

MINERALOGICAL EVOLUTION AND LEACHING BEHAVIOUR OF A HEAP OF BOTTOM ASH AS A FUNCTION OF TIME – INFLUENCE ON ITS VALORIZATION

D. Blanc^{*}, L. Gonzalez, M. Lupsea-Toader and C. de Brauer

Université de Lyon, INSA-Lyon, DEEP (Déchets Eaux Environnement et Pollutions – Wastes Water Environment Pollutions), 20 avenue Albert Einstein, F-69621 Villeurbanne, France

*Corresponding author

email: denise.blanc@insa-lyon.fr

telephone number 00 33 (0)4 72 43 88 41

fax number 00 33 (0)4 72 43 87 17

Abstract

MSWI BA in France is reused as a substitute for natural aggregates in building material for road constructions. Before MSWI BA reuse, treatment operations are generally necessary such as ferrous and non-ferrous metals removal, ageing process, and particle size separation. BA valorization depends on the leaching behavior of the main MTE, which depends on pH. It's well known that ageing process influence the natural pH of the BA. Initial pH of fresh BA (around 12 – 13) may decrease until the pH value 8 reached for weathered BA. Ageing process is influenced by different parameters, for example the presence of ferrous metals because of their oxidation and the CO₂ content of the gaseous phase in the porosity of BA. Then, as the ferrous removal is more and more efficient and as the MSWI BA are stored in heaps, limiting the atmospheric exchange, the efficiency of ageing process is no longer certain. The main objective of this study was to measure the efficiency of the ageing process when BA are stored in heap. The mineralogical evolution and the leaching behavior of BA were observed during 7 months. To compare, two artificial ageing processes were carried out on the final sample. All the results showed that when the BA were stored in heap, the ageing process was not efficient. The evolution of pH was very low, showing that the carbonation didn't occur. On the contrary, 'artificial' ageing processes permit to diminish the pH value. Mineralogical characterization showed differences between all the samples. These differences permitted to explain the MTE leaching, especially for lead or antimony.

Keywords

MSWI BA, ageing process, heap, MTE, characterization.

Introduction

Currently, 14.2 million tons of municipal solid waste (MSW) are incinerated each year in France. On one hand incineration diminishes the mass and the volume (70% and 90% respectively) of MSW, on the other hand by-products are generated. Bottom ash (BA) is the main solid by-product, accounting for 80 wt % of total solid waste generated by incineration processes [1]. In France, approximately 3 million tons of MSWI BA are produced each year.

A common alternative to the MSWI BA storage in France, is its reuse as a substitute for natural aggregates in building material for road constructions. However, the high content of metal trace elements (MTE) and salts, potentially dangerous after release to the environment by leaching mechanisms, appeared to be the main restriction for BA reuse, especially because of new threshold limits in the French regulation [2]. The leaching behavior of the main MTE concerned by the threshold limit depends on pH. Chemical reactions that control the solubilization of the MTE as dissolution / precipitation reactions, complexation reactions, oxidation-reduction reactions and sorption / desorption mechanisms are influenced by pH [3-4]. Thus, pre-treatment operations, such as ferrous and non-ferrous metal removal, ageing process, and particle size separation, are generally necessary, in order to reach the environmental, mechanical, geotechnical and hydraulic performances for BA reuse.

It is well known that ageing influences the natural pH of BA. In fact, the initial pH of fresh BA (around 12 – 13) may decrease down to pH 8 for weathered BA. At the beginning, the pH is due to the solubilization of portlandite; in the end, carbonates and gypsum are precipitated [5-6]. The ageing

process is influenced by different parameters, such as the presence of ferrous metals because of their oxidation and the CO₂ content of the gaseous phase present in the porosity of MSWI BA. As the ferrous removal is more and more efficient and as the MSWI BA are stored in heaps, limiting the atmospheric exchange, the efficiency of ageing process is no longer certain.

The main objective of this study was to measure the efficiency of the ageing process when MSWI BA are stored in heap of 1200 tons. The mineralogical evolution and the leaching behavior of BA were observed during 7 months. Moreover, the ageing process was accelerated by using two different procedures: a 6 weeks 'natural' ageing process performed on a small sample (5 kg) with good atmospheric contact, and an 'artificial' carbonation with the application of a pure CO₂ flow through the MSWI BA. The leaching behavior of weathered MSWI BA was measured and used as reference.

Material and methods

Material

The MSWI BA samples were collected from a French MSWI plant. The waste treatment plant capacity is approximately 57 000 tons/year, which results in a monthly production of BA of about 1000 tons. In accordance with regulations, monthly productions of 40 mm sieved BA, from which ferrous and non-ferrous metals have been removed, are stored in separate heaps. The sampling was performed on one monthly batch of BA with a mechanical shovel. To ensure sample representativity, six samplings of about 100 kg were made on the heap, at 2 heights in 3 different points, at least 1 m deep. The 600 kg recovered were homogenized and quartered to obtain a sample of 60 kg. The residual moisture content was measured by drying at 105°C until the mass was constant. Next, the 60 kg sample was dried and a representative sub-sample (about 30 kg) was obtained by quartering the sample to a 1/2 split. Subsequent quartering was carried out to supply samples (7.5 kg) for various laboratory tests. Before analysis, the bottom ash sample was sieved to 4 mm and ferrous and non-ferrous metals were removed from the remaining fraction. The remaining fraction was then, crushed to 4 mm. About 1 kg of the sample thus obtained was crushed to 1 mm for X-ray diffraction (XRD) analyses.

