Influence of Chemical Pre-treatment on the Leaching Behaviour of Bottom Ash

Ola Hammoud, Denise Blanc, Maria Lupsea Toader, Christine de Brauer

ola.hammoud@insa-lyon.fr

5th International Conference on Sustainable Solid Waste Management – Athens – 21 June 2017
Fly Ash

- heterogeneous material
- inert residues (ceramics, bottle glass...)
- incineration products
- unburned MSWI residues
French decree from 18/11/2011*

*French decree from 18/11/2011 on the recycling of MSWI-BA in road materials based on the released quantities of pollutants (European leaching test EN12457-2)
Chemical pre-treatment

Objective

Reduce the released quantities of fines particles and inorganic contaminants

Removed by washing

Stabilised in the solid matrix

Chemical treatment

Stabilised in the solid matrix

Removed by washing
Materials and methods

Auvergne Rhône-Alpes, France
MSWI-BA (0-2 mm)

Chemical treatment

Raw-BA

H₂O

HCl

H₂O

H₂O

Leaching test
EN 12457-2

Treated-BA

H₂O stirring
24 hours
10 L/kg

Raw-BA

Treated-BA
Optimisation of various washing parameters

<table>
<thead>
<tr>
<th>Extractant</th>
<th>HCl concentration (mol.L⁻¹)</th>
<th>Washing time (hours)</th>
<th>L/S ratio (L.kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.18</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.5</td>
<td>3</td>
<td>5</td>
</tr>
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<td>EDTA</td>
<td>1</td>
<td>6</td>
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</tr>
<tr>
<td></td>
<td>1.50</td>
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Chemical pre-treatment washing protocol

- **Prewash**: Reduce the quantity of soluble elements
- **Acid extraction**: Destabilize the mineralogical phases
- **2 steps of rinsing**: Remove the elements trapped on the solid matrix
Efficiency of the chemical pre-treatment

- Released quantity (mg/kg DM)
  - Sb, Cr, Pb, Zn
  - Cl-, SO4-2-

- Raw BA
- Treated BA
- Thresholds for road material

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Modelling principles

Mineralogical assemblage = MSWI-BA

Solution

Phreeqc Interactive

Thermodynamic equilibrium

New mineralogical assemblage

Input data for the following step

[Elements] ; pH
Modelling vs. experimental

**Experimental and modelled results have the same order of magnitude**

**Modelling is reliable when the mineralogical assemblage is complete (e.g. Ca, Zn)**

- **Prewash** (H₂O, stirring 1 hour, 2 L/kg)
- **Extraction** (HCl, stirring 1 hour, 2 L/kg)
- **First rinsing** (H₂O, stirring 1 hour, 2 L/kg)
- **Second rinsing** (H₂O, stirring 1 hour, 2 L/kg)
- **Leaching test** (H₂O, stirring 24 hours, 10 L/kg)
- **Thresholds for road material** (French decree)
Conclusions & perspectives

➢ Efficient chemical pre-treatment protocol:
  ▪ HCl in small concentration (2M)
  ▪ low L/S ratio
  ▪ short contact time

➢ Dynamic rinsing is necessary to remove the traces of dissolved metals

➢ Improvement of the mineralogical assemblage: other characterisation methods (SEM-EDS, sequential extraction...)

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Thank you for your attention!

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## Optimisation of different washing parameters

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<td>1.00 1.50</td>
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### Released quantity (mg/kg DM)

![Graph showing released quantity of various elements (Sb, Cr, Pb, Zn, Cl⁻, SO₄²⁻, Mo, Ni, Cu) for Raw-BA and Treated BA. Red lines indicate thresholds.](image)
Optimisation of a chemical pre-treatment protocol

**Prewash**
- $\text{H}_2\text{O}$
- Stirring 1 h
- 2 L/kg

**Acid extraction**
- HCl 0.2 M
- Stirring 1 h
- 2 L/kg

**2 steps of rinsing**
- $\text{H}_2\text{O}$
- Stirring 1 h
- 2 L/kg

To reduce the quantity of soluble elements
To destabilize the mineralogical phases
To remove the elements which have been trapped on the solid matrix
Context

MSWI-BA

New decree of building construction

French decree from 18/11/2011

1. To have an other alternatives ways of valorization
2. To reduce the use of natural aggregates and also the price of construction materials

1. Competition with other natural materials
2. The environmental restrictions
3. The image of the materials as a waste and not as a product

Development of setup for the determination of the influence of different washing parameters on the leachable fraction of the main MTE

