

Article

Sequential Extraction of Incineration Bottom Ash: Conclusions Regarding Ecotoxicity

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Abstract: The classification of incineration bottom ash (IBA) as hazardous or non-hazardous according to ecotoxic hazard property HP14 is still under debate. In this context, only the compounds of Zn and Cu with the hazard statement code H410 are of relevance. With an approach based on the grouping of substances, it was shown that such substances are either readily water-soluble or slightly and sparingly soluble. The concentrations of readily soluble Cu and Zn compounds in IBA are far below the cut-off value of 0.1%. Slightly and sparingly soluble Zn and Cu compounds could be quantified in the first fraction of a four-step sequential extraction procedure. With the results from the complete sequence, the dimensionless synthesis toxicity index (STI) was calculated and was in the range of 494 to 1218 for the four investigated IBA samples. It was concluded that IBA can usually be classified as non-hazardous.

Keywords: incineration bottom ash; hazard properties; ecotoxicity; sequential extraction; synthesis toxicity index

1. Introduction

In the European Union, 225 million tons of municipal solid waste (MSW) were generated in the year 2019 [1]. Fortunately, 48% of this mass was recycled, but still, 24% is landfilled. The goal is to reduce the amount of landfilled waste to less than 10% in the year 2035. Slightly more than one quarter (27%) was treated in thermal waste treatment plants. Most relevant residue in thermal waste treatment is the incineration bottom ash (IBA). Blasenbauer et al. [2] presented data on municipal solid waste incineration for 22 European countries. According to that reference, 17.6 million tons of IBA are generated annually in 463 incineration plants, with a total capacity of 90 million tons of MSW. The main area of application is as a sub-base material for road construction [3,4], although there are reports of problems, e.g., swelling [5]. Further utilization pathways are as a cement substitute [6,7].

There are also legal regulations on waste at the European level. The Waste Framework Directive 2008/98/EC [8] defines a waste hierarchy with a priority sequence from prevention to disposal (Article 4), as well as by-products and the end-of-waste status (Articles 5 and 6). The European Commission is empowered to draw up a list of waste (LoW) and adapt it to the current state of scientific knowledge (Article 7). For IBA there are two entries (“mirror entries”) in the list of wastes: 19 01 11* (bottom ash and slag containing dangerous substances) and 19 01 12 (bottom ash and slag other than those mentioned in 19 01 11*). Hazardous waste (all entries with *) is waste that has one or more hazard-relevant properties. These properties (hazard properties HP1–HP15) are defined in EU Regulation (EU) No. 1357/2014 [9]. Examples are HP1: explosive, HP2: oxidizing, HP6: acutely toxic, and HP11: mutagenic. The definitions are aligned with Regulation (EC) No. 1272/2008 (a regulation on classification, labeling, and packaging of substances and mixtures, CLP) [10]. This connects waste legislation to legislation on chemicals. The classification and labeling system is explained in detail elsewhere [11]. With regard to the hazardousness of IBA, it has



Citation: Simon, F.-G.; Scholz, P. Sequential Extraction of Incineration Bottom Ash: Conclusions Regarding Ecotoxicity. *Appl. Sci.* **2024**, *14*, 5541. <https://doi.org/10.3390/app14135541>

Academic Editors: Luca Fiori and Fulvia Chiampo

Received: 29 April 2024

Revised: 7 June 2024

Accepted: 24 June 2024

Published: 26 June 2024



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been shown that, of the 15 hazard-relevant properties, only the property HP14 “ecotoxic” could be applicable [12–14].

The entry HP14 “ecotoxic” is defined by the following in Council Regulation (EU) No 2017/997 [15]: “Waste which presents or may present immediate or delayed risks for one or more sectors of the environment”. The further explanations in the regulation list the substances that lead to this classification. These are the substances to which the hazard statements H400, H410, H411, H412 and H413 are assigned. These substances are classified as acutely hazardous to water (H400) or chronically hazardous to water category 1 (H410), category 2 (H411), category 3 (H412), or category 4 (H413). Cut-off values of 1% (H400, H411, H412, H413) or 0.1% (H410) apply. If the concentration c is below the cut-off value, the substance is not counted. A waste is classified as hazardous according to HP14 if one of three sums results in a value greater than or equal to 25%:

- (1) $\Sigma c(\text{H400})$;
- (2) $100 \times \Sigma c(\text{H410}) + 10 \times \Sigma c(\text{H411}) + \Sigma c(\text{H412})$;
- (3) $\Sigma c(\text{H410}) + \Sigma c(\text{H411}) + \Sigma c(\text{H412})$.