Methods

Ageing process

Industrial ageing process: The procedure described above was carried out five times in order to obtain five samples at different ages. The heap of MSWI was stored on an uncovered platform. These samples were named IAT0, IAT2, IAT4, IAT6 and IAT7, where the numeral represented the ageing time in months.

Laboratory ageing process: A sample of 20 kg issued from the fifth sampling, i.e. IAT7 (7 months old), was moistened in order to obtain a residual moisture content of 12% to facilitate the carbonation process [7]. During a period of 6 weeks, the sample was moistened and mixed each week, ensuring a good atmosphere-surface exchange. The ageing evolution was followed by the measure of pH. After 6 weeks, a sample named LAT7 was obtained and characterized.

Laboratory artificial carbonation: A second sample of 2.5 kg issued from the fifth sampling, i.e. IAT7 (7 months old), was artificially carbonated in a lab-pilot described by Kaibouchi (2004) [8]. The MSWI-BA introduced in the pilot had a residual moisture content of 11% and was submitted to an ascendant flow of pure CO₂ (900 mL.min⁻¹). To limit the preferential pathways, a bidim[®] was introduced under the material. The carbonated sample obtained was named LCT7, characterized and compared to the IAT7 and LAT7 samples.

Solid characterization

Total Contents: Total elemental content was determined by inductively coupled plasma spectrometry (ICP-MS) after microwave-assisted digestion of 0.1 g of dry sample, with concentrated nitric acid (HNO₃), perchloric acid (HClO₄) and hydrofluoric acid (HF).

XRD: X-ray diffraction (XRD) analyses were conducted on three replicates of MSWI bottom ash samples using a BRUKER[®] D8 Advance instrument diffractometer. The samples were scanned from 0° to 70° 2θ at a scan rate of 0.02° (40)/s. A DIFFRACplus program BASIC Evaluation Package, version

EVA12, 2006 composition DIFFRACplus BASIC software package (Bruker AXS) and databases ICDD PDF-2 Release 2006 were used.

FT-IR: Fourier transform infrared spectroscopy (FT-IR) analysis was conducted on a Nicolet Magna 550 spectrometer. Each sample was mixed thoroughly with potassium bromide and pressed to create pellets for analysis. The spectra were recorded in the range of 400 to 4000 cm^{-1} , with 2 cm^{-1} resolution.

TG-DSC: Thermogravimetry coupled with differential scanning calorimetry (TG-DSC) was conducted in a LABSYS calorimeter (TG-DSC 1600, SETARAM) where the mass loss (TG) and DSC profiles are recorded simultaneously. Combustion took place under atmosphere with a temperature range from 25 to 850°C (ramp rate of 10 $^{\circ}\text{C}.\text{min}^{-1}$), using a gas (air) flow of 30 $\text{mL}.\text{min}^{-1}$. 20 mg of sample was placed in an Al_2O_3 crucible without a lid. Both TG and DSC baselines were corrected by subtracting the baselines recorded under identical conditions during a second run of the sample. All experiments were performed in triplicate.

Leaching procedure

Leaching test: The European standard leaching test EN 12457-2 is performed in a single batch at liquid-to-solid ratio L/S =10 $\text{L}.\text{kg}^{-1}$, with deionized water as leachant agitated for 24 h [9]. For this study, the leaching test was conducted on the < 4mm sieved fraction. The eluate was filtered through a 0.45 μm membrane filter. The pH of the eluate was measured immediately. The test was performed in triplicate.

Element concentrations: The concentrations of major and mineral trace elements in the eluates from the leaching tests were measured by inductively coupled plasma atomic emission spectroscopy (ICP–AES) and Ionic Chromatography (IC) for anionic species (Cl^- and SO_4^{2-}).

Results and discussion

Results were evaluated considering that the industrial ageing process was influenced by the size of the heap of more than 800 tons of MSWI BA. The weather conditions and the move of the heap between the third and the fourth sampling influenced the chemical and mineralogical changes, hence the leaching behavior. Thus, conclusions had to be interpreted, more as global trends of the evolution of the heap, than absolute results.

Evolution of the physico-chemical parameters

The residual moisture content and the pH of eluates after leaching tests on different samples were reported in Table 1. The residual moisture content measured for the five samples IAT0 to IAT7 were not significantly different. IAT2 and IAT6 were respectively sampled in winter and spring and their slightly higher water contents may be due to snow and rain precipitations.

