



Research article

Municipal solid waste incineration (MSWI) fly ash composition analysis: A case study of combined chelatatant-based washing treatment efficiency

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ABSTRACT

The challenge of sustainable use of MSWI residues such as fly ash is particularly acute. One of the possible uses of these residues in making secondary building materials. However, MSWI fly ash is highly contaminated with toxic elements such as Pb, Zn, Cd, Cu, etc. Its treatment to reduce the environmental impact is required before reuse or disposal. Here, the efficiency of a new three-step combined treatment with two complexing agents (ethylenediaminetetraacetate and gluconate) to increase the toxic-element elution from fly ash in contrast to conventional water-only treatments is shown. The compositions of raw and differently treated (reagent-combined and water-only treatments) MSWI fly ash were compared by macro- and microelemental, mineralogical, and microstructure analysis, in addition to the standard leaching test. The relevancy for such comprehensive analysis of MSWI fly ash prior and after treatments to minimize the environmental risks is shown. For Cd, Cu, and Zn, the combined treatment is proved to be 10–1000-fold more efficient than the water-only one. It was shown that the same WFA, which seems non-hazardous according to the leaching test after being washed with water, proves to be extremely hazardous when more properties are taken into account. Thus, it is relevant not only to study the leaching of WFA components and the factors affecting it, but also to pay detailed attention to amounts of elements remaining in the material after treatments.

1. Introduction

The utilization of waste residues challenge has been dealt with for over 25 years (Goumans et al., 1991). During the incineration process of municipal solid waste, ash residues are approximately 80% (w/w) bottom ash and 20% (w/w) fly ash (Wiles, 1995). High concentrations of chloride, sulfate, lead, zinc, copper, etc. turn waste fly ash (WFA) into a “hazardous waste” (Kamon et al., 2000; Nowak et al., 2013; van der Bruggen et al., 1998). Due to the landfill space reduction along with environmental regulations concerning potential leaching of various pollutants into ground waters (Lovell et al., 1991), these residues should be treated. To convert WFA into a safe material suitable for landfilling or reuse, it is necessary to reduce the leaching of potentially toxic elements (PTEs).

Main ways to achieve this goal have been: water washing in combination with solidification (Ferreira et al., 2002; Mangialardi, 2004, 2003), stabilization using various chemicals (Eighmy et al., 1998; Quina et al., 2010), adding silica fume to hydrated WFA pastes (Li et al., 2014), carbonation (De Boom et al., 2014; Ecke, 2003), and thermal treatments (Huber et al., 2016; Wey et al., 2006). However, recently,

metal extraction from WFA (Kersch et al., 2003; Pedersen, 2002) to retrieve valuable metals has become comparably attractive (Karlfeldt Fedje et al., 2012; Tang and Steenari, 2015). As metal concentrations in WFA are considerable, research has been focused on making this extraction as efficient as possible (Tang et al., 2017; Weibel et al., 2017). However, currently these methods are not being aimed to reduce the WFA contamination level.

Among other applications, the WFA is considered as a promising cement substituent in the production of concrete (Bertolini et al., 2004; Ginés et al., 2009; Mangialardi, 2004; Saikia et al., 2007) or lightweight artificial aggregates (Colangelo et al., 2015). WFA is conventionally water-treated (Aubert et al., 2006), and the subsequent leaching test estimates its suitability for reuse. However, the washing procedure is not very economically feasible, reported liquid-to-solid ratios (L/S) are high (above 10) (Hoi et al., 2011) or the procedure is not optimized, and the leaching test is not performed on the final product (containing WFA) to test the treatment efficiency (Bertolini et al., 2004). Moreover, unlike coal-combustion fly ash (CCFA) mostly consisting of spherical particles (Mishra and Das, 2010), WFA particles are not studied well. They presumably consist of an inert glassy core surrounded by a porous,

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partially dissolvable mineral matrix layer (Al, Si, and Ca are the main components) covered with easily soluble alkali-metal chlorides (Kitamura et al., 2016). Thus, washing WFA may decompose the matrix, which would lead to a PTE release. Hence, if the potentially soluble part of WFA does not dissolve entirely, WFA can be hazardous if washed again or incorporated in cement.

Thus, water-only treatments proved to be effective for readily soluble salts but not all PTEs. Several assisting agents (separately) for heavy-metal recovery (Zn, Pb, Cu, Mn, and Cd) from WFA were studied due to their high complexation constants (Martell and Sillén, 1971), and it was reported that disodium ethylenediaminetetraacetate (EDTA) and sodium gluconate are especially efficient for Zn and Pb (Ferreira et al., 2002). However, a detailed study on the effectiveness of these complexing agents and their combined use for WFA purification was not performed.

Therefore, the goal is to study the effectiveness of the combined use of chelatants (EDTA and gluconate) to improve PTE extraction from WFA while using lower water volumes. Apart from complexation constants, the agents were selected due to their ability to simulate the matrix decomposition of WFA particles, a process that might have occurred outdoors with assistance of environmental agents. The study involved the comparison of untreated and treated WFA by the standard leaching test and macro- and microelemental, mineralogical, and microstructure analyses, and the analysis of individual hazardous elements in the leachates and remaining WFA material.

2. Materials and methods

WFA was supplied by the municipal solid waste-to-energy incinerator plant of AVR-Van Gansewinkel (Duiven, the Netherlands).

2.1. Samples and reagents

Deionized water (a Milli-Q Academic system, Millipore) was used for the preparation of all the solutions and washing. Nitric acid (69%, for analysis, ISO-grade, AppliChem Panreac) was used for all the operations with ICP–AES. All standard solutions were from High Purity Standards. A mixture of ICP-AM-6 (100 mg/L of Al, Sb, B, Ba, Be, Cd, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, K, Na, Si, Pb, Tl, Sr, V, Zn) and ICP-MS-68B (100 mg/L of Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, Zr) standard solutions was used for the calibration in the range 0.01–10 mg/L. A mixture of an ICP-AM-15 standard solution (10,000 mg/L of Na, K, Ca, and Mg), P (10,000 mg/L), and S (10,000 mg/L) was used for the calibration in the range 1–100 mg/L. An internal standard solution of Sc (20 mg/L) was prepared from a standard solution (Inorganic Ventures, 1000 mg/L).

