Accelerated carbonation for treatment of MSWI bottom ash

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Abstract

Leaching of heavy metals from MSWI bottom ash exceeds some of the Flemish limit values for recycling the material as granular construction application. In particular, leaching of Cu, Zn and Pb often exceeds the limit value, with Cu being the most critical. In order to recycle bottom ash, treatment is therefore required. The bottom ash studied was divided on-site into four fractions using a large-scale wet sieving installation: a sludge fraction (Ø 0–0.1 mm), a sand fraction (Ø 0.1–2 mm) and two gravel fractions (Ø 2–6 and 6–50 mm). The two gravel fractions complied with the limit values after 3 months of natural ageing. The sand and sludge fraction did not reach the limit value for Cu. Four weeks of accelerated carbonation resulted in an important decrease of Cu leaching from these two fractions, although the limit value is still exceeded. In view of applying carbonation as one of the treatment methods in an integrated industrial application, two tests were additionally performed. The use of stack gas as carbonating medium was verified by setting up an accelerated carbonation experiment at the incineration plant. Also, the depth of carbonation was measured in a 10 cm thick sample of the sand fraction after different periods of treatment. After 3 months of natural ageing only the upper 4 cm underwent a significant carbonation, while after one week of accelerated carbonation the total sample was carbonated. A model was developed to predict these experimental results.
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1. Introduction

Bottom ash is the most important residue originating in the grate furnace of a municipal solid waste incinerator (MSWI) as it accounts for 80–90% of the total weight of all the residues. Although incineration enables to reduce the volume of the original waste by up to 90%, the produced amounts of bottom ash are still substantial. In Flanders (the northern part of Belgium, 5.95 million inhabitants) 3.2 million tons of municipal solid waste was collected in 2003 [1]. Roughly 1 million tons were incinerated, resulting in 270,000 tons of bottom ash.

Treatment of this bottom ash is important in view of sustainable waste management. Bottom ash can replace the sand or gravel fraction in concrete bricks or can be used as such in foundations [2]. For bottom ash to be recycled, it must comply with strict regulations, consisting of civil-technical and environmental requirements. In practice, the latter appear to be a problem as leaching of MSWI bottom ash exceeds some of the limit values for heavy metals, so that treatment is required.

Various treatment options applicable to waste incineration residues prior to their reuse or final disposal have been proposed [3], such as size separation, magnetic separation, washing, ageing/weathering, carbonation, chemical extraction, sintering, . . . The most commonly used method is natural ageing of bottom ash – which includes reactions as oxidation, carbonation, neutralisation of pH, dissolution, precipitation and sorption – through storage in stockpiles open to the atmosphere for a period of 1–3 months [4]. Carbonation has been recognised as one of the most important ageing processes [5] and involves the absorption of CO_2 by an initially alkaline material, which causes the pH to decrease and calcite to precipitate [6]. The carbonation reaction can be accelerated using a gas with a higher CO_2 percentage than air. Using the CO_2 from the stack gas of MSW incinerators might be an interesting option [7]. To introduce the CO_2 needed for carbonation, there are several possibilities: leading the CO_2-rich gas in counter-current over a thin layer of bottom ash on a moving belt, or blowing the gas through tubes in the bottom ash heaps [8].

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In this paper, natural ageing and accelerated carbonation are studied on the different fractions of bottom ash in order to evaluate their potential for decreasing heavy metal leaching. Accelerated carbonation was also performed on the sand fraction using the stack gas of the incinerator. In addition, the velocity of carbonation in a 10 cm layer of bottom ash fraction was investigated. A model for the carbonation reaction was developed and evaluated.

2. Materials and methods

2.1. Materials

The MSWI bottom ash used in this study underwent an on-site treatment after quenching. This wet treatment – consisting of various cut, sieve and wash units – separated the light organic fraction and the fraction larger than 50 mm from the main stream, and sent these back into the incinerator. The main stream again went through a wet sieving process to produce three fractions: Ø 0–2, 2–6 and 6–50 mm. Magnets removed ferrous material from the gravel fractions (Ø 2–6 and 6–50 mm). The eddy current technique was used to separate non-ferrous material from the 6–50 mm gravel fraction. The smallest fraction (Ø 0–2 mm) was separated in a sand fraction (Ø 0.1–2 mm) and a sludge fraction

(Ø 0–0.1 mm). The weight percentages of the sludge, sand and gravel fractions (Ø 2–6 and 6–50 mm) were 8%, 32%, 14% and 27%, respectively. After collection, the four fractions were dried at 50 °C for 9 days and stored in closed buckets to slow down further transformation reactions.

2.2. Characterization

The moisture content of each bottom ash fraction was determined by weighing a sample, drying the sample at 105 °C for 24 h and weighing it again.

