

Article

Release of Trace Elements from Bottom Ash from Hazardous Waste Incinerators

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Abstract: Bottom ash is the major by-product of waste incineration and can contain trace elements (As, Cd, Co, Cu, Cr, Mo, Ni, Pb, and Zn) with concentrations up to thousands of $\text{mg}\cdot\text{k}^{-1}$. In this study, a combination of different extractions and leaching tests (i.e., CH_3COOH and ammonium-EDTA (Ethylenediaminetetraacetic acid) extractions and pH_{stat} leaching tests) was used to investigate the potential release of trace elements from bottom ash samples derived from hazardous waste incineration plants. Although large variations have been found in the release of trace elements by different extractions, in general, the highest concentrations of most trace elements (except As and Mo) were released with the CH_3COOH extraction, whereas the release of As and Mo was highest with the ammonium-EDTA extraction. Kinetics of element release upon acidification based on a pH_{stat} leaching test at pH 4 could be related to the solid-phase speciation of some selected trace elements. The relatively high-potential mobility and elevated total concentrations of some trace elements imply a threat to the environment if these bottom ashes are not treated properly. Results of the present study may be useful to develop potential treatment strategies to remove contaminants and eventually recover metals from bottom ash.

Keywords: bottom ash; hazardous waste; kinetic release; potential mobility; trace elements; waste management

1. Introduction

When society moves towards more sustainable material cycles, recovery of metals from industrial waste can be an opportunity to turn waste into a valuable resource. It is estimated that numerous metals will be consumed in less than 50 years (Zn) or 100 years (Co, Cu, Ni, Mo, and Pb) if current rates of extraction are maintained [1]. However, sustainable reserves of these metals will remain for the future if they are recovered and the remaining reserves are used more efficiently [2]. Waste containing significant amounts of trace elements offers a potential for the recovery of these elements, since trace elements in anthropogenic matrices are often more labile compared to natural matrices (e.g., ores, rocks) [3]. Generally, the term “major elements” is used for elements which have concentrations greater than 1% and term “trace elements” has been used in geochemistry for chemical elements that occur in the Earth’s crust in amounts less than 0.1% ($1000 \text{ mg}\cdot\text{k}^{-1}$) [4]. In this study, the term “trace elements” is used to indicate particularly the elements As, Cd, Cr, Co, Cu, Mo, Ni, Pb, and Zn while the term “major element” is used to indicate the following elements: Al, Ca, Fe, K, Mg, P, S, and Si.

Waste incineration has been a preferred alternative in solid waste management since landfilling became more difficult to site due to high costs, diminishing land availability, and stricter regulations [5].

The bottom ashes (BAs) from waste incineration are often treated to recover the metals or they are reused in the cement and concrete industries to produce road construction materials in Europe and developed countries [6,7]. However, without any pretreatment, the residues which contain high amounts of leachable potentially toxic elements are also classified as hazardous wastes [8].

One of the key factors when evaluating the risks related to the management (e.g., disposal/reuse) of solid waste regarding environmental health and safety is the release of pollutants to the receiving environment. Co-disposal of different kinds of waste without knowing their leaching characteristics may pose a threat to environment, for example, the disposal of ash in an acidic environment increased the leaching of heavy metals and contaminated the ground water at the disposal site [9]. For this reason, leaching/extraction tests are commonly applied because they provide information about the potential release of constituents from solid materials to the liquid phase [10]. There are several extraction/leaching tests for solid materials, each with different purposes and implications. Among these tests, an ammonium-EDTA (ethylenediaminetetraacetic acid) extraction is usually used to determine the potential mobility of trace elements in soils and sediments as a consequence of complexation. Different types of EDTA (EDTA free acid, sodium-EDTA, and ammonium-EDTA) are used as extraction solutions [11]. Acetic acid (CH_3COOH) in different concentrations ($0.43 \text{ mol}\cdot\text{L}^{-1}$ or $0.11 \text{ mol}\cdot\text{L}^{-1}$) is often used to determine the fraction of elements in a soil or sediment that is susceptible to changes in acidity of the environment (e.g., through acid rain) [12]. Beside acetic acid, nitric acid is currently employed in pH-dependence or pH_{stat} tests to analyze the leachability of an element under acidic conditions since acetic acid is a weak acid that may form complexes.

For the sake of harmonization, ammonium-EDTA $0.05 \text{ mol}\cdot\text{L}^{-1}$ and CH_3COOH $0.43 \text{ mol}\cdot\text{L}^{-1}$ were selected as extraction solutions by the Standards Measurement and Testing (SM&T) Program to indicate respectively the “mobilizable/potentially available fractions” or the “acid extractable fractions” of elements in sediments and soils [13]. Since the release of trace elements from soils, sediments and waste materials is strongly influenced by pH, different types of tests are available to assess the release of elements due to changes in pH. While single extractions (e.g., the extraction with CH_3COOH) allow estimating element release at a single pH value, which is determined by the reagent and by the acid neutralizing capacity of the sample, pH_{stat} leaching tests allow investigating element release at a pre-defined pH value. In the standard pH_{stat} test [14], the release of trace elements is only assessed at one moment in time (after 48 h), which does not allow addressing the kinetics of the release of elements [14]. Hence, a detailed batch leaching test where the pH is kept at a preset value by using an automatic titration over time in conjunction with the analysis of the leachates at various times allows determining the release kinetics of elements due to changes in pH. This kind of test provides a more detailed assessment of time-dependent leaching behavior of trace elements.

Element leaching from BA has been the subject of many studies in different countries. An overview of some selected papers dealing with trace element leaching from BA which are relevant for the present study is provided in Table 1. It was found that leaching of trace elements from BA is pH-dependent and affected by accelerated ageing [15–17]. In developing countries, BA is sometimes treated differently from what is stipulated in legislation. For instance, some hazardous waste incinerators leave the BA covered at a dump site next to the plants (e.g., Ghana [18] and Vietnam). As for most developing countries, rapid industrial development has led to an increase in the generation of various types of industrial waste in Vietnam in recent years. However, data on the composition of BA from hazardous waste incinerators in Vietnam, as well as the potential release of trace elements from these materials are rather scarce, even though such studies provide essential information to select the most sustainable management options for this kind of waste, and eventually also contribute to the protection of the environment.

Table 1. Total concentrations (dry weight basis) of major and trace elements, mineral composition, organic carbon content (OC), and pH, and of studied BA compared to other studies. Average \pm standard deviation of 2 replicates.

