

Article

Grain-Size Specific Characterisation and Resource Potentials of Municipal Solid Waste Incineration (MSWI) Bottom Ash: A German Case Study

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Abstract: Municipal solid waste incineration (MSWI) is a major element of modern waste management and produces annually around 5.7 million tonnes of bottom ash (BA) in Germany. In order to save natural resources and protect the environment, utilisable materials need to be recovered from BA. It was the aim of the present study to determine metal and mineral resource potentials of MSWI BA based on a characterisation study of raw and aged BA of the MSWI plant in Kassel (Germany). The BA investigated consisted of 82.2% mineral materials, 16.3% metals, and 1.5% unburnt organic matter. Overall, 12.1% and 3.6% of the MSWI BA were theoretically recoverable as native ferrous (Fe) and non-ferrous (NFe) metals, respectively. Assuming state-of-the-art recovery technology, 10.7% and 2.0% of the BA were actually extractable as Fe and NFe metals. The processed BA, as a mixture, did not comply with current German limit values for use as a construction material mainly due to excessive soluble salt contents. Coarser grain size fractions were less contaminated, resulting in a utilisable potential of less than 30% of the BA as a construction material. Hence, grain-size specific processing routes need to be developed for MSWI BA to fully exploit its mineral resource potential.

Keywords: MSWI; bottom ash; characterisation; mineral fraction; metals; resource potential

1. Introduction

Municipal solid waste incineration (MSWI) is an important treatment method for non-recyclable waste in Europe. In 2016, about 50 million tonnes of municipal solid waste were incinerated in the European Union, which is about 40% of the total municipal solid waste treated [1]. After waste incineration, solid residues like bottom ash (BA) and fly ash remain. MSWI BA is the main solid residue and amounts to 20%–30% of the waste input and consists mainly of the mineral fraction (80–85%), ferrous metals (5–10%), non-ferrous metals (NFe) (2–5%), and unburned organic matter (OM) [2,3]. The vast majority of European MSWI plants operate wet BA discharge systems [4]. Wet discharged BA is characterised by the formation of new mineral phases and hardening processes. On the one hand, this leads to the solidification of the BA and thus immobilisation of heavy metals. On the other hand, potentially recoverable metals are bound in the mineral matrix [5]. MSWI BA is commonly processed in order to recover the metals contained. Due to its high water content, wet bottom ash must be stored (aged) prior to dry treatment. In Germany, the BA is currently stored for four weeks on average before processing, with a trend towards shorter aging periods [6]. Shorter aging facilitates the recovery of fine metals, which could otherwise be incorporated

into or conglomerated with minerals [7], but goes hand in hand with higher soluble contents of salts and less stable mineral phases [8,9]. After metal recovery, the residual mineral fraction is typically disposed of in landfills or utilised in technical constructions (mainly in road construction). Processed BA is used as a construction material in about half of the European countries [10]. The most common utilisation option for processed BA is as a subbase layer material in road construction. In Germany, 34% of the 5.7 million tonnes of MSWI BA produced in 2017 was utilised in such technical constructions (road subbase layers and embankment construction). More than half of the BA (59%) was disposed of in landfills or used as landfill construction material. The remaining 7% was used as underground backfill material [3].

Due to the general importance of MSWI as a waste treatment method, numerous studies on the compositions of BA exist (e.g., [11–13]), but only recently detailed grain size-specific characterisation studies have been performed on BA [14–17]. Such detailed characterisation studies are essential to determine the resource potential of BA and as a basis for the design of appropriate recovery processes. Due to the heterogeneity of MSWI BA [18], representative sampling is a critical issue for its characterisation [19]. As a consequence of the large effort required for sampling and analysis, there are only a few complete MSWI BA characterisation studies and no recent ones for German MSWI plants. So far, most studies on resource recovery from MSWI BA focused on metals, due to their economic value and the environmental benefits of metal recycling [20–25]. Nevertheless, the mineral fraction of MSWI BA is also a potential resource because its utilisation as a construction material can conserve landfill space and primary resources [26–28]. However, it has been shown that soluble salts and heavy metals may be problematic for material use in technical constructions [28], or that the metallic aluminium content may also be problematic for use as aggregates in concrete due to its deteriorating effect on the compressive strength of the concrete [29,30]. To understand the resource potentials and contaminant levels in different grain size fractions of MSWI BA, grain-size specific information on the material composition, elemental contents and leaching behaviour is needed, but rare [31,32]. Furthermore, given the trend towards shorter aging periods before BA processing in Germany [6], such investigations should also take into account different properties of raw and aged BA with respect to metal recovery and the quality of the mineral fraction as a construction material. Despite the increasing interest in MSWI BA utilisation as a construction material, there are currently no studies available that provide a characterisation of its resource potential, particularly for different grain size fractions in raw and aged BA.

Although the overall composition of MSWI BA is well investigated, there is a lack of knowledge about grain-size specific characteristics of raw and aged BA with respect to material properties and resource potentials. Therefore, it is the aim of the present study to characterise the raw and aged MSWI BA from the MSWI plant in Kassel (Germany) as a function of the particle size to determine its theoretical and utilisable resource potentials. In particular, this study focusses on the utilisation of the mineral fraction given current regulations in Germany. Because the waste input and incineration technology (grate incineration) of the Kassel MSWI plant is typical for German MSWI plants [33], the case study findings can also be used to provide information about the characteristics and resource potentials of MSWI BA in Germany on a more general level.

2. Resource Potential of MSWI Bottom Ash

MSWI BA is a mix of materials from which metals such as iron, aluminium, copper, brass and steel as well as construction materials can be recovered. Studies on the resource potential of MSWI BA in Europe are reviewed and major findings on resource recovery from MSWI BA are summarised.

2.1. Metal Recovery Potential

The most abundant metals in the BA that can be recovered are iron, stainless steel, aluminium and copper. Their concentration basically depends on the composition of the incinerated waste. Total contents of Fe of 6 to 12 wt.% in the MSWI BA were reported in the literature [15,16,20]. The iron concentration increased with decreasing grain size [17,25,31]. Some other studies reported that higher iron concentrations were found in bigger grain sizes [16,34]. Aluminium was uniformly distributed across different grain sizes [17,31]. According to the literature, the content of the metallic aluminium was 1.2–1.7 wt.% and the non-ferrous metal fraction consisted of approx. 70% metallic aluminium [20,35,36]. The recovery of fine Al particles (<2 mm) is only possible to a minor degree using conventional processing technologies [5,36]. Metallic Al can pose a problem for BA utilisation as a construction material because it reacts with water to aluminate $\text{Al}(\text{OH})_4^-$ and hydrogen gas H_2 [30]. The hydrogen produced during this reaction leads to an increase in volume and swelling of the BA, which can cause damages in technical constructions [37]. Iron and aluminium may be present in a metallic form as native metals or chemically bound, which is relevant for recoverability as well as reactivity.

Copper, zinc, nickel, and lead were found in the BA in high concentrations, mainly in grain sizes below 4 mm [17,25,31]. Copper and zinc can be recovered from the BA. Moreover, alloys like brass, which can be found in the BA, contain copper and zinc. The melting point of Cu and Zn is in or below the range of waste incineration temperatures, which means that they melt during the combustion process and may form new alloys. Because these metals are toxic, they are also of concern as potential pollutants. Total contents of selected metals in MSWI BA from recent European studies reported in the literature are shown in Table 1. Precious metals are not contained in Table 1, despite their economic value and existing recovery options [4,22] because they are rarely addressed in characterisation studies due to the very large sample masses required [23,38] and their recovery requires above state-of-the art processing intensities.

Table 1. Total elemental contents of municipal solid waste incineration (MSWI) bottom ash (BA) reported in the literature. For Al and Fe, only the metallic contents are shown.

Element	Content (mg/kg)	Reference
Al (metallic)	12,000–17,000	[20,22,36]
Fe (metallic)	60,000–12,000	[15,16,20]
Cd	2.6–14	[22,31,39]
Cr	180–1500	[22,31,39]
Hg	0.5	[31]
Pb	540–970	[22,31,39]
Ni	120–640	[22,31]
Cu	700–5200	[20,22]
Zn	1600–3400	[20,22]

2.2. Utilisation of Processed Bottom Ash

The utilisation of processed MSWI BA is regulated differently in the European countries and has recently been reviewed by Blasenbauer et al. [10]. The majority of European countries permit the utilisation of MSWI BA outside landfills, but only half of them use BA in practice. All countries which permit and regulate the utilisation of the BA have requirements on the leaching contents that are specifically defined for BA. Only Austria has additional requirements on the total elemental (inorganic) contents [10]. Some other countries specify requirements related to total contents of organic compounds (Wallonia in Belgium, France, Lithuania, Poland). Heavy metals are more relevant for the utilisation of the MSWI BA than organic pollutants, because the heavy metals can leach out and cause environmental problems [40]. In general, it should be noted that soluble substance contents are not necessarily comparable among

different sources because of a variety of leaching tests applied in terms of liquid-to-solid ratio or grain size [10].

In Germany, only leaching contents of the MSWI BA are relevant for its utilisation in technical constructions. There are several German regulations and recommendations for the utilisation of MSWI BA. The most commonly used recommendation is LAGA M 20 [41], which addresses the utilisation of BA as a material in constructions with engineered containment (e.g., as a base layer under an impermeable layer in road construction). LAGA M 20 [41] is not legally binding, but is often adopted by the competent authorities. According to the recommendation, the leachable content of As, Pb, Cd, Cr, Cu, Ni, Hg, Zn, Cl^- and SO_4^{2-} should be analysed in order to check whether the material is suitable for utilisation in technical constructions or not. Furthermore, there is a regulation for the utilisation of BA as an aggregate in road construction, called TL Gestein-StB 04 [42]. The limit values are identical to LAGA M 20 [41], except for chloride, sulphate and chromium. There has also been an ongoing discussion about a draft regulation on the use of secondary building materials for more than decade in Germany. In this draft, the utilisation criteria and limit values for the application of recovered materials, including processed MSWI BA in buildings and constructions, are defined [43]. However, it is unclear whether and when this unifying regulation will come into force. The limit values of this draft regulation, TL Gestein-StB 04 and LAGA M 20, are shown in Table S1 of the Supplementary Information (SI).

2.3. MSWI Bottom Ash Characterisation and Sampling

Most studies on the resource potential of MSWI BA have investigated the raw MSWI BA [14,15,32]. An exception is the study by Loginova et al. [17], who investigated and characterised aged MSWI BA from the MSWI plant in Duiven, Netherlands as a function of the particle size. Moreover, Pfrang-Stotz and Reichelt [44] evaluated the quality of different raw and aged MSWI BAs with regard to their utilisation options. They studied the mineralogy, environmental compatibility and construction properties of the ashes [44]. However, none of the studies in the literature reviewed addressed the utilisation potential of the mineral fraction simultaneously for different grain-size fractions and aging periods.

In order to characterise heterogeneous materials, appropriate sampling is the key to representative analysis results. The composition of MSWI BA depends, among other factors, on the waste incineration input, which varies temporally and locally. As mentioned, the concentrations of some analytes can be very low, which requires large sample masses in order to determine their contents. In many cases, the size and number of samples (increments) are limited in practice, which may impair the analyses' representativeness. Correct sampling means that each particle has the same probability of ending up in the sample, as defined by Gy's sampling theory [45]. There are two types of sampling error. Systematic sampling errors result from incorrect sampling and can be avoided by correct sampling. Random sampling errors, also called correct sampling errors (CSE), are unavoidable and occur due to the heterogeneity of the material, even if the sampling is carried out correctly. In the theory of sampling, two types of heterogeneity are distinguished. The constitutional heterogeneity (CH) is related to the individual composition of the material. The distribution heterogeneity (DH) concerns the particle distribution in the material. Random sampling errors due to CH can be controlled through sample mass. Errors as a consequence of DH can be controlled through the number of increments that are combined to a mixed sample [35,45]. Therefore, for a complete characterisation of the highly heterogeneous MSWI BA, a large amount of material needs to be sampled to obtain representative results.

