



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 CaCO₃ 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 NH₄NO₃ 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.

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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 Micromeritics 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 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 optical 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 MINTEQA4.dat [20]. To the original MINTEQA4 database the following complexes and compounds were added: $\text{Cd}(\text{NH}_3)_2^{2+}$, $\text{Cd}(\text{NH}_3)_4^{2+}$, $\text{Zn}(\text{NH}_3)_2^{2+}$, $\text{Zn}(\text{NH}_3)_3^{2+}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$ from the PHREEQC database *llnl.dat*; $\text{Cu}(\text{NH}_3)_2^{2+}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, $\text{Cu}(\text{NH}_3)_4^{2+}$ from [21]; lactic acid [22]; $\text{Cu}(\text{lactate})^+$, $\text{Cu}(\text{lactate})_2$, $\text{Mn}(\text{lactate})^+$, $\text{Mn}(\text{lactate})_2$, $\text{Pb}(\text{lactate})^+$, $\text{Pb}(\text{lactate})_2$, $\text{Zn}(\text{lactate})^+$ and $\text{Zn}(\text{lactate})_2$ [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: de-ionised water ($18.2\text{ M}\Omega/\text{cm}^2$) 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 $0.45\ \mu\text{m}$ 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

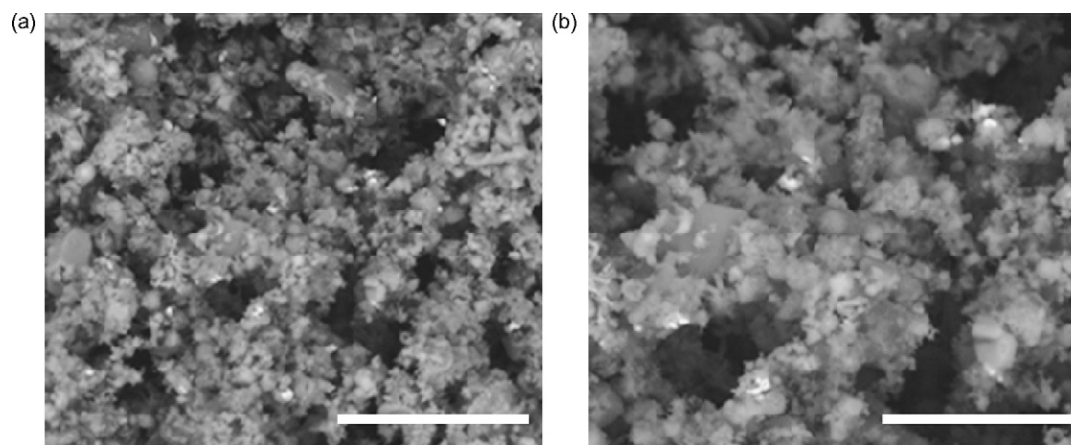


Fig. 1. SEM images (back scattered electrons) of the original ash (a) Magnification 5000 times. The bar corresponds to 20 μm . (b) Magnification 10,000 times. The bar corresponds to 10 μm .

amorphous, on the particle surfaces. The characterization of the resulting ash is vital as this can give valuable information about how the various leaching agents interact with the ash. This is important when analyzing leaching patterns and designing methods to effectively separate the leachate from the resulting ash.

The particle size distribution of the original ash had its maximum for particle sizes of 20–40 μm . Leaching by water or ethanol caused the average particle size to become approximately halved (10–20 μm) which would, theoretically, double the specific surface area as was also measured (Table 2). The electron micrographs in Fig. 1 shows that the single particles are generally smaller than indicated by the laser diffraction measurements but present in

aggregates. Probably the aggregated particles were separated by water or ethanol treatment. The particles are not very porous and the specific surface area is $5.1 \pm 0.2 \text{ m}^2/\text{g}$ (Table 2) which is comparable with other published data (2.2 and $5.6 \text{ m}^2/\text{g}$) [25].

