# Hydrocyclone separation as a tool for reduction of the amount of heavy metals in municipal solid waste incinerator (MSWI) residues

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*Municipal solid waste incineration residues such as fly ash and air pollution control residues are classified as hazardous waste and disposed of, although they contain potential resources. The most problematic elements in municipal solid waste incineration residues are leachable heavy metals and salts. Therefore, these residues usually do not meet the criteria for recycling as construction material or for landscaping, as they possess an environmental risk (and are classified as an H15 hazard material - waste capable by any means, after disposal, of yielding another substance, for example, leachate). Thus, an efficient treatment method should comprise a washing step to remove soluble chlorides, combined with an elimination step aiming to remove the heavy metals. As a consequence, it was proposed to use a cyclosizer device (hydrocyclone principle) for the separation of the incineration residues in order to prove the statement that the highest concentration of heavy metals can be found within the finest particles. Chemical and physical properties of two air pollution control residue samples and one fly ash sample were examined prior to sorting the samples into five size fractions by the cyclosizer. The results show that chloride salts can be removed from the residues during the cyclosizer separation process, and heavy metals were concentrated in the fine particle size fraction after the process. On the basis of these findings it can be assumed that removing the finest size fraction from the municipal solid waste incineration residues (fractions <12 µm and <14 µm respectively), will decrease the heavy metal content by* ***Hg*** *51* **ï** *60%;* ***Ag*** *32* **ï** *36%;* ***Cd*** *37* **ï** *46%;* ***Co*** *23* **ï** *27%;* ***Cr*** *30* **ï** *40%;* ***Cu*** *27* **ï** *37%;* ***Ni*** *21* **ï** *26%;* ***Pb*** *34* **ï** *42%;* ***Sb*** *44* **ï** *50%;* ***Zn*** *33* **ï** *40%. Concentrations of the heavy metals in the coarse fraction of these residues are below the regulatory limit, and therefore this study suggests that they can be used for recycling and reuse.*

***Keywords:*** *cyclosizer, waste incineration, MSWI residues, heavy metal, fly ash, APC*

## Introduction

The last two decades have seen a growing trend towards municipal solid waste incineration (MSWI) due to its unique benefits of mass and volume reduction of waste (Liu et al., 2016; Mikulį iÍ, 2016). There are several types of MSWI residues, though the finer fraction, referred to as fly ash (FA) and air pollution control (APC) residue, pose serious environmental problems (Yao et al., 2015; Raclavská et al., 2017).

Fly ash and APC residue consist of fine particles that contain significant amounts of leachable toxic elements, including heavy metals, chloride salts and sulphates (Saqib and Bäckström, 2016; Nowak et al., 2013).
The concentrations of metals in APC from combustion of municipal waste decrease in the following series: Zn > Cu > Pb > Sb > Cr > As > Cd (Saqib and Bäckström, 2016) or Zn > Pb > Cu > Cr > Ni > Cd, and the concentrations of Zn and Pb are higher by one order or more than those of other metals (Pan et al., 2013). Metals which are present in ion-exchangeable form are leached in the following order: Cd > Cu > Sb > Zn> As > Pb > Cr (Saqib and Bäckström, 2016). In addition, highly toxic organic substances and organic pollutants such as dioxins (PCDD), furans (PCDF) and PAHs are also present making the utilization of MSWI residues even more problematic (Saikia et al. 2007). Therefore, they usually do not meet the criteria for recycling as construction material or for possessing an environmental risk (and are classified as an H15 hazard material - waste capable by any means, after disposal, of yielding another substance, for example, leachate) (Aguiar et al., 2009). Several researchers have developed different treatment methods to decrease the leachability of the MSWI residues. These methods are generally classified as separation, stabilization/solidification and thermal techniques (Quina and Bordado, 2009). A limited number of studies mentioned fly ash and APC residue treatment using a hydrocyclone for their separation (Ko et al., 2013). Several studies recommended water washing the residues to remove soluble chlorides before applying another treatment (Mangialardi, 2003; Wang et al., 2010; Chen et al., 2017). A single washing, followed by washing of the filtration cake removes up to 99% of soluble chlorides according to a previous study (Hartmann, 2015). Recently authors have published the link between particle size and chemical composition of fly ash and they conclude that with decreasing particle size, the concentration of heavy metals increases (Wang et al., 2002; De Boom and Degrez, 2012). The distribution of major elements in different particle size fractions is less predictable (Fedje et al., 2010). The release of heavy metals into flue gas is related to chloride content in MSWI fly ash. Evaporation

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of Cd, Pb and Zn increases proportionally to increasing concentrations of chlorides in waste from MSWI (Chen et al., 2017).

Thus, an efficient treatment method should comprise a washing step to remove soluble chlorides, combined with an elimination step aiming to remove the heavy metals. As a consequence, it was proposed to use a cyclosizer device (hydrocyclone principle) for MSWI residue treatment. Apart from (Ko et al., 2013; Wang et al., 2002), there is a general lack of research in MSWI residue treatment by using a hydrocyclone or cyclosizer device. In addition to chlorides and heavy metals decrease, the question of high organic compound levels could be raised. However, the present study was limited to inorganic contaminants.

The objective of this study was to investigate the treatment of different MSWI residue samples to eliminate the hazard property H15 (reducing the chloride content) and mitigation of problematic elements (heavy metals, above all Hg and Pb). Three different residue samples were treated by using the cyclosizer device for separation. Chemical and physical properties of residue size classes were examined. The statement that the highest concentration of heavy metals can be found within the finest particles is to be investigated. Using these mineral processing methods for MSWI residue treatment could make it possible to eliminate the classification of the MSWI residues as an H15 hazard property material and re-categorize it from hazardous waste to non-hazardous waste. Therefore, treated MSWI residue is a promising material which can save the use of non-renewable natural resources and it is also cost-effective when there is no need to handle it as a hazardous material.

