

PhD
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Geochemical Aspects of Municipal Solid Waste Incineration Bottom Ash and Implications for Disposal

The incineration is considered to be the most appropriate method of municipal solid waste (MSW) treatment in Switzerland, and therefore is now a mandatory procedure. It reduces the waste mass significantly and causes a nearly complete destruction of organic compounds. The solid residues of incineration of municipal waste are mainly bottom ash and residues from air pollution control. In Switzerland about 650 000 t of municipal solid waste incineration (MSWI) bottom ash is produced per year.

The aim of this thesis was to perform a detailed mineralogical and chemical characterisation of bottom ash using modern geochemical and mineralogical methods. The main objective was to evaluate bottom ash for its reuse, metal recovery and its long-term behaviour in landfills. To investigate these aspects, analytical methods, new recovery techniques and the leaching behaviour were examined.

The heterogeneity of the MSW affects the composition of the bottom ash. Due to the short duration of the incineration process, the bottom ash material does not reach equilibrium conditions. The chemical composition of MSWI bottom ash is a direct function of the primary waste feed. Conversely, the mineralogical composition strongly depends on incineration conditions such as the firing temperature and the duration of the process because new mineral phases are formed during incineration.

Bottom ash is composed of various minerals, metals, glass and organic compounds. The main crystalline phases of bottom ashes are silicates (e.g. quartz, pyroxene, feldspar, melilite, monticellite) and oxides (e.g. spinel-group minerals, hematite). In addition, various carbonates, hydroxides, sulphates, sulfides and phosphates were detected. These crystalline components are either refractory minerals or phases newly formed during incineration. The amorphous part (glass) of bottom ash comprises between 40 and 50%. From a petrologic point of view the main chemical composition is comparable to an ultrabasic rock. However, trace element concentrations differ completely. Bottom ash is for example strongly enriched in heavy metals (Cd, Cu, Pb and Zn) or halogenides (Cl, Br).

The very complex composition of bottom ash causes major difficulties for their chemical analysis. The suitability of standard methods used in geoscience for rock analysis (e.g. quantitative X-ray fluorescence) is limited for bottom ashes. One of the major problems occurring is the sample preparation due to its content of metal particles. An extensive study of bottom ash analysis showed that a semiquantitative X-ray fluorescence method (UniQuant) solved many of the problems. The major advantages of UniQuant are the independence of a material dependent standardisation, the large number of analysed elements and possibilities to use different sample preparation methods. Tests with more than 30 approved international standards showed that the production of pressed powder tablets is a quick and suitable preparation method. Good results are achieved if the bottom ash powder is very fine-grained.

Bottom ash is rich in metals, it contains ~6 % Al, ~0.9% Cu, ~15 % Fe and ~0.5 % Zn. These high metal concentrations must be regarded as pollutants which may harm the environment. Metal recovery is not only economically interesting, it also lowers the pollution potential. In this study, both aspects were considered and discussed.

Before being able to recover metal particles from bottom ash, they have to be liberated from the surrounding matrix. A new fragmentation method (selective electrodynamic fragmentation SelFrag) was evaluated and compared to the conventional mechanical jaw crusher.

Six grain size-classes of the fragmented materials were processed with a magnetic separator. The liberated particles of the SelFrag are cleaner and in the nonmagnetic fraction copper is stronger enriched than in the jaw crusher processed material. The SelFrag technique processes material in water and this causes higher processing costs (waste water treatment). However, combining the SelFrag processing with a bottom ash washing procedure would reduce the loads of heavy metals, Cl and S in the deposited bottom ash. With the fragmentation and separation techniques chosen, no fraction could be produced that fulfills the requirements of an 'Inert'-type landfill (according to the Swiss ordinance on wastes).

Apart from the total content of a pollutant (e.g. heavy metals) its leaching behaviour is of major importance for the estimation of the pollution potential. The Swiss ordinance on wastes ('Technische Verordnung über Abfälle', TVA) defines a batch leaching test for the evaluation of a waste material and its disposal. This 'TVA-test' is performed using CO₂-saturated water. In this study, the interactions between bottom ash and the eluent was investigated. It was found that CO₂ is a very effective agent to lower the pH-value of an alkaline system. The influence of CO₂-saturated water (pH=4) to bottom ash is comparable with 0.07 m HNO₃ (pH=1.2). During the TVA-test, carbonates (especially calcite) precipitate. The filtrated eluate after the test is not at equilibrium with the atmospheric CO₂ partial pressure and thus CO₂ starts to degas immediately. By consequence the pH increases and further precipitation of carbonates is provoked. The precipitating carbonate crystals incorporate large amounts of heavy metals such as Zn. These findings imply for the TVA-test that the measured concentration in the eluate are lowered if the precipitation of carbonates from the eluate is not inhibited. The filtration of the eluate should never be performed using a vacuum pump because this causes a purging of CO₂ and forces carbonate precipitation. Moreover, the pH-value of the eluate has to be measured within some minutes after filtration and the eluate has to be stabilised immediately by acidification.

