

Treatment of incineration by-products for generating new building materials

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1. Introduction

The aim of this project is to find an application for the 0-4 mm fraction of municipal solid waste incineration (MSWI) bottom ash. MSWI bottom ash is a heterogeneous material, consisting of stony, glassy and ceramic particles, as well as ferrous and non-ferrous metallic fractions in lower amounts, and even unburnt materials. Its component oxides make it a suitable material for use in concrete/mortar mixtures. However, its unwanted contaminant elements need to be taken into account before this goal can be achieved. There are two ways in which the bottom ash can be used as building material- either as concrete raw material, or as part of a prefabricated concrete product. For the first direction, the bottom ash will be characterized in terms of its physical (particle size distribution, water content, specific surface area, shape etc.) and chemical (composition, leaching, pozzolanicity etc.) properties in order to assess its suitability as concrete constituent. For the second direction, washing treatments will be used in order to produce concrete that complies with the environmental legislation for building materials.

2. Experimental program

2.1. Raw Materials

At present, Municipal Solid Waste Incineration (MSWI) bottom ash is used in low-grade applications (e.g. road base) or landfilled. However, this material has a similar composition to cement and other concrete constituents, suggesting its applicability in this field.

Tab. 1: The oxide composition of the MSWI bottom ash in % mass, compared to the ones of commercially available binders (coal combustion fly ash, ground granulated blast furnace slag and CEM I 42.5N); R.O.=remaining oxides.

Oxide	MSWI bottom ash 2012	MSWI bottom ash 2013	Coal combustion fly ash	Blast furnace slag	CEM I 42.5 N
CaO	20	21	4.5	39	62
SiO ₂	36.5	34	55	35	20
Al ₂ O ₃	10.6	9.6	22	12.5	6
Fe ₂ O ₃	15.4	16.8	8	9	3.5
MgO	2.2	2.5	2	0.5	1.5
SO ₃	1.5	2.9	1.5	0.1	4.5
R.O.	13.8	13.2	7	3.9	2.5

Table 1 shows how the composition of the 0-4 mm bottom ash compares to the composition of commercially available binders (coal combustion fly ash, ground granulated blast furnace slag and a Portland cement, CEM I 42.5N). The selected bottom ash fraction has a composition very similar to blast furnace slag, which is the main component (70% by mass) of CEM III B, the most used cement type in the Netherlands. Moreover, due to properties such as high water demand, the use of MSWI bottom ash can lead to enhanced properties.

Tab. 2: Comparison between the leaching analysis of the MSWI bottom ash 0-4 mm and the requirements of the Soil Quality Regulation for shaped, non-shaped and IBC materials.

Element	MSWI bottom ash 2013 (mg/kg)	MSWI bottom ash 2010 (mg/kg)	Shaped materials (mg/m ²)	Non-shaped materials (mg/kg)	Isolation IBC materials (mg/kg)
Antimony (Sb)	0.22	0.15	8.7	0.32	0.7
Arsenic (As)	<0.05	<0.05	260	0.9	2
Barium (Ba)	0.69	0.27	1500	22	100
Cadmium (Cd)	<0.001	<0.001	3.8	0.04	0.06
Chromium (Cr)	0.12	<0.05	120	0.63	7
Cobalt (Co)	<0.03	<0.03	60	0.54	2.4
Copper (Cu)	14	5.8	98	0.9	10
Mercury (Hg)	<0.0004	<0.0004	1.5	0.02	0.08
Nickel (Ni)	0.24	0.18	81	0.44	2.1
Molybdenum (Mo)	1.1	1.1	144	1	15
Lead (Pb)	<0.1	<0.1	400	2.3	8.3
Selenium (Se)	<0.007	<0.007	4.8	0.15	3
Tin (Sn)	<0.02	<0.02	50	0.4	2.3
Vanadium (V)	<0.1	<0.1	320	1.8	20
Zinc (Zn)	0.48	<0.2	800	4.5	14
Chloride (Cl ⁻)	6200	5800	110000	616	8800
Fluoride (F ⁻)	2.4	2	2500	55	1500
Sulphate (SO ₄ ²⁻)	1700	8200	165000	1730	20000

An important aspect taken into account is the environmental impact of this by-product, since both concrete constituents and final concrete products need to comply with the legislation in force. Therefore, the leaching of contaminants needs to be studied, and its interaction with the hydration of cement quantified.

