Mercury in Vienna's waste incineration cluster and related problems for fly ash disposal

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SUMMARY: In Vienna thirteen lines of waste incineration are in operation. Altogether they annually utilize about 1 Million tons of municipal solid waste, hazardous waste and municipal sewage sludge. The total mercury input into the waste incineration plants is determined to be 700 kg per year. The combustion technologies used are grate furnaces, fluidized bed combustors and rotary kilns. All thirteen incineration lines s are equipped with wet flue gas cleaning systems. While the mercury contents of the filter cake generated by the (from wet flue gas cleaning systems generally exceed the limit value (20 mg/kg) for disposal at non-hazardous waste landfills, Hg contents in slag and bottom ash are far below those limit values. Fly ashes investigated at the different incineration plants show a somehow diverse picture with respect to Hg contents. At most plants Hg contents are in the range of 0.2 to 15 mg/kg and thus below the limit value for non-hazardous waste landfills. Only at incinerators that inject activated carbon into the flue gas upstream the bag house filter, increased Hg contents are observable. Lab scale tests demonstrate that acidic leaching (pH 3 - 10) of those fly ashes (with increased Hg contents) is not capable to sufficiently reduce the content of mercury. The reason for the non solubility of these mercury compounds is their appearance as metallic Hg^0 or their strong bond to the activated coke.

1. INTRODUCTION

Vienna's waste incineration cluster consists of 7 lines of grate furnaces, 4 lines of fluidized bed combustors and 2 rotary kilns operated at 4 different sites. Altogether at these 13 lines about 1 million tons of waste (municipal solid waste MSW, hazardous waste, and sewage sludge) are incinerated per year, whereby 45,000 tons of fly ash are produced. Due to Austrian legislation, namely (DVO,2008) and (AVVO,2003), MSW incineration fly ash is classified as hazardous waste and therefore has to be deposited on underground disposal sites or stabilized with Portland cement prior disposal at non-hazardous waste landfills.
In an ongoing research project (Christian Doppler Laboratory for Anthropogenic Resources)

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alternative treatment methods, that allow fly ash disposal at non-hazardous waste landfills without the addition of cement, are investigated. The main objectives of these treatment methods are the reduction of the total content of water soluble salts and mercury, as well as the leachability of selected heavy metals (Purgar,2013). For the disposal at non-hazardous waste landfill (Reststoffdeponie according to the Austrian landfill directive) the limiting mercury content is 20 mg/kg dry mass, as long as no stabilization measures are applied (DVO 2008). Considering these challenges (in particular the reduction of soluble salts) and the fact that all incinerators investigated are equipped with a wet flue gas cleaning system, a wet chemical fly ash decontamination process is envisaged. Such wet treatment method, utilizing the scrubber water, would easily allow removing water soluble salts and reducing the solubility of many heavy metals due to the reduction in the alkalinity of treated fly ash (IAWG, 1997). Hence, the only challenge that remains unclear when utilizing scrubber water for fly treatment is the reduction of the mercury content. Against this background the present paper aims firstly at evaluating the potential of wet acidic fly ash treatment for reducing the mercury content and secondly at assessing the overall significance of the total mercury flows in fly ashes in comparison to other residues from waste incineration.

Thereto two research approaches have been followed. In order to investigate the potential for reducing the mercury content by acidic leaching, similar to the FLUWA (Schlumberger,2013) process, laboratory tests have been carried out, whereby their design considered possible ratios between fly ashes generated and acidic scrubber water available. By determining the specification of the mercury compounds present in fly ashes and evaluating their potential removal rates under different conditions, the feasibility of an acidic leaching process with respect to the reduction of the mercury content has been assessed.

