

Article

Impact of Natural Weathering on Stabilization of Heavy Metals (Cu, Zn, and Pb) in MSWI Bottom Ash

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Featured Application: We identified the impacts of natural weathering on the quality parameters of bottom ash from municipal solid waste incineration, which are important for the use of bottom ash in civil engineering. Our findings will help reduce the amount of waste in landfills as well as handling costs.

Abstract: Bottom ash (BA) is the main residue left by municipal solid waste incineration (MSWI). As the circular economy is strengthened, the use of BA in civil engineering is increasing, but its successful use is hampered by heavy metal leaching. In this study, we investigated the influence of natural weathering (6 months) on the stabilization of heavy metals (Cu, Zn, and Pb) with different particle sizes in MSWI BA. Natural weathering is the most popular and cost-effective treatment method for BA. During this process, calcium carbonate (CaCO_3) is produced, which causes a reduction in heavy metal leaching. We used the following methods in the analysis: The fractionation of BA, XRF, and XRD; an extraction test (LST EN 12457-2:2003); and AAS. The results showed that the concentrations of all elements in BA decreased during natural weathering. An analysis of the mineralogical composition showed a very high (>20%) content of calcium carbonate (CaCO_3). The calcium carbonate content increased by 3.2% during weathering because the $\text{Ca}(\text{OH})_2$ in fractions <5.6 mm and <40.0 mm was hydrolyzed to CaCO_3 . Our analysis showed that the metal concentrations (Cu and Pb) in untreated MSWI bottom ash eluate exceeded the limit values, and thus it cannot be used in civil engineering. After three months of stabilization, the heavy metal concentrations were less than the limit values.

Keywords: municipal solid waste incineration; bottom ash; natural weathering; heavy metals; copper; zinc; lead



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1. Introduction

Incineration is one of the most effective technologies used for the treatment of municipal solid waste (MSW) in many industrialized countries [1–3]. After MSWI, several types of solid residue, such as bottom ash (BA), fly ash (FA), and boiler ash (BLA), are formed [4–7]. BA constitutes 85–90% of the total weight of all furnace residues [8–11].

BA is a highly heterogeneous mixture of slag, nonferrous and ferrous metals, glass and ceramics, other noncombustible matter, and a small amount of unburned organic matter (plastic, fiber, wood, etc.) [5,12]. The incineration process parameters, such as the furnace configuration, combustion temperature, quenching process, incineration waste composition, etc., affect the properties of BA [13,14]. Although BA is classified as nonhazardous waste by the European Waste Catalogue [15], most furnace ashes are disposed of in landfills because some elements, such as soluble salts (sulfates and chlorides) or heavy metals (Cu, Zn, Pb, and Ba), are often present in high concentrations in untreated (fresh) bottom ash [8,16–18]. BA can be used in civil engineering after pretreatment. The following pretreatment technologies can be applied: Water washing [17,19], full metal separation [20],

vitrification [21,22], or weathering (natural and accelerated) [1,16,23–25]. Almost all of these technologies incur substantial additional costs. Natural weathering is the most ecologically and economically beneficial method for the treatment of BA.

During natural or accelerated weathering processes, some characteristics (chemical and mineralogical) of BA particles undergo changes. BA is not an inert material, having a complex set of interactions with the ambient atmosphere and undergoing further chemical and mineralogical transformations [26]. When additional contact with atmospheric air (and thus atmospheric CO₂) occurs, various chemical reactions begin, resulting in the solidification, volume stability, and reactivity of BA [27]. The main reactions are hydrolysis, oxidation of some metals (e.g., iron, copper, and aluminum), carbonation, dissolution/precipitation of hydroxides and salts, complexation, sorption, neutralization of pH, formation of solid solutions, and mineral neoformation [28–30]. The stabilization processes depend on various conditions, including mineral composition, reaction temperature, the amount of CO₂ in the atmospheric air, BA particle size, etc. Furthermore, the moisture level (amount of water) in BA is an important parameter [11].

Natural weathering leads to chemical stabilization and reductions in the solubility and mobility of toxic elements through carbonation, oxidation, precipitation, and pH neutralization reactions [31]. However, certain chemical, legal, and technological barriers linked to the potential leaching of toxicity hamper its valorization in many countries because of the heavy metals contained in BA [32]. The environmental characterization we performed demonstrated the effect of increasing the curing time on decreasing the concentrations of leached metals. More detailed research on natural weathering processes should be conducted to ensure the metals remain stabilized over longer periods [33].

In this study, we investigated the influence of natural weathering on heavy metal (Cu, Zn, and Pb) stabilization for different particle sizes of MSWI bottom ash. We used the following methods in the analysis: Fractionation of BA, XRF, XRD, AAS, and extraction (leaching) tests.

2. Materials and Methods

2.1. BA Sampling and Characterization

We collected the BA samples from an MSW incinerator located in Klaipeda, Lithuania. The main stream was composed of household waste with a smaller proportion of commercial waste. The grate furnace incinerator operated at temperatures between 850 and 1100 °C with a capacity of 255,000 tons of waste per year. The BA samples were collected from different parts of the BA stockpiles in the storage room.

We determined the granulometric composition of BA according to the standards of LST EN 933-2:2001 [34] and LST EN 933-1:2012 [35]. For granulometric determination, we sieved the BA through 5.6, 11.2, 24.4, and 40.0 mm mesh sieves. We used a vibrating sieve shaker to facilitate fraction separation. Figure 1 shows the average percentage distribution of BA particles of the three samples and the accumulated distribution of BA particles in the samples.

We determined the moisture content in triplicate using the oven-drying method: After homogenization and weighting, a test portion (2 kg) was dried in the oven at 105 °C until it reached a constant mass. The moisture content (Figure 2) of the BA was then determined according to Willits (1951) [36].

