Immobilisation of MSWI Fine By-Products

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Abstract

Municipal solid waste incineration (MSWI) produces a number of by-products: fly ashes, bottom ash and air pollution control residues. All these materials contain certain levels of contaminants, such as heavy metals, chlorides and sulphates among others, which are higher than the accepted limits for environmental protection in the Netherlands. Therefore, these contaminants need to be immobilized before the consideration of MSWI by-products as possible building materials.
Immobilisate recipes were tested for mechanical and environmental properties. These recipes fulfilled all the required conditions of compressive strength, durability and leaching, as well as the volume condition of staying under 125% of the volumes of the employed wastes. It was shown that using bottom ash, which is a non-hazardous MSWI waste, into the immobilisates (without counting it as a waste to be treated, but as a component that aids immobilisation) lowered the needed cement amount while also leading to improved environmental properties.

Introduction

Incineration by-products from two municipal solid incineration plants in the Netherlands were collected and analysed in this project: a scrubber residue, two fly ashes, a contaminated gypsum and a filter cake. Bottom ash was also employed, but since this is usually a non-hazardous by-product, it was not considered as a waste to be conditioned. The selected binder was a CEM I 52.5 N, and two more alternative binders were analysed for comparison: a ground granulated blast furnace slag and a coal combustion fly ash. The following tests were done on all materials: PSD (for the powders), specific density, water content, chemical composition (XRF), chloride leaching (titration) and a cascade leaching test. The results of all these tests can be found in [1]. The oxide composition and leaching values of the filter cake and bottom ash can be found in Tables 1 and 2, respectively. Table 3 gives an overview of physical properties of all by-products.

Table 1. Oxide composition of the filter cake and bottom ash, obtained by XRF on dry mass; other oxide compositions of analysed materials can be found in [1].

[%]	MgO	Al_2O_3	SiO_2	SO_3	CaO	Fe_2O_3	Cl	Br
Filter cake	3.3	1.6	4.9	14.7	21.7	22.3	10.2	0.13
Bottom ash	2.3	10	34	7.6	26.2	13.1	0.06	-

Immobilisates were designed using all by-products mixed together, in order to meet the following criteria :

1. The compressive strength of the monolith after 28 days of curing must be at least 1 MPa.
2. By using binders, it must be shown that the immobilization actually.
3. The leaching of a block must comply with a leaching following NEN 7345 [2]. The specimen must not disintegrate during the duration of the diffusion test.

4. The volume of monolith must not exceed 125% of the volume of the volume of the waste materials to be conditioned.

Table 2. Comparison between the leaching analysis of the by-products and the requirements of the Landfill Ban Decree [3] and Soil Quality Decree [4].

Element	**Non-hazardous [mg/kg]**	**Hazardous [mg/kg]**	**Non-shaped materials [mg/kg]**	**IBC materials [mg/kg]**	**Filter cake [mg/kg]**	**Bottom Ash 0-2 mm [mg/kg]**
Sb	0.06-0.7	0.7-5	0.32	0.7	2.7	1.2
As	0.5-2	2-25	0.9	2	0.042	< 0.03
Ba	20-100	100-300	22	100	1.3	0.37
Cd	0.04-1	1-5	0.04	0.06	0.12	< 0.004
Cr	0.5-10	10-70	0.63	7	< 0.02	0.2
Cu	2-50	50-100	0.9	10	0.55	0.48
Hg	0.01-0.2	0.2-2	0.02	0.08	0.89	0.0012
Mo	0.5-10	10-30	1	15	0.44	0.63
Ni	0.4-10	10-40	0.44	2.1	< 0.02	0.038
Pb	0.5-10	10-50	2.3	8.3	0.32	< 0.003
Se	0.1-0.5	0.5-7	0.15	3	< 0.05	< 0.05
Zn	4-50	50-200	4.5	14	1	0.057
Cl^-	800-15000	15000-25000	616	8800	4610	1900
F^-	10-150	150-500	55	1500	6.4	11
SO_4^{2-}	1000-20000	20000-50000	1730	20000	1200	15000

Besides these, an exception was identified in the legislation for the leaching values of chlorides, bromides and sulphates, as follows:

a. The content of $Cl^-+Br^-+SO_4^{2-}$ (by mass) does not exceed 20%
or
b. The material is landfilled at least 3 meters away from the perimeter of the landfill.

Materials and methods

Materials were analysed for particle size distribution using laser granulometry, density using a He pycnometer and water content by drying at 105 °C until constant mass (Table 3).

