

Stable isotope evidence for the atmospheric origin of CO₂ involved in carbonation of MSWI bottom ash

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Abstract

Stable isotopes were used to constrain the origin of CO₂ involved in the ageing process of municipal solid waste incineration (MSWI) bottom ash under open-air conditions. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of CaCO₃ occurring in MSWI bottom ash samples of variable age and the $\delta^{13}\text{C}$ of the residual organic matter content were measured, and laboratory assessments made of the isotopic fractionation accompanying CaCO₃ neo-formation during accelerated carbonation experiments of bottom ash or pure lime with atmospheric or industrial CO₂. The results indicate that stable isotopic compositions exhibited by fresh and aged bottom ash samples reflect non-equilibrium processes resembling those described in the carbonation of concrete and mortar. They also lead to conclusions on the prevalent involvement of atmospheric CO₂ in the open-air carbonation of MSWI bottom ash.

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1. Introduction

The stability of municipal solid waste incineration (MSWI) residues has been extensively studied due to their widespread application in roadbeds, embankments and sub-base constructions, namely in The Netherlands, Denmark and France (Van Zomeren and Comans, 2004; Johnson et al., 1996; Piantone et al., 2004). In Europe, the definition and implementation of regulatory leaching tests for solid waste are on-going tasks. According to the ENV 12920 Standard, and using standardized leaching tests, a new approach needs to be applied

that, rather than setting pre-defined threshold values above which waste cannot be recycled, relies on the development of highly diagnostic predictive tests based on an assessment of the use scenarios. This requires detailed knowledge of the main physical and chemical changes and reactions involved in weathering transformations occurring during the ageing process of MSWI bottom ash.

Regarding ageing of Ca oxide-bearing residues generated in high temperature incinerators, the dominant process is the so-called carbonation process (Comans and Meima, 1994; Zevenbergen and Comans, 1994; Chandler et al., 1997; Meima and Comans, 1997) taking place as a result of the high chemical reactivity of Ca oxide (quick lime, CaO). Hydration of incineration residues induces the conversion of CaO to lime (Ca(OH)₂, portlandite),

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which is itself transformed into calcium carbonate (CaCO_3 , calcite). This process improves the environmental quality of the end material by lowering the original pH (from pH 12–13 to 8–10, near to those of CaCO_3 stability) and immobilising Pb and Zn.

To date, there is ample evidence that conducting carbonation tests on quick-lime-rich residues prior to leaching tests provides a reasonably acceptable simulation of the main ageing process. It is generally assumed that carbonation occurring in MSWI bottom ash as a result of open-air ageing on platforms is exclusively initiated and maintained by atmospheric CO_2 . However, this has not yet been clearly demonstrated and is still open to debate. CO_2 produced as a result of bacterial decomposition of the residual organic matter present in the MSWI bottom ash (below 5% for recyclable MSWI bottom ash and generally depending on efficiency of combustion; Belevi et al., 1992; Pavasars, 2000; Duge-nest et al., 1999; Ferrari et al., 2002) could also contribute to carbonation reactions.

Because CO_2 produced by aerobic biodegradation of petroleum-derived organic matter and also cellulose, lignin, is expected to be markedly depleted in ^{13}C relative to atmospheric CO_2 ($\delta^{13}\text{C} \approx -25\%$ compared to $\delta^{13}\text{C} \approx -7\%$; Hoefs, 1980), the predominant source of CO_2 involved in the carbonation of MSWI bottom ash may be recorded in the isotopic composition ($\delta^{13}\text{C}$) of newly formed CaCO_3 .

The main goal of this study was to investigate the use of stable isotopes to unravel the origin of the CO_2 involved in the ageing process of MSWI bottom ash under open-air conditions. The authors report herein the C and O isotope compositions of carbonates occurring in MSWI bottom ash samples of different ages and from various locations in France. The ageing process was also investigated through a series of accelerated carbonation experiments carried out on MSWI bottom ash samples as well as pure lime, in the presence of atmospheric or industrial CO_2 . The results provide constraints on isotopic fractionations accompanying the carbonation process.

2. Samples and methods

2.1. Bottom ash samples

The MSWI bottom ash samples used in the study (Table 1) came from 13 different sites located in France, mostly in the Parisian area. They were collected from incinerator refuse bottom ash pits after water quenching (F series), open-air maturation

platforms of variable ages (S and Y series) and road bases (T series). In all, 24 samples were gathered and represent ageing-maturation times ranging from a few days (incinerator output) to over 20 a (roadbed).

The field samples (around 50 kg) were protected from atmospheric carbonation in sealed canisters. They were dried at moderate temperature (50 °C), then crushed to 4 mm size after sorting any scrap Fe with a magnet, and then divided in a riffle splitter to obtain laboratory samples (around 3 kg).

The mineralogy of the studied samples is described in Piantone et al. (2004) and comprises the three classes of minerals typically encountered in MSWI bottom ash (Eusden et al., 1999): (i) unmelted refractory minerals and glass from household waste (quartz, feldspar, bottle glass, plaster, etc.); (ii) high-temperature minerals and glass from the melting induced by local high-temperature spots formed during waste combustion (quenched glass—bubbled or not, high-temperature Ca-bearing silicates, alumino-silicates, etc.); (iii) low-temperature minerals newly formed during ageing after bottom ash quenching, and essentially composed of carbonates, sulphates and/or ettringite, oxalates, Al and Fe hydroxides and zeolites. Further details on the mineralogy of the MSWI bottom ash samples studied and the associated literature can be found in Piantone et al. (2004).

Determinations of pH were done according to the NF ISO10390 procedure, by combining 5 g of MSWI with 50 mL of distilled water (decarbonated by boiling), followed by thorough mixing (1 h) and settling (1 h) before measurements.