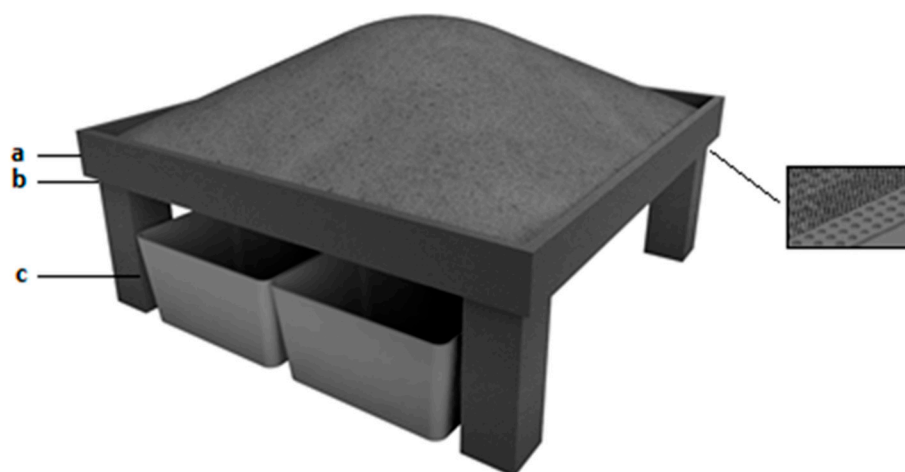


Figure 1. Laboratory stand used for MSWI bottom ash natural weathering experiments: (a) Storage tank for MSWI bottom ash; (b) holes, covered with plastic mesh, for leachate draining; (c) leachate collection tank.

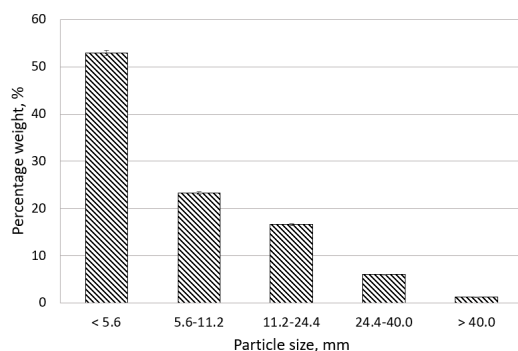


Figure 2. Fractional composition of BA (%).

The chemical compositions of the major and minor elements in MSWI BA were determined in triplicate by X-ray fluorescence spectroscopy (XRF) using an Axios mAX X-ray spectrophotometer. We performed the mineral composition analysis using a SmartLab X-ray diffractometer (Rigaku) with a 9 kW rotating Cu anode X-ray tube. X-rays were recorded in the 20–10–75 degree range using the Bragg–Brentano method.

We performed compliance leaching tests according to the standard LST EN 12457-2:2003 [37]. The samples, which were below 4 mm in size both originally and after pretreatment, were placed in contact with distilled water in capped glass bottles. The solid-to-liquid ratio was 1/10 (90 g of dry BA and 900 mL of distilled water), and the suspension was agitated for 24 h at room temperature (20 ± 5 °C). The solid residue was separated by filtration. We immediately detected the pH and conductivity of the eluate. We analyzed the concentrations of three metals (Cu, Zn, and Pb) by atomic absorption spectroscopy (AAS) according to LST EN ISO 15586:2004 [38].

2.2. Natural Weathering Experiments

We stabilized the heavy metals in five different fractions (<math>< 5.6</math>; $5.6-11.2$; $11.2-24.4$; $24.4-40.0$; <math>< 40.0</math> mm) of MSWI BA during natural weathering in ambient air conditions (the temperature and amount of precipitation were not constant). We filled five laboratory stands with 200 ± 5 kg of different fractions of fresh (untreated) BA. For comparison, we placed another stand (<math>< 40.0</math> mm) in the laboratory (the temperature and the amount of precipitation (60 mm per month) were constant).

We developed the laboratory stands for the study (Figure 1) for the natural weathering of bottom ash without restricted air circulation or precipitation, which consisted of two main parts: The bottom ash and slag storage tank and the leachate storage tank. We

installed accumulated filtrate outlets at the base of the bottom ash storage stand, which we covered with a dense mesh to prevent the bottom ash and slag particles from entering the filtrate. A total of 10 laboratory stands were filled with bottom ash: Two stands for each of the five fractions.

The bottom ash was exposed to natural (outdoor) conditions for 6 months and was thus affected by atmospheric precipitation. The leachate that formed and permeated through the bottom ash was collected in storage tanks. We observed precipitation throughout the stabilization process. The bottom ash was re-mixed once every 2 weeks to improve air circulation. Samples of bottom ash (4 ± 0.05 kg) were obtained once every two weeks.

Each bottom ash sample was dried, and its physical properties were determined: Density according to LST EN ISO 17892-2:2015; moisture according to LST EN 14524-2:2003; porosity and particle size distribution according to LST EN 933-1:2012. We determined the chemical composition of the bottom ash to evaluate any compositional changes during the stabilization process. The bottom ash eluate was also prepared according to LST EN 12457-2:2003. The metal content of the waste bottom ash eluate was determined by atomic absorption spectral analysis using a Buck Scientific 2010 VGP spectrometer.

3. Results and Discussion

3.1. Fractional Composition and Moisture Content of BA

The fractional composition of the MSWI BA is presented in Figure 1.

More than half ($52.94 \pm 0.1\%$) of the BA consisted of particles smaller than 5.6 mm. Particles of 5.6 to 11.2 and 11.2 to 24.4 mm represented $23.26 \pm 0.1\%$ and $16.58 \pm 0.1\%$ of the content, respectively. The largest (>40.0 mm) bottom ash particles comprised the smallest portion of the sample ($1.19 \pm 0.1\%$). Thus, BA is similar to the optimum distribution with a sand-like fraction and can be classified as a 0–25 mm material with good graduation [24].

The results of the determination of the moisture content of the different fractions are shown in Figure 3.

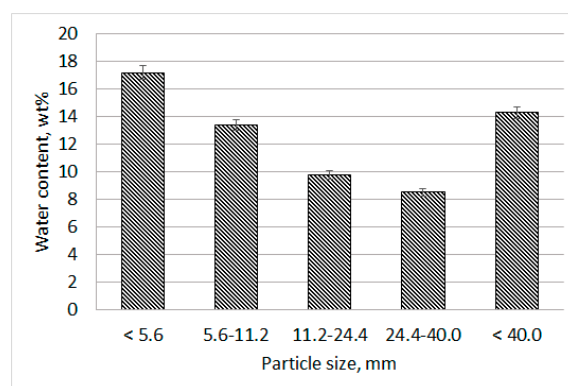


Figure 3. Water content in untreated MSWI bottom ash.

