

Investigating the Mineralogy of Bottom Ash using XRD and PARC

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Abstract:

Recycling MSWI bottom ash fines is challenging due to the high content of contaminants and other properties such as high porosity. In order to optimize treatments, it is necessary to understand the mineralogical composition of BA fines. Two different fines were investigated: dry sieved fine bottom ash (FBA 0-4mm) and filter cake (FC < 0.250mm) produced during the washing of bottom ash fractions above 4mm. The chemical composition of both samples was determined (XRF) as well as their leaching behavior (ICP-OES). The mineralogical composition was measured via XRD Rietveld quantification. SEM and EDX were used to acquire a spectral imaging set that was analyzed with the PARC (PhAse Recognition and Characterization) software. The result is a quantification of all phases present, including their chemical composition and can be compared with XRD results. The results show that FBA grains are coated in melilite slag that is created during incineration. Around 36wt% of the sample is X-Ray amorphous. It also leaches more chloride than FC. FC contains a high amount of calcite and sulphate minerals such as gypsum and ettringite. It leaches more sulphate than FBA as a result. The amorphous content is 63wt%. PARC allows some insight into the chemical composition of these amorphous phases, however, the comparison between Rietveld quantification and PARC shows big differences that could be improved by measuring larger areas and analyzing them in PARC.

Keywords: MSWI, Bottom Ash, Contaminants, XRD, SEM

1. Introduction

Waste incineration reduces the volume and weight of household waste and is used for energy generation. Bottom ash (BA) is the main residue of this process [1]. In many countries, BA is landfilled, but it is also increasingly recycled as part of developing a cyclical economy in the EU [2]. New applications are developed and the bigger fractions are now applied as aggregate in building materials for example [3–5]. However, the application of smaller fractions (below 4mm) in building materials remains a challenge [6].

The main problems can be their high porosity [7], metallic aluminum content [3] and the high amounts of contaminants. The porosity leads to high water absorption, which can cause problems with the rheological properties of concrete. Metallic aluminum generates hydrogen gas in contact with the high pH environment of cement and can lead to cracks and loss of strength. The fine fractions of BA also tend to be the most contaminated ones [8]. If they are used in building materials these high concentrations can exceed the limits set by the Soil Quality Degree in the Netherlands [9]. However, the fine fractions also show some reactivity when mixed with cement and could potentially be used as a cement replacement [10].

In order to improve the properties of BA several treatments were developed, such as slow milling [7] or washing [8]. Slow milling can reduce porosity and remove metallic aluminium, but is generally not very effective in terms of reducing the leaching of highly soluble contaminants. Washing can remove a large percentage of soluble contaminants, it is however not always sufficient, tends to reduce the reactivity of BA and can produce heavily contaminated fines. For this reason, it is necessary to investigate the properties of fine BA and their composition in order to understand the effectiveness of treatments and optimize potential applications. Two different BA types were investigated, namely fine bottom ash (FBA 0-4mm) that is separated out via dry sieving at the processing plant and FC (< 0.250mm) the filter cake produced from washing bigger BA fractions (Figure 1), a technique that is increasingly employed in the Netherlands. Both materials were analyzed using large area phase analysis based on SEM spectral imaging (PhAse Recognition and Characterization - PARC), X-ray diffraction (XRD), X-ray fluorescence (XRF) and leaching of PTE's.

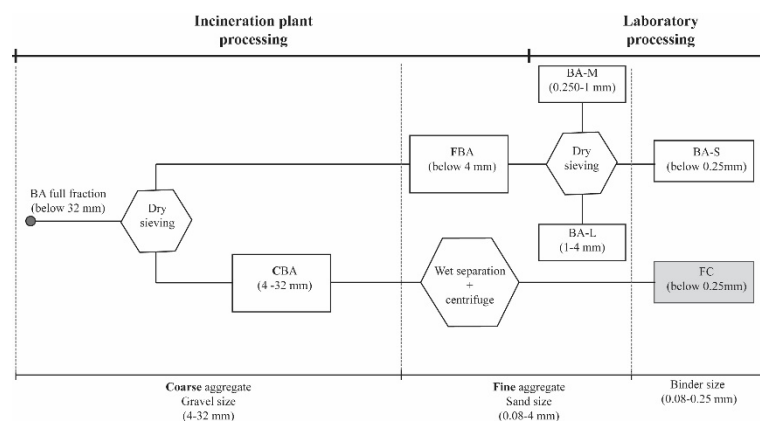


Figure 1: MSWI BA processing from the treatment plant to the laboratory scale, according to the different particle fraction obtained by sieving technique.