A complete list of hazardous substances can be found in Annex VI of CLP Regulation (EC) No. 1272/2008 [10]. The current version of the list (18th Adaption to Technical Progress, ATP18) contains 4372 entries. Of these, numerous substances have the hazard statements H400 and H410–413, but the vast majority of entries are, of course, irrelevant for the classification of bottom ash. The calculation rules for classification (1–3, see above) also indicate that the hazard statement H410 is particularly relevant for a substance. Even when the concentration of a substance with the hazard statement code H410 is just above the cut-off value of 0.1% the cumulative value of calculation rule (2) is already 10% because the concentrations of H410 substances are multiplied with the factor 100. As far as possible, H410 substances in IBA-only heavy metal compounds are to be considered. It is important to note that the concentrations c refer to the molar mass of the compounds rather than, e.g., leaching limits where the limit values are usually defined for an element (or ion). One exception is lead (Pb) where the concentrations apply to the element (“Note 1” in Annex VI of the CLP regulation). Therefore, only heavy metals with concentrations above approx. 500 mg/kg need to be considered for the HP14 classification (in the case of Pb: 1000 mg/kg). According to the literature data on the elemental composition of IBA, these are Cu, Zn, Pb, and Cr (at least when maximum values of the range are taken into account) [16–19]. Data for two samples from the present study together with the data from Hjelm et al. [16] are listed in the Supporting Information (SI, Table S1). Usually, it is not exactly known which chemical compound of the mentioned elements is present in IBA. However, this is needed for the HP14 classification. Otherwise, a “worst case” composition (related to the highest stoichiometric factor) has to be assumed [14], i.e., for Cu and Zn, the sulfates CuSO_4 and ZnSO_4 , with stoichiometric factors of 2.51 and 2.47, respectively. Elemental concentrations of 500 mg/kg each for Cu and Zn would result in a sum value of 24.9%, only slightly below the limit value of 25%. If crystal water were considered (Cu: penta-hydrate, Zn: hepta-hydrate) the sum would be above the limit value.

However, information on the composition of IBA can be obtained by an approach based on the grouping of substances [13]. For IBA, four substance groups can be defined: 1. elemental and alloyed metals, 2. readily water-soluble substances, 3. slightly and sparingly soluble substances, and 4. substances with strong chemical bonding. Elemental and alloyed Cu and Zn, at least the larger particles are, present in IBA and are usually recovered as the non-ferrous metals fraction [20]. Zn particles smaller than 1 mm are classified as H410, fine particles of Cu only as H411. The water-soluble fraction can be quantified with standard leaching procedures, e.g., at liquid to solid ratios (L/S) of 2 or 10 L/kg. Both sulfates of Zn and Cu belong to this group. In a recent publication, it was shown that for the above-mentioned metals the leached amount is well below the cut-off value of 1000 mg/kg even when the stoichiometric factors are applied [21]. Substance group 3 includes potential H410 substances. These are carbonates, hydroxides, and oxides of the listed elements, and are soluble in weak organic acids such as acetic acid. The

“worst-case” substances in group 3, i.e., those compounds with the highest stoichiometric factors, are $\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$ (factor 1.74) and ZnO (factor 1.24). ZnCO_3 would have a higher stoichiometric factor (1.92) but is classified as H411 only. Substances with strong chemical bonding, such as silicates or sulfides, are only soluble in strong acids (e.g., aqua regia) and have no hazard statement code for ecotoxicity.

Sequential extractions are a viable method for distributing elements into different substance groups, as outlined above. They were initially developed to investigate the chemical composition of soil and sediments [22]. The procedure was harmonized for the determination of extractable trace metals in sediments by the Community Bureau of Reference (BCR) [23], but is often modified. Haberl and Schuster [24] proposed a 7-step extraction procedure starting with water extraction and no pH adjustment. A comprehensive review on sequential extraction was presented by Filgueiras et al. [25]. Although the individual steps can vary, the common approach is using increasingly stronger leaching liquids within the sequence. Usually 4 fractions (F) are generated and analyzed: F1 bound to carbonates (weak acidic conditions), F2 bound to Fe- and Mn-oxides (reducing conditions), F3 bound to organic matter (oxidizing conditions), and F4, the residual fraction, only soluble in strong acids. Investigations on sequential extraction of IBA have already been conducted [24,26,27]. From the sequential extraction results, He and Kasina [27] determined a risk assessment code and an individual contamination factor. Ma et al. [28] used their results from sequential extraction with MSW IBA and sewage sludge incineration (SSI) fly ash to calculate the synthesis toxicity index (STI) [29,30]. The STI allows evaluation of the potential toxicity of heavy metals in ashes. It was shown that vitrification of the ashes lowered the STI by several orders of magnitude.

In the present study, four different bottom ashes from municipal solid waste incineration (MSWI) plants in Germany (IBA1–4), a fly ash from MSWI (waste code 19 01 13*) without flue gas cleaning products (FA), an SSI ash (SSA), and crushed sand (CS) from construction waste (waste code 17 01 07) were examined by a four-step sequential extraction procedure. The STI was calculated for all seven materials. For the four IBA samples, an assessment according to the hazard property HP14 (ecotoxicity) was carried out with a one-step extraction with an organic acid (maleic acid) at a pH of 4. This method could be an alternative to biotests in the classification of incineration bottom, according to the hazard property HP14.