Type of Bottom Ash	Unit	This Study [19]		[20]	[21]	[22]	[18]
		Hazardous Waste Incinerators		Industrial Wastes	Municipal Solid Waste Incinerators (MSWI)	Coal, Peat and Forest Residues	Hospital Medical Waste Incinerators
		AS1 *	AS2 **				
Al	%	6.06 \pm 0.33	2.90 \pm 0.12	-	6.4	1.22	
As	mg·kg ⁻¹	7 \pm 1	77 \pm 75	21.4	21	3.9	
Ca	%	1.91 \pm 0.02	3.85 \pm 0.18	6.26	9.7	-	
Cd	mg·kg ⁻¹	1 \pm 0.03	2 \pm 0.1	<0.3	14	<3.0	7.54
Co	mg·kg ⁻¹	928 \pm 23	63 \pm 11	7.8	67	2.9	
Cr	mg·kg ⁻¹	573 \pm 45	804 \pm 185	50.6	1158	10.9	99.30
Cu	mg·kg ⁻¹	1126 \pm 196	818 \pm 188	33.5	7743	16.9	
Fe	%	3.92 \pm 0.15	23.82 \pm 3.53	-	8.9	0.84	
K	mg·kg ⁻¹	3800 \pm 200	2400 \pm 2	2910	9000	-	
Mg	mg·kg ⁻¹	1900 \pm 6	7900 \pm 617	5850	15,000	-	
Mn	mg·kg ⁻¹	377 \pm 3	3597 \pm 259	1450	1000	425.0	
Mo	mg·kg ⁻¹	278 \pm 7	42 \pm 1	1.1	99	<1.0	
Ni	mg·kg ⁻¹	1373 \pm 77	233 \pm 22	24.3	356	6.3	
P	mg·kg ⁻¹	2000 \pm 47	1000 \pm 41	3430	4000	-	
Pb	mg·kg ⁻¹	63 \pm 4	817 \pm 85	5.1	1022	<3.0	143.80
S	mg·kg ⁻¹	1130 \pm 56	3820 \pm 348	1580	4950	59.4	
Zn	mg·kg ⁻¹	930 \pm 2	1461 \pm 291	340	7732	256.0	16,417.69
OC	%	3.24 \pm 0.01	0.95 \pm 0.04	-		<0.5	
pH		8.64 \pm 0.05	9.40 \pm 0.70	-			
Calcite	%	1.0	3.6	-	0.5		
Corundum	%	6.9	-	-	4.5		
Hematite	%	-	7.2	-	1.9		
Magnetite	%	3.1	13.1	-	4.2		
Mullite	%	1.9	-	-	-		
Quartz	%	10.3	7.8	-	31.4		
Rutile	%	-	2.6	-	0.8		

* = BA sample 1; ** = BA sample 2.

In the present study, BA samples that were previously partly characterized using chemical, mineralogical, and physical approaches [19] were further studied through a complementary extraction/leaching approach with focus on the potential release of trace elements under influence of acidification and complexation. Single extraction with ammonium-EDTA (0.05 mol·L⁻¹) and CH₃COOH (0.43 mol·L⁻¹), which are commonly applied to soils and sediments, were performed. The results of the single extractions were compared with the release of elements during pH_{stat} titration leaching at pH 4. This pH was chosen since it represents the worst-case scenario when the samples would become exposed to acidification at the disposal site (e.g., acid rain conditions, mixing with other acid wastes, etc.). The comparability of different extractions and leaching tests is determined by the main characteristics of the tests (the chemical reagent used, the duration of the tests, the liquid/solid (L/S) ratio). The tests used in this study are all conventional batch tests in which the leaching solution is not renewed, and the mixing is performed over a relatively short time period (hours to days) with the aim of reaching equilibrium conditions. The comparison of potential mobility of trace elements by different and extractions is not completely straightforward since operational conditions and reagents are different. The estimation of the potential trace elements' mobility is thus operationally defined by the extracting agents used [23].

The aim of the study is to investigate the usefulness of a different extraction/leaching approach focusing on the potential release of trace elements from BAs from hazardous waste incinerators under influence of acidification and complexation. The kinetic of release of the various elements under acidic conditions is also discussed and related to the solid-phase composition of the BA. It is not the purpose of the present paper to investigate the metal recycling from BA, since this would also require a detailed

economic and technological assessment. However, strategies for disposal or recycling of solid waste are also often based on the understanding of the leaching behavior of these materials [10]. In this study, the information deduced from the different methods was compared and evaluated. Results of the present study are helpful for the first steps in the evaluation the potential treatment strategies for these BAs. Results from extraction methods applied in the present study might be indicative for evaluation of options for metal recovery. Additionally, the investigation of release kinetics of trace elements under acidic conditions by a detailed batch leaching test is helpful to gain a better understanding of acid neutralization capacity as well as the solid-phase composition of the BA. Since this is just the first estimation for the usefulness of the CH_3COOH and ammonium-EDTA extraction, we use standardized conditions, using more diluted extraction agents and high liquid/solid (L/S) ratios instead of severe conditions with more concentrated agents and low L/S ratios. Moreover, mild extraction conditions are used since the chemical consumption should be minimized during BA washing for multiple reasons. Several studies have dealt with bottom ash from municipal solid waste incineration; however, bottom ash from hazardous waste incineration has not been the subject of many studies before. This paper will improve our understanding of the release of trace elements under different external factors that BAs may encounter during their processing or management. Extraction and leaching methods applied in the present study are standardized tests that have been developed for soils and sediments. Developing novel extractions for waste materials is not the purpose of the present study. However, the approach used in this study is useful to evaluate the fraction of metals that can be leached out from BA, in view of metal recovery and treated BA disposal/use. This approach is necessary for the development of appropriate waste management options, especially in countries facing inefficient waste and waste water treatment technologies, resulting in residual waste materials with considerable concentrations of valuable elements.

2. Materials and Methods

2.1. Material Characterization

The BA samples in the present study were collected from two hazardous waste incinerators in Ho Chi Minh City, South Vietnam. At the time of sampling, source material from the plant from which sample AS1 was collected included sludge from the waste water treatment of textile and printing ink production factories, and chemical containers. The general input for the incineration facility where AS2 was collected was sludge from waste water treatment of a textile dyeing factory, cloths containing chemical and lubricants, and out of date chemicals. After sampling, the BA materials were stored in plastic bags and brought to KU Leuven, Belgium for further treatment and laboratory analysis. More details about sampling and sample pretreatment and the determination of chemical and mineralogical composition of the samples can be found elsewhere [19]. In general, the composition of BA varies greatly and depends on the input material and the applied incineration technology. The BA samples in the present study were collected from two-stage incinerators having a quite low combustion temperature (550–650 °C) which can influence the complete burning of organic matter and the forming of metal oxides. Moreover, inputs of hazardous waste incinerators vary widely depending on the type of plants.

Some general characteristics (pH, total elemental concentrations, organic carbon content and mineralogical components) of these samples compared to other studies are summarized in Table 1. The fraction >2 mm determined by sieving was 12% for both samples. Mineralogical characterization was carried out by X-ray diffraction (XRD). According to XRD results, the studied BAs were mainly composed of oxides and Ca-, and Si-minerals. Magnetite (Fe_3O_4), quartz (SiO_2), and calcite (CaCO_3) were found in both samples. Corundum (Al_2O_3) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) were detected in sample AS1 and hematite (Fe_2O_3) and rutile (TiO_2) were found in sample AS2 (Table 1). Total element concentrations in these samples were compared to the composition of other BA from different sources including industrial wastes, MSWI, coal, peat and forest residues, and hospital medical

waste incinerators. Both samples were characterized by a low concentration of Ca and P compared to the composition of other BA. Iron concentration in AS2 was much higher compared to its concentration in AS1 and other BA (Table 1). The total element concentrations of some trace elements in the two BA samples were compared to the Flemish limit values for recycling of granular material in construction applications to evaluate whether the studied BAs would be suitable for being used in construction applications. Results indicated that Cu (sample AS1 and AS2), Ni (sample AS1) and Zn (sample AS2) exceeded the Flemish limit values for recycling of granular material in construction applications [24]. Moreover, according to the Vietnamese National Technical Regulation on Hazardous Waste Thresholds, As and Pb (sample AS2) exceeded the limit values [25]. This might raise concerns regarding the potential hazard of using this BA as a construction material if no pretreatment is applied.