Table 1 Residual moisture and pH values evolution for industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7)

Sample	IAT0	IAT2	IAT4	IAT6	IAT7	LAT7	LCT7
Residual moisture content (%)	21.8±1	23.6±0.1	21.4±0.2	23.5±0.1	21.9±0.5	12*	11*
pH	12.8±0.1	12.6±0.1	12.7±0.1	12.1±0.1	11.9±0.1	9.4±0.1	8.7±0.1

*adjusted values

All these values were too high to allow the weathering. In fact, the moisture can limit the transfer of gaseous phase in the porosity of MSWI BA, the surface exchange with the atmosphere and the weathering reactions, carbonation reaction for example [7, 8]. Indeed, the pH is globally constant during the first four months. A slight decrease of pH was observed for IAT6 and IAT7. However, the final pH of LAT7 and LCT7 were respectively 9.4 and 8.7. These values showed that with optimized conditions (optimal moisture content, high surface exchange between the atmosphere and the solid phases) weathering could occur, decreasing the pH. For LCT7, the pH value was characteristic for carbonated bottom ash and calcite buffering [10,11].

Evolution of the chemical and mineralogical composition

Total content evolution

The evolution of the total contents for major and MTE was reported in the Table 2. These results didn't show any significant variations all along the industrial ageing process (IAT0 to IAT7 samples) for major element content. A slight variation was observable for Ca and Si during the first four months. However, the values obtained for these two elements over the next months, confirm that these variations were not significant. The MTE content didn't show notable differences either, especially as the MTE contents are strongly dependent on "nugget effect" in spite of all the precautions taken during the sampling procedure.

Table 2 Evolution of the total content for industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7)

Sample	IAT0	IAT2	IAT4	IAT6	IAT7	LAT7	LCT7
Major Elements g.kg⁻¹							
Si	182.8	199.2	223.8	194.0	183.9	193.7	190.8
Ca	149.3	137.2	119.9	135.6	136.1	131.3	126.7
Fe	81.5	73.4	73.7	85.6	77.1	69.8	68.2
Al	45.7	45.6	38.5	45.3	39.9	45.9	49.2
Na	27.7	31.5	41.0	32.8	28.1	27	30.9
Mg	13.5	13.0	11.5	12.4	12.7	0.8	0.9
P	8.6	7.5	5.9	7.4	8.2	7.3	7.6
K	9.6	9.4	9.0	8.5	9.0	4.6	5.8
S	7	5.7	4.1	5.9	6.5	6.4	6.1
Mineral Trace Elements mg.kg⁻¹							
As	13.4	11.8	14.6	16.4	29.6	15.1	17.7
Ba	1102.0	938.8	1750	1131	1349	916.4	2962
Cr	827.9	698.1	633.8	734.6	671.9	675	479.3
Cu	4214	1697	1217	4130	2310	1266	2922
Mo	14.5	12.2	11.1	13.9	12.9	12	11.8
Ni	264.5	214.8	150.4	177.6	238.9	216.8	132.3
Pb	1207	812.8	925	1072.7	2036.4	736.9	1053.4
Sb	72.1	61.2	70.4	75.8	251.9	67.7	59
Zn	2413	2684	2712	2471	6433	2448	2620

During the first four months, Sb and Zn contents remained constant. Whereas Cr, Cu, Ni and Pb contents slightly decreased. This decrease might be due to surface washing phenomenon at the surface of the heap. Moreover, an increase of these MTE' contents in the samples IAT6 and IAT7 was observed, which can be attributed to the move of the heap. Indeed, the move of the heap can bring near the surface elements weakly drained since the beginning of the weathering.

Concerning the laboratory ageing of BA and carbonated BA, only slight differences have been observed for the major or mineral trace elements. A decrease of the total content of Fe, Mg and K was observed. Indeed, the total content of MTE was different for LAT7 and LCT7 sample, which is in accordance with literature [12].

Mineralogical evolution

The mineralogical evolution was observed by XRD and FT-IR analysis performed on different samples (Table 3 and Figure 1 respectively). Only slight differences for major mineralogical compounds were observed on IAT0 to IAT7 samples [13]. On the other hand, the carbonation was highlighted for the LCT7 sample.

For IAT0 to IAT7 samples, the gismondine, the quartz and the gehlenite were identified by XRD as major silicate phases in MSWI BA. With FT-IR analysis, the band of vibration Si-O (1088 cm^{-1}) attributed to quartz was present in all the samples. Indeed, the band of vibration Si-Ca (794 cm^{-1})

confirmed the presence of silicate phases. Because of glass alteration in basic conditions, the proportion of gismondine increased during the weathering process. The proportion of quartz detected by XRD increased rather in older samples. This result can be attributed to the depletion of amorphous silica in fresh bottom ash [14]. The proportion of the gehlenite didn't change during the weathering, and the tobermorite was not detected in the older samples. In agreement with the literature, all the results showed that the weathering procedure had no influence on the proportions of the silicate phases [11, 14]. The proportion of the quartz, the gehlenite and the gismondine remain practically constant in LAT7 and LCT7 samples. No evolution was observed on the band of Si-O or Si-Ca either. This means that silicate phases are very stable in bottom ash.