Despite their importance for MSWI BA characterisation, few studies in the literature have provided a detailed description of the sampling strategies applied. Morf et al. [22] and Huber et al. [32] took samples according to the Theory of Sampling, taking into account the material heterogeneity by calculating the required sample mass in order not to exceed a defined maximum sampling error. Morf et al. [22]

took the samples from a falling stream, which is the best sampling strategy for covering the material heterogeneity [45]. Most other studies were very brief on the sampling procedures [14–17] and the motivation for the sampling performed or the sampling plan were not elaborated on. This is a shortcoming in the literature because the representativeness of study results cannot be assessed and the comparability among different studies is impaired.

3. Materials and Methods

3.1. MSWI Plant

For the present research, BA was collected from the MSWI plant located in Kassel (Germany). Annually, around 175,000 Mg of waste are incinerated, consisting mainly of residual household waste and a minor share of commercial, business and industrial waste. The incineration plant has two combustion lines with a forward-moving grate. The combustion temperature in the oven is approx. 1000 °C, with an average residence time of waste of 2.5 h [33]. The plant has a wet discharge system for the BA. At the MSWI plant, approximately 44,000 Mg of fresh BA are produced per year, which is around 25% of the waste input and thus similar to other German MSWI plants [33]. The BA produced is subsequently transported to an external treatment plant and, after metal recovery, it is currently either used as material for road construction or deposited at a landfill.

3.2. Sampling

Sampling theory was applied [45] to obtain a representative sample of the Kassel MSWI BA. The sampling aim was to determine the content of non-ferrous metals, with a maximum relative standard error of 10%. Non-ferrous metals were chosen as analyte because they are essential for the resource potential of MSWI BA and are typically present at relatively low concentrations of 1–3% [16,20]. The required sampling mass was calculated to be around 1900 kg. Formulas and calculations are described in Section S.2 and Table S2 of the SI.

The sampling campaign was carried out at nine days over a period of four weeks in May and June 2019. The increments were taken at different random times of the day between 8 a.m. and 5 p.m. from the conveyor in order to obtain a sample that is representative for the whole sampled bulk material and to avoid biased samples due to periodic waste delivery times or periodic changes in the operating conditions of the plant. Both combustion lines of the plant were sampled in order to cover the full spectrum of the BA heterogeneity. Since the conveyor system receives BA from both ash dischargers, one discharger was switched off in order to take a defined quantity of material from the other discharger (Figure 1). This was applied several times per day in order to obtain independent increments. The sample mass was defined as the BA quantity on the conveyor after 10 min when the discharger was switched on. Then the whole amount of BA lying on the conveyor was taken. Forty single increments with an average mass of 43 kg were taken during the sampling campaign. The variation in the increment mass (10 min discharges of BA) is shown in Figure S1 of the SI. The total mass of the sample was finally 1.7 Mg. After separation of the coarse fraction (>31.5 mm) by sieving, around one third of the sieve throughput was immediately processed, another third (roughly) was stored indoors for later analyses of the aged BA, and the remaining material was discarded (scheme and mass flows are shown in Figure 2).

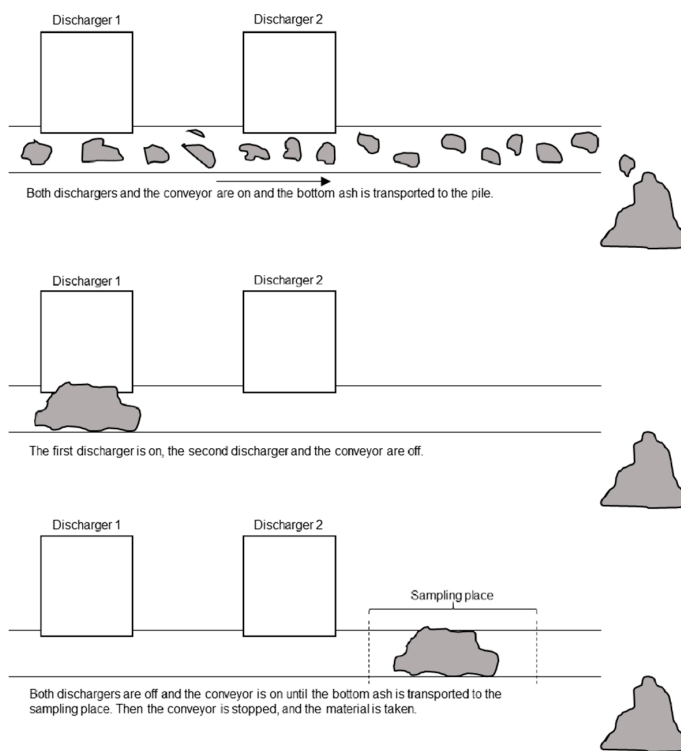


Figure 1. Scheme of sampling procedure for one increment.

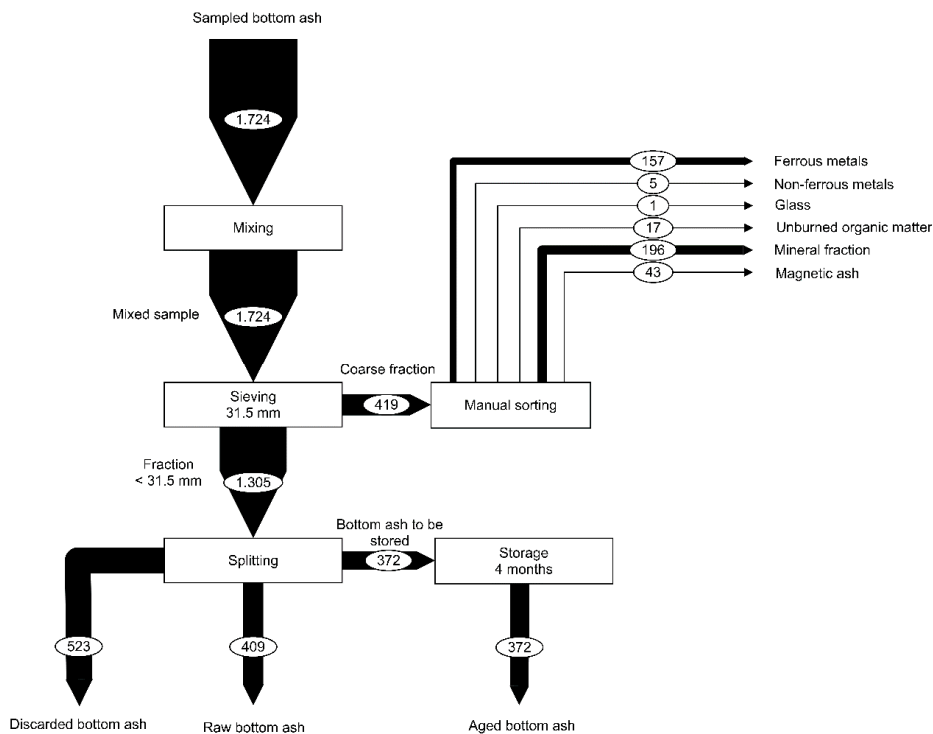
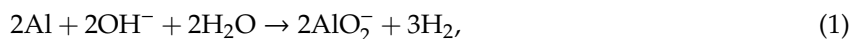


Figure 2. Scheme of the sample preparation with mass flows in kg shown as Sankey diagram (arrow width proportional to flow value).

3.3. Sample Preparation and Analysis

The fresh and aged BA were processed and analysed in the same way. The preparation process consisted of the following steps: drying, sieving, sorting (Figure 3). The mass flows for sample preparation and analysis are shown in Figures S2 and S3 of the SI for the raw and aged BA, respectively. All the sampled BA was initially sieved on a screen with a mesh size of 31.5 mm in order to remove coarse particles. The coarse fraction above 31.5 mm was manually sorted into ferrous metals, non-ferrous metals, glass, unburned organic matter, minerals and magnetic ash. The fraction smaller than 31.5 mm was either directly processed, stored for 4 months in barrels for subsequent processing, or discarded (Figure 2). After the drying process at 50 °C for at least 48 h, the particle size distribution was determined by sieving on screens with mesh sizes of 25, 20, 16, 8, 4, 2, 1, and 0.063 mm. Thereafter, the fractions over 2 mm were manually sorted into the following material fractions: ferrous metals, non-ferrous metals, mineral fraction (consisting of slag, ash, ceramics, demolition waste), glass, unburned organic matter, and magnetic ash (agglomerates of ferrous metals and minerals). The magnetic ash was regarded as a separate fraction because the ferrous metals contained are unavailable for manual sorting without crushing. The magnetic ash and mineral fractions were ground in a ball mill to liberate encapsulated metals and to prepare the samples for elemental analysis and leaching analysis. Visual identification of the non-ferrous metals in the fraction below 4 mm was not feasible. Therefore, in these grain size fractions, the metallic aluminium content was determined with the soda attack method, based on the reaction of metallic aluminium with NaOH (Equation (1)), as reported in previous studies [15,36,46]. The volume of the H₂ gas released from the reaction was measured and the aluminium content was calculated. Ten grams of the material below 4 mm was analysed (triple determination) using a sodium hydroxide solution with a concentration of 30 wt.%. The equations to determine the metallic Al content are shown in Section S.3 of the SI.



3.4. Chemical Analyses

X-ray fluorescence spectroscopy (XRF) was carried out with a handheld XRF device (Analyticon NITON XL3t) in order to determine total elemental contents. Non-ferrous metal particles were visually identified, and their elemental composition was determined by XRF analysis. Furthermore, the elemental composition of the mineral, magnetic fraction and the glass was also determined by XRF. Glass was not analysed for each grain size because the glass composition do not differ significantly among the grain sizes as Huber et al. (2019) have observed [31]. All samples were analysed using the analysis mode “Mining” for the mineral samples and “General Metals” for the metallic samples. Further investigations on the chemical composition were performed by mass spectroscopy with inductively coupled plasma (ICP-MS) on aqua regia dissolved samples in order to verify and complement the results of the XRF analysis. The determination of the total contents was carried out on three analysis samples (triplicates).

The eluates were prepared from the sieved and sorted materials, including the residual mineral fraction, the magnetic ash and the glass with a liquid-to-solid ratio of 10 L/kg [47]. This leaching test is required by several German recommendations and regulations such as LAGA M 20 and TL Gestein-StB 04 [41,42]. The eluates were filtrated through a 0.45 µm cellulose nitrate filter. The pH value was determined with a handheld device (Aqualytic AL 15). After the leaching test, the resulting solutions were analysed by ICP-MS for contents of Cr, Cu, As, Pb, Cd, Ni, Zn, Hg, and by ion chromatography (IC) for chloride and sulphate contents. The determination of the leaching contents was carried out in duplicates.

