

Ten-year chemical evolution of leachate and municipal solid waste incineration bottom ash used in a test road site

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ARTICLE INFO

Article history:

Received 2 March 2009

Received in revised form 18 July 2009

Accepted 20 July 2009

Available online 28 July 2009

Keywords:

Aggregate

Emission

Environmental impact

Modeling

MSWI

Waste

ABSTRACT

The use of municipal solid waste incineration (MSWI) bottom ash for road and car-park construction is an appropriate solution to reduce their disposal and the consumption of natural materials. In addition to leaching tests, the environmental impact assessment of such a waste recycling scenario critically needs for reliable long-term field data. This paper addresses a 10-year pilot site where MSWI bottom ashes have been used as road aggregates in Northern France (oceanic temperate climate). The paper focuses on the long-term evolution of leachate chemistry and the mineralogical transformations of MSWI bottom ash over 10 years. Data interpretation is supported by geochemical modeling in terms of main pH-buffering processes. The leachate pH and concentrations in major elements (Ca, Na and Cl) as well as in Al and heavy metals (Cu, Pb and Zn) quickly drop during the first 2 years to asymptotically reach a set of minimum values over 10 years; similar to those of a reference road built with natural calcareous aggregates. SO₄ release makes exception with a slightly increasing trend over time.

Carbonation induced by CO₂ inputs, which leads to the successive dissolution of portlandite, CSH and ettringite, is one of the main phenomenon responsible for the geochemical evolution of leachate. On the other hand, mineralogical observations and batch tests demonstrate a relative stability of the MSWI bottom ash inside the subbase layer. In particular, carbonation may be far to be completed and still in progress after 10 years. This is consistent with preferential rainwater flow and dilution at the road edges combined to diffusion inside the subbase layer.

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1. Introduction

The high demand of construction materials compared to the availability of natural materials, as well as the lack of available space for waste disposal, is a problem in many urbanized areas across the world. The use of by-products and wastes for road construction is an appropriate solution to reduce the amount of disposed materials and to provide for alternative construction materials. Municipal solid waste incineration (MSWI) residues produced from the household waste combustion, and reused for road and car-park construction, is a typical case (e.g. [1,2]). For instance, in France, reuse of MSWI residue started during the 1950s in the Parisian Region and spread all over the country during the 1980–1990s, a period during which many incinerators were built [3].

As for some other alternative materials (coal fly ash, blast furnace slag, etc.), the reuse of MSWI bottom ash as road aggregate

may impact the environment – both soil and water resources – by releasing salts and heavy metals (e.g. [1,2]). The acceptance criteria for recycling MSWI bottom ash in road construction usually depends on the leaching potential of the material, which is determined through standardized leaching tests (e.g. [2,4]). Batch tests are useful for determining the intrinsic properties of the waste with respect to one or several controlled parameters (e.g. pH). However, these static experiments that are performed on short duration (usually 48 h) on crushed materials are poorly representative of field conditions. Column tests that run over longer duration (weekly to monthly time scales) include a hydrodynamic facet more representative of site conditions. As an example, they can be used to assess scale effects of percolation on element release [4,5]. However, their 1D configuration is far to be as complex as field geometry that present boundary or edge effects for instance. Long-term processes such as carbonation are also not fully taken into account.

Therefore, in complement to lab leaching tests, long-term field scale experimentations are critically needed for supporting environmental impact assessment in a given recycling scenario. To our knowledge, only a few field scale studies have been recently published with respect to MSWI bottom ash reuse for road construction

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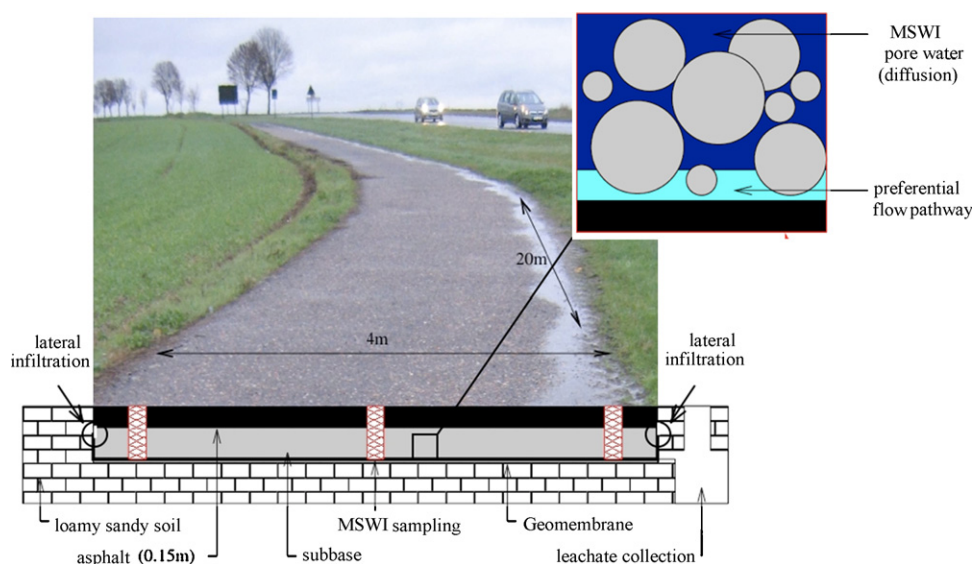


Fig. 1. Schematic transversal cross-section of the road with core sampling locations (subbase layers built either with MSWI bottom ash aggregate or calcareous aggregates).

[6–10]. In these studies, leachate sampling has been performed for relatively short durations (3 years at maximum). The present paper copes with a 10-year pilot site, dedicated to study the environmental impact of MSWI bottom ash valorized as road aggregates in Northern France. The paper focuses on the long-term evolution of leachate chemistry and mineralogical transformations of MSWI bottom ash over 10 years. Data interpretation is supported by batch test performed on core samples drilled after 10 years and geochemical modeling.

2. Field site and methods

2.1. Test road properties and materials

2.1.1. Description of the test road

The studied site consists of a small road characterized by a low traffic, about 10 vehicles per day, and built in 1997 at Hérouville (Parisian Region, France). The road is divided into two sections of 4 m wide and 20 m long. The first section contains a 25 cm thick subbase layer of MSWI bottom ash (dry weight of 31.2 tons). The second road section was built by using conventional calcareous aggregates (crushed natural limestone). This second section is used as a reference. The calcareous aggregate presents the same physical properties (granulation, hardness, etc.) than the MSWI bottom ash. Two complementary sections built with MSWI bottom ash stabilized by cement and hydrocarbon binders were also tested at Hérouville to investigate their potential improvement in environmental and geotechnical properties. The corresponding results are not discussed in this study.