Leaching of metals from the bottom ash fractions was tested using the EN 12457-2 test. In this test, 10 g of dry material was stirred in 100 ml of distilled water for 24 h. The NEN 7343 column test, formally required in Flanders as a compliance test for recycling as granular construction material, was also performed on the sand fraction to compare both tests. In the NEN 7343 test a column was filled with material and percolated with distilled water (acidified to pH 4) from bottom to top. The eluate was collected in seven fractions, corresponding to a total liquid to solid ratio (L/S) of 10 and requiring 3 weeks of testing. The procedure of both tests has already been described in more detail elsewhere [9]. After filtration of the leachates over a 0.45 μm membrane, the metals in the eluates were measured with a VG PlasmaQuad PQ-2 Plus ICP-mass spectrometer.

In order to evaluate the pH dependence of metal leaching from uncarbonated and carbonated (4 weeks) sand fraction, different volumes of concentrated HNO_3 or 1 M NaOH were added to the leachant to obtain different leaching pH's at the end of the EN 12457-2 test.

2.3. Natural ageing experiments

Samples of dried sand and gravel fractions were rehumidified to their original moisture content. As the dried sludge fraction was too solid to work with, natural ageing experiments were not performed on this fraction. Samples of 25 ± 1 g sand fraction and 50 ± 1 g gravel fraction (Ø 2–6 mm) were spread out in several Petri-dishes (Ø 90 mm), which resulted in layers of ca. 3 and 6 mm thickness, respectively. Samples of 120 ± 1 g gravel fraction (Ø 6–50 mm) were put in glass recipients (Ø 50 mm), resulting in layers of ca. 7 cm thickness. The Petri-dishes and glass recipients were placed in contact with atmospheric air (CO_2 percentage of 0.03 vol.%) in the laboratory. After 1, 2, 3, 4, 8 and 13 weeks, samples were removed and their moisture content was determined. Metal leaching was subsequently tested using the EN 12457-2 test. After filtration, leachates were analysed to determine pH and metal concentrations (using ICP-MS).

To study the depth of carbonation as a function of time, samples of sand fraction were put in several glass recipients of 10 cm height (Ø 100 mm) and also placed in contact with atmospheric air in the laboratory. After 2, 4, 7 and 12 weeks, a glass recipient was taken and the sample of 10 cm height was divided into 20 subsamples, each consisting of a subsequent layer of 0.5 cm. As carbonation is accompanied by a decrease of the leachate

pH, the latter parameter can be used to evaluate the extent of carbonation.

2.4. Accelerated carbonation experiments

Accelerated carbonation tests were carried out in a Sanyo MCO-17AI chamber to control the CO_2-percentage and the temperature in the atmosphere. The following optimal parameters were used: 10% CO_2 and 50 °C. The same amounts of samples and the same testing procedure (determination of moisture content, EN 12457-2 leaching test, filtration and determination of pH and metal concentrations in the eluates) were used as in the natural ageing experiment. Samples were removed from the chamber after 1, 2, 3 days and 1, 2, 3, 4 weeks. Additional samples were taken of the sand fraction after 1, 2, 3 and 6 h. As the accelerated carbonation experiment was performed on fresh bottom ash samples (with their initial ash moisture content), the experiment was also performed on samples of 25 ± 1 g sludge fraction, which resulted in layers of ca. 3 mm thickness in several Petri-dishes (Ø 90 mm). More details about the accelerated carbonation experiments and the determination of the optimal parameters are provided in former research [10].

As the stack gas of the incinerator contains 10% CO_2, its use as carbonating medium was verified by setting up an experiment at the incineration plant. More information about the flue gas treatment process of the particular incineration plant is provided elsewhere [11]. Stack gas (temperature 112 °C, humidity 21 vol.%) was pumped (flow rate 0.339–0.369 m³/min) through a column (Ø 48 mm, length 209 mm) packed with 481.6 g of sand fraction. After 1, 2, 3 days and 1, 2, 3, 4 weeks the column content was mixed and a sample of ca. 50 g was taken. Afterwards, the remaining material was mixed and loaded back into the column. The removed sample was replaced by inert silica wool. During the experiment, some problems occurred caused by condensation of the stack gas on the bottom ash. This condensate increased the resistance of the packed column, which resulted in several short interruptions of the experiment and a fluctuating flow rate of the stack gas through the packed column. A condensate sample was collected each time a sample of sand fraction was taken. After determining the moisture content, the samples of sand fraction were leached using the EN 12457-2 test. In the filtered eluates and the condensate samples pH and metal concentrations were determined.

The carbonation rate was studied on samples of sand fraction put in glass recipients of 10 cm height (Ø 100 mm) in the CO_2 chamber. After 1, 2, 3 days and 1, 2, 3, 4 weeks, a glass recipient was taken and tested in the same way as in the similar natural ageing test.

