Leaching Characteristics of Wood Biomass Fly Ash Cement Composites

Carević, Ivana; Štirmer, Nina; Trkmić, Marija; Kostanić Jurić, Karmen

Source / Izvornik: **Applied Sciences, 2020, 10, 1 - 17**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:237:827118

Rights / Prava: In copyright / Zaštićeno autorskim pravom.

Download date / Datum preuzimanja: **2024-10-02**

Repository / Repozitorij:

Repository of the Faculty of Civil Engineering, University of Zagreb

DIGITALNI AKADEMSKI ARHIVI I REPOZITORIJI

applied sciences

MDPI

Article

Leaching Characteristics of Wood Biomass Fly Ash Cement Composites

Ivana Carević [1], Nina Štirmer [1,*], Marija Trkmić [2] and Karmen Kostanić Jurić [3]

[1] Department of Materials, Faculty of Civil Engineering, University of Zagreb, 10000 Zagreb, Croatia; ivana.carevic@grad.unizg.hr
[2] Central Chemical and Technological Laboratory, HEP-Proizvodnja d.o.o., 10000 Zagreb, Croatia; marija.trkmic@hep.hr
[3] Tomting 2010 Ltd., 10000 Zagreb, Croatia; karmen.kostanic@tomting.hr
* Correspondence: nina.stirmer@grad.unizg.hr; Tel.: +385-1-4639-298

Received: 20 November 2020; Accepted: 29 November 2020; Published: 4 December 2020

Abstract: Wood biomass ash (WBA) represents an environmental and economic problem for energy producers, and there have been extensive studies of using WBA as a raw material in construction products. This study investigates the leaching characteristics of WBA cement composites based on testing results. Currently, 70% of WBA is landfilled, and the rest is primarily used in agriculture; therefore, this study also addresses the leaching as a component of environmental safety of these two primary WBA management approaches. An analysis of the leaching characteristics of WBA, monolithic, and crushed cement composites is performed by replacing 15% of the cement with WBA. The study was conducted using three WBA samples collected from different power plants. Increased values of leaching from the WBA itself are indicative of potential issues that could occur in the case of its disposal. The study concluded that the WBA could be potentially environmentally acceptable as a raw material in the concrete industry because the heavy metals are stabilized within the cement matrix.

Keywords: wood biomass fly ash; cement-based materials; heavy metals; leaching; environmental safety

1. Introduction

Recently, in Croatia and other European Union (EU) countries, the promotion of the advantages and possibilities for electrical and thermal energy generation has resulted in a significant increase in the number of power plants that use biomass (particularly wood biomass) as a renewable energy source (RES). Worldwide, RES usage is the greatest in the electricity sector, where biomass represents the third-largest renewable source and generates 493 TWh worldwide, and in the heat generation sector where 95% of the renewable energy comes from biomass [1]. Biomass combustion generates ash, including wood biomass ash (WBA). WBA represents an environmental and economic problem for energy producers: the costs of disposal continue to increase [2,3], while the EU is attempting to limit its disposal at landfills through various directives [4,5]. According to Directive 2008/98/EC on waste [4] and the new Directive (EU) 2018/851 [5], the priority for WBA management is preventing it from being created, then recycling it, and, lastly, disposing of it. An application for WBA reuse must be identified because prevention is infeasible due to the expected increase in the use of biomass as an energy source and legislative measures decrease disposal options.

During wood biomass combustion in a power plant, two primary types of WBA are generated: (1) wood biomass bottom ash, which is ash collected from the bottom of the combustion chamber, and (2) wood biomass fly ash that can consist of relatively coarse fly ash collected from the cyclone or boilers and fine fly ash collected from electrostatic filters or baghouse filters [6]. Fly WBAs and bottom WBAs have significant differences that should be considered prior to disposal. According to some authors [6–11], heavy metals (e.g., Zn, Cd, Pb, and Hg) and organic pollutant (PCDD/F, PAH) concentrations are higher for fly WBA than bottom WBA, meaning that each type of WBA requires a different disposal strategy [8,10]. According to [12], the greatest variations are of the volatile heavy metals concentrations such as Zn, Pb, and Cd, the concentrations of which increase as the particle size decreases. High Cd concentrations can have toxic effects on organisms in the soil, be taken up by plant cover, and, ultimately, enter the food chain [13]. A high share of Cd in some types of WBA also represents a potential health risk because it accumulates in the kidneys and affects bone density [14]. Exposure to high Zn concentrations can lead to toxic effects in brain cells [15], whereas any Pb exposure has an extremely negative impact on human health, especially cognitive function [16]. The leaching of Cu and Zn from fly WBA also damages lung tissue [17]. Furthermore, due to the leaching of heavy metals from WBA, its disposal creates a significant groundwater pollution problem [18].

Therefore, the responsible management of WBA requires an effective solution. Most studies of WBA recovery are in the field of soil enrichment [7,9,19,20]. In the EU, the use of WBA in agriculture is regulated by the criteria determined by national legislation (such as in Sweden, Finland, Germany, Austria, and Croatia) that specify limits for heavy metals based on the total content of elements in the ash [21–23]. Furthermore, WBA recovery presents an array of options for the construction industry: as a raw material for alkali activation [24–26], in the production of ceramic products [27,28], as a raw material for road construction [29–31] or as an aggregate/binder in concrete production [32–39]. Cement is the main component of concrete, one of the dominant materials used in the construction industry [40,41]. Cement production impacts the environment through its raw material processing requirements, which result in significant energy consumption accompanied by high CO_2 emissions. Recent research shows that the global clinker-to-cement ratio as a parameter for general estimation of CO_2 production, was 0.7 in 2018 [42]. On the other hand, authors [43] claimed that commercially available cement contains 20% substitute cement materials, including by-products from other industries (e.g., granulated blast furnace slag, fly ash from coal-fired thermal power plants, and silica fume), resulting in a cement-to-clinker ratio that is even higher. According to estimates given by [43], the use of substitute cement materials could reduce the CO_2 emissions from cement production by approximately 400 million tonne/year; therefore, applying WBA as a mineral admixture could contribute to the "greening" of the concrete industry, although there are current technical and commercial obstacles to its use [44]. When compared to the limit values according to EN 450-1 [45] for fly ash obtained from coal combustion, WBA has higher values of loss of ignition (LOI), CaO, MgO, alkali and sulphate components [6,46]. The morphology of WBA particles is also different from coal fly ash: WBA particles have irregular shapes and are porous compared to the spherical glassified particles of coal fly ash. Therefore, WBA currently cannot be used in concrete using the recommendations given for coal fly ash [45,46]. However, research has been further harnessed for the use of this potential supplementary cementitious materials (SCM) in the cement industry [47–49] as a tool and mitigation strategy for reducing carbon dioxide emissions associated with concrete production [50–53]. Intensive studies of using WBA as a raw material in construction products have been performed [47,54,55], but minimal information exists in the literature regarding the ecological impact of WBA through its life cycle [22,56]. Berra et al. [22] examined the suitability of pH-dependent leaching; they performed long-term dynamic leaching tests on samples where three different WBAs were used in the cement mixture. They suggested the use of long-term dynamic leaching tests on monolithic specimens containing solid wastes in order to evaluate the environmental quality of construction materials. Using different leaching methods (EN 12457-3 and using Artificial Sweat and Gastric Fluids) research [56] showed that utilization of tested fly ashes in covered and paved structures is still possible, although an environmental permit would be required. The most extensive research where biomass fly ash was used in the cement composites was done by [57] with combination of different leaching tests (tank leaching test, parallel batch extraction test at different L/S ratios and the pH dependence leaching test) under different application scenarios (using mortar in an environment where release of substances is controlled by diffusion, evaluate a second life stage in which the material is used in a granular form and response of leaching to the change in surrounding environmental conditions). From available literature [6,58] a large variation in the properties of local WBAs is observed depending on several factors such as the type of biomass used, the combustion technology, the temperature of the combustion and the location of the WBA collection. These variation also refer to heavy metals content in WBA samples that can present possible environmental risk [59]. Therefore, it is recommended to focus not only on a good technical performance but also on the release of contaminants in multiple life cycles of mortars that include biomass fly ash [57], which is addressed by this paper. When using WBA as a raw material in cement composites and in construction products, it is essential to determine its environmental impacts [30], which result from potentially enhanced contaminant leaching. The environmental acceptability of WBA as a potentially new raw material in the cement and concrete industry is related to the ability of the cement matrix to bind the contamination elements (in this case heavy metals) physically and chemically within the hydrate structure which should be analyzed. Each construction product within the EU must comply with European legislation [60], which ensures that any construction product for which there is a harmonised standard is CE-marked and possesses reliable information concerning its performance. One of the basic requirements of The Regulation (EU) 305/2011 [60] is "hygiene, health, and the environment", which means that every construction product must prove that during its use it is safe for health and the environment. Currently, in practice, construction products are not often tested for leaching. Construction products can potentially negatively impact the local environment by releasing hazardous substances into the soil or underground, sea, or surface waters. Hazardous substance releases require assessment, and, for the leaching of the hazardous substances previously discussed into the environment, the Technical Committee CEN TC 351 has developed laboratory tests that use demineralised water as eluent [61].

