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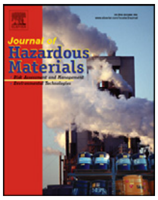

Removal of hazardous metals from MSW fly ash—An evaluation of ash leaching methods

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ABSTRACT

Incineration is a commonly applied management method for municipal solid waste (MSW). However, significant amounts of potentially hazardous metal species are present in the resulting ash, and these may be leached into the environment. A common idea for cleaning the ash is to use enhanced leaching with strong mineral acids. However, due to the alkalinity of the ash, large amounts of acid are needed and this is a drawback. Therefore, this work was undertaken in order to investigate some alternative leaching media (EDTA, ammonium nitrate, ammonium chloride and a number of organic acids) and to compare them with the usual mineral acids and water.

All leaching methods gave a significant increase in ash specific surface area due to removal of soluble bulk (matrix) compounds, such as $CaCO_3$ and alkali metal chlorides. The use of mineral acids and EDTA mobilised many elements, especially Cu, Zn and Pb, whereas the organic acids generally were not very effective as leaching agents for metals. Leaching using NH_4NO_3 was especially effective for the release of Cu. The results show that washing of MSW filter ash with alternative leaching agents is a possible way to remove hazardous metals from MSW fly ash.

1. Introduction

Incineration is, together with material recycling, one of the two most used management methods for municipal solid waste (MSW) [1]. The incineration results in both heat and electricity production, as well as a significant reduction in the waste volume. However, the produced ash can be a problem. Only in Sweden hundreds of tonnes of MSW fly ash are produced every year [1]. These fly ashes are usually classified as hazardous material due to their high content of toxic metals and soluble components, and therefore, have to be deposited in specialised landfills [2]. Land filling in sites with advanced leachate control are expensive, and therefore, there is a strong incitement to reduce the deposited amounts [1]. In Sweden a research program to promote the utilization of non-coal ashes is sponsored by the boiler companies and the Swedish Energy Agency [3]. Many of the projects have been successful, promoting the use of ashes and decreasing the need of land filling. However, these projects are mainly focused on relatively stable or non-hazardous ash fractions, such as biomass ashes and MSW bottom ashes while the utilization of MSW fly ash is still not investigated.

A number of methods to stabilize fly ash in order to reduce leaching has been suggested. Mixing of the ash with water may result in agglomeration of the material due to cementitious reactions. This type of treatment reduces the leaching of metals and sulphates but the leaching of chlorides is almost unchanged [4]. Another way to stabilize ash is sintering at about 1200 °C. The dense and partly glassy structure formed encloses the heavy metal species, thus, making them less available for leaching [5]. Thermal treatment also results in evaporation of volatile metal species. Results obtained by Jakob and co-workers showed that 100% of the ash content of Cd, Cu and Pb, as well as 50% of the Zn may be evaporated at temperatures around 1000 °C [6]. Thus, sintering gives a more stable residue but also creates a need for handling options for the vaporised metal compounds. In addition, it includes significant energy consumption.

Common methods for ash cleaning are based on wet treatment, i.e. enhanced leaching. Bio-leaching has been suggested for removal of metals from fly ashes [7–10], but unfortunately the L/S-ratios (liquid-to-solid-ratios) often have to be high as the active bio substances otherwise will not survive. The most widespread leaching method is acidic leaching using strong mineral acids as many metal compounds have high solubility at low pH [11–15]. However, due to the alkalinity of the ash large amounts of acid are needed.

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Table 1
Total amounts of main and minor elements in the original ash.

Main Element	Original ash, mg/kg dry ash	Minor element	Original ash, mg/kg dry ash
Si	32,700	Ag	<1
Al	22,200	As	80
Ca	363,000	Ba	770
Fe	5,602	Be	1
K	22,800	Cd	90
Mg	10,100	Co	20
Na	32,000	Cr	190
P	4,000	Cu	5400
Ti	1,860	Hg	3
S	7,000	Mn	574
		Mo	10
		Ni	30
		Pb	5730
		Sn	20
		Sr	500
		V	10
		Zn	5780
		Zr	40

Taken from Ref. [24].

Therefore, this work was undertaken in order to investigate the removal of metals from MSW fly ash using some alternative leaching media as well as mineral acids. The choices of alternative leaching media (EDTA, ammonium nitrate, ammonium chloride and a number of organic acids) were primarily based upon their possible ability to form complexes with metal ions. EDTA, as well as organic acids, forms complexes with many metals and have been used to study and reduce the impact from hazardous metals in both mine tailings and MSW ash [8,16–18]. The effectiveness and influences of the various leaching agents are investigated and discussed in this article.

2. Material and methods

2.1. Material

The ash sample was a textile filter ash from a bubbling fluidized bed (BFB) burning 100% MSW. Dry lime was added to the flue gas channel before the filter. Each day during a period of two weeks eight sub-samples from the filter ash were collected at random times. All samples were mixed and the final sample was stored in an airtight container. The element concentrations are shown in Table 1.