As shown in Fig. 1, both sections are covered with a slightly permeable bitumen (asphalt) layer of 15 cm thickness; according to the French recommendations for the use of MSWI bottom ash in road construction [11]. The bitumen cover is flat, i.e. characterized by a nil slope (to be compared to a reference 3% slope for the French public roads) in order to maximize rainwater infiltration. The bitumen cover did not present any major cracks after 10 years of utilization. The two road sections are completely embedded in the surrounding soil, a cultivated loamy and sandy soil. A polyethylene drainage liner (geomembrane) is located at the bottom of the subbase layer. This geomembrane does not completely cover the road sides or edges, allowing for lateral water infiltration into the subbase layer. The depth of the local aquifer varies seasonally, between 3 and 7 m beneath the road.

2.1.2. MSWI bottom ash

The studied MSWI bottom ash comes from a waste incineration facility from the Parisian Region (France). Prior to utilization, the MSWI bottom ash was screened to remove particles larger than 30 mm, magnetic materials, and metallic aluminum, and then weathered outdoor in heaps during 3 months. The MSWI bottom ash was classified “V”, i.e. a by-product suitable for valorization as road aggregates according to the French regulation. The bottom ashes are composed of glass, ceramics, natural rocks, metallic compounds and unburnt residues.

2.2. Field monitoring and sampling

2.2.1. Leachate monitoring

A slight inclination of the geomembrane drives leachate by gravity towards the collection system: punctually with hermetic bags used to avoid atmospheric exchange (minimizing carbonation or oxidation) and continuously with larger collectors of 700 L. Precipitation data were collected from a nearby MétéoFrance weather station. The electrical conductivity and the flow rate of leachate were measured and compared to precipitation in a few occurrences.

From 1997 to 2000, EUROVIA and INERIS monitored the road by sampling and analyzing leachate [12]. In 2007, the two road sections were monitored again in order to evaluate leachate chemistry after 10 years of utilization. Electrical conductivity, pH and redox potential were directly measured after sampling. The leachates were filtrated at 0.45 μm and stored at 4 °C (one half was acidified with ultra-pure nitric acid for metal analysis). Total alkalinity was determined using the Merck alkalinity test and dissolved organic carbon (DOC) using a total organic carbon analyser at the laboratory on the filtrated leachates. Anion concentrations were analyzed on the filtrated leachates by ion chromatography, and cation concentrations on the acidified filtrated leachates by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.2.2. Sampling of MSWI bottom ash from the road subbase layer

In order to evaluate the material evolution, MSWI bottom ash samples were collected after 10 years (October 2007) in the road subbase layer by drilling cores of 15 cm in diameter. Each core was further divided according to three depths: underneath the bitumen, in the middle of the layer and the bottom of the layer (Fig. 1). The drilled core samples were carefully packed in aluminum coated plastic bags to prevent carbonation, oxidation and dehydration.

Water content (humidity) was estimated by weight loss between bottom ash freshly sampled (in situ measurement) and after drying (lab measurement). Water content is expressed as a percentage of the dry material.

2.3. Chemical and mineralogical analyses

2.3.1. Batch leaching tests

The availability NF-X31-210 batch leaching test [13] was used as standard reference for characterizing the initial state of both the MSWI bottom ash and the calcareous aggregates (in 1997). The present MSWI bottom ash was classified “V” according to this French standard test. The sample is first homogenized, grinded to obtain a particle size below 4 mm and dried at 100 °C. A solid amount of 100 g is then mixed with 1 L of demineralized water (i.e. a liquid on solid ratio, L/S, of 10) in an airtight device, to avoid carbonation, under permanent agitation. The leachate is removed after 16 h and filtrated at 0.45 μm. The solid phase is again submitted to the same leaching process twice. The pH is measured for each of the three leachates. The total released mass of a given element (i.e. the sum of the three leachate) is normalized to 1 kg of dry material.

The drilled core samples taken from the 10-year old bottom ash layer were also submitted to batch leaching tests to estimate element release but also pore water chemistry for another study devoted to reactive transport modeling. Contrarily to the NF-X31-210 test, the MSWI bottom ash were neither crushed nor dried to prevent as much as possible any chemical artifacts and creation of new solid surfaces (e.g. breaking of calcite crusts formed by carbonation). Indeed, crushing may disturb the MSWI bottom ash granularity and texture that were acquired during 10 years of evolution. The L/S ratio was set to 5 as a compromise between minimizing dilution effect and collecting a satisfactory volume of solution for analyses. The batch tests were performed during 1 month to let the eluate chemistry reached a steady state (a near equilibrium state), which also helps to identify solubility-controlled processes. The batch test was also applied to a fresh MSWI bottom ash sample for comparison. It is worth noting that the leaching tests were made in 2008 and that, therefore, the fresh MSWI bottom ash does not strictly correspond to the material used for the test road construction in 1997. However, both bottom ashes came from the same incineration facility without any significant change in the bottom ash production but a slight evolution of municipal waste sorting.

2.3.2. Solid-phase analysis

The total element content (i.e. bulk chemistry) was analyzed by ICP-AES after LiBO₃ mineralizing in 2007. The ash samples were mixed prior to analysis. Mineralogical investigation were made by means of optical and scanning electronic microscopy (SEM-EDS) on thin section as well as by X-ray diffraction (XRD) on dried crushed materials. The fresh MSWI bottom ash of reference was similar but not exactly the same material used 10 years ago (see previous paragraph).

2.4. Interpretation by geochemical code

Some insights into the chemical processes occurring in MSWI bottom ash were investigated with the geochemical model CHESS [14]: (i) by calculating saturation index (SI) of the leachate with respect to primary and secondary minerals, (ii) by comparing experimental data with stability domains of minerals, and eventually (iii) by calculating the pH of the leachate with respect to a sequence of pH-buffering minerals. The MINTEQ thermodynamic database [15] was selected in that purpose, and enriched with additional data for cement phases (sulfo-aluminates, calcium silicates hydrates – CSH, etc.) as well as for lead hydroxide (see [16] for

Table 1
Elemental composition of MSWI bottom ash.

Oxide	[wt.%]	Trace metals	[ppm]
Na ₂ O	3.4	As	<10
MgO	1.9	Cd	5
Al ₂ O ₃	2.8	Cr	75
SiO ₂	40.5	Cu	960
SO ₃	0.86	Hg	0.1
K ₂ O	0.80	Pb	1495
CaO	31.5	Zn	1555
Fe ₂ O ₃	10.0		

further details). The B-dot model was used for activity correction because the pore water chemistry of the fresh MSWI bottom ash has a high ionic strength (0.7 molal). The B-dot model is indeed well adapted since it is parameterized for solutions of up to 3 molal ionic strength in which NaCl is the dominant solute.

