Mineralogical Analysis of MSWI Bottom Ash

K. Schollbach[1], Q. Alam[1], M.V.A. Florea[1], S.R. van der Laan[2], C.J.G. van Hoek[2] H.J.H Brouwers[1]

[1]Department of the Build Environment, Technical University Eindhoven, Eindhoven, P.O. Box 513, 5600 MB, Netherlands
[2]Tata Steel Europe, RD&T, Ceramics Research Centre, P.O. Box 10000, 1970 CA IJmuiden, The Netherlands

Corresponding Author: k.schollbach@tue.nl, Tel.:+31 40 247 8958, Fax: +31 40 243 85 95

Abstract

Strict legislative limits in regards to contaminants make it difficult to use Municipal Solid Waste Incineration bottom ash (MSWI BA) in building materials or landfill it in the Netherlands. The purpose of this investigation is to determine the mineralogical composition of BA fines (0-4 mm) which is usually the most contaminated fraction. Knowledge about the mineralogy can help determine where contaminants are bound in the material and how they will react to treatment or application in concrete. The main methods employed are XRD and SEM-EDX and the identified mineral phases fall into the categories of inert incineration residue, incineration or weathering product. However, further research is needed to identify all phases to allow for a complete quantification using Rietveld refinement in the future.

Keywords

MSWI bottom ash, XRD, SEM, mineralogy, composition

Introduction

In the Netherlands the majority of municipal solid waste is incinerated rather than landfilled, which reduces the volume of waste by up to 90% [1]. One of the solid residues produced this way is Municipal Solid Waste Incineration (MSWI) bottom ash, which is a very inhomogeneous material containing inert residues (ceramics, bottle glas or natural rocks), incineration products, weathering products as well as unburned MSWI residues [2].

It is well known that bottom ash (BA), especially the fines [1], can be heavily contaminated with a wide variety of metals, Cl^- or SO_4^{2-}. For this reason the Dutch legislation specifies different leaching limits for this material depending on its use. The leachate that is used as basis for testing is produced by mixing BA and water at a ratio of 1:10 in all cases.

If the BA is landfilled the Landfill Ban Degree [3] applies and the material can be divided into the categories: inert, hazardous, non-hazardous and beyond that too contaminated to be landfilled. If the BA is used as a building material the Soil Quality degree [4] applies and the categories are shaped, non-shaped and IBC (Table 1). IBC refers to material that is only used with additional insulation and will be abolished as a category by 200 and reduced to 50% by 2017.

Table 1) Dutch legal leaching limits for landfilled material according to the Landfill Ban Decree [3] and building materials according to the Soil Quality Degree [4].

	Landfill Ban Decree			Soil Quality Degree		
	inert	non-hazardous	hazardous	shaped	non-shaped	IBC
Contaminant	mg/kg	mg/kg	mg/kg	mg/m^2	mg/kg	mg/kg
As	0.5	2	25	260	0.9	2
Ba	20	100	300	1500	22	100
Cd	0.04	1	5	3.8	0.04	0.06
Cr	0,5	10	70	120	0.63	7
Cu	2	50	100	98	0.9	10
Hg	0.01	0.2	2	1.4	0.02	0.08
Mo	0.5	10	30	144	1	15
Ni	0.4	10	40	81	0.44	2.1
Pb	0.5	10	50	400	2.3	8.3
Sb	0.06	0.7	5	8.7	0.32	0.7
Se	0.1	0.5	7	4.8	0.15	3
Zn	4	50	200	800	4.5	14
Co				60	0.54	2.4
Sn				50	0.4	2.3
V				320	1.8	20
Cl^-	800	15	25	110000	616	8800
F^-	10	150	500	2500	552	1500
SO_4^{2-}	1000	20000	50000	165000	1730	20000
Br^-				6702	202	34

All of these legislative limits make it vital to find a combination of treatments and applications for Dutch BA. Knowing how contaminated the BA is and where the contaminants are bound is the basis for this and several studies have been done on the mineralogical composition of BA, especially the incineration products [5–9].

Characterization

Generally, the main elements in BA are Si, Ca, Al, Na, Mg, Cl, S and Fe although their ratio can vary considerably based on the source of the MSWI BA and the fraction that is analyzed. Table 2 shows the example of weathered BA fines (0-4 mm) determined with XRF. This fraction has an unusually high CaO content, as the amount of SiO_2 is usually higher than that of CaO.