In the Netherlands, there are two legislative documents that regulate the use of materials: Soil Quality Decree [1] and the Landfill Ban Decree [2]. Both decrees specify acceptable emission levels of both inorganic and organic compounds. The Soil Quality Decree sets limits for the composition and leaching of granular materials, designated as 'non-shaped', with respect to chloride, mercury, molybdenum and strontium, for example. If these requirements are not met, the granular material is considered as 'waste', and landfill of these materials is a remaining option. The composition and leaching are also leading in selecting the type of applicable landfill, namely for mineral or hazardous waste, and the relevant safety measures as laid down by the Landfill Ban Decree. By stabilization, e.g. combining different materials and adding primary binders (quicklime/hemi-hydrate/cement), a granular ('non-shaped') or a shaped product can be obtained for non-hazardous landfill, and sometimes it is even possible that the treated material meets the Soil Quality Decree requirements of a building material [3–7]. Table 2 compares the leaching of the MSWI bottom ash fraction 0-4 mm to the requirements of the Soil Quality Regulation.

The problem-contaminants of the selected bottom ash are antimony, copper, molybdenum and chlorides (highlighted in italics in Table 2). Copper oxide forms a heterogeneous solution with the clinker mineral C_3A and is physically entrapped by C_3A hydration products [8]. Kindness et al. [9] studied the immobilization of molybdenum using both model cement systems (mixtures of C_3S , C_2S , C_3A and gypsum) and real cement systems (Ordinary Portland Cement and Ground Blast Furnace Slag). After hardening of these systems in the presence of 2000 ppm molybdenum, the larger part was bound, while the rest stayed in solution as molybdate MoO_4^{2-} . Both antimony and chlorides are known to have an accelerating effect on cement hydration [10].

2.2. Experimental Process

The particle size distribution (PSD) was determined through dry sieving. The bottom ash samples were divided by dry sieving into 3 fractions: 0-0.125 mm, 0.125-1 mm and 1-4 mm. Each of the resulting 3 fractions was dried at 105 °C, milled to fine powder and analyzed by XRF using the OMNIAN method. Two additional fractions, 0.125-4 mm of each sample, were also analyzed for validating the measurements, with excellent results.

The following parameters were used for the washing treatment: liquid to solid ratio L/S=2, shaking speed 250 rpm, and a duration of treatment of 2 hours. Distilled water was used for the process and a shaking table Stuart SSL2 was employed, using a horizontal shaking movement for the washing of the three samples. XRF was employed to analyze the content of the solid samples after washing.

The chlorides from the leachates are automatically titrated (Titrino Metrohm 785 DMP) using a silver nitrate solution 0.01 M. Equation (1) represents the chemical process that takes place:



Silver chloride is formed as reaction product; the solubility of this chloride is very low, meaning that it will precipitate the chloride ions from the solution. The amount of needed silver nitrate is quantified, and based on it the amount of chlorides leached out of the bottom ash can be computed back, in mg Cl/ kg bottom ash.

3. Results and discussion

Figure 1 shows the PSD of the MSWI bottom ash on a logarithmic scale. Before sieving, the material was dried overnight at 105 °C to facilitate the dry sieving.

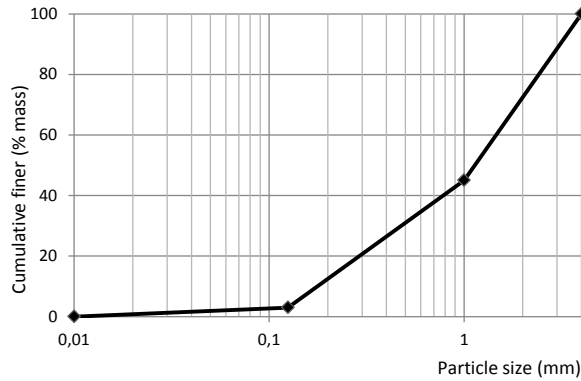


Fig. 1: Particle size distributions of the fresh bottom ash on a logarithmic scale

The cumulative PSDs of the fresh contains only 5.2% of the mass being represented by particles under 0.125 mm, while 65% by mass of the particles are over 1 mm.

It can be observed from Table 3 that there is a strong connection between the concentration of each constituent and the particle size. Some of the constituents have an ascending trend, increasing in concentration with the increase of particle size: Si, Fe, Mg (characteristic of natural gravel, for instance), while others have a descending trend: Ca, Al, Cu, S, Cl. The latter trend has been observed in literature for most anions and heavy metals, but on a larger particle size range [11,12].

Tab. 3: The oxide composition of the MSWI bottom ash in % mass, determined by XRF using the OMNIAN method; R.O.=remaining oxides.