3. Results and discussion

3.1. Mineralogical and chemical properties of the initial MSWI bottom ash

XRD analyses and SEM observations of the initial MSWI bottom ash samples indicate a broad spectra of minerals in agreement with literature, such as silicates (feldspars, gehlenite, mellite, quartz and pseudo-wollastonite), carbonates (calcite), sulfates (ettringite and gypsum), aluminum and iron oxyhydroxides (gibbsite and magnetite). The occurrence of cement-type phases (mainly portlandite and CSH [17,18]) was not directly determined by XRD analysis but consistent with the highly alkaline pH measured in batch tests.

The bulk chemical composition of the studied bottom ash (Table 1) is within the range of data compiled on a worldwide base by Jeong et al. [19]. The MSWI bottom ash is enriched in Ca–Fe–Si–O with relatively high amounts in Al and heavy metals Cu, Pb and Zn but relatively low contents in As, Cd and Hg. Table 2 presents the results of the availability NF-X31-210 batch leaching test applied in 1997 to the initial MSWI bottom ash and the calcareous aggregate used for building the test roads. The pH of the MSWI bottom ash is clearly alkaline (pH ~ 11.8), which indicates a rather low degree of maturation of the bottom ash [20]. The leached fractions in soluble salts are 2900 and 6960 mg/kg for NaCl and CaSO₄, respectively. Such high values are again typical of a fresh MSWI bottom ash. The release of the toxic metals Al (215 mg/kg), Cu (23 mg/kg), Pb

Table 2
Results of the availability NF-X31-210 batch leaching test applied to the MSWI bottom ash and the calcareous aggregate.

	MSWI bottom ash	Calcareous rock
pH	11.8/11.3/11.1	9.3/9.3/9.3
Conductivity [mS/cm]	2575/810/490	67/50/52
DOC [mg/kg]	1050	77
Major element [mg/kg]		
Ca	5134	237
Cl	1933	53
Na	991	54
SO ₄	1829	180
Metal [mg/kg]		
Al	215	5
As	<0.3 ^a	<0.3 ^a
Cd	<0.3 ^a	<0.3 ^a
Cr	0.4	<0.3 ^a
Cu	23.1	<0.15 ^a
Hg	<0.1 ^a	<0.1 ^a
Pb	8.3	<0.3 ^a
Zn	2.3	<0.3 ^a

^a Detection limits.

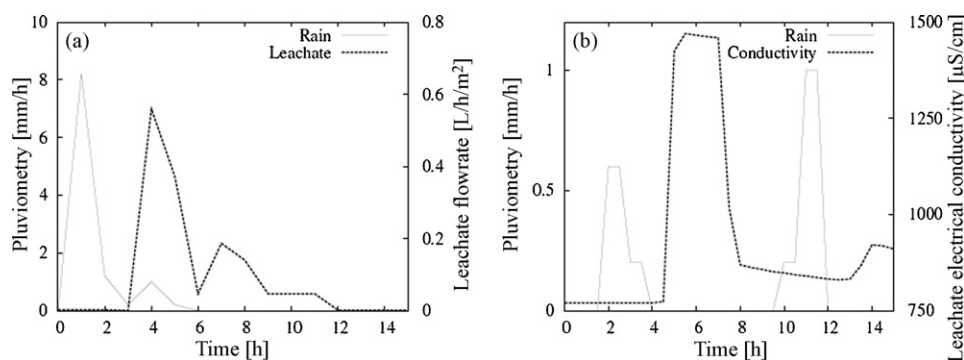


Fig. 2. Time response of the leachate flow rate (a) and electrical conductivity (b) with respect to successive rain events.

(8 mg/kg) and Zn (2 mg/kg) is also significant; Pb and Zn release being maximized by the high pH values [2,20]. As discussed below, there is a correlation between the high released fractions of Cu and dissolved organic matter (DOC, 1050 mg/kg). The release of As, Cd and Hg are weak and below the detection limits: <0.3 mg/kg for As and Cd, and <0.1 mg/kg for Hg. As expected from a natural limestone, the release of the major and metallic elements by the calcareous aggregate is low, and the pH much less alkaline, compared to the MSWI bottom ash.

3.2. Rainwater infiltration

The precipitation regime is typical of a temperate oceanic climate. The local average precipitation rate is about 700 mm/year for the 1998–2008 period. There has been an initial leachate production due to discharge by gravity during the very first weeks. Next, leachate volume is fairly well correlated to local precipitation in terms of intensity and frequency. Fig. 2 gives a typical example representative of successive rain events. The mean leachate flowrate is 90 L/m²/year when normalized to the road surface. This rate corresponds to an equivalent infiltration/rainfall ratio of approximately 15%. Several overflows of the 700 L collectors occurred between two consecutive sampling periods. The unknown volume of overflowed leachate led to large uncertainties on volume measurements, which did not allow for calculating flow rate and release fluxes. As a consequence, element release will only be expressed in terms of concentration throughout the paper.

The bitumen cover is a barrier against rainwater percolation through the bottom ash layer. The infiltration ratio of 15% is high compared with the ratio commonly measured for public roads, which is about 2–3%. However, this relatively high apparent infiltration ratio is most probably related to important edge effects with lateral inflows to the MSWI bottom ash layer. This lateral input is suspected to be a major source of leachate production, as theoretically assumed by different authors [1,21]. Such a preferential lateral flow is further supported by the short hydraulic response time (3–4 h) of leachate discharge (normalized flow rate) to a given rain event, as shown in Fig. 2. The decrease of leachate electrical conductivity (graph b of Fig. 2) between two successive rain events can be interpreted in terms of residence time and preferential lateral flow pathways (schematized in Fig. 1). The first more intense signal corresponds to the mixing between an infiltrated and diluted water circulating quickly into the preferential flow pathways along the geomembrane, and a pore water representative of the bottom ash. The second and weaker signal corresponds to the same kind of mixing, except that the pore water does not have sufficient time for diffusing from the granular bottom ash and/or reaching equilibrium with the MSWI bottom ash minerals nearby the preferential flow pathways. The lateral preferential flows is relevant to public road structures but the preferential flow above the geomembrane,

i.e. along the bottom of the bottom ash layer, is somehow an artifact of the present collection system.