2. Materials and Methods

IBA (IBA 1–3) was sampled at three waste incineration plants and at one substitute fuel plant (IBA 4) in Germany, all using grate firing for incineration. Sample size was in the range of 600–800 kg. SSI ash (SSA) was sampled at a German municipal sewage sludge incineration plant with 3 lines using stationary fluidized bed technology. The MSWI fly ash (FA) was provided by the operator of a MSWI plant in southern Germany also using grate technology. The fly ash was separated from the flue gas in a multicyclone after the boiler and before the spray dryer and the bag filter. Therefore, no flue gas cleaning products were contained in this fly ash. The crushed sand (CS) was purchased from a company in the construction materials recycling sector in southern Germany. The material is economically non-recyclable and accumulates as a by-product during the crushing process during the recycling of construction and demolition waste (C&D waste).

The IBA samples required careful and systematic processing due to strong inhomogeneity of the material. In the present study only the grain size fraction <16 mm was examined. FA, SSA, and CS required no crushing (ball milling only) because the grain size of the original material was already <2 mm.

In the first step, the entire sample quantity from four steel drums was formed into a cone on a heap. The cone was divided into four piles of approximately the same size using stainless steel blades and dividing plates. Two opposite piles were then combined and stored for further dividing steps, while the remaining two piles were returned to the

barrels. This procedure was repeated until a manageable quantity of approx. 20 kg was produced. All residues were shoveled back into the drums for further analysis.

The partial samples were dried on a dividing plate. After drying, scrap iron particles were removed from the samples using a magnet (scrap removal). The samples were then crushed to a particle size of <2 mm using a jaw crusher (Retsch BB300, Haan, Germany). Non-ferrous metal particles and unburned materials (e.g., paper or non-woven polymer materials) were removed from the crushed material by visual inspection. Compared to the initial large sample quantity, a manageable amount of material was now available, which could be further divided after sorting out impurities using a rotary sample divider. The crushed material was then finely ground in a ball mill (vibrating cup mill Retsch MM2000, Haan, Germany). It was important to separate the magnetic particles again with a magnet after grinding. Visible non-magnetic metal particles also had to be removed. In the final step, the resulting fine grain was sieved again to <0.25 mm and prepared for analysis. A 0.5 g portion of the sample was weighed into a polypropylene plastic centrifuge tube and the four extraction steps were carried out:

Fraction 1 (F1, weak acid soluble): (1) 40 mL acetic acid (0.11 M) per 1 g ash, i.e., L/S = 40 L/kg; (2) shaking for 16 h at 25 °C on an orbital shaker (Heidolph Instruments, Schwabach, Germany), liquid–solid separation by centrifugation at 1500 rpm, removal of the supernatant, washing of the residue with 5 mL of distilled water, and centrifuging separately.

It is important that the final pH is 4 to ensure that carbonates are digested [26,27]. The original recipe was devised for the application of sequential extraction with soil and sediments. However, the alkalinity of IBA is much higher than that of soil due to a high content of CaO, Ca(OH)₂, and CaCO₃ in the ashes. Necessary adjustments of the pH were performed with concentrated acetic acid.

Fraction 2 (F2, reducible fraction, substances bound to iron and manganese oxides): (1) 40 mL NH₂OH×HCl (0.5 M); (2) shaking for 16 h at 25 °C. Residues of the previous extraction were added to the hydroxylamine hydrochloride (CAS No. 5470-11-1). The samples were shaken in an orbital shaker for 16 h (overnight) at room temperature at 30 rpm. The solid fraction was separated from the liquid by centrifugation at 3000 rpm for 5 min. The solid residues were washed three times with distilled water in a centrifuge.

Fraction 3 (F3, Oxidizable fraction, substance bound to organic matter): (1). 10 mL H₂O₂ (8.8 M), (2). Shaking for 1 h at 25 °C, (3). Addition of further 10 mL H₂O₂ (8.8 M) and storage for one hour at 85 °C in a water bath, (4). Addition of 50 mL ammonium acetate (1 M; pH 2.0) and shaking for 16 h at 25 °C. After centrifugation of the mixture at 3000 rpm for 5 min, the solution could be decanted. The solid residues were washed three times with 5 mL distilled water each, and then centrifugation and decantation were repeated.

Fraction 4 (F4, Residue, soluble in strong acids): After the third fraction, solid residues were dried and then digested using aqua regia. The sample mass was significantly lower, at approx. 60% of the origin.

The cation concentrations within fractions F1–F4 of were analyzed using a Thermo Scientific iCAP 7000 ICP-OES equipped with an ASX-200 autosampler. Prior to sample measurements, calibration using external standards was necessary. For lower cation concentrations, additional ICP-MS measurements were carried out using a Thermo Scientific iCAP Qc instrument.