Optimisation of the L/S ratio

3 L/S ratio were tested: 2, 5 and 10 L/kg \{HCl 0.18 M; contact time 6 h; V<2 fraction \}

The leachability of most MTE increases with the decrease of pH

L/S = 2 L/kg has been selected for global chemical treatment for economical and environmental reasons
Optimisation of different washing parameters

L/S ratio, size particle fraction and contact time

- The leachability of most MTE increases with the decrease of pH
- L/S = 2 L/kg has been selected for global chemical treatment for economical and environmental reasons

- The release of most MTE decreases after treatment with HCl for all particle size fractions (expt Sb, Cr and As)

- Whatever the contact time, a reduction in the overall metal concentration was observed.
- More than 60% of MTE were released for short contact time with HCl
- The contact time of 1 h has been chosen for the global chemical washing

L/S = 2 L/Kg; V < 2 mm and t = 1 h
Development of setup for the determination of the influence of different washing parameters on the leachable fraction of the main MTE

Optimisation of contact time

4 washing time were tested: 1, 3, 6 and 24 h \{HCl 0.18 M; L/S = 10 L/kg; V<2 fraction\}

Whatever the contact time, a reduction in the overall metal concentration was observed.

More than 60% of MTE were released for short contact time with HCl.

The contact time of 1 h has been chosen for the global chemical washing.
Different size particle fractions were tested: V<2; V 2-5; V>5 \{HCl 0.18 M, L/S = 10 L/kg; 6 h\}

The release of most MTE decreases after treatment with HCl for all particle size fractions (expt Sb, Cr and As)
Modelling the washing protocol using the geochemical modelling tool PhreeqC

Study of the leaching behaviour of major elements

Both experimental and modelled results have the same order of magnitude

The modeling is more reliable when the assembly mineralogical is complete ex: Ca
Modelling the washing protocol using the geochemical modelling tool PhreeqC

Study of the leaching behaviour of major MTE

Chemical treatment applied in this study has been proven to be efficient for all MTE

Zinc shows a good coherence between experimental and simulated leaching behaviour (its assemblage is well defined)
An important quantity of chlorides and sulphates is solubilised during the pre-wash step; most of NaCl and KCl can be removed by simple washing and rinsing.
Perspectives

- Development of construction materials incorporating treated materials (concrete, cement mortar...)
- Environmental and mechanical evaluation of materials (MLT, compressive strength, slump test...)
- Modelling of scenario

REDUCE, REUSE, RECYCLE

INSA
How modelling BA?

Use a previous work

Definition of a mineral assemblage representative of BA

Geochemical modeling (Phreeqc)

Fluorite
Celestine
gypsum
brushite
Barite

dissolution - précipitation

Ks = f (T, pH)

Adaptation of the assembly

From total content
Optimisation of different washing parameters

Concentration of hydrochloric acid: **0.18 M, 0.5 M, 1 M, 1.5 M**
L/S = 10 L/kg, 6 hours contact time, V<2 fraction

The efficiency of the washing process

With the addition of the [HCl] for most elements (expt Sb and Mo)

At low alkaline pH, Sb and Cr are more stable
The behaviour of elements varies depending on the washing solution.

HNO₃ is a strong oxidizing agent.
EDTA is a complexing agent.

MTE have been trapped on the solid matrix so a rinsing step is necessary.
**Optimisation of different washing parameters**

**L/S ratio, size particle fraction and contact time**

- **L/S**
  - The leachability of most MTE increases with the decrease of pH
  - L/S = 2 L/kg has been selected for global chemical treatment for economical and environmental reasons

- **Size particle fraction**
  - The release of most MTE decreases after treatment with HCl for all particle size fractions (expt Sb, Cr and As)

- **Contact time**
  - Whatever the contact time, a reduction in the overall metal concentration was observed.
  - More than 60% of MTE were released for short contact time with HCl
  - The contact time of 1 h has been chosen for the global chemical washing

**L/S = 2 L/Kg ; V < 2 mm and t = 1 h**
Conclusions & perspectives

- Fine particle size is more charged in MTE

- **HCl with small concentrations, Low L/S ratio and a short contact time** are efficient to increase the efficiency of pre-treatment process

- A **dynamic rinsing** is necessary to remove the traces of metals
- Different characterisation (XRD, SEM...), are necessary to improve the mineralogical assemblage

- Incorporation of the treated materials in different formulations to know if we can recover them in building construction

- Perform different environmental and mechanical tests of this material (compressive strength, slump test...)

Chemical treatment

Raw-BA

H₂O

HCl

H₂O

Treated-BA

H₂O
Cellule solaire → Traitement chimique → Plaquette de silicium

KOH → H₂O → Solution de décapage → H₂O