Table 3 Proportion (%) calculated with Diffracplus software of major mineral phases detected by XRD analysis performed on industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7)

Mineralogical compounds	IAT0	IAT2	IAT4	IAT6	IAT7	LAT7	LCT7
Quartz SiO_2	5	7	8	14	14	15	12
Gismondine $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$	15	15	19	37	39	38	40
Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$	<5	6	<5	<5	6	5	6
Tobermorite $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_{12}$	13	9	ND*	ND	ND	ND	ND
Calcium hydroxide $\text{Ca}(\text{OH})_2$	< 5	<5	<1	<1	<1	ND	ND
Calcite CaCO_3	<5	5	6	7	9	10	13
Anhydrite CaSO_4	5	<5	ND	ND	ND	ND	ND
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	ND	ND	ND	<5	<5	<5	5
Ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	<5	<5	ND	5	8	<5	<1
Hydrocalumite $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}(\text{H}_2\text{O})_2$	ND	ND	ND	ND	<5	ND	ND

*ND = not detected

The calcite was also detected in all the samples and its relative proportion increased during the weathering, whereas the proportion of the calcium hydroxide decreased. Indeed, the calcite was formed because of the carbonation of the calcium hydroxide in contact with CO_2 from the atmosphere. The evolution of carbonation was revealed by the FT-IR analysis: the band of vibrations C-O (1427 and 874 cm^{-1}) attributed to the carbonate increased, while a progressive decrease of the band O-H (3643 cm^{-1}) attributed to the calcium hydroxide was observed. For the LAT7 and LCT7 samples, the carbonation was complete as the calcium hydroxide wasn't detected by XRD anymore. Moreover the band of vibrations C-O (1427 and 874 cm^{-1}) was higher for LCT7 sample, whereas the band of vibration of O-H (3643 cm^{-1}) disappeared.

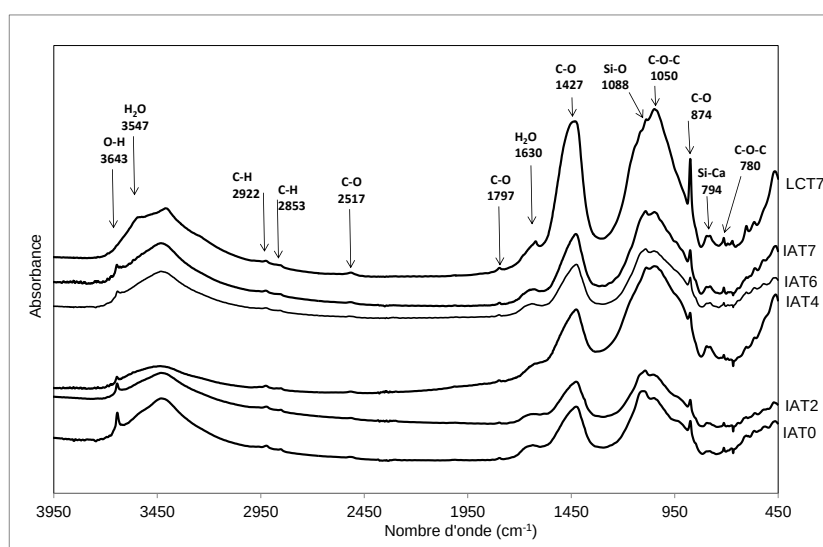


Fig. 1 FT-IR spectra of industrial ageing samples (from IAT0 to IAT7) and laboratory artificial carbonated sample (LCT7) - $450 - 3950$ cm^{-1} zone of the FT-IR spectra

The sulfate phases detected were essentially calcium sulfate phases (anhydrite, gypsum) or calcium aluminum sulfate phase (ettringite). In older samples (IAT4, IAT6 and IAT7), the anhydrite was not detected, whereas the gypsum was detected in slight proportion [15,16]. For the carbonated sample, a new band of vibration of H₂O (3547 cm⁻¹), attributed to the gypsum, was observed. The ettringite was detected in all the samples, with a slight increase with time. Indeed, the band of vibration of H₂O (1630 cm⁻¹) attributed to the ettringite is higher for older samples, than for IAT0 and IAT2 samples.

Thermal properties' evolution

The evolution of the thermal properties of bottom ash has been evaluated by TG-DSC. To analyze TG-DSC results (Figure 2), temperature zones were attributed to the decomposition of different compounds present in the bottom ash [7,17], as follows:

- Between 25 and 180°C, the slight endothermic effect, associated with a slight loss of mass (around 0.5%) mainly corresponds to the evaporation of the residual free water and the low bound water content, e.g. structural hydrates such as ettringite.
- Between 180 and 640°C, the combustion of organic matter takes place, giving rise to an extensive exothermic phenomenon. This phenomenon can be decomposed in two peaks. The first peak (180 – 375°C) is attributed to combustion of the aliphatic compounds and to decarboxylation. The second peak (375 – 640°C) is attributed to the combustion of more complex organic molecules with higher molecular weights, incorporating aromatic compounds. This peak also comes from the combustion of residual organic matter resulting from incomplete combustion in the incinerator [18,19,20,21].
- Between 640 and 800°C, a broad endothermic phenomenon is observed. This is mainly due to the decomposition of carbonates [18,22,23].