According to the technical guideline of the German associations for thermal waste treatment ITAD and operators of IBA treatment plants IGAM [31], the methodology of HP14 classification of IBA should be performed based on the grouping of substances. The decisive substance group 3 (slightly and sparingly soluble substances) contains the potential H410 substances, and should be quantifiable after selective extraction using a weak organic acid at pH 4, as above. Maleic acid is suggested rather than acetic acid, as described above for F1. Therefore, the four IBA samples were additionally examined by a selective extraction with maleic acid for the quantification of H410 substances.

All experiments were performed as triplicates.

3. Results

3.1. Sequential Extraction

The sequential extraction of mineral waste is an advanced method that allows a more in-depth analysis of the mobility and environmental availability of heavy metals such as copper, zinc, lead, and nickel. This method makes it possible to distinguish the bonding forms of these metals more precisely. While standard leaching with water identifies the readily soluble fractions, sequential extraction splits the metals into several fractions based on their binding to different matrix components of the mineral waste.

This differentiated approach is of great importance as it provides insights into the conditions under which metals can be mobilized, such as changes in pH or redox conditions. This is particularly relevant for the elements copper, zinc, lead, and nickel as potential toxic elements. Sequential extraction thus provides valuable information on the potential bioavailability and mobility of these metals, which is crucial for the assessment of environmental risks and the development of environmentally sound waste treatment and disposal strategies. It is important to emphasize that the fractionation was performed sequentially, with the residues of each step being used for the subsequent extraction.

Overall, sequential extraction enables a more comprehensive assessment of the chemical speciation of heavy metals in incineration ashes compared to selective extraction. Through this method, targeted measures can be developed to minimize the environmental impact of MSWI bottom ashes by considering the exact fractions and mobility patterns of the investigated metals. In the present study, an SSI ash, an MSWI fly ash and crushed sand from C&D waste have additionally been included in the investigation. Figure 1 shows the extracted amounts of the elements Cu, Zn, Pb, and Ni in the individual fractions F1 to F4. All concentrations have been measured with ICP-OES and calculated to leached content in mg/kg. The elements Cd and Cr exhibited much lower concentrations, and have been measured with ICP-MS (see Figure 2). The results for the elements As, Sb, V, Mo, Sn, and Co are displayed in the Supporting Information (SI, Figure S1).

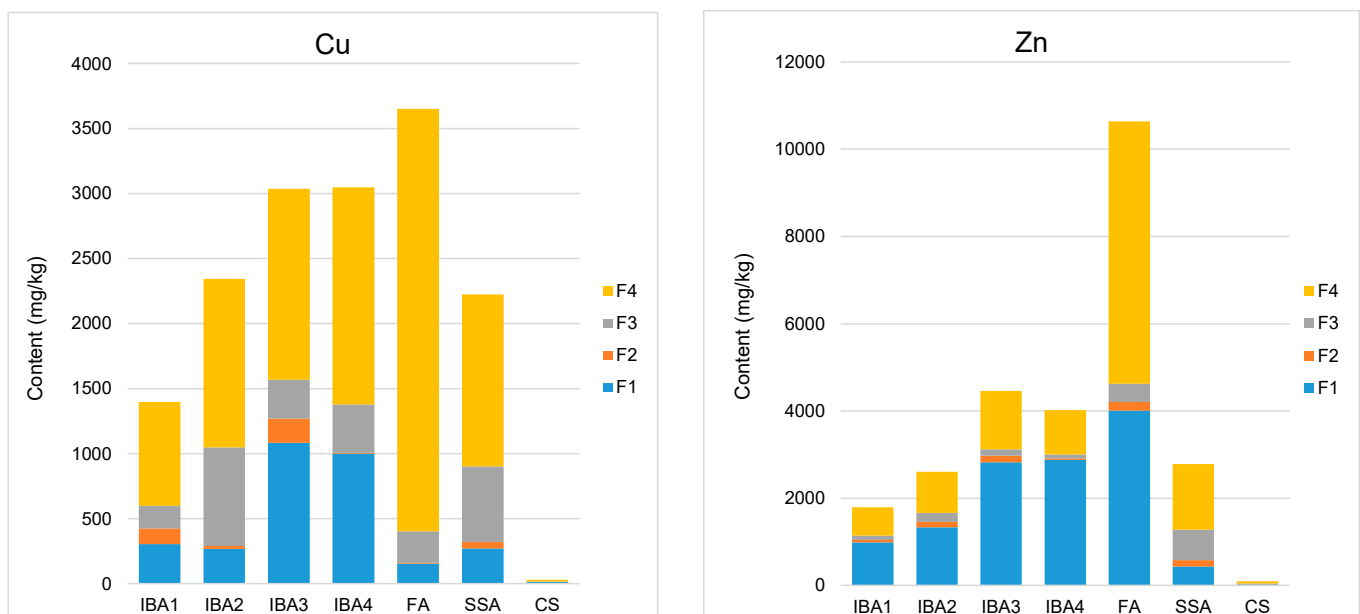


Figure 1. Cont.