Immobilisate recipes were designed using all investigated by-products (Table 1), CEM I 52.5 N as binder and water and mixed using a similar procedure to the one prescribed in [5] for mortars. Two types of compaction were then used: vibration in prismatic moulds (40x40x160 mm) and using an Intensive Compaction Test (ICT) similar to devices used in asphalt research. Demoulding of the latter took place immediately and the samples were then stored in water for 28 days. The prisms were demoulded after 24 hours and then stored in water until compressive strength tests were performed. Such curing conditions can be viewed as an additional treatment step for reducing contaminant leaching, similar to a washing step but with an increased efficiency [6-8].
A cascade test was performed for all samples (liquid to solid ratio, L/S 10, shaking for 24 hours with 250 rpm) and the leachate analysed according to NEN 7345 [2].

Table 3. Physical properties of the six investigated materials

	Fly Ash A	**Fly Ash B**	**Scrubber residue**	**Gypsum**	**Filter cake**	**Bottom ash**
D_{min} [μm]	13.32	10.76	10.76	9.34	n/a	18.22
D_{max} [μm]	25.75	16.95	16.95	18.30	n/a	2000
Density [g/cm^3]	2.68	2.12	2.12	2.74	1.08	2.59
Water content [%]	1.22	0.93	0.97	32.1	65.4	10.4

Results

The scope of the first batch of immobilisate recipes was to design a non-hazardous block, fit for the edges of the landfill. Moreover, these tests serve as a first impression on the acquired strength of such samples and an indication of how to minimize the cement content of an immobilisate while at the same time maximizing its waste content.

Table 4. Mechanical properties of the designed immobilisates

		Recipe 1		**Recipe 2**	
Age		**Flexural strength [MPa]**	**Compressive strength [MPa]**	**Flexural strength [MPa]**	**Compressive strength [MPa]**
7 days	average	**1.59+/- 0.102**	**8.15+/- 0.150**	**1.00**	**3.91+/- 0.06**
	min	1.49	8.01	1.00	3.85
	max	1.73	8.36	1.00	3.96
14 days	average	**1.81+/- 0.118**	**14.20+/- 1.510**	**1.19+/-0.06**	**5.27+/-0.10**
	min	1.66	11.51	1.13	5.28
	max	1.99	16.39	1.25	5.51
28 days	average	**2.18+/- 0.060**	**15.07+/- 0.563**	**1.67+/-0.64**	**7.21+/-0.75**
	min	2.12	13.94	1.02	7.04
	max	2.26	15.79	2.12	8.50

Two recipes were designed, using the guidelines stated in the Introduction, and termed Recipe 1 and Recipe 2. A final oxide composition with the main oxide contents (SiO_2, CaO, Al_2O_3, Fe_2O_3) within the range of commercial binders (Table 4) was sought. The ratio between the five fine residues was kept constant in all recipes. Both the cement and water contents were kept under 20% each in the total mass of the mix, so that the dry incineration by-products (including bottom ash) make up at least 60%. The bottom ash content was kept between 25 and 40% by mass of immobilisate. Recipe 2 contains less bottom ash and therefore more fine by-products than Recipe 1. Table 4 presents the strength test results of the obtained prisms after various curing periods.

Figure 1. Aspect of the ICT mixes after 28 days curing

Using the same dry mix as Recipe 2, ICT samples were tested using various water contents in order to determine the minimum water content for a high compaction mix. Table 5 lists the water contents, densities and 28-days compressive strengths of the ICT samples (Figure 1).

Table 5. Water content and densities of the obtained ICT samples

	ICT-1 [mg/kg]	**ICT-2 [mg/kg]**	**ICT-3 [mg/kg]**	**ICT-4 [mg/kg]**
Water [% mass of dry mix]	13.1	13.7	12.8	11.8
Density [g/cm^3]	2128	2128	2100	2083
Strength [MPa]	9.20	12.50	3.95	14.85

The leaching of all designed immobilisates was measured using the cascade test after 28 days of curing in water. Table 6 summarises the results for all designed recipes.

Besides measuring the leaching of the final immobilisates, chloride leaching was measured on the curing water, to determine a total leached chloride content. The scope was to simulate a diffusion test, which would be used on the final product, as detailed in the introduction. Only chlorides were measured, because the individual leaching of both sulphates and bromides from all by-products were well under the legal limits. Moreover, this value is not relevant if the exception criteria for the maximum concentration of chlorides, sulphates and bromides is used. If the criteria for the middle of the landfill is used, then just the leaching of the rest of the contaminants and the compressive strength are important factors. It was found that an average of ~60% of the leachable chlorides were released into the curing water. If curing was done to simulate landfill conditions (less than 100% humidity), these chlorides would partly still be available for leaching during a diffusion test.
However, for the inner landfill, the chloride leaching would not be a criteria.