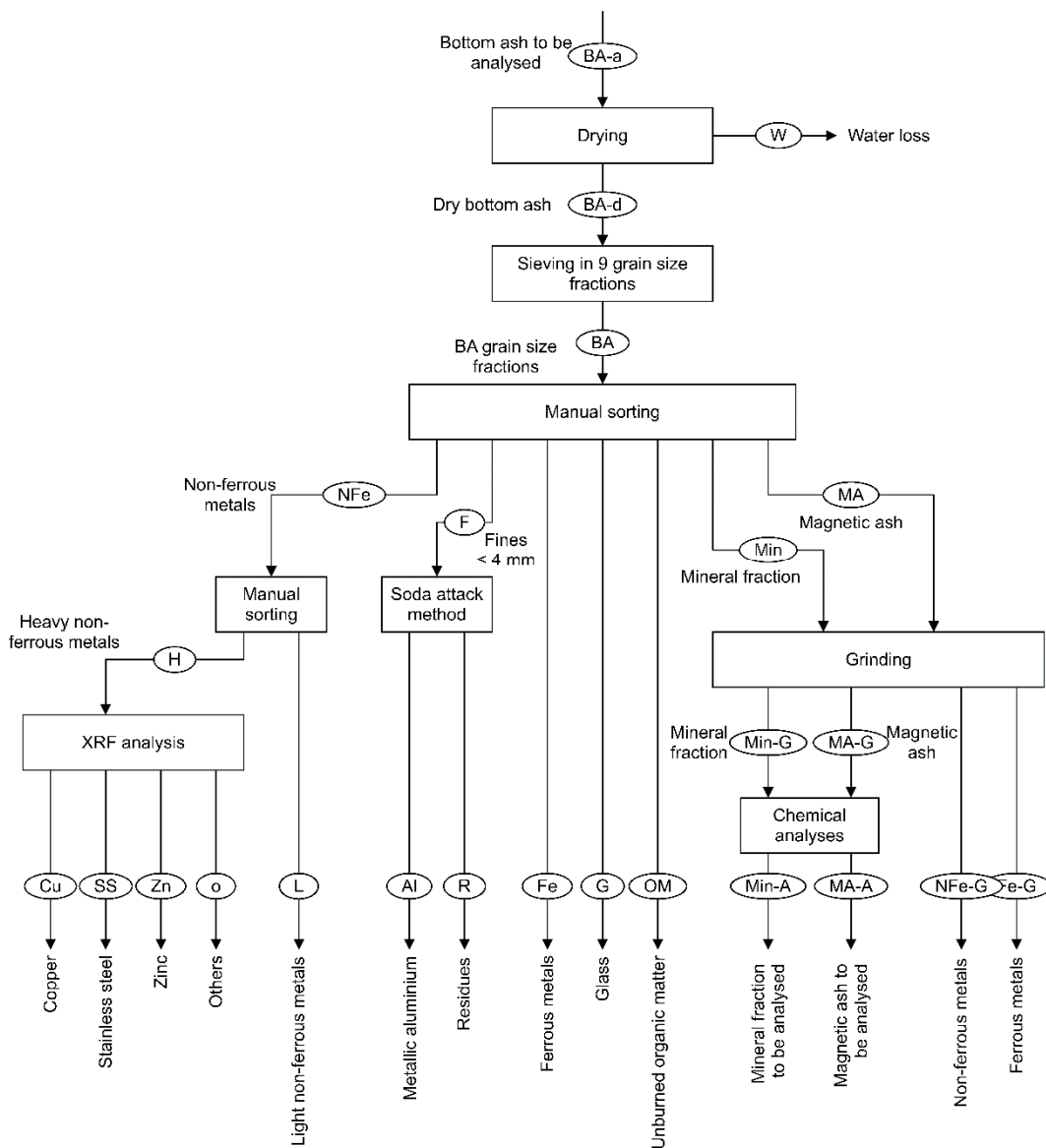


Figure 3. Scheme for further sample preparation and analysis. The same methodology for the raw and aged MSWI bottom ash was applied.

3.5. Determination of Resource Potentials

In the present study, the theoretical and the utilisable resource potential of MSWI BA are distinguished. The theoretical resource potential is defined by the total content of (native) metals > 2 mm and minerals. The utilisable resource potential is defined in view of technical and environmental conditions, which limit the actually recoverable material quantity. The utilisable resource potential therefore depends on applied processing technologies as well as regulatory frameworks. In the present study, the recoverable material fractions were determined based on the defined state-of-the-art BA treatment in Europe and in view of the legal framework in Germany. The latter is relevant for the utilisation of the mineral fraction only since there are no regulations on the quality of recovered metals from BA.

The utilisable resource potential of metals is determined by the recovery rates assumed for the state-of-the-art dry treatment plant according to Allegrini et al. [20] and the Best Available Techniques Reference Document for Waste Incineration [48]. It is assumed that only metals > 2 mm were recovered, as this is common in most German BA treatment plants [6]. The average recovery rates for particles above 2 mm were 85% for ferrous metals and 61% for non-ferrous metals. The grain size-specific recovery rates used for the analysis are shown in Table S3 of the SI. Precious metals are not considered in the utilisable resource potential due to their very low concentrations in the MSWI BA and their low importance regarding the quality of the mineral fraction. However, it should be noted that they may be economically very relevant for full valorisation [4,22].

The utilisable resource potential of the mineral fraction is defined for two different utilisation routes of the BA processed: on the one hand, as construction material in contained structures (such as road subbase layers) subject to the regulation of LAGA M 20 [41], and on the other, as aggregates in concrete subject to the regulation of TL Gestein-StB 04 [42]. For both options, the composition of the processed bottom ash is determined based on the metal recovery rates assumed for state-of-the-art BA treatment (see above). The processed BA thus contains the mineral fractions, the magnetic ash fraction as well as residual metal contents. The technical and mineralogical properties of the mineral fraction are not further considered for its utilisation, as previous studies [17,30,44] have shown that this should be feasible. The soluble contents in the residual mineral fraction after metal recovery were determined for each grain size fraction using the results from the leaching analysis. It was assumed that the residual metal contents have a negligible influence on the solubility of heavy metals because the leaching of heavy metals does not depend on the bulk content but is controlled by mineral solubility [49]. Moreover, the soluble amount of heavy metals is typically below 1% [19]. For the utilisable resource potential as a construction material in contained structures, the determined leaching concentrations of each grain size fraction were compared with limit values from LAGA M 20 [41]. Then the utilisable resource potential for this route was determined by considering the grain size fractions that comply with these limit values without further treatment. To determine the utilisable resource potential as aggregate in concrete, a mineral mixture was synthetically designed to produce a Fuller curve. The Fuller curve provides an ideal gradation for aggregates, resulting in optimum density and strength of the concrete mixture [50]. The approach for designing the Fuller curve is described in Section S.4 of the SI and the particle size distribution of the Fuller-curve-mixture is shown in Table S4 of the SI. Here, the coarse grain size fraction > 31.5 mm cannot be used. The residual metal and glass contents in the designed mixture were determined. Finally, the utilisable resource potential for the aggregate route is made up by the grain size fractions complying with limit values from TL Gestein-StB 04 [42] and with a maximum residual metallic aluminium concentration of 1% [51]. Both potentials were determined on a grain size-specific basis. Single different grain size fractions are not used as separate materials in practice, but as multistage sieving is applied in most treatment processes, the utilisation of a mixture of different grain sizes is applicable. Although theoretically feasible, the potential of the fine fraction as a raw meal substitute in cement production was not considered due to the lack of implementation [37].

3.6. Statistical Measures

In this study, spread and deviations were considered in order to assess the sampling, processing, and analysis. The relative difference was used to compare the compositions of the raw and aged BA by calculating the relative deviation between two values of the same characteristic, e.g., the content of ferrous metals in the raw and aged BA. As the raw and aged BA are the result of sample division, sample processing could be assessed in this way. The standard deviation (SD) and the relative standard deviation (RSD) were used to compare the nine daily samples in order to evaluate the temporal variation of the BA

composition. The SD and RSD measure the sample variability due to the heterogeneity of the material [52]. As far as the total elemental contents and the leaching contents are concerned, the standard deviation shows the deviations between the analysis samples and thus provides some indication about proper (i.e., non-selective) sample preparation. The standard error was used to compare the material composition between the nine daily samples and shows how well the determined content (e.g., metals, glass, etc.) corresponds to the actual content in the bulk material. Moreover, it is an indicator of the unavoidable sampling error. The relative standard error was used to plan and evaluate the sampling performed [45], as described in Section S.2 of the SI.

4. Results

4.1. MSWI Bottom Ash Characterisation

4.1.1. Particle Size Distribution

The particle size distribution of the raw and aged MSWI BA is shown in Figure 4. Both ashes are similar in their particle size distribution. The aged BA has a lower share over 8 mm and a higher share between 1 and 8 mm, compared to the raw BA. The share of very fine particles (below 1 mm) is lower in the aged BA. The results for both ashes show that approx. 20% of the BA is smaller than 2 mm and 25% is bigger than 31.5 mm. The daily variation in the mass of the grain size fractions, expressed as the standard deviation (Figure 4), is in the range of 0.1–1.5%, and thus relatively low. This indicates that the particle size distribution is not affected by the daily fluctuation of the waste input.

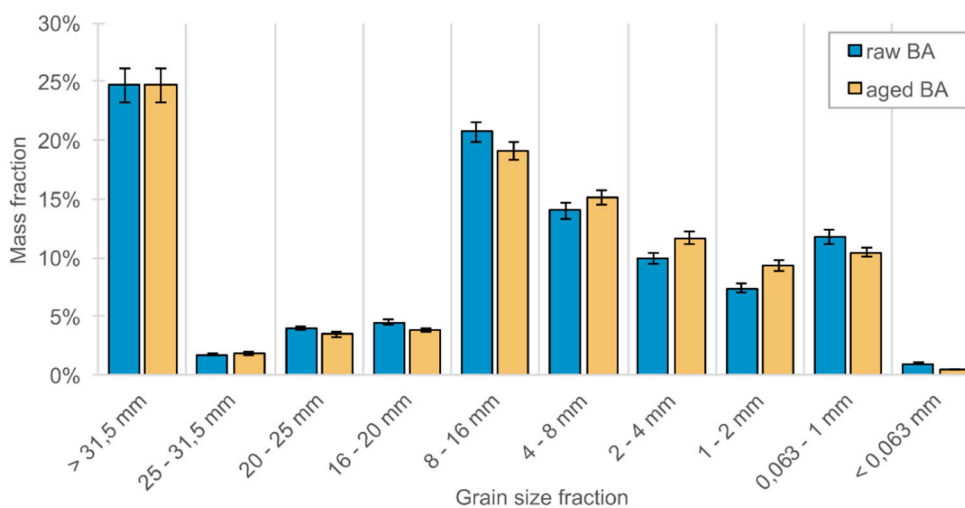


Figure 4. Grain size distribution of the raw and aged MSWI bottom ash. The error bars show the standard deviation over the nine daily samples.

4.1.2. Material Composition

The material composition of the MSWI BA investigated was determined by the manual sorting of six material groups above 2 mm grain size and resulted in 42.2% and 40.6% minerals (>2 mm), 13.8% and 16.5% magnetic ash (>2 mm), 14.3% and 14.1% ferrous metals (>2 mm), 2.0% and 2.2% non-ferrous metals (>2 mm), 6.1% and 5.0% glass (>2 mm), 1.4% and 1.6% unburned organic matter (>2 mm), and 20.2% and 20.2% fine materials (<2 mm) for the raw and aged samples, respectively (see Figure S4 of the SI). Hence, the material composition of the raw and aged BA is similar, with the largest relative difference of 19.2% for

magnetic ash (Table S5 of the SI). A detailed account of the material composition of the raw BA above 2 mm is provided by Figure 5 and its equivalent for aged BA (Figure S5 of the SI). All the mean values and statistical measures on the material composition of the raw and aged BA can be found in Table S5 of the SI.

Figure 5 illustrates that minerals make up the largest share of each grain size fraction. Ferrous metals have a share similar to minerals in the fraction above 31.5 mm, but there is a clear tendency towards decreasing ferrous metal contents with decreasing grain size. With respect to the distribution of non-ferrous metals, across grain size classes, no clear trend can be observed. The highest contents of non-ferrous metals were found in the grain sizes between 4 and 16 mm. The very low NFe metal content in the grain size fraction from 2–4 mm is partly caused by the lower identification rate during manual sorting of these small particles. Hence, native NFe metal contents are supposedly higher in this fraction and total contents were determined in further analyses (metallic Al by the soda attack method, total contents by elemental analysis), which are shown in Section 4.1.3. The main metal in the NFe metal fractions below 31.5 mm is aluminium, with concentrations between 23.7% and 58.6% and an average content of 35.2%. The concentration of copper in NFe metals above 2 mm is between 9.4% and 28.3%, and thus substantially lower than that of iron or aluminium. Selected metal contents (Al, Cu, Zn, stainless steel) of the non-ferrous metals in the raw and aged BA are shown in Figures S6 and S7 of the SI. Figure 5 also shows that most of the glass was found in grain sizes from 2 to 16 mm. The unburned organic matter was mainly found in the grain size fraction above 31.5 mm. In the size fractions below 31.5 mm, there is a tendency towards increasing contents of unburned organic matter with decreasing grain size.