The present study investigates the potential for WBA reuse or disposal by assessing leaching as a component of the environmental safety of (1) WBA disposal, (2) monolithic cement composites in a hardened state with 15% WBA as a cement replacement, and (3) crushed cement composites with 15% WBA as a cement replacement. Three WBA samples were obtained from different power plants that use different combustion technologies and use virgin wood as a biomass source. This case study serves as guidance for the implementation of the essential requirement "hygiene, health, and the environment" in the products' CE markings.

2. Materials and Methods

2.1. Materials

For the leaching test, wood biomass fly ash samples WBA1, WBA2, and WBA3 were selected and used to replace 15% of the cement in the cement composites; this proportion of WBA is considered acceptable because it does not degrade the composites' mechanical or durability properties [62]. Three samples were obtained from different plants, and their characteristics are provided in Table 1. A survey was performed during sampling, in which the respondents confirmed that they used virgin wood chips in their energy production [63].

The heavy metals content of each WBA and the cement are shown in Table 2 and discussed in detail in [6]. The heavy metals content in WBAs and cement (zinc, cadmium, chromium, nickel, lead, manganese, cobalt, barium, bismuth, strontium, and copper) was evaluated according to EN ISO 16968:2015 [64], while mercury contents were evaluated according to the standard ASTM D 6722-11 [65]. The WBA heavy metals concentrations that exceeded those for the cement are highlighted in bold italic. As clearly demonstrated, all the heavy metals concentrations of the chosen WBAs were higher than those of the cement except for Sr. Comparing the heavy metals concentrations of the studied WBAs with those of bottom WBAs [7,8,56,57,66–69], the Cd and Co concentrations are visibly higher for all three samples of tested fly WBAs.

Table 1. Plant characteristics.

Plant Designation	Plant Power (Electric and Thermal Energy)	Combustion Technology	Furnace Temperature (°C)	Additives Used during Combustion
1	4.6 MWel 10 MWth	Grate combustor + pulverized fuel combustor	700–750	-
2	2.75 MWel 15 MWth	Grate combustor	800	-
3	9.9 MWel 16 MWth	Bubbling fluidized bed	850	Quartz sand

Table 2. Comparison of the heavy metals content (mg/kg) in the tested wood biomass ash (WBA) and cement, with heavy metal values for fly WBA and bottom WBA from literature [7,8,56,57,66–69].

	Measured Values from WBA Samples			Cement	Values from the Literature	
	WBA1	WBA2	WBA3		Bottom WBA [7]	Fly WBA [7,8,56,57,66–69]
Zn (mg/kg)	***1850***	***314.7***	139	182.4	15–1000	34–17 470
Cd (mg/kg)	***3.1***	***2.6***	***6***	0.93	0.4–0.7	1–60
Cr (mg/kg)	50	***123***	61.7	63.9	<60	18–160
Ni (mg/kg)	79.6	***170.3***	35.2	68.7	40–250	20–102
Pb (mg/kg)	***79.9***	***101.4***	***37.8***	1.9	15–60	12–5318
Mn (mg/kg)	***6565***	***1660***	***942***	617.3	2500–5500	6000–9000
Co (mg/kg)	***11.2***	***26***	***15.8***	7.9	0–7	3–200
Ba (mg/kg)	***588.8***	***1437***	***545***	236.7	/	669–2210
Bi (mg/kg)	***44.8***	***2.8***	***25.2***	<0.02	/	/
Sr (mg/kg)	408.5	314.7	485	1775.4	/	667–1065
Cu (mg/kg)	***84.4***	***79.7***	***56.1***	30.6	15–300	27–920
Hg (mg/kg)	<0.003	0.01	***0.189***	0.042	0.4	0.1–1.1
HMI	20.57	17.27	13.67	6.49	/	/

For testing the monolithic samples using the dynamic surface leaching test (DSLT) method, CEM I 42.5 R cement, water, and the selected WBAs from the different plants replaced 15% of the cement per the EN 197-1 [70] standard.

2.2. Specimen Preparation and Testing Methods

The leaching tests and sample labels are shown in Table 3. Labels F1, F2, and F3 represent the samples obtained from the eluates of WBA1, WBA2, and WBA3, respectively. Crushed mortar samples M1, M2, and M3 had 15% of their cement replaced with WBA1, WBA2, and WBA3, respectively, and monolithic samples M15-1, M15-2, and M15-3 had 15% of their cement replaced with WBA1, WBA2, and WBA3, respectively. REF was a monolithic sample containing only cement as a binder, while M0 designates the crushed mortar sample without WBA.

Table 3. Test programme and sample labelling.

Testing Method	Tested Samples	Sample Designation after Testing
EN 12457-2:2005	Eluate of samples WBA1, WBA2 and WBA3	F1, F2, F3
	Crushed mortar with 15% of WBA replacement 1, 2 and 3 and reference mixture	M0, M1, M2, M3
CEN/TS 16637-2	Monolithic samples with 15% WBA replacement 1, 2 and 3 and reference mixture	REF, M15-1, M15-2, M15-3

The WBA leachate (F1, F2, and F3) and crushed cement mortar (M0, M1, M2, and M3) samples were tested according to the standard EN 124 57-2:2005 [71], wherein the liquid to solid phase ratio (L/S) was

10 for the granulated material that was exposed to the more direct action of water. The crushed mortar sample with 15% WBA was prepared according to the standard EN 196-1:2016 [72]. The composition of the mortar and storage of materials before usage followed the standard, which defines that the mass ratio of CEN components, standard sand, cement, and water is 3:1:0.5. The mortar contained 1350 ± 5 g of sand, 450 ± 2 g of cement, and 225 ± 1 g of water; 15% of the cement was replaced with WBA. The mortar was crushed and sieved to a particle size less than 4 mm to produce the crushed mortar samples.

Leaching testing per EN 12457-2:2005 [71] involved separating 20 g of WBA, placing it in a closed 250 mL bottle, and filling the bottle with 200 mL of solvent (deionised water) in order to attain a desired ratio of liquid/solid (L/S = 10). The glass bottle containing the sample-water mixture was rotated (mixed) for 24 h. After the mixing was complete, the mixture was allowed to settle for 15 ± 5 min. The eluate was then passed through a membrane filter with a pore diameter of 0.45 µm. Analysis of the heavy metals concentration using a spectrometer with excitation in inductively coupled plasma—ICP-OES (ICPE 9000, Shimadzu) was preceded by sample stabilisation with 65% nitric acid.