2. Material and Methods

2.1 Materials

MSWI bottom ash with a particle size below 4 mm (FBA) was provided by Heros Sluiskil B.V., the Netherlands together with the filter cake (FC) that is produced during washing of the bigger BA fractions (Figure 1). FBA is separated out via dry sieving at the plant due to its high content of contaminants and not washed. FBA was weathered for about 6 weeks at the plant after quenching.

2.2 Methods

The overall chemical composition of the two BA materials was determined via XRF (PANalytical Epsilon 3) using pressed powder. The composition of the leachates was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Varian 730-ES). XRD measurements were performed with a Bruker D4 and a Panalytical X'Pert Pro using Co-radiation ($K\alpha_1$ 1,7901Å). Both devices had fixed divergence slits with an opening of 0.5° and 0.04 rad soller slits. A step size of 0.02 was used. 10wt% of Si was added as an internal standard for the quantification of amorphous content.

Scanning electron microscopy (SEM) measurements combined with X-Ray microanalysis (EDX) was performed with samples prepared by mounting in epoxy and polished to a flat surface without the use of water. They were coated with carbon. The spectral imaging (SI) data sets for the PARC analysis were acquired using a JEOL JSM-7001F SEM using two 30 mm² SDD detectors (Thermo Fisher Scientific) and NORAN-System7 hardware with NSS.3.3 software. The SEM accelerating voltage was 15 kV, the beam current 6.2nA and the step size of the measurement 1µm. The PARC software enables the grouping of elemental spectra taken from each measured pixel according to elemental signals above a defined threshold and their ratio. These groups are then represented as color-coded phase maps [11].

The leachates of FBA and FC were produced according to the comparable standards NEN-EN 12457-4 and EN 12457 – 2 respectively. After filtration, the leachate acidified with HNO₃ and analyzed via ICP/OES according to NEN 6966. The Cl⁻ and SO₄²⁻ content was measured by ion chromatography (IC) (Thermo scientific Dionex ICS-1100). The concentration of all contaminants is given as mg per kg of dry solid (d.s.) BA.

3. Results and Discussion

The overall oxide composition of both BA products is given in Table 1. FBA (0-4mm) contains more than double the amount of SiO₂, as well as a slightly higher content of Al₂O₃ and Fe₂O₃. FC (<0.125mm) on the other hand has a higher CaO and SO₃ content. The phase composition (Table 1) shows that this difference is mainly due to the calcite, gypsum and ettringite content, while quartz is enriched in FBA (0-4mm).

The higher SiO_2 content can be explained by the higher quartz content (Table 1) of FBA. Quartz is mechanically resistant and tends to accumulate in the bigger fractions of BA. Calcite is produced during the weathering of BA. It has a low mechanical resistance and can be removed from the surface of bigger fractions during washing[8]. This way it tends to accumulate in the finer fractions. The high content of sulfate content is the result of sulfates getting dissolved during the washing of the bigger fractions and them being enriched in the filter cake FC also contains a very high amount of X-Ray amorphous phase compared to FBA as a result of the washing and hydration products forming that tend to be amorphous.

Table 1: XRF Oxide composition of both BA products together with their main phases determined via Rietveld quantification. All results are given in wt%.

	Oxides				Phases		
		FBA	FC			FBA	FC
		% wt.	% wt.			% wt.	% wt.
	MgO	1.9	1.9		Melilite	4.7	0.7
	Al_2O_3	10.6	8.8		Feldspar	5.7	1.4
	SiO_2	33.7	15.3		Calcite	13.5	17.4
	P_2O_5	1.4	1.1		Ettringite	0.2	10.4
	SO_3	1.0	2.5		Gypsum	0.2	2.6
	K_2O	0.9	0.9		Halite	0.8	0.4
	CaO	17.1	32.7		Apatite	6.5	-
	TiO_2	1.2	1.9		Quartz	12.5	2.1
	MnO	0.1	0.5		Hematite	3.8	1.2
	Fe_2O_3	12.2	10.3		Spinel	8.9	0.5
	CuO	0.3	0.6		Other	7.1	0.4
	ZnO	0.6	1.2		Amorphous	36.1	63.0
Other	0.4	0.5					
LOI	18.5	21.4					

The leaching behavior confirms the results obtained from XRF and XRD. The sulfate and chloride leaching for both materials is above or very close to the legal limit established by the Dutch Soil Quality Degree [12]. However, the sulfate leaching from FC (<0.125mm) is significantly higher than that from FBA (0-4mm), due to the high gypsum and ettringite content. The opposite is true for chlorides. FC only leaches about half the amount of FBA. This is likely a result of the fact that chlorides have a higher solubility than sulfates so that they are partially removed during the washing process that produces the FC.