Moisture analysis showed that the water content in the untreated BA ranged from 8.50% to 17.16%. The mean value was $12.60 \pm 0.39\%$. The amount of water in BA is not a stable value as the BA is cooled by water in an incinerator. Some of the water immediately evaporates from the hot bottom ash, while some is absorbed.

3.2. Chemical Composition of BA

The chemical compositions (major elements) of the five different fractions of BA, obtained by XRF, are provided in Table 1. The compositions are described as the weight percentages of each element.

Table 1. Major elements of five different fractions of untreated MSWI bottom ash (wt %).

Element	Fraction of MSWI BA (mm)				
	<5.6	5.6–11.2	11.2–24.2	22.4–40.0	<40.0
Na	2.890 ± 0.627	2.179 ± 0.113	2.194 ± 0.544	2.027 ± 0.339	2.603 ± 0.154
Mg	1.844 ± 0.400	1.390 ± 0.072	1.400 ± 0.348	1.293 ± 0.216	1.661 ± 0.098
Al	2.708 ± 0.075	2.597 ± 0.072	2.963 ± 0.070	4.028 ± 0.185	3.047 ± 0.225
Si	12.982 ± 0.088	19.947 ± 0.120	22.098 ± 0.127	21.925 ± 0.275	17.520 ± 0.295
P	0.876 ± 0.016	0.537 ± 0.014	0.391 ± 0.013	0.454 ± 0.032	0.632 ± 0.043
S	2.727 ± 0.019	1.422 ± 0.012	0.843 ± 0.009	0.779 ± 0.020	1.946 ± 0.041
K	0.792 ± 0.007	0.735 ± 0.007	0.899 ± 0.008	1.260 ± 0.022	0.809 ± 0.021
Ca	19.050 ± 0.115	14.453 ± 0.085	12.880 ± 0.073	12.965 ± 0.155	16.268 ± 0.245
Ti	0.826 ± 0.022	0.595 ± 0.019	0.478 ± 0.018	0.442 ± 0.044	0.610 ± 0.065
Fe	4.690 ± 0.032	4.272 ± 0.029	3.917 ± 0.026	4.510 ± 0.068	4.398 ± 0.085

The chemical analysis of the five different fractions of BA showed that the main elements (>10%) were silicon (Si) and calcium (Ca). The bottom ash also contained aluminum, magnesium, sodium, iron, and sulfur (1–8%). The above-mentioned elements of bottom ash were found in the oxide form (oxides, silicates, and sulfates).

A comparison between the chemical compositions of the different fractions of BA and the Earth's crust is depicted in Figure 4.

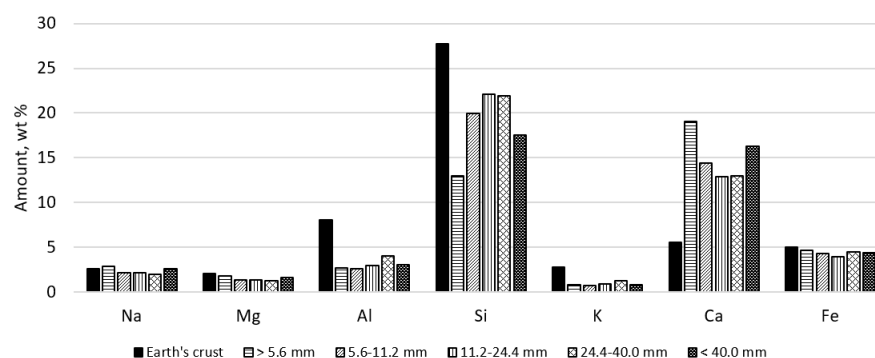


Figure 4. Major chemical elements of MSWI BA in comparison to the element abundances in the Earth's crust, based on [27].

Figure 4 shows that the amounts of the major elements found within all five different fractions of BA were close to the composition of the Earth's crust (with basaltic and other geological materials) [27,28]. We also found a wide range of metals that are hazardous to human health and the environment, such as titanium, chromium, manganese, nickel, copper, zinc, lead, and others. A comparison of the amounts of five heavy metals (Mn, Cu, Zn, Sr, and Pb) in the different untreated BA fractions is presented in Figure 5. In the <40 mm fraction, we performed tests in natural weathering (N) and laboratory aging (L) conditions.