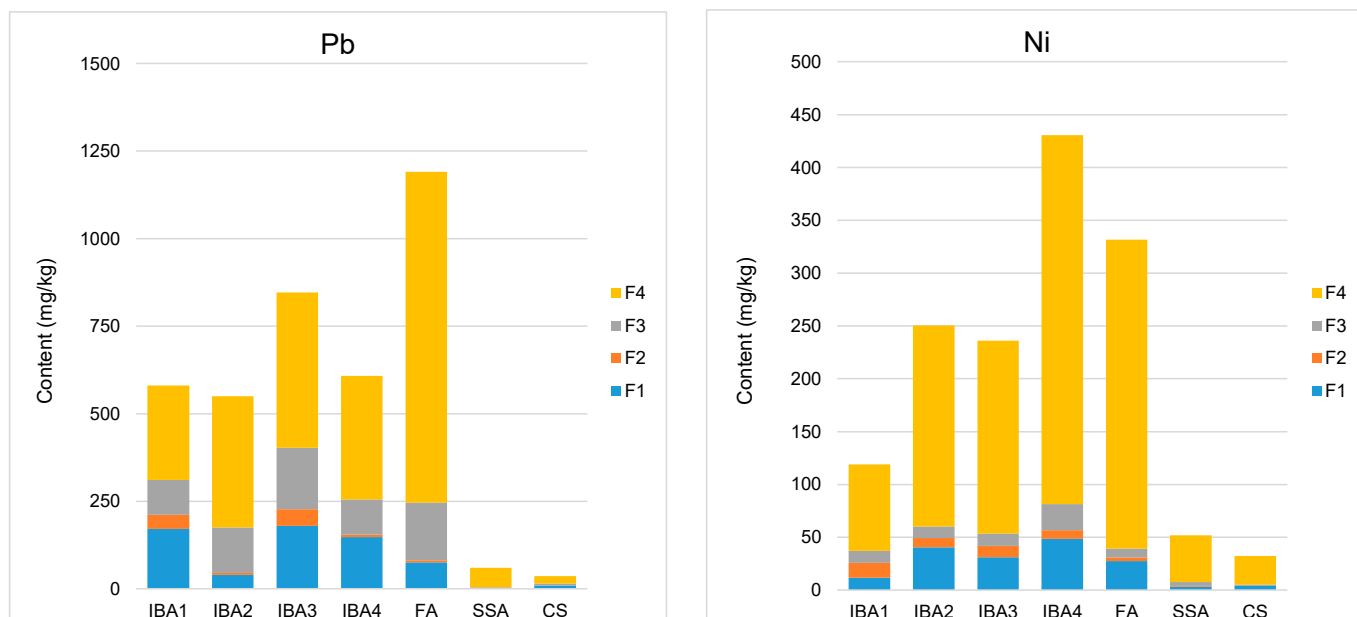


Figure 1. Extracted amounts of the elements Cu, Zn, Pb, and Ni in fractions F1–F4 after sequential extraction. The unit of the y-axis in all cases is mg/kg (note different scales).