For determining the leaching characteristics of the monolithic cement paste samples, testing was performed per the CEN/TS 16637-2 standard (DSLT method) [73], wherein the release of substances to the environment is primarily controlled by diffusion. Construction products suitable for the DSLT include facades (brick, concrete, wood panels, glazing, and coatings), roof coverings, pavement samples (from concrete, stone, asphalt, and concrete slabs), foundations (concrete blocks and concrete), coastal protection, gravel railroad sections (track ballast), and glass tiles [74]. The DSLT involves periodic leaching solution replacement, as specified by the standard, to ensure a substantial difference in concentration between the solid and liquid phases. As compared to a leaching test for granular materials, the DSLT requires more time but provides information on the kinetic mobility of the harmful substances and complex leaching mechanisms [75]. For the monolithic sample leaching tests per CEN/TS 16637-2 [73], cement paste samples were prepared according to the EN 196-3:2016 [76] standard, see Table 4.

Table 4. Paste mix details.

Sample Designation	Water, g	Cement, g	WBA, g	Standardized Consistency, %
REF	141.5	500	-	28.3
M15-1	217	425	75	43.4
M15-2	142	425	75	28.4
M15-3	160	425	75	32.0

After 3 days of ageing, leaching tests were performed on prism samples with dimensions of 4 × 4 × 16 cm. The leaching vessel was a closed polypropylene plastic container. The eluate sampling was performed at 0.25, 1, 2.25, 4, 9, 16, 36, and 64 days. Samples were submerged in demineralised and deionised water with a conductivity of less than 0.5 mS/m, such that the ratio of the volume of the liquid to the exposed mortar surface was L/S = 90 L/m^2, i.e., there was 90 L of solvent (deionised and demineralised water) to 1 m^2 of sample surface area. The solvent volume was obtained using the following expression:

$$V_l = (L/A) \times AV_1 = (\mathrm{L}/\mathrm{A}) \times \mathrm{A}, \tag{1}$$

where

surface area of the tested sample in m^2, and
L/A must be equal to 80 ± 10 L/m^2.

According to the standard, the distance between the solvent and the vessel bottom, i.e., the distance between the sample and the solvent surface, must be at least 20 mm. The solvent was removed from the vessel at specified times and replaced with the same amount of demineralised and deionised water until the end of the next period. The fluid removed was passed through a 0.45 µm filter paper.

The pH and electrical conductivity of the removed fluid and the mass of the monolithic DSLT sample were measured. The filtered fluid was prepared for heavy metals concentration testing using ICP-OES (acidification with nitric acid to below pH 2 before testing).

Leaching of the substance per unit of sample surface area is given by

$$V_l = (L/A) \times Ar_i = (\mathrm{ci} \times \mathrm{V/A}) \times 0.01, \tag{2}$$

where

period i—period time from 1 to n,
r_i—leaching value per unit surface area of the sample for the period i (i = 1 to 8), in mg/m^2,
V—solvent volume in L, and
A—surface area of the tested sample in m^2.

The leaching ratio is defined as the ratio of the leached metal concentration in the eluate to the total amount of metal measured in the tested material [77,78]:

$$V_l = \left(\frac{L}{A}\right) \times A \text{ Leaching ratio} = (c_i/c_{tot}) \times 100, \tag{3}$$

where

c_i = concentration of individual leached heavy metal (mg/kg) and
c_{tot} = content of individual heavy metal in WBA according to Table 2.

3. Results and Discussion

3.1. Discussion of the Application of WBA in Agriculture

Circular WBA management is ecologically and economically viable at the local level. Based on the conducted survey made under project "TAREC^2 Transformation of Wood Biomass Ash into Resilient Construction Composites", 61% of WBA is landfilled, while 38% is used in agriculture [63]. The heavy metals concentrations in WBA that are shown in Table 2 were compared with the limit values for heavy metals concentrations in some EU countries (Table 5) to evaluate the applicability of WBAs in agriculture.

Table 5. Heavy metals concentration limit values for the use of WBA in agriculture and forestry [mg/kg] [21,23].

Heavy Metal	Finland	Sweden	Denmark	Lithuania	Austria	Croatia
As	40	30	-	30	20	-
Cd	25	30	15	30	5–8	**0.7–3**
Cu	700	400	-	400	200–250	70–500
Pb	150	300	120	300	100–200	45–200
Zn	4500	7000	-	7000	**1200–1500**	**200–1800**
Cr	300	**100**	**100**	**100**	150–250	70–250
Ni	150	**70**	**30–60**	**70**	150–200	**25–100**
V	-	70	-	70	100	-
B	-	500	-	500	-	-
Hg	1.0	3	0.8	3	-	0.4–3
Co	-	-	-	-	100	-
Mo	-	-	-	-	20	-

In Croatia, the end-of-waste criteria are specified by the "Ordinance on by-products and end-of-waste status" (OG 11//14) [23], through which WBAs can obtain agricultural product status in three categories, depending on the levels of heavy metals allowed. None of the tested WBAs meet the heavy metals limit criteria for use in agriculture: the Cd concentrations in samples WBA1 (3.1 mg/kg) and WBA3 (6 mg/kg), the Zn concentration in sample WBA1 (1850 mg/kg), and the Ni concentration in sample WBA2 (170.3 mg/kg) were higher than the limit values in Table 5, prohibiting their use in agriculture. Notably, the tested WBA samples met only the criteria for application to forestry in Finland. Producing WBA in one country and using it in another as part of its circular management must be economically viable.

As shown in Table 2, the heavy metal index (HMI) was determined as an overall evaluation of the WBAs' heavy metals contents. The HMI was proposed by the authors of [6], wherein the heavy metals contents were normalised to the limit values for the standard potentially toxic elements (Cd, Hg, Cr, Cu, Pb, Ni, and Zn) to evaluate the use of waste products in agriculture [77]. Sample WBA1 has greatest HMI (18.2); it was collected from a power plant that uses a grate combustor and pulverised fuel combustor as its combustion technology (Table 1). The authors of [3] state that the temperatures in a grate combustor can reach 1000–1200 °C, while combustion temperatures in fluidised beds are somewhat lower (less than 900 °C); in pulverised fuel systems, the peak flame temperatures are commonly near 1600 °C, which is extremely high as compared to the other combustion systems. Because combustion temperature affects the chemical composition of the WBA, including the metals content (metals content increases with increasing temperature [33]), it could be expected that WBAs from power plants with pulverised fuel combustors cannot be used in agriculture. However, this should be investigated further.

3.2. Leaching from the WBA and Crushed Cement Composites with 15% WBA as Cement Replacement

When landfilling any waste, the appropriate procedures and criteria should be followed. In consideration that most WBA is currently disposed of as waste (70% in Europe and 61% in Croatia), the WBA leaching values were compared to the leaching value limits for the waste categories (inert, non-hazardous, and hazardous waste) prescribed in the "EU Directive 1999/31/EC" [78,79] and shown in Table 6.

Results of the heavy metals concentration testing of the WBA eluate samples (F1, F2, and F3) are given in Table 6 along with the results of the heavy metals concentration testing of the crushed mortar samples with 15% WBA used as a cement replacement (M0, M1, M2, and M3). These samples represent the end-stage of the construction material life cycle, disposal.

From Table 6, Zn and Cr had the highest concentrations of the WBA eluates (F1, F2, and F3). Significant Cr leaching was observed for all WBAs tested, especially for sample F1. By comparing the results for the heavy metals Pb, Ni, Zn, Cr, Cd, and Cu in the WBA eluates (F1, F2, and F3) with the values obtained for the crushed mortar samples (M1, M2, M3), when the WBA was incorporated into the cement mortar, significant decreases in the heavy metals concentrations were observed. This can be explained by the reduced heavy metals mobility, i.e., the incorporation of the heavy metals into the cement matrix [80], and confirms that the heavy metals were successfully encapsulated within the cement matrix. Based on the values obtained, assessments of the bonding of the heavy metals in the new environment (cement matrix) and environmental safety can be performed. The leaching ratio is a useful index for safety assessment: larger values for metal solidification, i.e., lower concentrations of leached metal, indicate a lower environmental impact and greater safety when using and disposing of the material.