As only some fly ash streams investigated are characterized by increased mercury contents (that prohibit a disposal at non-hazardous waste landfills) the origin of the mercury pollution, as well as its significance with respect to total mercury flows in combustion residues have been investigated. For the latter a detailed material flow analysis for mercury in Vienna's waste incineration cluster has been carried out. Thereto the combustion residues bottom ash, fly ash, filter cake and used activated coke have been evaluated for their mercury load. This information has been used together with data about mercury emission monitoring in order to assess the influence of waste feed, combustion technology and flue gas cleaning system on the mercury content in the resulting fly ash.

2. MATERIAL AND METHOD

2.1 Investigated Residue Streams

In Vienna 13 Lines of waste incineration are in operation. All these lines use an almost similar configuration of flue gas cleaning which is summarized in Figure 1. Detailed information about the investigated incinerators can be found in Böhmer (2006). Some of these 13 lines of waste incineration use a similar combustion technology as well as the same flue gas cleaning system. Additionally the waste input is the same. Therefore these 13 lines of incineration are grouped as follows:

The **first group** consists of two lines of waste incineration, utilizing together 232,000 tons of municipal solid waste (msw) annually. Besides flue gas about 48,000 t of slag, 8,100 t of fly ash and 270 t of filter cake (with a water content of 50 percent) are produced. As combustion technology grate furnaces are used (see Figure 1(A)). The heat transfer zone - Figure 1 (D) - from which boiler ash is subtracted, is followed by the flue gas cleaning system. Due to Austrian legal

restrictions boiler ash is classified as fly ash. 4,300 tons of boiler fly ash are recovered from the heat transfer zone each year (y). The flue gas cleaning system is accomplished, referring to Figure 1, as follows: An electrostatic precipitator (esp), where 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, beside other substances, hydrochloric acid and mercury is extracted. After this a fixed bed activated carbon adsorber is installed. 300 t per year of used activated coke, classified as hazardous waste, is utilized in the incinerators of group 4. Subsequent a selective catalytic reduction (scr) – system is installed.

The **second group** of incinerators, two lines of grate furnaces, are using almost the same system as the incinerators in group 1. Remarkable differences are: the boiler ash and the filter ash are collected together and a fixed bed carbon adsorber is omitted. Altogether these incinerators utilize 203,000 t of municipal solid waste per year, besides flue gas about 44,000 t/y of slag, 3,300 t/y of fly ashes and 270 t/a of filter cake (40% moisture) are generated. In Figure 1 these facilities are indicated by B, D, F (esp), G, I, and J.