2.2. Experimental accelerated carbonation

A subset of six samples (S1, S2, S4, F1, F2, F3) was used to perform experimental accelerated carbonation in the laboratory under controlled conditions according to Bodénan et al. (2000). This was done with the aim of investigating induced shifts in isotopic composition of CaCO_3 . Due to the presence of calcite in the samples and as the proportion of newly formed calcite may be very small compared to the initial MSWI content, it was necessary to use CO_2 gas with an isotopic composition significantly different to atmospheric CO_2 in order to monitor the carbonation process unambiguously. The procedure of Bodénan et al. (2000) was followed, with 1500 g of sample placed in a confined cell circulated with industrial CO_2 , at a pressure slightly above atmospheric pressure (1.2 atm.), for 6 h,

Table 1
Organic C content, calcite content, pH, and isotopic composition of calcite for untreated samples of naturally aged MSWI bottom ash

Ech.	Storage	Organic carbon, %	Calcite, %	pH	$\delta^{13}\text{C}/\text{PDB} \pm 0.1, \text{‰}$	$\delta^{18}\text{O}/\text{PDB} \pm 0.1, \text{‰}$	$\delta^{18}\text{O}/\text{SMOW} \pm 0.1, \text{‰}$
<i>F series</i>							
F1	Freshly produced	1.2	7.5	11.2	-17.4	-12.5	17.9
F2	Freshly produced	0.9	8.2	11.9	-14.8	-12.5	18.2
F3	Freshly produced	0.7	11.7	13.1	-12.1	-11.1	19.0
F4	Freshly produced	0.4	4.4	12.7	-8.4	-9.7	20.9
F5	Freshly produced	0.7	9.2	12.7	-11.2	-11.7	18.8
F6	Freshly produced	1.0	7.6	11.4	-14.8	-10.6	19.9
<i>S series</i>							
S1	>5 year old	1.1	8.2	8.7	-15.1	-11.6	20.4
S2	1–5 year old	0.9	7.5	9.9	-15.8	-11.1	19.5
S3	1–5 year old	0.7	5.8	11.2	-15.6	-12.1	18.4
S4	1–5 year old	0.1	10.0	12.8	-11.5	-10.9	19.6
S5	1–5 year old	1.3	13.1	nd	-13.1	-10.8	19.8
<i>Y series</i>							
Y1	<3 month old rehandled	2.4	20.9	10.9	-17.3	-13.8	16.6
Y2	<3 month old rehandled	3.4	17.5	11.6	-16.9	-14.6	15.8
Y3	<3 month old surface	3.9	26.0	10.1	-16.5	-13.6	16.8
Y4	<3 month old internal	3.9	21.5	11.4	-17.8	-12.6	17.9
Y5	<3 month old outer deposit	2.7	40.2	9.7	-22.0	-13.9	16.6
Y6	<3 month old	1.6	20.8	9.0	-18.0	-13.2	17.3
Y7	<3 month old	2.6	21.0	10.6	-15.7	-13.2	17.2
Y8	<3 month old	3.4	21.1	12.2	-15.0	-12.9	17.5
Y9	<3 month old	2.3	20.7	11.6	-15.5	-14.2	16.2
Y10	<3 month old	2.8	33.8	10.9	-18.0	-14.2	16.2
Y11	3 1/2 year old rehandled	3.0	17.9	10.6	-13.7	-10.9	19.6
<i>T series</i>							
T1	20-year old basement	0.9	8.2	9.0*	-18.3	-9.5	21.1
T2	20-year old basement	1.2	11.7	8.8*	-18.9	-8.9	21.7

nd, not defined.

* Data from François (2001).

exceeding the optimum time of the 3 h required to complete the reaction (Fig. 1). This protocol was applied to samples F1, F2, F3, S1 and S2. In the experiment involving sample S4, compressed air (instead of pure CO_2) was used and the experiment duration was extended to 14 days.

Similar experiments of accelerated carbonation were carried out on pure lime $[\text{Ca}(\text{OH})_2]$. The latter was synthesised by hydration of commercial calcium oxide (commercial crushed calcium oxide from marble, Merck® ref. 1.02109.1000). Due to the extreme instability of quick lime in open-air conditions, the commercial powder was first decarbonated beyond the stability limit for CaCO_3 and lime (900 °C for 4 h). It was then cooled in an inert atmosphere (dry N_2) and 5 g were hydrated for 2 h with 25 mL of deionised water (milliQ®) previously degassed from dissolved CO_2 (by bubbling with N_2). At every step of the synthesis procedure, a sample was collected, dried under N_2 atmosphere and

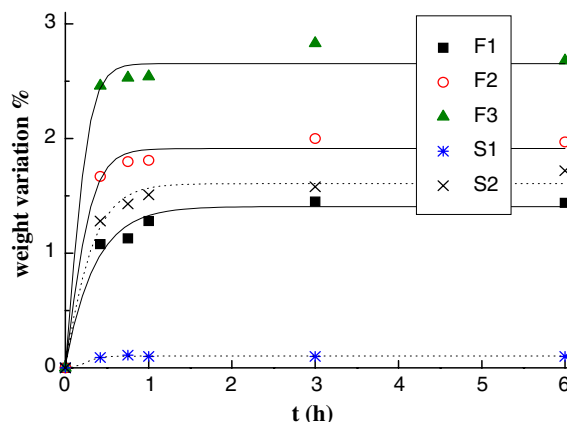


Fig. 1. Illustration of the weight variations for a set of selected samples of bottom ash exposed to industrial CO_2 . Keys: F1–F3, fresh samples derived from the incineration plant; S1 and S2, stocked samples from an old stock ageing platform.