The use of more aggressive leaching agents increased the surface area four to six times (Table 2). SEM images of these ash samples indicated precipitation of secondary compounds, crystalline or amorphous, on the particle surfaces. However, the residue from leaching with 3 M HCl (Fig. 2c) showed clean and clearly etched particle surfaces. This is consistent with the results given in Tables 3 and 5 showing that a large part of the calcium-containing compounds was removed by 3 M HCl. Thus, the ash matrix was

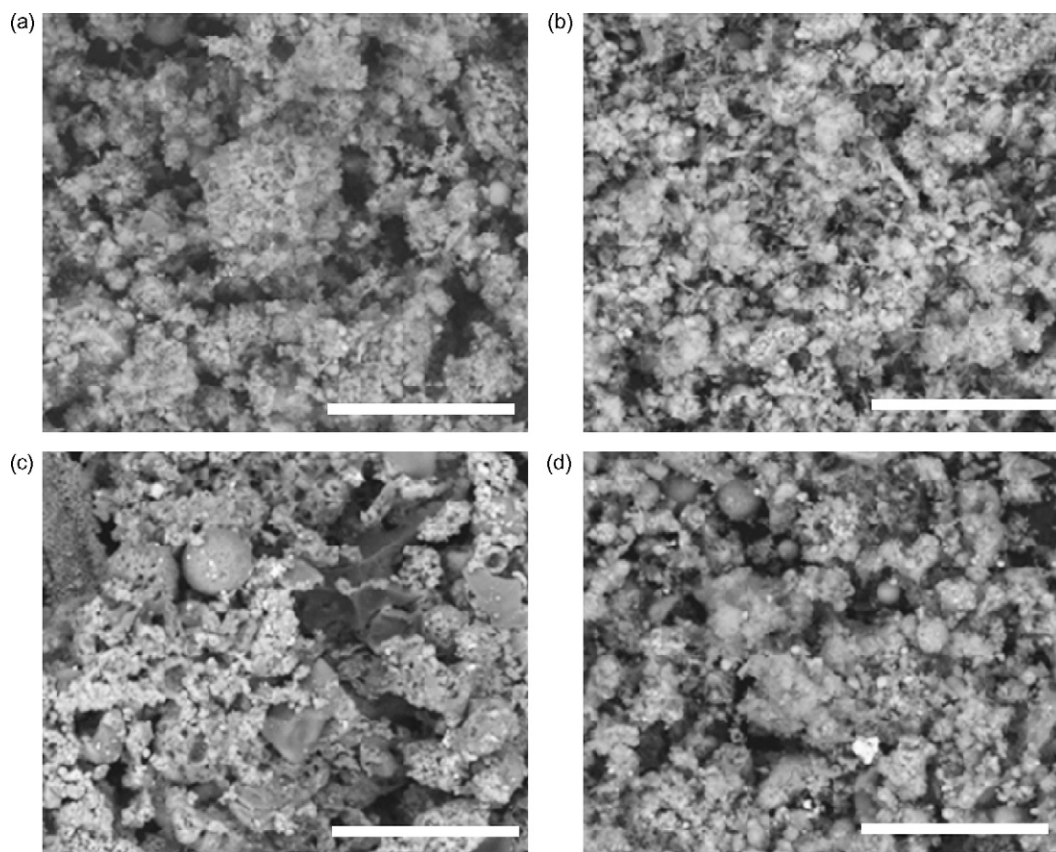


Fig. 2. SEM images (secondary electrons) of leached ash samples (magnification 5000 times) (a) ultra pure water (b) 1 M HCl (c) 3 M HCl and (d) 0.1 M EDTA with HNO_3 . The bar corresponds to 20 μm .

Table 2
Specific surface area of ash samples leached in different media for 24 h.

Leaching media	None	De-ionised water	0.1 EDTA with pH adjustment	0.1 M NH ₄ NO ₃	3 M NH ₄ NO ₃	1 M HCl	3 M HCl
Specific surface area, m ² /g	5.1	10.7	34.2	12.7	21.7	19.9	20.4

attacked by the acid creating pores and a large surface area. However, precipitation of secondary compound crystals on the particle surfaces during leaching with weaker leaching agents increased the specific surface area even more. It is likely that CaSO₄ or some other Ca compound like CaCO₃ could be an important part in the crystals

[18]. The FTIR results indicated the presence of major amounts of both SO₄²⁻, 1100–1200 cm⁻¹, and CO₃²⁻, 1400–1500 cm⁻¹, in all ash samples except in the ash sample leached with 3 M HCl (Fig. 3). That sample showed a large peak around 1620 cm⁻¹ which points at chemically bound water attached to SO₄²⁻ ions, i.e. gypsum vari-

Table 3
Crystalline compounds identified in original and leached ashes.