2.2. Extractions/Leaching Test

Extractions and leaching test were performed at room temperature (20 °C). The ammonium-EDTA extraction followed the protocol of the Standards, Measurement and Testing (SM&T) Program [26]. Ammonium-EDTA 0.05 mol·L⁻¹ solution was added to the dry sample with a liquid/solid (L/S) ratio of 10 (L·kg⁻¹). The suspension was shaken for 1 h in a reciprocal shaker, centrifuged (3500 rpm, 10 min), decanted and filtered (0.45 µm, Chromafil® PET-45/25, Macherey, Düren, Germany). The acid extractable fraction (generally considered to consist of exchangeable elements and elements bound to carbonates) was also based on the procedure described by the SM&T programme using an extraction with CH₃COOH 0.43 mol·L⁻¹ [27]. The CH₃COOH 0.43 mol·L⁻¹ solution was added to the dry sample to obtain a liquid/solid (L/S) ratio of 40 (L·kg⁻¹). The suspension was shaken for 16 h in a reciprocal shaker, centrifuged (3500 rpm, 10 min), decanted off and filtered (0.45 µm, Chromafil® PET-45/25, Macherey, Düren, Germany). After extraction, the pH of the extracts was measured with a pH Hamilton single-pore electrode.

The pH_{stat} leaching test was carried out employing an automatic multitrans titration system (Titro-Wico Multititrator, Wittenfield and Cornelius, Bochum, Germany). 80 g of dried sample was put in an Erlenmeyer flask together with 800 mL of Milli-Q water (L/S ratio = 10 L·kg⁻¹). Element release was measured at regular time intervals (0, 1, 3, 6, 12, 24, 48, 72 and 96 h). Bottom ash samples were first shaken for 30 min at the natural BA-pH (without acid addition) before the effective pH_{stat}- experiment was started. A sample of 5 mL of the suspension was taken over a filter (0.45 µm, Chromafil® PET-45/25, Macherey-Nagel GmbH & Co. KG, Düren Germany) by means of a syringe attached to a flexible tube at regular time intervals. This pH_{stat} test corresponds to the CEN/TS 14997 test [14], except that the leachate is not only sampled after 48 h, but at regular time intervals. Moreover, in the present study, the pH_{stat} tests were only performed at pH 4. The objective of this test was to examine the kinetic release of trace elements under acidic conditions, while the pH of the suspension (bottom ash suspended in water) is kept at a constant value (pH = 4) by continuous titration with HNO₃ (1 mol·L⁻¹). Due to the variety of processes occurring at landfills or open dumps such as sulfide oxidation, microbial activity, acidic deposition and reaction with atmospheric CO₂, the pH of ash in landfills may drop to a value as low as 3 to 5 [28]. Hence pH 4 was chosen to address a worst-case scenario of acidification.

2.3. Analysis and Quality Control

Single extractions with ammonium-EDTA 0.05 mol·L⁻¹ and CH₃COOH 0.43 mol·L⁻¹ were done in duplicate and the results are presented as a mean value. Blank solutions were also inserted in each batch of extractions. A certified reference material (BCR 483) was also analyzed for quality control (Table 2).

Table 2. Comparison of the results of the ammonium-EDTA 0.05 mol·L⁻¹ extraction and CH₃COOH 0.43 mol·L⁻¹ extraction of BCR 483 (average ± standard deviation of 2 replicates) and certified values.

Element	Ammonium-EDTA 0.05 mol·L ⁻¹ (This Work)	Ammonium-EDTA 0.05 mol·L ⁻¹ (Certified Values)	Acetic Acid 0.43 mol·L ⁻¹ (This work)	Acetic Acid 0.43 mol·L ⁻¹ (Certified Values)
Cd	20.7 ± 0.7	20.4 ± 1.3	19.6 ± 0.5	18.3 ± 0.6
Cr	37.6 ± 9.8	28.6 ± 2.6	26.3 ± 1.6	18.7 ± 1.0
Cu	192 ± 7	215 ± 11	38.2 ± 1.2	33.5 ± 1.6
Ni	24.2 ± 1.4	28.7 ± 1.7	25.5 ± 1.5	25.8 ± 1.0
Pb	189 ± 17	229 ± 8	1.9 ± 0.2	3.1 ± 0.25
Zn	529 ± 16	612 ± 19	659 ± 34	620 ± 24

The extracts/leachates were acidified immediately after the experiments, with concentrated HNO₃ to bring the pH < 2. The EDTA extracts were kept at 4 °C and not acidified prior to analysis to prevent precipitation of EDTA salts at low pH. Elemental concentrations (Al, Ca, Fe, K, Mg, P, S, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn) were measured by ICP-OES (Varian 720-ES). A Varian 720-ES instrument supplied with double-pass glass cyclonic spray chamber, concentric glass nebulizer SeaSpray and “extended high solids” torch was used. Solutions were introduced into the spectrometer using the Varian SPS3 sample preparation system. Calibration solutions were prepared from certified multi-element ICP standard stock solutions and from Plasma HIQU (High Quality) single element solutions from CHEM-LAB (Belgium). Blanks were also included in the calibration. All solutions were prepared from 18 MΩ·cm⁻³ ultra-pure water supplied from Millipore system and stabilized with ultra-pure nitric acid (CHEM-LAB). Sensitivity, linear dynamic range, and freedom from spectral interferences were taken into consideration during wavelength selection for each element. Each measurement was carried out with three replicates.

3. Results

In this study, although results and discussion mainly focus on trace elements (As, Cd, Co, Cr, Cu, Ni, Mo, Pb, and Zn), major elements (Al, Ca, Fe, K, Mg, P, S, and Si) are sometimes mentioned because of their relevance for interpretation of release mechanisms of elements of interest.

3.1. Single Extractions

The results of ammonium-EDTA and CH₃COOH 0.43 mol·L⁻¹ extractions for the studied BA samples are displayed in Table 3. Extractability is expressed in percent of an element extracted with ammonium-EDTA and CH₃COOH extraction relative to its total concentration in the (solid) sample. Ammonium-EDTA extraction was used to determine the potential mobility of trace elements as a consequence of complexation and used as an estimation of the “pool” of a specific element that can deliver elements from the solid phase to the solution [13]. Moreover, it can also give a rough indication on the bioavailability of some trace elements and it is sometimes used to assess the availability of trace elements to plants [29,30].

Among the examined trace elements, Cd (in AS1) and Pb (in AS2) showed the highest EDTA extractability (27 and 31% of the total content in the samples, respectively) while EDTA extractability of some other trace elements such as Co (3%), Ni (2–3%), Cr (0.2–0.6%) and Mo (10%) is rather similar despite of their difference in total concentrations in both samples (Table 3).

Table 3. Extractability (as% of total concentration) of elements from ammonium-EDTA and acetic acid extractions.