## Materials and methods

### Materials

The MSWI residue samples (two APC residues and one FA sample) used for measurements are referred to as APC 1, APC 2 and FA 3. MSWI residues samples were collected during the years 2013 and 2014. A detailed description of the samplesô origin is confidential. However, a description of the technologies used in the incineration plants is shown below:

**APC 1** ï The incineration plant consists of 3 lines of grate furnaces, a dry flue gas cleaning system with the addition of crushed activated coke into the flue gas stream before the baghouse filter, utilizing municipal solid waste (188,000 t/y). The main reason for the injection of activated coke is the removal of mercury and other pollutants. The annual solid residue amount is 47,500 t of slag, 3,700 t of APC residue and 190 t of filter cake with a water content of approximately 40 per cent.

**APC 2** ï The incineration plant consists of two lines of grate furnaces, a dry flue gas cleaning system and electrostatic precipitators, utilizing 203,000 t of municipal solid waste per year. The remaining dust (filter fly ash) is subtracted, followed by a wet chemical two-stage scrubber system. In the first stage, in an acidic environment, hydrochloric acid and mercury, as well as other substances, are extracted. After this, a fixed bed activated carbon absorber is installed. The remarkable differences are: the boiler ash and the filter ash are collected together, and a fixed bed carbon absorber is omitted. The annual solid residues amount is 44,000 t of slag, 3,300 t of APC residue and 270 t of filter cake with a water content of approximately 40 per cent.

**FA 3** ï The incineration plant uses a fluidised combustion technology, electrostatic precipitators and utilises almost exclusively refuse-derived fuel (RDF), with a capacity of 110,000 t/y. Boiler ash and filter ash are collected together. Annually 10,100 t of bottom ash and 11,200 t of fly ash emerge as a solid residue.

Colour of the samples varied from light grey to light brown (colour was influenced by the incineration technology and combusted materials). All the residue samples were alkaline with **pH** values from **12.2** to **12.4** and **density**: **APC 1 = 2.97 g/cm$^3$, APC 2 = 2.85 g/cm$^3$, FA 3 = 2.49 g/cm$^3$**. Good wettability was typical for all samples. The raw residue samples obtained from the MSWI plants were homogenised for further analysis and treatment.

### Methods

**Chemical analysis**. The chemical composition of the MSWI residues was determined by X-ray fluorescence (XEPOS III HE, Spectro) according to (CSN EN 15309, 2007). The analysis was conducted in the accredited laboratory Public Health Institute Ostrava, Czech Republic (ZUOVA). The MSWI samples (both raw and treated) were homogenised. The dry mass and the loss of ignition were established. The dry samples were ground to the size < 60 µm, and for the pellet preparation, the wax was added. The fluorescence analyses were conducted on the pelletised samples.

**Mineralogical analysis**. The phase composition of samples in the original state, after the removal of chlorides by washing, and after separation in hydrocyclone (APC1) were analysed using X-ray diffraction analysis. The verification of qualitative evaluation and also a semi-quantitative estimation of the composition of samples were determined by Rietveld analysis of diffraction data (software RayfleX Autoquan). Measurements were performed at the diffractometer Bruker AXS D8 Advance with 2ẽ /ẽ geometry, with Goebel mirror in the primary beam and with the energy dispersive detector SOL-XE. The results are presented together with estimates of statistical errors (statistical level 99%, i.e. 3ů).

Microanalysis of particles was performed by scanning electron microscope SEM, FEI Quanta 650 FEG equipped by analyzers EDX ï EDAX Apollo X, WDA ï LEXS, EBSD ï EDAX TSL, CL ï Gatan Mono 4. Polished sections were prepared for chemical analysis of particles. Chemical analysis of particles in separated grain size classes was focused on the identification of particles with the content of metals. The number of analysed particles in each class was 25.

**MSWI residue separation**. The separation was performed by using a cyclosizer (Metcon Laboratories, VSB-TUO). The cyclosizer is a precise laboratory apparatus for the rapid and accurate determination of particle size distribution within the sub-sieve range (Figure 1). Particles were separated according to their Stokesian settling characteristics by a principle based on the well-known hydraulic cyclone principle. The samples were sized at 100 µm before cyclosizing to achieve better separation results. Only the undersize fraction (< 100 µm) was used for the cyclosizer sorting. Separation size fraction boundaries were established according to the MSWI residue density (APC 1 = 2.97 g/cm$^3$, APC 2 = 2.85 g/cm$^3$, APC 3 = 2.49 g/cm$^3$), water temperature (10.1 °C) and flow speed (11.6 l/min). Approximately 180 L of water was used for the separation of 1.5kg of the sample. The S/L ratio was approximately 1:100.

The samples were sorted into five size fractions by the cyclosizer. The sixth size fraction was obtained by filtering the process water passing the No. 5 cyclone. Alternately, solids passing the No. 5 cyclone were determined by difference. The separated solids were settled, filtered, dried in ambient temperature and weighed to determine the size distribution.