	Alkali metal salts	Non-silicate Ca compounds	Ash silicates and aluminates	Bed sand components
Original ash, not leached taken from Ref. [24]	NaCl ^a KCl ^a KCaCl ₃ ^b	CaCO ₃ ^a CaSO ₄ ^b Ca(OH) ₂ ^a CaClOH ^a	Ca ₃ Al ₂ O ₆ ^b	SiO ₂ ^b
Leaching agent	Crystalline compounds identified in the residue after leaching			
Ultra pure water	NaCl ^b	CaCO ₃ ^a Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇	SiO ₂ ^b
1 M HCl	NaCl	CaCO ₃ ^a CaSO ₄ Ca(OH) ₂ ^b	Ca ₂ Al ₂ SiO ₇ Ca ₃ Al ₂ O ₆ ^b	SiO ₂ ^b KAlSi ₃ O ₈ ^b
3 M HCl		CaSO ₄ ^b	Ca ₂ Al ₂ SiO ₇ Ca ₃ Al ₂ O ₆ ^a (Fe,Mg)SiO ₃	SiO ₂ ^a KAlSi ₃ O ₈ ^a
1 M HNO ₃	NaCl ^b	CaCO ₃ ^a CaSO ₄ ^a	Ca ₂ Al ₂ SiO ₇ ^a Ca ₃ Al ₂ O ₆ ^a	SiO ₂ KAlSi ₃ O ₈
3 M HNO ₃		CaSO ₄ ^b	Ca ₂ Al ₂ SiO ₇ Ca ₃ Al ₂ O ₆ ^a (Fe,Mg)SiO ₃	SiO ₂ ^a KAlSi ₃ O ₈ ^a
1.5 M H ₂ SO ₄	K ₂ SO ₄	CaSO ₄ ^a CaSO ₄ (H ₂ O) _{0.5} CaSO ₄ (H ₂ O) ₂ ^b		
0.2 M acidic process water		CaCO ₃ ^a CaSO ₄	Ca ₂ Al ₂ SiO ₇ ^a Ca ₂ SiO ₄ ^a	SiO ₂
0.1 M Formic acid		CaCO ₃ ^a CaSO ₄ ^b Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇ ^b Ca ₂ Al ₂ O ₅	
0.1 M Acetic Acid		CaCO ₃ ^a CaSO ₄ ^b Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇ Ca ₂ Al ₂ O ₅	
0.1 M Lactic acid	NaCl KCl ^b	CaCO ₃ ^a CaSO ₄ Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇ Ca ₂ Al ₂ O ₅	
1 M Lactic acid	NaCl ^a	CaCO ₃ ^a CaSO ₄ ^a	Ca ₂ Al ₂ SiO ₇ ^a Ca ₃ Al ₂ O ₆ ^a	SiO ₂
0.5 M Oxalic acid		CaSO ₄ ^a Ca(CO ₂) ₂ (H ₂ O) _{2.2} ^a		SiO ₂ ^b
0.1 M NH ₄ Cl	NaCl ^b	CaCO ₃ ^a CaSO ₄ ^b Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇ ^a Ca ₂ Al ₂ O ₅	SiO ₂ ^b
0.1 M NH ₄ NO ₃		CaCO ₃ ^a Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇	SiO ₂
3 M MH ₄ NO ₃		CaCO ₃ ^a CaSO ₄	Ca ₂ Al ₂ SiO ₇ ^a Ca ₃ Al ₂ O ₆ ^a	SiO ₂
0.1 M EDTA without pH adjustment	NaCl ^a	CaCO ₃ ^a CaSO ₄ ^a Ca(OH) ₂ ^a	Ca ₂ Al ₂ SiO ₇ ^a Ca ₃ Al ₂ O ₆	SiO ₂ ^b KAlSi ₃ O ₈ ^b
0.1 M EDTA with pH adjustment	NaCl ^b	CaCO ₃ ^a CaSO ₄ ^a	Ca ₂ Al ₂ SiO ₇ ^a Ca ₃ Al ₂ O ₆ ^a	SiO ₂

^a Major.