2.2. Equipment

2.2.1. Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma atomic emission spectrometry (ICP–AES) provides rapid and highly sensitive multielemental quantification of MSWI fly ash with high accuracy and precision (Alba et al., 1997; Saqib and Bäckström, 2016). An ICP–OES 5100 SVDV spectrometer (Agilent Technologies) was operated in the axial mode (the auxiliary gas flow, 1.2 L/min; coolant gas flow, 14 L/min; nebulizer gas flow, 0.8 L/min). All emission lines were measured simultaneously.

2.2.2. Flameless atomic-absorption spectrometry coupled with pyrolysis

An RA-915 + Mercury Analyzer (Ohio Lumex Co.), a portable multifunctional atomic absorption spectrometry (AAS) instrument with Zeeman high-frequency modulation of polarization for background correction, with a RP-91C pyrolysis attachment (Lumex) was used for mercury determination.

2.2.3. X-ray diffraction analysis

The WFA mineralogical composition was determined by X-ray Diffraction (XRD) using a Bruker D2 PHASER (Co tube, 1.79,026 [Å]) with a LYNXEYE 1-D detector and fixed divergence slits. The XRD measurements were performed on pre-dried powdered samples. Phase identification was performed using X'Pert HighScore Plus 2.2 and the PDF-2 database.

2.2.4. Scanning Electron Microscopy

Scanning Electron Microscopy (Phenom ProX, PhenomWorld) with a backscattering electron (BSE) detector with a spot size of 4.0 and a voltage of 15.0 kV was used. The samples prior to analysis were covered with a 14 nm gold layer by means of a SOP K575X Dual Turbo sputter coater.

2.2.5. Ion chromatography

Ion chromatography (IC) was selected as a standard method for chloride and sulfate in leachates (Ito et al., 2008). A Thermo Scientific Dionex ion chromatograph 1100, 2 × 250 mm AS9-HS ion-exchange columns, the isocratic flow (0.25 mL/min) was used. Ion detection was accomplished by measuring a suppressed conductivity making use of an electrolytically regenerated suppressor (Thermo Scientific Dionex AERS 500 2 mm). As eluent, a 9 mM solution of sodium carbonate was used.

2.2.6. Auxiliary equipment

An XP 504 analytical balance (Mettler Toledo), 15-D0438 riffle boxes (sample splitters, CONTROLS Group), an SM-30 shaking table (Edmund Bühler GmbH), a UF 260 drying oven (Memmert), and a Multiwave 3000 (Anton Paar) microwave oven for digestion with a 60-bar rotor were used throughout. Automatic Eppendorf Research pipettes (Eppendorf International) were used for the preparation of calibration solutions. A-class polypropylene volumetric flasks (Vitlab) with volume (50.00 ± 0.12) mL and (100.00 ± 0.20) mL and polypropylene test tubes (Axygen) were used for the preparation of calibration and test solutions.

2.3. Procedures

2.3.1. Microwave-assisted acid digestion

The M-MVI 80-2008 standard method of microwave-assisted acid digestion for measurements of mass fractions of elements in samples of soils and bottom sediments by ICP–AES and AAS was used. The digestion procedure was adapted specifically for these samples. The volumes of 9 mL of conc. HCl, 3 mL of conc. HNO₃, and 0.5 mL of conc. HF (ISO-grade, AppliChem Panreac, Spain) were added to the samples (150–200 mg), the mixtures were placed in high-pressure vessels, and were heated for 1 h in a microwave oven.

2.3.2. Sample preparation

Fresh WFA samples were used for analyses and treatments. The material was oven-dried at 105 °C to a constant mass. Next, the WFA fraction above 500 µm was sieved out (3.8% w/w), because it contained significant amounts of unburned carbon. LOI at 550 °C of the fraction above 500 µm is 16.84. Next, the material was randomly divided with a sample splitter: the first half was saved for treatments; the second half was used for the standard leaching test and microwave-assisted acid digestion. Subsequently, treated samples were collected and subjected to the standard leaching test, ICP–AES, AAS, and XRD analysis again to assess the treatment efficiency and examine its impact on WFA composition.

2.3.3. Standard leaching test

The standard leaching test (EN 12457-4, 2002) was performed on untreated WFA and the fraction below 500 µm (5 replicates of 40 g each) to evaluate the level of PTEs, chloride, and sulfate. This test was also used to evaluate the combined (COMBY) and water-only (WATER-

