Relevance of MSWI fly ash total composition analysis: A case study of washing pretreatments

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Abstract.

In recent years, a challenge of recycling MSWI residues (such as fly ash) is particularly acute. One of the possible ways is the use of such residues in secondary building materials. However, MSWI fly ash is highly contaminated with various toxic elements such as Pb, Zn, Cd, Cu, etc. Therefore, before these residues can be reused or even discarded, it is necessary to treat them to reduce the environmental impact. The aims of this study are to test the efficiency of several complexing agents that might be added to water to increase the metal elution from fly ash and to highlight the necessity of the total analysis of the fly ash in case of determining its environmental impact. Composition of raw and differently treated (combined, based on EDTA and sodium gluconate, and aqueous-only treatments) MSWI fly ash were analyzed by ICP–AES and AAS, ion chromatography, XRD, and SEM. The results showed that for some metals the combined treatment is 10–1000-fold more efficient than the aqueous one. At the same time, the combined treatment makes it possible to determine how high the latent hazard of MSWI fly ash might be, the property, which cannot be assessed with the aqueous-only treatment.

Keywords: MSWI fly ash; Potentially Toxic Element; Chemical properties; Environmental impact; Treatment; Leaching

1 Introduction

The challenge of the utilization of waste residues has been dealt with for over 25 years [1]. During the incineration process, the residues are distributed as approximately 80% (w/w) of bottom ash and 20% (w/w) of fly ash (WFA) [2]. Due to an increase in landfilling prices along with environmental regulations concerning potential leaching of various pollutants into ground waters [3], these residues should be treated to match the legislation. It is known that the most polluted part is WFA [4]. Vast concentrations of chloride, sulfate, and such metals as lead, zinc, copper, etc. [5] turn this category of residues into a “hazardous waste”. To convert WFA into a safe or inert material suitable for either further landfilling or reuse, it is necessary to significantly reduce the leaching of potentially toxic elements (PTEs).

Since the beginning of WFA treatment development, the main ways to achieve this goal have been: water washing in combination with solidification [6,7], stabilization using various chemicals [8,9], silica fume [10], carbonation [11,12], and thermal treatments [13,14]. However, recently, metal extraction from the WFA by various methods has become comparably attractive [15,16]. As metal concentrations in WFA are considerable, research has lately been focused mainly on making this extraction as efficient as possible [17,18]. Nevertheless, there is, as well, a decent number of studies investigating the reuse of WFA as a substituent for cement in the production of concrete [19,20] or lightweight artificial aggregates [21]. Conventionally, WFA is water-treated [22], and the subsequent leaching-test results for this washed WFA show whether it is suitable for reuse. However, existing studies contain several liabilities or vaguely presented information, namely: a) the washing procedure is not very economically feasible (L/S ratios are too high) [23], b) the WFA washing procedure (L/S and time) is not indicated, and c) the leaching test is not performed on the final product (containing WFA) [24].

The study [25] showed that MSWI FA particles have a structure consisting of a glassy “skeleton” core, surrounded by a partially dissolvable “muscle” layer (Al, Si, and Ca are the main matrix components), and this “body” is covered with a shell mainly consisting of alkali metal chlorides. Thus, during washing of WFA, the matrix is being decomposed, which therefore leads to a major PTE release. Hence, as long as the potentially soluble part of WFA does not dissolve entirely, WFA can potentially be hazardous.

The aim of this study is to investigate chemical properties of WFA and assess the efficiency of two complexing agents (sodium gluconate and EDTA) to elute PTEs and matrix elements. The idea is that these chelating agents accelerate the washing out of the matrix of WFA particles, a process that would naturally have occurred outdoors but much more slowly.
2 Materials and Methods

2.1 Samples and reagents

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

Deionized water (a Milli-Q Academic system, Millipore, France) was used for the preparation of all the solutions and washing. Nitric acid (69%, for analysis, ISO-grade, AppliChem Panreac, Spain) was used for all the operations with ICP–AES. All standard solutions were from High Purity Standards (USA). 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, Pb, Ti, 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 (10000 mg/L of Na, K, Ca, Mg), P (10000 mg/L), and S (10000 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, USA, 1000 mg/L).