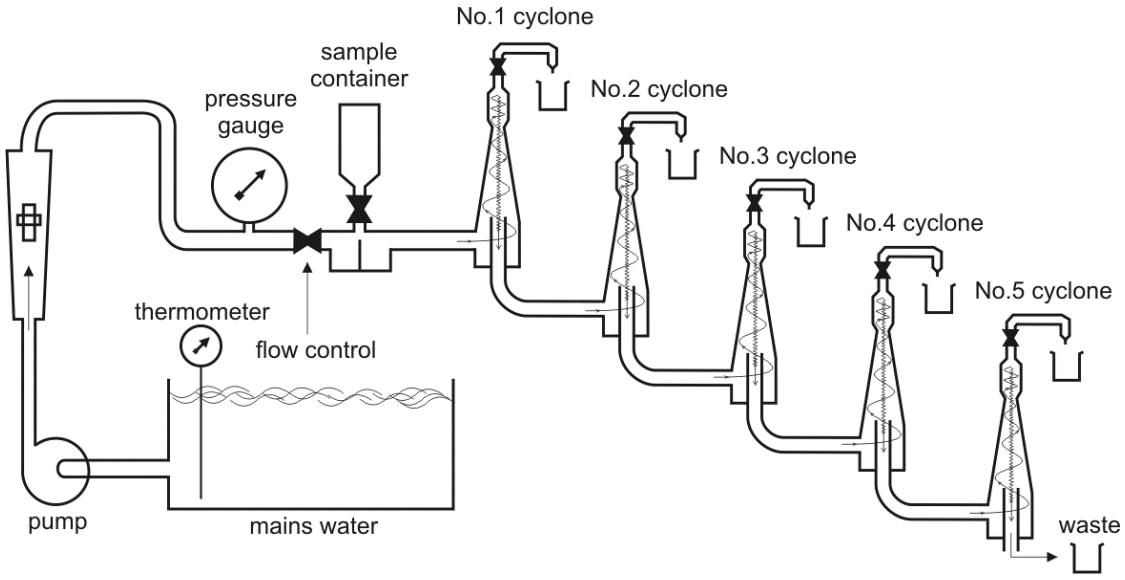


*Fig. 1. The diagrammatic arrangement of the cyclosizer device*

**Size fractions**

**APC 1** and **APC 2:** 1 (49 ï 100 µm); 2 (34 ï 49 µm); 3 (23 ï 34 µm); 4 (16 ï 23 µm); 5 (12 ï 16 µm); 6 (< 12 µm)

**FA 3:** 1 (55 ï 100 µm); 2 (39 ï 55 µm); 3 (26 ï 39 µm); 4 (19 ï 26 µm); 5 (14 ï 19 µm); 6 (< 14 µm)

## Results and discussion

### Untreated MSWI residue characteristics

Chemical and physical analyses of untreated samples were performed to obtain essential characteristics. The chemical composition of MSWI residues is strongly influenced by the flue gas cleaning technology and by the material that is combusted. Concentrations of major components, especially chlorides, can significantly influence APC and FA behaviour for further treatment. The amount of the major components expressed in wt.%

was calculated in terms of oxides. Concentrations of the major components can be found in Table 1. The concentrations of heavy metals in unprocessed MSWI residues are presented in Table 2.

Generally, calcium had the highest representation within all of the MSWI residue samples (13.5 ï 21 wt.% present as CaO), which may be associated with the lime injected during the flue gas cleaning process. Furthermore, high chloride concentrations can be considered as a significant characteristic of MSWI solid residues (APC 1 ~ 14.1 wt.% and APC 2 ~ 9.7 wt.%). Lower chloride concentrations for FA 3 (2.6 wt.%) is in relation to the combusted material, as waste-derived fuel is primarily combusted in this incineration plant. However, FA 3 sample showed high concentrations of Al, Fe, Mg, P and Si.

*Tab. 1. Major fly ash components concentrations in wt.%*

| Major MSWI residues components [wt.%] | | | |
|---|---|---|---|
| | APC 1 | APC 2 | FA 3 |
| $SiO_2$ | 10.17 | 13.65 | 31.52 |
| $Al_2O_3$ | 13.05 | 14.70 | 25.37 |
| $Fe_2O_3$ | 2.18 | 3.88 | 7.60 |
| CaO | 18.84 | 21.10 | 13.57 |
| MgO | 0.77 | 0.86 | 2.43 |
| $Na_2O$ | 14.39 | 10.97 | 4.05 |
| $K_2O$ | 6.32 | 4.69 | 1.60 |
| sulphates | 8.13 | 4.92 | 2.53 |
| chlorides | 14.10 | 9.73 | 2.62 |
| heavy metals | 2.14 | 1.95 | 0.77 |
| LOI | 9.80 | 13.49 | 7.91 |

Heavy metals: the sum of Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, and Zn
LOI: loss on ignition

*Tab. 2. The content of heavy metals (mg/kg) in unprocessed MSWI residues*

| Heavy metal content [mg/kg] | | | |
|---|---|---|---|
| | APC 1 | APC 2 | FA 3 |
| Hg | 37.1 | 16.8 | 1.9 |
| Ag | 18.2 | 11.4 | 3.1 |
| Cd | 237 | 181 | 12.2 |
| Co | 26 | 26 | 36.7 |
| Cr | 656 | 558 | 254 |
| Cu | 820 | 908 | 1550 |
| Ni | 51.9 | 60.4 | 56.9 |
| Pb | 2800 | 2580 | 1370 |
| Sb | 773 | 719 | 128 |
| Zn | 15900 | 14400 | 4210 |

MSWI residue obtained from the plant using baghouse filter technology for flue gas cleaning (APC 1) generally had the highest concentrations of heavy metals among the samples. Baghouse filters are usually located at the end of the flue gas cleaning process. Furthermore, in the case of APC 1, crushed activated coke is injected into the flue gas stream before the baghouse filter, which absorbs heavy metals, especially mercury, and other pollutants. The highest concentration of Hg (37.1 mg/kg) was found for APC 1. This concentration considerably exceeds the limit for Hg in a non-hazardous waste landfill (limit value of 20 mg/kg) (Purgar et al., 2014). In addition, Cd, Cr, Pb and Zn concentrations were highest in APC 1 sample.