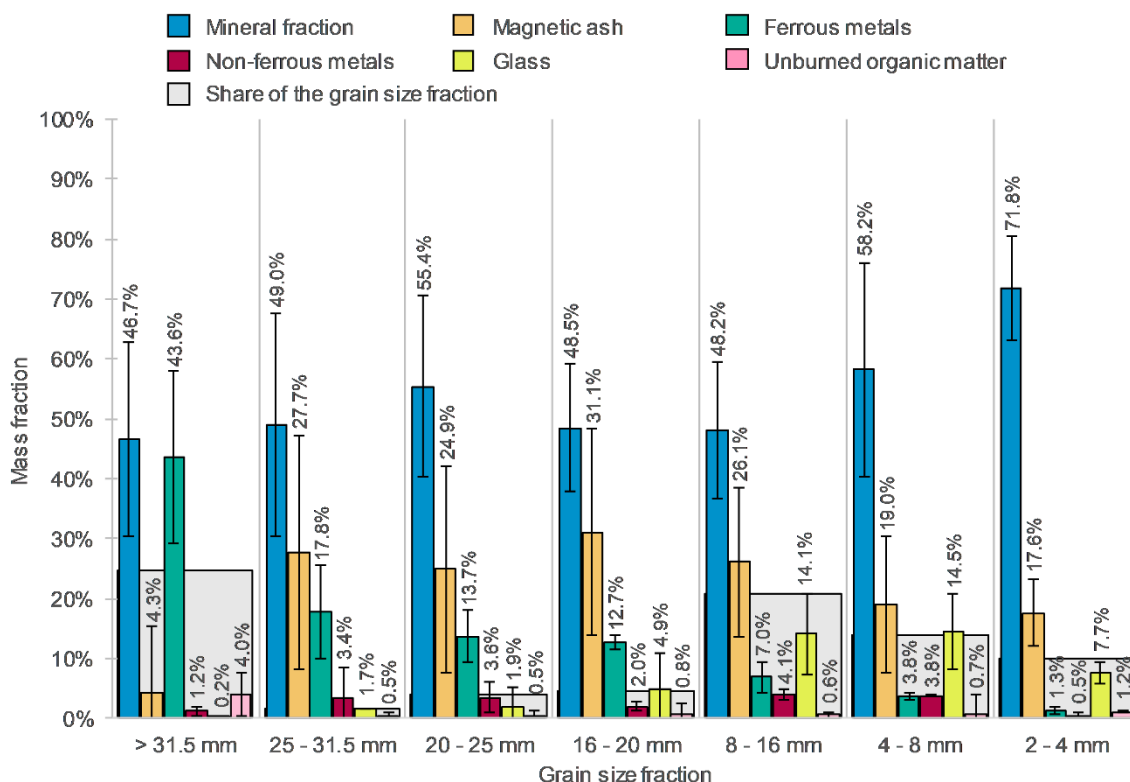


Figure 5. Composition of the raw MSWI bottom ash as a function of the particle size; error bars show the standard deviation over the nine daily samples.

The standard deviation illustrated in Figure 5 presents the daily deviation of the material composition. It is higher for material fractions with higher concentrations such as the mineral fraction and the magnetic ash. With regard to the relative standard deviation (Table S5 of the SI), it can be stated that the daily variation is most significant for the unburned OM, magnetic ash, glass and ferrous metals. The relative standard error for NFe content over the nine daily samples is 4.7% and 5.0% for the raw and aged BA, respectively (Table S5 of the SI). Thus, the sampling goal of a maximum relative standard error of 10% could be achieved by the present characterisation study. The RSE is below 10% for all material fractions, except for the unburned organic matter (23.5% and 19.1% in the raw and aged BA, respectively, in this case). Thus, the fundamental sampling error is acceptable for all relevant materials.

4.1.3. Total Contents

The total elemental contents of the MSWI BA investigated were determined for 33 elements (see Tables S6–S16 of the SI). The contents of Al, Fe, Cu, Zn, Cr, Ni, Pb and Cd as metals of economic or environmental interest are exemplarily shown for different grain size fractions and the BA in total in Figure 6. Because native metal contents are essential for recovery, they are distinguished from chemically bound metal contents. From Figure 6, it can be seen that the contents of metallic aluminium and copper increase with decreasing grain size. The same tendency can be observed for zinc below 31.5 mm. Contrarily, the contents of metallic iron, chromium and nickel decrease with decreasing grain size and show a strong correlation because of chromium and nickel being constituents of stainless steel. Iron and zinc in the coarse grain size fraction above 31.5 mm are mainly present in metallic form (see Figure 6). Their contents correlate with each other because zinc is used to protect steel against corrosion. Metallic aluminium makes up 40% and 29% of all Al in the raw and aged BA (Tables S15–S17 of the SI), respectively, which is in line with the literature values (e.g., Xia et al. [21] reported that Al_2O_3 is 60–70% of the total Al amount). Copper is mainly found as native metal (Figure 6), and its contents differ significantly between the raw and aged BA in the grain sizes below 16 mm. For Cd and Pb, no clear correlation between raw and aged BA, metallic and mineral content, and grain size could be observed. The total content of Pb in the raw and aged BA is almost identical, while Cd has a slightly higher concentration in the aged BA. Both elements are enriched in the finer grain size fractions below 4 mm.

The SD for the triplicate analysis (Figure 6) is higher for elements with low concentrations such as Cd and Pb because of the lower homogeneity of the analysis samples. In view of the high SD observed for the metallic and chemically bound shares of Cd and Pb, these results should be seen as tentative. In the case of Al, Cu, Zn, Pb, and Cd as chemically bound elements, larger SDs can be observed, indicating that these elements are irregularly distributed in the mineral phases. The ranges clearly overlap with differences between the raw and aged BA, hence, statements about higher or lower contents of these elements in raw and aged BA are less certain.

4.1.4. Leaching Concentrations

The leaching concentration is an important parameter for BA utilisation as construction material. Therefore, the leaching concentrations of chloride, sulphate, Cu, Zn, Cr, Ni, Pb and Cd as well as the pH value were analysed for different grain size fractions of the mineral and magnetic ash fractions in the raw and aged BA (see Figure 6). The results show that chloride and sulphate contents in the eluate of the aged BA are slightly lower than for the raw BA. Chloride concentrations in the eluate increase with decreasing grain size. A slight increase in the solubility of the sulphates during the aging process can be seen in the grain size fractions above 31.5 mm, between 8 and 16 mm, and below 0.063 mm. From Figure 7, it can be seen that the concentrations of copper, chromium and nickel increased after aging, while zinc, lead and cadmium concentrations were lower in the eluate of the aged BA. The contents of the elements investigated

in the eluate increase with decreasing grain size, with the finest fraction below 0.063 mm being the most contaminated. A full account of the elemental concentrations analysed in the leaching tests for the mineral and magnetic ash fractions can be found in Tables S18–S22 of the SI.

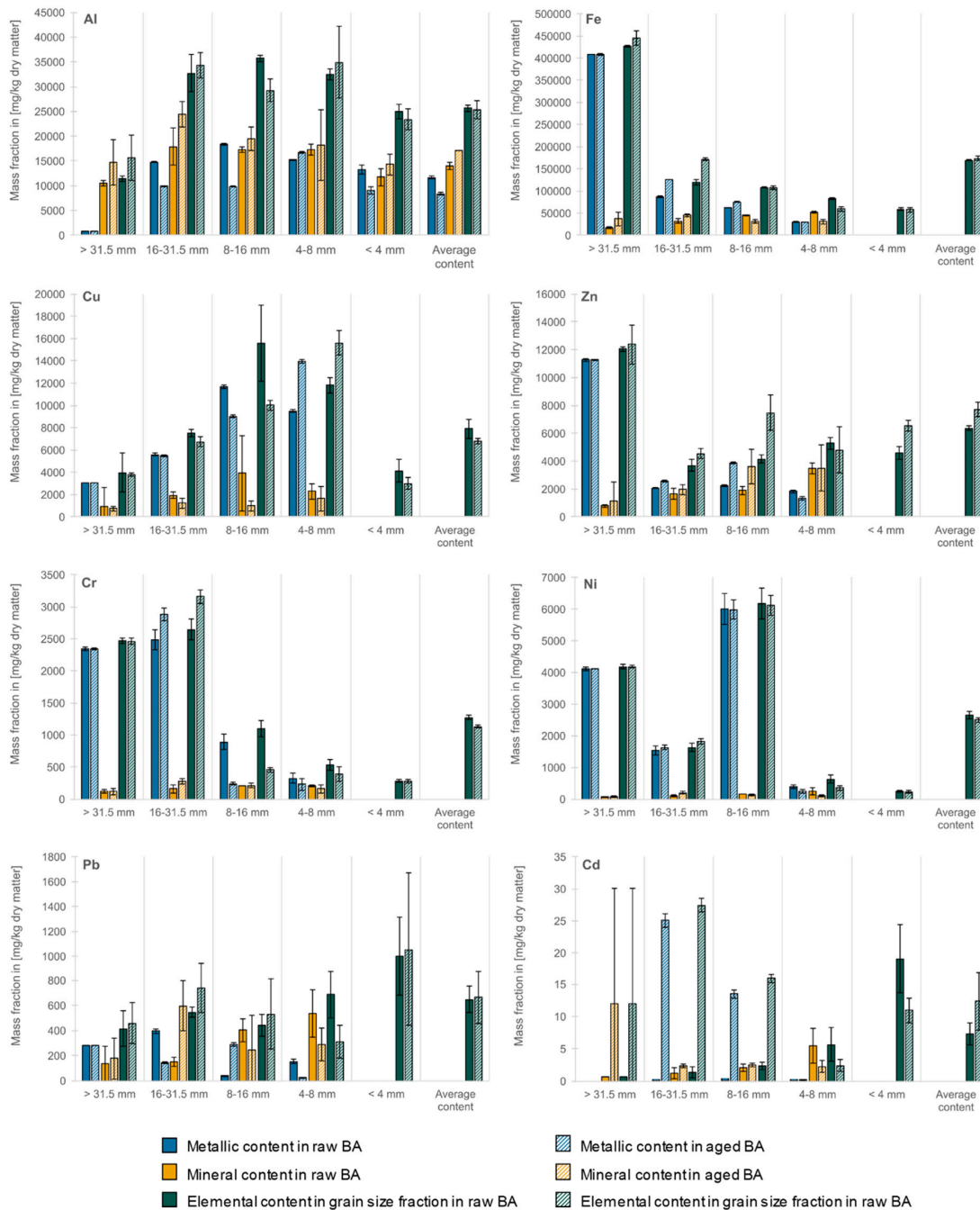


Figure 6. Total contents of Al, Fe, Cu, Zn, Cr and Ni in different grain size fractions and for the BA as a whole. Metallic and mineral contents are distinguished. The error bars show the standard deviation over three chemical analyses.