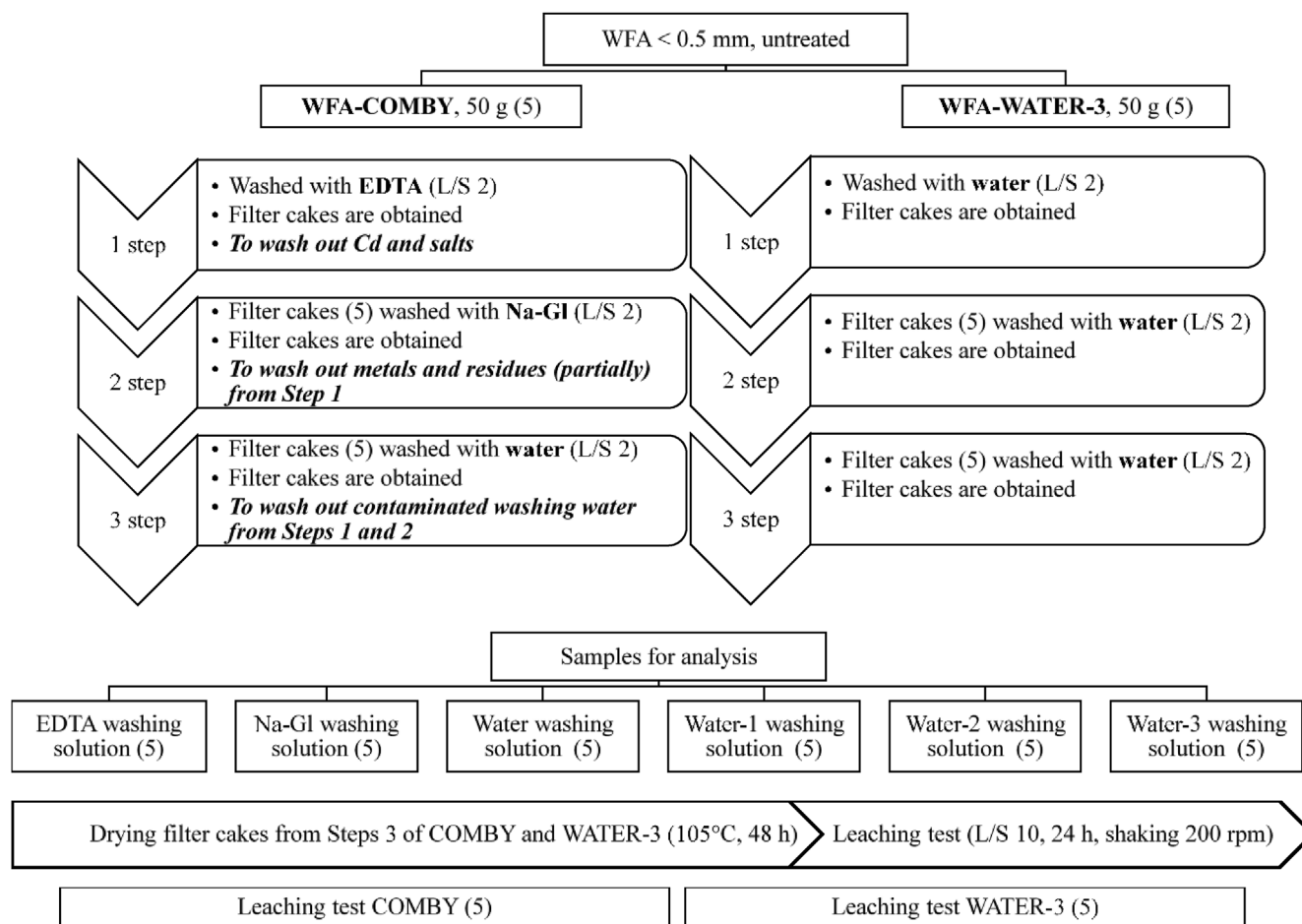


Fig. 1. Scheme of WATER-3 and COMBY treatments and analysis (figures in parentheses denote the number of replicates for each stage).

3) treatments (Section 3.2.4 below). After the standard leaching test (24 h shaking, L/S 10, 200 rpm), the samples were filtered through 17–30 and 0.2- μm filters to prepare leachates for ion chromatography and ICP–AES/AAS.

2.3.4. COMBY and WATER-3 treatment procedures

To test the efficiency of complexing agents, individual solutions of EDTA and sodium gluconate (Na-GI) were used. A WFA sample (40 g) was added to 200 mL of 0.05M EDTA and shaken for 20 min (200 rpm). The mixture was filtered (17–30 and 0.2- μm filters), and the washing water was collected for further analysis. The same procedure was repeated for another WFA portion, but Na-GI instead of EDTA was used.

Fig. 1 illustrates the scheme for both treatments consisting of three steps. WATER-3 serves as a reference, it follows all steps from COMBY, but instead of the additive solutions deionized water was used. Due to the dissolution of soluble components, in all cases L/S was taken with respect to the initial sample mass.

3. Results and discussion

3.1. Untreated WFA properties

3.1.1. Comparison of leaching vs. bulk element composition

The results for bulk WFA element contents (Table 1) show that the samples are highly contaminated and pose a potential hazard. Such high PTE contents in WFA allowed us to test the efficiency of complexant-based treatments. The standard leaching test results (L/S 10) on the untreated WFA show that Cr, Pb, Cd, Mo, and Zn concentrations exceed the legislation limits (LL) significantly (leachate pH 13).

Table 1

PTEs in the WFA: their total content, leaching, and legislation limits (LL).

Element	Total content	Leaching	LL (Dutch Soil Quality Decree, 2007)	Times over LL (for leaching)
	mg/kg	mg/kg	mg/kg	
Sb	1500 \pm 100	< 0.02	0.32	–
As	60 \pm 1	< 0.1	0.9	–
Ba	1500 \pm 100	2.9 \pm 0.3	22	–
Cd	300 \pm 10	0.10 \pm 0.01	0.04	2.5
Co	22 \pm 1	< 0.1	0.54	–
Cr	290 \pm 10	1.9 \pm 0.2	0.63	3
Cu	1500 \pm 100	0.10 \pm 0.01	0.9	–
Hg	< 0.001	< 0.001	0.02	–
Mo	30 \pm 1	6.7 \pm 0.7	1	6.7
Ni	130 \pm 10	< 0.01	0.44	–
Pb	3500 \pm 100	26 \pm 3	2.3	11.3
Se	15 \pm 1	< 0.02	0.15	–
Sn	630 \pm 10	< 0.02	0.4	–
V	60 \pm 2	< 0.05	1.8	–
Zn	19,000 \pm 200	21 \pm 2	4.5	4.7

However, they are only a small fraction of the total PTEs present in WFA, and despite a significant content of Sb, Cd, Cu, their leaching is below the quantification limits. These elements are probably embedded in WFA particles rather than are at its dissolvable surface layer.

In addition to high metal concentrations, WFA leachates after the standard leaching test contain large amounts of chloride (110 \pm 10 g/kg) and sulfate (50 \pm 1 g/kg). It is similar to the previous findings, where the effectiveness of a water treatment is shown (Colangelo et al.,

2012; De Boom and Degrez, 2015; Mangialardi, 2003; Mulder, 1996). However, the standard leaching test is not always sufficient to bring the sulfate content/leaching down to a level acceptable by the environmental legislation (Dutch Soil Quality Decree, 2007). Thus, from the values of leachable and bulk contents of PTEs, the standard leaching test should be complemented with a more detailed characterization.

3.1.2. Mineralogical composition and microstructure

According to XRD data, the crystalline components of untreated WFA are mainly anhydrite, quartz, halite, sylvite, and calcite. The pH 13 evidences that lime might be present as well. However, it gives very low XRD signals, probably due to fine dispersity, thus, its identification is hindered (Thongsanitgarn et al., 2014; Wang et al., 2010). The changes due to treatments are presented below (Section 3.2.2).

Fig. S1 (Supplementary Information) presents a general overview of the untreated WFA (< 500 μm). It consists of porous particles of irregular shape, and the fraction of fine particles (< 50 μm) is predominant, which agrees with the granulometric analysis (56.8% w/w is below 63 μm). To investigate if particle-size fractions of WFA differ in the microstructure, the material was divided into three fractions: < 40, 40–250, and 250–355 μm .