Much of the Si is usually bound in quartz (SiO_2), which is a common component. The reasons for this are that quartz is inert under the incineration conditions, it is very common in nature and also used in in a wide variety of industrial products. Other inert residues are waste glass, ceramics, metals, soil and rock minerals [10]. Unburned organic residues like plastics or paper can also occur. The amount of metal present is usually greatly reduced by magnetic separation and subsequent recycling.

The products of MSWI can be separated into amorphous and crystalline phases [1, 6, 8-9, 11-12]. Amounts of up to 85% incineration products with a high amount of vesicles have been reported. Based on microscopy analysis, Dykstra Eusden et. al. [13] distinguish between transparent, Si-rich and opaque Ca and Fe-rich glassy phases.

Table 2) Composition of MSWI BA fines (0-4 mm)

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO
wt%	1.4	1.6	12.1	13.5	1.7	5.1	1.1	32.4	1.6	0.1	0.2

Oxide	Fe_2O_3	NiO	CuO	ZnO	SrO	ZrO_2	BaO	PbO	Cl	LOI
wt%	7.2	0.02	0.4	1.0	0.10	0.05	0.1	0.2	1.5	18.4

The most common crystalline phases resulting out of incineration are melilite group minerals and spinel group minerals.

After incineration of BA, which creates CaO, it is rapidly quenched in water. The quenching makes them quite unstable under atmospheric conditions with a high pH. For this reason the BA is weathered by exposing it to atmospheric CO_2 for several weeks or months [14]. The typical reaction taking place is given below, but other, complex reactions with unburned organic matter, bacteria and water take place at the same time.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The carbonation decreases the pH, precipitates Ca and makes Calcite ($CaCO_3$) a common component of weathered BA. Other phases reported to occur in weathered BA in appreciable amounts are aluminum hydroxide precipitates and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) [5].

For the heavy metal contaminants it was shown that carbonation reduces the Cu concentration as well as that of Cd, Pb, Zn and Mo (Meima and Comans, 1999; Zevenbergen and Comans, 1994). According to Wei et. al. [7], the majority of heavy metals are concentrated in the non-silicate minerals. Particularly Cr, Zn and Mn are bound in spinel. Cu is tightly associated with dissolved organic content (DOC) [15] and sorption on other secondary minerals. Fe, Sn and Zn seem to be associated with metallic inclusions in a silicate glass matrix.

Generally, the leaching behavior of BA greatly depends on the carbonation/weathering of BA incineration products and the secondary minerals that are formed along with the variation on pH during those processes and a detailed knowledge of the phases and processes is necessary. In this project the focus will be on the finer fractions of BA, as they are the most contaminated. The ultimate goal is to use the material to substitute cement creating an environmental concrete with less CO_2 production as well as immobilizing contaminants.

Methodolgy and Material

The BA was supplied by Heros Sluiskil B.V. (NL) and was in the range of 0 to 4mm which was sieved with the following result 4.7wt% (>4 mm), 41.7wt% (1-4 mm), 49.5wt% (0,125-1 mm) and 4.1 (<0,125 mm). The chemical composition was measured using a PANalytical Epsilon 3X XRF using pressed powder tablets (Table 2). LOI was determined by heating fraction to 1100°C for 2h. The density of the BA fration was determined with a He-Pycnometer and is 2.65g/cm^3. XRD measurements were done with a D5000 using CuK_α radiation, automatic divergence slits with a step size of 0.02 and a spinning sample.