2.5. Modelling of the carbonation rate (see Nomenclature list)

2.5.1. Model

Carbonation, the reaction of CO_2 and $Ca(OH)_2$ leading to $CaCO_3$ and H_2O, is controlled by two mechanisms: CO_2 diffusion from the air through the porous system up to the reaction front (at each particle) and the reaction of diffused CO_2 with

$Ca(OH)_2$ after dissolution in the thin water film surrounding each particle [7,8,12,18]. These two mechanisms correspond to the first and second term in Eq. (1), the differential equation describing the carbonation process.

$$\varepsilon_{air} \frac{\partial C_{CO_2}^g}{\partial t} = D_{eff} \frac{\partial^2 C_{CO_2}^g}{\partial x^2} - R_{CO_2} \tag{1}$$

A constant porosity ε_{air} and effective diffusion coefficient D_{eff} are assumed. The reaction term R_{CO_2} is modelled as a second order reaction in CO_2 and $Ca(OH)_2$ with both concentrations in the liquid phase ($R_{CO_2} = \varepsilon_{water} k_r C_{CO_2}^l C_{Ca(OH)_2}^l$). The porosity ε_{water} is essential for unit conformity. The CO_2 concentration in the liquid phase is converted into the corresponding value in the gaseous phase using the Henry's law (temperature: 25 °C for natural ageing experiment and 50 °C for accelerated carbonation experiment). Assuming a constant $Ca(OH)_2$ concentration in the reaction term R_{CO_2} (this means that whenever some dissolved $Ca(OH)_2$ reacts with CO_2, new $Ca(OH)_2$ dissolves), the reaction kinetics becomes pseudo-first order ($R_{CO_2} = \varepsilon_{water} k C_{CO_2}^g$) and Eq. (1) may be integrated analytically.

As the objective of the model is to calculate pH, a second differential equation Eq. (2) needs to be integrated. The reaction term $R_{Ca(OH)_2}$ is identical to R_{CO_2} except for the assumption here of a constant CO_2 concentration (instead of constant $Ca(OH)_2$ concentration in R_{CO_2}).

$$\frac{\partial C_{Ca(OH)_2}^l}{\partial t} = -R_{Ca(OH)_2} \tag{2}$$

From here, pH can be easily calculated as the assumption is made that pH is controlled by the dissolution of $Ca(OH)_2$. As pH control is not exerted by $Ca(OH)_2$ for carbonated materials, but rather by $CaCO_3$, deviations from experimental and predicted pH values can be expected, particularly for the higher carbonation degrees. However, as the model was used to calculate not only pH for carbonated materials, but also for uncarbonated and partly carbonated materials, the assumption of pH control by $Ca(OH)_2$ was considered valid for a simple model. An iterative scheme is developed to solve the differential system of Eqs. (1) and (2) and implemented in Matlab.

2.5.2. Determination of the model parameters

Several parameters need to be determined for the differential system of Eq. (1) and (2) to be solved. Both porosities ($\varepsilon_{air} = 0.51$ and $\varepsilon_{water} = 0.22$) were calculated from the dry bulk density ($\rho_{dry} = 0.66$ kg/l), wet bulk density ($\rho_{wet} = 0.88$ kg/l) and absolute density of the bottom ash fraction ($\rho_{absolute} = 2.41$ kg/l) by Eqs. (3) and (4). The dry and wet bulk densities were determined by weighing a volume of 1 l of non compacted dry respectively wet sand fraction. The absolute density was measured with a pycnometer according to BS 812 [13].

$$\varepsilon_{air} = \frac{V_{air}}{V_{air} + V_{water} + V_{bottom\ ash}}$$
$$= \frac{(1/\rho_{wet}) - (\rho_{dry}/\rho_{wet})(1/\rho_{abs}) - ((\rho_{wet} - \rho_{dry})/\rho_{wet})}{(1/\rho_{wet})} \tag{3}$$

$$\varepsilon_{\text{water}} = \frac{V_{\text{water}}}{V_{\text{air}} + V_{\text{water}} + V_{\text{bottom ash}}} = \frac{((\rho_{\text{wet}} - \rho_{\text{dry}})/\rho_{\text{wet}})}{(1/\rho_{\text{wet}})} \tag{4}$$

Other parameters were taken from literature: the effective diffusion coefficient D_{eff} [14] and the Henry constants [15]. The effective diffusion coefficient of CO_2 in pores is known to be strongly correlated with the relative humidity. As no specific information was available for the bottom ash used, the effective diffusion coefficient of CO_2 in concrete pores was assumed (1E−8 m²/s). Further research should determine the exact effective diffusion coefficient in the bottom ash sand fraction. The initial CO_2 concentration was calculated using the ideal gas law, assuming the presence of 0.03% CO_2 in air. The initial $Ca(OH)_2$ concentration was calculated by means of the initial pH. One parameter, the reaction rate constant k_r, was considered as the only degree of freedom and used to fit the experimental results.

3. Results and discussion

3.1. Characterization of the bottom ash fractions

Immediately after sampling, the bottom ash fractions had a moisture content (m/m) of 39.6% (Ø 0–0.1 mm), 26.6% (Ø 0.1–2 mm), 5.0% (Ø 2–6 mm) and 4.4% (Ø 6–50 mm). After drying in view of storage, the moisture content (m/m) was about 6.0%, 2.5%, 0.4% and 0.1%, respectively. As shown in Table 1, Flemish leaching limit values are exceeded for Cu, Zn, Pb, Cd, Ni, Ba, Mo and Sb. For the latter three elements, however, limit values have only been informally proposed. The leaching concentrations of Cu, Zn and Pb – the three metals mostly exceeding limit values – were initially exceptionally high for this type of bottom ash. Leaching values of different batches of fresh sand fraction usually range from 3 to 7 mg/kg dry matter (DM) for

Cu and from 0.5 to 3 mg/kg DM for Zn and Pb. Cu leaching is the most critical and will therefore be focused on.