**Mineralogical phase analysis**

The main mineral phases in fly ashes from MSWI form anhydrite, calcite, halite, and sylvite, calcium silicate, mayenite, and calcium aluminium silicate (Zhou et al., 2015). Mineralogical phase analysis of fly ashes is important from the point of view of determination of their puzzolan properties when utilised in the construction industry and also for determination of the form of chlorides occurrence that is important information for their removal because they represent the limiting factor for utilization of fly ashes (replacement of Portland cement in concrete). Chlorides form an important mineral phase of fly ashes from MSWI. They are present most often as halite (NaCl) and sylvite (KCl). Halite occurs in fly ashes in amounts from 2.4% (APC 3) to 12% (APC 1), sylvite is present in amounts from 4.3% (APC 2) to 7% (APC 1). Other crystalline phases in fly ashes from MSWI include anhydrite ($CaSO_4$) 2.61 ţ 5.74%, calcite ($CaCO_3$), quartz ($SiO_2$), periclase (MgO), hematite ($Fe_2O_3$) and silicate phase. The samples APC 1 and 2 have larnite ($Ca_2SiO_4$) 12% and alumosilicate: gehlenite ($Ca_2Al[AlSiO_7]$) 6.58 ï 8.06%. The sample APC 3 contains muscovite ($KAl_2[AlSi_3O_{10}](F,OH)_2$) and sanidine ($K[AlSi_3O_8]$). Amorphous component forms 37 ï 48% in APC 1 and 2, in fly ash APC 3 it is up to 64%. After removal of chlorides by washing, there appeared in fly ashes: tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) in amounts of 3 ţ 6% and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) in concentrations up to 3%, formed during washing

of fly ash as a result of reaction of calcium aluminate with calcium sulphate (Chindaprasirt et al., 2013). The content of calcite in APC1 and APC2 increased after washing from 11 to 15%.

The sample APC1 separated in the cyclosizer proved that the amount of amorphous component increased (up to 55%) in comparison with APC1 in the original state (37.1%). The highest amount of amorphous component was found in the particle size class over 63 µm (59.1%), and the lowest amount was found in the particle size class from 12 to 28 µm. The content of the amorphous component increases again in particles of the size below 12 µm. In a relationship with the content of the amorphous component in individual particle size classes, it was determined the highest amount of gehlenite (9%), larnite (14%), anhydrite (6%) and halite (1.3%) in the particle size class from 12 to 28 µm. The highest amount of quartz was determined in the class over 63 µm. The highest content of calcite and periclase was determined in the class below 12 µm. Separation of APC1 in cyslosizer did not cause a significant enrichment of phases with puzzolan properties. The concentrations of halite varied in the range from 0.25 to 1.31%, and the lowest amounts were found in the class over 63 µm (0.52%) and below 13 µm (0.25%).

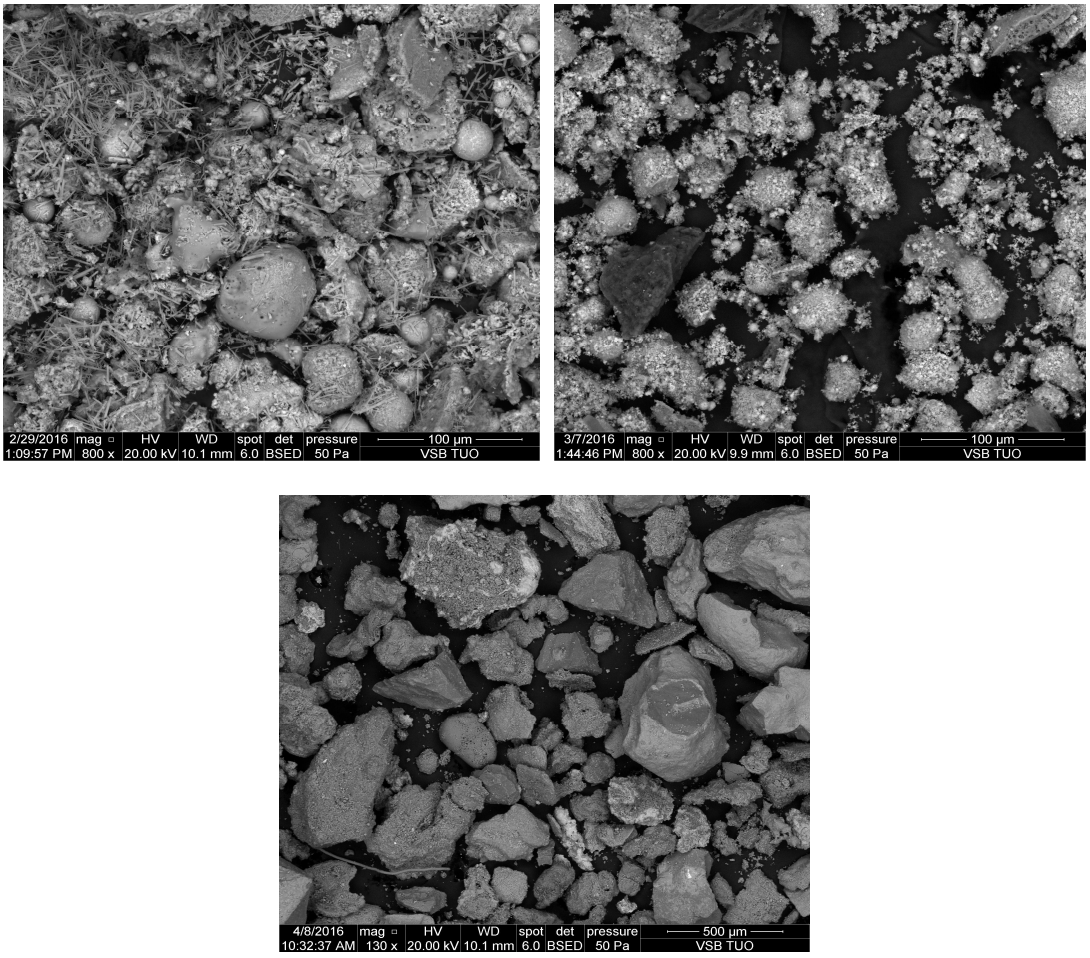


*Fig. 2. Scanning electron microphotographs: APC1 – original sample (upper left), APC1 after separation in cyclosizer, particle size class 25 – 45 µm (upper right), sample after washing – extraction by water, removal of 98% water-soluble chlorides (below).*

Nature of metal occurrence in particles of fly ash before the beginning of chloride removal by washing or separation in cyclosizer was studied by chemical analysis of particles. It was found that metals are present prevalently in the form of native metals (Pb), oxides: CuO, SnO, ZnO, $FeO_x$, PbO, or mixed phases: Pb-Al-O, Pb-Ca-O, Cr-Fe-O, Cr-Fe-Ca, Cr-Zn-$O_x$, Sn-Fe, Fe-Ca-O, and Fe-Cr. The analysis of particles after separation in cyclosizer proved that even when particles are separated according to the size, they are covered by particles of chloride of size from 1 to 2 µm. The same trend appears in all particle size classes from cyclosizer. The highest concentrations of chloride (17-21%) were determined in particles of size over 63 µm. The highest number of particles containing Zn was found in the particle size class from 63 µm to 1 mm (91%) and in the finest class below 25 µm (73%). The number of particles containing Zn in other particle size classes was 45%. The highest average concentration of Zn was determined in particles over 1 mm (9.15%). The particles with the highest average concentrations of Si (8.02%) and Al (3.92%) occur in the particle size class < 25 µm.