3.3. Evolution of leachate chemistry over time

3.3.1. General trend

Fig. 3 shows that pH and most of the elemental concentrations significantly decrease during the first 2 years, then more gradually to eventually reach a set of minimum values after 10 years. SO₄ concentration makes exception and presents a slightly increasing trend over time. A maximum concentration peaks occur at 3 months, which is consistent with the characteristic time derived from the ratio of the subbase layer porosity on the mean flowrate. Data spreading probably comes from variations in water residence time according to the precipitation regime, as discussed in Section 3.2.

3.3.2. Dissolved salt release (Na–K–Cl)

Cl concentration decreases from a maximum value of 4000 mg/L after 3 months, to 300 mg/L after 2 years, and 100 mg/L after 10 years, as shown in Fig. 3. Chloride is essentially a conservative element that is present as dissolved salts (NaCl and KCl) in the initial pore water of MSWI bottom ash. Not shown in Fig. 3, K and Na release present a similar trend than Cl. Dissolved salt release is controlled by hydrodynamics, essentially a diffusion process inside the bottom ash layer combined to a weak lateral flow towards the collection system, as mentioned above. However, the molal ratio Na/Cl that is initially close to unity increases over time progressively. This suggests another sources of Na release on the long-term, such as the slow dissolution of glassy particles.

3.3.3. Evolution of pH

The evolution of leachate pH is partly dependent on the hydrodynamics of rainwater infiltration, as discussed for chloride release, but is also driven by carbonation processes. CO₂ input is due to the gaseous diffusion of atmospheric CO₂ into the subbase layer that is under unsaturated hydric conditions [22]. To a lesser extent, microbiological respiration may also yield an in situ production of CO₂ [23]. There are three main pH-buffering minerals according to literature on MSWI bottom ash weathering [17,18]: portlandite (Ca(OH)₂) for fresh unweathered bottom ash with leachate pH greater than 12, ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) for quenched bottom ash with leachate pH close to 10.5, and calcite (CaCO₃) for carbonated bottom ash with leachate pH close to 8. Though the amorphous CSH cannot be identified by XRD, it is likely that these cement-type phases also control the pH in the range 10–11.5 [17,18].

The pH-buffering sequence is illustrated in Fig. 4 by means of a simple CHES calculation. A more relevant modeling would require a reactive transport approach and the present modeling is illustra-

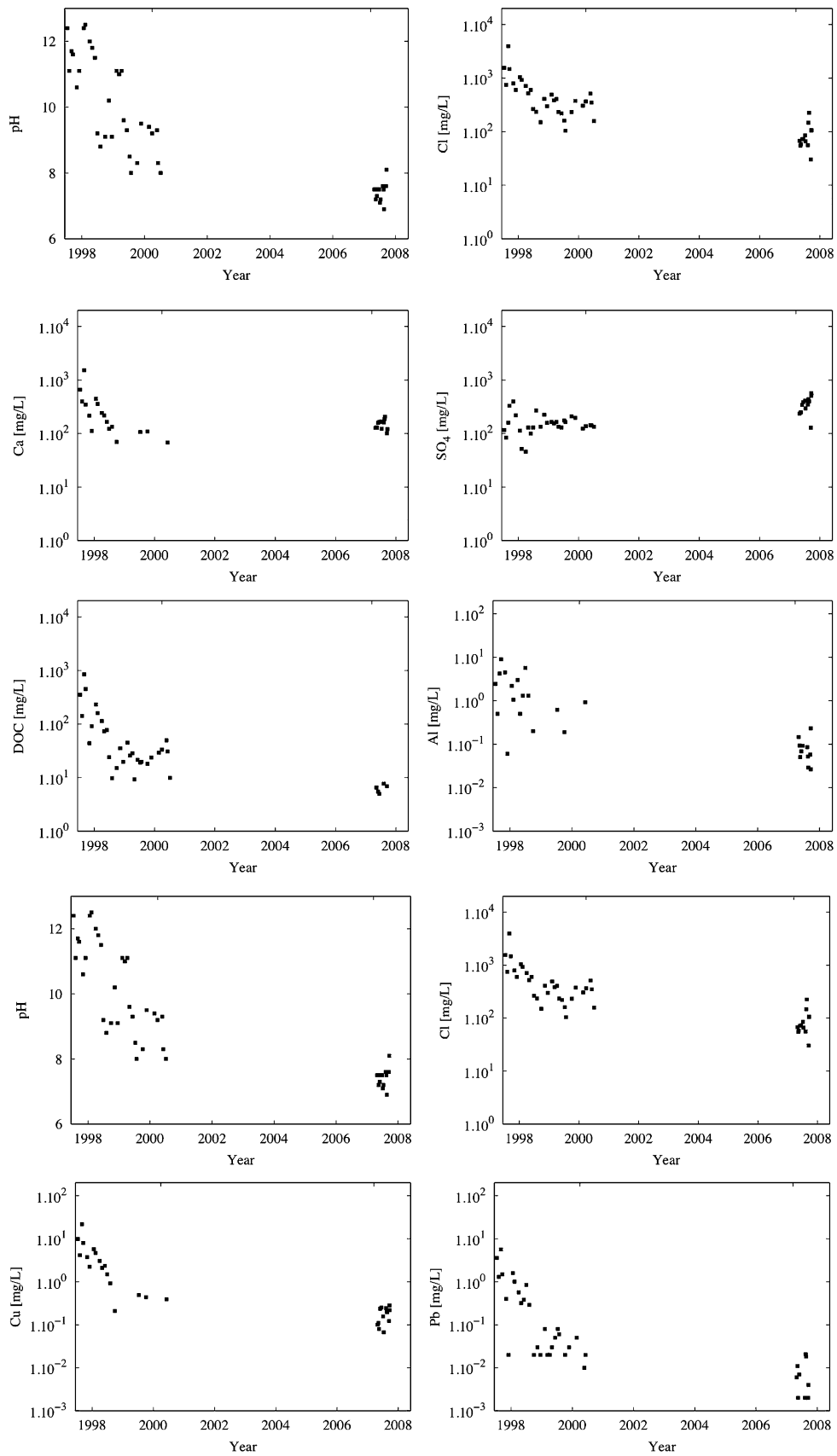


Fig. 3. Measured pH and element concentrations in leachate of the road section built with MSWI bottom ash.