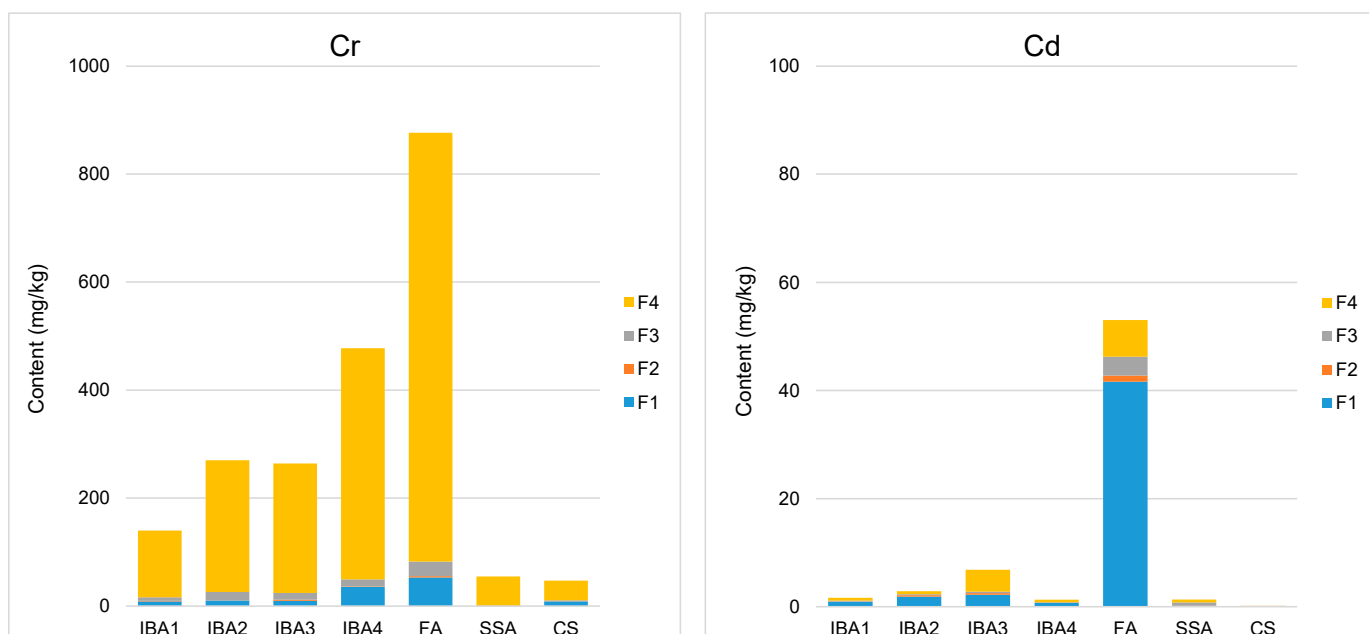


Figure 2. Extracted amounts of the elements Cr and Cd in fractions F1–F4 after sequential extraction, measured using ICP-MS. The unit of the y-axis in all cases is mg/kg (note different scales).

As can be seen from Figure 1, for Cu, the four incineration bottom ashes IBA1–4 show different solubilities between 267 and 1084 mg/kg in fraction F1. Sample SSA is comparable to IBA2 in all fractions F1–F4; the fly ash shows a low solubility of Cu in fraction F1, although the total content is the highest. Thus, there are fewer Cu species soluble in weak organic acids in the fly ash (FA). Cu species that are soluble in the reducible fraction F2 are hardly present in any of the ashes analyzed; their solubility is limited to a maximum of 185 mg/kg. However, it must always be taken into account that the compounds soluble in fraction F1 are no longer present at this point. Under oxidative conditions in F3, at 173–759 mg/kg, significantly more Cu compounds dissolve than previously in fraction F2. The largest proportion, at 798–3248 mg/kg, is the residue that was quantified in fraction F4

using aqua regia digestion. In comparison to the ashes, the examined crushed sand showed a very low solubility of Cu species in all four fractions of up to 13 mg/kg only.

As the selective extraction already showed, Zn species in waste incineration ashes are already highly soluble in weak organic acids such as the 0.1 M acetic acid used here (see Figure 1). In each of the four IBA samples, the majority of the total Zn content dissolved in this first fraction F1 at 990–2877 mg/kg. However, the SSI ash, at only 435 mg/kg, has a significantly lower solubility, especially in relation to the total Zn concentration. This suggests that other Zn compounds that are not soluble in weak organic acids are predominantly present in SSA. At 4005 mg/kg, a larger proportion of the total Zn content is dissolved in the fly ash, although this accounts for less than half of it. In the second fraction, F2, all ashes are similar; the solubility of Zn is relatively low, similar to that of Cu in F2. In contrast to copper, however, the solubility of Zn under oxidative conditions in fraction F3 is also low and, therefore, plays a subordinate role in the overall analysis. It was striking that the majority of Zn species were only soluble in sample FA in fraction F4 at 6012 mg/kg, which means that the composition of the Zn species in the fly ash must differ significantly from that of the IBA, where only a small proportion was still present in the residue. Zn could also hardly be detected in the crushed sand (CS) at up to 53 mg/kg, similar to Cu.

In the case of Pb, hardly any trend differences could be detected between IBA and FA, see Figure 1. The picture here was similar to that for Cu, with 40–180 mg/kg dissolved in fraction F1 in these five samples and fraction F2 being negligibly small. At 100–176 mg/kg, more Pb species were again dissolved in fraction F3. The majority of Pb was only dissolved in fraction 4 with up to 944 mg/kg in FA. In contrast to Cu and Zn, the total concentration of Pb in SSA is relatively low at only 60 mg/kg. CS also only contains a total of 36 mg/kg Pb.

As the selective extraction and the aqua regia digestion have already shown, Ni is present to an even lesser extent in HMVA, but also in FA, see Figure 1. The ratio between the individual fractions showed a low solubility of 12–49 mg/kg in fraction F1, which, however, is usually much higher than in fractions F2 and F3. The majority of the Ni species (82–349 mg/kg) only dissolves in the residual fraction F4. In comparison, the Ni concentrations in SSA and CS are again lower than in IBA and FA, at a total of 52 and 32 mg/kg, respectively.

To classify the toxicity (see Section 3.2) of the ashes and the crushed sand, the solubilities of Cd and Cr are also shown in Figure 2. It should be noted that ICP-MS was used as the quantification method due to the low concentrations, which nevertheless have a major influence on the classification of the samples with regard to hazards and toxicity. With the exception of fly ash with 42 mg/kg, Cd is only soluble in fraction F1 in very low concentrations of 0–2 mg/kg. Fraction F2 is again negligibly low; in fraction F3, the solubility is below 1 mg/kg; an exception here is again FA, with approx. 4 mg/kg. In fraction F4, too, only low solubilities of 0–6 mg/kg could be detected.

