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## Effect of Organic Carbon in MSWI Bottom ash on the Mobilization of Heavy Metals

Nowadays municipal solid waste incineration (MSWI) plants are playing a major role in the waste management activities. In Switzerland, since 2000, it is not allowed to deposit MSW material without thermal treatment. Incineration activities reduce the waste volume by 90% and waste mass by 80%, leading to the production of two main by products: Bottom ash and Fly ash. Generally, 700'000 tons of municipal solid waste incineration (MSWI) Bottom ash are produced every year.

Municipal solid waste incineration Bottom ash are currently disposed in type D landfills in Switzerland. Rain water is constantly interacting with Bottom ash and seepage waters are produced. Heavy metals and the organic part (TOC) of MSWI bottom ash might get mobilized in aqueous solution as "dissolved organic carbon – metal" complexes, leading to a potential contamination of soil and groundwater.

The aim of the thesis was to take representative bottom ash samples from four plants in the area of Bern and to characterize them in detail. A special focus was given to the role of the organic carbon in the solid residues and to reveal a plausible transition between total organic carbon (TOC) and dissolved organic carbon (DOC). The dissolved organic carbon is known to be responsible for heavy metal complexation (e.g. Cu), increasing the potential leaching risk of soil and groundwater contamination.

The heterogeneity of MSWI bottom ash is strongly dependent on the primary waste feed. Therefore, to obtain a representative sample from all plants, three weeks sampling campaign was planned by collecting 42 bottom ash samples of 30-40 Kg each, at a minimum period of 12 hours. Approximately, one ton of bottom ash was sampled for each plant. The material was then crushed, sieved and split below 5 mm size, with the final scope of obtaining four equal samples (A-B-C-D), representative for each plant. All metal particles (<2 mm), which could not pass through the sieves, have been analyzed separately via total digestion and inductively coupled plasma optical emission spectroscopy (TD-ICP-OES). The analyses show that the most common metal is aluminum, followed by iron, copper and zinc. In two plants, the metals fraction below 2 mm were more enriched in silicates or glass particles and hence depleted in pure metals.

Bottom ash are composed of refractory (e.g. quartz, feldspars, etc.) and newly formed minerals (e.g. melilites, spinels, etc.); additionally, they contain organic components and amorphous glass. The firsts survive the burning process and therefore are considered as highly reactive material. The seconds are the most common melting product of MSWI bottom ash, highly enriched in Si, Ca, Na, Fe and Al.

X-ray fluorescence analyses performed on Bottom ash powder pills revealed a general chemical overview of the four samples. From a petrologic point of view these samples are comparable to an ultrabasic volcanic foidite even more depleted in SiO<sub>2</sub>.

The variability in composition of major oxides (e.g. CaO in relation to municipal solid waste), minor oxides (e.g. P<sub>2</sub>O<sub>5</sub> linked to sewage sludge) and trace elements concentrations (e.g. Zn associated with car-scrap disposal) is highly related to the amount and type of waste disposed in the plants.

The main crystalline phases identified belong to silicates (e.g. quartz, feldspar, melilite, and wollastonite) and to the oxides group (e.g. iron and aluminum oxides). Using X-ray diffraction

and scanning electron microscopy techniques, carbonates (e.g. calcite) and cementitious phases (e.g. ettringite, hydrocalumite, portlandite and lime) were detected. This suggests that the four bottom ash samples were already partially altered by hydration and carbonation processes. The components are either refractory minerals already present in the input waste or newly formed melt products. Amorphous glass phases are strongly abundant in all four samples (more than 70 wt.%). Apart from the chemical composition of the solid Bottom ash, their leaching potential risk was of major importance during this study. In Switzerland, the Swiss ordinance on waste (Verordnung über die Vermeidung und die Entsorgung von Abfällen, VVEA) delineates two batch-leaching tests for the evaluation of the mobilization potential of solid waste material. Even though the tests are not prescribed for bottom ash, the results showed comparable values with seepage waters collected from a natural landfill site (Teufftal), where slags are commonly disposed. Test 1 is accomplished between bottom ash and CO<sub>2</sub>-saturated water, while test 2 is performed using bottom ash constantly mixed with pure-water. Both tests are performed in a Liquid:Solid ratio of 10, for a period of 24 hours. The results show how the mobility of the single chemical components is strongly pH dependent and associated to the electrical conductivity (EC) of the aqueous solution. The newly formed mineral phases, associated with the main reaction products (e.g. ettringite, lime, portlandite, hydrocalumite, etc.), are responsible for the incorporation of chemical constituents (i.e. heavy metals) and for the strong pH and EC buffering of the pure water.

