INFLUENCE OF CHEMICAL PRE-TREATMENT ON THE LEACHING BEHAVIOUR OF BOTTOM ASH

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Abstract

The valorisation of municipal solid waste incineration bottom ash is conditioned by its intrinsic content in pollutant elements such as BTEX, PCBs, hydrocarbons… and by potential release of mineral trace elements. An important percentage of bottom ash is currently not valorised because of regulation constraints. In this context, the objective of our study is to evaluate the influence of chemical pre-treatment on the leaching behaviour of bottom ash.

Firstly, the influence of different parameters on the efficiency of the chemical treatment has been investigated. Based on these results an optimised protocol has been developed, consisting of several steps of washing and rinsing. Secondly, for a better understanding of the leaching mechanisms involved, the leaching behaviour of this material has been modelled, using the geochemical modelling tool Phreeqc®.

The results show that the pre-treatment protocol defined is effective for most elements. There is a good coherence between experimental and simulated data for elements such as calcium and sulphur – these elements have been well described in the mineralogical assemblage. Results are less convincing for other elements (e.g. antimony) for which not enough data exists yet, in order to correctly define their geochemical speciation in the MSWI-BA.

To conclude, a short washing step with a hydrochloric acid solution 0.2M and a low liquid-to-solid ratio, followed by two rinsing steps, shows an important decrease in the leachability of MTE and anions from bottom ash.

Keywords

Municipal solid waste incineration; bottom ash, mineral trace elements, chemical treatment, leaching behaviour, geochemical modelling

Introduction

The production of municipal solid waste has been increasing over time due to urbanization. Efficient management of this waste is required in order to reduce its volume. Currently, the most spread process for the treatment of municipal solid waste is incineration, which is a thermal method that aims to recover energy from waste. Municipal waste incineration produces two types of solid residues: bottom ash, called MSWI-BA here after, and fly ash issued from air pollution control. All incineration residues are toxic, as they contain hazardous compounds: dioxins, mineral trace elements (MTE) and soluble salts such as chlorides and sulphates [1]. While the valorisation of fly ash is limited because of its high content in pollutant compounds [2], the bottom ash is widely used as backfill material [3, 4]. In France, the mostly spread application of bottom ash are the road base formulations. The thresholds for such valorisation are stated in the French decree from 18/11/2011 [5]. The pollutant potential of MSWI-BA is evaluated by leaching tests performed according to the EN 12457-2 standard [6].

A more interesting but not developed valorisation domain is the construction – bottom ash could be integrated in construction products’ formulations. In France, no regulation exists in this sense yet. In order to define reliable formulations, the material needs to be characterised at micro scale. MSWI-BA is composed of particles of variable sizes, including glass fragments, pieces of ceramic, unburned pieces and scrap. It is porous, angular with a rough texture and lighter than natural aggregates [7]. From the chemical point of view, the bottom ash has a heterogeneous nature, which differs depending on the origin of the waste and the type of the incinerators used during the process. MSWI-BA is in majority composed of silica, iron, aluminium, calcium, sulphates, chlorides...
etc. Besides these major compounds, bottom ash contains also MTE in small quantities, such as arsenic, copper, antimony, cadmium etc. [7-9]. The high leachability of these trace elements from MSWI-BA can lead to problems related to human health and the environment – once leached at contact with water, MTE can diffuse in the ground and underground water [10].

In this context, it is important considering pre-treatment methods of bottom ash before its valorisation. In France, only techniques aiming at the extraction of the soluble fraction are recognised by the authorities to open new ways of valuation as secondary raw material. As a consequence, our approach consists in chemical washings. The chemical washing of MSWI-BA has been previously tested by several authors [11-14]. It has been shown that very fine particles and mobile organic and inorganic contaminants (organic acids, MTE and salts) potentially leachable, can be removed by washing, or stabilised in the solid matrix, thus reducing the released quantities from the treated material. The present work serves three purposes: (i) to study the influence of different washing parameters on the leachable fraction of the main MTE, (ii) to optimize and implement a treatment including several washing and rinsing steps, (iii) to model the washing protocol using the geochemical modelling tool PhreeqC®, in order to better understand the geochemical composition of the MSWI-BA.