Cr is present more frequently overall in the ashes, whereby almost all species for this element are only dissolved in fraction F4. Fraction F1 also has a relevant solubility of up to 53 mg/kg; fraction F2 is negligibly small; and fraction F3, with up to 27 mg/kg, is also relevant for the overall classification of the samples with regard to toxicity. With a solubility of up to 794 mg/kg, the residue of fraction F4 contains the largest proportion of Cr species, as already mentioned.

The results clearly showed that Zn and Cd are elements that are mainly transferred to the fly ash in the process of municipal solid waste incineration [32,33]. Crushed sand from C&D waste recycling showed only negligible heavy metal contamination.

3.2. Calculation of Synthesis Toxicity Index (STI)

With the data from Section 3.1 the (dimensionless) STI can be calculated according to Equation (1) [28–30]. The needed parameters T_i , C_N and E_j are listed in Table 1.

$$STI_M = \sum_{i=1}^n \left(T_i \left(\sum_{j=1}^n E_j Q_i^j \right) / C_N^i \right) \quad (1)$$

Table 1. Model parameters for the calculation of the synthesis toxicity index (STI).

| Heavy Metals | Cu | Zn | Pb | Ni | Cr | Cd |
|-----------------------------|-----|-----|-----|-----|-----|-----|
| T_i | 5 | 1 | 5 | 5 | 2 | 40 |
| C_N (mg/kg) | 200 | 300 | 240 | 190 | 350 | 0.8 |
| Bioavailability coefficient | F1 | F2 | F3 | F4 | | |
| E_j | 7 | 5 | 2 | 0 | | |

T_i is the toxicity coefficient of the element i ; the bioavailability coefficient E_j with j is the step of the sequential extraction; Q is the extracted amount of element i in step j ; and C_N is the risk screening value of element i .

The bioavailability coefficient E is highest for F1 because this fraction is readily mobilizable under natural conditions. On the contrary, E is zero for F4 because this content cannot be mobilized in the environment. The toxicity coefficient is highest for Cd and as low as 1 for Zn. The risk screening value C_N acts as a threshold value and can be associated with background values of the elements in the natural environment. The numerical values and the listed elements have been adopted unchanged from the work of Ma et al. [28]. Although arbitrarily set, the values consider the environmental properties of the different elements and the intended purpose of the test conditions in the sequential extraction. A comprehensive discussion of the values for the model parameters can be found elsewhere [30].

The calculation results are listed in Table 2. The numerical values of parameter E_j , i.e., the extracted amount of the respective element in counted fractions F1–F3 are listed in Table S2 in the Supporting Information (SI). It is clearly visible that the MSWI fly ash has the largest value for the STI. Actually, fly ash from MSWI is commonly classified as hazardous waste. That with the most impact in the calculation has the element Cd with the highest risk screening value C_N and toxicity coefficient T_i . This also led to the higher value for STI of IBA3 in comparison to the other IBA samples. On the contrary, CS has the lowest STI. There is almost no contamination with heavy metals. The utilization as secondary building material is only affected by the presence of polyaromatic hydrocarbons and sulfate [34]. The STI of SSA is lower than that of IBA due to lower heavy metal contents, at least when municipal sewage sludge is incinerated [35].

Table 2. Results of the STI calculation for the seven tested materials.

| Sample | STI |
|--------|--------|
| IBA1 | 494 |
| IBA2 | 882 |
| IBA3 | 1218 |
| IBA4 | 576 |
| FA | 15,366 |
| SSA | 219 |
| CS | 38 |

3.3. Selective Extraction with Maleic Acid

To quantify just the potential H410 substances a selective (one step) extraction with maleic acid was executed with the four IBA samples [31]. Identical sample preparation as for the sequential extraction was performed (L/S = 40 L/kg). The results are displayed in Table 3. Multiplication with the stoichiometric factors for $\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$ and ZnO resulted in the content of the respective H410 substances. According to calculation rule 2 (see Section 1) the concentrations of all H410 substances have to be multiplied by 100. If the result is below 25%, the waste is classified as non-hazardous relative to hazard property HP14. Actually, this was the case for the four tested IBA samples.

Table 3. Extracted amounts of the elements Cu and Zn after selective extraction with maleic acid at pH 4 and conversion to the respective “worst-case” substances used for the calculation of the HP14 sum (calculation rule 2).

| Sample | Cu (mg/kg) | Zn (mg/kg) | $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (mg/kg) | ZnO (mg/kg) | HP14 Sum (%) |
|--------|---------------|---------------|--|----------------|-----------------|
| IBA1 | 430.82 | 1113.02 | 749.62 | 1380.14 | 13.8 |
| IBA2 | 597.34 | 1132.59 | 1039.37 | 1404.41 | 24.4 |
| IBA3 | 559.60 | 1231.01 | 973.71 | 1526.45 | 15.3 |
| IBA4 | 746.52 | 886.56 | 1298.95 | 1099.33 | 24.0 |

The values in Table 3 are different from those for F1 in the sequential extraction experiments. The numeric values for the graphs of the results (Figure 1) are listed in the Supporting Information. Values of around 2800 mg/kg were measured for Zn in F1 for IBA 3 and 4, resulting in a HP14 sum above 25%. Samples IBA 1 and 2 are also well below the limit value in the sequential extraction experiments. For a comparison of IBA extraction with maleic acid and acetic acid, the volume of data is not sufficient.

