term	Component									
	Ca ¹	Cr ¹	Cu ¹	Mo ¹	Pb ¹	S	Sb ¹	Zn	Cl ⁻	DOC ¹
CO ₂	-	+	+	+	0	+	+	0	0	+
CO ₂ × pH	-	+	+	+	0	+	+	0	0	+
CO ₂ × time	0	0	-	0	0	0	-	0	0	0
CO ₂ × temp	0	0	-	0	0	-	0	0	0	-

CO₂, pretreatment with CO₂ in excess; 0, no effect on component mobility; -, negative effect; + positive effect

¹Data were log₁₀ transformed

thereof. A pretreatment with CO₂ followed by leaching at high pH resulted in the highest mobilizations of Cr, Cu, Mo, S, and Sb. When an interaction between CO₂ and leaching time or leaching temperature or both was observed (Cu, S, and Sb), the mobility of the elements was reduced as the time or, the temperature level, or both were being increased.

CO₂ treatment was also the dominating factor in the release of DOC. Treatment with CO₂ as well as interactions between the treatment with CO₂ and leaching pH increased the amount of DOC in the leachate, whereas the opposite resulted from the interaction of CO₂ and leaching temperature. Ultrasound treatment had a significantly positive effect ($\alpha = 0.05$) on the release of Cl⁻ only.

Discussion

Critical components

The effect of carbonation on the mobility of nine components is discussed in this study, i.e., Ca, Cr, Cu, Mo, Pb, Sb, Zn, Cl^- , and SO_4^{2-} . The leaching of Cr, Cu, Mo, Sb, Cl^- , and SO_4^{2-} from SGT-BA (Table 3) exceeded the limit values for the acceptance of waste at landfills for inert waste.² In addition, Ca was included because of its involvement in the formation of secondary minerals like calcite (CaCO_3), anhydrite (CaSO_4), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 0.003 \cdot 26\text{H}_2\text{O}$) in the bottom ash.^{13,14} Because Pb and Zn could be demobilized by substitution in these neoformed minerals¹³ or affected by pH changes¹ resulting from carbonation, these elements were also included in the study.

Moderate carbonation

Moderate carbonation effected the transition of SGT-BA from alkaline to material equilibrated at a pH level of $\text{pK}_{\text{Calcite}}$. During the diffusion testing of solidified SGT-BA, the leachate pH developed differently for solidified moderately carbonated specimens compared to solidified as-sampled specimens (Fig. 3). Initially, during frequent replenishments of the acidic leachant, the pH of both leachates was almost neutral. On increasing the intervals between the replenishments, the increase in leachate pH for solidified as-sampled SGT-BA was more pronounced than for solidified moderately carbonated SGT-BA. At the end of the test, the pH of the solidified moderately carbonated SGT-BA was 8.21 ± 0.06 ($n = 3$), and for the solidified as-sampled SGT-BA the pH was 11.10 ± 0.14 ($n = 2$). Because the solidified moderately carbonated SGT-BA sustained the pH level during the diffusion test, even after eight replenishments with acid leachant (Fig. 3), there was no indication of any excess of carbonation. At the end of the diffusion test, the solidified as-sampled SGT-BA approached an endpoint pH of 11.25 ± 0.16 , as measured in SGT-BA samples before carbonation at an L/S ratio of $10 \text{ l (kg ash)}^{-1}$. This indicates that the alkalinity of SGT-BA was not consumed (Fig. 3) during the testing. Because the pH measured in the bottom ash before the treatment was not close to the level of $\text{pK}_{\text{Calcite}}$, it can be assumed that if any natural carbonation occurred during the six months storage, it probably had only a minor effect on the leaching.

To assess the effect of moderate carbonation on the mobility of the tested components, two methods were combined. First, to simulate leaching-controlling conditions after landfilling or during reuse, the material was compacted and tested using diffusion leaching.¹¹ Second, to assess the potentially leachable amount of these components, milled material was tested using an availability test.⁹ Moderate carbonation increased the cumulative release of Ca, Pb, SO_4^{2-} , Zn, and Cl^- from the solidified material, whereas the release of Cr, Cu, Mo, and Sb (all defined as critical) decreased (Table 4). As described by Fick's second law of

diffusion,¹⁵ the release of a component from a solid material over time depends on (1) the soluble fraction of the component (the *availability* of the component) as determined by the availability test (Fig. 2), and (2) the diffusion coefficient. Component availability is the potentially leachable amount from the waste through diffusion over a very long period. The effective diffusion coefficient was determined using the diffusion test and was used to describe the release rate from the solid matrix (in Table 5 presented as the negative logarithm pD_e). Such an approach was assumed to indicate whether changes in the release after carbonation were the result of changes in the availability of a component or changes in the retention of a component in the solid matrix.