Element	AS1 (%)		AS2 (%)	
	EDTA	CH ₃ COOH	EDTA	CH ₃ COOH
Major elements				
Al	0.2	4	1	20
Ca	87	100	45	87
Fe	1	7	0.1	2
K	5	10	8	19
Mg	25	47	7	50
Mn	9	23	1	11
P	13	13	5	12
S	98	100	36	37
Trace elements				
As	14	< 6	2	< 0.5
Cd	27	65	< 3	< 3
Co	3	17	3	25
Cr	0.6	3	0.2	4
Cu	22	33	11	29
Mo	10	6	10	< 0.9
Ni	2	15	3	27
Pb	9	< 1	31	42
Zn	20	43	6	29

Although Cd reached the highest extractability in AS1, its concentration in the EDTA extract was below limit of quantification (LOQ) in AS2. Arsenic also had a low EDTA-extractable fraction (2%) in sample AS2, but in sample AS1, 14% of the total As concentration was extracted. Similar to As and Cd, Zn also displayed a higher extractability in sample AS1 (20%) compared to sample AS2 (6%). Results of As and Cd were in accordance with Ca and S, since both Ca and S reached a high extractability in AS1 (87–98%), and a slightly lower extractability in AS2 (36–45%). A study of ash from coal combustion, Nugteren (2008) [31] reported that As, Cd, and Mo are belonging to the group of elements which are associated with calcium oxides and sulfates. However, FEG-EPMA analyses of the bottom ash samples indicated that Mo (in AS1) was related to Fe-bearing phases, while As and Cd could not be observed during solid-phase characterization with FEG-EPMA [19]. The extractability of Cu (AS1 and AS2) and Pb (AS2) was quite high compared to other trace elements. The high EDTA extractability of Cu and Pb (respectively 22% (in AS1) and 31% (in AS2) of their total content in the samples) might be explained by the high complexation constants for these two elements with EDTA ($\log K = 17.8$ and 18.3 , respectively) [12].

The concentrations of elements extracted with CH₃COOH varied between the two BA. Besides Cd (in AS1) and Pb (in AS2), Zn and Cu showed a high extractability (29–65% of their total concentration). In contrast, Cr, As and Mo display a low extractability ($\leq 6\%$). It should be mentioned that Pb and Cu are characterized by a higher stability for mononuclear monoligand and biligand complex systems with CH₃COOH compared to other metals [32,33]. However, the high extractability of Cd, Pb, Zn, and Cu can be a combination of both high stability of the acetate complexes and the drop of pH during extractions. In both samples, Co and Ni were released in similar amounts (15–17% for AS1 and 25–27% for AS2, respectively) possibly because they originate from the same host phases, namely Fe-alloys or Fe-oxides [19].

For both single extractions, Ca and S (in AS1) showed the highest extractability among the examined elements. Ca and S in AS1 were totally extracted during the CH₃COOH 0.43 mol·L⁻¹ extraction. In general, major cations present in the solid samples may be one of the factors affecting trace element extraction efficiency due to their competition to form complex compounds with EDTA [34].

The dissolution of calcite can consume EDTA in calcareous soils, lowering the extraction efficiency for trace elements [35]. In the present study, important amount of Ca (87%) was extracted with ammonium-EDTA (Table 3), possibly affecting the extraction efficiency of the reagent.

3.2. Acid Neutralization Capacity (ANC) and Trace Element Release at pH 4

The $ANC_{pH4, 96h}$ (i.e., the amount of acid added to maintain a pH of 4 until 96 h after the start of the pH_{stat} titration) of sample AS2 ($936 \text{ mmol}\cdot\text{kg}^{-1}$), was nearly double to the $ANC_{pH4, 96h}$ of sample AS1 ($510 \text{ mmol}\cdot\text{kg}^{-1}$). The higher amount of calcite as determined by XRD in sample AS2 (3.2%) most likely explains the difference in ANC between both samples. Although the pH change during the extraction with CH_3COOH $0.43 \text{ mol}\cdot\text{L}^{-1}$ might provide an indication of the ANC of the two BA samples, the difference in the final pH of the CH_3COOH extracts was not that high (final pH of 3.26 and 3.44 for AS1 and AS2 respectively). The initial pH of the CH_3COOH solution was 3.02. The reason for this small difference in pH, despite the important difference in ANC, might be the short duration of the CH_3COOH extraction test (16 h) in which the slow buffering reactions are not fully considered [36]. Hence, pH_{stat} leaching tests, performed for a longer period (96 h in the present study) likely allow a better estimation of ANC from BA samples. It should also be mentioned that weathering of BA (natural or artificial) is responsible for increasing the buffering capacity of the BA [15]. Several studies have shown that leaching for several metals appears to be less important than from fresh BA after weathering [37,38]. However, a study about the carbonation (artificial weathering) of BA from municipal solid waste incinerator, Van Gerven et al. (2005) [39] reported an increase in the leaching of Cr and a constant leaching of Mo and Sb after carbonation of BA. Therefore, ANC of a BA is very important and should be better estimation to investigate the release of trace metal upon external addition of H^+ .

The evolution of ANC and the release of Ca with time in both samples during pH_{stat} leaching are displayed in Figure 1.

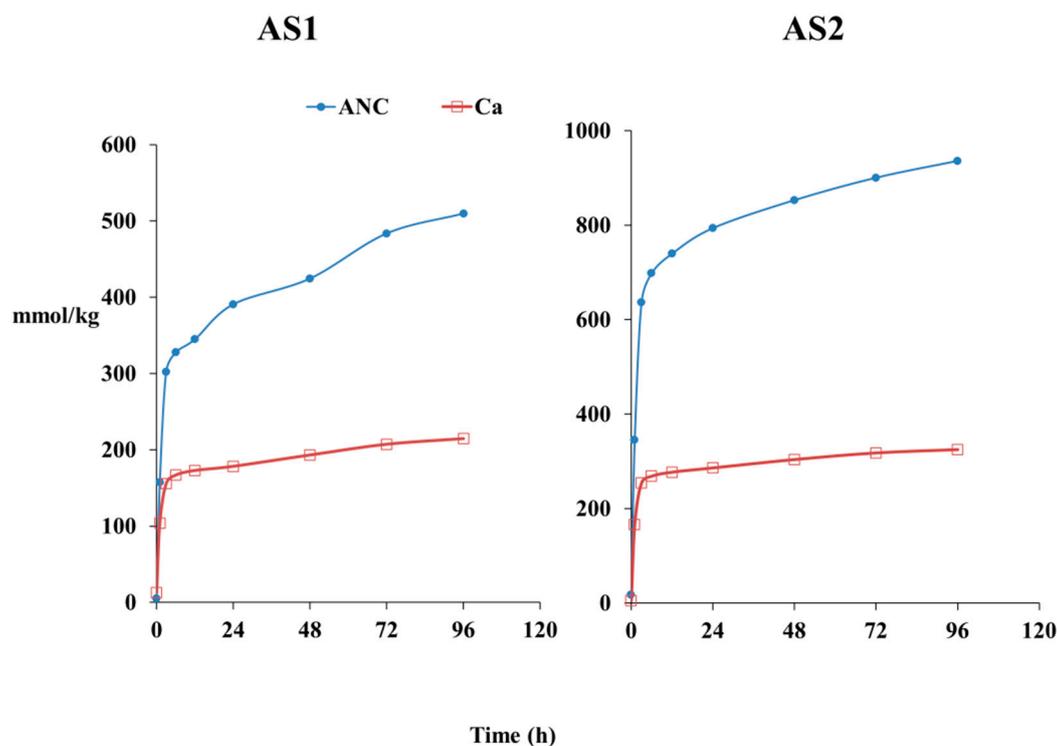


Figure 1. Evolution of ANC and Ca during pH_{stat} leaching test (pH 4).