Figure 1 shows that the Cr leaching values were significantly high in the WBA eluates, but when the WBA was used in the cement composites, these values decreased substantially. The same trend was observed for the other metals (Cd, Cu, Pb, and Zn) except Ni, the concentration of which was 27.42% greater in the M2 sample than in the reference mixture. Large values for Cr leaching from the WBAs themselves were observed in [57], but the authors concluded, through the testing of crushed mortar, that the metals chemically bond in the mineral phase or are absorbed by the cement matrix, and the same was observed when coal ash was used in concrete. However, the testing of WBA eluates in [81] did not reveal Cr leaching or deviations from limit values.

Table 6. Heavy metal concentrations and limited values for the individual waste categories [78,79].

	Eluate of Samples WBA1, WBA2 and WBA3, mg/kg			**Crushed Mortar with 15% WBAs 1, 2 and 3, and the Reference Mixture, mg/kg**				**Leaching Limit Values Based on WAC (Waste Acceptance Criteria), mg/kg, L/S = 10**		
	F1	**F2**	**F3**	**M0**	**M1**	**M2**	**M3**	**Inert Waste**	**Non-Hazardous Waste**	**Hazardous Waste**
Cd	0.02	0.107	<0.01	0.056	0.02	0.061	0.108	0.04	1	5
Cr	8.35	6.681	4.10	1.241	0.07	1.081	0.778	0.5	10	70
Cu	0.48	0.12	0.034	0.23	0.18	0.33	0.31	2	50	100
Ni	0.04	0.047	0.051	0.024	0.04	1.449	<0.006	0.4	10	40
Pb	<0.05	3.41	0.010	<0.05	<0.05	<0.05	0.224	0.5	10	50
Zn	0.63	15.722	0.086	1.172	0.02	0.652	1.137	4	50	200

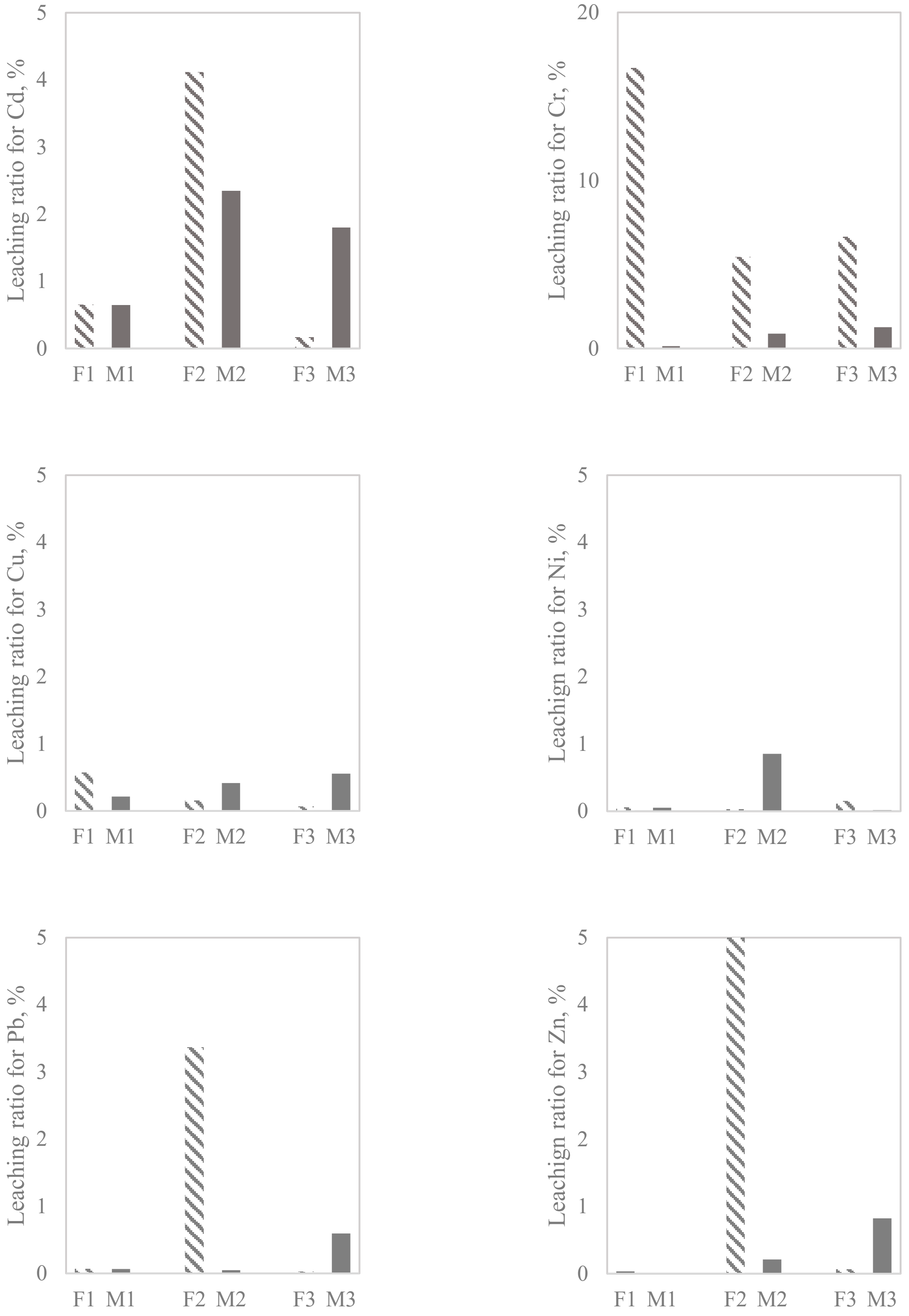

Figure 1. Ratio of leached metal in the crushed cement composite compared to the primary samples (WBA eluates F1, F2, and F3).

WBA leaching values (F1, F2, and F3) were compared to the leaching limit values for certain waste categories (inert, non-hazardous, and hazardous wastes) prescribed in the EU Directive 1999/31/EC [78,79] and are shown in Table 6 along with the results of the heavy metals concentration testing of the crushed mortar samples with 15% WBA used as a cement replacement (M0, M1, M2, and M3). These samples represent the end-stage of the construction material life cycle, disposal. Comparing the WBA eluate results shown to the limit values for the individual waste categories (using the conversion factor L/S = 10 L/kg), none of the tested WBA eluates (F1, F2 and F3) was in the inert waste category, based on at least one of their analysed parameters, respectively Cr values for F1, F2 and F3 were high and close to the limit for non-hazardous waste. For the case of disposal, the WBA leaching results obtained illustrate the vital importance of compliance with disposal procedures and the need for systematic control and testing to prevent local environmental pollution.

3.3. Leaching from the Monolithic Cement Samples

The leaching characteristics of WBA used in cement composites was assessed by the cumulative leaching of heavy metals during a 64 d testing period, with the results shown Figure 2 and expressed as mg per m^2 of the surface area. The cumulative testing values are provided in Table A1 (Appendix A).