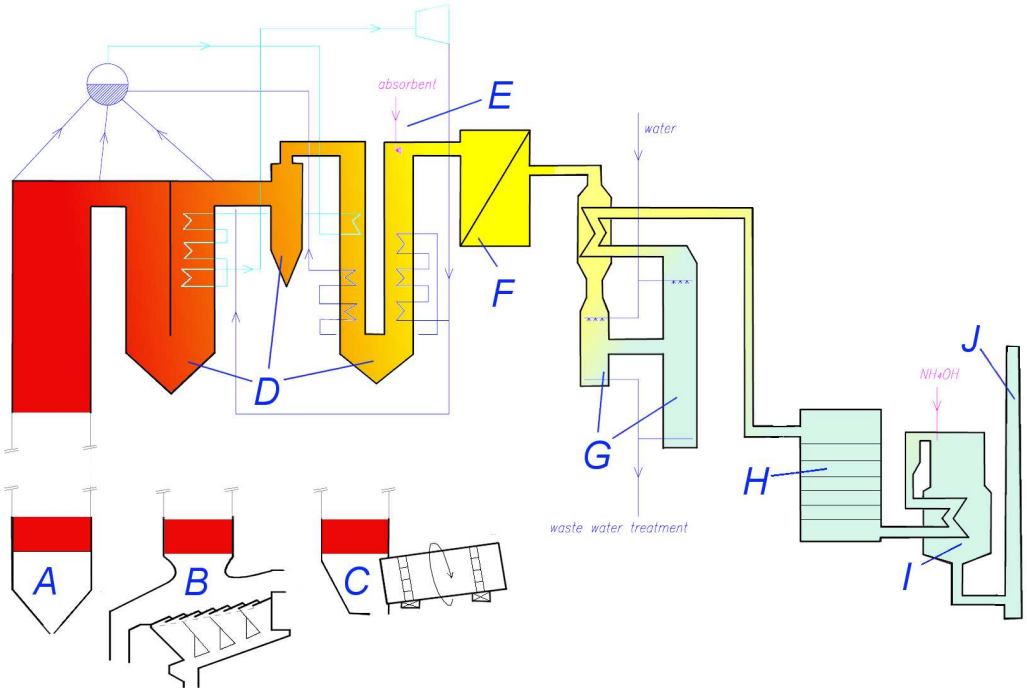

Figure 1. Scheme of thermal waste treatment plant configurations, A: fluidized bed combustor, B: grate furnace, C: rotary kiln, D: raw particle collection in the heat transfer zone, E: dry flue gas cleaning system, F: electrostatic precipitator (esp) or bag house filter (bhf), G: wet scrubbers, H: fixed bed coke adsorption, I: selective catalytic reduction J: chimney, modified from [Purgar 2013a].

The **third group** of incinerators, consisting of 3 lines of grate furnaces, is also utilizing MSW (188 000 t/y). Concerning Figure 1, these facilities can be described by B, D, E, F (bhf), G, I, and J. The most remarkable difference to the incinerators of group one and two is the addition of crushed activated coke into the fly gas stream before the bag house filter. The main reason for this injection of activated coke is the removal of mercury and other pollutants. The annual solid residues amount to 47,500 t of slag, 3,700 t of fly ash and 190 t of filter cake with a water content of approximately 40 percent. At the acidic scrubbers annually 28,000 m³ of a solution with a pH – value of 1.1 are subtracted.

The **fourth group** of incinerators consists of 6 lines using different fuels as well as different combustion technologies. For further investigations they are considered within one group, since all of them share parts of the flue gas cleaning system. The most important part of the shared equipment is the waste water treatment facility. The purification of the wastewater of these 6 lines results in 2,300 t/y of filter cake with a water content of approximately 50 percent. It is not possible to assign mercury loads of the filter cake generated to single incineration lines. The fourth group is divided into 3 subgroups: **4a**, **4b** and **4c**. Two lines of rotary kilns (**4a**) at site four are mainly utilizing hazardous wastes. Their common capacity is about 100,000 t/y. The rotary kilns are equipped with a electrostatic precipitator, a two stage wet flue gas cleaning system followed by an activated carbon adsorption facility before the flue gas is finally cleaned in the collective SCR-system of group 4. Annually 2,500 t of fly ash are produced and about 16 000 t of slag. Filter ash and boiler ash are collected together. Concerning Figure 1 these facilities can be described by C, D, F (esp), G, H, I, and J. Group 4 includes also three fluidized bed combustors (**4b**) that utilize almost exclusively sewage sludge. In the year 2005 and 2006 169,000 t of sewage sludge have been treated whereby 16,200 t of fly ash have been generated. Because of the closed gas distributor there is no bottom ash generated. Due to the plant operator these conditions have not changed crucial since 2005. The flue gas cleaning system is comparable to the one of the rotary kilns (4a) described above.
Another fluidized bed combustor (**4c**) is related to group 4. It utilizes primarily exclusively refused derived fuel (RDF) and partly sewage sludge with a capacity of 110,000 t per year. Annually 10,100 t of bottom ash and 11,200 t of fly ash emerge. The flue gas path is similar to the subgroups 4a and 4b. Boiler ash and filter ash are collected together. Concerning Figure 1 the facilities of group 4b and 4c can be described by A, D, F (esp), G, H, I, and J.

Due to the low load of mercury in the exhaust gas and in the wastewater of the investigated sites (Stoiber,2011) these Hg flows have been neglected within this work.