We performed XRD phase analysis on residual BAs after pH_{stat} leaching (at $\text{pH} = 4$) to assess leaching related to changes in major solid phases. XRD phase analysis on the residual BAs after the pH_{stat} leaching (at $\text{pH} = 4$) showed that some peaks of calcite (CaCO_3) decreased in intensity (Figure 2). This suggests that main mineral phases in the BAs were stable at $\text{pH} 4$, except small change was observed for calcite. Possibly, the dissolution of other mineral phases was too small to be detected by the XRD technique.

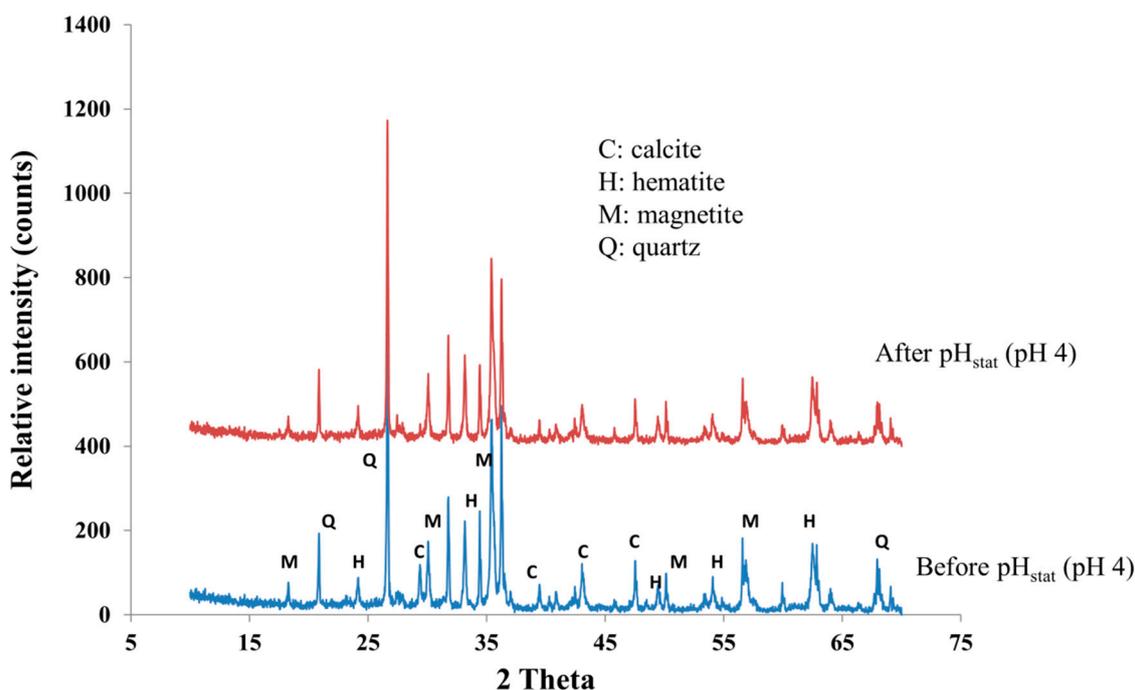


Figure 2. XRD patterns of original sample and sample after the pH_{stat} test ($\text{pH} = 4$, sample AS2).

In the following section, leachability refers to the concentration in the final leachate (after 96 h) expressed in percent of an element leached relative to its total concentration in the (solid) sample (Table 4) except for Mo in sample AS2 since its concentration in the leachates decreased to values below the LOQ from 3 h onward. For the latter, the concentration in the leachate after 1 h was used.

In both BA samples, despite the high total concentration, Al, Fe, and P exhibit very low leachability ($<0.5\%$) compared to other major elements, such as Ca, K, Mg, Mn, and S ($>2\%$). This suggests that no significant dissolution of Al-Fe-P containing minerals occurred during the pH_{stat} leaching test. Release of some selected major and trace elements during pH_{stat} leaching are displayed in Figures 3 and 4. Cadmium concentrations in the leachates from both samples were below LOQ likely due to the low total Cd-concentrations ($\leq 1.5 \text{ mg}\cdot\text{kg}^{-1}$).

Table 4. Leachability (as% of total concentration) of elements in the pH_{stat} test (after 96 h or, except for Mo in sample AS2, after 1 h).

Heading	AS1 (%)	AS2 (%)
Major Elements		
Al	0.1	0.4
Ca	45	34
Fe	0.3	0.02
K	5	7
Mg	14	14
Mn	5	2

Table 4. Cont.

Heading	AS1 (%)	AS2 (%)
P	0.03	0.04
S	54	22
Trace Elements		
As	<1	<1
Cd	<6	<3
Co	3	6
Cr	0.04	0.02
Cu	3	2
Mo	1	0.3
Ni	3	6
Pb	<0.2	1
Zn	9	3