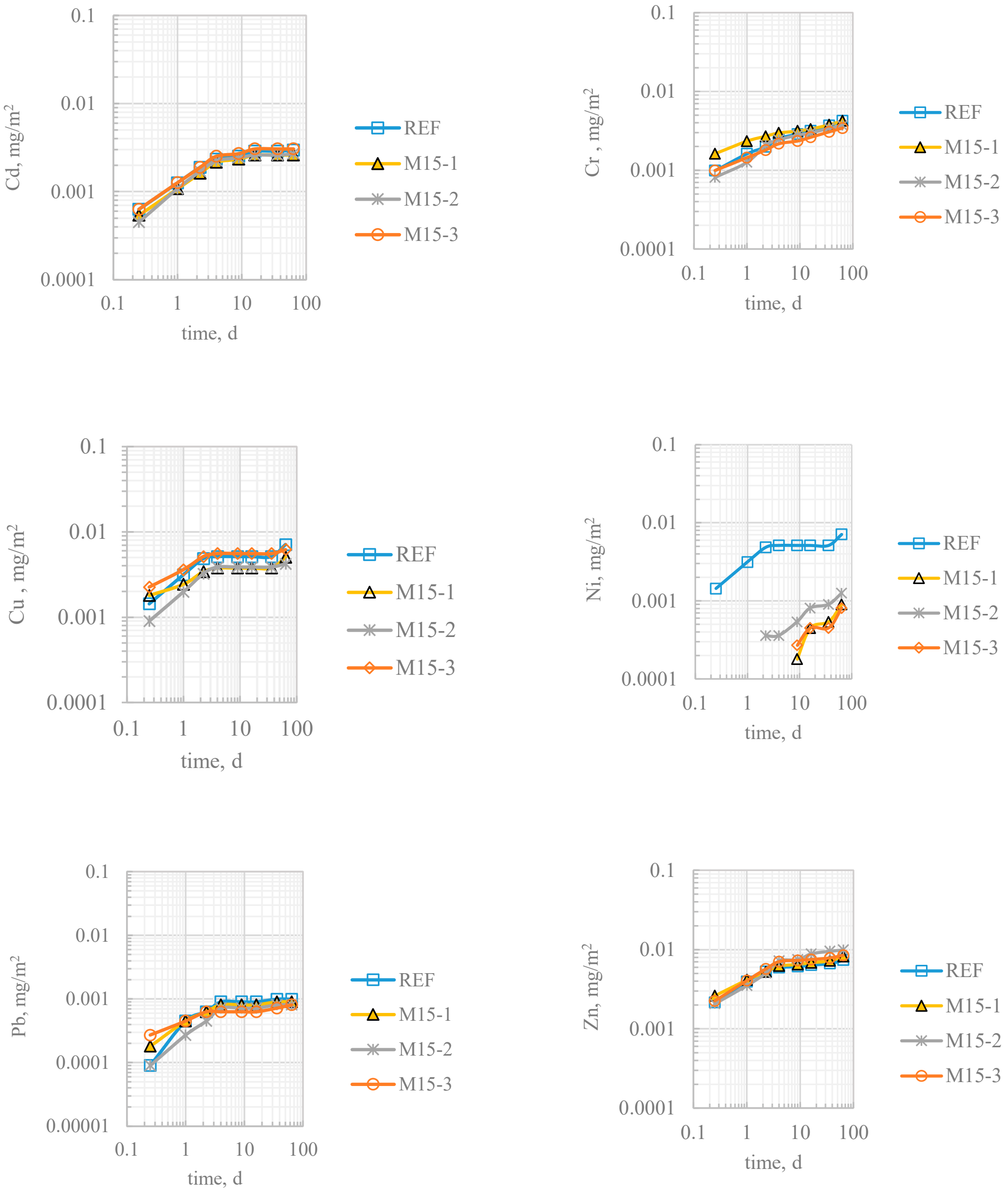

Figure 2. Cumulative leaching of heavy metals from the monolithic samples over time.

By examining the heavy metals leaching results over time, a trend of decreasing heavy metals concentrations can be observed up to the 7th time step of the test (at 36 d), as shown in Table A1. The exception to this trend was Ni; in the 8th time step (at 64 d), its concentration slightly increased.

The initial leaching that occurs on the outer surface of the monolithic sample causes the initially larger concentration values. Over time, the heavy metals leaching occurs due to the diffusion of the heavy metals ions from the cement matrix, which was observed after the 8th time step of the testing and agrees with [66]. In most cases, the heavy metals leaching became insignificant after long-term submersion [82]. The leaching values reducing over time indicates that the heavy metals leaching initially comes only from the surface layer of the sample. Significantly more time must elapse before the metal from the interior part of the sample is released to the external environment, due to slowed diffusion, the effect of the metals bonding to hydration products, and the reduced leaching of the majority of the heavy metals given the high pH value of the sample interior [83–87]. Stronger initial leaching of the heavy metals from monolithic samples containing WBA was observed by [66], and the authors suggested that the heavy metals leaching was probably caused by the diffusion of heavy metal ions from the cement matrix. Surface leaching, dissolution, and diffusion are the three dominant mechanisms for releasing heavy metals from the cement matrix [88]. The strong linear relationships observed between the cumulative leaching and time for Cr ($R^2 = 0.99$ for all mixtures) and Zn ($R^2 = 0.92 - 0.97$) indicate diffusion-controlled leaching. For Ni, delayed leaching in the initial phase [84] with subsequent diffusion-controlled leaching was observed.

Cumulative leaching values for mixtures M1-15, M2-15, and M3-15 for metals Cd, Cr, Cu, and Pb are equal to or less than those of the reference mixture, as shown in Table 7. The WBA mixtures' cumulative Zn leaching values were 11.06% (M1-15) to 34.3% (M2-15) higher than reference mixture, demonstrating the sensitivity of the Zn leaching to substituting the cement with WBA. The cumulative leaching values for Ni were less than the reference mixture except for sample M2-15, for which the value was 27.42% greater than the reference. Leaching is heavily dependent on the pH value of the solution, i.e., the leaching increases as the pH value of the solution decreases [39]. The mineralogical phases of the metal oxides present in the WBA affect their sensitivity to the presence of H+ ions in leaching. At lower pH values, there is an increase in heavy metals leaching [39]. During the testing, the pH values of the eluate were between 10.8 and 11.7. The demineralised water becomes highly alkaline when it encounters concrete, especially when, as in this case, there is no water flow [82].

Table 7. Values of cumulative leaching in mg/m^2 for mixtures REF, M1-15, M2-15 and M3-15 after 64 days, and the limit values for cumulative leaching per [66,84,89].

	REF	**M1-15**	**M2-15**	**M3-15**	**Soil Quality Regulation**
Element	**(mg/m^2)**	**(mg/m^2)**	**(mg/m^2)**	**(mg/m^2)**	**Limit Values for Ready-Made Construction Materials (mg/m^2)**
Cd	2.99	2.61	2.70	3.06	3.8
Cr	4.23	4.23	3.69	3.42	120
Cu	7.11	5.04	4.23	6.22	98
Ni	0.99	0.90	1.26	0.81	81
Pb	0.99	0.90	0.81	0.81	400
Zn	7.37	8.19	9.90	8.47	800

In the absence of national legislation regarding limit values for leaching from monolithic products, the cumulative leaching values per sample surface area obtained for certain metals were compared to the Dutch limit values given in the guideline: "Soil Quality Degree" [66,84,89] (see Table 7). Despite the increased levels of some metals (Zn and Ni) observed for the mixtures containing WBA as a partial substitute for cement, the leaching of the cement composites with 15% WBA was significantly below the limit values provided in the Dutch guidelines [66,84,89], i.e., the tested values of heavy metals leaching are acceptable. These results concur with those of [22,57] when pure wood biomass was used for combustion.

4. Conclusions

This study analysed the impact of using WBA in cement composites regarding leaching characteristics by examining three cases: (1) the leaching of the WBA itself (WBA eluate), (2) the leaching of the crushed mortar that contained 15% WBA as a partial cement replacement, and (3) the leaching of the monolithic samples with 15% WBA as a partial cement replacement, per the proposed standard CEN/TS 16637-1.

Based on the testing, the following conclusions were reached:

- As an overall quality measurement, the heavy metals index (HMI), indicates that the WBAs from power plants using a pulverised fuel combustor cannot be used in agriculture, although this should be further investigated.
- By comparing the test values from the WBA leaching to the limit values for the individual waste categories, it was found that all of the examined WBAs failed to meet the criteria for categorisation as inert waste based on at least one analysed parameter.
- The values for heavy metals leaching for the monolithic samples with 15% WBA as a substitute for cement are less than those for the reference sample, excepting Zn, but still lower than the specified criteria. All tested samples meet the criteria given in "Soil Quality Degree".
- During various stages in the life cycle of cementitious building materials containing WBA, the heavy metals are stabilized in the cement matrix, and therefore WBA could be used in the construction sector following the basic construction requirement of "hygiene, health, and the environment".