Materials and methods

About the studied bottom ash

The bottom ash used in this study was recovered from an energy enhancement unit located in the Auvergne-Rhône-Alpes region in France. Most of the waste comes from household, industry and water treatment plants. The furnace is equipped with a moving grate incinerator, which produces about 60 tons of bottom ash per day. 300 kg of MSWI-BA were recovered for this study – for representative sampling, 10 to 20 kg bottom ash were collected daily over one month. The MSWI-BA were then dried for one week at 80 °C. Ferrous and non-ferrous metals were removed by magnetic separation and by eddy current. The samples were prepared by quartering in order to obtain homogeneous subsamples. Three particle size fractions were prepared by sieving, respectively 0-2 mm fraction (V<2), 2-5 mm fraction (V2-5) and larger than 5 mm fraction (V>5).

Leaching behaviour of bottom ash

Based on the French decree from 18/11/2011 [5], the leachability of the studied material before and after chemical treatment was evaluated, according to the European standard leaching test EN 12457-2 [6]. Powdered material was agitated in a rotary eluent in contact with demineralised water at a liquid-to-solid ratio (L/S) of 10 L.kg⁻¹ during 24 h. The mixture was next filtered through a 0.45-μm cellulose acetate membrane. The concentrations of several major and trace elements in the eluates were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for metals and Ion Chromatography (IC) for the anions. All elements mentioned in the 18/11/2011 decree [5] were measured. The leaching test was performed in triplicate.

Optimisation of the chemical washing process

Various washing parameters have been studied: the nature of the washing solution and its concentration, the washing duration and the L/S ratio. The washing efficiency has been evaluated on all granulometric fractions [15]. Table 1 shows the values tested for the various parameters. After each test, the material was vacuum filtered through a 0.45-μm membrane, dried at 80 °C during 24 hours and tested according to the EN 12457-2 standard described above [6]. The concentrations of MTE and anions in the eluates were measured by ICP-MS and Cl.

| Table 1 Values of the different parameters tested during the washing treatment of MSWI-BA |
|-----------------------------------------------|-----------------|-----------------|---------------|-----------------|
| Extractant (concentration) | HCl (0.18 M) | HNO₃ (0.5 M) | EDTA (0.05 M) |               |
| Washing time (h)          | 1               | 3               | 6             | 24             |
| HCl concentration (mol.L⁻¹) | **0.18**        | 0.50            | 1.00          | 1.50           |
| L/S ratio (L.kg⁻¹)        | 2               | 5               | 10            |               |
| Granulometric fraction (mm) | V<2             | V2-5            | V>5           |               |


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The optimal set of parameters has been chosen based on the efficiency of the treatment process (see results in the next section), i.e. hydrochloric acid solution at 0.18 mol.L$^{-1}$, during 6 hours with a L/S ratio of 10 L.kg$^{-1}$ (in bold in table 1).

**Pre-treatment protocol**

A general pre-treatment protocol, comprising several stages of pre-wash, extraction and rinsing, has been studied. This protocol includes the following steps:

- Pre-wash with water: stirring during 60 min; L/S = 2 L.kg$^{-1}$
- Extraction with HCl (washing): 0.18M, stirring 60 min; L/S = 2 L.kg$^{-1}$
- First rinsing with water: stirring 60 min; L/S = 2 L.kg$^{-1}$
- Second rinsing with water: stirring 60 min; L/S = 2 L.kg$^{-1}$.

After each step, the eluates have been separated by centrifugation and then by filtration on a 0.45 μm cellulose acetate membrane. The concentrations of MTE and anions in the filtrates were analysed by ICP-MS and CI, respectively. Next, the MSWI-BA samples were dried at 80 °C for 24 hours and submitted to a leaching test with water according to the EN 12457-2 standard.