2.2 Determining the Mercury Contents

Over a period of 4 years fly ash, slag and filter cake samples were collected on a daily basis by the plant operator and merged to mixed samples for each stream, which have been analyzed in the plant operator's laboratory every two months. Hence, the mercury content of the incerination residues have been determined every second months. The total content of mercury has been determined by digesting the ash samples in aqua regia (concentrated nitric acid and hydrochloric acid). After digestion the sample has been analyzed using cold vapor – AAS (Atomic Absorption Spectroscopy) with a detection limit of 0.1 mg / kg referring to dry matter (dm). The average mercury content of the used coke from the fixed bed activated carbon adsorber was determined by 64 measurements of single samples.

2.3 Material Flow Analysis

The annual mean Hg – loads of the different incineration residues (L) and their related uncertainties (U) are determined using the following equation $L \pm U = m\ (c \pm u)$, whereby m is the mass flow of the incineration residue per year and c is the median value of the Hg – contents determined for this residue. u is the uncertainty of the concentration c. Except for one data set (Hg content of the fly ash of group three) no outlier is removed for the calculation of the median values. The uncertainty (u) is determined as follows: The 25 percent and the 75 percent percentile of c is calculated. For the determination of the 25 percent percentiles all values equal the detection limit were set to zero. The

75 percent percentile is calculated based on values used for the determination of the median value *c*. The uncertainty (*u*) is the difference to the median value (*c*) of the 25 or 75 percent percentile, whichever is larger. Deviations for the mass flows have not been considered.

2.3 Wet Chemical Mercury Extraction

A single sample of fly ash, from one of the incinerators of group three, has been collected and analyzed for its mercury content applying the procedure described above. Furthermore in an agitated non heated batch reactor fly ash and deionized water has been mixed with a liquid to solid ratio (*LS*) of 10 and stirred for 30 minutes. Additionally a certain amount (1.8, 3.6 and 5.4 mol/kg fly ash) of hydrochloric acid (HCl) was added. After thirty minutes the liquid and solid phase were separated with a büchner funnel, filter paper (blue ribbon) and a standard laboratory vacuum pump. To determine the extracted amount of Hg the filtrate has been analyzed using ICP-OES. This amount has subsequently been related to the total contents of mercury of the fly ash sample investigated.

3. RESULTS AND DISCUSSION

In Figure 2 the median (*c*) as well as the 25 and 75 percentile concentrations of mercury of the investigated incineration residues are summarized.