2.2 Equipment

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. An RA-915+ Mercury Analyzer (Ohio Lumex Co.), a portable multifunctional atomic absorption spectrometer with Zeeman high-frequency modulation of polarization for background correction, with a RP-91C pyrolysis attachment (Lumex) was used for mercury determination. The mineralogical composition of the WFA was determined by X-ray Diffraction (XRD) using a Bruker D2 PHASER (a Cu tube, 1.79026 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. Scanning electron microscope (Phenom ProX, PhenomWorld) with a voltage of 15.0 kV and a backscattered electron (BSE) detector with a spot size of 4.0 was used. Prior to analysis, the samples were covered with a 14 nm gold layer by means of a SOP Turbo sputter coater K575X Dual. A Thermo Scientific Dionex ion chromatograph 1100 (2×250 mm AS9-HS ion-exchange columns; 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 solution of sodium carbonate was used (Na2CO3, 9 mM).

2.3 Procedures

Prior to analysis, the WFA was stored in sealed plastic containers for 1 week. Further, the material was oven-dried at 105 °C to a constant mass. Next, the WFA was sieved into two size fractions (above and below 500 μm) to exclude the coarser fraction containing significant amounts of unburned carbon (LOI (550 °C) of the fraction above 500 μm is 16.84, w/w is 3.8%). Further, the material was randomly divided with a sample splitter: the first half was saved for treatments; the second half was used for a leaching test and autoclaved acid digestion. Subsequently, treated samples were collected and subjected to the leaching test and ICP–AES and AAS analysis again to assess the treatment efficiency and examine the treatment impact on WFA composition.

Total analysis of WFA was made according to M-MVI 80-2008 standard method (Method for performing measurements of mass fractions of elements in samples of soils and bottom sediments using atomic emission and atomic absorption spectrometry). 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), placed in high-pressure vessels, and the mixtures were heated for 1 h in a microwave oven.

To test the efficiency of the complexing agents, disodium ethylenediaminetetraacetate (EDTA) and sodium gluconate (Na-Gl) were used. Both solutions were prepared with a concentration of 0.05 M. A sample of the WFA (40 g) was added to 200 mL of 0.05 M EDTA and shaken for 20 minutes (200 rpm). The mixture was filtered (17–30 μm and 0.2-μm), and the liquid (washing water) was collected for further analysis. The whole procedure was repeated for another portion of the WFA, but Na-Gl instead of EDTA was used.

The leaching test (according to EN 12457-4 (26)) was performed on untreated WFA, fraction below 500 μm (5 replicates of 40 g each) to evaluate the level of contaminants (PTEs, chloride, and sulfate), and later, on WFA samples subjected to combined and aqueous treatments. After finalizing the leaching (24 h of shaking, 200 rpm, L/S = 10), all the samples were filtered through 17–30 μm and 0.2-μm filters to prepare leachates for subsequent analyses by ion chromatography and ICP–AES/AAS. Filter cakes after the first step of filtration were stored and dried for further analysis.
3 Results and discussion

3.1 Properties of untreated MSWI FA

3.1.1 Comparison of leaching vs total composition of untreated WFA

The results of the leaching test (Table 1) on the untreated WFA show that the greatest hazard is the leaching of Cr, Pb, Cd, Mo, and Zn. Their concentrations in leachates exceed the legislation limits (LL) significantly. Therefore, based on these data, it can be concluded that the WFA needs a treatment which would minimize the leaching of those components. At the same time, firstly, it is noticeable that the leached quantities are negligible compared to the total content of a particular PTE (especially Zn and Pb). Secondly, it is evident that with a significant content of certain components (Sb, Cd, Cu), their leaching is below the limit of quantification. Thus, it can be indirectly concluded that these elements are embedded in WFA particles rather than present at its dissolvable surface layer.

In addition to high concentrations of metals, the WFA leachates also contain large amounts of chloride (110 ± 10 g/kg) and sulfate (50 ± 5 g/kg). In most papers on this topic [27,28], the effectiveness of a water treatment is shown. However, even this treatment is not always sufficient to bring the sulfate content/leaching down to a level acceptable by the environmental legislation [29].