Cu, Pb, and Zn exhibited low mobility from solidified as-sampled SGT-BA because pD_e was calculated at greater than 12.5 (Table 5). A statistical evaluation on the effect of carbonation on diffusivity through comparison of pD_e values would not be reliable because the release of elements exhibited diffusion-controlled leaching in too few replicates. From the results obtained, whether the observed difference in pD_e for Pb (Table 5) was caused by the treatment or the data variability between samples was inconclusive. Chandler et al.¹ noted that high pD_e values (here observed for Cu, Pb, and Zn) were associated with relatively high standard deviations. Tortuosity is a material property that indicates the actual path length of diffusing ions through the solid matrix. Any changes in this factor would point to changes in the physical retention, possibly affecting diffusivity. Fernández Bertos et al.¹⁶ describe changes in the porous structure and tortuosity of MSWI residues resulting from carbonation, as well as a less pronounced effect on bottom ash than that on APC residues. In this study, however, the average values of tortuosity for solidified SGT-BA differed by 19%, although the difference was not significant ($\alpha = 0.05$) because of the relatively high data variability between solidified as-sampled specimens. Therefore, it cannot be expected that moderate carbonation of SGT-BA would lead to physical retention of components in the solid matrix.

Whereas the availability of Pb in moderately carbonated SGT-BA increased only about 35% (Fig. 2), the cumulative release increased by over 150% (Table 4). The increase in cumulative release is thus partly due to the lowered capacity of the material to chemically retain Pb. A similar discussion could be applied to Ca, Zn, and SO_4^{2-} .

A pD_e value of less than 9.5 indicates low retention of a component in the material and possibly questions the applicability of the diffusion test. For Cl^- , pD_e was just at this threshold. In diffusion tests, Cl^- is considered as an inert species. This is confirmed here, since the cumulative release approached the availability of Cl^- . Nevertheless, Cl^- was identified as a component following a diffusion-controlled pattern for both solidified moderately carbonated and solidified as-sampled SGT-BA. Even though the diffusivity of Cl^- was largely unaffected by moderate carbonation (Table 5) and changes in availability are within a relatively large standard deviation (Fig. 2), results show an increase of 22% in Cl^- leaching from solidified material after moderate car-

bonation (Table 4). Goni and Guerrero¹⁷ suggest that carbonation destabilizes Friedel's salt ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \times 10\text{H}_2\text{O}$), possibly leading to the release of Cl^- .

Because the release of Cl^- could not be decreased by moderate carbonation and is limited mostly by its availability in the ash, a pretreatment method (e.g., washing) to remove part of the available Cl^- could be the most efficient method for decreasing the salt content in leachates from reused or disposed MSWI bottom ash.

Moderate carbonation decreased the availability of Cr, Mo, Sb, and SO_4^{2-} (Fig. 2). However, as defined through the applied protocol, availability is the cumulative release at pH 7 and pH 4 and as such does not reflect a change in mobility due to carbonate formation, since carbonates are dissolved at pH 4. Rather, it reflects a redistribution of elements in mineral phases, from which Meima et al.¹⁸ performed their investigations. Changes in the availability of Cr, Mo, and Sb led to a decrease in their cumulative leaching from solidified SGT-BA (Table 4). The transition of Cr into a less mobile trivalent state under the conditions of the diffusion leaching test [pH from neutral to 8.21 ± 0.06 ($n = 3$), Fig. 3] might also have affected its mobility, as has been discussed in recent work.¹⁹

Moderate carbonation was anticipated to considerably lower the mobility of carbonate formers such as Pb,^{20,21} a hypothesis that was disproved in the diffusion tests. pH changes in bottom ash were shown¹⁹ to be an important factor affecting the leaching of Pb and Zn. Solidification also played an important role in the demobilization of Pb and Zn. The treatment decreased the availability of Pb from moderately carbonated SGT-BA by more than one order of magnitude (Fig. 2). Cu exhibited similar changes in its availability, although its demobilization on solidification was not as pronounced as that of Pb. Moderate carbonation decreased the cumulative release of Cu by more than half (Table 4).