Table 2 compares the metal concentrations obtained with the two different leaching tests performed on the sand fraction (stored and 2 weeks carbonated). For Pb and Cu leaching, the difference between the two tests seems important. This is probably due to the heterogeneous character of the sand fraction (see also Table 1), which manifests itself most using the one-stage extraction test (small sample amount). However, as both tests have a similar effect on metal leaching and taking into account the long test duration and the large sample volume needed for the column test, the use of the one-stage extraction test (EN 12457-2) is justified.

3.2. Natural ageing

During natural ageing, the leachate pH of samples of sand fraction gradually decreases from 12.1 to 10.7 (after 3 months). Their moisture content (m/m) decreases from 26.6% (at the start) to 2.4% after 1 week and then gradually decreases further to 2%. The effect of natural ageing on Cu leaching for samples of sand fraction is shown in Fig. 1. Three months of natural ageing is clearly not sufficient for Cu to reach its limit value of 0.5 mg/kg DM in these samples. Moreover, the leaching of Cr increases from 0.2 mg/kg DM to 1.1 mg/kg DM. Leaching of Zn and Pb decreases within the first week to below the limit value. Other (informally regulated) metals such as Mo, Sb and Ba still exceed their limit value after 3 months of ageing.

The gravel fractions show a more fluctuating pH path. During the first week, the moisture contents (m/m) decrease from 5% (Ø 2–6 mm) and 4% (Ø 6–50 mm) to 0.8% and 0.4%, respectively, and then remain constant. Table 3 [16] shows the average leaching values of the two gravel fractions after 3 months of natural

Table 1

Leaching concentrations (mg/kg DM) and leachate pH of fresh bottom ash fractions (October 2003) using the EN 12457-2 extraction test, together with the Flemish limit values (regulated metals and non-regulated metals) for recycling of granular material in construction applications

	Flemish limit value	Sludge fraction (Ø 0–0.1 mm)	Sand fraction (Ø 0.1–2 mm)	Gravel fraction (Ø 2–6 mm)	Gravel fraction (Ø 6–50 mm)
pH		12.9	12.1 ± 0.2	9.7	9.2
Regulated metals					
As	0.8	<0.01	<0.01	<0.01	<0.01
Cd	0.03	**0.035**	<0.01	<0.01	<0.01
Cu	0.5	**217.40**	**38.85 ± 3.39**	**2.40**	**0.72**
Cr	0.5	0.27	0.16 ± 0.06	0.04	0.04
Hg	0.02	n.a.	n.a	n.a.	n.a.
Ni	0.75	**4.03**	0.17 ± 0.06	0.04	0.02
Pb	1.3	**18.78**	**7.62 ± 1.78**	0.09	0.08
Zn	2.8	**21.61**	**3.76 ± 0.79**	0.18	0.20
Non-regulated metals					
Ba	1.6	**7.18**	**7.46 ± 0.53**	**2.11**	1.02
Co	0.25	<0.01	<0.01	<0.01	<0.01
Mo	0.2	**2.41**	**1.12 ± 0.12**	**0.28**	0.18
Sb	0.1	0.08	**0.47 ± 0.20**	**0.67**	**0.59**
Se	0.04	<0.01	<0.01	<0.01	<0.01
V	0.8	0.62	0.54 ± 0.11	0.46	0.18

n.a., not analysed. The values of the sand fraction are given as an average of 15 samples, together with the standard deviation. Measurements exceeding the limit value are in bold.

Table 2
Leaching concentrations (mg/kg DM) and leachate pH of stored (March 2004) and carbonated (during 2 weeks) bottom ash sand fraction obtained by two different leaching tests (NEN 7343 column test and EN 12457-2 one-stage extraction test) together with the Flemish limit values (regulated and non-regulated metals) for recycling of granular material in construction applications

	Flemish limit value	Stored sand fraction		Carbonated sand fraction	
		NEN 7343	EN 12457-2	NEN 7343	EN 12457-2
pH		11.7–12.5	12.1	7.6–8.4	8.6
Regulated metals					
Cu	0.5	**39.22 ± 0.92**	**29.26 ± 1.79**	**7.98 ± 0.41**	**8.14 ± 0.48**
Zn	2.8	**2.97 ± 0.43**	**2.81 ± 0.21**	1.76 ± 0.06	1.63 ± 1.10
Pb	1.3	**12.39 ± 1.10**	**4.8 ± 0.07**	0.09 ± 0.01	0.60 ± 0.71
Cr	0.5	0.02 ± 0.01	0.08 ± 0.02	0.02 ± 0.01	0.05 ± 0.02
Ni	0.75	0.17 ± 0.01	0.12 ± 0.06	0.30 ± 0.04	0.22 ± 0.03
Non-regulated metals					
Mo	0.2	**1.00 ± 0.01**	**0.75 ± 0.02**	**0.72 ± 0.02**	**0.52 ± 0.01**
Sb	0.1	**0.17 ± 0.01**	**0.32 ± 0.03**	**0.98 ± 0.03**	**0.95 ± 0.02**
V	0.8	0.19 ± 0.04	0.23 ± 0.03	0.37 ± 0.01	0.33 ± 0.01
Ba	1.6	**5.19 ± 0.24**	**6.15 ± 0.46**	0.56 ± 0001	1.16 ± 0.23