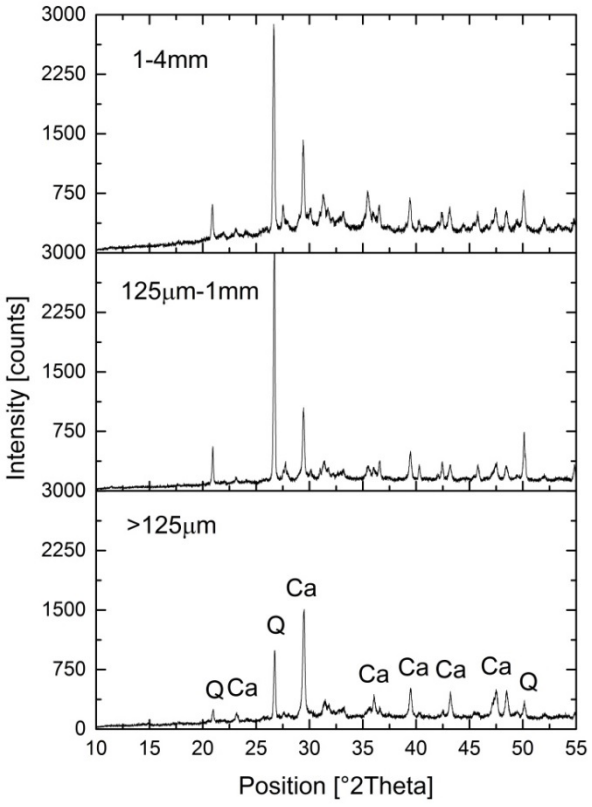

Figure 1) XRD-diffractograms of 3 fractions of weathered BA separated out of a 0-4 mm fraction. Ca-Calcite, Qz – Quartz

Metallic Al in the ash can lead to the production of hydrogen gas in a highly alkaline environment like cement paste, leading to cracking. For this reason the metallic aluminum content in all three fraction of BA was determined by treating the BA with a 3M NaOH solution and collecting the hydrogen in a closed system. The result was 1.39 wt%. No Al could be detected in the finest fraction, while 0.35 wt% were found in the 1-4 mm fraction and 1.04 wt% in the 1-0.125 mm fraction. BSE-SEM and EDX measurements of the 0-4 fraction were done by Tata Steel Netherlands with a JEOL JSM-7001 and a Noran System 7 EDS system. The sample was cast in resin and polished without water.

Results and Discussion

The chemical analysis of the BA shows the unusually high CaO content compared to other MSWI BA [1,7, 16]. A reason can be that only the 0-4 mm fraction is analysed and calcite has a tendency to accumulate in the finest fractions. This trend can also be seen in the XRD measurements of the BA in Figure 1. Quartz tends to accumulate in the bigger fractions due to its good mechanical resistance.

Other minerals identified in the BA fractions are given in Table 3, where the general composition is given. Spinel and melilite minerals can be identified as the main crystalline incineration products along with hematite (Fe_2O_3). Muscovite ($KAl_2(OH,F)_2(AlSi_3O_{10})$ is a common mica mineral found in a variety of rocks and is used in paints, plastics or cosmetics as a filler. Wollastonite is a mineral with many industrial applications, for example in ceramics, but it could also be a product of MSW incineration.

A widely practiced treatment of BA to reduce the contaminants is washing with varying amounts of water and different durations. More information about the washing treatment and its effectiveness is available from Alam et al [17].

The contact of this BA with water leads to the formation of ettringite as can be seen in Figure 2. The formation occurs very fast and seems to be independent of the amount of water used for washing. But after 72h and an L/S of 10 the ettringite peaks disappear again. The mineral most likely dissolved due to pH changes in the solution. The same phenomenon occurs independently of the fraction washed.

Table 3) Mineral phases in BA fines (0-4 mm) as identified with XRD

Mineral	Formula	Type
Quartz	SiO_2	inert residue
Calcite	$CaCO_3$	weathering
Magnetite (Spinel)	$Fe^{2+}Fe^{3+}{}_2O_4/Fe_3O_4$	incineration
Hematite	Fe_2O_3	incineration
Gehlenite (Melilite)	$Ca_2Al(AlSiO_7)$	incineration
Bassanite	$CaSO_4 \cdot 0.5(H_2O)$	weathering
Muscovite	$KAl_2(OH,F)_2(AlSi_3O_{10})$	inert residue
Wilhendersonite (Zeolite)	$K_2Ca_2\ (H_2O)_{10}\ (Al_6Si_6O_{24})$	weathering
Wollastonite	$CaSiO_3$	incineration/inert residue