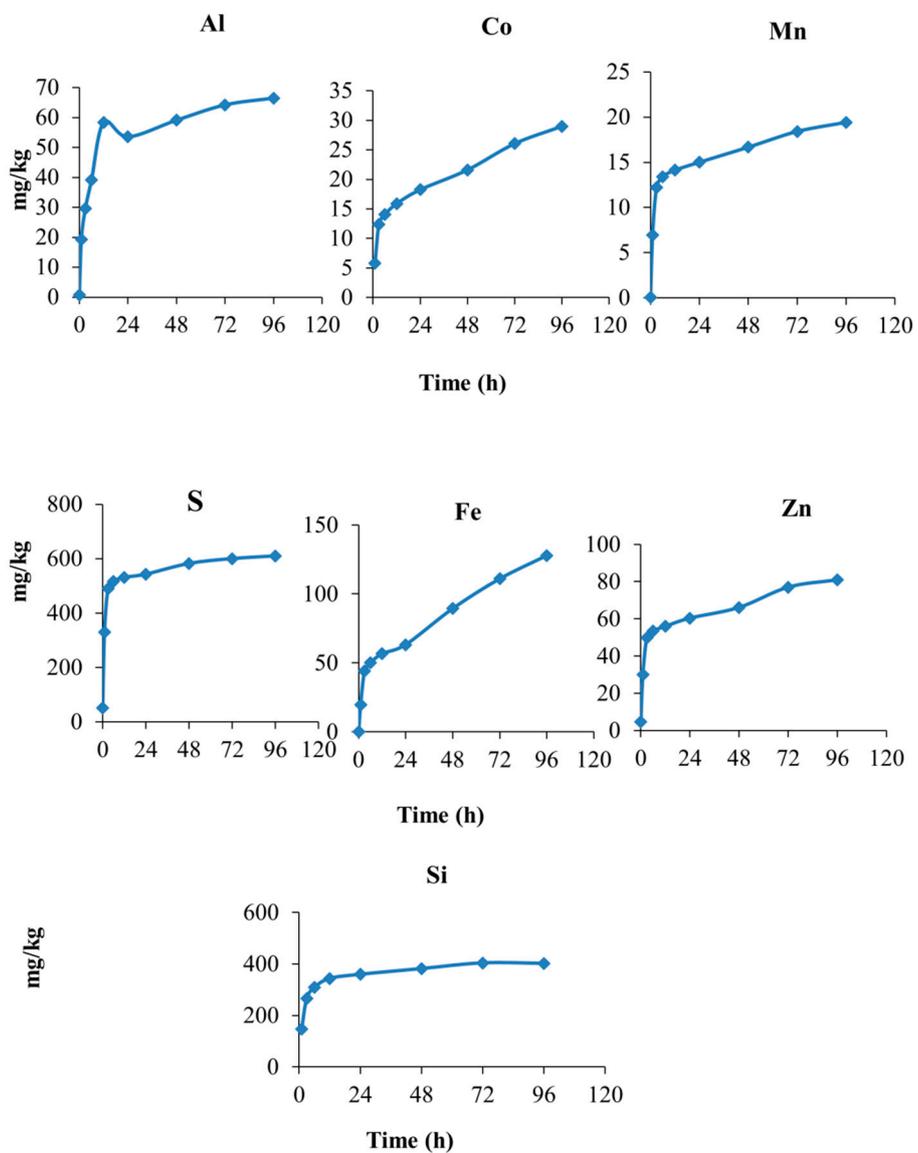


Figure 3. Release of major elements and some selected trace elements from AS1 during pH_{stat} leaching (at pH 4).

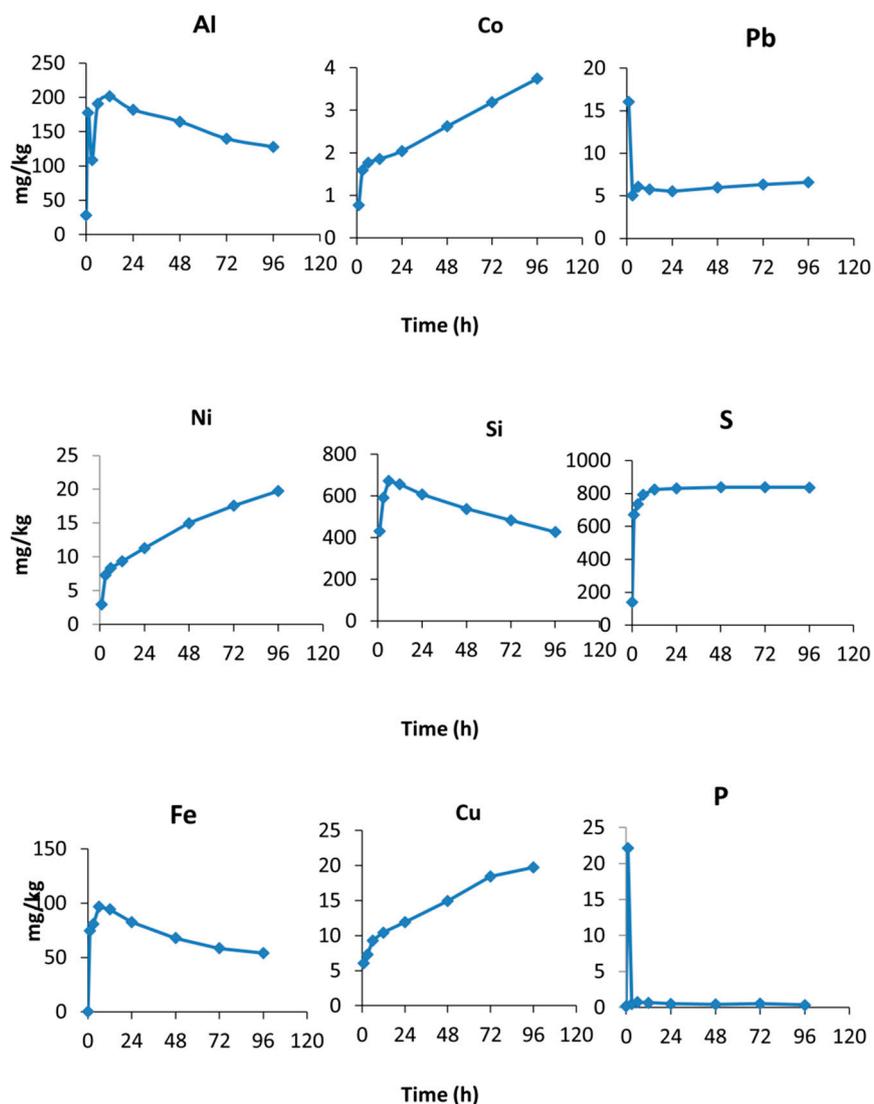


Figure 4. Release of major elements and some selected trace elements from AS2 as a function of time during pH_{stat} leaching (at pH 4).

In the leachate of sample AS1, As and Pb were below LOQs while released Cr concentration was very low (0.04% or $0.3 \text{ mg}\cdot\text{kg}^{-1}$ was released at pH 4). The leachability of Co, Cu, Mo, and Ni varied between 1–3%. The highest leachability was observed for Zn (9%).

In sample AS2, most of trace elements were only detected in the leachates after 1 h except Cr, Mo and Zn which were already released immediately from the start of the experiment. Arsenic concentrations in the leachate varied just around LOQ while Mo was released at the beginning of the pH_{stat} experiment, but the concentration decreased below LOQ after 3 h of leaching. Nickel exhibits the highest leachability (8%), while other trace elements such as Co, Cu, Pb and Zn show a moderate leachability (1–6%). Chromium exhibited a low leachability (0.02%) despite its high total concentration ($804 \text{ mg}\cdot\text{kg}^{-1}$). This indicates that most of the trace elements in the BAs do not occur in readily soluble forms, even if the external pH is lowered to a value of 4.

4. Discussion

4.1. Potential Release of Trace Elements Based on Different Extractions/Leaching Test

The results after 48 h of pH_{stat} leaching in this study corresponds to the standard pH_{stat} test CEN/TS 14997 test [14] at pH 4. Therefore, comparing the release of trace elements by the CH_3COOH extraction, ammonium-EDTA extraction and after 48 h of pH_{stat} leaching provides information on the potential release of trace elements in BA samples based on standardized extraction/leaching tests. The release of some selected trace elements from CH_3COOH $0.43 \text{ mol}\cdot\text{L}^{-1}$ and ammonium-EDTA $0.05 \text{ mol}\cdot\text{L}^{-1}$ extraction compared to the amount of these trace elements extracted with pH_{stat} leaching test (determined with 48 h) is displayed in Figure 5.