The values are given as an average of two samples with their standard variation. Measurements exceeding the limit value are in bold.

ageing. As they comply with the limit values after natural ageing, they are used as granular material in foundations.

The results of the natural ageing test to study the carbonation rate as a function of time, are shown in Fig. 2(a). The results after 7 weeks of natural ageing are not given as Fig. 2(a) would become unclear. After 3 months of natural ageing, only the upper
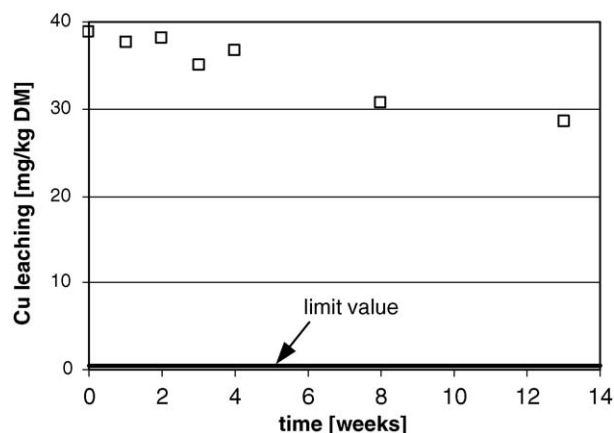

Fig. 1. Cu leaching as a function of time during natural ageing (sand fraction, November 2003–February 2004).

Table 3
Average leaching concentrations (mg/kg DM) of the gravel fractions after 3 months of natural ageing for the period April 2002–May 2003 (at the incinerator plant)

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Flemish limit value	0.8	0.03	0.5	0.5	0.02	0.75	1.3	2.8
Gravel fraction (Ø 2–6 mm)	0.02	<0.01	0.03	0.34	–	0.03	0.03	0.03
Gravel fraction (Ø 6–50 mm)	0.02	<0.01	0.04	0.32	–	0.04	0.04	0.10

4 cm underwent significant carbonation. The modelled result of this natural ageing test is shown in Fig. 2(b). In spite of the many assumptions made (see Section 2.5), the model predicts the trend of pH decrease. As the model only takes into account the carbonation reaction, the correspondence between experimental results and modelling indicates that carbonation is indeed one of the most important reactions in the natural ageing process. However, the simple model cannot predict the experimental results accurately. Besides the limits of the model itself (mainly the assumption of the pH control by $Ca(OH)_2$ dissolution and the assumed effective diffusion coefficient), this implies that also other reactions (for example adsorption on newly formed minerals, complexation, hydrolysis and dissolution/precipitation [3,4,17–20]) must play a role in the ageing process.