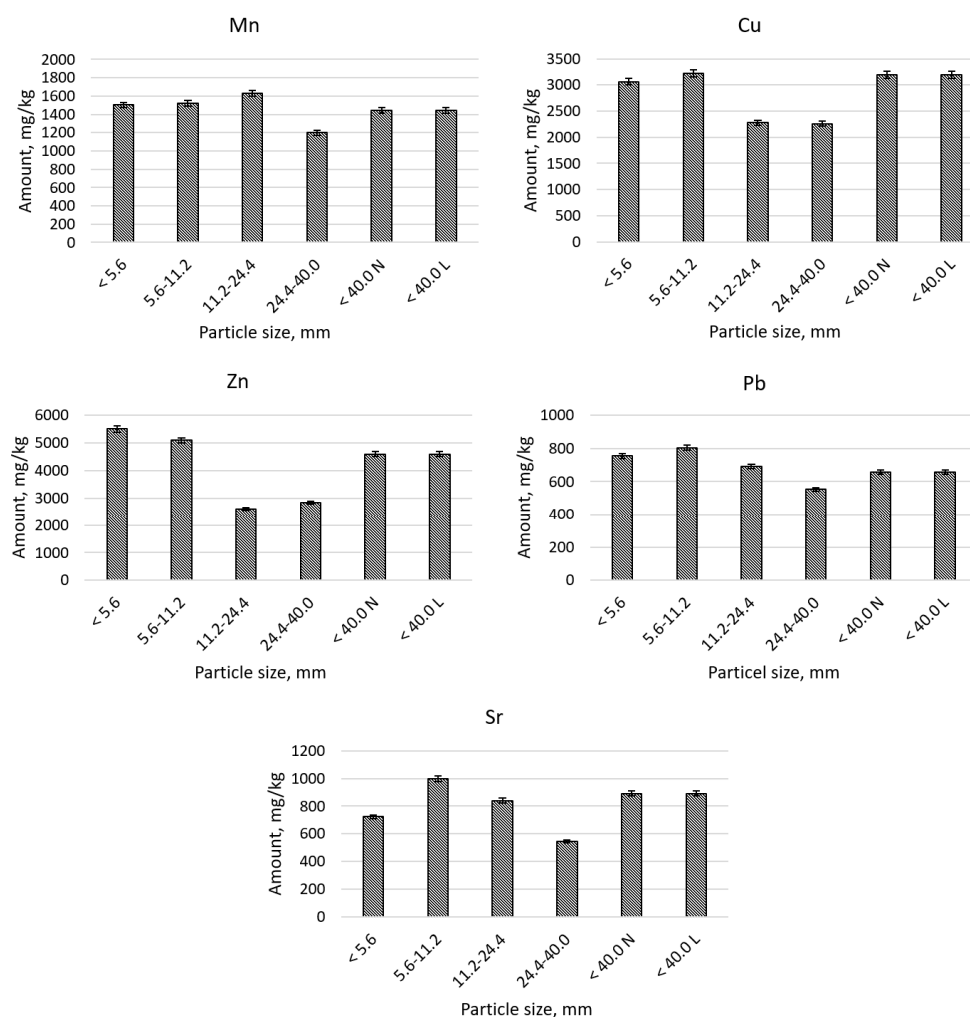


Figure 5. Amounts of heavy metals in different bottom ash fractions ($mg\ kg^{-1}$): Mn; Cu; Zn; Pb; Sr.

The chemical composition analysis showed that zinc (Zn) was present in untreated BA in high concentrations ($2596\text{--}5504\ mg\ kg^{-1}$). The maximum concentrations of three metals (Cu, Pb, and Sr) were found in the 5.6–11.2 mm fraction, with values of 3223 ± 129 , 805 ± 40 , and $1000 \pm 25\ mg\ kg^{-1}$, respectively. The highest concentration of Zn ($5504 \pm 152\ mg\ kg^{-1}$) was found in the smallest BA fraction (<math><5.6\ mm</math>).

Figure 5 shows that bottom ash particle size and heavy metal distribution did not have a direct relationship. These results showed that the bottom ash fractions did not have a substantial effect on the amounts of heavy metals.

3.3. Leaching of Untreated MSWI Bottom Ash

The pH levels of the different fractions of untreated BA eluate were determined via the single-stage leaching method (LST EN 12457-2:2003). The pH values of the samples varied from 10.55 to 12.48. The lowest pH value (10.55) was found in the 11.2–22.4 mm fraction and the highest (12.48) in the <math><5.6\ mm</math> fraction. The pH of the BA mixture (<math><40.0\ mm</math>) was closest to the pH of the eluate of the smallest fraction (<math><5.6\ mm</math>). With these pH values, the solution was quite close to the equilibrium solubility of portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$). The presence of $Ca(OH)_2$ in BA is caused by calcination reactions in the furnaces. Natural or synthetic calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), or anhydrite ($CaSO_4$) generates CaO and CO_2 or SO_2 . Later, most of the generated CaO is hydrolyzed as a result of quenching and forms the corresponding hydroxide [28].

Using the atomic adsorption spectral analysis method (AAS), we determined the concentration of three metals (Cu, Zn, and Pb) in the five BA fractions (Figure 6). We found

the highest Cu concentration ($217.800 \pm 10.890 \mu\text{g L}^{-1}$), and a high concentration of Pb ($124.522 \pm 9.614 \mu\text{g L}^{-1}$) was also found in the <40.0 mm fraction. We found the highest Pb concentration in the <5.6 mm fraction ($145.625 \pm 7.281 \mu\text{g L}^{-1}$). After analyzing the Zn concentration in the untreated BA eluates, we observed the highest zinc content occurred in the <40.0 mm fraction ($239.700 \pm 11.950 \mu\text{g L}^{-1}$).

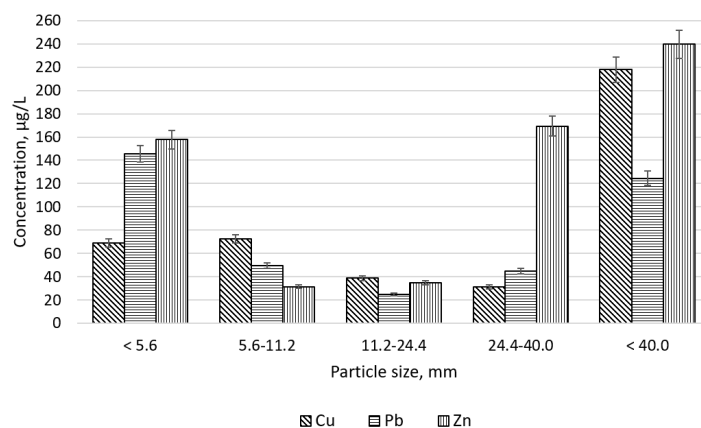


Figure 6. Concentrations of heavy metals in the different fractions of untreated bottom ash eluate.

Chemical composition and leaching tests (Figures 5 and 6) showed that the highest metal concentrations occurred in the fraction eluates, which had the highest amounts of these metals in the solid phase of BA.

3.4. Effect of the BA Natural Weathering

We determined the effect of natural weathering on the different BA fractions using analyses of the chemical and mineralogical compositions, and leachate and eluate parameters.

The chemical compositions of the different untreated BA fractions and those after 3 and 6 months of natural weathering are shown in Table 2 and Figure 6 in terms of major and minor elements (provided in the oxide form) by the percentage of weight and trace elements in milligrams per kilogram. Additionally, we weathered the <40.0 mm fraction under laboratory conditions (constant precipitation amount and temperature) for comparison. The main part of BA (more than 65% by weight) consisted of the following element oxides: SiO₂, CaO, Al₂O₃, and Fe₂O₃. We noted that all element (except Fe₂O₃ and TiO₂) concentrations decreased during natural weathering.

Table 2. Bulk chemical composition of untreated BA and BA after 3 and 6 months of weathering.