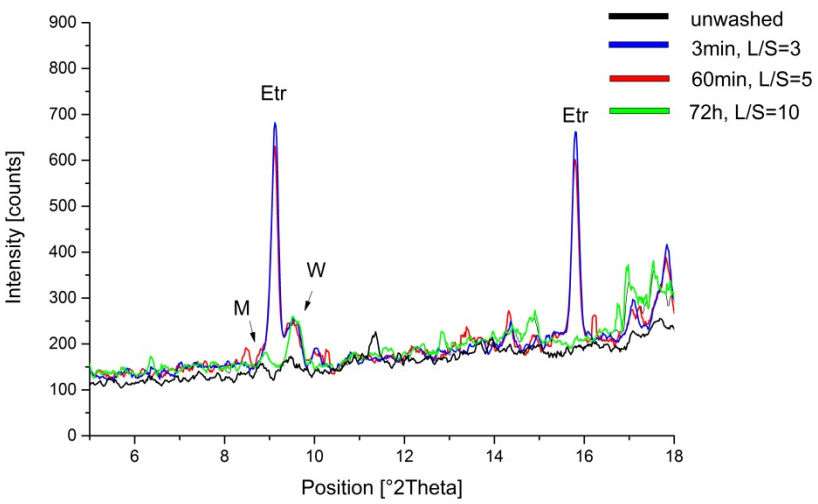

Figure 2) Ettringite peaks in washed Ba fraction (1-4mm) at different liquid to solid ratios (L/S) and varying times. M – Muscovite, W – Wollastonite, Etr – Ettringite

In general, it is very difficult to track the mineralogy of BA using only XRD, because many phases can occur at the same time in low concentrations, making it difficult to distinguish them. A SEM/EDX analysis can be helpful in distinguishing between these phases. Figure 3 shows a SEM BSE image of a grain of BA slag with several embedded crystalline phases. EDX analysis (Table 4) shows the composition of the marked areas.

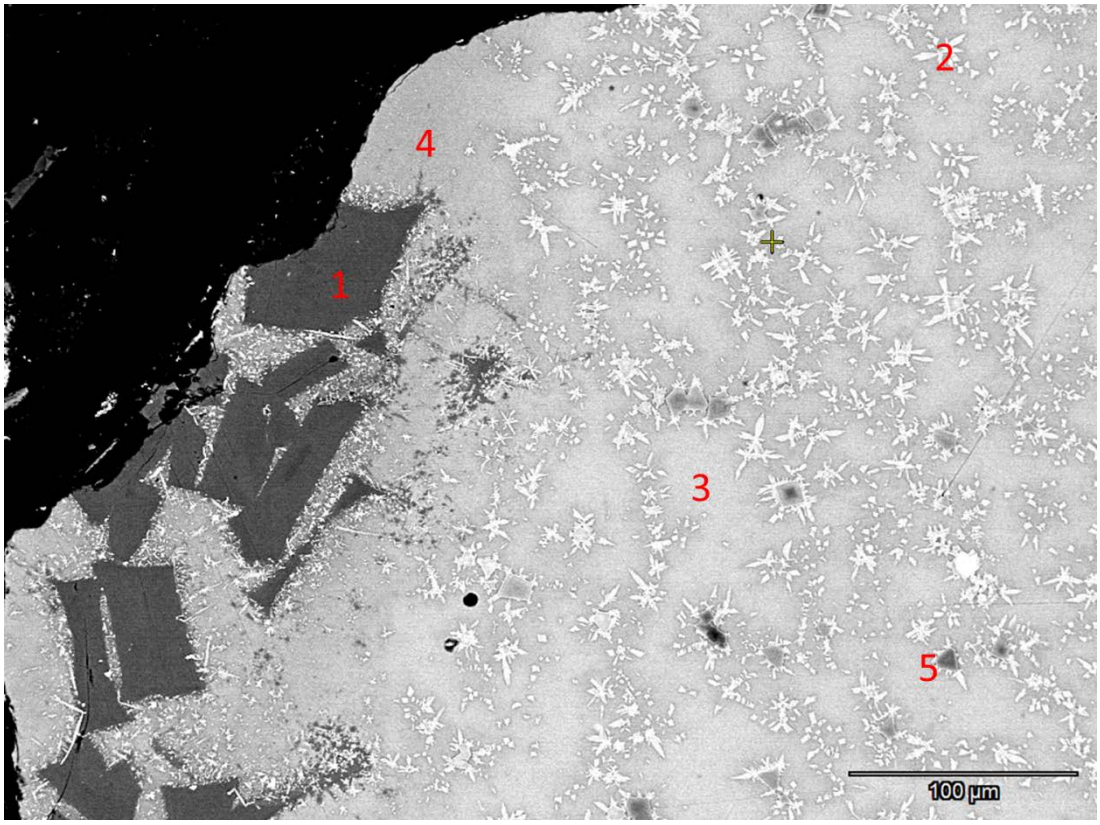

Figure 3) SEM-BSE image of a BA grain. Several crystalline phases are embedded in a glassy phase. 1 – wollastonite, 2 – clinopyroxene, 3 – glassy phase, 4 – glassy phase, 5 - spinel

The general composition of the dark rectangular crystal corresponds with that of wollastonite, which is also visible in the XRD measurements. The bright, acicular crystals have a composition similar to minerals in the clinopyroxene group, esseneite ($CaFeAlSiO_6$) in particular.