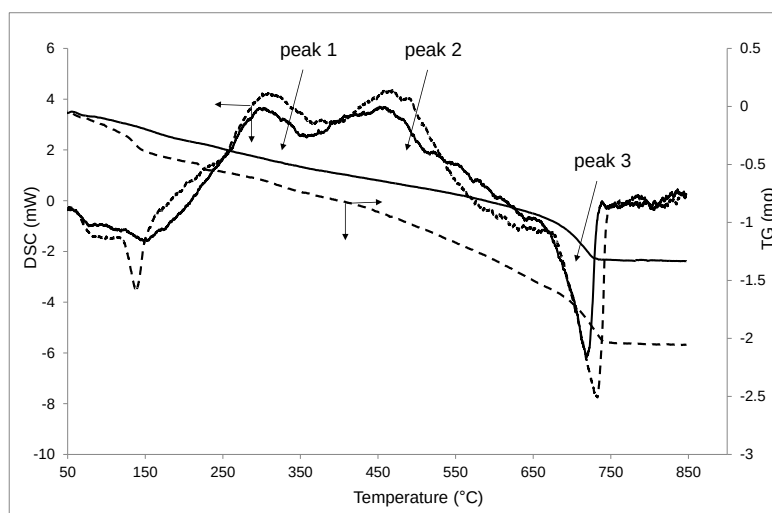


Fig. 2 TG-DSC thermograms of IAT7 (continuous) and LCT7 (dashed) samples.

Temperature range from 25 to 850°C

- ramp rate of 10°C.min⁻¹ under air flow of 30 mL.min⁻¹.

The percentage of mass loss due to the combustion of organic matter ($\Delta m_1 + \Delta m_2$) and the decomposition of carbonates (Δm_3) were reported in Table 4 for all the samples. A slight decrease of the loss of mass due to the combustion of organic matter (OM) was observed during the first four months of industrial weathering (samples IAT0 to IAT4). Moreover, the ratio $\Delta m_2/\Delta m_1$ slightly increased, and this result was a sign of the stabilization of OM [17,20]. Concerning the samples IAT6 and IAT7, the loss of mass due to the decomposition of OM increased. This result can be explained by the shifting of the heap – the OM at the center of the heap was not decomposed because of the lack of oxygen. Nevertheless, the values of the ratio $\Delta m_2/\Delta m_1$ indicated that the OM was stabilized with an evolution of aromatic structures due to the increase of humic acids [17,20,23]. During the laboratory ageing process, the OM was well stabilized – the highest ratio $\Delta m_2/\Delta m_1$ was measured for the LAT7

sample. On the contrary, the ratio for the artificial carbonated sample was intermediate, which indicated that the stabilization of OM was not achieved for this sample.

All these results were consistent with the FT-IR results. Indeed, the bands of vibration of C-H (2925 and 2849 cm^{-1}) attributed to the aliphatic methylene and the band of vibration of C-O-C (1049 cm^{-1}) attributed to the polysaccharides can be observed for all the sample on Figure 1, attesting the presence of residual OM. Moreover, for the LCT7 sample, these bands of vibration were slightly more intense, as was the loss of mass due to the combustion of OM on thermogravimetric analysis.

Table 4 Loss of mass of the peaks 1, 2 and 3 of TG-DSC curves of the industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7)

Sample	IAT0	IAT2	IAT4	IAT6	IAT7	LAT7	LCT7
Δm_1^* (%)	1.08	1.15	1.00	1.20	1.20	1.45	1.77
Δm_2 (%)	1.03	1.39	1.21	1.83	1.74	2.43	2.39
$\Delta m_1 + \Delta m_2 = \text{OM}^{**}$ (%)	2.11	2.54	2.21	3.03	2.94	3.88	4.16
$\Delta m_2 / \Delta m_1$	0.95	1.21	1.21	1.52	1.45	1.68	1.35
Δm_3 (%)	3.55	2.94	1.85	2.26	2.02	2.99	3.74

* Δm_i represents the loss of mass for the peak i in %

**OM = Organic Matter

The loss of mass associated to the decarbonation (peak 3) fluctuated during the weathering (IAT0 to IAT7 samples), which is in contradiction with the XRD and the FT-IR results. Other thermal phenomenon can also occur at this temperature range and disrupt the analysis of loss of mass of decarbonation. For example, the oxidation of iron oxide and the formation of hematite leads to an increase of mass [18]. The high content of carbonate in the IAT0 sample might be due to the *in situ* carbonation at the exit of the furnace. At this point, the temperature of bottom ash was between 450 and 650°C and the CO_2 content of the combustion gaseous phase was high [24]. The higher loss of mass associated to the decarbonation was obtained for the artificial carbonated sample (LCT7). This result was consistent with the XRD result.