Oxide	MSWI bottom ash 0-0.125 mm	MSWI bottom ash 0.125-1 mm	MSWI bottom ash 1-4 mm	MSWI bottom ash 0-4 mm
CaO	44.7	34.9	28.2	33.1
SiO ₂	12.1	21.7	27.4	23.2
Al ₂ O ₃	8.1	8.4	7.7	8.2
Fe ₂ O ₃	14.8	17.1	19.3	17.7
MgO	1.4	1.7	2.4	1.9
CuO	0.6	0.5	0.5	0.5
SO ₃	6.1	5.0	2.9	4.4
Cl	2.4	1.7	1.0	1.5
R.O.	9.8	9.0	10.6	9.5

The current results demonstrate that this is also applicable on narrower PSDs, suggesting that the material can be further improved by removing the smallest (and implicitly more contaminated) size fraction. Figure 2 shows the variation of constituent concentration with particle size. Figure 2d shows the cumulative distribution of SiO_2 in the two bottom ash samples, the percentage of each fraction by mass being correlated with its silica content. Taking the PSD into account renders identical distributions for all oxides and anions for the two bottom ash sources, which indicates that the two samples can be considered equivalent in terms of composition in further research.

Given the results above, the following steps were proposed: the washing of the 0.125-1 mm and 1-4 mm fractions, as well as separately washing the complete 0-4 bottom ash sample. The finest fraction represents only 3-5% by mass of the total PSD and, because of its high contaminant concentrations, will not be upgraded. The 0.125-1 mm fraction has a PSD equivalent to that of a 0-1 sand, and is expected to be used as sand replacement after an optimized washing step. The 1-4 mm fraction is the cleanest in terms of contaminants and could also be used as sand replacement in mortar/concrete mixes, after its leaching is brought under the legal requirements. The investigation of the complete PSD is attempted in order to find a single solution for the whole sample, which would be technically easier to employ in practice.

A first observation after the washing and filtering of the three samples was that a lot more fines were generated through this process than were separated through dry sieving. Table 4 shows the mass percentage of fines in each fraction before and after the washing process.

The difference between the percentages of fines determined for the washing treatment and for the initial PSD during characterization can be due to the heterogeneity of the material and to the sampling method. In any case, the 0.125-1 and 1-4 mm fractions do not contain any fine particles (under 0.125 mm) after the dry sieving process. However, after the washing treatment, the amount of fine particles separated is relatively high.

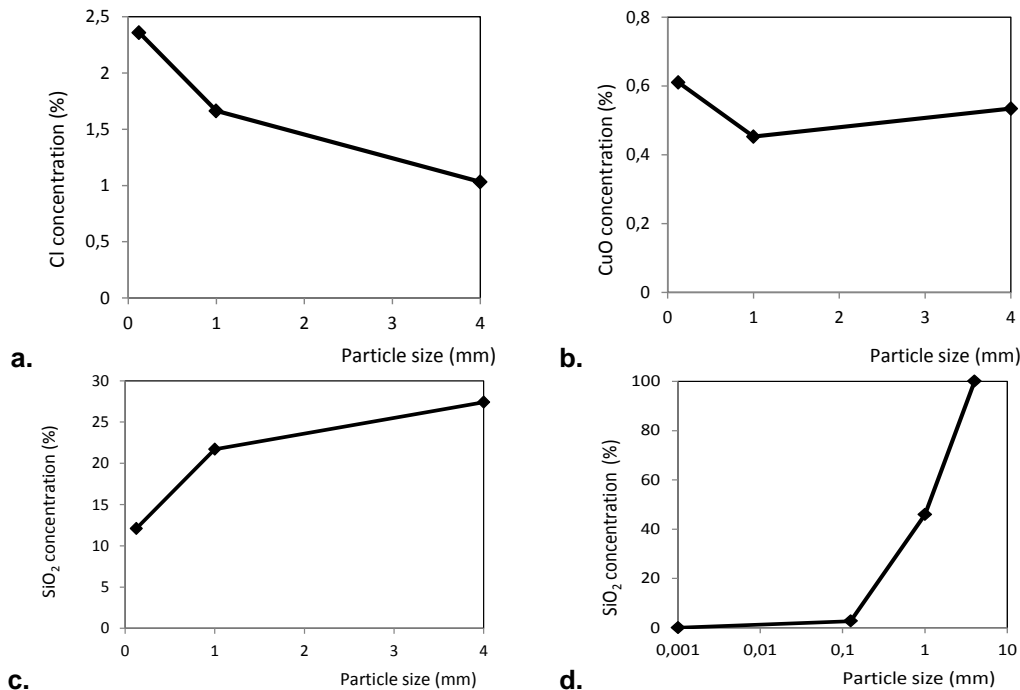


Fig. 2: The distribution of constituents in the bottom ash fractions: a. Cl, b. CuO, c. SiO_2 , d. cumulative SiO_2

Furthermore, fine particles were lost also during the filtering process, and are expected to be able to separate even more fine particles through a dry sieving of the coarser fraction after washing and drying.