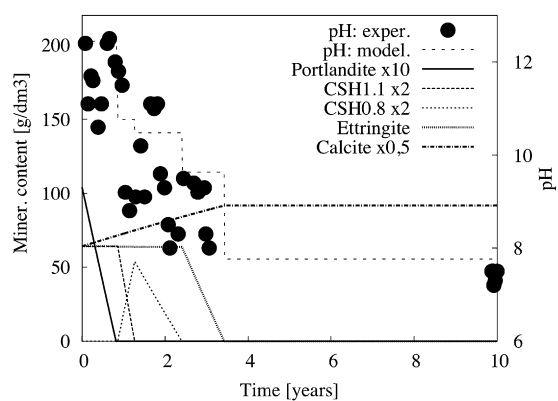
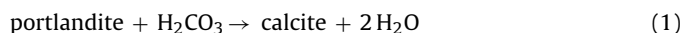
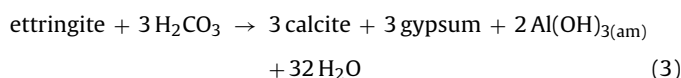
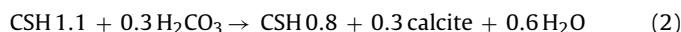


Fig. 4. Illustration by CHES modeling of pH evolution in leachate assuming 1 dm³ of MSWI bottom ash, a temperature of 20 °C, a constant input of CO₂ (30 mmol/dm³/year) and a set of pH-buffering minerals: portlandite (1 wt.%), CSH (2.5 wt.%) and ettringite (5 wt.%).

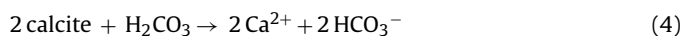
tive only. One dm³ of MSWI bottom ash is assumed to be slowly carbonated by CO₂ input. A zero order input rate, $d[\text{CO}_2]/dt = k$ was considered in CHES since the diffusion process cannot be modeled by a geochemical model alone. A mean rate constant k of 30 mmol/dm³/year approximately fits the measured pH evolution of leachate reported in Fig. 4. Temperature is fixed to 20 °C. A semi-quantitative proportion of pH-buffering minerals for the initial bottom ash can be deduced from XRD and batch analyses: portlandite (1 wt.%), CSH (2.5 wt.%), ettringite (5 wt.%) and calcite (10 wt.%). During the first months, portlandite dissolution gives a constant pH of 12.3 according to the following reaction:



Once portlandite is fully depleted, CSH dissolution and ettringite dissolution give a pH around 10.5 and 9.5, respectively, according to the following reactions:



These two reactions seem to have been active over 2 years in the test road. Reaction (3) yields gypsum (CaSO₄) and aluminum hydroxide (Al(OH)₃) precipitation, whereas calcite is an end-product of the reactions (1)–(3). On the long-term, calcite buffer the leachate pH around 8 at the atmospheric CO₂ pressure (4×10^{-4} atm) according to the following reaction:



In this simple modeling approach, calcite content increases from 10 to 13.5 wt.% as a result of the carbonation of the fresh bottom ash phases.

Table 3 tabulates the saturation indices (SI) calculated for a selection of representative leachates. Due to uncertainties, leachate is assumed to be in thermodynamic equilibrium with respect to a given mineral if the SI of this mineral ranges between -0.5 and 0.5 log unit. A positive SI (over-saturation state) indicates that the given mineral may precipitate as a secondary mineral. A negative SI (under-saturation state) indicates that the given mineral is not stable with respect to leachate chemistry and may dissolve at some kinetic rate (provided the mineral is effectively present in the material). The high pH of the first leachate (pH 12.4) is in good agreement with portlandite equilibrium. Once pH drops to 11, leachate becomes under-saturated with respect to portlandite but may be in equilibrium with CSH 1.1, a CSH of intermediate Ca/Si

Table 3

Saturation indices (SI) calculated with CHES for a selection of leachate representative of the successive weathering stages. The figures written in italic indicate that the mineral is close to equilibrium ($-0.5 < \text{SI} < 0.5$).

	~1 month	~9 months	~2 years	~10 years
pH	12.4	11.4	9.2	7.6
Calcite	–	–	–	<i>0.1</i>
CSH 0.8	–0.6	–0.9	–	–5.1
CSH 1.1	0.6	–0.1	–	–7.0
CSH 1.8	<i>0.5</i>	–1.8	–	–14.2
Portlandite	–0.1	–2.4	–7.0	–10.5
Gehlenite	–6.4	–7.7	–	–17.2
P-wollastonite	1.2	0.7	–	–5.7
Quartz	–3.5	–1.7	–	<i>0.1</i>
Amorphous Al(OH) ₃	–3.9	–3.2	–0.3	–0.5
Ettringite	6.3	0.2	–7.4	–16.7
Gibbsite	–2.3	–1.6	1.3	1.1
Gypsum	–0.9	–1.2	–1.0	–0.6
Cerussite	–7.1	–4.9	<i>0.1</i>	–2.1
Litharge	–1.9	–2.0	–1.6	–7.5
Pb(OH) ₂ (s)	–0.1	<i>0.2</i>	<i>0.2</i>	–5.4
Pb ₂ (OH) ₃ Cl	–1.1	–0.8	2.0	–8.2
Tenorite	2.1	1.6	1.4	<i>0.2</i>

ratio, as well as with ettringite. At pH 9.5 or below, ettringite is no more stable but aluminum hydroxides (gibbsite and amorphous Al(OH)₃) are not far from equilibrium. This is in agreement with Eq. (3). Gypsum is not far from equilibrium in leachate. Calcite remains in equilibrium with leachate, especially on the long-term when pH is close to neutrality.

The leachate data are also reported on the stability diagrams of Al and SO₄, calculated with CHES, in Fig. 5. The experimental data are not far from the theoretical lines of ettringite, Al(OH)₃ and gypsum solubilities. This is in agreement with the mineralogical evolution of MSWI bottom ash addressed by Eq. (3): a progressive dissolution of ettringite follows by a precipitation of aluminum hydroxide and gypsum.

As written above, data spreading is mainly due to the precipitation regime. However, to a lesser extent, temperature also have a seasonal effect on pH. According to CHES modeling, the pH of a leachate buffered by portlandite (or ettringite) drops by approximately 0.5 unit when temperature increases from 5 to 20 °C.

3.3.4. Release of solubility-controlled major elements

Ca leachate concentration continuously decreases from an initial maximum value of 1500 mg/L to a mean long-term values of 150 mg/L, as shown in Fig. 3. Though scattered, SO₄ concentrations starts from a maximum peak of 400 mg/L, drops to 150 mg/L in average during the first 3 years and eventually increases to 300 mg/L after 10 years. The initial release of Ca and SO₄ is probably linked to a soluble sulfate salt (anhydrite) dissolved in the pore water of MSWI bottom ash. Afterwards, Ca and SO₄ release may be solubility-controlled by ettringite, CSH, gypsum and calcite as previously found for leachates of MSWI bottom ash landfill [18]. As seen in the SO₄ stability diagram of Fig. 5, the leachates are slightly under-saturated with respect to gypsum. This under-saturation state may again be due to a dilution effect produced by a preferential rainwater infiltration along the geomembrane (edge effect).