Fraction (mm)	Element							
	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	TiO ₂	P ₂ O ₅	SO ₂
5.6 mm								
Untreated	27.700 ± 0.189	26.655 ± 0.161	6.506 ± 0.046	5.117 ± 0.142	1.093 ± 0.010	1.375 ± 0.037	2.007 ± 0.036	6.818 ± 0.048
3 months	27.424 ± 0.517	26.834 ± 0.424	6.222 ± 0.141	5.454 ± 0.409	1.029 ± 0.028	1.348 ± 0.125	1.740 ± 0.100	5.967 ± 0.120
6 months	26.376 ± 0.517	26.104 ± 0.433	6.293 ± 0.129	5.407 ± 0.413	0.910 ± 0.026	1.315 ± 0.117	1.844 ± 0.101	4.368 ± 0.098
5.6–11.2 mm								
Untreated	42.670 ± 0.257	20.223 ± 0.119	6.108 ± 0.041	5.587 ± 0.135	1.014 ± 0.009	0.992 ± 0.032	1.231 ± 0.033	3.555 ± 0.031
3 months	34.441 ± 0.603	23.054 ± 0.375	6.388 ± 0.124	5.483 ± 0.413	0.906 ± 0.026	1.128 ± 0.111	1.534 ± 0.098	3.528 ± 0.085
6 months	32.526 ± 0.592	22.634 ± 0.357	6.372 ± 0.126	5.121 ± 0.397	0.836 ± 0.025	1.184 ± 0.114	1.731 ± 0.102	3.321 ± 0.079

Table 2. Cont.

Fraction (mm)	Element							
	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	TiO ₂	P ₂ O ₅	SO ₂
11.2–24.4 mm								
Untreated	47.272 ± 0.271	18.022 ± 0.103	5.601 ± 0.037	5.599 ± 0.132	1.241 ± 0.011	0.797 ± 0.029	0.896 ± 0.031	2.108 ± 0.022
3 months	44.377 ± 0.752	18.057 ± 0.285	5.428 ± 0.110	5.476 ± 0.403	1.134 ± 0.031	0.786 ± 0.097	0.790 ± 0.087	2.101 ± 0.069
6 months	42.474 ± 0.699	16.891 ± 0.275	5.288 ± 0.114	5.372 ± 0.406	0.988 ± 0.028	0.773 ± 0.100	0.708 ± 0.084	2.049 ± 0.064
24.4–40.0 mm								
Untreated	46.902 ± 0.588	18.141 ± 0.2682	6.748 ± 0.097	7.612 ± 0.350	1.739 ± 0.030	0.737 ± 0.074	1.041 ± 0.073	1.949 ± 0.050
3 months	43.536 ± 0.752	16.359 ± 0.268	6.519 ± 0.100	7.404 ± 0.457	1.657 ± 0.040	0.731 ± 0.072	1.042 ± 0.091	1.652 ± 0.056
6 months	36.081 ± 0.620	16.753 ± 0.252	6.067 ± 0.122	7.958 ± 0.441	1.247 ± 0.031	0.715 ± 0.071	0.657 ± 0.089	1.470 ± 0.056
<40.0 mm natural weathering								
Untreated	37.479 ± 0.631	22.763 ± 0.343	6.288 ± 0.122	5.757 ± 0.425	1.116 ± 0.029	1.018 ± 0.108	1.449 ± 0.100	4.865 ± 0.103
3 months	33.703 ± 0.617	22.947 ± 0.366	6.384 ± 0.136	5.508 ± 0.419	0.928 ± 0.027	1.123 ± 0.111	1.558 ± 0.101	4.418 ± 0.099
6 months	31.850 ± 0.503	22.947 ± 0.366	6.193 ± 0.124	5.404 ± 0.394	0.832 ± 0.024	1.594 ± 0.102	1.558 ± 0.101	4.677 ± 0.099
<40.0 mm laboratory ageing								
Untreated	37.479 ± 0.631	22.763 ± 0.343	6.288 ± 0.122	5.757 ± 0.425	1.116 ± 0.029	1.018 ± 0.108	1.449 ± 0.100	4.865 ± 0.103
3 months	34.279 ± 0.623	24.263 ± 0.160	6.252 ± 0.128	5.487 ± 0.406	1.083 ± 0.028	0.101 ± 0.106	1.496 ± 0.101	4.800 ± 0.103
6 months	33.569 ± 0.616	24.641 ± 0.163	6.176 ± 0.123	5.418 ± 0.395	1.059 ± 0.027	0.980 ± 0.101	1.615 ± 0.104	4.847 ± 0.103

The concentrations of metals, including the main elements, in all the fractions of BA, decreased during natural weathering (Figure 7). We found the largest decreases in Mn, Cu, and Sr in the <40.0 mm fraction for both weathering types (natural and laboratory conditions). The Mn concentration was lower by 678 ± 159 and 725 ± 162 mg kg⁻¹, Cu by 1096 ± 125 and 1088 ± 122 mg kg⁻¹, and Sr by 346 ± 125 mg kg⁻¹ for natural and laboratory conditions, respectively. The decreases in Zn concentration in both <40.0 mm fractions were similar: 1121 ± 112 mg kg⁻¹ (natural weathering) and 1119 ± 110 mg kg⁻¹ (laboratory ageing). Decreases in the Pb concentrations of these fractions were relatively low: From 104 ± 12 to 142 ± 15 mg kg⁻¹ after 6 months of weathering. The highest decrease in Zn concentration (2359 ± 140 mg kg⁻¹) was found in the 5.6–11.2 mm fraction after 6 months of natural weathering.

We concluded that heavy metal concentrations in laboratory-aged BA decreased more rapidly than in naturally weathered BA during the first 3 months. Our analysis showed that heavy metal loss from BA in both conditions (natural weathering and laboratory aging) was similar after 6 months of the weathering (aging) process.

As mentioned above, various complex reactions occur during the MSWI BA weathering (aging) process, such as pH neutralization, secondary element formation, sorption, etc. These reactions can affect the leaching of macro- and micro-elements from BA [37]. These reactions can be represented by changes in the mineralogical composition (Table 3).