Author Contributions: Conceptualization, I.C. and N.Š.; methodology, I.C.; validation, I.C., M.T. and N.Š.; formal analysis, I.C.; investigation, K.K.J.; data curation, I.C., M.T. and K.K.J.; writing—original draft preparation, I.C. and K.K.J.; writing—review and editing, M.T. and N.Š.; visualization, M.T. and N.Š.; supervision, N.Š.; funding acquisition, N.Š. All authors have read and agreed to the published version of the manuscript.

Funding: This research was performed as a part of the research project IP-2016-06-7701 "Transformation of Wood Biomass Ash into Resilient Construction Composites", which was funded by the Croatian Science Foundation.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Results of the leach testing of the monolithic samples, by time increment.

				REF (mg/L)				
days	**0.25**	**1**	**2.25**	**4**	**9**	**16**	**36**	**64**
Cd	0.007	0.007	0.007	0.005	0.002	0.004	<0.001	0.001
Cr	0.011	0.007	0.004	0.006	0.004	0.003	0.006	0.006
Cu	0.016	0.019	0.019	0.003	<0.001	<0.001	<0.001	0.022
Ni	<0.001	<0.001	<0.001	0.001	0.003	0.002	<0.001	0.005
Pb	0.001	0.004	0.002	0.003	<0.001	<0.001	0.001	<0.001
Zn	0.024	0.02	0.015	0.007	0.002	0.003	0.003	0.008
				M15-1 (mg/L)				
days	**0.25**	**1**	**2.25**	**4**	**9**	**16**	**36**	**64**
Cd	0.006	0.006	0.006	0.006	0.002	0.003	<0.001	<0.001
Cr	0.018	0.008	0.004	0.003	0.002	0.002	0.005	0.005
Cu	0.02	0.007	0.011	0.004	<0.001	<0.001	<0.001	0.014
Ni	<0.001	<0.001	<0.001	<0.001	0.002	0.003	0.001	0.004
Pb	0.002	0.003	0.002	0.002	<0.001	<0.001	0.001	<0.001
Zn	0.029	0.017	0.012	0.011	0.003	0.004	0.004	0.011

Table A1. *Cont.*

M15-2 (mg/L)								
days	**0.25**	**1**	**2.25**	**4**	**9**	**16**	**36**	**64**
Cd	0.005	0.007	0.007	0.006	0.002	0.002	<0.001	0.001
Cr	0.009	0.005	0.009	0.004	0.004	0.002	0.005	0.003
Cu	0.01	0.012	0.014	0.007	<0.001	<0.001	<0.001	0.004
Ni	<0.001	<0.001	0.004	<0.005	0.002	0.003	0.001	0.004
Pb	0.001	0.002	0.002	0.003	<0.001	<0.001	<0.001	<0.001
Zn	0.023	0.016	0.017	0.024	0.003	0.015	0.008	0.004
M15-3 (mg/L)								
days	**0.25**	**1**	**2.25**	**4**	**9**	**16**	**36**	**64**
Cd	0.007	0.007	0.007	0.003	0.002	0.004	<0.001	<0.001
Cr	0.011	0.005	0.004	0.004	0.002	0.003	0.005	0.004
Cu	0.025	0.015	0.017	0.005	<0.001	<0.001	<0.001	0.007
Ni	<0.001	<0.001	<0.001	<0.001	0.003	0.002	<0.001	0.004
Pb	0.003	0.002	0.002	<0.001	<0.001	<0.001	0.001	0.001
Zn	0.025	0.02	0.018	0.015	0.003	0.002	0.004	0.007

References

1. World Bioenergy Association Global Bioenergy Statistics 2014. *Glob. Bioenergy Stat.* **2014**, *40*. [CrossRef]
2. Bohrn, G.; Stampfer, K. Untreated Wood Ash as a Structural Stabilizing Material in Forest Roads. *Croat. J. For. Eng.* **2001**, *35*, 81–90.
3. van Loo, S.; Koppejan, J. *The Handbook of Biomass Combustion and Co-Firing*, 2nd ed.; Earthscan: London, UK, 2012; ISBN 978-1-84407-249-1.
4. European Parliament and the Council of the European Union Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certian Directives. *Off. J. Eur. Union* **2008**, *L 312/3*, 99–126.
5. European Parliament and the Council of the European Union Directive (EU) 2018/851 of the European Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC on waste. *Off. J. Eur. Union* **2018**, *L150/109*, 31.
6. Carević, I.; Serdar, M.; Štirmer, N.; Ukrainczyk, N. Preliminary screening of wood biomass ashes for partial resources replacements in cementitious materials. *J. Clean. Prod.* **2019**, *229*, 1045–1064. [CrossRef]
7. Pitman, R.M. Wood ash use in forestry—A review of the environmental impacts. *Forestry* **2006**, *79*, 563–588. [CrossRef]
8. Rajamma, R.; Ball, R.J.; Tarelho, L.A.C.; Allen, G.C.; Labrincha, J.A.; Ferreira, V.M. Characterisation and use of biomass fly ash in cement-based materials. *J. Hazard. Mater.* **2009**, *172*, 1049–1060. [CrossRef]
9. Steenari, B.M.; Lindqvist, O. Stabilisation of biofuel ashes for recycling to forest soil. *Biomass Bioenergy* **1997**, *13*, 39–50. [CrossRef]
10. Ukrainczyk, N.; Vrbos, N.; Koenders, E.A.B. Reuse of Woody Biomass Ash Waste in Cementitious Materials. *Chem. Biochem. Eng. Q.* **2016**, *30*, 137–148. [CrossRef]
11. Berra, M.; Mangialardi, T.; Paolini, A.E. Reuse of woody biomass fly ash in cement-based materials. *Constr. Build. Mater.* **2015**, *76*, 286–296. [CrossRef]
12. Obernberger, I.; Supancic, K. Possibilities of ash utilisation from biomass combustion plants. In Proceedings of the 17th European Biomass Conference & Exhibition, Hamburg, Germany, 29 June–3 July 2009.
13. Amjad, M.; Khan, S.; Khan, A.; Alam, M. Soil contamination with cadmium, consequences and remediation using organic amendments. *Sci. Total Environ.* **2017**, *601–602*, 1591–1605. [CrossRef]
14. Khan, A.A.; de Jong, W.; Jansens, P.J.; Spliethoff, H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process. Technol.* **2009**, *90*, 21–50. [CrossRef]
15. Plum, L.M.; Rink, L.; Haase, H. The Essential Toxin: Impact of Zinc on Human Health. *Int. J. Environ. Res. Public Health* **2010**, *7*, 1342–1365. [CrossRef] [PubMed]