Table 2

Experimental conditions, calcite content and isotopic composition of calcite following accelerated carbonation tests on MSWI bottom ash samples and pure lime

Ech.	CO ₂	Time	Calcite, %	$\delta^{13}\text{C}/\text{PDB} \pm 0.1, \text{‰}$	$\delta^{18}\text{O}/\text{PDB} \pm 0.1, \text{‰}$	$\delta^{18}\text{O}/\text{SMOW} \pm 0.1, \text{‰}$
<i>F series</i>						
F1	Industrial 1	6 h	11	-29.4	-15.0	15.4
F2	Industrial 1	6 h	12	-27.0	-13.0	17.5
F3	Industrial 1	6 h	15	-27.6	-15.5	14.8
<i>S series</i>						
S1	Industrial 1	6 h	8	-16.0	-10.8	19.7
S2	Industrial 1	6 h	9	-26.2	-11.2	19.4
S4	Compressed air	342 h	28	-15.0	-12.5	18.0
<i>Portlandite</i>						
CAO-6	Atmospheric	11 days	nd	-16.7	-17.9	12.4
CAO-10	Atmospheric	14 days	nd	-11.2	-16.2	14.2
CAO-11	Atmospheric	17 days	nd	-18.3	-17.6	12.7
CAO-12	Atmospheric	17 days	nd	-18.4	-17.3	13.1
CAO-13	Atmospheric	17 days	nd	-20.5	-17.0	13.3
CAO-4	Industrial 1	1 h 30 min	nd	-56.8	-29.6	0.4
CAO-8	Industrial 2	4 h	nd	-49.4	-33.9	-4.1

analysed by IR spectrometry for control purposes. The Ca(OH)₂ compound obtained in this manner was submitted to two different procedures of experimental accelerated carbonation (Table 2).

- (i) In experiments CAO-6, CAO-10, CAO-11 to 13, carbonation was carried out by bringing the sample into contact with air (i.e. atmospheric CO₂) for 11–17 days. For the first tests (CAO-6 and CAO-10) the solid and humid synthetic lime was collected on a filter (Durapore GVWP 0.22 μm , diameter 45 mm) and simply exposed to ambient air. Later, Ca(OH)₂ samples were placed in Petri dishes (diameter 90 mm) in a reservoir continuously flushed by humidified air.
- (ii) In experiments CAO-4 and CAO-8, a lime milk was submitted to an ascending flow of industrial CO₂ gas for 1 h 30 min (CAO-4) and 4 h 30 min (CAO-8), then filtered and dried in an N₂ atmosphere. The two experiments used two different industrial CO₂ gases referred to as no. 1 and no. 2.

The progress of the accelerated carbonation experiments, conducted on both MSWI bottom ash samples and pure lime, was checked by FTIR (Fourier transformed infra red) analysis of samples before and after treatment using a Bruker Equinox spectrometer, with a spectral resolution of 4 cm⁻¹. The high sensitivity of IR spectrometry provided an excellent means for monitoring the transformation of lime

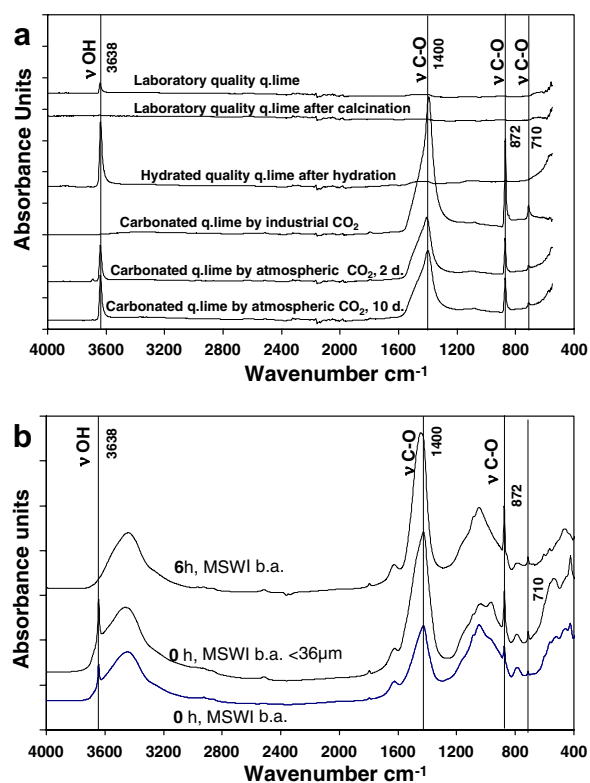


Fig. 2. Monitoring carbonation effects on (a) lime and (b) MSWI bottom ash by FTIR (Fourier transform infrared spectroscopy), S4 sample. Lime is identified by the ν OH band (3638.8 cm⁻¹) and calcite by the ν C–O bands at 1400.6, 872.0 and 710.0 cm⁻¹. Each spectrum represents the cumulative addition of 32 acquisition scans.

(η OH band at 3638.8 cm^{-1}) to CaCO_3 (η C–O bands at 1400.6 , 872.0 , 710.0 cm^{-1}) during experimental carbonation (Fig. 2a and b).

2.3. Organic carbon analysis

Organic C content was determined on bulk samples in accordance with the ISO 10694 Standard (1995). Typically, a quantity of 250 mg of sample was decarbonated in boiling 20% HCl. The insoluble residue was combusted in air at high temperature (above $900\text{ }^\circ\text{C}$), and the resulting C was measured as CO_2 by IR spectrometry using a LECO CS125 detector. The precision is $\pm 10\%$ for a total organic C content of about 1%.

2.4. Isotopic analysis of carbonates and organic carbon

Carbon and O isotope compositions of carbonates were determined according to McCrea (1950). Samples were digested in concentrated anhydrous phosphoric acid (H_3PO_4 , 100%) under vacuum at $25\text{ }^\circ\text{C}$ for 4 h. The CO_2 resulting from carbonate dissolution was purified by conventional cryogenic techniques and the isotopic ratios were measured on a Finnigan MAT 252 mass spectrometer, using reference CO_2 gas calibrated against the international standard NBS19. In the following description, the results are expressed in δ units (‰) and reported against the international PDB and SMOW standards (Pee Dee Belemnite for $\delta^{13}\text{C}$ and Sea Mean Ocean Water for $\delta^{18}\text{O}$). The analytical uncertainty on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ determinations is respectively $\pm 0.5\text{‰}$ and 0.2‰ .

Isotopic analysis of CaCO_3 was conducted on bulk powders. The small amount of organic matter present in the samples was previously verified so as not to affect the accuracy of the isotopic data on three test samples. Two MSWI bottom ash samples, containing 0.8% and 1.1% organic C, were treated with Na hypochlorite to remove the organic matter. The same treatment was also applied to one pure CaCO_3 standard. For the three test samples, the isotopic compositions measured before and after treatment were identical.