The mineralogical composition analysis (Table 2) showed a very high (>20%) content of two minerals, calcite (or otherwise calcium carbonate) (CaCO₃) and quartz (SiO₂), in BA. The quartz content remained almost unchanged (0% decrease) during weathering, while the calcite content increased by 3.2%. As the calcium content increased, other calcium-containing compounds such as anhydride (Ca(SO₄)) decreased. Comparing these results to those obtained by other scientists [1,5,16,36], we concluded that the mineralogical composition of BA from other countries is similar.

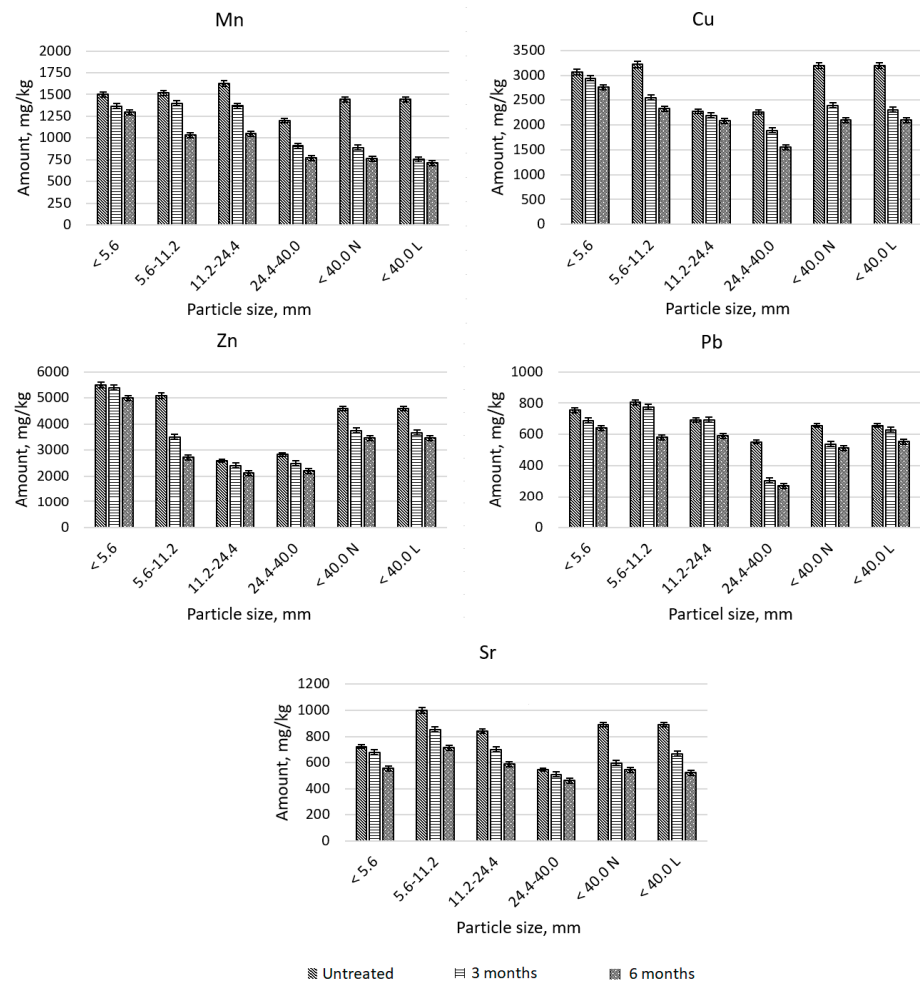


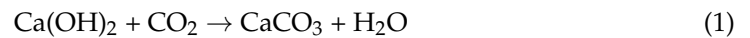
Figure 7. Amounts of heavy metals in different bottom ash fractions during natural weathering (mg/kg): Mn; Cu; Zn; Pb; Sr.

Table 3. Mineral compositions of untreated BA and BA after 3- and 6-month laboratory aging.

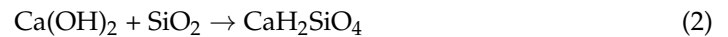
Mineral	Chemical Formula	Untreated Sample	Laboratory Ageing	
			3 Months	6 Months
Carbonates				
Calcite	CaCO ₃	XXXX	XXXX	XXXX
Oxide				
Quartz	SiO ₂	XXXX	XXXX	XXXX
Hematite	Fe ₂ O ₃	X	X	X
Magnetite	Fe + 2Fe + 3O ₄	XX	XX	XX
Silicates				
Diopside	CaMgSi ₂ O ₆	X	XX	XX
Gehlenite	Ca ₂ Al ₂ SiO ₇	XX	XX	XX
Akermanite	Ca ₂ Mg(Si ₂ O ₇)	X	X	X
Microcline	K(AlSi ₃)O ₈	X	X	X
Phosphates				
Hydroxylapatite	Ca ₅ (PO ₄) ₃ (OH)	X	X	XX
Sulfates				
Anhydrite	Ca(SO ₄)	X	X	X

Note: XXXX—very high amount (>20%); XXX—high amount (10–20%); XX—medium amount (5–10%); X—small amount (trace) (<5%).

The mineralogical changes in bottom ash during the stabilization process can be explained by the following formula:

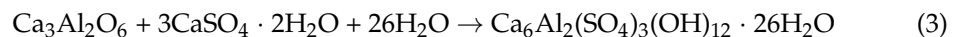


One of the major processes for the stabilization of BA is carbonization (Formula (1)), which occurs in two steps: First, carbon dioxide is absorbed into the water in the pores of BA. Then, calcium carbonate is formed by calcium hydroxide (Ca(OH)_2) reacting with dissolved CO_2 (water is necessary for the reaction) [39,40]. Later, the formation of calcium silicate hydrates is possible (Formula (2)):



The analogous formation of calcium aluminate hydrates occurs. Other scientists [26,27] have shown that calcium silicates and calcium aluminate hydrates have a high sorption capacity for heavy metals.