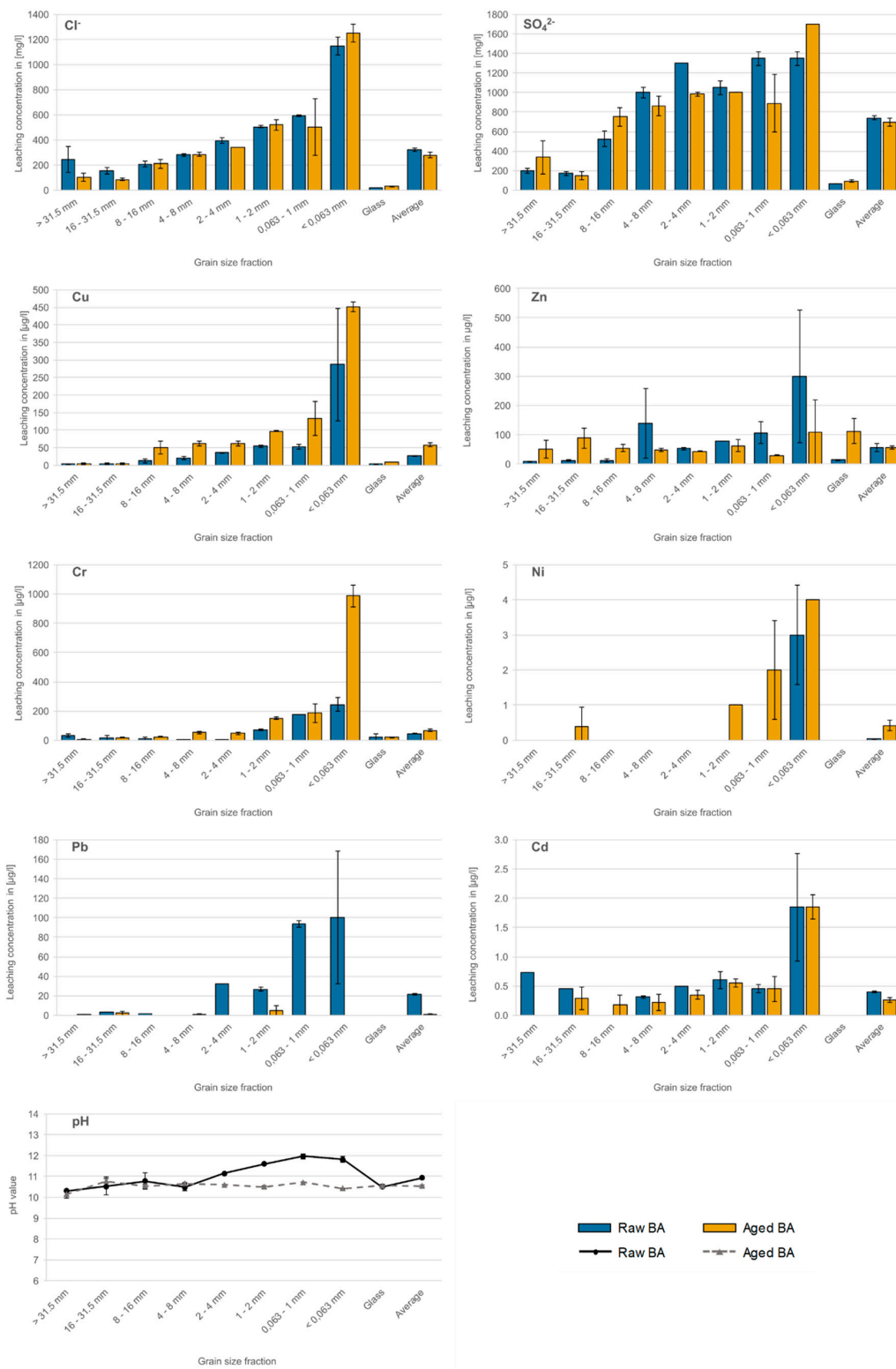


Figure 7. Leaching concentrations of the mineral fractions and glass of the raw and aged bottom ash as a function of the particle size. Error bars show the standard deviation of four analysis samples (two for the mineral and magnetic fraction each).

The standard deviations over the analysis samples are larger for finer grain sizes (Figure 7). However, despite the partly large SDs of Cu, Zn and Ni concentrations, the differences between raw and aged BA are substantial and overlap with the ranges of \pm one SD only for individual grain size fractions.

In comparison to existing limit values of LAGA M 20 [41] (see Table S1 of the SI), it can be stated that the concentrations of salts are generally above the limit values of 250 mg/L for chloride and 600 mg/L for sulphate for all grain size fractions below 8 mm and with regard to the average concentration over all grain sizes as well. With respect to heavy metal concentrations in the eluate, the LAGA M 20 limit values are exceeded by grain size fractions below 0.063 mm in the case of chromium (limit value: 200 μ g/L) for raw and aged BA and copper (limit value: 300 μ g/L) for aged BA. For raw BA, lead concentrations are above the limit value of 50 μ g/L for grain size fractions below 1 mm. It should be noted that for Pb and Cr in the finest fraction of the raw BA, the standard deviation ranges overlap with the limit values mentioned. Furthermore, the mean value of zinc below 0.063 mm is only very slightly below the limit value of 300 μ g/L in the case of raw BA, and standard deviation ranges exceed the limit value (see Figure 6). Given the observed spread, limit values for copper may also be critical for the eluate of very fine fraction (<0.063 mm) of the raw BA.

4.2. Resource Potentials

4.2.1. Metal Recovery

The theoretical resource potential is equivalent to the contents of pure metals above 2 mm grain size that are not chemically bound. Metals that are conglomerated with mineral phases are also potentially recoverable after crushing to release them. For ferrous metals, the theoretical resource potential amounts to around 12% of the mass of the BA investigated (12.2% for raw and 12.0% for aged BA), with more than 75% of it present in the coarse fraction above 31.5 mm (see Figure 8). For non-ferrous metals, the theoretical resource potential is 3.8% for the raw and 3.5% for the aged BA, with the largest contributions made by the fractions between 4 and 16 mm (see Figure 8). With regard to the individual non-ferrous metals > 4 mm, 0.7% aluminium, 0.3% copper, 0.1% brass and 0.8% stainless steel are potentially recoverable from the raw MSWI BA investigated (Figure S6 of the SI). In the aged BA above 4 mm, the theoretical resource potential of the NFe metals is 0.4%, 0.2%, 0.2% and 0.9% for aluminium, copper, brass, and stainless steel, respectively (Figure S7 of the SI).

In practice, not all metals contained in the BA can be recovered due to sorting efficiencies below 100%. The recoverable fractions depend on the technologies applied for metal recovery. Here, the utilisable resource potential was determined assuming conventional state-of-the-art technology for metal recovery, with no recovery below 2 mm grain size (Table S3 of the SI). The resultant utilisable resource potentials are shown in Figure 8 and amount to 10.8% and 10.7% for ferrous metals and 2.1% and 1.9% for non-ferrous metals in the case of raw and aged BA, respectively.

4.2.2. Minerals Utilisation

The theoretical resource potential of the MSWI BA is 86.2% and 86.6% for the raw and aged BA, respectively (Figure 9). These values are equivalent to the contents of the mineral fraction, magnetic ash, glass and a residual content of metals after metal recovery in a state-of-the-art treatment plant. The utilisable resource potential as construction material in contained structures is 27.9% and 22.9% for the raw and aged BA, respectively. The relatively low potential results from the high salt concentrations in the eluate of most grain size fractions below 31.5 mm. Only the grain size fractions from 8 to 16 mm for the raw BA and 16 to 31.5 mm for the aged BA comply with the limit values of LAGA M 20 [41] (see Figure S8 of the SI). The aging did not improve the quality of the BA with regard to soluble salts.

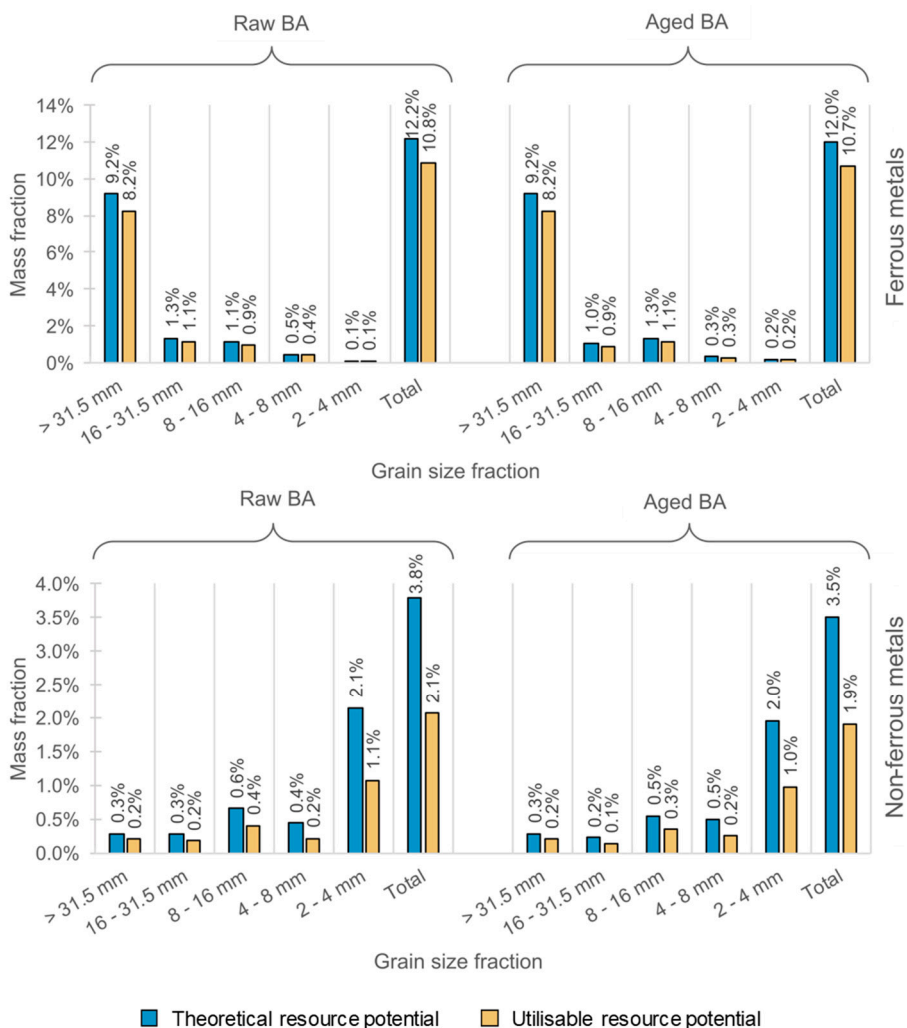


Figure 8. Contribution of the single grain size fractions to the resource potentials and total resource potentials of ferrous (**top**) and non-ferrous metals (**bottom**) in the raw and aged MSWI bottom ash.

With respect to the utilisation as aggregate in concrete, the suitability of grain size fractions to be used in a Fuller curve was evaluated and resulted in utilisable potentials of 0.0% and 8.1% in the raw and aged BA, respectively (Figure 9). The particle size distribution of the Fuller-curve mixture is shown in Figure S9 of the SI. Critical leaching concentrations are those of soluble salts and chromium, which do not comply with the limit values from TL Gestein-Stb 04 [42] for most fractions (Figure S10 of the SI). Based on these limit values, only the coarse grain size fractions (above 16 mm) are utilisable. However, the metallic aluminium content is above 1% in all grain size fractions of the raw BA (Figure S11 of the SI), impairing the utilisation of all grain size fractions of the raw BA as aggregate in concrete. In the aged BA, only the grain size fraction 16–31.5 mm satisfies the technical and environmental requirements for utilisation. The glass content determined is 7.2% and 5.3% in the raw and aged BA, respectively (Figure S12 of the SI).