The possible presence of minor amounts of carbonate other than CaCO_3 , potentially capable of reacting with phosphoric acid during the 4-h digestion period, was investigated. Five samples (F1, F2, F3, S1, S2) were submitted to a prolonged acid digestion of 24 h in order to promote extensive dissolution of any non-calcitic carbonate. The isotopic

compositions determined following 4-h and 24-h digestion protocols are identical or very close (within 0.4‰), indicating that non-calcitic carbonates, if present, are not likely to significantly affect isotopic determinations for CaCO_3 .

Phosphorolysis of bulk samples may generate gases other than CO_2 produced by carbonate dissolution, in particular SO_2 produced from sulphides or sulphates and N_2O from nitrous species, which may interfere with isotope measurements. The results of experiments specifically conducted with SO_4 (BaSO_4) and NO_3 ($\text{NH}_4(\text{NO}_3)$) indicate that the acid digestion protocol used in the study did not introduce any artefact in O isotope determinations.

The isotopic determinations presented in this paper were performed on aliquots of 60–120 mg of untreated bulk dried samples, ground to $<80\text{ }\mu\text{m}$ (F, S, T series) or $<50\text{ }\mu\text{m}$ (Y series). The CaCO_3 assays reported in Tables 1 and 2 were derived from CO_2 yields after 4 h acid digestion at $25\text{ }^\circ\text{C}$ (based on experimental calibration). The data acquired are consistent with CaCO_3 assays derived from bulk sample calcimetry.

The isotopic composition of organic C was determined on the two samples (Y3, Y4) exhibiting the highest organic C contents (4%). Samples were first treated with HCl 5 N to remove calcite, and then filtered, washed with distilled water and dried. An amount of $300\text{ }\mu\text{g}$ of calcite-free bulk sample was then converted to CO_2 by combustion for isotopic determinations, using an on-line coupled EA/CF-IRMS Thermo Finnigan unit. Calibration of the unit was done by use of carbonate and oil international standards (NBS18, NBS 19 and NBS 22).

3. Results and discussion

3.1. Raw MSWI bottom ash samples

The organic C content, CaCO_3 content, pH and isotopic composition of CaCO_3 of the 24 untreated MSWI bottom ash samples investigated are compiled in Table 1. The $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ values are shown in Fig. 3, along with isotope compositional fields reported in the literature for CaCO_3 from various relevant contexts.

The samples studied yielded $\delta^{13}\text{C}$ values ranging from -8‰ to -22‰ , averaging $-15.6\text{‰} \pm 2.9\text{‰}$, and $\delta^{18}\text{O}$ values between $+15\text{‰}$ and $+22\text{‰}$, averaging $18.7\text{‰} \pm 1.7\text{‰}$. Samples within a same age range (i.e. in a same series) have rather consistent isotopic compositions, with ranges in $\delta^{13}\text{C}$ and

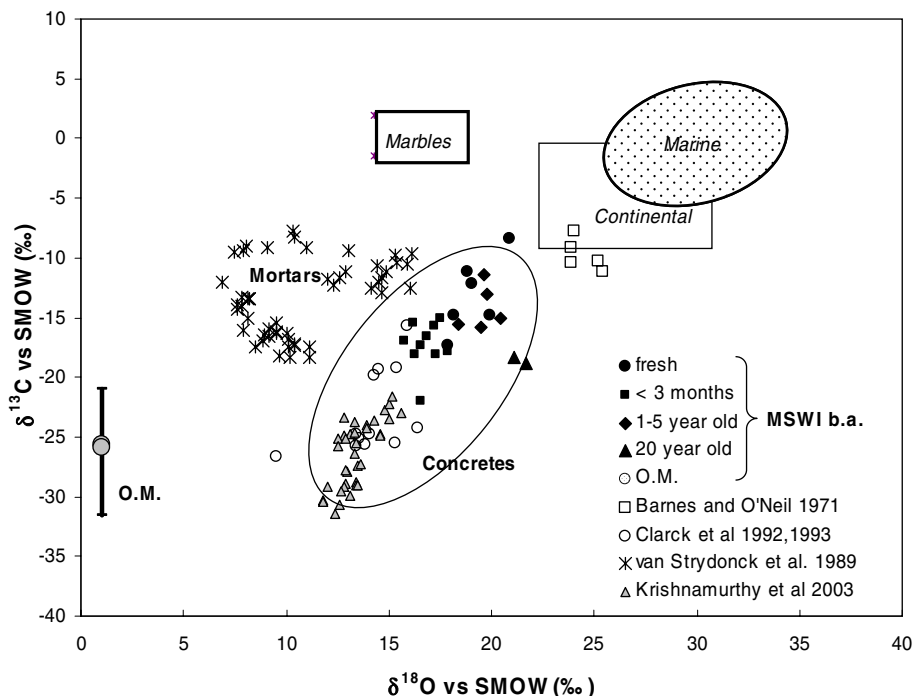


Fig. 3. Isotopic compositions of calcite in naturally aged MSWI bottom ash samples and comparison with reported $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values for carbonates in relevant natural and artificial contexts: marine and continental carbonates (Carpenter and Lohmann, 1995; Faure, 1986; Mayayo et al., 1996), marbles (metamorphosed limestones) (Hecht et al., 1999; Faure, 1986), vein filling carbonates from Maqarin (Clark et al., 1992, 1993), travertines (Barnes and O'Neil, 1971) from alkaline springs, carbonates from mortars (Van Strydonck et al., 1989) and concretes (Krishnamurthy et al., 2003). The $\delta^{13}\text{C}$ of organic C in 2 Y series samples are reported (grey circles) as well as the isotopic composition of residual organic matter potentially present in the samples (O.M., Bird and Gröcke, 1997; Deines, 1980).