^b Trace.

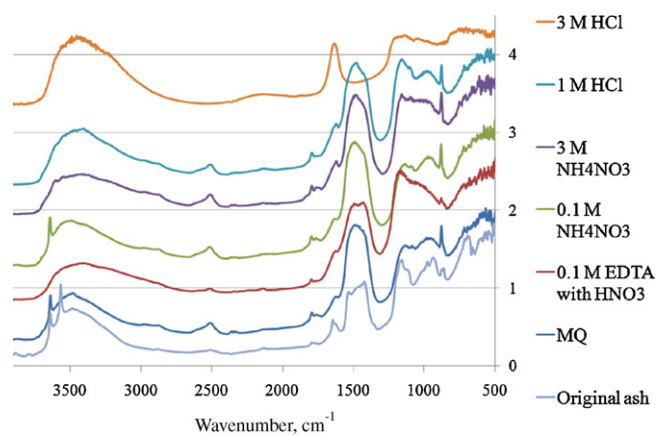


Fig. 3. FTIR spectra of original and leached ash samples.

eties. However, no gypsum could be identified in the XRD analysis (Table 3). This could be due to the small size of the crystals (Fig. 2) which may make them X-ray amorphous. The smaller FTIR peaks around 1760 cm^{-1} and 2500 cm^{-1} found in most leached ashes could be due to CaCO_3 and the peaks around 3640 cm^{-1} found for the original ash as well as for the material leached with de-ionised water and $0.1\text{ M NH}_4\text{NO}_3$ are proposed to be $\text{Ca}(\text{OH})_2$.

The crystalline compounds in the original ash and in ash residues after the leaching tests are shown in Table 3. As a result of lime addition calcium compounds, such as CaCO_3 and $\text{Ca}(\text{OH})_2$ dominate in the original ash. The presence of quartz (SiO_2) is due to elutriated bed sand particles. Both NaCl and KCl were identified as in other investigations of MSW filter ashes [26,27]. The mineralogy of the ash residues after leaching tests is dominated by aluminium silicates and remaining calcium compounds (CaCO_3 , $\text{Ca}(\text{OH})_2$ and CaSO_4) in addition to some secondary compounds, such as calcium oxalate and gypsum. Precipitation from the pore solution is probably the reason that NaCl was found in most of the leached ash samples. It might look as if the aluminium silicates were formed during the leaching tests but this cannot have been the case. Probably, the diffraction patterns of aluminium silicates were hidden in the background of the data for the original ash. The general crystalline structure of the leached ashes, with quartz and various Ca_xAl_y oxides and silicates, is more or less similar independent of the leaching agent used. This indicates that the residue after leaching will have a rather stable basic matrix.

3.2. Leaching

This discussion of the results from the experiments with different leaching media is based mainly on the composition of the samples taken after 24 h (Tables 4 and 5). In most cases the 6 h leaching was somewhat lower.

The acid neutralising capacity of the ash is high, a value of $10\text{ mmol H}^+/\text{g dry matter}$ was obtained from the pH-static titration experiment at pH 7 (Fig. 4). Equilibrium, which was defined to prevail when the acid consumption rate fell below $1\ \mu\text{l}/\text{min}$ (10^{-7} moles of H^+ per min) was reached after about 14 h. However, the main part of the acid was consumed within 30 min. This indicates that most of the alkaline compounds, like CaCO_3 and $\text{Ca}(\text{OH})_2$, are easily available. A minor part of the alkalinity is caused by compounds that are less soluble or enclosed in the ash matrix. Two minor buffering regions can be identified and are probably due to the carbonate system with $\text{p}K_{a1} = 6.4$ and $\text{p}K_{a2} = 10.3$ [21]. Van Herck et al. reported a similar acid neutralising capacity ($<12\text{ mmol H}^+/\text{g ash}$) for a MSW filter ash [11].