16. Marx, S.K.; Stromsoe, N. Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives. *Environ. Pollut.* **2016**, *213*, 283–298. [CrossRef] [PubMed]
17. Cenni, R.; Janisch, B.; Spliethoff, H.; Hein, K.R. Legislative and environmental issues on the use of ash from coal and municipal sewage sludge co-firing as construction material. *Waste Manag.* **2001**, *21*, 17–31. [CrossRef]
18. da Luz Garcia, M.; Sousa-Coutinho, J. Strength and durability of cement with forest waste bottom ash. *Constr. Build. Mater.* **2013**, *41*, 897–910. [CrossRef]
19. Pesonen, J.; Kuokkanen, T.; Rautio, P.; Lassi, U. Bioavailability of nutrients and harmful elements in ash fertilizers: Effect of granulation. *Biomass Bioenergy* **2017**, *100*, 92–97. [CrossRef]
20. Mellbo, P.; Sarenbo, S.; Stålnacke, O.; Claesson, T. Leaching of wood ash products aimed for spreading in forest floors—Influence of method and L/S ratio. *Waste Manag.* **2008**, *28*, 2235–2244. [CrossRef]
21. Lanzerstorfer, C. Characterization of Fly Ashes from Biomass Combustion with Focus on Their Utilization. Ph.D. Thesis, University of Natural Resources and Life Sciences, Vienna, Austria, 20 May 2016.
22. Berra, M.; Paolini, A.E.; Mangialardi, T. Environmental quality of hardened wood fly ash-cement mixtures. *Proc. Inst. Civ. Eng. Waste Resour. Manag.* **2016**, *169*, 3–13. [CrossRef]
23. Republic of Croatia Ministry of Environmental and Nature. Protection Ordinance on by-products and end-of-waste status (OG 11/14). *Off. Gazzete* **2014**, *114*, 1–10.
24. Candamano, S.; De Luca, P.; Frontera, P. Production of Geopolymeric Mortars Containing Forest Biomass Ash as Partial Replacement of Metakaolin. *Environments* **2017**. [CrossRef]
25. Rajamma, R.; Labrincha, J.A.; Ferreira, V.M. Alkali activation of biomass fly ash-metakaolin blends. *Fuel* **2012**, *98*, 265–271. [CrossRef]
26. Abdulkareem, O.A.; Ramli, M.; Matthews, J.C. Production of geopolymer mortar system containing high calcium biomass wood ash as a partial substitution to fly ash: An early age evaluation. *Compos. Part. B* **2019**, *174*, 106941. [CrossRef]
27. Fernández-pereira, C.; De Casa, J.A.; Gómez-barea, A.; Arroyo, F.; Leiva, C.; Luna, Y. Application of biomass gasification fly ash for brick manufacturing. *Fuel* **2011**, *90*, 220–232. [CrossRef]
28. Kizinievic, O.; Kizinievic, V. Utilisation of wood ash from biomass for the production of ceramic products. *Constr. Build. Mater.* **2020**, *127*, 264–273. [CrossRef]
29. Cabrera, M.; Agrela, F.; Ayuso, J.; Galvin, A.P.; Rosales, J. Feasible use of biomass bottom ash in the manufacture of cement treated recycled materials. *Mater. Struct.* **2016**, *49*, 3227–3238. [CrossRef]
30. Zagvozda, M.; Dimter, S.; Rukavina, T.; Grubeša, I.N. Possibilities of bioash application in road building. *Građevinar* **2018**, *70*, 393–402. [CrossRef]
31. Sarkkinen, M.; Kujala, K.; Kemppainen, K.; Gehör, S. Effect of biomass fly ashes as road stabilisation binder. *Road Mater. Pavement Des.* **2018**, *19*. [CrossRef]
32. Batt, A.S.; Garg, A. Partial Replacement of Wood Ash with Ordinary Portland Cement and Foundry Sand as Fine Aggregate. *J. Civ. Environ. Eng.* **2017**, *7*, 1–5. [CrossRef]
33. Yang, Z.; Huddleston, J.; Brown, H. Effects of Wood Ash on Properties of Concrete and Flowable Fill. *J. Mater. Sci. Chem. Eng.* **2016**, *4*, 101–114. [CrossRef]
34. Naik, T.R.; Kraus, R.N.; McCormick, S. Recycling of Wood Ash in Cement-Based Construction Materials. 2001. Available online: https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.1059.9743&rep=rep1&type=pdf (accessed on 3 December 2020).
35. Elahi, M.; Qazi, A.U.; Yousaf, M.; Akmal, U. Application of wood ash in the production of concrete. *Sci. Int.* **2015**, *27*, 1277–1280.
36. Naik, T.R.; Kraus, R.N. Wood Ash: A New Source of Pozzolanic Material. *Concr. Int.* **2003**, *25*, 55–62.
37. Elinwa, A.U.; Mahmood, Y.A. Ash from timber waste as cement replacement material. *Cem. Concr. Compos.* **2002**, *24*, 219–222. [CrossRef]
38. Chowdhury, S.; Maniar, A.; Suganya, O.M. Strength development in concrete with wood ash blended cement and use of soft computing models to predict strength parameters. *J. Adv. Res.* **2014**, *6*, 907–913. [CrossRef] [PubMed]
39. Udoeyo, F.F.; Inyang, H.; Young, D.T.; Oparadu, E.E. Potential of Wood Waste Ash as an Additive in Concrete. *J. Mater. Civ. Eng.* **2006**, *18*, 605–611. [CrossRef]

40. Biernacki, J.J.; Bullard, J.W.; Sant, G.; Banthia, N.; Glasser, F.P.; Jones, S.; Ley, T.; Livingston, R.; Nicoleau, L.; Olek, J.; et al. Cements in the 21st Century: Challenges, Perspectives, and Opportunities. *J. Am. Ceram. Soc.* **2017**, *100*, 2746–2773. [CrossRef]
41. Popović, K.; Rosković, R.; Bjegović, D. Cement production and sustainable development. *GRAĐEVINAR* **2003**, *55*, 201–206.
42. International Energy Agency; Levi, P.; Vass, T.; Mandová, H.; Gouy, A. Cement. 2020. Available online: https//www.iea.org/reports/cement (accessed on 26 November 2020).
43. UN Environment; Scrivener, K.L.; John, V.M.; Gartner, E.M. Eco-Efficient Cements: Potential, Economically Viable Solutions for a Low-CO2, Cement-Based Materials Industry. *Cem. Concr. Res.* **2018**, *114*, 2–26. [CrossRef]
44. IEA Bioenergy. Options for Increased Use of Ash from Biomass Combustion and Co-Firing. Available online: https://www.ieabioenergy.com/wp-content/uploads/2019/02/IEA-Bioenergy-Ash-management-report-revision-5-november.pdf (accessed on 3 December 2020).
45. *EN 450-1: Fly Ash for Concrete—Part 1: Definition, Specifications and Conformity Criteria*; The European Committee for Standardization (CEN): Brussels, Belgium, 2012.
46. *ASTM C618 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use*; ASTM International: West Conshohocken, PA, USA, 2019; pp. 3–6.
47. Carević, I.; Baričević, A.; Štirmer, N.; Bajto Šantek, J. Correlation between physical and chemical properties of wood biomass ash and cement composites performances. *Constr. Build. Mater.* **2020**, *256*. [CrossRef]
48. Sigvardsen, N.M.; Geiker, M.R.; Ottosen, L.M. Phase development and mechanical response of low-level cement replacements with wood ash and washed wood ash. *Constr. Build. Mater.* **2020**, *121234*. [CrossRef]
49. Fusade, L.; Viles, H.; Wood, C.; Burns, C. The effect of wood ash on the properties and durability of lime mortar for repointing damp historic buildings. *Constr. Build. Mater.* **2020**, *212*, 500–513. [CrossRef]
50. Juenger, M.C.G.; Snellings, R.; Bernal, S.A. Supplementary cementitious materials: New sources, characterization, and performance insights. *Cem. Concr. Res.* **2019**, *122*, 257–273. [CrossRef]
51. Li, J.; Zhang, W.; Li, C.; Monteiro, P.J.M. Eco-friendly mortar with high-volume diatomite and fl y ash: Performance and life-cycle assessment with regional variability. *J. Clean. Prod.* **2020**, *261*, 121224. [CrossRef]
52. Miller, S.A.; Moore, F.C. Climate and health damages from global concrete production. *Nat. Clim. Chang.* **2020**, *10*, 439–443. [CrossRef]
53. Monteiro, P.J.M.; Miller, S.A.; Horvath, A. Produce and use with care—Towards sustainable concrete. *Nat. Publ. Gr.* **2017**, *16*, 698–699. [CrossRef]
54. Medina, J.M.; Sáez del Bosque, I.F.; Frías, M.; Sánchez de Rojas, M.I.; Medina, C. Characterisation and valorisation of biomass waste as a possible addition in eco-cement design. *Mater. Struct.* **2017**, *50*, 1–13. [CrossRef]
55. Pavlíková, M.; Zemanová, L.; Pokorny, J.; Lojka, M.; Sedmidubsky, D. Valorization of wood chips ash as an eco-friendly mineral admixture in mortar mix design. *Waste Manag.* **2018**, *80*, 89–100. [CrossRef]
56. Manskinen, K.; Nurmesniemi, H.; Pöykiö, R. Occupational risk evaluation of using bottom ash and fly ash as a construction material. *J. Hazard. Toxic Radioact. Waste* **2011**, *16*, 79–87. [CrossRef]
57. Tosti, L.; van Zomeren, A.; Pels, J.R.; Comans, R.N.J. Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material. *Resour. Conserv. Recycl.* **2018**, *134*, 25–33. [CrossRef]
58. Sigvardsen, N.M.; Kirkelund, G.M.; Jensen, P.E.; Geiker, M.R.; Ottosen, L.M. Impact of production parameters on physiochemical characteristics of wood ash for possible utilisation in cement-based materials. *Resour. Conserv. Recycl.* **2019**, *145*, 230–240. [CrossRef]
59. Hansen, H.K.; Pedersen, A.J.; Ottosen, L.M.; Villumsen, A. Speciation and mobility of cadmium in straw and wood combustion fly ash. *Chemosphere* **2001**, *45*, 2–7. [CrossRef]
60. EU Office Regulation of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC. *Off. J. Eur. Union* **2011**, *88*, 5–43.
61. Kosson, D.S.; Van Der Sloot, H.A.; Sanchez, F.; Garrabrants, A.C. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environ. Eng. Sci.* **2002**, *19*, 159–204. [CrossRef]