Fig. S2 (Supplementary Information) shows particles of irregular shape with a relatively small surface area. This fraction (40–250 μm) contains a larger number of spherical particles (about 10%). Fig. S3 (Supplementary Information) portrays particles of the 250–355 μm fraction. In general, their shape resembles those from finer fractions. However, there are also agglomerates of smaller particles, glued together, including spherical (Fig. S3, circled in white). There are also flat particles with porous structures. It is noteworthy that WFA morphology does not change significantly in the range of 40–355 μm .

3.2. Selection of complexing agents

Na-GI and EDTA were selected because they are less aggressive than strong acids or bases, change the pH within 1.5 points only, which is important if being compared with water, and show their effectiveness in the extraction of Zn and Pb from WFA (Colangelo et al., 2012; Ferreira et al., 2002). Thus, besides eliminating chloride and sulfate, these treatments elute PTEs. To test their effectivity, three independent treatments were performed (L/S 5; 20 min): water only, EDTA (0.05M), and Na-GI (0.05M).

The results (Fig. 2) show that, firstly, each of them efficiently elutes different metals, and secondly, they different affect the standard leaching test results for the treated material. Na-GI is more effective in

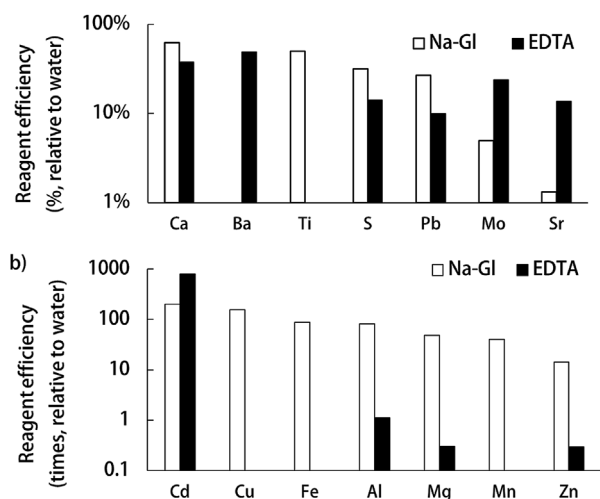


Fig. 2. Reagent efficiency relative to water: a) for elements, it is comparable to water) b) for elements, it is much higher than for water.

most cases (except for Ba, Sr, Mo, and Cd). It is vital to acknowledge its ability to elute major WFA matrix elements, calcium, aluminum, and iron. This may lead to matrix decomposition releasing an additional portion of PTEs, which could not be released during the standard leaching test or treatment with water. PTEs, which showed the excess over the LL according to the standard leaching test, were Cr, Cd, Mo, Pb, and Zn. However, significant amounts of Cu (by Na-GI) and Cd (by EDTA) can also be liberated from WFA due to high stability constants ($\log\beta_{1,\text{Cu-EDTA}} = 18$; $\log\beta_{1,\text{Cu-GI}} = 36$; $\log\beta_{1,\text{Cd-EDTA}} = 17$; and $\log\beta_{1,\text{Cd-GI}} = 10$) (Dojindo, 2017; Sawyer, 1964; Warwick et al., 2005). Being complementary, both agents were used sequentially in one treatment (COMBY) to elute the maximum number of PTEs.

3.3. Components not present in leachates or washing waters

In this section, we sum up the data on the elements that were below the limit of quantification (LOQ, which for all the elements was lower than the LL) in the leachates for all the kinds of applied treatments.

3.3.1. Arsenic

According to the literature (Jankowski et al., 2006), the maximum leaching of As is observed at pH 10 and does not change significantly after the continuation of the leaching test for more than 22–23 h. Thus, a standard leaching test (24 h) should be sufficient to detect and determine As. In general, the above-mentioned paper concludes that leaching increases with pH. However, another study (van der Hoek et al., 1994) drew completely opposite conclusions. Eventually, it was concluded that several parameters are responsible for As leaching, and not just pH. Most likely, as As accumulates in different WFA phases, its solubility is largely determined by the availability. In this study, the total amount of As in the WFA is not so significant (about 60 mg/kg), and leaching is absent in all experiments. It seems that this might be addressed to the fact that As is encapsulated in the silicate matrix (Hulett et al., 1980; Senior et al., 2000). Thus, comparing the leaching test results with the total As content shows that As is quite firmly immobilized and does not pose a further threat.

3.3.2. Cobalt

The leaching of Co is minimal at pH 8–12 (Jankowski et al., 2006). On one hand, it seems that the leaching test is not able to adequately assess the environmental impact of cobalt because under standard (for ash) conditions Co should not be leached out (pH 10–13). On the other hand, it is noteworthy that the mass ratio of arsenic to cobalt in the WFA is at the level of their ratios in such probable mineral phases as cobaltite CoAsS , safflorite $(\text{Co,Fe})\text{As}_2$, or skutterudite CoAs_3 . It might be assumed that cobalt can be enclosed together with arsenic in the silicate matrix, and thus, poses no further threat.

3.3.3. Nickel

According to the existing data, the maximum leaching of Ni is observed at pH 0–4 and 10–12 (Dijkstra et al., 2004). At the same time, there are data reporting that nickel in WFA is distributed between the silicate and magnetic fractions (Izquierdo and Querol, 2012). Judging by the fact that the leaching of Ni in all the samples is below LOQ, it can be concluded that it might be as well immured in the silicate matrix, dissolution of which in natural conditions is quite hindered.

3.3.4. Tin, selenium, and vanadium

Some studies (Hou et al., 2006; Jung and Osako, 2009) suggest that the ability of Sn to be mobilized is supposed to be high at pHs above 10. However, in this study, despite considerable total amount of Sn in the WFA (around 0.6 g/kg), the leaching from all the samples was very low. Probably, it also indicates that the silicate matrix of WFA is enriched with Sn. Trace amounts of Se (15 mg/kg), as well as its leaching below the LOQ and LL for all the samples indicate that it is likely, in our case, that Se is also enclosed in the silicate matrix. It is reported (Spears,

2004) that the major source of vanadium in WFA is glass. Given its trace contents in the investigated ash, as well as the lack of leaching in all samples, it can be concluded that it is also enclosed in the silicate matrix.