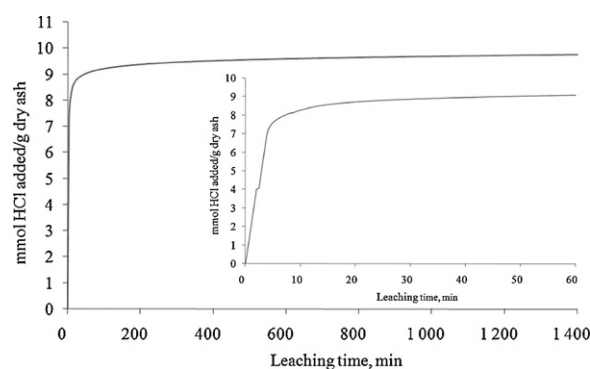


Fig. 4. Acid consumption rate/g dry ash during the pH-static experiments at pH 7. Magnification of the first hour as inset.

Due to the buffering by alkaline Ca compounds a high pH was measured in many leachates.

The ammonium–ammonia buffering system is most effective in the pH range between 8 and 10 [21] which agrees with the measured pH 8.3 in the 3 M ammonium nitrate leachate.

Calcium, potassium and sodium are released in significant amounts in all leaching media, even in water (Tables 4 and 5). This was expected since they are present as soluble salts and earlier work have shown high total water extractable amounts of these elements, as well as for the anions Cl^- and SO_4^{2-} [24]. The only leaching medium that did not transfer Ca effectively to the water phase was sulphuric acid since $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ was formed as secondary compounds [22].

EDTA is known to be an effective complexing agent but the optimal binding properties for various metals depend on the pH of the solution [28]. The PHREEQC modelling carried out here shows that in the EDTA solution with no pH adjustment almost all EDTA was associated with Ca. The fraction of Ca-EDTA complexes decreased with decreasing pH, resulting in possibilities for other ions to form complexes with EDTA which agrees with the experimental results (Table 5). Similar effects, i.e. the complex forming substance being preferably associated with Ca^{2+} , were seen in the equilibrium calculation results for acetate and formate.

Iron, manganese, aluminium and silicon show similar behaviour in the tests. Most leaching media had no or very little effect whereas 3 M HCl, 3 M HNO_3 and $1.5\text{ M H}_2\text{SO}_4$ removed 36–98% of these elements, all in solutions with $\text{pH} \approx 0$. At pH 7 (Table 4) only small fractions of Si were released and almost no Al or Fe. However, 19% of the Mn was leached, which according to the equilibrium calculations is present mainly as Mn^{2+} and to a minor part as a soluble chloride complex. A number of manganese oxides were suggested as solubility determining phases for Mn at pH 7. Similar leaching of Mn (25%) was obtained with the EDTA solution with end pH 8.2

Table 4

Fraction of ash components released from the ash after 24 h leaching by pH-static titration at constant pH 7 with 0.1 M HCl and with final L/S-ratios of 120. All results are given as % released of total amount in the dry ash.

Major elements	% Released	Minor and trace elements	% Released
Al	<1	Cd	100
Ca	80	Co	12
Fe	<1	Cr	9
K	100	Cu	3
Mg	37	Mn	19
Na	63	Mo	97
Si	9	Ni	26
Ti	<1	Pb	1
		Sn	2
		V	3
		Zn	23

Table 5
Fraction of major and minor ash components released from the ash after 24 h leaching with various leaching agents. Figures in brackets refer to fraction of major and minor ash components released from the ash after 24 h leaching with pre-washing using ultra pure water. All results are given as % released of total amount in the dry ash.