Batch leaching tests like the TVA-test have a typical running time of 1–2 days. Due to this short duration it is not clear whether the results obtained are significant for the medium- to long-term behaviour of bottom ash in a landfill. Flow through experiments (column experiments) are more suitable for such evaluations. Two column experiments with compacted bottom

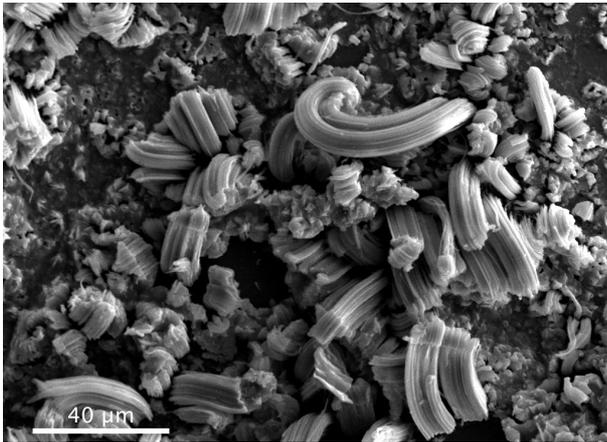
ash were conducted over a period of 850 days. One of the bottom ash samples was stabilised with 2% of cement. Because of the flow rate used, the experimental duration corresponds to 116 years of weathering in a landfill. Within the first 20 days of experimental leaching, the concentration of most ions decreased strongly. Afterwards, the concentrations stabilised at a low level. The pH-value at the effluent side of the columns remained in the high alkaline range (11–12) during the entire experiment. These findings indicate that short-time leaching tests like the TVA-test are capable of producing results which are meaningful for the medium-term leaching behaviour of bottom ash in a landfill. Furthermore, it shows that the washing of bottom ash prior the disposal would clearly improve the leaching quality.

Tracer experiments performed at the beginning and at the end of the column experiments showed that the flow-regime homogenises with time. This results from material dissolution and the disappearance of preferential flow paths.

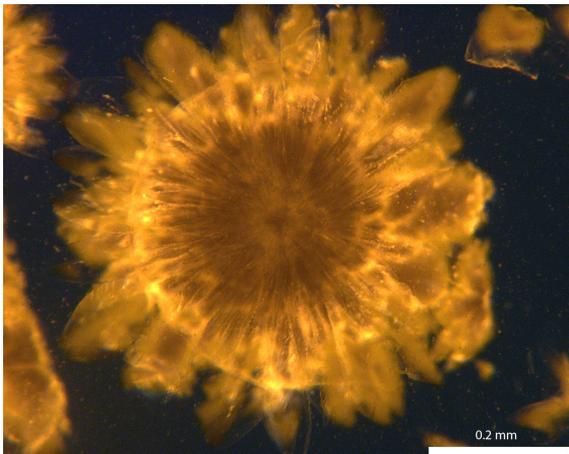
Investigation of the eluate evolution along the column profiles showed that distinct pH-fronts develop due to weathering reactions. In the first few centimeters of the columns, the

eluate pH was neutralised whereas towards the effluent side of the columns it remained alkaline. The extent of the pH-neutralised domain is dominated by the dissolution of pH-buffering phases like carbonates and hydroxides. It was found that many chemical constituents are mobilised in the pH-neutralised part of the columns. However, mobilised heavy metals precipitate immediately when the pH increases. Geochemical simulation indicates that these precipitated minerals are metal-hydroxides. The cement stabilisation does not increase the leaching quality significantly. Lower eluate concentrations of several heavy metals (Cr, Co, Pb and Zn) in the cement stabilised bottom ash were recorded only during the first 20 days of leaching. Conversely, the pH-neutralised zone in the cement stabilised bottom ash develops faster because pH-buffering minerals are encapsulated and the accessibility to the eluent is reduced.

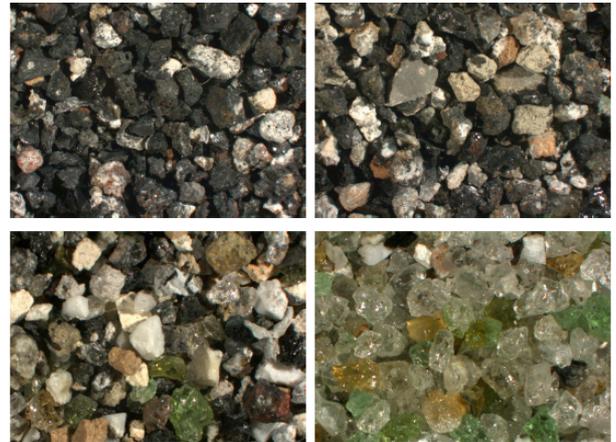
These results imply that an alkaline environment improves the leaching quality of bottom ash in a landfill. Therefore the high acid neutralising capacity (ANC) of the bottom ash (ca. 2 to 3 mol per kg) is important because it reduces the mobilisation of heavy metals.



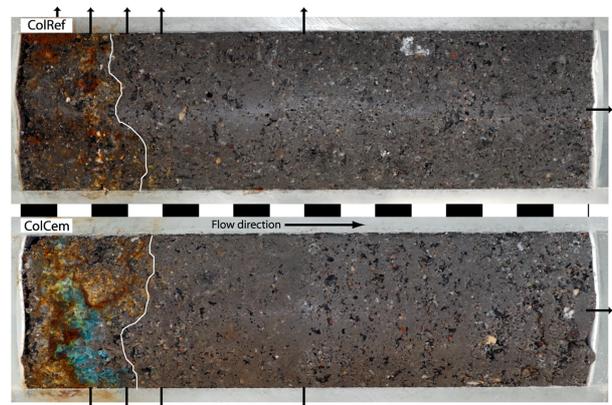
Efflorescing minerals at the surface of a polished bottom ash thin sections (SE images). Calcite efflorescing from new formed glass (bottom ash 'ZHHa')



Cathodoluminescence images of precipitated calcite from the 48 h TVA eluate of bottom ash sand (BASand). Zoning indicates different trace element content



Magnetic separates of grain-size fraction 1–2 mm (SelfFrag processed). From top left to bottom right: strong, medium, weak and non-magnetic fraction.



Photographs of the opened columns ColRef (top) and the ColCem (bottom) after leaching. The flow direction was from left to right. The white line indicates the extension of the alteration fronts and the black arrows show the positions of the sampling sites. The lengths of the columns are 16 cm.