**Geochemical modelling**

All stages of the treatment protocol described above, followed by leaching tests, have been modelled using the specific geochemical modelling software PhreeqC® version 3 [16], coupled with the LLNL database (Lawrence Livermore National Laboratory). The solid is represented by an assembly of mineral phases, called mineralogical assemblage; it is put into contact with the liquid phase, called solution. The mineralogical assemblage defined by Gonzalez [17] for the modelling of MSWI-BA has been used as input data in this study. The calculations were made assuming thermodynamic equilibrium. All steps of the washing protocol defined above have been modelled with the corresponding parameters (L/S, solution, concentration etc.). The mineralogical assemblage resulting from one step is used as input data for the following step. The pH of the liquid phases reached at thermodynamic equilibrium and concentrations of different elements (major elements, MTE and anions) are compared to the concentrations measured experimentally. A final step simulates the leaching test performed on treated bottom ash.

**Results and discussions**

**Leaching behaviour of bottom ash before chemical treatment**

The leaching behaviour of MSWI-BA has been tested as described in the sections above, according to the EN 12457-2 standard [6]. Figure 1 shows the results for the three granulometric fractions studied here. The thresholds for secondary road base use [5] are satisfied for all MTE, as well as for sulphates, for all granulometric fractions. Only the chlorides exceeded the thresholds for fine and intermediate particle size.

For most elements (except antimony), the release increases with the decrease of the particle size, thus the most charged fraction is the V<2. For the majority of the elements the fine fraction (V<2) is the most charged with MTE [18-20], thus presenting the highest release. Vaporisation and condensation during the incineration process of wastes, leads to the accumulation of MTE in the fine particle size as metal oxides or combined with anions [20]. Less MTE are released from coarse particles, compared to the fine fraction for two main reasons: (i) they contain a high percentage of glass fragments and unburned pieces and (ii) the available contact surface is smaller than that of the fine fraction. Coarse particles might contain metal or metal alloys (e.g. copper wires, lead base alloys for soldering), metal oxide particles adherent to the surface of larger particles, or as additives used in the formulation of ceramics.
Influence of the different washing parameters on the chemical pre-treatment of bottom ash

In this section, the optimisation of various parameters of the chemical pre-treatment process, i.e. the nature of the washing solution, the concentration of the chosen washing agent, the L/S ratio and the contact time is presented. All tests have been performed in triplicate and are plotted along with the standard deviation, where this is coherent. The results are expressed in mg of leached element per kg of dry matter (DM) of bottom ash and are compared to the leaching fraction of raw MSWI-BA (V<2) and to the secondary road base thresholds.

Optimisation of the washing solution

Three different washing solutions were tested on the finest fraction of MSWI-BA (V<2) which has exhibited the highest released concentrations during the leaching tests (see figure 1). Figure 2 shows that the behaviour of elements varies depending on the washing solution. However, not all exhibit the same behaviour, e.g. arsenic, barium, molybdenum and nickel leach in higher concentrations after treatment with nitric acid, while lead and cadmium are more soluble after treatment with EDTA. HNO$_3$ is known to be a strong oxidizing agent. On the other hand, EDTA plays the role of a complexing agent known for its ability to chelate metals [21]. Concerning HCl, the chloride anions might complex with lead ions forming a water insoluble species, e.g. PbCl$_2$ [22]. EDTA proved to be inefficient in stabilising MTE, thus the release is higher after treatment (figure 2). Moreover, EDTA is not biodegradable and more expensive. HCl proved to be the best treatment agent, which reduces the release for most MTE. Hydrochloric acid has been selected for further tests.

Fig. 1 Leaching behaviour of the three fractions (cf. NF EN 12457-2); comparison with secondary road base thresholds according to the 18/11/2011 decree; in hatched the values below or equal to the limit of quantification

Fig. 2 Leachable fraction before (raw-BA) and after washing with HCl, HNO$_3$ and EDTA; in hatched the values below or equal to the limit of quantification
All three chemical agents used have interacted with the solid matrix either to solubilize the elements, thus reducing their total content), or to destabilise certain components, thus increasing their release during the following leaching test. In all cases, solubilised heavy metal ions might have been trapped on the solid matrix during the treatment process. A rinsing step proved to be necessary, in order to remove all traces of the chemical agent and other dissolved elements. The global protocol is described later.