Evolution of the leaching behavior

The leaching behavior of bottom ash has been evaluated according to the European standard leaching test EN 12457-2 [9]. The leachable fractions were plotted in Figure 3 for main major elements and in Figure 4 for several MTE, chlorides and sulfates. The results in Figure 4 were compared to the threshold limits in the French regulation (11/18/2011 decree) – to evaluate the reuse of bottom ash as substitute for natural aggregate in road construction.

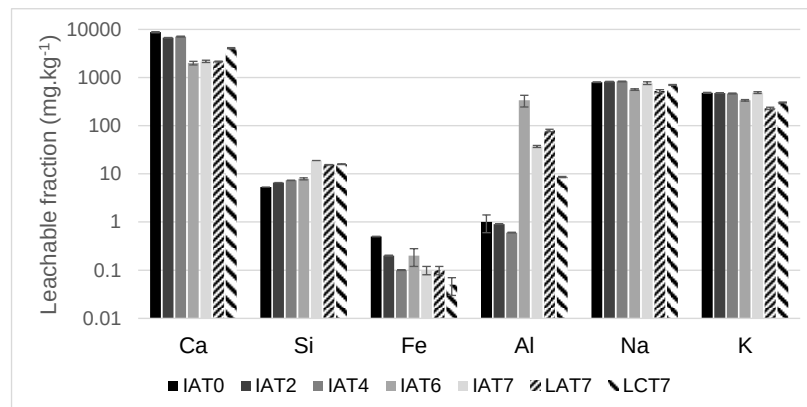


Fig. 3 Leachable fraction of Ca, Si, Fe, Al, Na and K for the industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7) - L/S ratio 10 L.kg^{-1} ; contact time 24h

The solubility of calcium depended on the pH of the eluates. During the first four months of the industrial weathering, it was higher than 12.4. The calcium hydroxide was precipitated and detected by XRD. After four months, the pH was lower than 12.4 – the calcium was precipitated as other mineral phases (ettringite for example) and its solubility changed [25]. The solubility of silicium remained low and slightly increased all along the industrial weathering. Silicium was bound to phases which had slow kinetics of dissolution depending on pH values (alumino-silicates phases, quartz...). For the sample IAT7, when the pH became lower than 12, the solubility of silicium was higher. The solubility of iron and aluminum was highly dependent on the move of the heap, with a clear difference between the results obtained for the IAT4 and the IAT6 samples. The leaching of sodium and potassium remained constant and high all along the weathering, suggesting that a portion of the sodium and the potassium were bound to stable and soluble phases like sylvite (KCl) or halite (NaCl) [26,27].

Concerning the ageing process, the leaching of major elements was not influenced by the laboratory ageing process. On the contrary, for the sample artificially carbonated (LCT7), the solubility of calcium, aluminum and iron were different. This result might be due to the precipitation of different phases (calcite, gypsum...) and the increase of solubility of iron and aluminum may be due to elemental metal oxidation [5,12,28,29].

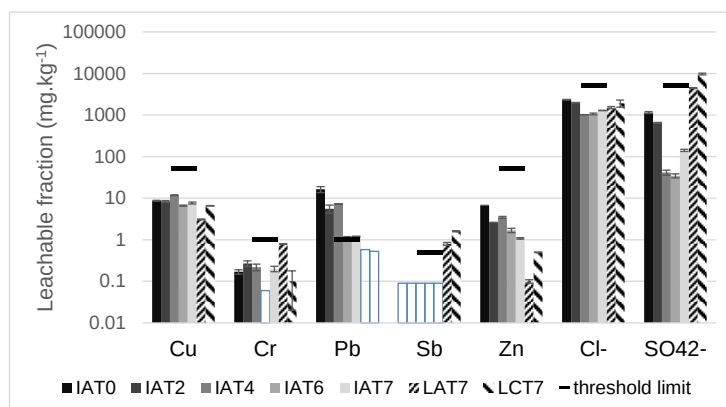


Fig. 4 Leachable fraction of Cu, Cr, Pb, Sb, Zn, Cl⁻ and SO₄²⁻ for the industrial ageing samples (from IAT0 to IAT7), laboratory ageing sample (LAT7) and laboratory artificial carbonated sample (LCT7) - L/S ratio 10 L.kg⁻¹; contact time 24h

– In white bars values below or equal to the limit of quantification

The leaching of *copper* slightly varied during the industrial weathering. A light decrease was observed for the LAT7 sample. During the laboratory ageing process (LAT7 sample), the OM was stabilized (*cf.* TG-DSC results) and the copper adsorbed on the organic matter was dissolved. Thus, copper could be adsorbed by the HFO (Hydrous Ferric Oxides) and the AAM (Amorphous Aluminum Minerals), which decreased its leachability. Indeed, this phenomenon was improved by the decrease of the pH value, which increased the adsorption surface [10,30].

The leaching of the *chromium* was very weak in all the samples. As a matter of fact, this MTE is mainly bound to silicate phases, which dissolved very slowly. After laboratory ageing process, the release of chromium increased. The chromate anion (CrO₄⁻) can substitute the sulfate (SO₄²⁻) in mineral phases as the Cr-monophase, the hydrocalumite and/or the ettringite. Thus, with the decrease of the pH value, due to the laboratory ageing process, the dissolution of these mineral phases facilitated the leaching of chromium or sulfates. On the other hand, with the artificial carbonation, and for a pH between 8 and 9, crocoite could precipitate and decrease the leaching of chromium [31,32].