<table>
<thead>
<tr>
<th>Element</th>
<th>Total content</th>
<th>Leaching</th>
<th>LL [29]</th>
<th>Times over LL</th>
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<tr>
<td></td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td></td>
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<tr>
<td>Sb</td>
<td>1500 ± 100</td>
<td>&lt; 0.02</td>
<td>0.32</td>
<td>-</td>
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<tr>
<td>As</td>
<td>60 ± 1</td>
<td>&lt; 0.1</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>1500 ± 100</td>
<td>2.9 ± 0.3</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>300 ± 10</td>
<td><strong>0.10 ± 0.01</strong></td>
<td>0.04</td>
<td>2.5</td>
</tr>
<tr>
<td>Co</td>
<td>22 ± 1</td>
<td>&lt; 0.1</td>
<td>0.54</td>
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<tr>
<td>Cr</td>
<td>290 ± 10</td>
<td><strong>1.9 ± 0.2</strong></td>
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<td>3</td>
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<tr>
<td>Cu</td>
<td>1500 ± 100</td>
<td>0.10 ± 0.01</td>
<td>0.9</td>
<td>-</td>
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<td>6.7 ± 0.7</td>
<td>1</td>
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<td>Ni</td>
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<td>0.44</td>
<td>-</td>
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<tr>
<td>Pb</td>
<td>3500 ± 100</td>
<td><strong>26 ± 3</strong></td>
<td>2.3</td>
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<tr>
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<td>&lt; 0.02</td>
<td>0.15</td>
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<tr>
<td>Sn</td>
<td>630 ± 10</td>
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<td>0.4</td>
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<td>V</td>
<td>60 ± 2</td>
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<tr>
<td>Zn</td>
<td>19000 ± 200</td>
<td><strong>21 ± 2</strong></td>
<td>4.5</td>
<td>4.7</td>
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</table>

Table 1 Potentially toxic elements in the WFA: total content, leaching, and legislation limits (LL); PTEs with concentrations in leachates exceeding the LL are given in **bold**

3.1.2 Mineralogical composition of untreated WFA

According to XRD data, untreated WFA mainly consists of: anhydrite, quartz, halite, sylvite, and calcite; minerals commonly found in MSWI FA [30,31]. Additionally, the pH of 13 of untreated WFA evidences that lime might be present as well. However, it gives very low XRD signals, probably due to fine dispersity, and, therefore, its identification is hindered [32,33]. The amorphous content in the investigated WFA is not significant.

3.1.3 SEM of untreated WFA

Figure 1a and b show a general overview of the untreated WFA (< 500 µm) on a different scale. These figures illustrate that the WFA consists of porous particles of an irregular shape, and the fraction of fine particles (<50 µm) is very large, which agrees with the granulometric analysis data (56.8 % (w/w) is below 63 µm). However, spherical particles of relatively small size (≤ 50 µm) are also present but their share is not significant. Figure 2 shows how certain characteristic particles of WFA look like.
3.1.4 Complexing agent selection

The analysis of the WFA showed that the water treatment is inevitable due to extremely high concentrations of Cl– (around 110 g/kg) and SO₄²⁻ (around 50 g/kg). We conducted an experiment (treatment) with water only and, in parallel, with the addition of complexation agents. Na-Gl and EDTA were selected because they act relatively gently (much less aggressively than strong acids or bases), only slightly change the pH (which is important if being compared with water), and also showed their effectiveness in metal extraction (Zn and Pb) from MSWI FA [6,34]. Thus, besides eliminating chloride and sulfate, these treatments can wash out some PTEs. To assess how the specific reagent affects the WFA as a whole (morphologically) and from the point of washing out of the components, three independent treatments were performed (L/S = 5, 20 min): water, EDTA (0.05 M), and Na-Gl (0.05 M).

3.2 Leaching of matrix components and contaminants for various treatments

Figures 3 and 4 illustrate the ability of the two agents to wash elements out of the WFA. In all the cases, at least one of the reagents was more effective than water. As can be seen, Na-Gl in most of cases (except Ba, Sr, Mo, and Cd) proved to be more efficient than EDTA. It is vital to acknowledge its ability to wash out calcium, aluminum, and iron. Presumably, along with the matrix decomposition, an additional portion of PTEs is washed out that could not be released during the leaching test/treatment with water only, which has a relatively low washout ability to those elements.