3.4. Two-reagent and water-only treatment comparison

Treatment parameters are the time of contact, L/S, and the number of steps. The priority task was to make a treatment which ensures the efficient chloride elution because its concentration is 100-fold higher than the LL. For a decrease in the chloride level by 98–99%, 15–30 min of washing is enough (Colangelo et al., 2012; De Boom and Degrez, 2015; Hoi et al., 2011; Mangialardi, 2004). In several studies, several-steps washing with L/S 1–3 proved to be more efficient than single-step ones with larger L/S (De Boom and Degrez, 2015; Ferone et al., 2013; Mangialardi, 2004; Vu et al., 2012). In most papers on this topic, the number of washing steps is limited to 2–3 (De Boom and Degrez, 2015; Hoi et al., 2011). Given that the studied WFA is severely polluted (Table 1) and retains a large water amount (about 30% after being in contact with water for about 20 min), we used a three-step washing procedure to remove the contaminated water. To minimize its amount, L/S 2 (relative to the initial sample mass) was used at each step. This ratio was selected empirically by obtaining a WFA–water paste with a viscosity low enough for its rapid mixing. EDTA was used at the first step as it elutes large amounts of Cd (ca. 1000-fold higher than the LL), and this also provided more iterations of rinsing out the contaminated water after this step. During the second step, Na-Gl was applied, and during the third, distilled water. All three steps together (¹EDTA/²Na-Gl/³water) comprise COMBY. For the sake of comparison, a WATER-3 treatment was applied. The procedure is the same as COMBY but instead of additives, only distilled water was used at all steps.

3.4.1. Treatment results (elution)

Fig. 3 shows the step-by-step elution for certain elements during both treatments. Taking into consideration that, for almost all metals, each step provides a significant PTE liberation, the number of steps cannot be less than three. The elution character for these two

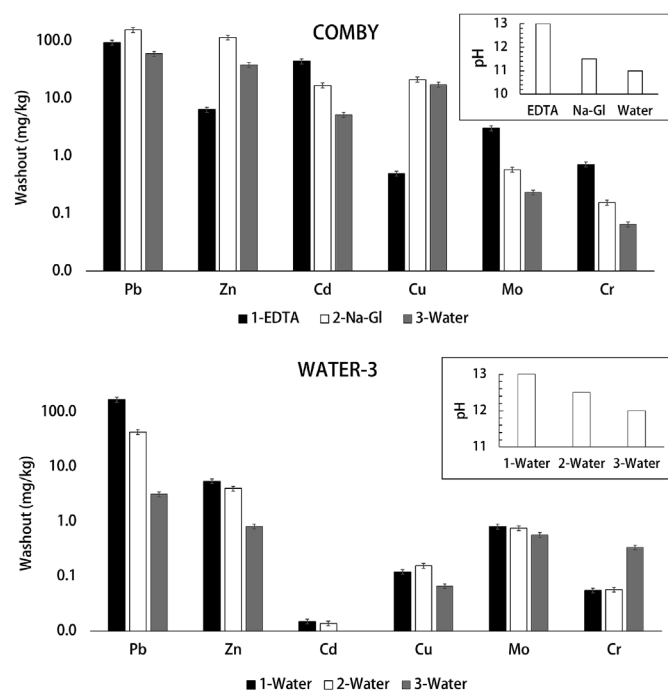


Fig. 3. Elution of metals during WATER-3 and COMBY treatments for each step; insets: pH of the washing waters during each step.

treatments differs for all metals (Fig. 3). For WATER-3, the concentrations of almost all the metals decrease in each step. This could be attributed to a change in pH at each step, however during COMBY pH drops are similar (see Fig. 3 insets). For COMBY, the pH after the first step decreases more than with WATER-3. This probably occurs due to the removal of alkaline compounds (mainly Ca) with EDTA. A pH change after the second step is the same, so the elution of such metals as Pb and Zn would have to be even less than in the first step (Quina et al., 2009), but it is the opposite. Thus, it is worthwhile to look for another reason for such an elution character.

Fig. S4 (Supplementary Information) illustrates the efficiency of COMBY and WATER-3 for chloride and sulfate. For chloride, the difference is within the error range; but for sulfate, the difference in the second step is quite noticeable. More intensive sulfate leaching compared to water may be due to the chelation of calcium with Na-Gl, as anhydrite is one of WFA main components. Fig. S4 shows that three steps with L/S 2 are nearly sufficient for removing chloride from WFA. In both treatments, a decrease in leachable sulfate concentration is evident; Na-Gl removes a larger amount of sulfate due to binding with calcium, and, unlike for chloride, still a significant amount of sulfate is liberated at the final stage of both treatments. The value at the third step is in a rather good agreement with the solubility of CaSO₄ (2 g/L) produced from anhydrite.

3.4.2. Mineralogical and element composition of treated WFA

Fig. 4 shows XRD spectra of treated WFA in comparison with untreated WFA, all samples were oven-dried (105 °C). Table 2 indicates the relative peak heights to show how a treatment changes the WFA matrix.

A primary WFA component is anhydrite (Bayuseno and Schmahl, 2011; Wan et al., 2006). It is worth mentioning how its share varies with the treatment type. It increases significantly both in WFA-WATER-3 and WFA-COMBY samples (due to the elution of readily soluble salts; approx. 20% w/w); however, the peak (ca. $2\theta = 29$) for WFA-WATER-3 is much higher than for WFA-COMBY. Thus, COMBY removes this component from the WFA matrix much better than WATER-3 due to high chelatabilities of EDTA and gluconate with calcium (Martell and Sillén, 1971; Sawyer, 1964). Nevertheless, CaSO₄ remains the main component of treated samples. Because this compound simultaneously possesses good sorption properties and is capable of considerably dissolving in water (Section 3.2.1), a very slow emission of PTEs into ground waters in the case of improper disposal cannot be excluded entirely.

The next main component is calcite (Bayuseno and Schmahl, 2011; Wan et al., 2006). Fig. 4 shows that, because of the sodium and potassium chloride elution, its share increases, and its content is higher for WFA-WATER-3. This is confirmed by Fig. 2, which shows the higher ability of COMBY to elute calcium compared to water.

High signals of halite (NaCl) and sylvite (KCl) are in line with the previous data (Bayuseno and Schmahl, 2011; Wan et al., 2006), and agree with the leaching data for chloride (about 110 g/kg) and the total element composition (Na, ca. 75 g/kg; K, ca. 50 g/kg, Fig. 5).

The last WFA main component is quartz (Bayuseno and Schmahl, 2011; Wan et al., 2006). Its content also varies in concordance with a decrease in the contents of soluble salts (ca. 77 g/kg in untreated and 93–96 g/kg in treated WFA, Fig. 5). Its share is larger after treatments (Table 2), and the WFA-COMBY sample has slightly more quartz due to a smaller fractions of anhydrite and other water-soluble phases.