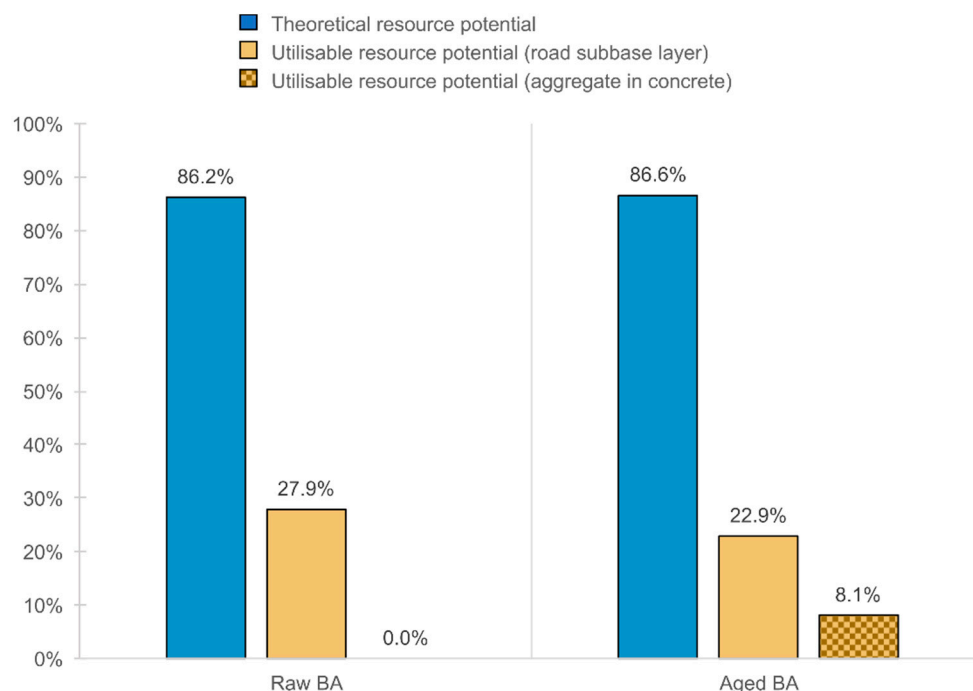


Figure 9. Resource potentials of the mineral fraction of the raw and aged BA.

Although the contents of sulphates and chlorides in eluate were slightly reduced after aging (Figure 7 and Figures S8 and S10 of the SI), they are still above the limit values and are an obstacle for BA utilisation. The leaching concentrations of copper, zinc, lead, nickel, and cadmium are below the limit values for utilisation as a construction material in contained structures and as aggregate in concrete. With respect to utilisation as aggregate in concrete, chromium can pose a problem for the utilisation of the BA because its concentrations in the fine fraction, and thus in the whole Fuller-curve mixture, are higher than the limit values, even after aging. Concerning the results for both utilisation routes, neither the raw nor the aged BA can be utilised as a complete aggregate mixture without further treatment or without mixing the fractions from MSWI BA with other materials such as recycled aggregates from other waste or natural aggregates. Both options exist in practice and enable higher utilisation rates for processed BA, but were not considered during the assessment of the resource potentials.

5. Discussion

5.1. Sampling and Processing

The partly significant differences, expressed as the standard deviation, in the nine daily samples regarding the material composition (Figure 5 and Table S5 of the SI) indicate that MSWI BA composition is subject to substantial daily variations. If a representative composition of the BA for a longer period, e.g., one year, is required, further effects such as seasonal variations need to be considered. Due to the moderate deviations between the material contents of the raw and aged BA, expressed as the relative difference, it can be stated that the sample division was carried out properly in this study. Furthermore, the relative standard errors below 10% for all material fractions, except for the unburnt OM, indicate a good representativeness of the material composition over the sampling period and thus generally acceptable sampling errors (Table S5 of the SI). The substantial variation in the content of unburned organic matter over the nine daily

samples (Table S5 of the SI) shows that the content of unburnt organic matter is sensitive to changes in the input and operating conditions of the MSWI plant.

It was expected that the raw and aged MSWI BA would show negligible differences in their total elemental composition. This cannot be observed for all elements analysed. Elements with concentrations below 0.1%, such as Pb and Cd, show larger differences between the raw and aged BA. This may be explained by the larger sample mass required for elements with lower concentrations due to their more heterogeneous distribution in the bulk material. Differences between the total contents of these elements in the raw and aged BA are therefore compromised by the chosen sample size and the strong heterogeneity of the BA.

5.2. Characterisation

The fraction of fine particles (<2 mm) of the MSWI BA investigated is lower than previous studies reported [5,15,16,20]. Because the comparison with other German BA characterisation studies [34,53] shows similar particle size distributions, the lower share of fine particles may be explained by differences in national waste management systems.

The trend of decreasing ferrous metal contents with decreasing grain size observed in the present study has also been reported in previous studies [32]. The total content of ferrous metals is higher than in other studies [16,20,54], which was not expected because of extensive source separation of waste in Germany. One possible explanation for the relatively high iron contents compared to other studies could also be the fact that the very coarse fraction, which is rich in iron, was not included in many characterisation studies [32], leading to an underestimation of the iron content in those cases.

The total content of copper shows significant differences in the raw and aged BA. Copper and its alloys have melting temperatures in the temperature range of waste incineration plants. Due to the circulation of the waste in the furnace, partially molten Cu particles come into contact with solid particles, resulting in a dissipative distribution of the copper [55]. This process affects the distribution heterogeneity of copper in the BA, resulting in larger uncertainties as to the Cu content analysis. This could be observed for copper in the raw and aged BA (Figure 6).

The decrease in soluble salts after aging can be explained by the chemical reactions taking place during the aging process. The main process during aging, the carbonation, may play an important role in reducing the solubility of the chloride ions [56]. Trends showing increasing contents of soluble chlorides with decreasing grain size are in line with the results from other studies [17]. The enrichment of soluble salts in the fine fraction may present an obstacle for the utilisation of the MSWI BA [37], as observed in the present study. Quicker et al. [34] and Pfrang-Stotz and Reichert [44] reported that the copper concentration in eluate decreases during aging. The opposite was observed in the present study. Copper has a cationic leaching pattern and its concentration increases with decreasing pH value [56]. The lower pH after aging may correlate with the higher copper solubility. Moreover, the oxidation level of copper in the aged BA was lower (Table S17 of the SI), which also correlates with the higher solubility. The substantial decrease in soluble Zn and Pb after aging can be explained by their insertion in the crystal lattice of calcite during the carbonation process [44,57].

5.3. Resource Potentials

5.3.1. Metals

Approximately two thirds of the aluminium in the BA is chemically bound in the mineral matrix. The higher mineral contents correspond to lower metallic aluminium contents in the aged BA compared to the raw BA. However, the chemically bound Al does not contribute to the metal resource potential.

Copper, iron, chromium, nickel, and zinc are mainly present in metallic form, which indicates that they are potentially recoverable. Chemically bound Cu and Zn are not considered within the metal resource potential because they cannot be recovered with conventional technologies [21].

The determined content of metallic aluminium in the grain sizes above 4 mm is relatively low in comparison with the reported literature data [16,20,22,32]. The total aluminium contents (metallic and chemically bound) are also lower than in previous studies [25,31]. A possible explanation for this is the separate collection of packaging materials and the deposit return system in Germany. Aluminium from packaging is expected to be in the medium grain sizes of the BA. For instance, in Austria, the Czech Republic and Switzerland, there are no deposit return systems for Al beverage cans, thus more aluminium cans end up in the residual waste. This may explain higher aluminium contents reported for Austrian, Czech and Swiss BA [16,22,32]. In Denmark, however, there is a deposit return system for aluminium cans, but reported Al contents of the BA were still above the values found in the present study [20]. Hence, the differences in Al contents cannot be explained only by the presence or absence of deposit systems for Al beverage cans, but other factors such as incinerated waste types and incineration technology may also be relevant.

Whereas metallic aluminium could be detected in finer fractions by the soda attack method, other NFe metals between 2 and 4 mm could not be identified during manual sorting. Hence, the theoretical resource potentials and utilisable resource potentials for NFe metals would increase if complete identification was possible. However, even if all the elemental Cu and Zn in the 2–4 mm fraction was present as native metals, this would increase the theoretical potential by 3% and the utilisable potential by 1% (Tables S9 and S13 of the SI). Consequently, neglecting native metals in this grain size fraction does not have a strong effect on the overall metal resource potentials.

The resource potential of metals below 2 mm was not considered. Nevertheless, it should be stated that the metals in these grain size fractions are potentially recoverable [58] by more extensive treatment. Currently, such treatment is applied only in a few treatment plants [38].

Precious metals were also not considered in the present study, although they may significantly contribute to the resource potential from an economic point of view [4,23]. Despite their typically very low concentrations in the BA (e.g., 2.2 mg/kg Au in BA < 5 mm [22]), their economic value may be higher than that of abundant metals such as iron or aluminium [4]. However, for their recovery, advanced processing is required, which was not considered in this study.

5.3.2. Mineral Fraction

The theoretical resource potential of the MSWI BA is equivalent to the amount of processed BA, which was more than 85% of the original mass in the present case. The utilisable potential of the MSWI BA was much lower for both utilisation routes than the theoretical potential in this study. Only a few grain size fractions could meet the respective requirements for use as material in technical constructions or aggregate in concrete. Because mixing with other mineral materials (recycled or natural) as well as further treatment was not considered in the directly utilisable potentials, the major part of the BA investigated could not be used. However, in practice, such manipulation and processing can be applied to enhance utilisation, for instance, by wet processing [31,37]. During wet processing, soluble salts such as chloride and sulphate are transferred to the finest fraction and removed as filter cake [59]. Holm and Simon [59] reported that 70% of the sulphate is transferred to the filter cake. Yang et al. [60] stated that the soluble chloride content can also be reduced by 70% by washing. Furthermore, the agglomerated fine particles that are enriched in contaminants as heavy metals can also be removed from the bigger fractions [61] and transferred to the filter cake. As a result, the whole BA as a mixture could be utilised if such treatment was applied. However, wet processing may have a deteriorating effect on NFe metal recovery using eddy

current separators [59]. Hence, current processing technologies for NFe metals recovery, especially Al, in the small grain size fractions < 2 mm need to be adapted in the case of wet processing [62]. To further decrease the metallic aluminium content, which also deteriorates the quality of the minerals, washing in alkaline conditions can be applied [37].

Müller and Rübner [30] reported on alkali–silica reactions in concrete specimens with MSWI BA. The reactions were related to the bottle glass contained in the BA (15%) and caused gel formation, which was accompanied by cracks inside the glass fragments. However, cracks in the concrete specimens due to the alkali–silica reactions were not observed during the nine months of investigations [30]. As the glass content in the Fuller-curve-mixture is lower than in the study of Müller and Rübner [30], it is expected that glass would not affect the concrete if the MSWI BA was used as aggregate. However, long-term investigations with MSWI BA concrete would be necessary to verify this.

6. Conclusions

The grain-size specific characterisation of the BA of the Kassel MSWI plant showed similar particle size distribution and material composition for the raw and aged BA. The raw BA consisted of 42.2% mineral fraction, 13.8% magnetic ash, 14.3% ferrous metals, 2.0% non-ferrous metals, 6.1% glass, 1.4% unburned OM and 20.2% fines below 2 mm in size. In comparison, the aged BA consisted of 40.6% mineral fraction, 16.5% magnetic ash, 14.1% ferrous metals, 2.2% non-ferrous metals, 5.0% glass, 1.6% unburned OM and 20.2% fine materials below 2 mm in size. Most of the ferrous metals in both cases were found in the coarse grain size fraction above 31.5 mm, whereas non-ferrous metals were primarily present in the medium and fine fractions.

The characterisation study was performed using a defined sampling strategy, which was confirmed by generally acceptable relative standard errors of less than 10%. Furthermore, significant variation between the individual daily samples of the MSWI BA was observed, which highlights the importance of temporally distributed sampling of MSWI BA.

Theoretical metal resource potentials of the MSWI BA, i.e., the contents of native metals above 2 mm, were 12.1% and 3.6% on average with respect to Fe and NFe metals. The utilisable potentials were determined to be 10.7% and 2.0% on average for Fe and NFe metals, respectively. However, the latter depend strongly on the applied recovery technology and therefore vary for different processing plants.