Total organic carbon (TOC) was measured according to DIN15936 and DIN19539 methods. The specific proprieties of organic carbon in the solid MSWI Bottom ash were investigated, while the main target was to distinguish the elemental carbon from the organic carbon. The DIN19539 method was found to be appropriate to distinguish the TOC species in assimilable organic carbon (TOC400) and residual organic carbon (ROC). Only the assimilable organic carbon is assumed to be reactive and tends to dissolve into aqueous solution. Therefore, a good correlation between TOC400 in solid Bottom ash and DOC in aqueous eluates was observed.

Dissolved organic carbon facilitates the leaching of several heavy metals and namely copper (Cu<sup>2+</sup>) shows a perfect correlation with DOC.

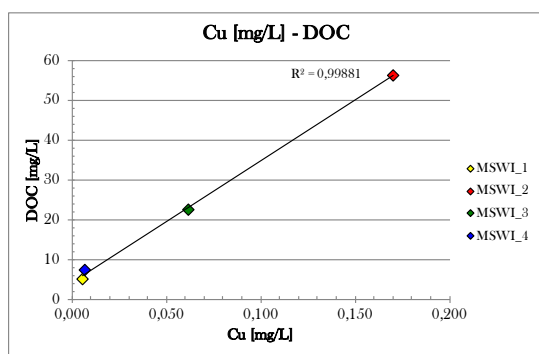
To get a more detailed insight into the role of the DOC species, as fulvic acids and humic acids, additional DOC separation was performed. These two main DOC species differ in molecular size (NMWL). The size of fulvic acids is smaller (1K to 10K Dalton) than humic acids (10K to 100K Dalton). They both have many carboxyl (COOH) and hydroxyl (COH) groups, although fulvic acids (FA) are smaller, they are more reactive due to a higher exchange capacity. Therefore, the leachates were ultra-filtered using Amicon 4mL ultracentrifugation filters with molecular-weight cutoff of 10K. The results show that, apparently, 89% of the copper and 90% of the DOC are concentrated in the filtrated eluate solution, below 10'000 Dalton. Conclusively, it has not been proven that copper binds to fulvic acid molecules only, but it has been shown that copper tends to bind preferentially to organic molecules that are smaller than 10'000 Dalton.



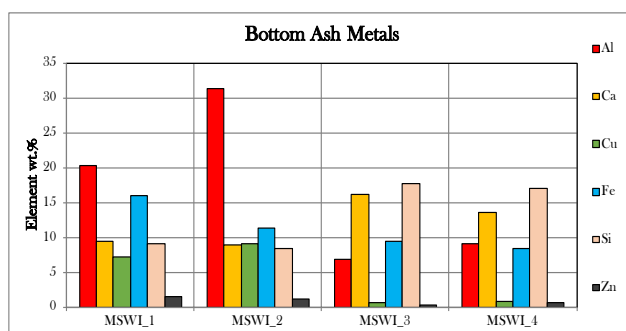
TVA CO<sub>2</sub> Eluate Test performed on the 4 MSWI Bottom ash. From left to right: MSWI\_1, MSWI\_4, MSWI\_2 and MSWI\_3.



Bottom ash metals (>2 cm) manually separated from the MSWI\_4 slags.



XY diagram between copper dissolved in the TVA-H<sub>2</sub>O eluate and DOC in mg/L for the 4 MSWI bottom ash



Bottom ash metals fraction between 1000-200 μm size, totally digested into solution for quantitative inductively coupled plasma optical emission spectrometry (ICP-OES) chemical analyses. The metals concentrations are expressed in wt.%.