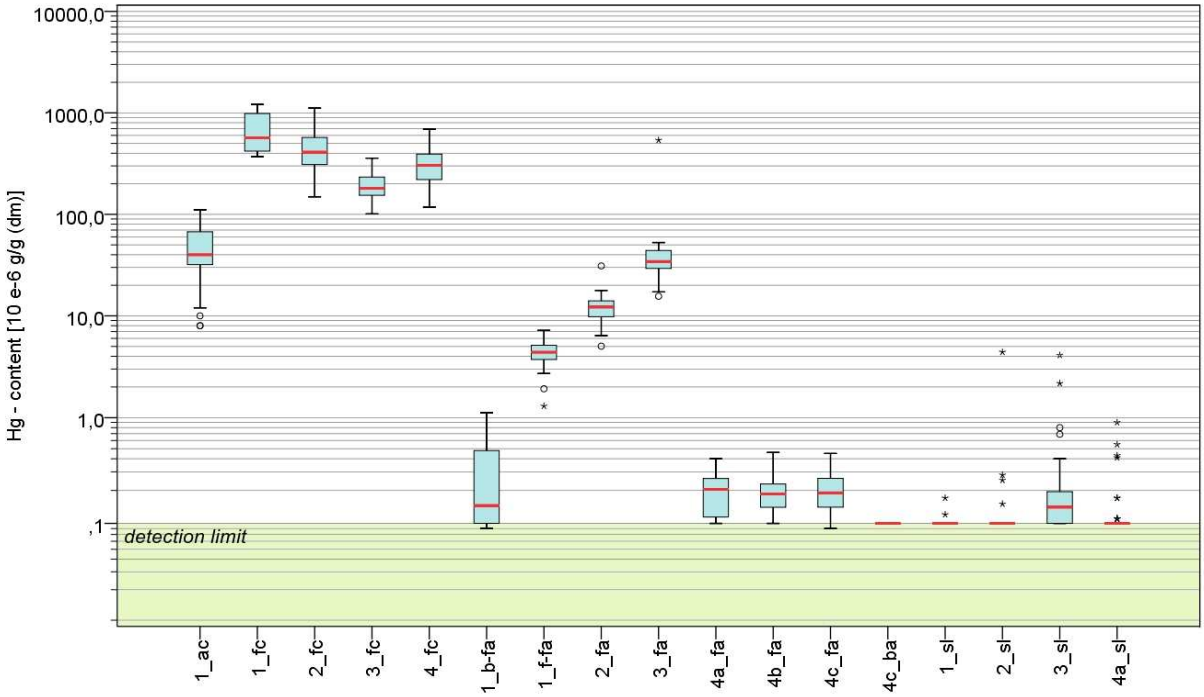

Figure 2. Mercury content of the in the investigated incineration residues, dm: dry matter, Notation abscissa: incinerator group _ residue stream, ac: activated coke, fc: filter cake, b-fa: boiler fly ash, f-fa: filter fly ash, fa: boiler and filter fly ash, ba: bottom ash, sl: slag, boxplot: minimum - 25% percentile – median – 75% percentile – maximum and mild outliers ° and strong outliers *.

While the Hg – concentration in used activated coke and filter cake exceed the limiting value (20 mg / kg dm) for a disposal at a non-hazardous waste landfill (Reststoffdeponie according to the

Austrian landfill directive), the Hg – content in slag and bottom ash is far below this limit value. On the other hand a wide range of Hg – concentrations (0.1 – 50 mg/kg dm) in fly ashes is observable. It can be seen, that only fly ash generated at incinerators of group three, exceed the restrictions, regarding mercury, for a deposition at non-hazardous waste landfills. Information, whether the fuel input, the combustion technology, the flue gas cleaning system or a combination of these factors is the reason for this increased Hg – contents, can be derived from Figure 3. The incinerators of group 2 and 3 are all using a grate furnace as combustion technology and have almost the same fuel composition, though the transfer coefficients for Hg into fly ash ranges from 0.36 for group 2 until 0.92 for group 3. This finding demonstrates that the dry flue gas cleaning system (injection of crushed coke or activated carbon) upstream the bag house filter causes the increased Hg contents in the fly ash of group 3.