Table 4) Chemical composition of the areas marked in Figure 5, measured with EDX.

Compound	1 Wt.%	2 Wt.%	3 Wt.%	4 Wt.%	5 Wt.%
Na_2O	3.84	1.66	2.81	3.51	0.4
MgO	5.75	4.77	2.75	3.32	10.33
Al_2O_3	9.54	13.03	12.46	10.03	51.94
SiO_2	39.33	27.31	31.27	35.71	0.58
P_2O_5	0.35	0.72	1.78	1.88	0.75
SO_3	0.12	0.64	0.7	0.72	0.43
Cl	0	0.02	0.12	0.13	0
K_2O	0	0.35	0.43	0.65	0
CaO	33.92	16.53	19.99	20.71	0.56
TiO_2	0.14	3.06	1.56	2.13	0.65
MnO	0.2	0	0.13	0.21	0.39
Fe_2O_3	6.8	31.9	26	21.02	33.96

In nature esseneite has been observed to crystallize out of high temperature, quenched sediments in contact with combusted coal [18]. Similar conditions can also apply in an MSW incinerator and the paragenesis of wollastonite and esseneite has been reported in vitrified wastes before [19]. Surrounded by the esseneite crystals and marked as 5 in Figure 3, spinel crystals with the composition $(Mg,Fe)Al_2O_3$ can be seen. Traces of Mn and Cl as additional contaminants can be found in the material but further examination using SEM/EDX is required.

Conclusion and Outlook

In conclusion it can be said, that in the investigated BA (0-4mm) inert residues, incineration products and weathering products can be detected using XRD and SEM. Ca has a tendency to accumulate in the finer fractions in the form of calcite ($CaCO_3$), while Si accumulates in the bigger fractions in the form of quartz. The identifies incineration products were magnetite, hematite, melilite and probably wollastonite. Inert residues were quartz and muscovite, while basanite and zeolite were identified as likely weathering products. Washing the BA fractions forms ettringite within 3 minutes, which shows that there are reactive aluminum sources in the material. The ettringite dissolves again when the material is washed as L/S=10 for 72 h. Using SEM/EDX on a polished BA sample the crystallization of spinel and esseneite out of a glassy matrix can be observed.

Because BA is a complex mixture of many minerals, further SEM/EDX studies of the material are planned, including chemical and phase mapping. Rietveld quantifications of the minerals is planned with the goal of quantifying not only the crystalline phases, but also the amorphous contents of BA.

This knowledge will be combined with other methods such as sequential extraction [20] to determine where contaminants are bound in the BA and how treatment effects the mineralogy of the pure material

and or when it is used in concrete. The ultimate goal of the project is the safe and efficient use of BA in environmental concrete in accordance with Dutch legislature.

Acknowledgements

This project is funded by STW (Stichting voor de Technische Wetenschappen, the Netherlands) as part of the project "Environmental concretes based on treated MSWI bottom ashes", project number 10019729.

References

[1] J. M. Chimenos, M. Segarra, M. Fernandez, and F. Espiell, "Characterization of the bottom ash in municipal solid waste incinerator," *J. Hazard. Mater.*, vol. 64, no. 3, pp. 211–222.

[2] C. S. Kirby and J. D. Rimstidt, "Mineralogy and Surface Properties of Muicipal Solid Waste Ash," *Environ. Sci. Technol.*, vol. 27, no. 4, pp. 652–660.

[3] *Besluit stortplaatsen en stortver boden afvalstoffen,VROM.* Den Haag: Ministerie van Volkshuisvesting, Ruimtelijke Ordeling en Milieubeh, 2012.

[4] *Regeling bodemkwaliteit, VROM*. Den Haag: Ruimte en Milieu. Ministerie van Volkshuisvesting, Ruimtelijke Ordeling en Milieubeheer., 2013.