Along with the carbonization reaction, a sulfate formation reaction plays an important role in the stabilization of BA. During the sulfate reaction, calcium sulfate dissolves in pore water and is transported. Subsequently, an aqueous sulfate phase such as gypsum is formed. Due to the increased reaction of sulfates with aluminum compounds, during the formation of the calcium aluminate phase, ettringite forms in the pore water (Formula (3)):



The reactions described above are illustrated by a graph depicting the dependence of pH on the calcium oxide concentration in the eluates (Figure 8). Six months after the beginning of the stabilization process, all pH and Ca concentration values decreased. The graph shows that Ca(OH)_2 in the <5.6 m and <40.0 mm fractions was hydrolyzed to CaCO_3 during the stabilization process.

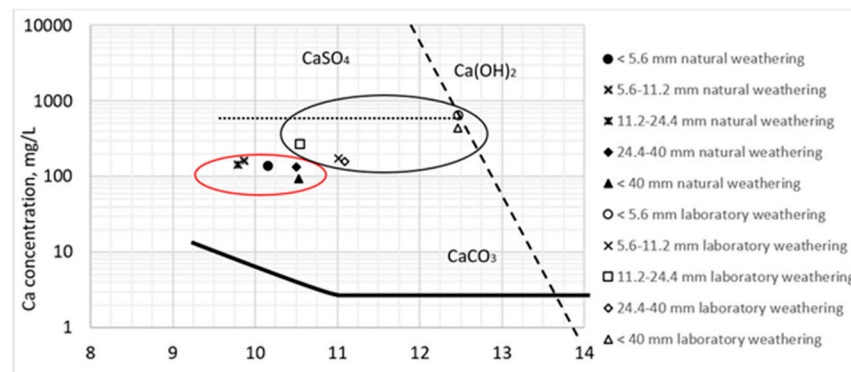


Figure 8. Changes in calcium solubility and pH during 6 months of natural weathering of BA eluates as a function of particle size.

The concentrations of copper (Cu), lead (Pb), and zinc (Zn) in the BA eluates and filtrate during natural weathering and laboratory aging are shown in Figures 8–10. We compared the metal concentrations with the limit values (in an eluate) that would enable BA to be used in civil engineering in Lithuania [41].

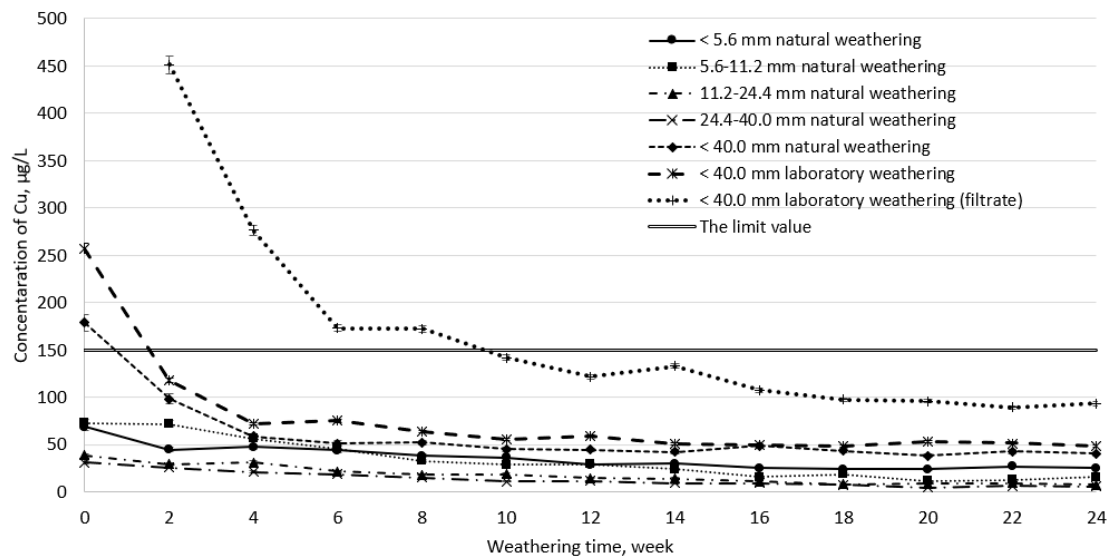


Figure 9. Concentration of copper (Cu) in different fractions of BA eluate and leachate during natural weathering and laboratory aging.

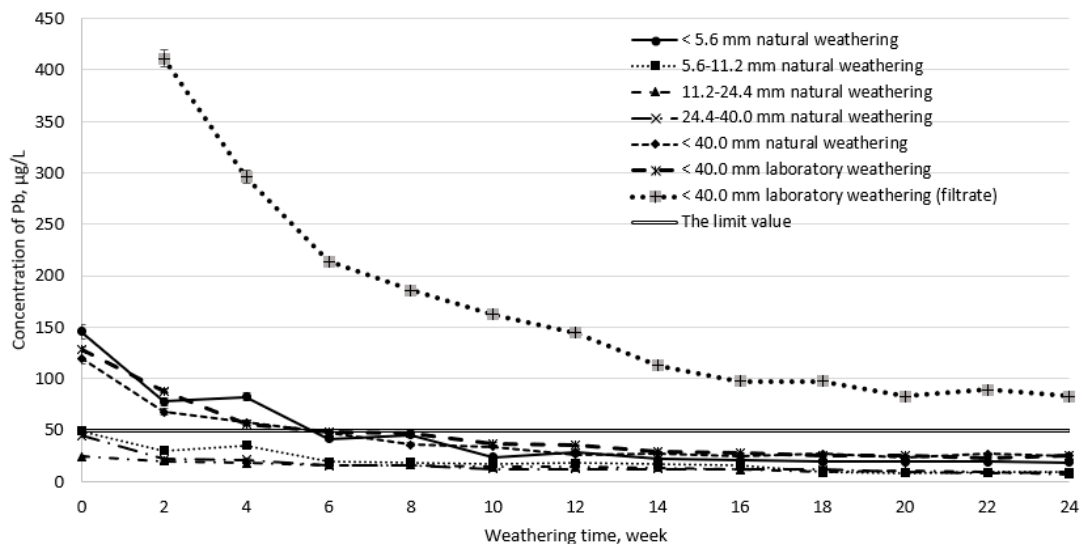


Figure 10. Concentration of lead (Pb) in different fractions of bottom ash eluate and leachate during natural weathering and laboratory aging.