After the separation in cyclosizer, the microanalysis identified the particles containing Cu, Co and V, while particles containing Pb were not identified. Water-soluble salts of Pb were probably formed in the environment of the saturated chloride solution (Ye et al., 2017). From the results of microanalysis it follows that during the separation in cyclosizer, chlorides were not sufficiently effectively removed, which was caused by the short time of contact between water and particles (approximately 20 minutes). Hartmann et al. (2015) determined that leaching after one hour had the efficiency of 72% for the chloride removal, and only after 24 hours, it reaches 94%. Pan et al. (2008) report recovery of 86% after two hours of leaching. During the direct washing (24 hours), the efficiency of 98% was achieved at the ratio L/S=10:1 (Figure 2).

**Water leachate**

Landfill criteria and acceptance limits are not uniform within the European Union. Valid European legislation was used for the MSWI residue waste category evaluation (European Council Decision 2003/33/EC). Water leachate was prepared according to (CSN EN 12457-2, 2003) and compared to the limits according to (European Council Decision 2003/33/EC) in Table 3.

The total leachable fraction was by far largest for the APC 1 and was dominated by chlorides of Ca, Na and K, APC 2 was very similar. The APC 1 and APC 2 sample contained soluble forms of Pb in significant amounts. A comparison of the amounts of elements dissolved in the leachate revealed that the main sources of metal ions are likely to be chlorides. However, in the high pH range, Pb, as well as many other metals, show amphoteric behaviour and thus dissolve as oxo-anions. Such processes may also take place during a leaching test (Abbas et al., 2001). According to Takaoka et al. (2005), Pb and Zn mainly exist as water-soluble $PbCl_2$ and $ZnCl_2$ in MSWI residues. Furthermore, Ko et al. (2013) reported that only a small amount of Pb and Zn from MSWI fly ash could be transferred to the liquid phase, but Cr and Cu mostly remain in the solid phase (Hsiao et al., 2002). Higher concentrations of Pb found in the leachate from APC 1, and APC 2 in this study are in agreement with Ko et al. (2013). Nevertheless, a higher amount of Cr was found in a liquid phase in this study. Cr(VI) may have been dissolved and then transformed into a less soluble form in a secondary reaction such as reduction to Cr(III) in MSWI residue leachate (Abbas et al., 2001).

*Tab. 3. Water leachate results of untreated MSWI residue samples, compared with European waste landfill limits (values exceeding the non-hazardous limits are highlighted)*

| Parameter | Unit | MSWI residues | | | Limits (2003/33/EC) | | |
|---|---|---|---|---|---|---|---|
| | | APC 1 | APC 2 | FA 3 | I | NH | H |
| pH | [-] | 10.64 | 11.63 | 9.43 | - | - | - |
| D.S. | [mg/kg] | 30925 | 19495 | 4055 | 4000 | 60000 | 100000 |
| DOC | [mg/kg] | 42.7 | 46.2 | 51.5 | 500 | 800 | 1000 |
| $Cl^-$ | [mg/kg] | **101046** | **89653** | 14927 | 800 | 15000 | 25000 |
| $SO_4^{2-}$ | [mg/kg] | **23200** | 11500 | 6680 | 1000 | 20000 | 50000 |
| F- | [mg/kg] | 46.5 | 49.4 | 5.1 | 10 | 150 | 500 |
| As | [mg/kg] | 0.9 | 0.1 | 0.3 | 0.5 | 2 | 25 |
| Ba | [mg/kg] | 6.1 | 5.8 | 5.0 | 20 | 100 | 300 |
| Cd | [mg/kg] | 0.005 | 0.331 | 0.015 | 0.04 | 1 | 5 |
| Cr | [mg/kg] | **12.4** | 2.0 | 9.8 | 0.5 | 10 | 70 |
| Cu | [mg/kg] | 0.2 | 0.2 | 0.2 | 2 | 50 | 100 |
| Hg | [mg/kg] | 0.022 | 0.009 | 0.005 | 0.01 | 0.2 | 2 |
| Mo | [mg/kg] | **33.7** | 4.5 | 4.4 | 0.5 | 10 | 30 |
| Ni | [mg/kg] | 0.2 | 0.2 | 0.2 | 0.4 | 10 | 40 |
| Pb | [mg/kg] | **59.9** | **39.7** | 0.3 | 0.5 | 10 | 50 |
| Sb | [mg/kg] | **4.10** | 0.419 | 0.050 | 0.06 | 0.7 | 5 |
| Se | [mg/kg] | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 | 7 |
| Zn | [mg/kg] | 17.4 | 22.0 | 0.5 | 4 | 50 | 200 |
| Phenol index | [mg/kg] | 15.8 | 0.2 | 0.1 | 1 | - | - |

D.S.: dissolved solids; I = Inert; NH = Non-Hazardous; H = Hazardous

Generally, it was found that the concentrations of heavy metals in the solid phase were higher than those in the liquid phase, which is in agreement with (Ko et al., 2013). These findings support the premise that the hydrocyclone separation process can transfer water-soluble salts from MSWI residues to liquid phases while preserving most of the heavy metals in solid phases.