The leaching of Sb from the FC is also above the limit set by the Soil Quality Degree and can be explained by the affinity of Sb for minerals such as calcite and ettringite [13].

Both FC (<0.125mm) and FBA (0-4mm) contain high amounts of amorphous phase from incineration, weathering, and washing that cannot be differentiated via XRD. For that reason, PARC measurements were done on both materials. This method also provides information about the microstructure of the material as well as the distribution of phases and their composition. Since both samples are very inhomogeneous and include many different phases, most of which are only present in small amounts, only the major phases are included here.

PARC measurements of FBA were presented previously (Figure 2) [14] and show a rim of melilite or amorphous phases with a melilitic composition around bigger, more homogenous grains. These phases are formed from slag during the incineration process.

Table 2: Leaching behavior of both BA products together with the limits imposed by the Dutch Soil Quality degree. All results are given in mg/kg d.s. Values that exceed the limit are bolded.

Element	SQD Limits	FBA	FC
Sb	0.32	0.22	2.4
As	0.9	< 0.05	< 0.3
Ba	22	0.7	0.4
Cd	0.04	< 0.001	< 0.02
Cr	0.63	0.12	0.2
Co	0.54	< 0.03	< 0.02
Cu	0.9	14	1.3
Pb	2.3	< 0.1	0.1
Mo	1	1.1	0.7
Ni	0.44	0.24	0.07
Se	0.15	< 0.007	< 0.2
Sn	0.4	< 0.02	< 0.1
V	1.8	< 0.1	< 0.1
Zn	4.5	0.48	0.4
Cl-	616	6200	2966
SO ₄ ²⁻	1730	1700	21179

Figure 3 shows a representative field of the PARC measurement of FC. As expected the particle size is much smaller on average. However, minerals with a higher hardness (e.g. quartz) tend to be present as bigger grains, while calcite, in particular, is present as very small particles. The particles themselves are also more homogenous due to their small size.

The average composition and amount of some of the most common phases is given in Table 3 for FBA and Table 4 for FC.