In the case of construction materials, the theoretical potential is constituted by the residual fraction of the BA after metal separation and amounted to 86–87%. The processed BA was not utilisable as a whole, neither as construction material in contained structures nor as an aggregate in concrete because it did not comply with limit values of current German regulations. Therefore, the utilisable resource potentials were identified on a grain-size specific basis. Only larger grain size fractions could be used because leaching concentrations of salts were too high in the fine fractions. Overall, less than 30% of the BA was directly utilisable as a construction material in contained structures and less than 10% could be used as aggregate in concrete. In the case of use in concrete, the content of metallic aluminium posed an additional restriction, apart from soluble salts. Aging did not have any significant effect on the utilisation potentials regarding leaching concentrations. Thus, legal compliance of BA as a construction material was not facilitated by longer aging.

In order to enable the utilisation of the processed BA, further manipulation or processing would be required to reduce the contents of soluble salts as well as to minimise residual metal contents. The grain size-specific characterisation performed in this study constitutes a basis for defining grain-size specific processing routes for purposes of producing utilisable BA qualities. In order to assess the actual use of BA as construction material and identify suitable applications, further investigations on its mineralogical

and technical properties are needed. Such investigations should reflect different MSWI and BA treatment settings to provide a broad basis for the assessment of mineral utilisation options of processed BA.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-9276/9/6/66/s1>, Figure S1: Distribution of the mass of the increments in the nine daily samples and in the whole sample, Figure S2: Mass flows in [kg] determined by the analysis of the raw MSWI BA smaller than 31.5 mm, Figure S3: Mass flows in [kg] determined by the analysis of the aged MSWI BA smaller than 31.5 mm, Figure S4: Total material composition of the raw and aged MSWI BA; error bars show the standard error of the nine daily samples, Figure S5: Composition of the aged MSWI BA as a function of the particle size; error bars show the standard deviation of the nine daily samples, Figure S6: Composition of the non-ferrous metals in the grain size fractions over 4 mm in the raw MSWI bottom ash, Figure S7: Composition of the non-ferrous metals in the grain size fractions over 4 mm in the aged MSWI BA, Figure S8: Leaching concentrations for evaluation of the utilisable resource potential as construction material in contained structures (such as road subbase layers) under the regulation of LAGA M 20, Figure S9: Particle size distribution of the Fuller-curve mixture, Figure S10: Leaching concentrations for evaluation of the utilisable resource potential as construction material in contained structures (such as road subbase layers) under the regulation of TL Gestein-StB 04, Figure S11: Content of metallic aluminium in the Fuller curve mixture, Figure S12: Glass content in the Fuller-curve mixture, Table S1: Limit values for recycling of mineral residues and wastes in Germany according to different regulations and recommendations, Table S2: Assumed values for calculating the HIL, Table S3: Assumed recovery rate of the metals for assessment of the utilisation potential of the mineral fraction after metal recovery, Table S4: Cumulative particle size distribution after Fuller for aggregate with spherical shape, where $P(d)$ is the percentage passing a sieve with mesh size diameter d , Table S5: Statistical measures of the material contents of the raw and aged MSWI BA > 2 mm considering the nine daily samples, Table S6: Mass fraction of all elements analysed in the non-ferrous metals fraction above 4 mm of the raw BA in (mg/kg dry matter), Table S7: Mass fraction of all elements analysed in the ferrous metals fraction above 4 mm of the raw BA in (mg/kg dry matter), Table S8: Mass fraction of all elements analysed in mineral fraction above 4 mm of the raw BA in (mg/kg dry matter), Table S9: Mass fraction of all elements analysed in the mineral fraction below 4 mm of the raw BA in (mg/kg dry matter), Table S10: Mass fraction of all elements analysed in the non-ferrous metals fraction of the aged BA in (mg/kg dry matter), Table S11: Mass fraction of all elements analysed in the ferrous metals fraction of the aged BA in (mg/kg dry matter), Table S12: Mass fraction of all elements analysed in the mineral fraction above 4 mm of the aged BA in (mg/kg dry matter), Table S13: Mass fraction of all elements analysed in the mineral fraction below 4 mm of the aged BA in (mg/kg dry matter), Table S14: Mass fraction of all elements analysed in the glass fraction of the raw and aged BA in (mg/kg dry matter), Table S15: Concentration of metallic aluminium in the grain sizes below 4 mm of the raw BA, determined by soda attack method, Table S16: Concentration of metallic aluminium in the grain sizes below 4 mm of the aged BA, determined by soda attack method, Table S17: Share of the mineral content of the metals in the raw and aged MSWI BA, Table S18: Leaching concentrations in the mineral fraction above 4 mm of the raw BA, Table S19: Leaching concentrations in the mineral fraction below 4 mm of the raw BA, Table S20: Leaching concentrations in the mineral fraction above 4 mm of the aged BA, Table S21: Leaching concentrations in the mineral fraction below 4 mm of the aged BA, Table S22: Leaching concentrations in the glass of the raw and aged BA.

Author Contributions: I.V. was involved in all parts of the study, including conceptualisation, investigation, visualisation, writing of the original draft, reviewing and editing. D.L. was mainly involved in conceptualisation, interpretation and discussion of results, writing of the original draft, reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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References

1. Eurostat. Waste Treatment 2016. Available online: https://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_wastrt&lang=en (accessed on 13 February 2020).
2. CEWEP. Bottom Ash Factsheet. Available online: <https://www.cewep.eu/bottom-ash-factsheet/> (accessed on 4 March 2020).
3. ITAD. Reststoffe (Residues). Available online: <https://www.itad.de/wissen/reststoffe> (accessed on 5 April 2020).

4. Böni, D.; Morf, L.S. *Thermo-Recycling: Efficient Recovery of Valuable Materials from Dry Bottom Ash*; ZAR: Hinwil, Switzerland, 2018.
5. Bunge, R. Aufbereitung von Abfallverbrennungsaschen—Eine Übersicht (Processing of municipal solid waste incineration bottom ash—An overview). In *Mineralische Nebenprodukte und Abfälle (Mineral by-Products and Waste)*; Thomé-Kozmiensky, K.J., Ed.; TK: Neuruppin, Germany, 2016; ISBN 9783944310282.
6. Kuchta, K.; Enzner, V. Metallrückgewinnung aus Rostaschen aus Abfallverbrennungsanlagen: Bewertung der Ressourceneffizienz (Metal Recovery from Bottom Ash From Waste Incineration Plants: Assessment of Resource Efficiency). Available online: <https://entsorgergemeinschaft.de/tileviewer.html?d=17&pc=54> (accessed on 7 December 2018).
7. Bunge, R. Recovery of Metals from Waste Incinerator Bottom Ash. 2019. Available online: https://www.umtec.ch/fileadmin/user_upload/umtec.hsr.ch/Dokumente/Metals_from_MWIBA_6_2019.pdf (accessed on 30 March 2020).
8. Astrup, T. Pretreatment and utilization of waste incineration bottom ashes: Danish experiences. *Waste Manag.* **2007**, *27*, 1452–1457. [[CrossRef](#)] [[PubMed](#)]
9. Meima, J.A.; Comans, R.N.J. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash. *Environ. Sci. Technol.* **1997**, *31*, 1269–1276. [[CrossRef](#)]
10. Blasenbauer, D.; Huber, F.; Lederer, J.; Quina, M.J.; Blanc-Biscarat, D.; Bogush, A.; Bontempi, E.; Blondeau, J.; Chimenos, J.M.; Dahlbo, H.; et al. Legal situation and current practice of waste incineration bottom ash utilisation in Europe. *Waste Manag.* **2020**, *102*, 868–883. [[CrossRef](#)] [[PubMed](#)]
11. Hjelmar, O.; Johnson, A.; Comans, R.N.J. Incineration: Solid residues. In *Solid Waste Technology & Management*; Christensen, T.H., Ed.; Wiley: Chichester, UK, 2011; pp. 430–462. ISBN 9781405175173.
12. Chandler, A.J.; Eighmy, T.T.; Hjelmar, O.; Kosson, D.S.; Sawell, S.E.; Vehlow, J.; Van der Sloot, H.A.; Hartlén, J. *Municipal Solid Waste Incinerator Residues*; Elsevier: Amsterdam, The Netherlands, 1997; ISBN 9780080537184.
13. Knorr, W. *Rückstände aus der Müllverbrennung (Residues from Waste Incineration)*; Erich Schmidt: Berlin, Germany, 1999; ISBN 3503048588.
14. Caviglia, C.; Confalonieri, G.; Corazzari, I.; Destefanis, E.; Mandrone, G.; Pastero, L.; Boero, R.; Pavese, A. Effects of particle size on properties and thermal inertization of bottom ashes (MSW of Turin’s incinerator). *Waste Manag.* **2019**, *84*, 340–354. [[CrossRef](#)]
15. Del Valle-Zermeño, R.; Gómez-Manrique, J.; Giro-Paloma, J.; Formosa, J.; Chimenos, J.M. Material characterization of the MSWI bottom ash as a function of particle size. Effects of glass recycling over time. *Sci. Total Environ.* **2017**, *581–582*, 897–905. [[CrossRef](#)]
16. Šyc, M.; Krausová, A.; Kameníková, P.; Šomplák, R.; Pavlas, M.; Zach, B.; Pohořelý, M.; Svoboda, K.; Punčochář, M. Material analysis of Bottom ash from waste-to-energy plants. *Waste Manag.* **2018**, *73*, 360–366. [[CrossRef](#)]
17. Loginova, E.; Volkov, D.S.; Van de Wouw, P.M.F.; Florea, M.V.A.; Brouwers, H.J.H. Detailed characterization of particle size fractions of municipal solid waste incineration bottom ash. *J. Clean. Prod.* **2019**, *207*, 866–874. [[CrossRef](#)]
18. Chimenos, J.M.; Segarra, M.; Fernández, M.A.; Espiell, F. Characterization of the bottom ash in municipal solid waste incinerator. *J. Hazard. Mater.* **1999**, 211–222. [[CrossRef](#)]
19. Astrup, T.; Christensen, T.H. *Waste Incineration Bottom Ashes in Denmark: Status and Development Needs by 2003*; Affald Danmark & Environment & Resources DTU, Technical University of Denmark: Copenhagen, Denmark, 2005.
20. Allegrini, E.; Maresca, A.; Olsson, M.E.; Holtze, M.S.; Boldrin, A.; Astrup, T.F. Quantification of the resource recovery potential of municipal solid waste incineration bottom ashes. *Waste Manag.* **2014**, *34*, 1627–1636. [[CrossRef](#)]
21. Xia, Y.; He, P.; Shao, L.; Zhang, H. Metal distribution characteristic of MSWI bottom ash in view of metal recovery. *J. Environ. Sci. (China)* **2017**, *52*, 178–189. [[CrossRef](#)]
22. Morf, L.S.; Gloor, R.; Haag, O.; Haupt, M.; Skutan, S.; Di Lorenzo, F.; Böni, D. Precious metals and rare earth elements in municipal solid waste—sources and fate in a Swiss incineration plant. *Waste Manag.* **2013**, *33*, 634–644. [[CrossRef](#)] [[PubMed](#)]