$\delta^{18}\text{O}$ values generally not exceeding $\approx 7\text{‰}$ (except for $\delta^{13}\text{C}$ values of F series samples, which vary by over $\approx 9\text{‰}$). The isotopic domains defined for each of the four age series show significant overlap. Fresh and intermediate-age (1–5 y) samples have identical isotopic compositions ($-8\text{‰} < \delta^{13}\text{C} < -17\text{‰}$; $18\text{‰} < \delta^{18}\text{O} < 21\text{‰}$). Recent (<3 months) and old (20 y) samples show, respectively, the lowest (16–18‰) and highest (21–22‰) $\delta^{18}\text{O}$ values, and slightly lower $\delta^{13}\text{C}$ values (-22‰ to -15‰) on average than other samples (-17‰ to -8‰) (Fig. 3). It is noted that the highest $\delta^{13}\text{C}$ value in the set of data is exhibited by the recent sample F4, and the lowest value by sample Y5, which represents the carbonate crust deposited/newly formed at the surface of the ageing MSWI bottom ash (Table 1). No particular age trend is apparent in the isotope data (Fig. 3). In addition, there is no significant correlation between CaCO_3 isotopic composition and either organic C content or CaCO_3 content for the samples studied.

The $\delta^{13}\text{C}$ values of residual organic C measured for two samples of MSWI bottom ash (Y series)

are identical, averaging $-25.7\text{‰} \pm 0.3\text{‰}$ PDB, and consistent with what one might expect for the residual, burned or unburned, organic matter (cellulose or lignin) in MSWI bottom ash (see below). There is no distinct relationship between pH and isotopic signature, but one notes that samples from the fresh series exhibit a positive correlation between $\delta^{13}\text{C}$ and high pH values (11–13) (Table 1).

Calcium carbonate in MSWI bottom ash exhibits isotopic composition distinct from typical marine, continental and metamorphic calcium carbonates, in particular due to more negative $\delta^{13}\text{C}$ values (Fig. 3). In contrast, the field of CaCO_3 isotopic composition defined by the MSWI bottom ash samples studied falls within the $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ domain reported by Létolle et al. (1990) for carbonates found in weathered concretes. In addition, it fits in well with the positively-sloped trend defined by carbonates newly formed in (hyper-)alkaline conditions and/or in the presence of mineral phases such as portlandite-ettringite (Barnes and O'Neil, 1971; Létolle et al., 1990; Clark et al., 1992, 1993; Macleod et al., 1991; Krishnamurthy et al., 2003) (Fig. 3).

This observation is consistent with the fact that MSWI behaves as concrete during carbonation. The bottom ash often contains significant amounts of cement phases, such as lime, ettringite, CSH [calcium silicate hydrate gel] and stratlingite (Speiser et al., 2000; Delville, 2003), which are typical of concrete and mortar, and induce the development of highly alkaline pHs.

The $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ values measured for CaCO_3 newly formed in the fresh and aged MSWI bottom ash samples of this study are not as low (in particular as far as $\delta^{13}\text{C}$ values are concerned) as those of carbonates developing on concrete constructions and described in Macleod et al. (1991) and Krishnamurthy et al. (2003). They also differ, particularly the $\delta^{18}\text{O}$ values, from isotopic compositions reported by Van Strydonck et al. (1989) for carbonates formed in lime mortars as a result of hardening processes.

3.2. Experimental carbonation of MSWI bottom ash

Calcium carbonate abundance and isotopic composition of the six MSWI bottom ash samples submitted to accelerated experimental carbonation in the laboratory are compiled in Table 2 and presented in Fig. 4. Most samples show an increase in

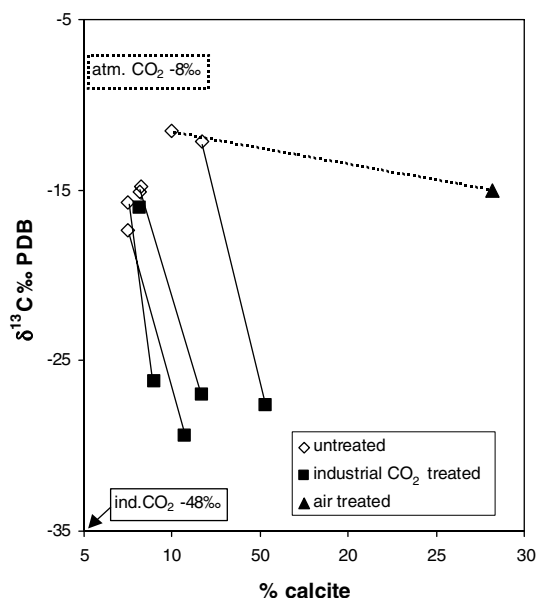


Fig. 4. Plot of $\delta^{13}\text{C}$ values as a function of calcite content prior to and after accelerated carbonation experiments performed on MSWI bottom ash samples.

CaCO_3 content of around a few percentage, relative to their untreated counterparts. S4, which was subjected to the longest duration experimental carbonation, shows a very significant increase of 18% in CaCO_3 content (Fig. 4).

Treated samples exhibit CaCO_3 – $\delta^{18}\text{O}$ values identical or similar (i.e. within 2‰) to those of their untreated counterparts (Tables 1 and 2). In contrast, it appears that the main effect of the experimental carbonation treatment is a significant decrease in CaCO_3 – $\delta^{13}\text{C}$ (Fig. 4). $\delta^{13}\text{C}$ values of CaCO_3 in samples treated with industrial CO_2 range from -26‰ to -29‰ , and are 10‰ to 16‰ lower than those of untreated samples (Fig. 4). The only exception to this is sample S1, for which both the amount of CaCO_3 and the $\delta^{13}\text{C}$ value do not change, reflecting a lack of newly formed CaCO_3 in agreement with other results (Bodéan et al., 2000). Sample S4, the experimental carbonation of which was carried out under compressed air, also shows a decrease in $\delta^{13}\text{C}$, but less significant (i.e. 4‰ ; Fig. 4).