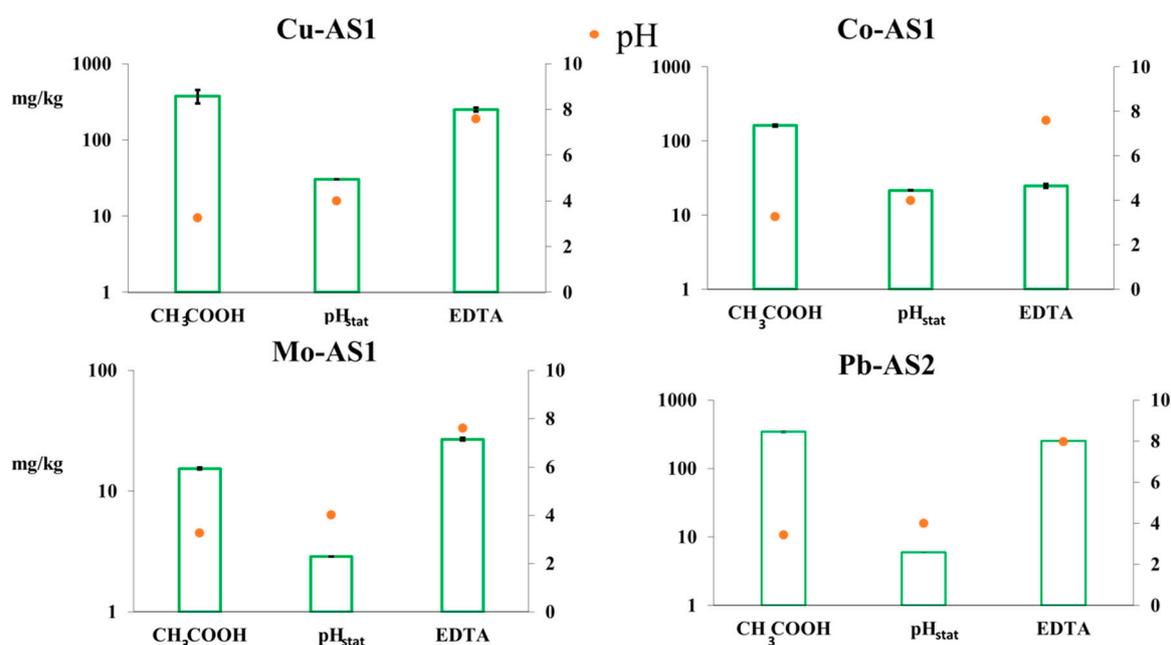


Figure 5. Release of Cu-Co-Mo (in AS1) and Pb (in AS2) after acetic acid $0.43 \text{ mol}\cdot\text{L}^{-1}$ and ammonium-EDTA $0.05 \text{ mol}\cdot\text{L}^{-1}$ extraction compared to the amount of these trace elements released by the pH_{stat} leaching test (after 48 h).

Most of trace elements showed the highest extractability with CH_3COOH , while As and Mo were most effectively extracted with ammonium-EDTA. The high amount of trace elements (except As and Mo) that were extracted by CH_3COOH can be explained by the low pH (pH = 3.26–3.44) of the CH_3COOH extract. Acidification has a pronounced effect on the release of trace elements from the studied BAs. Removal or recovery of trace elements from ash by acid leaching has been studied to find out the most effective leaching agent [24,40,41]. However, this recycling option suffers from some drawbacks such as the use of large amounts of acid due to the high ANC of ashes and the generation of wastewater. The more important extraction of As and Mo by ammonium-EDTA compared to CH_3COOH extraction and pH_{stat} leaching at pH 4 is related to the fact that they may occur as oxyanions which are known to be leached more under alkaline conditions than in acidic conditions. The pH of the CH_3COOH extract is 3.26 (AS1) and 3.44 (AS2), whereas the pH of the solution of the pH_{stat} leaching test was continuously kept at 4. Contrarily, the pH of the ammonium-EDTA extract is neutral to slightly alkaline with values of 7.59 (AS1) and 7.98 (AS2). Some trace elements such as Cd, Cu, Ni, Pb, and Zn can form complexes with dissolved organic carbon (DOC) which may enhance the leaching of these elements. Increased Cu leaching from MSWI bottom ash by DOC complexation was observed by [42,43]. Cu in AS1 exhibited a slightly higher mobility at alkaline pH values (9–11) compared to neutral pH, which can be related to the fact that Cu forms organometal complexes with

dissolved organic matter in the leachates of sample AS1 at high pH [19]. Unfortunately, data of DOC in the leachates are not available; hence, the possible effects of complexation with DOC could not be evaluated in the present study.

The relatively high-potential mobility of Cu, Pb and Mo deduced from the ammonium-EDTA extraction, in combination with elevated total concentrations of Cu and Mo (in AS1) and Pb (in AS2) indicate a higher possibility of recovery of these metals from the BA. Up to 250 mg Cu/kg and 27 mg Mo/kg (in AS1) and 251 mg Pb/kg (in AS2) were released by the ammonium-EDTA extraction.

Removal of contaminants from ashes by washing with chelating agents (e.g., citrate buffer, EDTA or oxalate buffers) has been suggested since chelating agents can remove significant amounts of contaminants present in mobile forms in the outer layer of the ash particles [22]. Pre-washing with water, increasing the concentration of EDTA and increasing the extraction time even increase the extractability [41]. A high extractability of Cu (100%), Pb (94%) and Zn (40%) was observed from the fly ash with pre-water washing followed by a 24 h extraction with EDTA $0.1 \text{ mol}\cdot\text{L}^{-1}$ (end pH 8.2 and L/S $5.0 \text{ L}\cdot\text{kg}^{-1}$) [41]. However, it is worth noting here that results for fly ash are not directly transferable to the BA samples in this work due to the differences in particle size, chemical composition, and mineralogy. Extraction efficiency obtained in the present study can probably be improved, by increasing the concentration of the EDTA solution, adapting the extraction time, L/S ratio, temperature, etc. It was not the purpose of the present study to investigate the optimal condition for maximal element recovery from the BA samples. However, the result show that the extractions used in the present study can be used for a relatively cheap and fast screening of the potential of element recovery from waste materials.

4.2. Kinetics of Trace Element Release during Leaching Test at pH 4

Understanding the kinetics of trace elements release is important for predicting the environmental risks associated with these elements over time. Kinetic leaching experiments performed on solid materials have shown that element leaching can be described by two steps, representing a fast release process followed by a slow process [44]. In this study, time-dependent leaching behavior of trace elements could be divided into three types (Figure 6), considering fast and slow release processes.

Type 1 includes elements which are released slowly, and steady state is not reached (e.g., Co and Ni in both samples, as well as Cu in AS2 and Zn in AS1). This type of element release is related to the desorption of elements that are strongly bound to solid phases or to the slow dissolution of solid phases. Similar leaching patterns of Co and Ni from both samples support the hypothesis that they might come from the same host phase or that they are retained by similar binding mechanisms. Compositional analysis by EPMA-EDS indicated that Fe, Co, and Ni co-existed in the analyzed spots in sample AS1 [19]. The slow release of Ni and Co is most likely due to the fact that Ni and Co are occluded in stable phases such as Fe-alloys and Fe-oxides and thus showed a slow mobilization under acidic environmental conditions. Similar time-dependent leaching patterns of Fe, Co, and Ni (Figure 3) from sample AS1 support this hypothesis. Although the Fe content of sample AS2 was much higher (24%) compared to that of sample AS1 (4%), it should be mentioned here that the total concentration of Co and Ni in AS2 is not that high (63 mg Co/kg and 233 mg Ni/kg), and Ni and Co did not show a release pattern similar to Fe in sample AS2. In sample AS1, Zn occurs in Si-rich phases which might be related to quartz, mullite or amorphous phases [19]. The release pattern of Zn during the pH_{stat} leaching test in this study (Figure 3) is quite similar to the release of Zn from glass phases as observed by [45]. Moreover, quartz and mullite are known as stable phases under neutral and mildly acid conditions while Zn was observed to leach up to 9% in pH_{stat} leaching test (Table 4). Therefore, Zn might be associated with amorphous or poorly crystalline phases, which are more easily dissolved than stable phases.