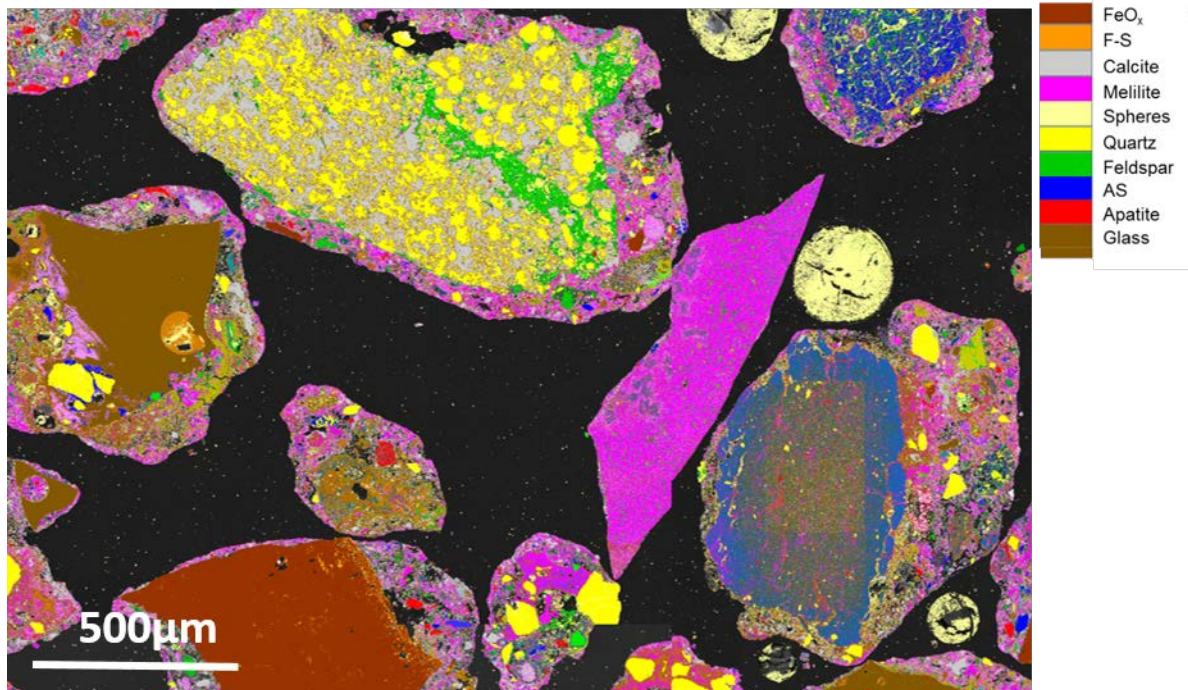


Figure 2: PARC image of FBA (0-4mm) including the main phases. Phases that could not be identified as a mineral are given a name in cement notation based on the main oxides in the phases. Glass denotes industrial soda-lime glass while spheres are porous SiO₂ rich incineration products similar to fly ash [14].

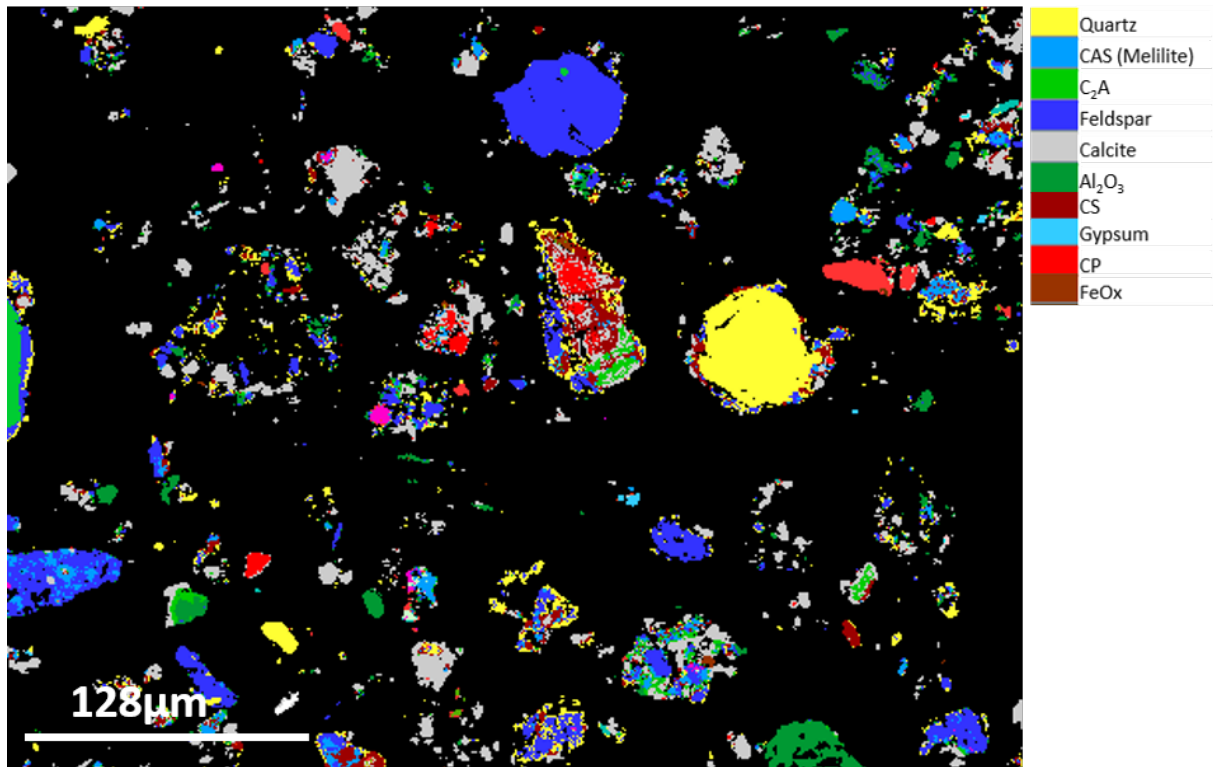


Figure 3: PARC image of FC (<0.125mm) including the main phases. Phases that could not be identified as a mineral are given a name in cement notation based on the main oxides in the phases.