3.3. Accelerated carbonation

3.3.1. Laboratory scale experiments

Fig. 3(a) and (b) show the time evolution of the leachate pH and moisture content (m/m) of sludge and sand fraction samples subjected to accelerated carbonation. Within the first 24 h an important pH decrease occurs, afterwards the pH slowly decreases further to around 8.5. The moisture content (m/m) decreases during the first 3 days from 39.6% (sludge fraction) and 26.6% (sand fraction) to 13.8% and 6.5%, respectively, and then remains constant. The overall influence of accelerated carbonation on Cu leaching is significant (Fig. 4): from 40 to 4 mg/kg DM for the sand fraction and from 217 to 21 mg/kg DM for the sludge fraction, with the main decrease taking place within the first 24 h. However, leaching still exceeds the Flemish limit value of 0.5 mg/kg DM. A similar evolution of pH and Cu leaching for the sand fraction is already described elsewhere [21]. Accelerated carbonation has very little influence on the gravel fractions because they consist of more inert material, such as SiO_2, hence the lower leachate pH of the fresh fractions (Table 1).
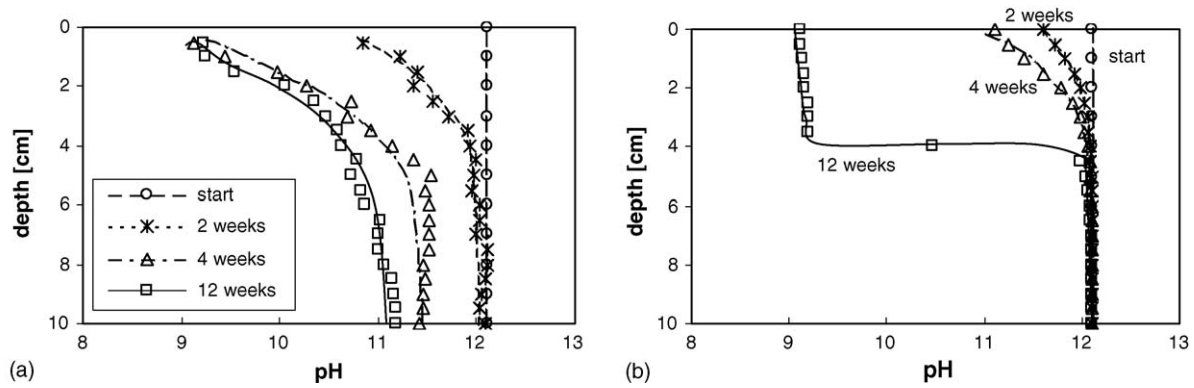
Fig. 2. (a) Experimental results of natural ageing test; (b) modelled results of natural ageing test. The results after 7 weeks are not given.
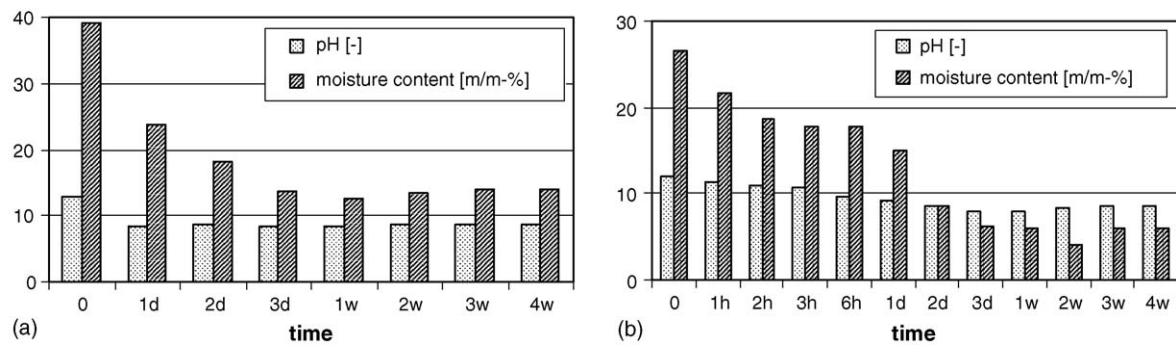

Fig. 3. pH and moisture content as a function of time during accelerated carbonation: (a) sludge fraction, (b) sand fraction.

To explain the change of Cu leaching from samples of sand fraction exposed to accelerated carbonation for different periods of time (Fig. 4), several parameters have to be considered. As carbonation causes the pH to decrease and metal carbonates to form, these two parameters were investigated. Fig. 5 shows the Cu leaching as a function of pH, both for uncarbonated and carbonated (during 4 weeks) sand fraction. The experimental results in the pH range from 8 to 12 suggest that both pH decrease and carbonate formation are important factors. However, as calculations with the geochemical speciation program Visual Minteq cannot explain Cu leaching completely [18], other factors must be taken into account. Complexation with organic material [22–24] and sorption to Al-/Fe-oxides [22,25]

are two factors that are reported to influence Cu leaching but that are not considered in the Visual Minteq calculations. These factors are still under investigation.

For the other regulated metals (Zn, Pb, Ni and Cr), the limit values are complied with within the first hours of accelerated carbonation. For the amphoteric elements Zn and Pb, this is caused by the pH decrease as a consequence of carbonation. Both pH decrease and carbonate formation cause Ni leaching to decrease. Cr, forming chromate, behaves as oxyanion and has a specific leaching behaviour [10].

3.3.2. Use of stack gas from the incinerator

Accelerated carbonation was also performed using stack gas from the incinerator. As already mentioned in Section 2.4 the
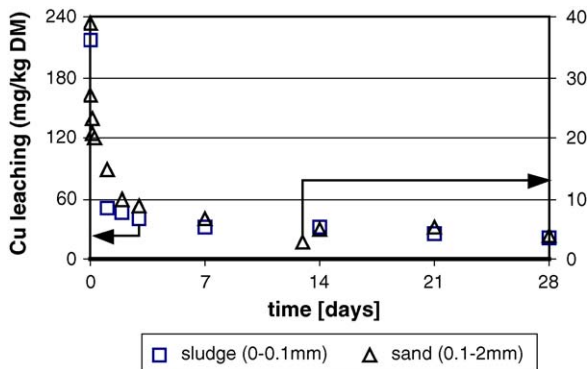

Fig. 4. Cu leaching as a function of time during accelerated carbonation (sand and sludge fraction, October 2003).
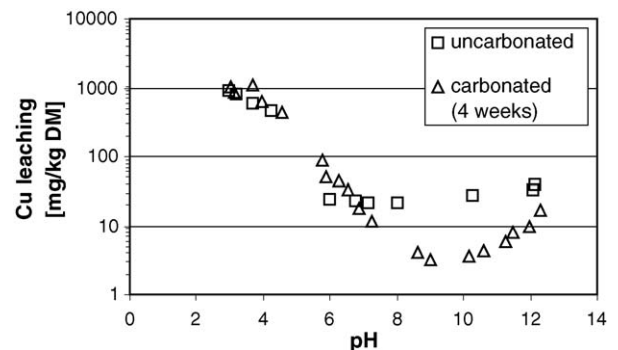

Fig. 5. pH-variation test of Cu (sand fraction).