All other minerals in Fig. 4 are present in WFA in fairly small amounts. No new phases are detected in the treated WFA. A significant content of aluminum (33–45 g/kg) coincides with the presence of melilite and feldspar; sphalerite and willemite might be the origin of zinc (19–23 g/kg); the sources of iron (15–21 g/kg) and titanium (11–15 g/kg) are presumably ilmenite, rutile, and sitinakite; magnesite is for magnesium (12–17 g/kg); and the presence of apatite might explain moderate concentrations of phosphorus (7–10 g/kg).

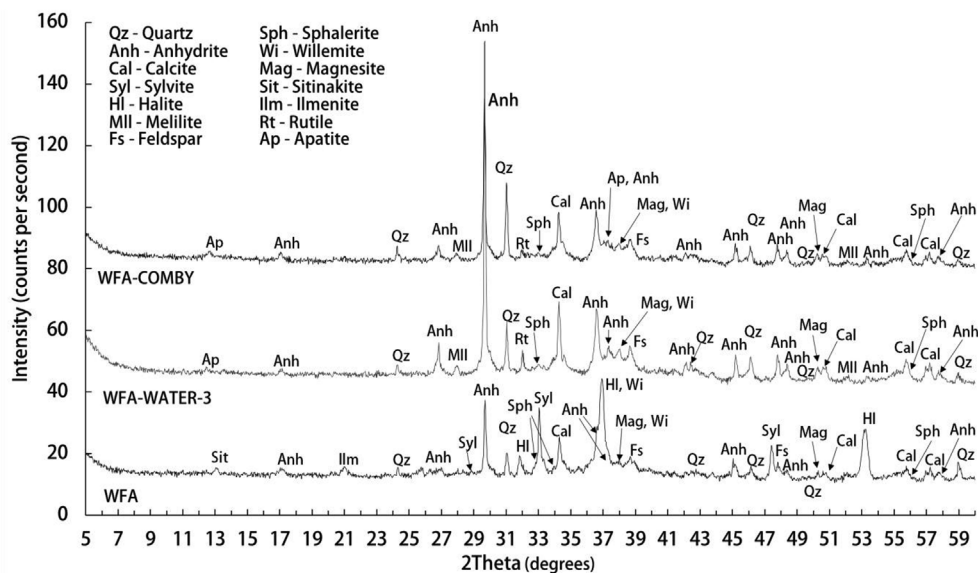


Fig. 4. Mineralogical composition of the untreated WFA and WFA after WATER-3 and COMBY treatments. For the sake of convenience, the intensity scale is expressed in square-root values and shifted upwards.

Table 2
Main minerals in untreated and treated WFA.

Mineral	Sample		
	WFA	WFA-WATER-3	WFA-COMBY
Halite	High	–	–
Anhydrite	Low	High	Medium
Sylvite	High	–	–
Calcite	Low	High	Medium
Quartz	Low	Medium	High

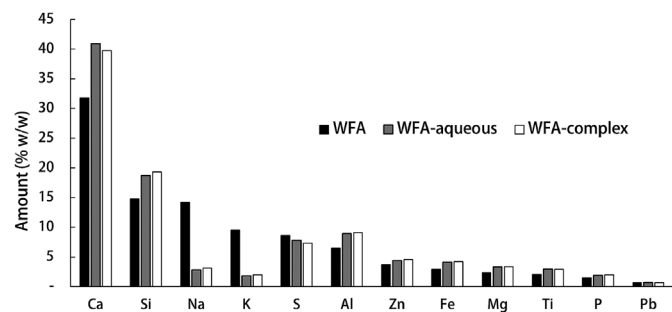


Fig. 5. Total element composition (major components) of untreated WFA, WATER-3-treated WFA, and COMBY-treated WFA.

Fig. 5 shows the bulk WFA composition after COMBY and WATER-3 treatments. It confirms the mineralogical analysis and leaching behavior. The contents of calcium and silicon are slightly higher in treated samples due to a noticeable decrease in the proportion of sodium, potassium (Fig. 5), and chloride. Sulfur content (the main source is supposedly anhydrite) is slightly lower after treatments (by eluting sulfate, as shown above). The percentages of almost all the main components (Al, Zn, Fe, Mg, Ti, and P) are also slightly higher after treatments. While the elution of zinc during the treatments is abundant, a very significant Zn amount remains bound in the treated WFA (22 ± 1 g/kg) (Fig. 5). After treatments, there is still also a high Pb content (3.2 ± 0.2 g/kg). Because these elements pose a potential risk, even in a combination with the standard leaching test, the bulk element analysis is required to determine the treatment effectiveness, and to consider other ways of WFA reuse because it contains large quantities of

valuable metals.

Thus, both treatments show effective chloride removal. However, some differences in the treated WFA due to the presence of EDTA and Na-GI do not affect the final macro-composition considerably.

3.4.3. Microstructure of treated WFA

As discussed in Section 3.1.2, the untreated WFA consists of particles with a rather complex shape and a large surface area, which, nevertheless, has a fair share of smooth surface. Fig. S5 (Supplementary Information) illustrates the changes during the second and third steps of WATER-3. Spherical particles appear smoother as the porous outer layer is removed, and agglomerated particles (Fig. S3b, Supplementary Information) are liberated. During this process, an increase in the number of particles, and, therefore, a new surface accessible for dissolution, might affect the PTE leaching.

Fig. S6a (Supplementary Information) shows changes in WFA particles after washing the untreated WFA with EDTA. Comparing this figure with Figs. S2 and S3 shows how much the surface of particles has changed. If a large part of the untreated WFA was quite smooth (Fig. S6); here, the whole surface has become scabrous, so its area has increased significantly. This may explain PTE elution enhancement during the second step of COMBY. Fig. S6b displays the shape of a WFA particle after the last step of COMBY. To a relatively large porous particle, several small spherical particles are attached (in the centre). This agglomerate may be formed during the drying process after treatment, or this structure was there originally, but only several washing steps have revealed it. During the further use or disposal, this agglomerated particle might fall apart completely resulting in an increase in the number of particles, and, therefore, in the new surface available for PTE leaching.