The measured $\delta^{13}\text{C}$ reported in Table 2 for treated samples reflects the C isotopic composition of the two generations of CaCO_3 : (1) the primary CaCO_3 , formed on-site as a result of natural ageing and initially present in the untreated sample, with a $\delta^{13}\text{C}$ of around -16‰ (Table 1); and (2) the secondary CaCO_3 , newly formed during experimental accelerated carbonation and which ought to be markedly depleted in ^{13}C relative to primary CaCO_3 so as to explain the lower $\delta^{13}\text{C}$ values of treated samples compared to untreated ones. Mass balance calculations yield $\delta^{13}\text{C}$ values of -55‰ , -53‰ and -82‰ , respectively, for secondary calcite newly formed in experiments involving samples F1, F2 and F3 and industrial CO_2 no. 1 (with $\delta^{13}\text{C} = -48\text{‰}$) and of -17‰ in the experiment involving sample S4 and air CO_2 (with $\delta^{13}\text{C} = -8\text{‰}$). S1 and S2 were not considered in these calculations because the amount of secondary newly formed CaCO_3 in these two samples is extremely low, i.e. $<1.5\%$.

The $\delta^{18}\text{O}$ values measured for CaCO_3 in the treated samples also reflect the mixing of two generations of CaCO_3 . However, they are not very different to those of the untreated samples, in spite of various $\delta^{18}\text{O}$ for industrial CO_2 and atmospheric CO_2 (respectively 13‰ and 41‰). One can conclude that both generations have rather similar $\delta^{18}\text{O}$ values (i.e. within a few ‰) and thus the fractionation factor is very weak.

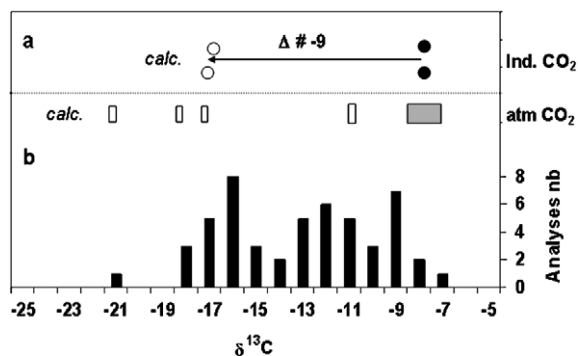


Fig. 5. $\delta^{13}\text{C}$ of calcite formed during experimental carbonation of pure lime with (a) industrial CO_2 (only the fractionation factor Δ is reported on the upper part of the schema in order to minimize the scale) and (b) with atmospheric CO_2 . The histogram derived from literature data (Van Strydonck et al., 1989; Pachiardi et al., 1986) is given for comparison.

3.3. Experimental carbonation of lime

The isotopic compositions of calcium carbonates formed by experimental carbonation of lime are reported in Table 2 and the $\delta^{13}\text{C}$ values are presented in Fig. 5 and compared with literature data. Newly formed CaCO_3 in the presence of air (experiments CAO-6, CAO-10 to CAO-13; atmospheric CO_2 $\delta^{13}\text{C} = -8\text{‰}$) yields $\delta^{13}\text{C}$ values of -20.5‰ and -11.2‰ . These values are within the range of $\delta^{13}\text{C}$ values measured for untreated MSWI bottom ash samples (Fig. 3). Newly formed CaCO_3 in the presence of industrial CO_2 yields $\delta^{13}\text{C}$ values of -56.8‰ for industrial CO_2 no. 1 (experiment CAO-4; $\delta^{13}\text{C}_{\text{CO}_2} = -48\text{‰}$) and -49.4‰ for industrial CO_2 no. 2 (experiment CAO-8; $\delta^{13}\text{C}_{\text{CO}_2} = -40\text{‰}$). These values correspond to an intrinsic Δ ranging around -9‰ . The data obtained in experiments made with industrial CO_2 are more consistent. The scattering of data from experiments in open air may be related to different factors: (i) particle clustering that hampers carbonation; (ii) humidity that controls reactivity of lime and therein kinetics. Thus a larger interface and more humidity (CAO-10 to CAO-13 tests) yields lower $\delta^{13}\text{C}$.

The above results indicate that CaCO_3 formed during experimental carbonation of lime is systematically depleted in ^{13}C relative to the CO_2 used in the reaction, regardless of its C isotopic composition (industrial or air). It implies that CaCO_3 precipitation, under experimental conditions, is accompanied by a systematic negative fractionation of carbon isotopes. The magnitude of this fraction-

ation, expressed as ε ($\varepsilon \approx \delta^{13}\text{C}_{\text{CaCO}_3} - \delta^{13}\text{C}_{\text{CO}_2}$), is in the range of -11.5‰ to -3‰ , respectively -11.5‰ to -3‰ in experiments with air, -9‰ to -8‰ in experiments with industrial CO_2 .

The $\delta^{13}\text{C}$ values of newly formed calcium carbonates by reaction experiments of lime and atmospheric CO_2 in this study are comparable to values reported for calcium carbonates formed during experimental carbonation of mortars (Van Strydonck et al., 1989) or quick lime (Pachiardi et al., 1986) at low temperature over periods of months to years. Fig. 5 is a histogram of $\delta^{13}\text{C}$ values ($n = 51$) reported in Van Strydonck et al. (1989) and in Pachiardi et al. (1986), which illustrates the spreading (-21‰ to -7‰) and the multi-modal character of the distribution. This is interpreted by the authors as reflecting a strong kinetic effect in relation to the variation in quick lime content of the different samples, the rate of CO_2 diffusion and the rate of CaCO_3 precipitation. This kinetic effect induces an isotopic fractionation, which grows with an increasing CaCO_3 precipitation rate. The lowest $\delta^{13}\text{C}$ value of -21‰ (i.e., $\varepsilon \approx -13\text{‰}$) reported by Pachiardi et al. (1986) corresponds to experimental conditions most favourable to the kinetic effect (maximised contact surface between CO_2 and quick lime). One of the modes in Fig. 5 corresponds to an isotopic fractionation of around -9‰ , consistent with the fractionation observed in the present experiments, notably those performed with industrial CO_2 .