In the present investigation, only the grain size fraction <16 mm was used. The classification of IBA according HP14, however, is based on the complete ash. It is known that heavy metal content is significantly lower in the coarse fraction [17–19], so that the results presented in Table 3 can be considered as upper value, i.e., IBA is usually to be classified as non-hazardous.

4. Discussion

The classification of IBA as hazardous or non-hazardous according to hazard property HP14 ecotoxicity is still under debate because there are still no generally accepted methods for the assessment. Biotests with aquatic and terrestrial microorganisms are often suggested for ecotoxicity assessment [36]. Here, the exact chemical composition need not be known. Observed here is the effect of the aqueous leachate of the test material on the selected organisms. In the cited work, the leachate was prepared with an L/S of 10 L/kg and then diluted by factors of 2, 4, and 8. The leachate of a moderately aged IBA has a pH of 11 [21], and even with a dilution by a factor of 8, the resulting test solution has a pH higher than 8.5, which is, however, recognized as the maximum pH for biotests. At higher pH values, the test organisms already show effects due to the pH. The provided procedures for the application of biotests are not uniform in Europe. In Austria, the leachate is diluted by a factor of 1000 in compliance with the methods described in CLP [10], i.e., the final L/S is 10,000 L/kg or, finally, 100 mg IBA per L [37]. With this approach, IBA is, not surprisingly, usually classified as non-hazardous.

There are approaches to elucidate the chemical composition of IBA by X-ray methods such as XAS, XRD, and XANES. The latter method even requires radiation from a synchrotron light source [38–40]. Although useful results are gained, the methods are not applicable for commercial analytical laboratories.

This is different for the two methods applied in the present study. With the 4-step sequential extraction, the mobilization behavior of the relevant heavy metals can be examined. For the HP14 classification, even a one-step extraction (here, called selective extraction) might be sufficient. For IBA, only the elements Zn and Cu are of relevance because the solid content of all other heavy metals is below the cut-off value of 0.1% even when stoichiometric factors are applied to convert them to chemical compounds. In this context, it is strange that for Pb the elemental concentration counts and no conversion is needed (“Note 1” in CLP, see above), although the toxicity coefficient T_i of Pb (see Table 2) is as high as for Cu and higher as for Zn. Further, setting a cut-off value (here, 0.1%) leads to non-consideration of other heavy metals rather than Cu and Zn. However, a longer list of heavy metals is under consideration for landfilling or utilization of IBA [21].

In the series of experiments performed in the present study, the limit value for a classification as hazardous waste was exceeded for two samples due to Zn concentrations of around 2800 mg/kg extracted at pH 4. In both cases, the sum of all 4 fractions was then above 4000 mg/kg, which is above the medium value for Zn presented by Hjelm et al. [16]. This could be the result of insufficient sample homogenization or the presence of small brass particles. In general, a sample size of 0.5 g for the described extractions is low in comparison to standardized leaching tests with L/S ratios of 2 or 10 L/kg. Here, the sample sizes are 500 or 100 g of waste material, respectively. Anyway, the results in the present study indicate that IBA is to be classified as non-hazardous waste. Actually, this has no implication on the possible utilization of IBA, where mainly the leaching behavior is decisive [2]. However, a classification of IBA as hazardous waste would complicate handling and transport. Further, this would negatively influence the acceptance of the material.

In a recent publication [21], it was shown that in Germany, IBA can be landfilled on a landfill class DK I [41] and utilized according to quality class HMVA-2 of the secondary building material ordinance [42].

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14135541/s1>, Figure S1: Extracted amounts of the elements As, Sb, V, Mo, Sn, and Co in fractions F1–F4 after sequential extraction; Table S1: Total content of substances in the test material in mg/kg; Table S2: Extracted amounts in the fractions F1–F4 to be used as E_j for the calculation of the STL.

Author Contributions: Conceptualization, F.-G.S.; methodology, F.-G.S.; validation, F.-G.S. and P.S.; investigation, P.S. and F.-G.S.; writing—original draft preparation, F.-G.S. and P.S.; writing—review and editing, P.S.; visualization, F.-G.S.; supervision, F.-G.S.; project administration, F.-G.S.; funding acquisition, F.-G.S. All authors have read and agreed to the published version of the manuscript.

Funding: Please add: This research was funded by German UMWELTBUNDESAMT (UBA’s Refo-Plan 2020), grant number 3720333050.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Chemical analyses and sample preparation were performed by Katja Nordhaus, Maren Riedel, Anna Böwe, Bianca Coesfeld, Inga Simon, and Ruisi Ling.

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

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