Fig. S7 (Supplementary Information) shows a structure of particles after WATER-3 (all three steps). It is worth noting that such structures were not observed at any of the previous steps. Based on XRD data, the formation of significant quantities (enough to form such large particles) of new phases was not observed during the treatment. Perhaps, it is a structure of some WFA particles which was hidden before under the layers of soluble components. Only calcite of all main minerals that form WFA can have a similar needle structure (Braissant et al., 2003; Wang et al., 1999). Besides, it would not dissolve in water (during treatments). It is possible that the reagents used in COMBY and contributing to the elution of calcium, help to dissolve such structures.

Table 3

Standard leaching test results for untreated WFA and after treatments (for metals which concentrations exceed the legislation limit (LL)); underlined, more than the LL; bold, became worse after the treatment; italicized, became better after the treatment.

Element	Leaching test		Leaching test results (after treatments)	
	WFA untr.	LL	COMBY	WATER-3
mg/kg				
Cd	<u>0.10 ± 0.01</u>	0.04	10 ± 1	< 0.02
Cr	<u>2.0 ± 0.2</u>	0.63	<i>0.50 ± 0.05</i>	4.4 ± 0.4
Cu	0.10 ± 0.01	0.9	3.6 ± 0.4	< 0.02
Pb	<u>21 ± 2</u>	2.3	85 ± 9	< 0.05
Mo	<u>6.7 ± 0.7</u>	1	<i>1.4 ± 0.2</i>	3.3 ± 0.3
Zn	<u>21 ± 2</u>	4.5	38 ± 4	<i>0.40 ± 0.04</i>
g/kg				
Cl ⁻	<u>110 ± 10</u>	0.62	<i>1.6 ± 0.2</i>	<i>1.9 ± 0.2</i>
SO ₄ ²⁻	<u>50 ± 5</u>	2.4	<i>19 ± 2</i>	<i>16 ± 2</i>

Therefore, they are not observed in the case of COMBY. Another possible explanation of such structures (yet demanding further research) might be the formation of hydration products (Wang et al., 2007). It is important to come to understanding how such a vast formation of a new and highly developed surface would affect the leaching of PTEs.

Thus, during the treatments, the WFA microstructure undergoes changes that may affect its further properties. Both treatments wash a rather deep surface layer off, significantly increasing the total surface area. During COMBY treatment, the WFA surface changes from partially smooth to rugged and scabrous compared to WATER-3.

3.4.4. Standard leaching test results on treated WFA

Table 3 presents the standard leaching test results (L/S 10) for both treatments. Only elements with concentrations above the LL are shown. It is worthwhile to give a small remark regarding the LLs for chloride and sulfate. In this study, the environmental legislation for CCFA (LL (sulfate), 30,000 mg/kg; LL (chloride), 1000 mg/kg) could have been applied (Doudart de la Grée et al., 2015) because WFA is closer in some properties to CCFA rather than to MSWI bottom ash. However, because hereby no evidence of complete WFA similarity to CCFA was presented, the legislation criteria for non-shaped building materials were used instead, see Table 3 (Dutch Soil Quality Decree, 2007). It is rather negligible in the context of this study because the goal was not to demonstrate the WFA leaching results after a treatment, but to show what changes the WFA undergoes. The treatment selection or other decision regarding the further utilization of WFA can be made using these criteria though. Therefore, the LL values are taken for clarity, so that the challenge level can be estimated.

Table 3 shows that COMBY causes a strong increase in the PTE leaching except for Cr and Mo. In general, COMBY, which elutes matrix elements such as Ca, Fe, Al, Mg, and Zn, promotes the liberation of PTEs enclosed in the matrix (Fig. 2). At the same time, WATER-3 elutes orders of magnitude less amounts of these matrix elements, keeping PTEs inside. Therefore, after WATER-3, the concentrations of a considerable number of PTEs (except for Cr and Mo) are below the LL. Both treatments were not targeted to completely elute anions. Table 3 shows that both treatments were similarly effective in eluting chloride (COMBY, 99%; WATER-3, 98%), and close to each other for sulfate elution (COMBY, 62%; WATER-3, 68%).

Table 3 shows that Cd leaching from the untreated WFA (using the standard leaching test) is only twofold higher than the LL (0.10 mg/kg). However, COMBY increased Cd leaching by about 100 times (10 mg/kg), while during WATER-3 it has decreased by more than fivefold (< 0.02 mg/kg). At the first two steps of WATER-3, a very small amount of Cd was liberated (0.03 mg/kg, Fig. 3), while during COMBY it was much larger at all the three steps (67.0 mg/kg). As at three steps of COMBY, the eluted Cd amount is decreasing (45, 17, and 5 mg/kg,

respectively), while the matrix component elution at the 1st step for water and EDTA is similar, it might be concluded that EDTA transformed all available Cd to soluble species on the surface layers. If some additional Cd sources would have been uncovered by dissolving the matrix, an increase in its concentration at each subsequent step would have been observed. The ability of Na-GI to elute Cd is also significant (0.10 mg/kg), although less than of EDTA due to a lower complexation constant (Section 3.2), and despite its use in the second step of COMBY, an increase in concentration also did not occur. As WATER-3 is reagent-free, only a small amount of soluble Cd got into the washing water (0.04 mg/kg), and the standard leaching test indicates WFA-WATER-3 as apparently non-hazardous. However, a very significant increase in the cadmium leaching using chelating agents shows that such a “clean” WFA may have a hazard under the action of environmental substances (Buffle et al., 1977).

Fig. 3 shows that a significant amount of Cr (0.7 mg/kg) is liberated at the 1st step of COMBY, less at the second step (0.2 mg/kg), and at the third step a negligible amount (0.1 mg/kg) is eluted, and according to the standard leaching test results its level satisfies the regulations. At the same time, for WATER-3, a small amount (0.1 mg/kg) of Cr is liberated at the first two steps, and at the third step its amount increases threefold. Eventually, WFA-COMBY leaches twofold Cr (4.4 mg/kg) as the untreated WFA (2.0 mg/kg). The solution pH decreases during the treatment; however, at pH 8–13, Cr leaching does not vary this much (Quina et al., 2009). On the other hand, Fig. 6 illustrating a comparison of Mg, Al, and Fe leaching at all steps, reveals that it is 2–3-fold larger at the first step of COMBY (and Mg is not released at all at the first step of WATER-3), and at the 2nd and 3rd steps for COMBY, the elution of these components is 1–2 orders of magnitude higher than that of WATER-3. It might be suggested that Cr is encapsulated in the matrix. Thus, as for Cd, the standard leaching test with L/S 10 does not show how much Cr will potentially leach out later, during the use of WFA-based materials.