3.4. Kinetic fractionation of carbon isotopes

The results of carbonation experiments of lime indicate that CaCO_3 produced by the reaction $\text{Ca}(\text{OH})_2 + \text{CO}_2 \Rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ does not precipitate in isotopic equilibrium. The reaction is accompanied by a negative kinetic fractionation of C isotopes of between -11.5‰ and -3‰ . The observed kinetic fractionation is consistent, in direction and magnitude, with the fractionation documented for CaCO_3 precipitation at low temperature in (hyper)-alkaline conditions on the basis of theoretical and experimental grounds (Barnes and O'Neil, 1971; Turner, 1982; Usdowski and Hoefs, 1990; Létolle et al., 1988, 1990). This kinetic effect has been described and discussed in detail in studies of natural carbonation processes taking place in industrial concretes. Létolle et al. (1988, 1990), in particular, indicate that the kinetic effect is primarily linked to the differential diffusion

of ^{13}C and ^{12}C molecules occurring in the water film at the lime-water interface, resulting in a theoretical fractionation of $\varepsilon \approx -11\text{‰}$. Using this ε value predicts a $\delta^{13}\text{C}$ value of about -19‰ for CaCO_3 precipitated by the reaction of lime and air CO_2 , i.e. very close to some of the values obtained in this study (Table 2).

Overall, it appears that the present experimental results are generally consistent with those of previous published studies and confirms the existence of a kinetic fractionation of C isotopes of around -10‰ between newly formed CaCO_3 and gaseous CO_2 during carbonation of lime in alkaline and low-temperature conditions. The documented kinetic fractionation is symmetrically opposite to equilibrium fractionation, which would be around $+9.8\text{‰}$ according to Deines (1980).

The results of carbonation experiments conducted on MSWI bottom ash samples under similar experimental conditions are in agreement with those performed on pure lime. The secondary CaCO_3 produced in these experiments was depleted in ^{13}C with respect to the CO_2 involved in the carbonation process by several ‰. The mass balance calculation for the single most-efficient experiment (S4 in Table 2), which generated 18% newly formed CaCO_3 , yields a C isotope fractionation of $\approx -9\text{‰}$ ($\varepsilon \approx \delta^{13}\text{C}_{\text{calcium carbonate}} - \delta^{13}\text{C}_{\text{CO}_2} \approx -17 + 8 \approx -9\text{‰}$), similar to that documented in experiments conducted on lime. The authors conclude from this observation that CaCO_3 precipitation in experimental carbonation of MSWI bottom ash takes place with a similar negative kinetic fractionation of C isotopes. This implies that at least some residual lime was present in the MSWI samples used in the experiments (except for S1, the experimental carbonation of that did not produce any CaCO_3).

3.5. Implications for natural carbonation of MSWI bottom ash

Based on the above discussion, it is concluded that the precipitation of CaCO_3 following reaction of quick lime, and hydrated lime with CO_2 during open-air ageing of MSWI bottom ash, must occur with a similar negative kinetic fractionation of C isotopes. This is consistent with the fact that the naturally aged MSWI bottom ash samples investigated in this study show $\delta^{13}\text{C}$ values similar to those of CaCO_3 precipitated in concretes and mortars (Fig. 3) as a result of interactions between lime and atmospheric CO_2 at normal surface tempera-

ture and alkaline pH (Pachiaudi et al., 1986; Létolle et al., 1990).

The $\delta^{13}\text{C}$ value of atmospheric CO_2 varies between -11‰ and -7‰ , depending on the contribution of anthropogenic industrial CO_2 (released by burning fossil fuel into the air) (Mook, 1986; Don-garrà and Varrica, 2002; Widory and Javoy, 2003). Considering a kinetic fractionation of about -9‰ for low temperature–high pH carbonation of lime, CaCO_3 formed from atmospheric CO_2 during open-air ageing of MSWI bottom ash should exhibit $\delta^{13}\text{C}$ values in the range of -20‰ to -16‰ . The range of $\delta^{13}\text{C}$ values measured for all of the samples investigated in this study (-22‰ to -8‰) is largely consistent with the expected range and further supports the conclusion that the prevalent source of CO_2 in the maturation process of MSWI bottom ash is atmospheric CO_2 .

The conclusion that non-equilibrium processes are involved during open-air carbonation of MSWI bottom ash is also supported by $\delta^{18}\text{O}$ data. If it is assumed that CaCO_3 formed during open-air ageing derives its O_2 exclusively from local rain water. Using $\delta^{18}\text{O}$ between -5‰ and -8‰ for rainfall over the different MSWI sites and a mean annual air temperature of $\approx 17\text{ °C}$, $\delta^{18}\text{O}$ values between 22‰ and 25‰ are obtained for equilibrium CaCO_3 , i.e. higher values than the $\delta^{18}\text{O}$ values of $16\text{–}22\text{‰}$ (Table 1) measured for the samples studied. This constitutes additional evidence that non-equilibrium processes control CaCO_3 precipitation during carbonation of MSWI bottom ash, in a manner very similar to that described by Rafai et al. (1991) for carbonation of concrete, and that the O_2 in newly formed CaCO_3 is not provided solely by rainfall water. Furthermore, the scattering of MSWI bottom ash can be explained by the contribution of two processes of carbonation: carbonate precipitation by CO_2 absorption onto hydrated lime (2/3 O_2 provided by atmospheric CO_2 and 1/3 by water (Létolle et al., 1990 and Dietzel et al., 1992) and of Ca precipitated by direct carbonation, such as in alkaline springs from alkaline rocks (Barnes and O'Neil, 1971; Dietzel et al., 1992).