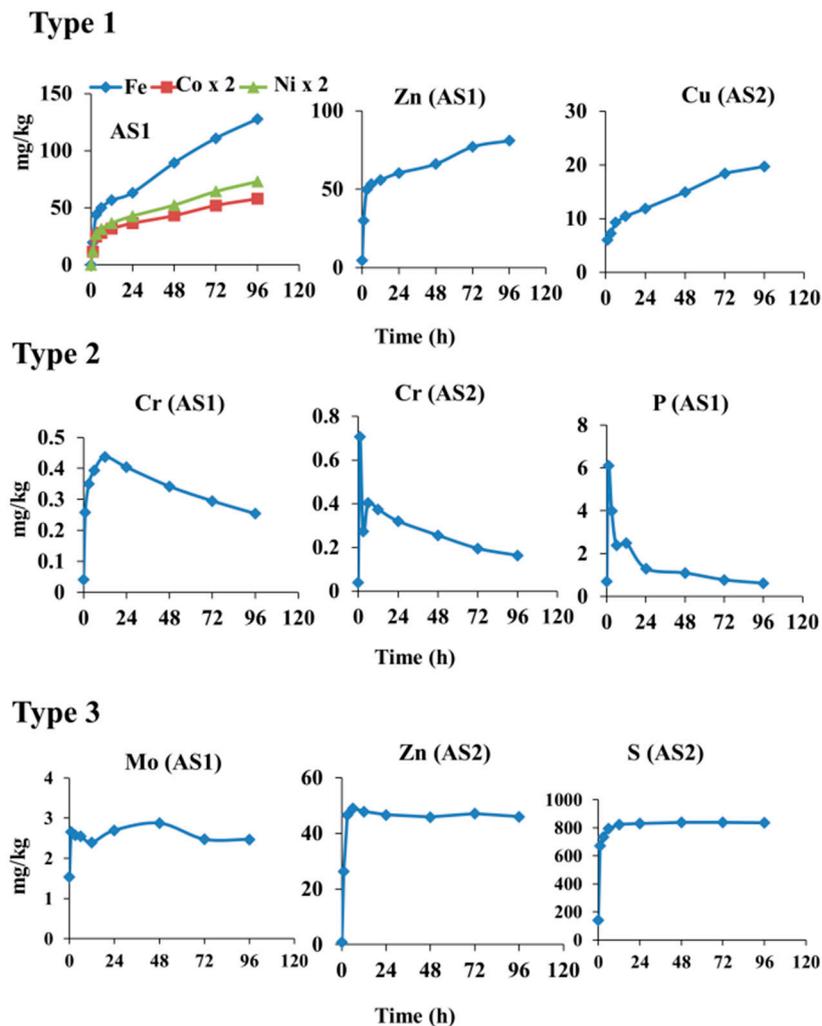


Figure 6. Release of Fe (AS1), P (AS1), S (AS2) and some selected trace elements illustrating three different types of time-dependent leaching behavior during pH_{stat} leaching (at pH 4). Co and Ni concentrations were multiplied by a factor of 2 for a better visualization.

Release of elements according to “type 2” is characterized by an initial release at the beginning of the pH_{stat} leaching test, followed by a decrease in dissolved concentrations over time. This type of release is related to precipitation reactions or re-adsorption onto solid phases (e.g., Cr and P in both samples). This is the case for example when elements forming oxyanions (e.g., chromate) are re-adsorbed on positively charged reactive surfaces at acidic pH. This phenomenon could not be assessed in the single extraction test (e.g., CH_3COOH extraction) due to the short duration of the extraction and the fact that only the final leachate was analyzed.

The last type of leaching pattern (“type 3”) is related to elements which are released rapidly, and steady state seems to be reached after more or less 6 h (e.g., Cu–Mo in AS1 and Zn in AS2). Mo was also observed in Fe-rich phases in sample AS1 by FEG-EPMA; however, its leachability was higher compared to other elements associated with Fe-rich phases. The release kinetics of Mo (AS1) during pH_{stat} leaching is also faster than Co and Ni (Figure 3) suggesting that this element might not be incorporated into crystalline phases but is distributed on the surface of Fe-rich phases. Although Zn-bearing phases were not identified by XRD and FEG-EPMA in sample AS2 [19], the release behavior of Zn during pH_{stat} leaching was similar to S (Figure 6), suggesting that Zn may also exist in S-rich phases or that Zn and S are bound to a solid phase in a similar way.

It can be deduced from the pH_{stat} test that release mechanism of elements from BA are probably related to the surface processes on the solid material such as desorption and re-adsorption, or to solubility of mineral phases. When pH is lower, desorption happens since the presence of hydrogen ions displaces metals that bound on the solid surfaces [46]. Precipitation or re-adsorption onto solid phases is observed for some elements which form oxyanions such as Cr and P. It was concluded by [47] that solid solution formation is frequently believed to be a controlling mechanism for oxyanion leaching, for example for Cr (VI) in MSWI bottom ash.

5. Conclusions

In the present study, two BA samples characterized by a different mineralogical and chemical composition and with a different ANC were investigated applying some standardized extractions/leaching tests (CH_3COOH extraction, ammonium-EDTA extraction, and pH_{stat} leaching test). A high extractability of trace elements (except As and Mo) was observed in the CH_3COOH extraction which also resulted in the lowest pH among the experiments. pH_{stat} leaching allows investigating the kinetics of element release under acidic conditions and can be linked to the solid-phase characteristics of some selected trace elements. Nickel and Co are occluded in stable phases such as Fe-alloys and Fe-oxides while Zn might be associated with amorphous or poorly crystalline phases. Moreover, Zn may also exist in S-rich phases. Based on the results obtained in this study, some preliminary treatment to remove trace elements (e.g., by washing) or immobilize trace elements from the ash should be applied to the studied BAs before landfilling. This is necessary to avoid contamination of the environment, both as consequence of the high total concentrations and because of the relatively high mobility (as deduced from single extractions) of Cu-Mo (in AS1) and Pb (in AS2). Additionally, the potential recovery of some metals should be explored. The extractions and leaching tests applied in this study, which are generally used for preliminary screening in assessment of elemental mobility, could also be used for a first estimate of the potential recovery of valuable elements from waste materials. The approach used in this study is helpful for the development of appropriate waste management options, especially in countries facing inefficient waste and waste water treatment technologies, resulting in residual waste materials with considerable concentrations of valuable elements.

Author Contributions: T.T.T.D. designed and performed the experiments. T.T.T.D. interpreted the results with significant contribution of Valérie Cappuyns. T.T.T.D. wrote the paper and significant contribution to writing was made by V.C. and R.S.E.V. performed ICP-OES analysis.

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