PTEs, which showed the excess over the LL according to the leaching test, were Cr, Pb, and Zn. However, the examination for the washout ability of the agents revealed that significant amounts of Cu and Cd can also be washed out of the WFA by means of Na-Gl (Cu) and EDTA (Cd). According to these findings, it was decided to use both reagents sequentially (a combined treatment) to get rid of the maximum number of PTEs.
The results showed that, firstly, each of the two reagents efficiently wash out different metals, and secondly, they have different effects on the results of the leaching test conducted on the treated material.

3.3 Total element composition of untreated and treated WFA

Mineralogical and total element analyses of untreated WFA as well as of WFA subjected to aqueous and combined treatments were conducted to investigate their impact on the WFA. From Figure 5 several features confirmed by other data (mineralogical analysis and the leaching test) can be observed. Calcium and silicon amounts are slightly higher in the treated samples due to a noticeable decrease in the proportion of sodium, potassium (also can be seen in Figure 5), and chloride. The sulfur content (the main sources are supposedly anhydrite and sphalerite) is slightly lower as a result of treatments (by washing out sulfate). Further, percentage of almost all the main components (Al, Zn, Fe, Mg, Ti, P) is also slightly higher after treatments.

In conclusion, the aqueous and combined treatments have similarities because they are both water-based. They are fairly effective in the chloride removal. However, they also have differences due to the presence or absence of reagents (EDTA and Na-Gl), which do not affect the final composition of the WFA significantly; however, some differences can be seen. In the case of the aqueous treatment, the WFA is a little bit more enriched with anhydrite, and calcium in general. In the case of the combined treatment, anhydrite still prevails, but the share of quartz is slightly higher.

Taking into consideration the quantitative analysis of the main components, it is worth noting that there is a high content of Zn (22 ± 1 g/kg) and Pb (3.2 ± 0.2 g/kg) remaining in the WFA after treatments. Because these elements pose a potential risk, even in a combination with the leaching test, it is necessary to subject WFA to a total element analysis. Firstly, it is needed to determine how effective was the treatment, and secondly, to consider other ways to reuse WFA, based on the fact that it contains large quantities of valuable metals.

3.4 SEM of treated WFA

To understand how the treatments affect the surface of the WFA, a SEM analysis was carried out. Figure 6 shows a structure of a particle after the final step of the aqueous-only treatment. It is worth noting that at any of the preceding steps, such structures
were not observed. 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 under the layers of soluble components. Only calcite of all main minerals that form WFA can have a similar needle structure [35,36]. Besides, it would not dissolve in water during treatments. It is possible that the reagents used in the combined treatment contributing to the elution of calcium (Figure 3) help to dissolve such structures. Therefore, they are not observed in the case of the combined treatment. Another possible explanation of such structures (yet demanding further research) might be the formation of hydration products [37]. 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.

Fig. 6 SEM image of the WFA particle after the aqueous treatment

In conclusion, during the treatments, the WFA undergoes changes that may affect its further properties. Both treatments wash a rather deep surface layer off, significantly increasing the surface area of the particles.

4 Conclusions

Thus, in this article, mineralogical composition, total element content, leaching properties, and morphology of MSWI fly ash are studied. The metal elution ability of two complexing agents (sodium EDTA and gluconate) from the WFA is assessed.

- The main contaminants among cations found in WFA are Cd, Cr, Mo, Pb, and Zn. Their leaching exceeds the legislation limit 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 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 irregular developed shape (about 90% visually) and spherical particles (about 10% visually);
- The ability to elute metals from the WFA of gluconate is especially efficient (10–200 times higher than of water) for Cd, Cu, and Zn; and the elution ability of EDTA is the most efficient for Cd (800 times higher than of water).

In conclusion, it is necessary to attract special attention to the fact that the same WFA, which, according to the leaching test results (not reported in this paper), looks safe from almost all points after being washed with water, at the same time, seems to be extremely hazardous (it matches the criteria for an even higher-hazard category than the untreated one). This article aimed to show that it is necessary not only to study the leaching of certain components and the factors that affect them, but also to pay attention to the amount of the elements remaining inside the WFA after various treatments. The aim underneath this research is to draw attention to the issue of MSWI FA 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 all the data provided will be of help in resolving issues related to treating, processing, and utilizing of WFA.

This study will be continued and elaborated on the following parts:
• The comparison of the combined and aqueous-only treatments: their ability to elute metals from WFA;
• The effect of treatments on the mineralogical and total composition of WFA;
• The study of differently treated WFA and its leaching properties.

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6 References