Leaching agent	End pH	Al	Ca	Fe	K	Mg	Na	Si	Cu	Mn	Pb	Zn
Water L/S 50	12.4	<4	31	<1	100	<1	71	4	<1	<1	14	3
Mineral acids												
1 M HCl L/S 5	11.7	<4	30	<1	64	<1	44	4	<1	<1	23	<1
3 M HCl L/S 5	<0	76 [30]	63 [40]	63 [43]	86 [15]	64 [11]	58 [10]	44 [46]	100 [87]	71 [56]	100 [42]	77 [54]
1 M HNO ₃ L/S 5	11.8	<4	40	<1	84	<1	53	1	<1	<1	23	<1
3 M HNO ₃ L/S 5	<0	67 [28]	61 [39]	48 [37]	82 [14]	58 [11]	55 [9]	36 [44]	100 [81]	66 [51]	96 [32]	72 [51]
1.5 M H ₂ SO ₄ L/S 10	0.4	60	2	81	100	82	67	58	100	98	5	100
0.2 M acetic process water L/S 5	12.0	<1	19	<1	92	<1	53	<1	<1	<1	1	<1
Organic acids												
0.1 M formic acid L/S 5	12.3	<4	19	<1	83	<1	54	3	<1	<1	25	<1
0.1 M acetic acid L/S 5	12.2	<4	17	<1	70	<1	52	2	<1	<1	32	<1
0.1 M lactic acid L/S 5	12.3	<4	17	<1	69	<1	50	2	2	<1	30	<1
1 M lactic acid L/S 5	12.0	<4 [1]	37 [22]	<1 [1]	100 [10]	<1 [1]	66 [3]	<1 [1]	23 [24]	<1 [1]	43 [2]	1 [1]
0.5 M oxalic acid L/S 5	11.6	<4	31	<1	100	<1	53	1	1	<1	1	<1
Special complex forming agents												
0.1 M NH ₄ Cl L/S 5	12.2	<4	19	<1	83	<1	54	2	<1	<1	27	<1
0.1 M NH ₄ NO ₃ L/S 5	12.0	<4	21	<1	89	<1	53	2	<1	<1	23	<1
3 M NH ₄ NO ₃ L/S 5	8.3	<4 [1]	53 [14]	<1 [1]	77 [10]	16 [1]	41 [3]	4 [2]	100 [68]	<1 [1]	1 [1]	29 [16]
0.1 M EDTA without pH adjustment L/S 5	12.3	<4	19	<1	82	<1	35	2	<1	<1	34	1
0.1 M EDTA with pH adjustment L/S 5	8.2	<4 [5]	65 [31]	<1 [12]	97 [10]	40 [1]	40 [1]	5 [4]	100 [75]	25 [26]	94 [37]	40 [34]

(Table 5). According to equilibrium calculations this is primarily due to formation of chloride complexes and only to a small part to EDTA binding Mn ions.

Zinc was most effectively removed (40–100% removal) from the ash by sulphuric acid, 3 M HCl, 3 M HNO₃ and the pH-adjusted EDTA solution. In the leaching media with high-end pH only a few % of the Zn content was removed, whereas at pH 7 23% of Zn was transferred to the water phase (Table 4). These data indicate that the Zn-containing compounds present are insoluble at pH 11.5–12.5, partly soluble at pH 7–8 and very soluble at pH below 1.

The leaching of Zn is probably due to dissolution of oxidic Zn minerals like ZnO or Zn₂SiO₄, both of which are soluble in slightly acidic media and are suggested to be the main components of Zn in this ash based on speciation by synchrotron based X-ray spectroscopy [22,29].

Zn forms amine complexes as well as Cu and the Zn that was found in the pH 8.3 water phase after leaching with 3 M NH₄NO₃, e.g. 29% of the total Zn content, was present in soluble ammine complexes according to equilibrium modelling.

The release of lead in water (pH 12.4) was modest, e.g. 14% whereas 20–40% was released by formic, acetic and lactic acid (pH 12.0–12.3). According to literature data [11] and our PHREEQC modelling results soluble Pb(OH)₃⁻ and Pb(OH)₄²⁻ complexes are formed at high pH which explains part of these results. Dissolution of Pb(OH)₂ has been suggested to be the source for the hydroxide complexes in solution [11]. In our equilibrium calculations Pb(OH)₂ was indeed indicated as solubility controlling phase and this tendency decreased with increasing pH, as the formation of Pb(OH)₃⁻ is favoured over Pb(OH)₂ at high pH [21].

The pH 7 leaching removed only 1% of Pb, according to modelling as soluble chloride and carbonate complexes. Solubility controlling solids suggested were molybdate, vanadate and carbonate.

The 3 M solutions of HCl and HNO₃ as well as the pH 8.2 EDTA solution (Table 5) removed all Pb. However, leaching with H₂SO₄ and oxalic acid both led to precipitation of PbSO₄ and PbC₂O₄ also found in other work on MSW fly ash [8,18].

Pb does not form ammine complexes, which was reflected in the limited release of Pb by the NH₄NO₃ solutions. The slightly alkaline pH may also have decreased the leaching of Pb [13,15].