Not shown in Fig. 3, Si concentration is globally constant over time and ranges from an initial value of 5 mg/L to a final one of 2 mg/L. Gehlenite (Ca₂Al₂SiO₇), pseudo-wollastonite (CaSiO₃) and quartz are all primary minerals of MSWI bottom ash. Gehlenite is systematically not stable (under-saturated) with respect to the leachate, whatever the pH (Table 3). Pseudo-wollastonite is stable at alkaline pH but unstable at neutral pH. The opposite is true for

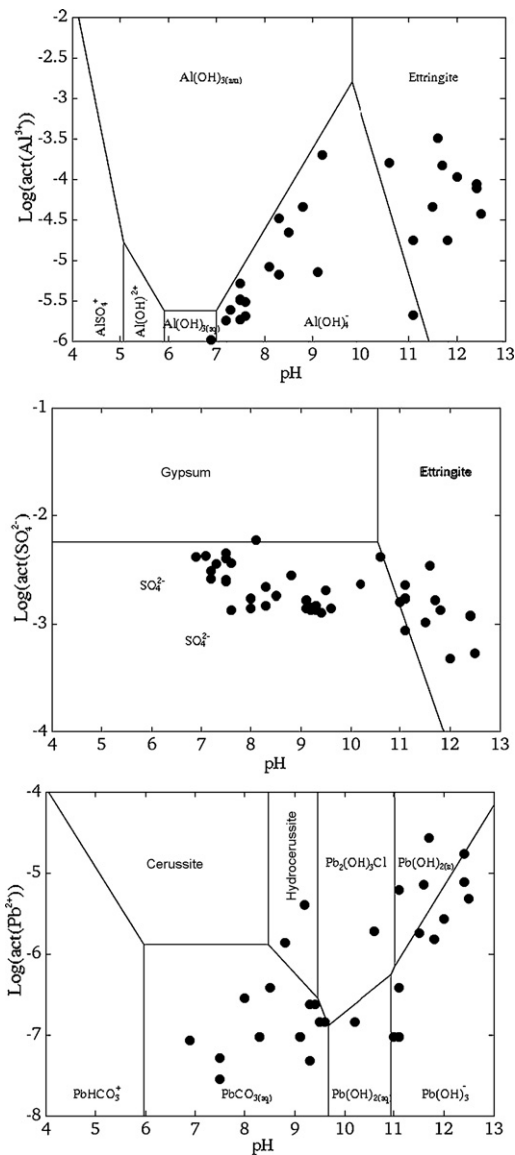


Fig. 5. Leachate data reported on the stability diagrams of Al, SO₄ and Pb calculated with CHESS ($T=20^{\circ}\text{C}$, $[\text{Al}]=3 \times 10^{-5}$ mol/L, $[\text{Ca}]=2.5 \times 10^{-3}$ mol/L, $[\text{Cl}]=10^{-2}$ mol/L and $[\text{SO}_4]=10^{-3}$ mol/L).

quartz. At neutral pH, leachate is in equilibrium with quartz and slightly under-saturated with respect to chalcedony.

3.3.5. Release of dissolved organic carbon

As shown in Fig. 3, the release of dissolved organic carbon (DOC) is similar to the release of dissolved chloride salts. DOC is also mostly present in the pore water of the MSWI bottom ash. The DOC leachate concentration is about 500 mg/L the first month and rapidly decreases over time to reach a final mean value of 10 mg/L after 10 years.

3.3.6. Release of Al and heavy metals

There is a clear correlation between DOC and Cu concentrations in leachate during the first 3 years. This is linked to the strong complexation affinity of dissolved organic matter, especially fulvic acids, for Cu ions [24]. Cu concentration varies from an initial value of 100 mg/L to a mean value of 0.18 mg/L after 10 years, the later concentration indicating an equilibrium with tenorite (CuO, Table 3). The temporal evolution of Cu concentrations as well as its correlation with DOC concentrations are in good agreement with

Table 4
Chemistry of leachate collected from the test road (MSWI bottom ash aggregates) and from the reference road (calcareous aggregates) after 10 years; means, minimum and maximum of 10 data.

	MSWI bottom ash		Calcareous rock	
	Mean	(min–max)	Mean	(min–max)
pH	7.3	(6.9–7.6)	7.6	(7.0–8.0)
Conductivity [mS/cm]	1.2	(0.6–0.7)	0.6	(0.4–0.8)
DOC [mg/L]	6.0	(5.2–6.9)	–	–
Alkalinity [mg _{HCO₃} /L]	115	(98–134)	280	(110–622)
Major [mg/L]				
Ca	149	(101–207)	85	(56–127)
Cl	89	(30–225)	5	(4–12)
K	29	(16–50)	7	(3.0–12)
Na	95	(33–199)	5	(3.5–7.5)
SO ₄	329	(129–511)	25	(10–35)
Metal [mg/L]				
Al	0.070	(0.027–0.146)	0.021	(0.005–0.048)
Cr	0.007	(<0.001 ^a –0.020)	0.001 ^a	(<0.001 ^a –0.002)
Cu	0.177	(0.084–0.250)	0.011	(<0.001 ^a –0.027)
Fe	0.016	(<0.002 ^a –0.032)	0.017	(0.003–0.032)
Pb	0.007	(0.001 ^a –0.021)	0.004	(<0.001 ^a –0.015)
Zn	0.054	(0.021–0.104)	0.023	(0.015–0.057)

^a Detection limits.

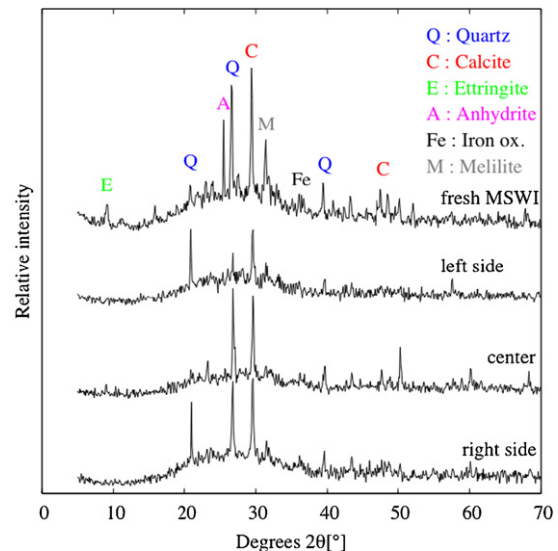


Fig. 6. Comparison of XRD diagrams of the initial and 10-year-old MSWI bottom ash samples.