3.6. Implication for organic matter contribution to MSWI bottom ash ageing

The possibility that the apparent evolution towards lower $\delta^{13}\text{C}$ (and $\delta^{18}\text{O}$) values observable in Fig. 3 reflects an increased contribution of ^{13}C -depleted organic C during maturation resulting

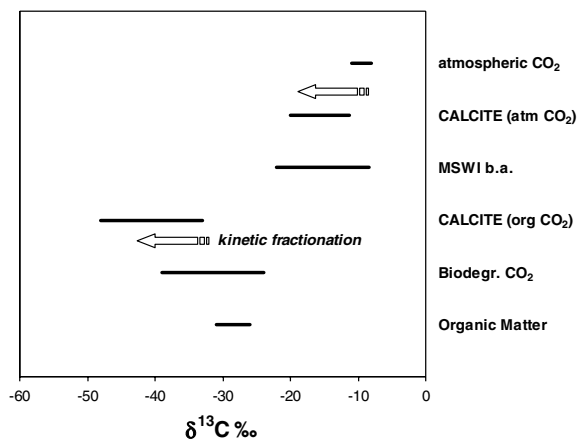


Fig. 6. $\delta^{13}\text{C}$ for different C sources and expected $\delta^{13}\text{C}$ values for calcite formed during natural ageing of MSWI bottom ash. The domain of untreated MSWI bottom ash samples is also reported (MSWI). The arrows depict direction and magnitude of kinetic fractionation of C isotopes during the carbonation process (see text).

from a gradual bacterial-mediated degradation of residual organic matter (Dugonest et al., 1999; Ferrari et al., 2002) is ruled out for the reasons developed below and depicted in Fig. 6.

Any residual organic matter potentially present in the MSWI bottom ash would be expected to show low $\delta^{13}\text{C}$ values, in the range of -31‰ to -25‰ . This is because residual organic matter is essentially composed of vegetation debris made of lignite and cellulose, with $\delta^{13}\text{C}$ values of around -26‰ (Deines, 1980; Macko et al., 1991; Loader et al., 2003) and/or remnants of petroleum-derived products primarily made of carboxylic acids, *n*-alkanes, “phthalate steroids” and PAH’s (polycyclic aromatic hydrocarbons) (Dugonest et al., 1999) with $\delta^{13}\text{C}$ ranging from -31‰ to -28‰ (Lichtfouse et al., 1997; Hirner and Lyon, 1989). This is supported by the measurements performed in this study yielding $\delta^{13}\text{C}$ values of $\approx -26\text{‰}$ for two samples (see Section 3.1). Considering that (i) combustion of organic matter is not expected to modify the $\delta^{13}\text{C}$ values of the residual C beyond $\pm 2\text{‰}$ (Turekian et al., 1995; Bird and Gröcke, 1997) and (ii) C isotope fractionation accompanying bacterial aerobic degradation of organic matter is nil (O’Malley et al., 1994; Mansuy et al., 1997; Mazeas et al., 2002) or small (-5 to -6‰ according to Conrad et al. (1994) and Hall et al. (1999)), any CO_2 evolved from degradation of residual organic matter in the MSWI bottom ash would show markedly negative $\delta^{13}\text{C}$ values, in the range of -39‰ to -24‰ . Since CaCO_3 precipi-

tation under the conditions prevailing in ageing MSWI bottom ash follows a negative kinetic C isotope fractionation (see above), any CaCO_3 formed from organically derived CO_2 would have extremely low $\delta^{13}\text{C}$ values, in an approximate range of -50‰ to -40‰ (Fig. 6). This scenario is not supported by the C isotope compositions reported in this study and is therefore considered unlikely to be of any significance for the samples investigated.

Other, more basic, considerations do not favour an assumed contribution of organically derived CO_2 . Any bacteria present in municipal waste prior to incineration would not survive the high temperature reached in the incinerators (i.e. 1000 °C). Consequently, bacteria would have to be introduced into the incineration residues after cooling. In France, bottom ash residues are cooled by immersion in water. The latter process triggers the instantaneous hydration of CaO to $\text{Ca}(\text{OH})_2$, which rapidly produces very alkaline conditions ($\text{pH} > 11$) as soon as the residue is removed from the water bath. Such a high pH environment does not favour bacterial development and therefore the rate of biotic colonization is unlikely to be sufficiently high to induce pervasive degradation of organic matter shortly after the production of MSWI bottom ash. The rapid kinetics of lime carbonation compared to biotic colonization pleads in favour of inorganic carbonation.

4. Conclusions

The C and O isotope composition of CaCO_3 occurring in MSWI bottom ash was determined for a set of 24 samples of variable age (fresh to 20 a old) and residual organic content (0–4%), in order to constrain the origin of the CO_2 involved in the carbonation process. Stable isotope compositions of CaCO_3 newly formed experimentally during accelerated carbonation of MSWI bottom ash samples and of pure lime in the laboratory under controlled conditions were also determined in order to investigate isotopic shifts potentially induced during carbonation reactions.

The results of this study lead to the following observations.

1. Naturally aged MSWI bottom ash samples show a range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (averaging— $15.6\text{‰} \pm 2.9\text{‰}$ and $18.7\text{‰} \pm 1.7\text{‰}$, respectively), with no distinct correlation with age or organic content.

2. The domain of CaCO₃ isotopic composition determined for the MSWI bottom ash samples investigated is consistent with the δ¹³C and δ¹⁸O values reported for carbonates occurring in weathered concrete and fits the trend defined by carbonates newly formed in alkaline conditions.
3. The stable isotope composition of CaCO₃ newly formed during experimental carbonation of pure lime or MSWI bottom ash is kinetically controlled, and reflects a kinetic fractionation for C isotopes of between −11.5‰ and −3‰ in air and −9‰ relative to the pure CO₂ gas used in the experiment.

The integration of these observations with prior knowledge of kinetic fractionation induced during precipitation of CaCO₃ at high pH leads to the conclusions that (i) CaCO₃ precipitation during natural carbonation of MSWI bottom ash does not occur in isotopic equilibrium, and (ii) recorded C isotopic compositions reflects the atmospheric origin of CO₂ involved in the carbonation process. No evidence was found in support of any significant contribution of CO₂ originating from the degradation of residual organic matter.

The demonstrated atmospheric source of the CO₂ participating in the ageing of MSWI bottom ash must be taken into account for establishing accelerated maturation procedures and associated norms aiming to develop predictive models of maturation.

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