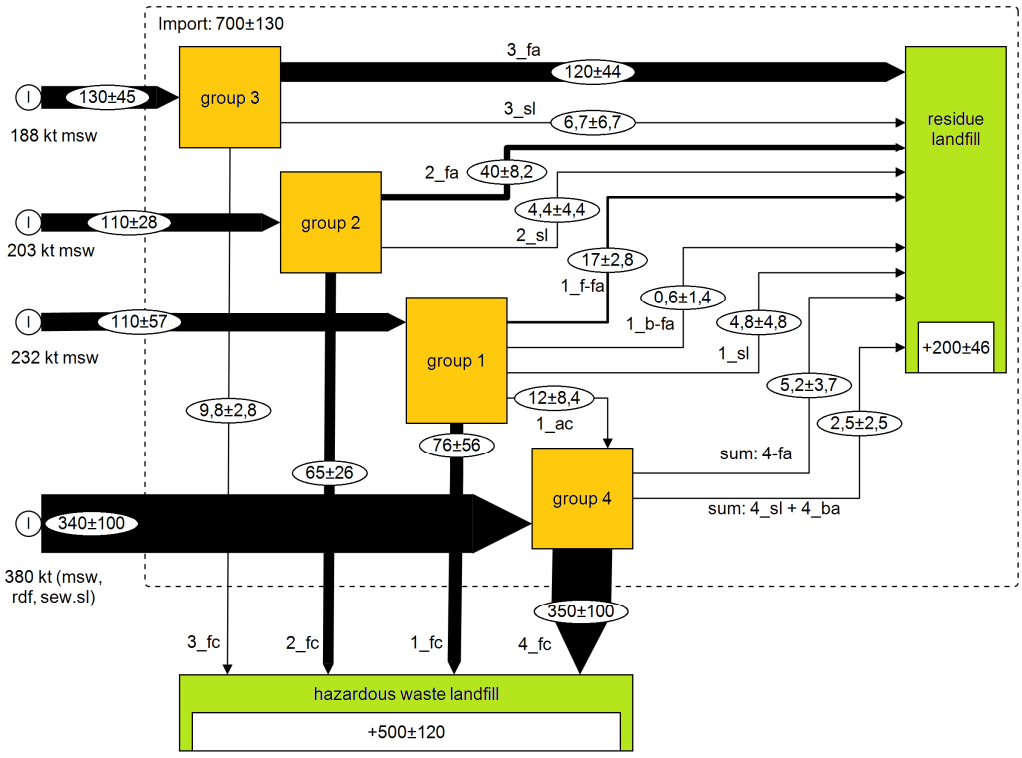

Figure 2. Mercury streams (L±D) in Vienna's waste incineration cluster in kg per year, Notation: incinerator group_residue stream, ac: activated coke, fc: filter cake, b-fa: boiler fly ash, f-fa: filter fly ash, fa: boiler and filter fly ash, ba: bottom ash, sl: slag.

For those fly ashes that cannot be landfilled at non-hazardous waste landfills (also considering other parameters than the Hg –concentration) a wet chemical treatment can be envisaged. A wet chemical treatment is mainly aimed at reducing the content of soluble salts and neutralize the fly ash in way, that a number of amphoteric heavy metals are non soluble at a subsequent eluat test, mandatory for disposal on a residue landfill. Also the reduction of the total content of heavy metals is achieved depending on the acidity of the extraction conditions. Mercury is adsorbed on fly ash or activated coke as $HgCl_2$, Hg_2SO_4 and Hg^0 (Karpf, 2006). According to (Merck, 2011) and (IFA, 2014) more than 0.5 g of the pure substances ($HgCl_2$ and Hg_2SO_4) except for Hg^0 are soluble in 1 liter water at 25°C. Realizing a process, similar to the FLUWA–process, described in (Schlumberger, 2013), at the incinerators of group 3, result in a *LS* ratio of 10 to 20. With the acidic scrubber water 1.8 mol of HCl per kg Fly ash are available for neutralization and acidic extraction. As described above an extraction of Hg from the fly ash has been investigated at laboratory scale, realizing a LS ratio of 10 an and an addition of 1.8 mol of HCl per kg of fly ash. Not to exceed the threshold parameter of 20

mg /kg approximately halve of the mercury of the fly ash of group 3 (3_fa) has to be extracted and therefore found in the liquid phase of the extraction procedure. By realizing a LS ratio of 10 in the extraction reactor a minimum concentration of 1.5 mg/l in the acidic filtrate has to be detected in order to ensure that the remaining Hg content is below the limit values of 20 mg/kg dm. The concentration of mercury in the filtrate measured was equal or below the detection limit of 0.1 mg/kg. Also a doubled and tripled addition of HCl in comparison to (1.8 mol HCl/kg fly ash) did not increase the concentration of Mercury in the filtrate. It is indicated that the non solubility of these mercury compounds results from its appearance as metallic Hg^0 or its strong bond to the activated coke. It follows that a wet chemical decontamination process without any additional thermal or stabilizing treatment will not be feasible to reduce the mercury concentrations of fly ashes from group 3.

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