The leaching of *lead* was high, the threshold limit was exceeded. Its mobilization decreased with weathering, because of the formation of stable complexes with hydroxyl ion (Pb(OH)₃⁻ and Pb(OH)₄²⁻) when pH value exceed 12. For LAT7 and LCT7 samples, the leaching of amphoteric MTE highly decreased. *Zinc* presented very similar behavior and may be precipitated as carbonate phases.

During the industrial weathering, *antimony* was not leached. The laboratory ageing process and the complete carbonation had a negative effect on the leaching of antimony, threshold limits were exceeded for LAT7 and LCT7 samples. When antimony is precipitated as *romeite*, the leaching of antimony is facilitated by the decrease of pH [1,29,31,32].

The leaching of *chloride* decreased during the first four months of industrial weathering, and then remained almost constant. During the first month, the leaching of chloride depended on very soluble salts (MgCl_2 , KCl , NaCl ). Chloride was precipitated in phases such as Friedel's salt and hydrocalumite. The solubility of these phases is dependent on the pH value and because of the decrease of pH with complete carbonation or laboratory weathering, the leaching of chloride increased [31,33,34].

The leaching of *sulfates* quickly decreased during the first months, and then, remained almost constant. First, soluble phases were dissolved ($\text{CaSO}_4(\text{aq})$, NaSO_4 and KSO_4). Then, sulfates were precipitated in ettringite, anhydrite or gypsum, with pH dependent solubility. These mineral phases were detected by XRD in LAT7 and LCT7 samples. Thus, the complete carbonation had a negative effect on the leaching of sulfates [4,31].

Conclusion

In this study, the weathering at industrial scale of a MSWI BA stored in a heap was monitored during 7 months. The results showed a very weak evolution, due to the limited exchanges with the atmosphere. Besides, the weathering of the same MSWI BA was carried out at laboratory scale. The evolution of the pH was accelerated. The mineralogy and the leaching behavior of the MTE were changed. Moreover, we highlighted that the complete carbonation has a negative effect towards the leaching behavior, except to amphoteric MTE.

Acknowledgments

The authors wish to thank Suez Environment for their financial support.

References

- [1] Cornelis. G.. Van Gerven. T.. Vandecasteele. C.. Antimony leaching from MSWI bottom ash: Modelling of the effect of pH and carbonation. *Waste manag.*, 32. 278-286 (2012)
- [2] Ministère de l'écologie, du développement durable, du transport et du logement. Arrêté du 18/11/2011 relatif au recyclage en technique routière des mâchefers d'incinération de déchets non dangereux. *Journal Officiel* n°0277 du 30 novembre 2011
- [3] Quina. M.J.. Bordado. J.C.M.. Quinta-Ferreira. R.M.. The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues. *Waste manag.*, 29. 2483-2493 (2009)
- [4] De Windt. L..Dabo. D.. Lidelöw. D.. Badreddine. R.. Lagerkvist. A.. MSWI bottom ash used as basement at two pilot-scale roads: comparison of leachate chemistry and reactive transport modeling. *Waste manag.* 31. 267-280 (2011)
- [5] Chimenos. J.M.. Fernandez. A.I.. Miralles. L.. Segarra. M.. Espiell. F.. Short-term natural weathering of MSWI bottom ash as a function of particle size. *Waste manag.* 23. 887-895 (2003)
- [6] Meima. J.A.. Comans. R.B.. Geochemical Modeling of Weathering Reactions in Municipal Solid Waste Incinerator Bottom Ash. *Environ. Sci. Technol.* 31. 1269-1276 (1997)
- [7] Rendek. E.. Influence des proceeds de la filière traitement thermique sur les caractéristiques et les évolutions bio-physico-chimiques des MIOM. PhD thesis INSA LYON. (2006)
- [8] Kaibouchi. S.. Mâchefers d'Incinération d'Ordures Ménagères : contribution à l'étude des mécanismes de stabilisation par carbonatation et influence de la collecte sélective. PhD thesis INSA LYON. (2004)
- [9] European standard. EN 12457-2: Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm (without or with size reduction) (2002)