**Optimisation of the concentration of hydrochloric acid**

Four different concentrations (0.18 M, 0.5 M, 1 M and 1.5 M) have been tested for the chosen washing agent, i.e. hydrochloric acid. The results are presented in figure 3 for the fine fraction (V<2). The efficiency of the washing process decreases with the increase of the concentration of acid for most elements. During the acid extraction MTE are replaced by H⁺ ions, thus becoming soluble. Chromium and antimony present a different behaviour. They are known to be stable in this range of pH, i.e. low alkaline pH, which explains the small variations with the concentration of the acid. Concerning the behaviour of Cl⁻ ions, their concentration increases with the increase of concentration of the washing agent. On the other hand, sulphates are soluble in acid solutions and easily leachable.

**Fig. 3** Leachable fraction before (raw-BA) and after washing (fraction V< 2) with HCl at 0.18 M, 0.5 M, 1 M and 1.5 M; in hatched the values below or equal to the limit of quantification

**Optimisation of the L/S ratio**

Three L/S ratios have been tested on the V<2 fraction using HCl 0.18 M solution during 6 hours (see figure 4). With some exceptions (chromium and antimony), the efficiency of washing increases with the decreasing of the L/S ratio. This behaviour has been also observed on fly ash by Huang et al. [22]. The quantity in moles of acid compared to the material mass increases with the L/S ratio, which leads to a smaller alkaline pH in the eluates. The leachability of most MTE increases with the decrease of pH in this range [18, 23-24]. Concerning the anions, the test has been performed only at ratio L/S = 2 L.kg⁻¹. For economic and environmental reasons, the L/S = 2 L.kg⁻¹ value has been selected for the global chemical treatment process of bottom ash.
Fig. 4 Leachable fraction before (raw-BA) and after washing of the fraction V<2 for the L/S ratios of 2, 5 and 10 L.kg⁻¹; in hatched the values below or equal to the limit of quantification

**Optimisation of the washing time**

Different contact durations have been tested on the V<2 fraction, with HCl 0.18 M and L/S = 10 L.kg⁻¹. The results show small variations in the release of elements. Whatever the contact time, a reduction in the overall metal concentration in the eluates is observed relative to the initial release from raw bottom ash. Similar results have been obtained by Huang et al. [22] on fly ash – more than 60% of MTE were released for low contact time with HCl, thus further leaching reveals unnecessary. The contact time of 1 hour has been chosen for this study.

**Influence of the washing on the particle size fraction**

The leaching of all considered particle size fractions before and after treatment with HCl 0.18 M solution has been tested (see figure 5). Similar results have been obtained by Gonzalez [17] and Chen et al. [25]. These results are very similar to those presented in figure 1, performed with the same experimental parameters, i.e. HCl, 0.18 M, L/S = 2 L.kg⁻¹, 6 hours (blue vs. red representation), thus confirming the reproducibility of the tests. Except arsenic, chrome and antimony, the general behaviour shows that for all particle size fractions the release of MTE decreases after treatment.

Fig. 5 Leachable fraction before (raw-BA) and after treatment for all particle size fractions; in hatched the values below or equal to the limit of quantification
Global chemical pre-treatment process for bottom ash

The optimisation study presented above allowed the development of a complete washing protocol, in order to meet the industrial demands (efficient, economic and environmental friendly). The most efficient extracting agent proved to be a slightly concentrated hydrochloric acid (0.2 M). Parameters such as contact time and L/S ratio presented small variations. For economic and environmental reasons (excessive production of liquid effluents to be treated later), the washing time was fixed at 1 hour and the L/S ratio at 2 L.kg⁻¹. The washing step is followed by two steps of rinsing with water, in order to remove the pollutants which have been previously solubilised and trapped in the solid phase. The global protocol has been detailed in the section § Materials and methods. This protocol has been next modelled; the results are presented below.