[5] P. Piantone, F. Bodénan, and L. Chatelet-Snidaro, "Mineralogical study of secondary mineral phases from weathered MSWI bottom ash: implications for the modelling and trapping of heavy metals," *Appl. Geochemistry*, vol. 19, no. 12, pp. 1891–1904.

[6] P.-Y. Mahieux, J.-E. Aubert, M. Cyr, M. Coutand, and B. Husson, "Quantitative mineralogical composition of complex mineral wastes–Contribution of the Rietveld method," *Waste Manag.*, vol. 30, no. 3, pp. 378–388.

[7] Y. Wei, T. Shimaoka, A. Saffarzadeh, and F. Takahashi, "Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases," *J. Hazard. Mater.*, vol. 187, no. 1–3, pp. 534–543.

[8] P.-Y. Mahieux, J.-E. Aubert, M. Cyr, M. Coutand, and B. Husson, "Quantitative mineralogical composition of complex mineral wastes - Contribution of the Rietveld method," *WASTE Manag.*, vol. 30, no. 3, pp. 378–388.

[9] A. P. Bayuseno and W. W. Schmahl, "Understanding the chemical and mineralogical properties of the inorganic portion of MSWI bottom ash," *Waste Manag.*, vol. 30, no. 8–9, pp. 1509–1520.

[10] T. T. Eighmy, J. D. Eusden, K. Marsella, J. Hogan, D. Domingo, J. E. Krzanowski, and D. Stampfli, "Particle Petrogenesis and Speciation of Elements in MSW Incineration Bottom Ashes," in *Environmental Apsects of Construction with Waste Materials*, 1994, vol. 60, pp. 111–136.

[11] V. Ettler, Z. Johan, M. Vítková, R. Skála, M. Kotrlý, G. Habler, and M. Klementová, "Reliability of chemical microanalyses for solid waste materials," *J. Hazard. Mater.*, vol. 221–222, pp. 298–302.

[12] C. Speiser, T. Baumann, and R. Niessner, "Characterization of municipal solid waste incineration (MSWI) bottom ash by scanning electron microscopy and quantitative energy dispersive X-ray microanalysis (SEM/EDX)," *FRESENIUS J. Anal. Chem.*, vol. 370, no. 6, pp. 752–759.

[13] J. D. Eusden, T. T. Eighmy, K. Hockert, E. Holland, and K. Marsella, "Petrogenesis of municipal solid waste combustion bottom ash," *Appl. Geochemistry*, vol. 14, no. 8, pp. 1073–1091.

[14] J. A. Meima, R. D. van der Weijden, T. T. Eighmy, and R. N. J. Comans, "Carbonation

processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum," *Appl. Geochemistry*, vol. 17, no. 12, pp. 1503–1513.

[15] J. A. Meima and R. N. J. Comans, "The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering," *Appl. Geochemistry*, vol. 14, no. 2, pp. 159–171.

[16] K. Schollbach, Q. Alam, V. Caprai, M. V. A. Florea, S. R. van der Laan, C. J. G. van Hoek, and H. Brouwers, "Combined Characterisation of MSWI Bottom Ash," in *PROCEEDINGS OF THE THIRTY-EIGHTH INTERNATIONAL CONFERENCE ON CEMENT MICROSCOPY*, 2016, pp. 74–82.

[17] Q. Alam, K. Schollbach, M. V. A. Florea, and H. J. H. Brouwers, "Removal of heavy metals and chlorides from municipal solid waste incineration bottom ashes by applying washing treatment," in *4th International Conference on Sustainable Solid Waste Management*, 2016.

[18] M. A. Cosca and D. R. Peacor, "Chemistry and structure of esseneite (CaFe3+AlSiO6), a new pyroxene produced by pyrometamorphism," *Am. Mineral.*, vol. 72, no. 1, pp. 148–156.

[19] E. Bernardo, L. Esposito, E. Rambaldi, A. Tucci, Y. Pontikes, and G. N. Angelopoulos, "Sintered esseneite-wollastonite-plagioclase glass-ceramics from vitrified waste," *J. Eur. Ceram. Soc.*, vol. 29, no. 14, pp. 2921–2927.

[20] A. Tessier, P. G. C. Campbell, and M. Bisson, "Sequential Extraction Procedure For The Speciation Of Particulate Trace-Metals," *Anal. Chem.*, vol. 51, no. 7, pp. 844–851.