Table 6. The leaching contaminants of all immobilisates after 28 days curing in water

Element	Recipe 1 [mg/kg]	Recipe 2 [mg/kg]	ICT-1 [mg/kg]	ICT-2 [mg/kg]	ICT-3 [mg/kg]	ICT-4 [mg/kg]
As	< 0.05	0.16	0.03	0.032	0.03	0.031
Ba	1.1	1.5	1.9	2.2	1.9	2.8
Cd	< 0.004	0.024	0.026	0.046	0.026	0.039
Cr	0.15	0.2	0.35	0.43	0.33	0.6
Co	< 0.01	< 0.01	0.01	0.01	0.01	0.01
Cu	0.28	0.72	0.79	1.1	0.78	1.1
Hg	< 0.0004	< 0.0004	0.0004	0.00073	0.0004	0.00064
Mo	1.1	0.92	1.5	1.8	1.5	1.6
Ni	0.053	1.5	0.055	0.06	0.053	0.059
Pb	0.23	0.064	1.2	1.8	1.2	1.7
Sb	< 0.03	< 0.03	0.18	0.31	0.18	0.25
Se	< 0.05	< 0.005	0.05	0.05	0.05	0.05
Sn	< 0.05	0.096	0.12	0.21	0.13	0.16
V	< 0.02	< 0.02	0.02	0.026	0.02	0.022
Zn	0.08	1.80	2.1	3.4	2.1	2.9
Cl^-	5200	12	17600	22300	17400	32500
F^-	12	150	12	12	11	12
SO_4^{2-}	5700	10800	11000	11000	11000	11000
Br^-	68	10000	230	270	300	400
CN^-	< 0.01	< 0.01	0.01	0.01	0.01	0.01

Discussion and conclusions

Recipes 1 and 2 qualify as non-hazardous materials (Table 2). Moreover, both immobilisates also qualify for IBC materials, and could therefore be crushed and used for instance in sub-road applications. Therefore, these products could be used either as blocks or as crushed granulate for the exterior of a new landfill. Both these recipes fulfil the strength requirement criteria for shaped products; recipe 1 achieves a very high strengths for such materials, so the use of Recipe 2 is recommended in order to maximise the reuse of fine contaminated by-products.

The four ICT samples (Figure 1) achieved very different compressive strength and chloride leaching contents, despite having the same dry mix proportions and rather similar water contents. The scope of these trials was to determine a minimum water content for immobilisation. The added water amounts were chosen to achieve workable mixes, while keeping their moisture content just enough for proper compaction. While solid samples were indeed achieved, the added water was not sufficient to ensure cement hydration and therefore immobilisation of the contaminants. There are multiple causes for this effect, the main one being the high water consumption of the scrubber residue.
Therefore, in order to achieve proper immobilisation, the water content should be based, besides particle sizes and finess and water/cement ratio, also on the water needed for waste reactions. To conclude, a water content closer to 20% by mass of total mix (as used in Recipes 1 and 2) is recommended.

It needs to be pointed out that all recipes proposed in this study have been mixed, compacted and cured under laboratory conditions, using standard moulds. If casting large monoliths or directly landfilling these mixes, the

heat generation, hydration and strength development will not be uniform and they cannot be predicted with any accuracy based on small scale laboratory testing.
Water curing will lead to leaching of contaminants in the curing water; this step can be seen as a treatment step, in order to achieve lower leaching values of the final product. This step would imply minimum water volumes (compared to washing the materials before immobilization) and no drying step is needed. However, the curing of immobilisates in air is also possible if the landfill exception criteria are taken into account. In this case, the curing time can be shortened to 7 days or even less, since the immobilisate surpass the required compressive strength at this age.

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References

[1] Florea, M.V.A. Quaas, L.C. Brouwers, H.J.H.: MSWI by-products and immobilisates as concrete constituents. Int. Conf. Adv. Cem. Concr. Technol. Africa, Dar es Salaam, Tanzania. (2016).

[2] NEN 7345:1995 nl:Leaching characteristics of solid earthy and stony building and waste materials - Leaching tests - Determination of the leaching of inorganic components from buildings and monolitic waste materials with the diffusion test.

[3] Landfill Ban Decree - Besluit stortplaatsen en stortverboden afvalstoffen,VROM, Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordeling en Milieubeheer. (2012).

[4] Soil Quality Decree - Regeling bodemkwaliteit, VROM, Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordeling en Milieubeheer. (2013).

[5] EN 196-1 Methods of testing cement. Determination of strength. (2005).

[6] Florea, M.V.A.: Environmental Interactions of Cement-Based Products. Int. Conf. Adv. Cem. Concr. Technol. Africa, Dar es Salaam, Tanzania. (2016).

[7] Quaas, L. C., “Eco-concrete, M1 report, TUe,” 2015.

[8] Mangialardi, T., “Disposal of MSWI fly ash through a combined washing-immobilisation process.,” J. Hazard. Mater., vol. 98, pp. 225–240, 2003.