Modelling of the pre-treatment process of bottom ash

Study of the evolution of pH and the mineralogical assemblage

Figure 6 shows the evolution of the pH for each step of the treatment process. The lowest pH is observed for the extraction step, which is justified by the acidity of the extracting agent. The eluate however, has an alkaline pH (8.32), which confirms the large buffer capacity of bottom ash. The increasing of pH during the two rinsing steps and the final leaching show that the thermodynamic equilibrium is not achieved. Despite previous washing steps, the pH obtained in the leaching test remains above 10.

Concerning the theoretical evolution of the pH, the model shows that after the extraction step the pH remains constant at 11.21. This is explained by the fact that the calculations are performed with the hypothesis of thermodynamic equilibrium. Several phases are completely dissolved during the extraction step, conducting to an identical assemblage as input data for the first and the second rinsing. The pH obtained after the final leaching is slightly different (11.23), as the leaching ratio L/S has changed from 2 to 10 L.kg⁻¹. The 2 pH units difference between the model and the experiment for the extraction step could also be explained by the thermodynamic hypothesis used in the model. Bottom ash has shown a strong buffer capacity, taking up to a week to reach the thermodynamic equilibrium [17]. This hypothesis being too restrictive, an improvement of the model could be obtained by modelling dissolution kinetics for several phases.

The leaching behaviour of major elements

The methodology for modelling such complex materials starts by validating the mineralogical assemblage based on the chemical behaviour of major elements present in the solid phase [26-28]. Therefore, the leaching behaviour of the major elements present in the bottom ash was evaluated during the different stages of the washing process. Figure 7 shows that both experimental and modelled results have the same order of magnitude. However, depending on the element, the results are more or less convincing. Elements for which the mineral assemblage is
almost complete, like calcium, aluminium and sulphur are well represented. On the other hand, the mineral assemblage for silicium is more complex, and the results are less convincing for this element.

![Fig. 7](image)

**Fig. 7** Leachable fractions of major elements during the treatment protocol; experimental (not hatched) and modelled (hatched) results

*The leaching behaviour of MTE*

The chemical treatment applied in this study has proven efficient for all MTE – the release has decreased, compared to the leaching behaviour of raw bottom ash (see figure 8). Modelling has led to the same conclusions as in the case of elements, namely that well-defined elements in the assemblage, such as zinc, show good coherence between experimental and simulated leaching behaviour. On the other hand, elements such as lead or copper, are not well modelled. Further characterisation methods, such as acid neutralization capacity (ANC) leaching tests [29] or sequential extractions [30], combined with characterisation technical (XRD, SEM etc.), need to be used, in order to affine the knowledge of the mineralogical assemblage of this material.

![Fig. 8](image)

**Fig. 8** Evolution of the leachable fraction of MTE during the treatment protocol; experimental (not hatched) and modelled (hatched) results

*The leaching behaviour of chlorides and sulphates*

The results obtained for anions are presented in figure 9. An important quantity of chlorides and sulphates is solubilised during the pre-wash step, mainly because most of the NaCl and KCl can be removed by simple water washing [22]. This solubilisation is well represented by modelling. However, because of the thermodynamic equilibrium hypothesis, all chlorides are solubilised in the first two steps of the treatment, which leads to zero release during the rest of the protocol. This observation is not valid for experimental data.
Conclusions

For accomplishing the valorisation of bottom ash in construction, efforts need to be made in order to stabilise this material over time. In this sense, a chemical pre-treatment has been developed in the current study. The influence of different washing parameters on the leachable fraction of the main MTE was studied. A complete washing protocol consisting of 4 steps (pre-wash, acid extraction and two rinsings) has been defined. A dynamic rinsing would be necessary in order to remove the traces of metals solubilized during the extraction with HCl and adsorbed or wedged on the solid phase. It has been observed that a low L/S ratio increases the efficiency of the pre-treatment process, reducing the production of effluents. On the other hand, the contact time does not have a great impact on the efficiency of the treatment – a short contact time is preferable. Finally, the modelling of the complete washing protocol helped at understanding the geochemical composition of this complex material. The results confirm that in order to make this model reliable, it is imperative to define a complete mineralogical assemblage of MSWI-BA.

References