Copper was not released in water or dilute acids but 100% released when the amount of acid added was large enough to create a very low pH (Table 5). The 1 M lactic acid solution gave higher release of Cu (23%) than the other organic acids used (Table 5). No published data on ash leaching by lactic acid have been found, but modelling using PHREEQC showed that lactate preferably forms complexes with Cu and Pb before Zn and Mn. This can explain the leaching patterns obtained. The release of Cu from MSW bottom ash due to formation of organo-copper complexes have been pointed out in several papers [17]. Especially the dissolved organic matter (DOM) from the ash has been shown to bind Cu in solution [30].

There was a sharp difference between Cu leaching by the EDTA solutions with end pH 12.3 (<1%) and 8.2 (103%). The equilibrium speciation by PHREEQC showed that the major dissolution of Cu probably has been caused by EDTA complexation. Literature data on EDTA leaching of MSW filter ash has indicated significant leaching for Cu (60–70%), Pb (70–90%) and Zn (50–100%) using EDTA [25,31]. The pH did not affect the leaching much but generally an acidic environment somewhat enhanced leaching [25].

The 3 M solution of NH₄NO₃ seemed to give a rather specific release of Cu, probably due to the formation of copper amine complexes, like [Cu(NH₃)₄]²⁺ [21] (Table 5). The stability of such complexes in this solution was also confirmed by equilibrium calculations. NH₄NO₃ is often used to leach and predict bioavailability of minor elements in soils and Cu is frequently found to form amine complexes especially at neutral and alkaline pH [32–34]. The more or less selective leaching of Cu by 3 M NH₄NO₃ (Table 5) is inter-

esting as it indicates a possibility to recover Cu from ash. Further studies on Cu extraction from ashes leached with NH_4NO_3 are in progress and the preliminary results show high potential for selective and effective extraction of Cu. The methodology and results will be presented and discussed in a following paper.

3.3. Pre-washing and leaching

Pre-washing of the ash with water was applied with the aim to decrease the influence from soluble major elements. Optimization of the washing time showed that most of the leachable Ca, K and Na were released within 60 min. Zhang et al. found an optimal time of 30 min, when washing an MSW filter ash, resulting in the release of 48% of Ca, 76% of K and 67% of Na [18]. It has also been shown that an L/S ratio of 400 gave an almost complete release of Ca, K and Na in this ash [24]. However, such high L/S-ratios may not be feasible in a practical process, and therefore, lower L/S values were used in this work.

The pH of the leachates produced in the leaching step was generally not much different from those recorded in the first test series (Table 5) with the exception of the low pH EDTA experiment. With pre-washing the end pH of that test became lower than 8 due to HNO_3 addition.

In most cases pre-washing resulted in the same or lower amounts of both major and minor elements being released in the following leaching step (Table 5). Pre-washing could separate particles from aggregates and dissolve parts of the ash matrix so that previously encapsulated species can be released. However, such changes in the ash structure also give a larger surface and more sites where metal ions can be adsorbed or co-precipitate with matrix compounds [35]. In these experiments these counter-acting effects may be the reason for the decreased leaching by acids and complex formers. The only exception was a somewhat increased leaching for Fe in the low pH EDTA solution which can be due to an increased porosity in the ash or to the lower amount of Ca present in combination with the lower pH as this favours the complex formation between EDTA and other metal ions.

4. Conclusions

- Leaching of ash increases the specific surface area which can increase or decrease the release of metal ions. This is partly due to the porous ash structure obtained after leaching of soluble major compounds such as CaCO_3 .
- Low pH in the leachates as obtained with the strong mineral acids resulted in high leaching of many elements.
- Organic acids were generally not effective as leaching agents for metals.
- The choice of leaching agent and its complex forming ability affects the leaching of many metals. Leaching by EDTA can probably be optimized to give good removal of some metals, such as Cu and Pb.
- Leaching using NH_4NO_3 was especially effective for Cu, indicating a possibility to recover Cu from ash.

Washing of MSW filter ash with various leaching agents seems to be a possible way to remove hazardous metals, which may promote utilization of such ashes. As the leaching agents used showed different efficiencies for different metal ions, this can be utilized to customize optimized leaching methods. The metal can then be returned to the material cycles in society and re-used.

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