2.2. Analytical methods

The shapes and morphologies of ash particles before and after leaching were examined by scanning electron microscopy (SEM). The microscope used was a FEI Quanta 200 FEG ESEM, operated at 2 kV for secondary electron imaging and 10 kV for back scattered electron imaging.

Particle size distributions were determined using a Malvern 2600c laser diffractometer and specific surface area per weight unit were determined using $N_{2(g)}$ and the BET (Brunauer, Emmet, Teller) five point method and a Micrometritics ASP, Accelerated Surface Area and Porosimetry System, 2010 instrument.

The main crystalline compounds in the original and leached ashes were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a position sensitive detector. Identification of compounds was carried out according to the Joint Committee of Powder Diffraction Standards database [19].

Chemical information about functional groups in original and leached ash samples was obtained using Fourier transform infrared spectroscopy (FTIR). A Nicolet Magna-IR 560 spectrometer with an insert cell for diffuse reflectance spectroscopy was used. Each sample was scanned 64 times with a resolution of $2.0\,\mathrm{cm}^{-1}$ and the datum was averaged.

Analysis of leachates for their metal ion content was carried out using ICP-MS (inductively coupled plasma mass spectrometry), ICP-OES (inductively coupled plasma optic emission spectrometry) and AAS (atomic absorption spectrometry).

Chemical speciation of aquatic species in the leachates was investigated using the thermodynamic equilibrium program PHREEQC, version 2.15.0-2697, with a modified version of the database MINTEQ.v4.dat [20]. To the original MINTEQ database the following complexes and compounds were added: $Cd(NH_3)^{2+}$, $Cd(NH_3)_2{}^{2+}$, $Cd(NH_3)_4{}^{2+}$, $ZnNH_3{}^{2+}$, $Zn(NH_3)_2{}^{2+}$, $Zn(NH_3)_3{}^{2+}$ and $Zn(NH_3)_4{}^{2+}$ from the PHREEQC database llnl.dat; $Cu(NH_3)_2{}^{2+}$, $Cu(NH_3)_3{}^{2+}$, $Cu(NH_3)_4{}^{2+}$ from [21]; lactic acid [22]; $Cu(lactate)^+$, $Cu(lactate)_2$, $Mn(lactate)^+$, $Mn(lactate)_2$, $Pb(lactate)^+$, $Pb(lactate)_2$, $Zn(lactate)^+$ and $Zn(lactate)_2$ [23].

2.3. Leaching experiments

The consumption of acid needed for neutralisation of the fly ash was determined by pH-static titration at constant pH 7 with 0.1 M HCl for 24 h. The final L/S-ratios were around 120. Except for measuring the amount of H^+ consumed by the ash, the water phase was analysed by ICP-OES for relevant elements.

Ash samples were leached with twelve leaching agents: deionised water ($18.2\,\mathrm{M}\Omega/\mathrm{cm}^2$) and HCl, HNO_3, H_2SO_4, EDTA, NH_4Cl, NH_4NO_3, acetic acid, formic acid, lactic acid and oxalic acid in various concentrations. In addition, an acidic solution from a flue gas cleaning process was included as a possible leaching medium. Generally, no pH control of leachates was applied except in the EDTA leaching where the initial pH was adjusted to below zero. The leaching experiments were carried out in glass beakers for 24 h with 5 g of ash under continuous stirring. The L/S ratio used was five except for the test with sulphuric acid where the L/S ratio was increased to ten to avoid problems with gypsum formation and in the water leaching where an L/S of 50 was used based on earlier results [24].

After 6 and 24 h leaching, a leachate sample was extracted using a syringe. The sample was filtrated through a membrane filter with 0.45 μm pore diameters. At the 6 h sampling a volume of leaching agent corresponding to the volume removed was added to the leaching experiment to keep the L/S ratio constant. After 24 h, the remaining ash was separated from the leachate by the same method of filtering. The ash was then washed with de-ionised water before drying at 105 °C.

Pre-washing with water at L/S 50 for 1 h was applied in some experiments. After removal of the water phase by decanting, the ash residue was leached with 3 M HCl, 3 M HNO_3, 3 M NH_4NO_3, 1 M lactic acid and 0.1 M pH-adjusted EDTA solution, respectively. These leaching media were chosen based on the results from the first test series. The pre-washing time had previously been optimized to maximize the leaching of Ca, K and Na.

3. Results and discussion

3.1. Changes in general ash characteristics due to leaching

Generally the results from the physical characterisations methods showed that the average ash particle size and specific surface area were affected by leaching. The extent of this effect depended on how aggressive the leaching medium was, i.e. what pH the leachate acquired or how much it could form soluble complexes with Ca and other matrix elements. Another effect that was observed was formation of secondary compounds, crystalline or