Table 4
Experiment at the incineration plant (use of stack gas) vs. CO_2 chamber: pH and leaching of metals (mg/kg DM) as a function of time

Time (days)	pH	Cu	Cr	Ni	Pb	Zn	Ba	Mo	Sb	V
Incineration plant										
0	11.9	36.0	0.2	0.1	5.3	2.7	7.6	1.9	0.7	0.2
1	10.5	16.0	0.2	0.1	0.1	0.2	1.4	1.2	1.9	0.3
2	10.4	15.8	0.2	0.1	0.1	0.1	1.4	1.2	1.9	0.3
3	9.7	13.2	0.1	0.2	0.1	0.2	1.3	1.2	1.8	0.3
7	9.6	4.6	0.2	0.1	1.0	1.6	0.8	0.2	1.3	0.2
14	9.1	3.8	0.2	0.1	0.3	0.8	0.9	0.2	1.4	0.1
21	8.9	5.4	0.1	0.1	0.7	1.4	0.7	0.1	1.2	0.1
28	8.6	4.3	0.1	0.1	0.3	0.7	0.5	0.1	1.3	0.1
CO_2 chamber										
0	12.5	38.0	0.2	0.2	8.3	3.8	7.5	1.1	0.5	0.6
1	9.2	14.8	0.3	0.3	1.4	2.9	2.1	1.1	2.3	1.2
2	8.7	9.9	0.1	0.1	0.1	0.4	1.6	0.9	1.6	0.9
3	7.9	8.9	0.2	0.2	1.2	2.4	1.9	0.8	1.4	0.9
7	7.9	6.8	0.1	0.2	0.2	0.7	1.5	0.7	1.2	0.8
14	8.4	5.1	0.1	0.2	0.1	0.6	1.4	0.7	0.9	0.8
21	8.6	5.2	0.1	0.1	0.2	0.8	1.5	0.7	1.1	0.8
28	8.6	4.0	0.1	0.1	0.1	0.5	1.3	0.6	0.8	0.7

Fig. 6. Accelerated carbonation (moving belt) (after [8]).

supplied bottom ash is totally carbonated and stabilized before reuse [26].

3.3.3. Study of the carbonation rate

The practical set-up for accelerated carbonation can be achieved in different ways. In Fig. 6, one option (leading the stack gas in counter-current over a layer of bottom ash on a moving belt) is shown. In this process several parameters influence the carbonation rate, namely the thickness of the layer of bottom ash, the velocity of the moving belt (or the residence time of the bottom ash on the belt) and the CO_2 percentage in the flue gas. For this reason, the study of the carbonation rate in a 10 cm thick sample of sand fraction was performed. After one week of accelerated carbonation, the total sample was carbonated (Fig. 7(a)).

Modelling of this test would allow variation of the different parameters and calculation of the optimal parameters without having to perform new experimental tests. Fig. 7(b) shows the modelled results of the accelerated carbonation test. As in the case with the natural ageing test, the model predicts the trend of pH decrease, however, not accurately. The deviations from experimental and modelled results appear to be particularly relevant for the higher carbonation degrees, which may probably be explained by the assumption of pH control by $Ca(OH)_2$ dissolution. Presumably, better prediction by the model could be obtained if the amount of carbonate species formed instead of pH was taken as the control variable of the carbonation process. However, also other assumptions made, mainly the constancy of the $Ca(OH)_2$ concentration in the reaction term R_{CO_2} (to simplify the model as no numerical integration methods were needed), the assumed effective diffusion coefficient, taking into account only the global reaction of CO_2 with $Ca(OH)_2$ and considering the reaction rate constant as degree of freedom limit the use of this model. Hence calculation of optimal parameters is not yet performed in this stage of the development of the model.