23. Muchova, L.; Bakker, E.; Rem, P. Precious metals in municipal solid waste incineration bottom ash. *Water Air Soil Pollut. Focus* **2009**, *9*, 107–116. [[CrossRef](#)]
24. Gisbertz, K.; Hilgendorf, S.; Friedrich, B.; Heinrichs, S.; Rießmann, D.; Pretz, T. Maximising metal recovery from incineration ashes. In Proceedings of the European Metallurgical Conference EMC 2013, Munich, Germany, 23 June 2013.
25. Deike, R.; Ebert, D.; Warnecke, R.; Vogell, M. Abschlussbericht zum Projekt Recyclingpotentiale bei Rückständen aus der Müllverbrennung; (Final Report on the Project “Recovery Potentials of Residues from Waste Incineration”). 2012. Available online: https://www.itad.de/wissen/studien/20130110_deike-hmvarcyclingpotentialabschlussbericht.pdf (accessed on 6 February 2020).
26. Lynn, C.J.; Dhir OBE, R.K.; Ghataora, G.S. Municipal incinerated bottom ash characteristics and potential for use as aggregate in concrete. *Constr. Build. Mater.* **2016**, *127*, 504–517. [[CrossRef](#)]
27. Van der Wegen, G.; Hofstra, U.; Speerstra, J. Upgraded MSWI bottom ash as aggregate in concrete. *Waste Biomass Valor* **2013**, *4*, 737–743. [[CrossRef](#)]
28. Hjelmar, O.; Holm, J.; Crillesen, K. Utilisation of MSWI bottom ash as sub-base in road construction: First results from a large-scale test site. *J. Hazard. Mater.* **2007**, *139*, 471–480. [[CrossRef](#)] [[PubMed](#)]
29. Keppert, M.; Pavlík, Z.; Cerný, R.; Reiterman, P. Properties of concrete with municipal solid waste incinerator bottom ash. In *2012 IACSIT Coimbatore Conferences*; IACSIT Press: Singapore, 2012; pp. 127–131.
30. Müller, U.; Rübner, K. The microstructure of concrete made with municipal waste incinerator bottom ash as an aggregate component. *Cem. Concr. Res.* **2006**, *36*, 1434–1443. [[CrossRef](#)]
31. Huber, F.; Blasenbauer, D.; Aschenbrenner, P.; Fellner, J. Chemical composition and leachability of differently sized material fractions of municipal solid waste incineration bottom ash. *Waste Manag.* **2019**, *95*, 593–603. [[CrossRef](#)]
32. Huber, F.; Blasenbauer, D.; Aschenbrenner, P.; Fellner, J. Complete determination of the material composition of municipal solid waste incineration bottom ash. *Waste Manag.* **2020**, *102*, 677–685. [[CrossRef](#)]
33. Thomé-Kozmiensky, E. *Abfallverbrennungsanlagen: Deutschland (Waste Incineration Plants: Germany)*; TK Verlag Karl Thomé-Kozmiensky: Neuruppin, Germany, 2018; ISBN 978-3-944310-38-1.
34. Quicker, P.; Stockschröder, J.; Zayat-Vogel, B.; Pretz, T.; Garth, A.; Deike, R.; Ebert, D.; Gellermann, C.; Brämer, T.; Ratering, S.; et al. *Möglichkeiten Einer Ressourcenschonenden Kreislaufwirtschaft Durch Weitergehende Gewinnung von Rohstoffen Aus Festen Verbrennungsrückständen Aus der Behandlung von Siedlungsabfällen (Possibilities of a Resource-Efficient Recycling Economy by Further Extraction of Raw Materials from Solid Combustion Residues from the Treatment of Municipal Solid Waste)*; Umweltbundesamt: Dessau-Roßlau, Germany, 2018.
35. Morf, L.; Gloor, R.; Skutan, S. *Sampling, Sample Preparation and Analysis of Solid Residues from Thermal Waste Treatment and Its Processing Products*; Methods Report; 2018; Available online: https://zar-ch.ch/fileadmin/user_upload/Contentdokumente/Oeffentliche_Dokumente/Sampling_methods_EN.pdf (accessed on 11 December 2019).
36. Biganzoli, L.; Ilyas, A.; van Praagh, M.; Persson, K.M.; Grosso, M. Aluminium recovery vs. hydrogen production as resource recovery options for fine MSWI bottom ash fraction. *Waste Manag.* **2013**, *33*, 1174–1181. [[CrossRef](#)]
37. Joseph, A.M.; Snellings, R.; Van den Heede, P.; Matthys, S.; de Belie, N. The use of municipal solid waste incineration ash in various building materials: A belgian point of view. *Materials (Basel)* **2018**, *11*, 141. [[CrossRef](#)]
38. Hu, B.; Rem, P.; Van de Winckel, T. Fine Heavy Non-Ferrous and Precious Metals Recovery in Bottom Ash Treatment 2008. Available online: https://www.iswa.org/uploads/tx_iswaknowledgebase/paper38.pdf (accessed on 6 December 2019).
39. Pfandl, K.; Stockinger, G.; Höllen, D.; Pomberger, R. Rohstoffpotenzial von MVA-Rostaschen für Metallrückgewinnung und Karbonatisierung (Raw material potential of municipal solid waste incineration ashes for metal recovery and mineral carbonation). *Österr Wasser Abfallw* **2018**, *70*, 147–160. [[CrossRef](#)]
40. Dou, X.; Ren, F.; Nguyen, M.Q.; Ahamed, A.; Yin, K.; Chan, W.P.; Chang, V.W.-C. Review of MSWI bottom ash utilization from perspectives of collective characterization, treatment and existing application. *Renew. Sustain. Energy Rev.* **2017**, *79*, 24–38. [[CrossRef](#)]

41. LAGA. Anforderungen an die Stoffliche Verwertung von Mineralischen Reststoffen/Abfällen (LAGA M 20) (Requirements for the Recycling of Mineral Residues/Waste). 2003. Available online: https://www.laga-online.de/documents/m20_nov2003u1997_2_1517834540.pdf (accessed on 5 February 2020).
42. FGSV. *Technische Lieferbedingungen für Gesteinskörnungen im Straßenbau (Technical Delivery Conditions for Aggregates in Road Construction)*; TL Gestein-StB 04, Ausg. 2004; Forschungsgesellschaft für Straßen- und Verkehrswesen (Road and Transportation Research Association (FGSV)): Köln, Germany, 2005; ISBN 3937356436.
43. Referentenentwurf des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit: Verordnung zur Einführung einer Ersatzbaustoffverordnung, zur Neufassung der Bundes-Bodenschutz- und Altlastenverordnung und zur Änderung der Deponieverordnung und der Gewerbeabfallverordnung (Ordinance on Groundwater Protection, Mineral Waste Utilization and Federal Soil Protection and Contaminated Sites, Draft Mutual Release. MantelV). 2017. Available online: https://www.bmu.de/fileadmin/Daten_BMU/Download_PDF/Gesetze/mantelv_text.pdf (accessed on 5 February 2020).
44. Pfrang-Stotz, G.; Reichelt, J. Einfluss geänderter Stoffströme in der Abfallwirtschaft auf die zukünftige Qualität und die Verwertungsmöglichkeiten von Müllverbrennungsschlacken (Influence of Changed Material Flows in Waste Management on the Future Quality and Recycling Possibilities of Waste Incineration Slags). *Forsch. Karlsr.* **2005**. [CrossRef]
45. Gy, P. *Sampling of Heterogeneous and Dynamic Material Systems: Theories of Heterogeneity, Sampling, and Homogenizing*; Elsevier: Amsterdam, The Netherlands, 1992; ISBN 9780080868370.
46. Aubert, J.E.; Husson, B.; Vaquier, A. Metallic aluminum in MSWI fly ash: Quantification and influence on the properties of cement-based products. *Waste Manag.* **2004**, *24*, 589–596. [CrossRef] [PubMed]
47. DIN EN 12457-4. *Characterization of Waste—Leaching—Compliance Test for Leaching of Granular Waste Materials and Sludges—Part 4: One Stage Batch Test at a Liquid to Solid Ratio of 10 l/kg for Materials with Particle Size Below 10 mm (without or with Size Reduction)*; Deutsches Institut für Normung e.V.: Berlin, Germany, 2003. (In Germany)
48. European Commission. *Best Available Techniques (BAT) Reference Document for Waste Incineration*; Publications Office of the European Union: Brussels, Belgium, 2019.
49. Hyks, J.; Astrup, T. Influence of operational conditions, waste input and ageing on contaminant leaching from waste incinerator bottom ash: A full-scale study. *Chemosphere* **2009**, *76*, 1178–1184. [CrossRef] [PubMed]
50. Wriggers, P.; Moftah, S.O. Mesoscale models for concrete: Homogenisation and damage behaviour. *Finite Elem. Anal. Des.* **2006**, *42*, 623–636. [CrossRef]
51. CUR. AEC-Granulaat als Toeslagmateriaal voor Beton (Processed Municipal Incinerator Bottom Ash as Aggregate for Concrete): CUR-Aanbeveling 116:2012. Available online: <https://www.cur-aanbevelingen.nl/cur-aanbeveling-116> (accessed on 11 March 2020).
52. Esbensen, K.H.; Wagner, C. Sampling quality assessment: The replication experiment. *Spectrosc. Eur.* **2016**, *28*, 20–25.
53. Grünbein, M.; Wegkamp, D.; Rüßmann, D. Steigerung der Wertstoffseparation von Rostaschen aus der Nassentschlackung durch Optimierung konventioneller Technik (Increase in recyclables separation of bottom ash from the wet purification by optimizing conventional technology). In *Mineralische Nebenprodukte und Abfälle: Aschen, Schlacken, Stäube und Baurestmassen*; Thomé-Kozmiensky, K.J., Ed.; TK: Neuruppin, Germany, 2015; ISBN 9783944310213.
54. Muchova, L. Wet Physical Separation of MSWI Bottom Ash. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands, 2010.
55. Breitenstein, B. Das “RENE-Verfahren” zur Rückgewinnung von NE-Metallen aus feinkörnigen Rostaschen der Thermischen Abfallbehandlung und Energetischen Verwertung (The “RENE process” for Recovery of Non-Ferrous Metals from Fine-Grained Bottom Ashes from the Municipal Solid Waste Incineration). Ph.D. Thesis, Clausthal University of Technology, Clausthal, Germany, 2017.
56. Luo, H.; Cheng, Y.; He, D.; Yang, E.-H. Review of leaching behavior of municipal solid waste incineration (MSWI) ash. *Sci. Total Environ.* **2019**, *668*, 90–103. [CrossRef]

57. Freyssinet, P.; Piantone, P.; Azaroual, M.; Itard, Y.; Clozel-Leloup, B.; Guyonnet, D.; Baubron, J.C. Chemical changes and leachate mass balance of municipal solid waste bottom ash submitted to weathering. *Waste Manag.* **2002**, *22*, 159–172. [[CrossRef](#)]
58. Holm, O.; Wollik, E.; Johanna Bley, T. Recovery of copper from small grain size fractions of municipal solid waste incineration bottom ash by means of density separation. *Int. J. Sustain. Eng.* **2017**, *3*, 1–11. [[CrossRef](#)]
59. Holm, O.; Simon, F.-G. Innovative treatment trains of bottom ash (BA) from municipal solid waste incineration (MSWI) in Germany. *Waste Manag.* **2017**, *59*, 229–236. [[CrossRef](#)] [[PubMed](#)]
60. Yang, S.; Saffarzadeh, A.; Shimaoka, T.; Kawano, T. Existence of Cl in municipal solid waste incineration bottom ash and dechlorination effect of thermal treatment. *J. Hazard. Mater.* **2014**, *267*, 214–220. [[CrossRef](#)] [[PubMed](#)]
61. Alam, Q.; Florea, M.V.A.; Schollbach, K.; Brouwers, H.J.H. A two-stage treatment for Municipal Solid Waste Incineration (MSWI) bottom ash to remove agglomerated fine particles and leachable contaminants. *Waste Manag.* **2017**, *67*, 181–192. [[CrossRef](#)] [[PubMed](#)]
62. Stockinger, G. Nassaufbereitung von Abfallverbrennungsaschen-Betriebsergebnisse einer großtechnischen anlage in Österreich (Wet processing of MSWI bottom ash—Results of a large-scale plant in Austria). In *Mineralische Nebenprodukte und Abfälle (Mineral By-Products and Waste)*; Thomé-Kozmiensky, K.J., Ed.; TK: Neuruppin, Germany, 2016; ISBN 9783944310282.



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