Table 3: Average composition and amount of some of the major phases in FBA (0-4mm) as determined via PARC. Phases that could not be identified as a mineral are given a name in cement notation based on the main oxides in the phases.

Oxides	FeOx	Calcite	Melilite	Quartz	Feldspar	CAS 1	CAS 2	CS 1	CS 2
MgO	0.38	1.22	2.40	0.38	2.46	1.76	9.79	3.19	3.49
Al ₂ O ₃	1.32	6.90	18.05	0.87	24.91	20.14	15.40	3.41	7.56
SiO ₂	1.87	6.75	28.44	94.34	43.76	10.52	32.97	42.52	30.18
P ₂ O ₅	0.13	1.47	1.50	0.10	0.99	1.52	1.19	0.92	1.78
SO ₃	0.48	5.63	3.15	0.90	2.10	8.66	1.07	0.42	2.57
Cl	0.24	1.69	1.28	0.10	1.51	2.56	1.17	0.35	1.62
K ₂ O	0.08	0.39	1.03	0.16	2.64	0.69	0.75	0.30	0.85
CaO	2.33	66.87	33.16	0.64	11.14	45.20	27.10	38.99	37.80
TiO ₂	0.35	1.53	1.27	0.07	0.98	1.24	1.07	1.25	1.68
MnO	0.22	0.41	0.07	0.03	0.10	0.08	0.07	0.25	0.18
Fe ₂ O ₃	91.18	3.44	5.85	1.00	4.38	3.18	5.09	4.60	7.14
Cu ₂ O	0.26	0.25	0.19	0.07	0.30	0.26	0.27	0.13	0.28
ZnO	0.30	0.45	0.51	0.11	0.72	0.75	0.68	0.47	0.64
Other	0.87	3.00	3.12	1.22	4.01	3.43	3.37	3.19	4.23
Amount (area %)	12.23	8.83	14.14	12.64	3.51	5.65	4.24	3.43	7.80

Table 4: Average composition and amount of some of the major phases in FC (<0.125mm) as determined via PARC. Phases that could not be identified as a mineral are given a name in cement notation based on the main oxides in the phases.

Oxides	Calcite	Quartz	CAS	C ₂ A	CS	A	AS
MgO	2.5	1.2	2.4	2.7	2.3	2.5	1.4
Al ₂ O ₃	7.9	4.6	22.3	17.1	10.3	52.4	24.7
SiO ₂	10.2	82.3	31.5	10.3	27.4	16.3	54.0
P ₂ O ₅	2.8	0.0	2.3	1.4	5.4	2.0	0.8
SO ₃	3.1	1.3	0.9	0.8	0.9	0.9	1.0
Cl	1.3	0.7	1.0	0.8	1.1	2.1	0.6
K ₂ O	0.3	0.0	1.0	0.2	0.3	0.7	1.5
CaO	59.8	4.5	26.8	35.4	33.9	11.6	7.0
TiO ₂	1.9	0.3	1.9	4.5	1.8	0.7	0.5
MnO	0.3	0.2	0.4	0.6	1.0	0.4	0.1
Fe ₂ O ₃	6.5	3.3	5.4	21.7	11.6	5.6	4.0
Cu ₂ O	0.4	0.3	0.5	0.6	0.4	0.8	0.5
ZnO	0.8	0.5	0.9	1.2	0.9	1.5	0.5
Other	2.2	0.8	2.9	2.7	2.9	2.6	3.6
Amount (area %)	25.1	19.22	5.4	2.8	7.48	7.76	24.01

A direct comparison between Rietveld quantification and PARC is difficult because the resolution of PARC is limited to around 1µm. It also cannot differentiate between amorphous and crystalline phases, while Rietveld cannot give information about the composition of the amorphous content. Another problem is that only a limited area can be analyzed with PARC, while XRD gives information about a much larger sample volume.

The best phases for a comparison are calcite and quartz. The calcite content determined with PARC is 8.8 area% for FBA, while the result from Rietveld refinement is 13.5 wt%. For FC it is 25 area% and 17.5 wt% respectively. For quartz, the results from PARC are 12.5 area% for FBA and 19.2 area% for FC. Rietveld quantification gives the amount as 12.5 wt% (FBA) and 2.1 wt% (FC). It is likely that measuring a larger area of the FC sample would improve the results.