**Cyclosizer separation**

Quantitative analysis of sample yield was calculated using an initial weight of 80 g of sample. Results of the quantitative analysis (recovery rate) are shown in Table 4, and heavy metal yield results are shown in Figure 3.

*Tab. 4. Recovery rates of MSWI residue samples after separation using a cyclosizer*

| Particle size range [µm] | | APC 1 | APC 2 | FA 3 | APC 1 | APC 2 | FA 3 |
|---|---|---|---|---|---|---|---|
| APC 1 & APC 2 | FA 3 | [g] | [g] | [g] | [%] | [%] | [%] |
| 49-100 | 55 ï 100 | 4.1 | 6.5 | 4.6 | 5.1 | 8.1 | 5.7 |
| 34-49 | 39 ï 55 | 6.5 | 9.0 | 8.8 | 8.2 | 11.3 | 11.0 |
| 23-34 | 26 ï 39 | 11.0 | 12.7 | 13.9 | 13.7 | 15.9 | 17.4 |
| 16-23 | 19 ï 26 | 9.0 | 9.1 | 11.1 | 11.2 | 11.3 | 13.9 |
| 12-16 | 14 ï 19 | 5.7 | 5.2 | 7.3 | 7.2 | 6.6 | 9.1 |
| < 12 | < 14 | 19.7 | 22.2 | 31.2 | 24.6 | 27.8 | 39.0 |
| Dissolved solids | | 24.0 | 15.2 | 3.2 | 30.0 | 19.0 | 4.0 |
| Sum | | 80 | 80 | 80 | 100 | 100 | 100 |

Elemental concentration in the size fractions was determined by using X-ray fluorescence analysis. The yield of the heavy metals chosen (Hg, Ag, Cd, Co, Cr, Cu, Ni, Pb, Sb a Zn) was calculated from the recovery rate of that size fraction (Table 4) and heavy metal concentrations in that size fraction. It can be concluded that the heavy metals tended to distribute into the size fractions in the same way for all fly ash samples, with the highest concentrations observed in two specific size fractions ï the oversize fraction (> 100 µm) and in the smallest size fraction (< 12 µm and < 14 µm respectively). Rönkkömäki et al. (2008), and Lanzerstorfer (2015) reported the same trend in the heavy metal distribution in the oversize and sub-sieve fraction for Cd and Zn. Moreover, according to Lanzerstorfer (2015), Pb is concentrated in the finest fraction of MSWI fly ash. Barbosa et al. (2013) examined fly ash samples from biomass incineration and showed an increasing concentration of all elements (except Hg) with decreasing particle size. Dahl et al. (2009) reported the tendency of increasing concentration with decreasing particle size for Zn but found no such consistent trend for Cd and Co.

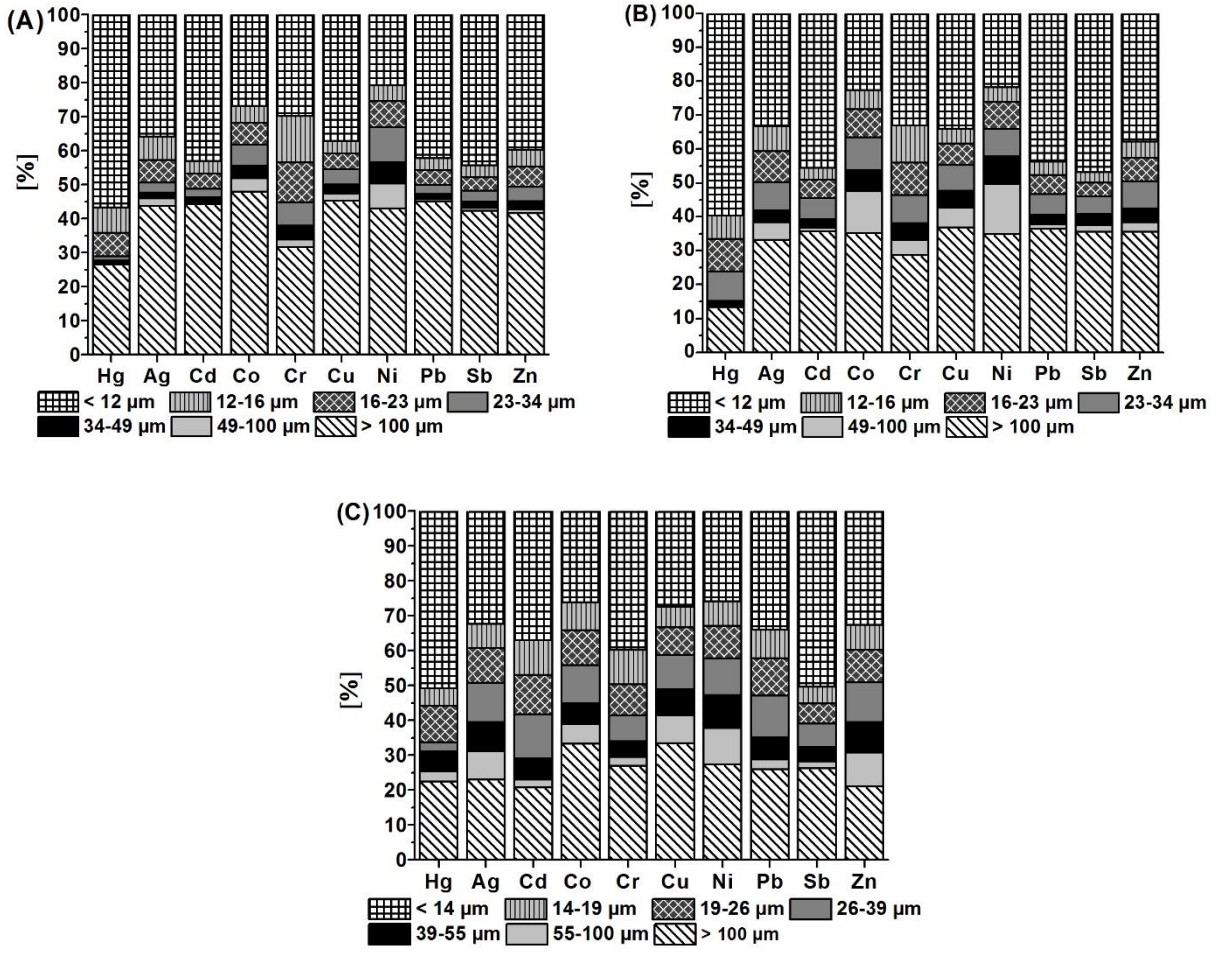


*Fig. 3. Heavy metal yield after sieving and separation using a cyclosizer: (A) APC 1, (B) APC 2, (C) FA 3*