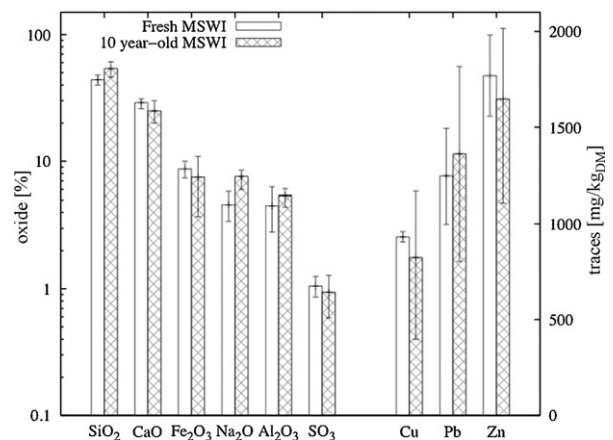


Fig. 7. Comparison of total contents in major elements and some heavy metals of the initial and 10-year-old MSWI bottom ash samples.

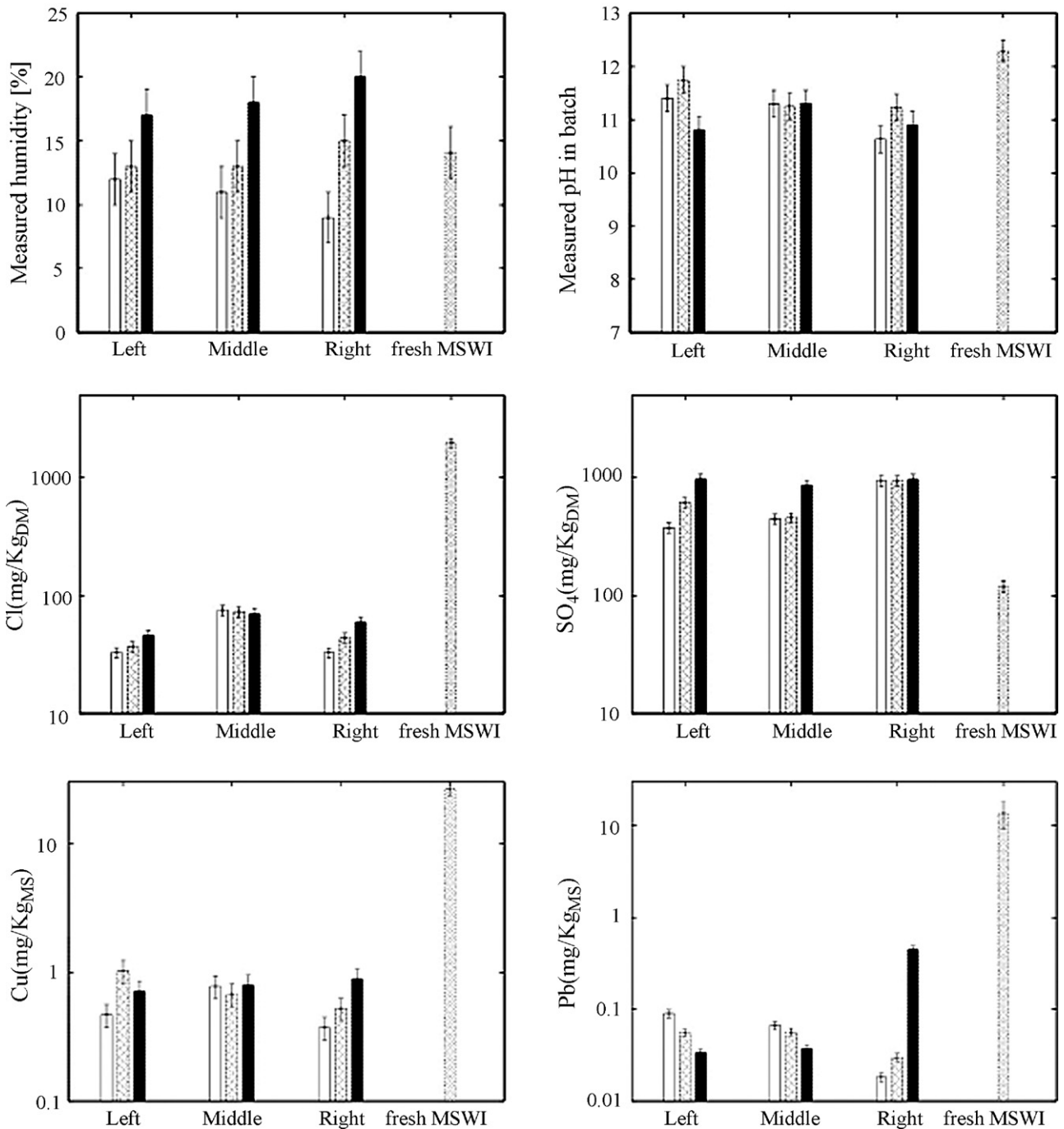


Fig. 8. Water content (humidity) of the 10-year-old MSWI bottom ash samples and comparison of the batch test results applied to the initial and 10-year-old bottom ash samples (surface \square , middle \boxtimes , and bottom \blacksquare of the subbase layer).

the data obtained by Lidelöw and Lagerkvist on a similar test road [8].

Al leachate concentration starts from a maximum values of 10 mg/L and constantly decreases to a mean long-term value of 0.07 mg/L (Fig. 3). Leachate is not far from equilibrium with ettringite, and from equilibrium with $\text{Al}(\text{OH})_3$ at a later stage, as shown in Fig. 5.

Pb concentration also decreases almost exponentially over time, from an initial value of 5 mg/L to a final mean value of 0.007 mg/L. Pb release can be correlated to solubility-controlling minerals: $\text{Pb}(\text{OH})_2$, for $\text{pH} > 12$, and $\text{Pb}_2(\text{OH})_3\text{Cl}$ for $10 < \text{pH} < 12$. Leachate is under-saturated with respect to cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) at the neutral pH reached on the long-term.

Co-precipitation with calcite [25], sorption processes [26], or simply dilution effect may explained such an under-saturation state. Not shown in Fig. 3, Zn concentration in leachate quickly drops during the first months from a maximal value of 0.6 mg/L to reach a mean concentration of 0.05 mg/L over time.

The leachate content in As, Cd and Hg were analyzed during the first 3 years only. The measured concentrations were below the detection limits: < 0.01 mg/L for As and Cd and < 0.001 mg/L for Hg. Only four data were available for three first years. Cr concentration was 0.04 mg/L at 1 month then ranged from 0.01 to 0.02 mg/L. This is not sufficient to draw an evolution with time. However, Cr concentration does not decrease after 10 years of evolution with a mean value of about 0.01 mg/L (Table 4).