Another observation is the remarkable similarity between the three separated fine fraction regardless of the size of the initial fraction that was washed, on one side, and the composition of the 0-0.125 mm fraction of the unwashed bottom ash (Table 3), on the other. The main differences between these washed fine fractions and the original one is, as expected, the decrease in the content of certain contaminants: Cu, SO₃ and Cl⁻. Another difference is the slightly modified Al/Fe ratio, which can be explained by the fact that some of the iron cations have been removed by the washing process.

Tab. 4: Amount of fines (<0.125 mm) in each bottom ash fraction before and after washing

Size fraction	MSWI bottom ash (%mass)	MSWI washed bottom ash (%mass)
0.125-1 mm	0	18
1-4 mm	0	8
0-4 mm	2.7	19

When comparing the three coarse fractions, the same similarity in composition can be observed; however, the differences are more notable, with the 0-4 washed coarse fraction having average values in between the ones of the 0.125-1 mm and 1-4 mm washed coarse fractions. This was to be expected, because the 0-4 mm sample is composed roughly of 50% by mass of each of the other two fractions. When comparing the three washed coarser fractions to their unwashed correspondents (Table 3), the same trend as in the case of the fine fractions can be observed: Cu, SO₃ and Cl⁻ decrease in concentration with the increase of particle size, together with Ca and Fe, which suggests an association of these two cations with the anions, while Si, Al and Mg are present in higher concentrations as the particle size increases. The latter can be explained by the generation of “cleaner” coarser fractions, through the removal of contaminants.

An XRD analysis could bring more insights into the mineralogy of the samples. Another important observation concerns the cumulative distribution of components in the washed fractions. Similar to the validation of the compositions of the original (unwashed) bottom ash fractions, a computation of cumulative distributions was used to validate the washed compositions. The split into fine and coarse fractions of the washed 0.125-1 mm and 1-4 mm samples were taken into account (Table 5) and re-combined; the resulting cumulative compositions compared to the ones of the 0-4 washed fractions (fine and coarse). However, this time these validations lead to interesting results. When comparing just the fine fractions, as expected, the 0-4 mm washed fine fraction has a composition very close to an average of the 0.125-1 mm and 1-4 mm fine fractions (because also their contribution in the whole 0-4 fraction was almost equal). The same holds true for the coarse washed fractions. However, when taking into account the cumulative distributions using the mass split described in Table 5, the results do not fit to the initial, unwashed fractions. Some of the constituents were removed through the washing process, which explains the mismatch, but the content of SiO₂, which should not have been leached out, can be used as an equivalent internal standard for validation.

Tab. 5: Composition of all separated fractions after washing in % mass; each initial fraction has been divided into fine and coarse fractions as explained above

Oxide	MSWI bottom ash 0.125-1 mm Fine	MSWI bottom ash 0.125-1 mm Coarse	MSWI bottom ash 1-4 mm Fine	MSWI bottom ash 1-4 mm Coarse	MSWI bottom ash 0-4 mm Fine	MSWI bottom ash 0-4 mm Coarse
CaO	45.7	21.6	41.3	18.2	43.3	20.6
SiO ₂	13.8	35.0	15.8	38.4	15.4	35.1
Al ₂ O ₃	17.0	16.1	20.5	14.4	17.7	14.5
Fe ₂ O ₃	6.5	11.3	4.4	10.8	7.0	12.8
MgO	2.6	3.8	3.5	5.2	2.9	3.4
CuO	0.6	0.3	0.4	0.3	0.5	0.3
SO ₃	5.9	3.4	6.6	2.5	5.8	2.7
Cl	0.4	0.2	0.4	0.2	0.4	0.2
R.O.	7.5	8.3	7.1	10.0	7.0	10.4

This possibility needs to be investigated further, by measuring the SiO₂ content using DSC [13, 14] and analyzing the leachate in order to compute a total mass balance after the washing step.

4. Conclusions

MSWI bottom ash 0-4 was analyzed and treated in order to become a building material. The contaminants that leached more than the Dutch legal limit were Cu, Mo, Cl⁻ and SO₄²⁻. It was shown that the distribution of the contaminants follows certain trends with particle size distribution.

After a washing step, the contaminant anions were shown to be drastically reduced in the final samples. The washing process generated significant amounts of fines which were not present before this step, by liberating fines from the larger particles. Regardless of the size fractions from which they were separated, these fines has a similar composition to the initial bottom ash fine fraction.

A global conclusion from these washed compositions is that certain elements, such as Fe, SO₃, Cl, K, are easily removed by washing, which suggests that they were probably present in anionic combinations (which are soluble in water). An XRD analysis could bring more insights into the mineralogy of the samples. Leaching tests will be performed to study the reduction of the contaminant cations. DSC measurements should be performed in order to relate the internal silica content to leached out elements and compute a mass balance for each element after the washing process.

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