On the basis of these results it can be assumed that after removal of the finest particles (fractions < 12 µm and < 14 µm respectively), the heavy metal content would be decreased by: ***Hg*** 51 ï 60%; ***Ag*** 32 ï 36%; ***Cd*** 37 ï 46%; ***Co*** 23 ï 27%; ***Cr*** 30 ï 40%; ***Cu*** 27 ï 37%; ***Ni*** 21 ï 26%; ***Pb*** 34 ï 42%; ***Sb*** 44 ï 50%; ***Zn*** 33 ï 40%. Theoretical mercury concentration for APC 1 would then be 16.32 mg/kg and for APC 2

13.72 mg/kg. These concentrations are within the Austrian landfill limit for mercury disposal (20 mg/kg), according to the Austrian Landfill statutory body (BGBl. II Nr. 104/2014).

Hydrocyclone separation is not a zero-waste technology. At the end of the process, wastewater containing high concentrations of salts (especially chlorides) and some heavy metals are generated; thus, it is essential to carry out wastewater treatment and recycling. However, high chloride-containing wastewater can be used for salt recovery or can be treated by adding sodium aluminate ($NaAlO_2$) to form insoluble Friedelôs salt at high pH conditions (Abdel-Wahab, 2002). The treated water can then be reused in the hydrocyclone separation process.

The above results demonstrate that hydrocyclone separation technology is promising for MSWI residue treatment and the heavy metal content reduction. However, the optimal separation boundary and separation efficiency should be investigated further. Therefore, it is proposed to build a pilot-scale hydrocyclone device for separating MSWI residues to confirm or deny the results stated in this paper.

## Conclusion

Three MSWI residue samples from different incineration plants were examined within this study. Chemical and physical properties of two APC residue samples and one fly ash sample were examined. Higher content of heavy metals was found in the samples, ranging from 0.77 (FA 3) to 2.14 wt.% (APC 1). Therefore, a unique separation process was applied to reduce the heavy metals content. The separation into six size fractions was performed by using a cyclosizer. The results show that chloride salts can be removed from the MSWI residues during the cyclosizer separation process by simple water extraction process, when the value of ratio S:L = 1:10 is reached and the time of contact with water is sufficient, i.e. more than one hour. Furthermore, heavy metals were concentrated in the fine particle size fraction after the process. On the basis of these findings, it can be assumed that removing the finest size fraction from the MSWI residues (fractions < 12 µm and < 14 µm respectively), will decrease the heavy metal content by up to 60% for Hg (APC 2). In addition a significant decrease of other heavy metals was observed as well (namely Sb > Cd > Pb > Zn > Cr > Cu > Ag > Co > Ni). Hydrocyclone separation seems to be a very promising method that could be used for the reduction of heavy metal content in the MSWI residues. The coarse particles of the MSWI residues had Hg concentrations below the regulatory limit. Therefore, it can be suggested that they may be used for recycling and reuse. However, use of this process on an industrial scale and its economic value needs to be further investigated, which was not a part of this study.

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## References

Abbas, Z., Steenari, B.M. and Lindqvist, O. (2001). A study of Cr(VI) in ashes from fluidized bed combustion of municipal solid waste: leaching, secondary reactions and the applicability of some speciation methods. *Waste Management*, 21(8), pp. 725-739.

Abdel-Wahab, A. and Batchelor, B. (2002). Chloride removal from recycled cooling water using ultra-high lime with aluminium process. *Water Environmental Research*, 74, 2002, pp. 256-263.

Aguiar Del Toro, M., Calmano, W. and Ecke, H. (2009). Wet extraction of heavy metals and chloride from MSWI and straw combustion fly ashes. *Waste Management*, 29(9), pp. 2494-2499.

Austrian Landfill Statutory Body, Deponieverordnung (2008). *BGBl. II Nr. 104/2014 ï Nr. 39.* Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien.

Barbosa, R., Dias, D., Lapa, N., Lopes, H. and Mendes, B. (2013). Chemical and ecotoxicological properties of size-fractionated biomass ashes. *Fuel Processing Technology*, 109, pp. 124-132.

Chen, W., Kirkelund, G.M., Jensen, P.E. and Ottosen, L.M. (2017). Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. *Waste Management*, 68, pp. 240-251.

Chindaprasirt, P., Thaiwitcharoen, S., Kaewpirom, S. and Rattanasak, U. (2013). Controlling ettringite formation in FBC fly ash geopolymer concrete. *Cement and Concrete Composites*, 2013, 41, pp. 24-28.

Dahl, O., Nurmesniemi, H., Pöykiö, R. and Watkins, G. (2009). Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. *Fuel Processing Technology*, 90 (7-8), pp. 871-878.

De Boom, A and Degrez, M. (2012). Belgian MSWI fly ashes and APC residues: A characterisation study. *Waste Management*, 32(6), pp. 1163-1170.

European Council Decision (2003). *European Council Decision 2003/33/EC - Establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of Annex II* to Directive 1999/31/EC.

Fedje, K.K., Rauch, S., Cho, P. and Steenari, B.M. (2010). Element associations in ash from waste combustion in fluidized bed. *Waste Management*, 30, pp. 1273-1279.