62. Chowdhury, S.; Mishra, M.; Suganya, O. The incorporation of wood waste ash as a partial cement replacement material for making structural grade concrete: An overview. *Ain Shams Eng. J.* **2015**, *6*, 429–437. [CrossRef]
63. Milovanović, B.; Štirmer, N.; Carević, I.; Baričević, A. Wood biomass ash as a raw material in concrete industry. *Građevinar* **2019**, *71*, 505–514. [CrossRef]
64. *EN ISO 16948: Solid Biofuels—Determination of Total Content of Carbon, Hydrogen and Nitrogen*; The European Committee for Standardization (CEN): Brussels, Belgium, 2015.
65. *ASTM D6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis*; ASTM International: West Conshohocken, PA, USA, 2011.
66. Berra, M.; De Casa, G.; Orso, M.D.; Galeotti, L.; Mangialardi, T.; Paolini, A.E.; Piga, L. Reuse of Woody Biomass Fly Ash in Cement-Based Materials: Leaching Tests. In *Recycling of Biomass Ashes*; Springer: Berlin/Heidelberg, Germany, 2011; pp. 133–146. ISBN 978-3-642-19353-8.
67. Dr. Art Ragauskas Chemical Composition Biomass Fly Ash: DC Chemical Composition Biomass Fly Ash: MicroElements. Available online: http://biorefinery.utk.edu/technical_reviews/ (accessed on 26 June 2017).
68. Ole, H.; Margareta, W.; Andersson, M.T.; Jutta, L.-Y.; Ebba, W.; Rihm, T. *Treatment Methods for Waste to be Landfilled*; Nordic Council of Ministers: Copenhagen, Denmark, 2009.
69. Demirbaş, A. Heavy metal contents of fly ashes from selected biomass samples. *Energy Sources* **2005**, *27*, 1269–1276. [CrossRef]
70. *EN 197-1:2011 Cement—Part 1: Composition, Specifications and Conformity Criteria for Common Cements*; The European Committee for Standardization (CEN: Brussels, Belgium, 2011.
71. *EN 12457-4:2002: Characterization of waste—Leaching—Compliance test for Leaching of Granular Waste Materials and Sludges—Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 l/kg for Materials with Particle Size below 4 mm (without or with Size Reduction)*; The European Committee for Standardization (CEN): Brussels, Belgium, 2002.
72. *EN 196-1:2016: Methods of Testing Cement—Part 1: Determination of Strength*; The European Committee for Standardization (CEN): Brussels, Belgium, 2016.
73. *CEN/TS 16637-2: Horizontal Dynamic Surface Leaching Test (DLST) for Determination of Surface Dependent Release of Substances from Monolithic or Plate-Like or Sheet-Like Construction Products*; The European Committee for Standardization (CEN): Brussels, Belgium, 2014.
74. *CEN/TS 16637-1:2014: Construction Products—Assessment of Release of Dangerous Substances—Part 1: Guidance for the Determination of Leaching Tests and Additional Testing Steps*; The European Committee for Standardization (CEN): Brussels, Belgium, 2014.
75. Barbir, D. *Studija Utjecaja Štetnih Otpada na Procese Hidratacije i Fizikalo-Kemijska te Mehanička Svojstva Cemetnih Kompozita (in Croatian)*; Sveučilište u Splitu Kemijsko tehnološki fakultet: Split, Croatia, 2013.
76. *EN 196-3:2016: Methods of Testing Cement—Part 3: Determination of Setting Times and Soundness*; The European Committee for Standardization (CEN): Brussels, Belgium, 2016.
77. Technical Office for Agriculture, Working group Compost—Consulting and Development. Heavy Metals and Organic Compounds from Wastes Used as Organic Fertilisers—Annex 2 Compost Quality Definition—Legislation and Standards. Available online: https://ec.europa.eu/environment/waste/compost/pdf/hm_annex2.pdf (accessed on 3 December 2020).
78. Ministry of Environment and Nature of the Republic of Croatia. Regulation on the methods and conditions for waste disposal, categories and working conditions for landfill sites (OG 114/2015). *Off. Gazzete* **2015**, *114*, 1–10.
79. The Council of the European Union Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. *Off. J. Eur. Commun.* **2003**, *L 11/27*, 1–23.
80. Achternbosch, M.; Bräutigam, K.; Hartlieb, N.; Stemmermann, P. Impact of the use of waste on trace element concentrations in cement and concrete. *Waste Manag. Res.* **2005**, *23*, 328–337. [CrossRef]
81. Barbosa, R.; Lapa, N.; Dias, D.; Mendes, B. Concretes containing biomass ashes: Mechanical, chemical, and ecotoxic performances. *Constr. Build. Mater.* **2013**, *48*, 457–463. [CrossRef]
82. De Grauw, A.; Marion, A.; De Lane, M. Study of the leaching behaviour of paving concretes: Quantification of heavy metal content in leachates issued from tank test using demineralized water. *Cem. Conrete Res.* **2005**, *35*, 951–957. [CrossRef]

83. Shi, H.; Kan, L. Leaching behavior of heavy metals from municipal solid wastes incineration (MSWI) fly ash used in concrete. *J. Hazard. Mater.* **2009**, *164*, 750–754. [CrossRef]
84. Sollars, B.C.J.; Perry, R.; Fellow, F. Cement-based Stabilization of Wastes: Practical and Theoretical Considerations. *Water Environ. J.* **1989**, *3*, 125–134. [CrossRef]
85. Yu, Q.; Nagataki, S.; Lin, J.; Saeki, T.; Van der Sloot, H.A.; Van Zomeren, A.; Meeussen, J.C.L.; Hoede, D.; Rietra, R.P.J.J.; Stenger, R.; et al. *Environmental Criteria for Cement Based Products Phase I: Ordinary Portland Cement Phase II: Blended Cements and Methodology for Impact Assessment*; ECN Publication; ECN-E–11-020; Energy Research Centre of the Netherlands: Petten, The Netherlands, 2011.
86. Yu, Q.; Nagataki, S.; Lin, J.; Saeki, T.; Hisada, M. The leachability of heavy metals in hardened fly ash cement and cement-solidified fly ash. *Cem. Concr. Res.* **2005**, *35*, 1056–1063. [CrossRef]
87. Li, X.D.; Poon, C.S.; Sun, H.; Lo, I.M.C.; Kirk, D.W. Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. *J. Hazard. Mater.* **2001**, *82*, 215–230. [CrossRef]
88. Gwenzi, W.; Mupatsi, N.M. Evaluation of heavy metal leaching from coal ash-versus conventional concrete monoliths and debris. *Waste Manag.* **2016**, *49*, 114–123. [CrossRef]
89. Ministry of Infrastructure and Water Management Netherland: Soil Quality Regulation. Available online: https://rwsenvironment.eu/subjects/soil/legislation-and/soil-quality-decree/ (accessed on 3 December 2020).

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).