The main disadvantage of using artificial carbonation at a moderate level as a stabilization method for SGT-BA prior to reuse or landfilling is its inability to demobilize Cl^- and SO_4^{2-} . The release of SO_4^{2-} even increased four times (Table 4). The increase in cumulative leaching of Ca and SO_4^{2-} on moderate carbonation might be the result of the decomposition of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \times 26\text{H}_2\text{O}$). Other aging processes such as remineralization^{21,22} might have a demobilizing effect. However, these processes are usually time consuming and much less controllable than carbonation.

Severe carbonation

Washing has been considered as a method to separate critical components from MSWI bottom ash and thus meet the environmental standards for reuse.²³ This work reveals that using an excess of CO_2 can enhance the success of such washing. The lower and upper levels of pH, temperature, leaching time, and ultrasound treatment (Table 2) were set to extreme values, although considered reasonable for MSWI bottom ash washing.

Treating suspended SGT-BA with an excess of CO_2 (severe carbonation) increased the mobility of all critical elements except Cl^- (Table 6). Also, a higher amount of DOC was mobilized on severe carbonation. The leaching of Pb and Zn was not affected as Ca was being demobilized. It was found that for all elements affected by severe carbonation, the higher the pH during the subsequent leaching, the more distinct the effect of CO_2 on element mobility (Table 6). DOC is known to form complexes with metals.²⁴⁻²⁷ Metal mobility may be increased as a result of complex formation with DOC; metal speciation may be affected by the complexation. Given that severe carbonation increased both the mobility of critical metals and DOC, the effect of complexation with DOC on metal mobility should be evaluated further.

For elements such as Cr, Cu, S, and in particular Sb, treatment with CO_2 had a greater impact than pH and all the other factors investigated. It might be worth testing whether washing with CO_2 is sufficient for the bottom ash to meet the acceptance criteria of inert waste at landfills.² In this respect, Mo could be a key element because of the minor impact of severe carbonation on its mobility (Fig. 4). To optimize the washing process, the interaction of CO_2 treatment with pH, time, and temperature should be considered. A short retention time (2 h) at a low temperature (20°C) might even favor the extraction of Cu, S, and Sb, although it might not lessen the degree of leaching for other critical components.

Outlook

Flue gas from incineration of MSW is a promising source of CO_2 for the carbonation of MSWI residues. However, the presence of oxygen, for instance, might risk mobilizing Cr, as proven for APC residues.^{6,19} It may therefore be interesting to investigate the effect of other gas components on the performance of the carbonation process and the effect on the leaching of contaminants.

In terms of SGT-BA treatment, the separation of critical components with an excess of CO_2 achieved an advantage over stabilization using moderate carbonation, maintaining the high mobility of Cl^- in all carbonation experiments. However, washing transfers the problem of contamination to a liquid phase, thereby requiring a leachate treatment unit and incurring additional costs. The L/S ratio required for successful washing is thus another critical factor. At the Division of Waste Science and Technology, the authors performed such studies on the optimization of leaching factors. The data are currently under evaluation and will be presented soon.

Conclusions

Artificial carbonation was tested as a treatment method on MSWI bottom ash generated at the stoker grate type incinerator Dåva kraftvärmeverk in Umeå, Sweden. For this

material (SGT-BA), it was concluded that from a regulatory point of view, the mobility of Cr, Cu, Mo, Sb, Cl⁻, and SO₄²⁻ was critical. Cl⁻ in SGT-BA had a high mobility. Even from solidified SGT-BA, the ion was released at a mean effective diffusion coefficient of $pD_e = 9.4 \pm 0.1$. Carbonation did not affect the mobility of Cl⁻. Except for highly mobile Cl⁻ and SO₄²⁻, calcite equilibrium resulting from moderate carbonation was proven to be effective in demobilizing other critical components (Cr, Cu, Mo, and Sb). The release of Cr, Mo, and Sb was affected through a decrease in their potentially leachable amounts (availability). The potential of SGT-BA to physically retain contaminants did not significantly change after moderate carbonation. Severe carbonation enhanced the separation of critical components (except Cl⁻), i.e., about fivefold for Sb and about twofold for Cr, Cu, and S. Yielding a mobility increase of only about 27%, the treatment had a minor effect on Mo. Nevertheless, the prospect is good that enhancing wet extraction of SGT-BA with an excess of CO₂ might be a feasible treatment option to meet regulatory criteria stipulated for inert waste at landfills. However, an impact assessment of other leaching factors such as the L/S ratio and complexation between DOC and metals as well as an economic assessment are still needed.

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