As with the other elements, the concentration of copper in the eluates decreased with increasing stabilization time (Figure 9). In the <40.0 mm fraction, the Cu concentration in the eluate exceeded the leaching limit value ($150 \mu\text{g L}^{-1}$), with values of 257.12 ± 5.14 and $178.60 \pm 3.57 \mu\text{g L}^{-1}$. For the filtrate formed by stabilizing the <40.0 mm BA fraction in the laboratory for up to 10 weeks, the Cu concentrations (172.32 ± 3.45 to $451.25 \pm 9.02 \mu\text{g L}^{-1}$) were above the limit values. Our experimental studies showed that the copper concentrations decreased rapidly (19.5–72.0%) during the first four weeks of the process. As the stabilization duration increased, the concentration change slowed and became almost stable after 16 weeks from the beginning of weathering (aging). After 24 weeks, all the BA eluate fractions had a Cu concentration $<50 \mu\text{g L}^{-1}$.

In three fractions (<5.6 mm with natural weathering; <40.0 mm with natural weathering and with laboratory aging), after 4 weeks, the lead concentrations were higher than the leaching limit value ($50 \mu\text{g L}^{-1}$) (Figure 10). The highest concentration of Pb occurred after 2 weeks in the laboratory-aged BA filtrate ($411.25 \pm \mu\text{g L}^{-1}$). Even after 24 weeks, the concentration of Pb in the filtrate was higher than the leaching limit value. The concentrations

of Pb in all the eluate fractions decreased during stabilization and did not exceed the limit value. The concentrations of lead in the fractions became almost stable and did not exceed $25 \mu\text{g L}^{-1}$ after 12 weeks of the weathering process.

The concentration of zinc in the BA filtrate and the eluates of the different fractions did not exceed the limit value of $300 \mu\text{g L}^{-1}$ during the stabilization process (Figure 11). Compared to the other metals, the concentration of zinc in the eluates decreased the most rapidly, with a remarkable decrease (from 19.5% to 78.5%) already noticeable after two weeks of the weathering process. Compared to the concentration in the untreated bottom ash eluates, the zinc concentration in the <40.0 mm fraction was 93.9% and 91.5% smaller after 24 weeks under natural weathering and laboratory aging conditions, respectively.

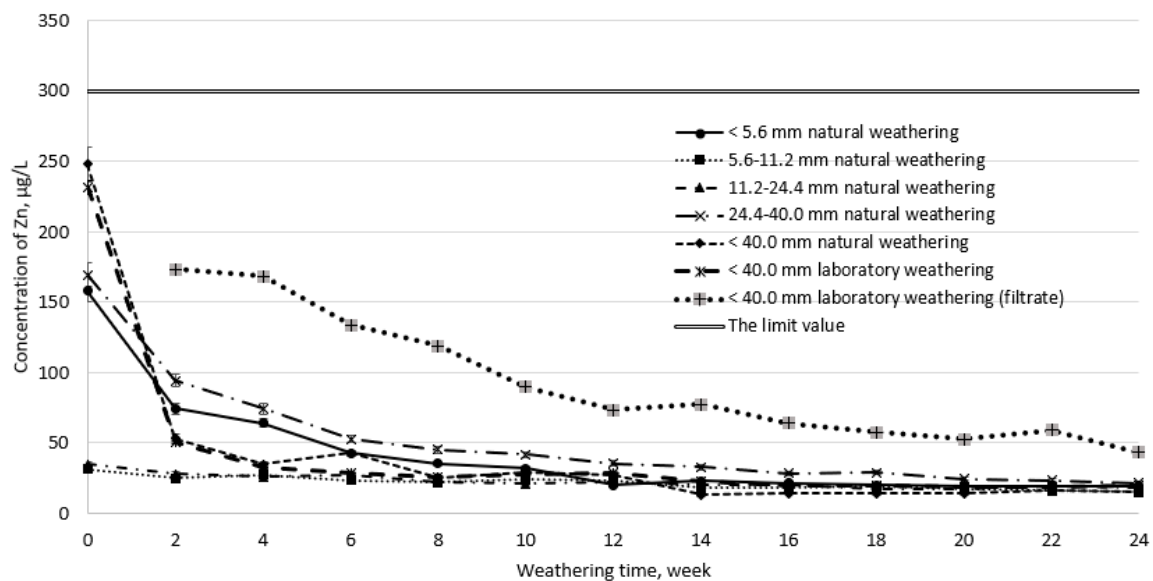


Figure 11. Concentration of zinc (Zn) in different fractions of bottom ash eluate and leachate during natural weathering and laboratory aging.

From this experimental research, we concluded that the metal concentrations in untreated MSWI bottom ash eluates exceed the limit values; therefore, they cannot be used in civil engineering. Three months is long enough to conduct heavy metal stabilization in MSWI BA. After the natural weathering process, the heavy metal concentration was lower than the limit values.

4. Conclusions

We presented the results of experimental research on MSWI BA quality parameters and the impact of natural weathering on heavy metal stabilization. On the basis of our results, the following conclusions were drawn.

The quantities of the major elements in all five investigated fractions of BA are close to the composition of the Earth's crust.

No direct relationship exists between bottom ash particle size and heavy metal distribution. These results showed that the bottom ash fractions do not have a significant effect on the amounts of heavy metals present.

The concentrations of all the elements (major, minor, and trace) in BA decreased during natural weathering. The largest decrease in heavy metals was found in the <40.0 mm fraction of stabilized (natural weathering) BA. Therefore, BA should not be fractionated before natural weathering.

After experimental analysis, we found that heavy metal concentrations decreased more rapidly under laboratory ageing (temperature and precipitation amount were constant) during the first three months than under natural weathering. This may have occurred because of the relatively more intensive precipitation under laboratory conditions.

The heavy metal decreases in BA under both conditions were similar after 6 months of the weathering process.

The accelerated carbonation during natural weathering resulted in a remarkable decrease in heavy metal leaching.

The changes in the MSWI BA quality parameters seen during natural weathering (the temperature and precipitation amount are not constant) and laboratory aging (the temperature and precipitation amount are constant) were similar. From this, we concluded that natural aging is a more cost-effective method to treat bottom ash, as it does not require constant temperature retention or additional water resources.

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