-
- [10] Arickx. S., De Borger. V., Van Gerven. T., Vandecasteele. C., Effect of carbonation on the leaching of organic carbon and of copper from MSWI bottom ash, *Waste manag.* 30, 1296-1302 (2010)
 - [11] Piredda. M., Stabilization of MSW combustion residues by accelerated carbonation treatment and their potential carbon dioxide sequestration. PhD thesis Università degli studi di Cagliari (2011)
 - [12] Santos. R.M., Mertens. G., Salman. M., Cizer. O., Van Gerven. T., Comparative study of ageing, heat treatment and accelerated carbonation for stabilization of municipal solid waste incineration bottom ash in view of reducing regulated heavy metal/metalloid leaching. *J. of Env. Manag.* 128, 807-821 (2013)
 - [13] Gori. M., Bergfeldt. B., Pfrang-Stotz. G., Reichelt. J., Sirini. P., Effect of short-term natural weathering on MSWI and wood waste bottom ash leaching behaviour. *J. of Haz. Mat.* 189, 435-443 (2011)
 - [14] Bayuseno. A.P., Schmahl. W.W., Understanding the chemical and mineralogical properties of the inorganic portion of MSWI bottom ash, *Waste Manag.* 30, 1509-1520 (2010)
 - [15] Chimenos. J.M., Fernandez. A.I., Nadal. R., Espiell. F., Short-term natural weathering of MSWI bottom ash, *J. of Haz. Mat.* B79, 287-299 (2000)
 - [16] Polettini. A., Pomi. R., The leaching behavior of incinerator bottom ash as affected by accelerated ageing. *J. of Haz. Mat.* B113, 209-215 (2004)
 - [17] Achour. F., Caractérisation de la matière organique dans les ordures ménagères. Recherche d'indicateurs de stabilité. PhD thesis INSA LYON (2008)
 - [18] Delville. N., Etude minéralogique et physico-chimique des mâchefers d'incinération des ordures ménagères en vue d'une utilisation en technique routière. PhD thesis, Université Blaise Pascal, Clermont-Ferrand (2003)
 - [19] Smidt. E., Tintner. J., Application of differential scanning calorimetry (DSC) to evaluate the quality of compost organic matter. *Thermochimica Acta.* 459(1-2), 87-93 (2007)
 - [20] Melis. P., Castaldi. P., Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. *Thermochimica Acta.* 413, 209-214 (2004)
 - [21] Otero. M., Calvo. L. F., Estrada. B., García. A. I., Morán. A., Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants. *Thermochimica Acta,* 389(1-2), 121-132 (2002)
 - [22] Carrasco-Hurtado. B., Corpas-Iglesias. F.A., Cruz-Pérez. N., Terrado-Cepeda. J., Pérez-Villarejo. L., Addition of bottom ash from biomass in calcium silicate masonry units for use as construction material with thermal insulating properties. *Constr. And Build. Mater.* 52, 155-165 (2014)
 - [23] Smidt. E., Meissi. K., Tintner. J., Ottner. F., Interferences of carbonate quantification in municipal solid waste incinerator bottom ash: evaluation of different methods. *Environ. Chem. Lett.* 8, 217-222 (2010)
 - [24] Rocca. S., van Zomeren. A., Costa. G., Dijkstra. J.J., Comans. R.N.J., Lombardi. F., Mechanisms contributing to the thermal analysis of waste incineration bottom ash and quantification of different carbon species. *Waste Manag.* 33, 373-381 (2013)
 - [25] Saffarzadeh. A., Shimaoka. T., Wei. Y., Gardner. K.H., Musselman. C.N., Impacts of natural weathering on the transformation/neoformation processes in landfilled MSWI bottom ash: A geoenvironmental perspective. *Waste Manag.* 31, 2440-2454 (2011)
 - [26] Dijkstra. J.J., van der Sloot. H., Comans. R.N.J., The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. *Applied Geochemistry.* 21, 335-351 (2006)
 - [27] Guerin. L., Devenir des polluants inorganiques contenus dans les résidus solides issus de la combustion des déchets ménagers. Spéciation et élaboration de tests de mobilité en vue de leur stockage ou de leur valorisation. PhD thesis Université de Toulon et du Var. (2002)
 - [28] Meima J.A., van der Weijden. R.D., Eighmyc. T.T., Comans R.N.J., Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Applied Geochemistry.* 17, 1503-1513 (2002)
 - [29] Arickx. S., Van Gerven. T., Vandecasteele. C., Accelerated carbonation for treatment of MSWI bottom ash. *J. of Hazard. Mat.* B137, 235-243. (2006)
 - [30] Yao. J., Li. W.B., Tang. M., Fang. C.R., Feng. H.J., Shen. D.S., Effect of weathering treatment on the fractionation and leaching behavior of copper in municipal solid waste incinerator bottom ash. *Chemosphere.* 81, 571-576 (2010)
 - [31] Todorovic. J., Svensson. M., Hermann. I., Ecke. H., Artificial carbonation for controlling the mobility of critical elements in bottom ash. *J. Mater Cycles Waste manag.* 8, 145-153 (2006)

-
- [32] Van Gerven. T.. Van Keer. E..Arickx. S.. Jaspers. M.. Wauters. G.. Vandecasteele. C.. Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling. Waste manag. 25. 291-300 (2005)
- [33] Ahn. J.W.. Um. N.I.. Han. G.C.. You. K.S.. Cho. H.C.. Effect of carbonation in removal of chloride from municipal solid waste incineration bottom ash. Geosystem Eng. 9(4). 87-90 (2006)
- [34] Nilsson. M. Andreas. L. Lagerkvist. A.. Effect of accelerated carbonation and zero valent iron on metal leaching from bottom ash. Waste manag. 51. 97-104 (2016)