Considering the standard leaching test results (Table 3), for untreated WFA Cu leaching was below the LL, but after COMBY it has increased significantly. The character of Cu elution differs from cadmium (for which the standard leaching test results after treatments were similar, Fig. 3 and Table 3). Apart from very high complexation constants, the reason for such an elution character is also the matrix decomposition, elements are liberated 10-fold less effectively at the first step of COMBY, as if blocking Cu leaching. For WATER-3, these components are liberated only slightly, so approximately the same Cu elution is observed at all three steps.

After WATER-3, the concentration of Pb in leachates is less than the LL; however, after COMBY, the WFA looks extremely hazardous (Table 3). In addition, even in the case of WATER-3, much more Pb is liberated at the first (168.8 mg/kg) and subsequent (43.5 and 3.2 mg/kg) stages than during the standard leaching test on the untreated WFA (Fig. 3, contact times are 20 min at every washing step and 24 h for the standard leaching test). This can be explained by the fact that during the standard leaching test, calcium salts can re-precipitate (e.g. CaSO₄), with which Pb salts tend to co-precipitate (Lu et al., 2012). Thus, in a

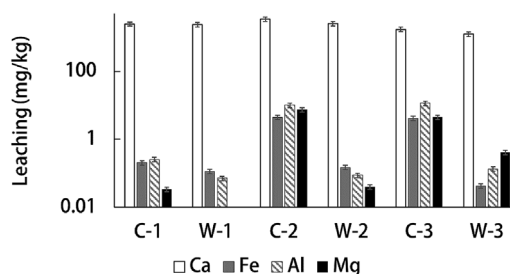


Fig. 6. Matrix components elution during COMBY (marked C) and WATER-3 (marked W) treatments.

short time of COMBY this does not happen, and all available Pb transfers to the solution. This phenomenon is not observed for other metals because their chlorides and sulfates have rather high solubilities.

Mo concentration in leachates have decreased after both treatments, and for COMBY it was close to the LL (Table 3). The elution character in both cases as well indicates a link to the elution of matrix components: in WATER-3 it is slow, so at all steps a similar amount of metal is liberated (0.8, 0.8, and 0.6 mg/kg, respectively); for COMBY, a much larger amount is eluted immediately (3.1 mg/kg), presumably, because of a high complexation constant ($\log\beta_{1,Mo-EDTA} = 20$) (Martell and Sillén, 1971), and at the following steps it decreases (0.6 and 0.2 mg/kg). The standard leaching test for the untreated WFA showed 6.7 ± 0.7 mg/kg of Mo, and the mass balance for treatments and liberated/left amounts for COMBY was $3.9 \pm 0.4/1.4 \pm 0.1 = 5.3 \pm 0.5$ mg/kg, and for WATER-3 was $2.2 \pm 0.2/3.3 \pm 0.3 = 5.5 \pm 0.5$ mg/kg, indicating that, probably, the rest of Mo (Table 1) is encapsulated in the silicate matrix and is unlikely to pose further threat.

For WATER-3, Zn level has decreased to an environmentally acceptable level (Table 3). However, for COMBY, it has become twofold worse than before the treatment. During WATER-3, it is very probable that only readily soluble Zn species are eluted, and at every step the elution decreases (5.5, 4.0, and 0.8 mg/kg). For COMBY, there is no significant Zn leaching at the first step (6.4 mg/kg), but at the second one, 18-fold higher amounts of the metal eluted (115.4 mg/kg). This can result from the matrix elements beginning to be effectively liberated at the Na-Gl step of COMBY, entailing enhanced Zn leaching.

4. Conclusions

Thus, mineralogical composition, total element content, leaching properties, and morphology of untreated and treated WFA are studied. As a whole, the efficiency of a three-step combined treatment with two complexing agents (ethylenediaminetetraacetate and gluconate) to increase the toxic-element elution from fly ash in contrast to conventional water-only treatments is shown.

- The main minerals found in the untreated WFA are anhydrite, quartz, halite, sylvite, and calcite. The high pH of 13 might indicate the presence of lime.
- The WFA major elements are Ca, Si, Na, K, S, and Al, and it is also enriched with Pb (3.5 g/kg) and Zn (19 g/kg).
- The WFA mainly consists of particles with an irregularly developed shape (about 90%) and spherical particles (about 10%).
- The main metal impurities in the WFA are Cd, Cr, Mo, Pb, and Zn. Their leaching exceeds the legislation limits by 3–11 times. The leaching of anions exceeds the corresponding limits by 25–1000 times. Leaching of chloride is 110 g/kg, and sulfate is 50 g/kg.
- The ability of gluconate to elute metals from the WFA is especially efficient (10–200-fold higher than of water) for Cd, Cu, and Zn; and EDTA is the most efficient for Cd (800-fold higher than of water).
- The ability of combined treatment to elute metals in comparison with water-only is 40% higher for Pb, 15 times higher for Zn, 1800 times higher for Cd, 115-fold higher for Cu, and 2 times higher for Mo and Cr.
- During both treatments, the WFA surface changes from smooth to scabrous. Both treatments wash a rather deep surface layer off, significantly increasing the surface area of the particles.
- As a result of combined treatment, the WFA has become even more hazardous than before the treatment. In the case of water-only treatment, the WFA appears to be much cleaner than before the treatment.

It is necessary to highlight that the same WFA, which, according to the leaching test results, looks non-hazardous from almost all points after being washed with water, proves to be extremely hazardous (it

matches the criteria for even more hazardous category than the untreated one). This study shows that it is beneficial not only to study the leaching of certain components and the factors which affect them, but also to pay attention to amounts of elements remaining in WFA after treatments. Because the WFA might have a latent hazard in some cases, and in some it is not hazardous after even minor processing. The aim underneath this research is to draw attention to the issue of WFA processing once again. If the extraction of metals turns out to be economically feasible for a certain country, it would be rather insubstantial to incorporate the material in concrete. We believe that these findings will help in issues related to treating, processing, and utilizing WFA. For further research, it is expedient to study the mechanisms of mutual elution of matrix components and PTEs in detail, as well as to investigate the structure of WFA and how, if used as secondary building materials, it affects the target material properties.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2019.01.096>.

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