stack gas had a high percentage of humidity (21 vol.%), which resulted in condensate formation on the bottom ash. Heavy metal concentrations and pH were measured in these condensate samples. The pH ranged from 7.0 to 7.9. Heavy metal concentrations were high in the first condensate sample, but the total concentration of each of the heavy metals decreased to less than 1 ppm in the subsequent samples and thus negligible. As the first sample consisted of only 120 ml, it was not taken into account either. However, this condensate problem has to be dealt with when one wants to perform accelerated carbonation with the stack gas as it causes an amount of wastewater. Collecting the water in the stack gas before leading it over the bottom ash would be an appropriate solution. Due to the water in the stack gas, the moisture content (m/m) in the samples periodically taken from the column increases from 26.6% at the start to 33.7% after 1 day and 36.2% at the end of the experiment (4 weeks). The Table 4 shows the evolution of pH and Cu leaching of the different samples of sand fraction (without taking into account the condensate samples) in comparison with the results obtained in the CO_2 chamber. The decrease of pH and Cu leaching is slightly faster in the CO_2 chamber, but the results appear comparable. This conclusion is also applicable to the leaching of the other regulated metals (also shown in Table 4). Although accelerated carbonation cannot yet improve the leaching characteristics of the sand fraction enough to comply with Flemish regulation, the availability of CO_2 containing gas is an important advantage of this treatment technique from an industrial point of view. Besides, other benefits could be considered if the (totality of) bottom ash was treated using stack gas from the incinerator: a part of the CO_2 would be removed from the stack gas (Kyoto Protocol) and the accelerated carbonation treatment would significantly reduce storage duration. Moreover, it would ensure that the
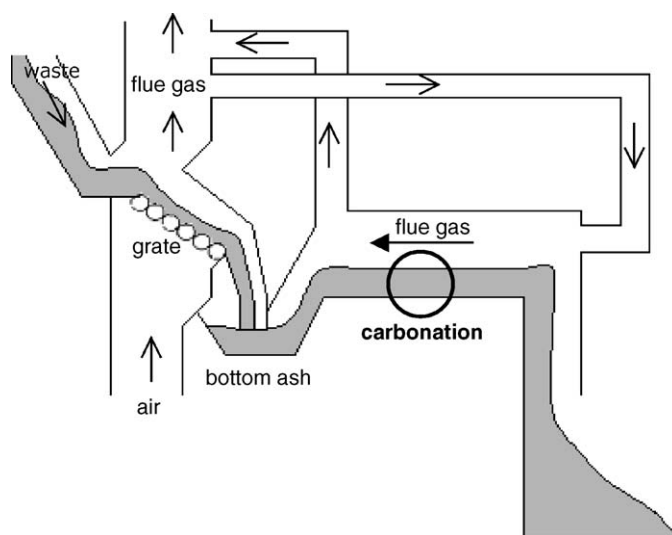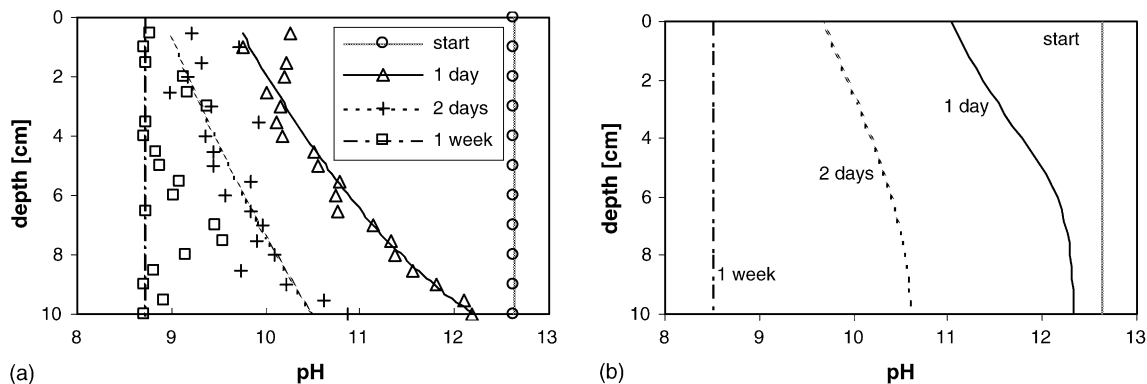
Fig. 7. (a) Experimental results of accelerated carbonation test; (b) modelled results of accelerated carbonation test.

4. Conclusions

Leaching concentrations of Cu, Zn, Pb, Mo, Sb and Ba – with Cu being the most critical – are too high in different size fractions of bottom ash in Flanders.

Three months of natural ageing is an adequate treatment for the gravel fractions in view of recycling. However, it is not sufficient for the sand and sludge fraction to comply with the limit values. Cu and Cr leaching still exceed the limit value after this treatment. Accelerated carbonation may have potential for the treatment of the bottom ash sand and sludge fraction. Cu leaching decreases significantly within 4 weeks of accelerated carbonation, with the main decrease taking place within the first 24 h, but the limit value is not complied with. However, all other regulated metals besides Cu, do reach the limit value using the accelerated carbonation technique. It has been shown that accelerated carbonation can be performed using stack gas from the incinerator. Thus, the bottom ash quality is improved and at the same time the emission of the greenhouse gas is lowered. Possibly a combination of accelerated carbonation with other techniques (e.g. extraction or heating) in an integrated treatment installation could result in a Cu leaching to below the limit value.

The carbonation reaction was modelled, to study the velocity of carbonation in view of an industrial application. In spite of the many assumptions made (pH control by Ca(OH)$_2$ dissolution, effective diffusion coefficient derived from concrete materials, consideration of the reaction coefficient as a degree of freedom), the model shows that carbonation is indeed a major reaction in the ageing process of bottom ash. The model shows a pH decrease similar to the experimental results, but the assumptions provided above need to be modified or removed for the model to become applicable.

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