4. Conclusion

The composition of two different BA products was investigated: fine dry sieved bottom ash FBA (0-4mm) and filter cake FC (<0.125mm) that is produced during washing of bigger fractions. FC contains more CaO and SO₃, while FBA is enriched in SiO₂. XRD Rietveld quantification shows that this is due to the presence of sulfate minerals such as gypsum and ettringite in FC, as well as a higher quartz content in FBA. Leaching tests support these results. The sulfate leaching from FC is about 12 times higher than from FBA, while chloride leaching from FC is only half.

Both BA products also contain a large amount of X-Ray amorphous phase (63 and 36wt% respectively). For this reason, PARC analysis was performed which is based on SEM spectral imaging. It shows the different microstructure and allows some insight into the composition of the amorphous content of both FBA and FC. For FBA the amorphous phase is mostly melilitic in nature as a result of the slag that is formed during incineration. This also seems to be the case for FC, however further study is needed to differentiate between melilitic phases and possible hydration products that are formed during the washing. The PARC measurement should also be extended to a bigger area in the future to achieve phase contents that are in better agreements with the Rietveld quantification.

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6. Literature

- [1] C.C. Wiles, "Municipal solid waste combustion ash: State-of-the-knowledge," *J. Hazard. Mater.*, vol. 47, no. 1–3, pp. 325–344, May 1996.
- [2] M. States and G.D.P. Co, "Europe 2020 targets," *Europe*, no. April, p. 2020, 2011.
- [3] U. Müller and K. Rübner, "The microstructure of concrete made with municipal waste incinerator bottom ash as an aggregate component," *Cem. Concr. Res.*, vol. 36, no. 8, pp. 1434–1443, 2006.
- [4] W.-T. Kuo, C.-C. Liu, and D.-S. Su, "Use of washed municipal solid waste incinerator bottom ash in pervious concrete," *Cem. Concr. Compos.*, vol. 37, no. 1, 2013.
- [5] J. Pera, L. Coutaz, J. Ambroise, and M. Chababbet, "Use of incinerator bottom ash in concrete," *Cem. Concr. Res.*, vol. 27, no. 1, pp. 1–5, 1997.
- [6] P. Tang, M.V.A. Florea, P. Spiesz, and H.J.H. Brouwers, "Application of thermally activated municipal solid waste incineration (MSWI) bottom ash fines as binder substitute," *Cem. Concr. Compos.*, vol. 70, pp. 194–205, 2016.
- [7] V. Caprai, M.V.A. Florea, and H.J.H. Brouwers, "Evaluation of the influence of mechanical activation on physical and chemical properties of municipal solid waste incineration sludge," *J. Environ. Manage.*, 2017.
- [8] Q. Alam, M.V.A. Florea, K. Schollbach, and H.J.H. Brouwers, "A two-stage treatment for Municipal Solid Waste Incineration (MSWI) bottom ash to remove agglomerated fine particles and leachable contaminants," *Waste Manag.*, p. , 2017.
- [9] *Soil Quality Decree. Regeling Bodemkwaliteit*, VROM, Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, 2013.
- [10] K.L. Lin and D.F. Lin, "Hydration characteristics of municipal solid waste incinerator bottom ash slag as a pozzolanic material for use in cement," *Cem. Concr. Compos.*, vol. 28, no. 9, pp. 817–823, 2006.
- [11] C.J.G. van Hoek, J. Small, and S.R. van der Laan, "Large area phase mapping using PhAse Recognition and Characterization (PARC) software," *Micros. Today*, vol. 24, no. 3, 2016.
- [12] *Regeling bodemkwaliteit*, VROM. Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer., 2013.
- [13] G. Cornelis, T. Van Gerven, and C. Vandecasteele, "The effect of calcium-bearing minerals on the solubility of molybdate and antimonate in alkaline wastes," in *International Conference on Engineering for Waste Treatment*, 2005.
- [14] K. Schollbach, Q. Alam, V. Caprai, M.V.A. Florea, S.R. van der Laan, C.J.G. van Hoek, and H.J.H. Brouwers "Combined Characterisation of MSWI Bottom Ash," in *Proceedings of the Thirty-Eight International Conference on Cement Microscopy*, 2016, pp. 74–82.