3.4. *In situ* MSWI bottom ash evolution

The bitumen cover does not present any major cracks after 10 years, which involves that no important swelling occurred in the MSWI bottom ash subbase. The XRD diagrams of Fig. 6 do not show any noticeable difference too, except anhydrite and ettringite depletion. The increase of calcite yield by carbonation of the fresh bottom ash phases is at maximum of 3.5 wt.% according to the simplified modeling approach of Section 3.3. The related decrease of the MSWI bottom ash porosity should not significantly modify the hydraulic properties. Comparison of SEM observations of the initial and 10-year-old MSWI bottom ashes, which did not indicate any evolution of mineralogy and texture, goes in that direction.

Total element contents of the initial and 10-year-old bottom ashes are within the same orders of magnitude (Fig. 7), which globally demonstrates a low release of both major elements (Ca, Fe and Si) and heavy metals (Cu, Pb and Zn). This statement was further investigated by batch leaching tests performed on the 10-year-old MSWI bottom ash. The main results are reported in Fig. 8.

The pH values (pH ~ 11) of the 10-year-old samples are lower than the pH value (pH ~ 12.3) obtained for fresh bottom ash in similar L/S conditions, but are significantly higher than leachate pH after 10 years (pH ~ 8). The discrepancy between the batch and leachate pH values may be explained by the preferential flow pathways taking place at the edges of the road from the one hand, and a relative isolation of the bottom ash inside the subbase layer from the other hand. This means that the carbonation process may not be fully achieved in the subbase bottom ash, even after 10 years. This is in agreement with the Lidelöv and Lagerkvist's study where carbonation was hampered by the limited infiltration and gas exchange through the compacted bottom ash subbase of a test road [8].

Cl concentrations (~70 mg/kg) of the 10-year-old bottom ash calculated from the batch test results are much lower than the initial value (~2000 mg/kg). The highest Cl concentration (~90 mg/kg) is found directly underneath the bitumen cover and the lowest (~50 mg/kg) at the bottom of the subbase layer. These results are fully consistent with a similar investigation performed by Bendz et al. [9]. The significant decrease of Cl concentration inside the bottom ash subbase cannot be explained by an advective flow of rainwater alone because the cumulative flow is too weak. Chloride ions diffuse inside the subbase bottom ash layer to the geomembrane boundaries (bottom and edges) where low preferential flows take place.

SO₄ release is higher for the 10-year-old samples than for the MSWI initial bottom ash. This may be related to a pH control. In the pH range 10–12.5, the lower the pH, the higher the SO₄ concentration (Fig. 5). On the contrary, Cu and Pb releases are lower for the 10-year-old bottom ash than for the initial sample. This supports the assumption that the easily leached fractions of Cu and Pb are released during the very first years, as discussed in Section 3.3.

The profile of water content (humidity) measured on the drilled core samples is also reported in Fig. 8. Unsaturated water conditions prevail inside the MSWI bottom ash layer since the water content ranges from 10 to 20 wt.%. Water content increases with depth but without any edge effects.

4. Environmental significance

Table 4 presents the leachate data collected from the test road section (MSWI bottom ash aggregates) and from the reference road section (natural calcareous aggregates) after 10 years. The reference road section is useful to characterize the chemical background of natural aggregates used in road construction as well as the pos-

sible contribution of traffic pollution. The chemical properties of the two types of leachate are very similar: neutral pH, weakly mineralized fluids, low concentrations in heavy metals. The SO₄ and Cu concentrations are slightly higher in the MSWI bottom ash leachate. Therefore, there is no relevant release of the measured toxic metals (Al, Cr, Cu, Pb and Zn) by the MSWI bottom ash subbase layer after 10 years at the Hérouville site. In addition, the leachate content in As, Cd and Hg that were analyzed during the first 3 years only were below the detection limits. Nevertheless, this potentially low environmental impact have to be balanced by the fact that (i) metallic Al was removed from the fresh MSWI bottom ash (Al release could have been different otherwise) and (ii) the leaching of oxyanions that were not measured in this study (e.g. Sb) may increase as pH drops during carbonation [27,28].

One problematic environmental issue may correspond to the maximum concentration peak measured in leachate during the first 3 months following the road construction, in particular high Al, Cu and Pb concentrations of 5, 10 and 5 mg/L, respectively. However, the potential environmental impact should be weak and localized over such a short period. Metal fluxes, the product of concentration by water flow, are indeed restricted by the infiltration flow, which is basically low due to the bitumen cover protection and impermeability.

An additional environmental concern is the relative stability of MSWI bottom ash inside the subbase layer demonstrated by both the mineralogical observations and batch tests. In particular, carbonation processes, which are known to decrease the aggressiveness of such alkaline materials (e.g. [29]), may be far to be completed and still in progress after 10 years.

5. Conclusions

The leachate pH and concentrations in major elements (Ca, Na and Cl) as well as in Al and the measured heavy metals (Cu, Pb and Zn) quickly drop during the first 2 years to asymptotically reach a set of minimum values over 10 years; which are similar to those of a reference road built with natural calcareous aggregates. For instance, Cl release after 10 years is about 40 times as small as initially. SO₄ release makes exception with a slightly increasing trend over time. There is no relevant release of Al, Cr, Cu, Pb and Zn from the MSWI bottom ash layer after 10 years at Hérouville site. Beside the potential increase of oxyanion release while pH drops, a problematic environmental issue may correspond to the maximum concentration peak measured during the first 3 months following the road construction. However, the potential environmental impact should be weak over this period because the bitumen cover protection and impermeability prevent any significant leachate flow.

It can be assumed that carbonation induced by CO₂ atmospheric inputs, which leads to the successive dissolution of portlandite, CSH and ettringite, is the main phenomenon responsible for the geochemical evolution of leachate. On the other hand, mineralogical observations and batch tests demonstrate a relative stability of the MSWI bottom ash inside the subbase layer. In particular, carbonation may be far to be completed and still in progress after 10 years. A relatively short hydraulic response of leachate production to a rain event, as well as the discrepancy between the leachate pH and batch test pH data clearly indicate that preferential flow and dilution effects take place at the road edges in combination to diffusion processes inside the subbase layer. The generalization of the environmental significances raised by this field study, and the few other similar ones published in literature, requires comparing the leachate quality and production of the different pilot sites. Work along these lines is in progress by means of a reactive transport modeling of MSWI bottom ash evolution.

Acknowledgements

The constructive comments of three anonymous reviewers are gratefully acknowledged and one of the authors thanks his colleagues, Sabine Liorzou and Médard Thiry from Ecole des Mines de Paris, for leachate sampling and analyses.

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