Hartmann, S., Koval, L., Ġkrobánková, H., Matýsek, D., Winter, F. and Purgar, A. (2015). Possibilities of municipal solid waste incinerator fly ash utilisation. *Waste Management and Research*, 33(8), pp. 740-747.

Hartmann, S., Matysek, D., Stary, M. and Skrobankova, H. (2015). Removal of Chlorides from Waste Incineration Residues. *InŨynieria Mineralna-Journal of the Polish Mineral Engineering Society*, 16(1), pp. 145-150.

Hsiao, M.C, Wang, H.P., Wei, Y.L, Chang, J-E. and Jou, C.J. (2002). Speciation of copper in the incineration fly ash of a municipal solid waste. *Journal of Hazardous Materials*, 91(1-3), pp. 301-307.

Ko, M.-S., Chen, Y.-L. and Wei, P.-S. (2013). Recycling of municipal solid waste incinerator fly ash by using hydrocyclone separation. *Waste Management*, 33(3), pp. 615-620.

Lanzerstorfer, Ch. (2015). Cyclone fly ash from a grate-fired biomass combustion plant: Dependence of the concentration of various components on the particle size. *Fuel Processing Technology*, 131, pp. 382-388.

Liu, S-J., Guo, Y.-P., Yang, H.-Y., Wang, S., Ding, H. and Qi, Y. (2016). Synthesis of a water-soluble thiourea-formaldehyde (WTF) resin and its application to immobilize the heavy metal in MSWI fly ash. *Journal of Environmental Management*, 182, pp. 328-334.

Mangialardi, T. (2003). Disposal of MSWI fly ash through a combined washing-immobilisation process. *Journal of Hazardous Materials*, 98(1-3), pp. 225-240.

Mikulļiĺ, H., von Berg, E., Vujanoviĺ, M., Wang, X., Tan, H. and Duiĺ, N. (2016). Numerical evaluation of different pulverized coal and solid recovered fuel co-firing modes inside a large-scale cement calciner. *Applied Energy*, 184, pp. 1292-1305.

Nowak, B., Aschenbrenner, P. and Winter, F. (2013). Heavy metal removal from sewage sludge ash and municipal solid waste fly ash - A comparison. *Fuel Processing Technology*, 105, pp. 195-201.

Pan, J.R., Huang, Ch., Kuo, J.J. and Lin, S.H. (2008). Recycling MSWI bottom and fly ash as raw materials for Portland cement. *Waste Management*, 28, pp. 1113-1118.

Pan, Y., Wu, Z., Zhou, J., Zhao, J., Ruan, X.,Liu J. and Qian, G. (2013). Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China. *Journal of Hazardous Materials*, 261, pp. 269-276.

Purgar, A., Fellner, J., Hahn, M., Hartmann, S., Lederer, J., Rechberger, H. and Winter, F. (2014). Mercury in Vienna´s waste incineration cluster and related problems for fly ash disposal. In *Proceedings Venice 2014, Fifth International Symposium on Energy from Biomass and Waste*, Venice, Italy.

Quina, M. J. and Bordado, J. C.M. (2009). Quinta-Ferreira, R. M., The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues. *Waste Management*, 29(9), 2009, pp. 2483-2493.

Raclavská, H., Corsaro, A., Hartmann-Koval, S. and Juchelková, D. (2017). Enrichment and distribution of 24 elements within the sub-sieve particle size distribution ranges of fly ash from wastes incinerator plants. *Journal of Environmental Management*, 203, pp. 1169-1177.

Rönkkömäki, H., Pöykiö, R., Nurmesniemi, H., Popov, K., Merisalu, E., Tuomi, T. and Välimäki, I. (2008). Particle size distribution and dissolution properties of metals in cyclone fly ash. *International Journal of Environmental Science*, 5(4), pp. 485-494.

Saikia, N., Kato, S. and Kojima, T. (2007). Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash. *Waste Management*, 27(9), pp. 1178-1189.

Saqib, N. and Bäckström, M. (2016). Chemical association and mobility of trace elements in 13 different fuel incineration fly ashes. *Fue*l, 165, pp. 193-204.

Standards Czech (2003). *Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 I/kg for materials with particle size below 4 mm (without or with size reduction)*, CSN EN 12457-2:2003 (83 8005), Czech Standard.

Standards Czech (2007). *Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence*, CSN EN 15309, Czech Standard.

Takaoka, M., Yamamoto, T., Tanaka, T., Takeda, N., Oshita, K. and Uruga, T. (2005). Direct Speciation of Lead, Zinc and Antimony in Fly Ash from Waste Treatment Facilities by XAFS spectroscopy. *Physica Scripta*, T115, pp. 943-954.

Wang, K.-S., Sun, C.-J. and Yeh, C.-C. (2002). The thermotreatment of MSW incinerator fly ash for use as an aggregate: a study of the characteristics of size-fractioning. *Resources, Conservation and Recycling*, 35(3), pp. 177-190.

Wang, L., Jin, Y., Nie, Y. and Li, R. (2010). Recycling of municipal solid waste incineration fly ash for ordinary Portland cement production: A real-scale test. *Resources, Conservation and Recycling*, 54, (12), pp. 1428-1435.

Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S. and Xi, Y.Q. (2015). A comprehensive review on the applications of coal fly ash. *Earth-Science Reviews*, 141, pp. 105-121.

Ye, M., Li, G., Yan, P., Zheng, L., Sun, S., Huang, S., Li, H., Chen, Y., Yang, L. and Huang, J. (2017). Production of lead concentrate from bioleached residue tailings by brine leaching followed by sulfide precipitation. *Separation and Purification Technology*, 183, pp. 366-372.

Zhou, J., Wu, S., Pan, Y., Zhang, L., Cao, Z., Zhang, X., Yonemochi, S., Hosono, S., Wang, Y., Oh, K. and Qian, G. (2015). Enrichment of heavy metals in fine particles of municipal solid waste incinerator (MSWI) fly ash and associated health risk. *Waste Management*, 43, pp. 239-246.