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Zinc recovery from Waste-to-Energy fly ash – A pilot test study

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ABSTRACT

Zinc recovery from MSWI fly ash using acidic leaching and chemical precipitation was studied at pilot scale. The leached fly ash was re-incinerated in order to destroy toxic dioxins. 75–150 kg/h of fly ash from a Swedish Waste-to-Energy plant was mixed with scrubber liquids from the same flue gas treatment system in a continuously stirred vessel. The resulting slurry was dewatered in a vacuum belt filter. Hydroxide precipitation of the produced leachate, at a pH of around 9, followed by filtration of the formed crystals in a membrane filter press produced a filter cake with up to 80 wt% $Zn(OH)_2$ in dry solids, calculated from Zn(tot). Up to 70% of the zinc content in the fly ash could be recovered. Two 4-hour full scale ash re-incineration tests were performed: leached fly ash was mixed with the waste at a ratio corresponding to a situation where all the fly ash was continuously re-incinerated. The tests showed only an 8% mass increase of produced fly ash, which means that most of it ended up in the bottom ash, although some elements could potentially accumulate in the system if all the fly ash was to be continuously re-incinerated. No negative effects were observed on the bottom ash quality, which suggests that a large portion of the toxic fly ash could be transformed into the bottom ash fraction.

1. Introduction

EU policies and legislation aim towards a more sustainable society and circular economy. The EU Waste Hierarchy described in Directive 2008/98/EC sets the priorities for different waste treatment approaches needed to reach these goals: material recycling and energy recovery are preferred over final disposal. Fly ash from municipal solid waste incineration (MSWI) is a problematic residue due to its content of soluble salts (mainly chlorides), metals (such as Cd, Cu, Hg, Pb and Zn), and dioxins (PCDD/Fs). Currently, these fly ashes are usually classified as hazardous waste and landfilled. Prior to landfilling, the fly ash is often stabilized to decrease potential leaching. One option is to mix the fly ash with sludge from the wet flue gas treatment (FGT) and create a so-called Bamberg cake. Another method, used at Langøya in Norway, involves mixing the fly ash with waste sulfuric acid. The resulting gypsum-rich product is used to fill and stabilize an old lime mine. In Germany, the fly ash is sometimes landfilled in old salt mines after mixing with e.g. $MgCl_2$.

Landfilling is not a sustainable treatment option, in particular as the fly ash contains valuable metals, including zinc (Zn) and copper (Cu), in significant concentrations, which could be recovered and re-used. The metals are mainly present as oxides and chlorides, and can therefore not be recovered by mechanical methods. Instead, leaching or thermal processes must be used. Thermal treatment is costly and has mainly been used without metal recovery in Japan (Lindberg et al., 2015). Chemical leaching based on the 3R process (Vehlow et al., 1990), on the other hand, is more widely used. The focus has been on Zn in particular and there are currently several initiatives using similar solutions for metal recovery from fly ash (Schlumberger et al., 2007, Karlfeldt Fedje et al., 2014, Rasmusen 2015, Bakke 2018). The procedures are all based on acidic leaching, but the metal recovery step differs. At present there is one plant in Switzerland where high purity Zn metal is recovered from MSWI fly ash (Schlumberger et al., 2007, Schlumberger et al., 2012). At that plant, a complex process of solvent extraction and electrolysis is used to produce pure zinc metal. A better option may be to generate a Zn-rich product that could be refined using existing metal industry production lines. Earlier studies at laboratory scale by our group have shown that 70% of the Zn can be recovered from fly ash using similar technology, but producing a Zn-rich product instead of pure Zn metal (Karlfeldt Fedje et al., 2014). Life cycle assessment-based calculations have

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also been carried out, and show that compared to current fly ash management, i.e. landfilling, Zn recovery would be beneficial both from environmental (avoiding about 1500 tons of CO_2-equivalent emissions/year) and economic (saving 0.9 million Euro/year) perspectives (Karlfeldt Fedje et al., 2014).

Among the studied scenarios, the most favourable alternative is Zn recovery combined with re-incineration of the washed ash (Karlfeldt Fedje et al., 2014). Some of the main benefits of this approach are the decreased need of both landfilling and mining of virgin Zn, but also that toxic dioxins that may be present in the fly ash are destroyed. It is known that dioxins are thermally degraded during incineration, but that they can be formed in the boiler deposits and then partly adsorbed in the fly ash (Hunsinger et al., 2002, van Caneghem et al., 2014, Lindberg et al., 2015). As dioxins are hydrophobic, they remain on the ash particles during leaching. When the leached ash residue is re-incinerated, the temperature and residence time is high enough to destroy the dioxins, and most of the ash residue is converted to bottom ash (Vehlow et al., 1990, Schlumberger et al., 2007).

The aim of this project was to scale up the suggested laboratory-scale Zn recovery method, i.e. leaching and precipitation (Karlfeldt Fedje et al., 2014), to pilot scale and to find optimal process conditions. In addition, full scale re-incineration tests were performed by returning fly ash residue to the furnace, with the goal of degrading dioxins and converting the residue to bottom ash without negatively influencing the quality of the generated ashes.

2. Materials and methods

All fly ash and scrubber liquids used in this study were sampled from a Waste-to-Energy plant in south western Sweden, to provide realistic conditions and the basis for a full-scale design at this and similar plants. The waste is incinerated in four grate fired furnaces with steam boilers, producing electricity and district heating. The flue gas treatment systems consist of electrostatic Precipitator (ESP), district heating economizer, HCl-scrubber stage, alkaline (SO_2) scrubber stage and condensing scrubber, gas reheater and bag house filter with activated carbon, and lime injection. About 550 000 ton waste is incinerated annually, which gives rise to about 15 000 ton fly ash and 100 000 ton bottom ash.

2.1. Pilot tests: fly ash leaching

Fly ash was collected from a silo where the ESP fly ash from all four lines is stored before it is mixed with sludge from the wet flue gas treatment in a Bamberg mixer. In total, 10 m^3 ash was collected over several weeks, to account for the variations in ash composition. The ash was stored in 11 big bags containing about 600 kg each. The compositions of the ash samples are provided in Table 1. The mineral composition is dominated by chlorides of Na and K as well as Ca carbonates and sulfates (Lassesson et al., 2014).

The ash samples were leached in 11 different campaigns, named A-K, where one big bag of fly ash was treated in each campaign. Scrubber liquids collected from the flue gas cleaning system were used as leaching and/or washing agents in the experiments, i.e. HCl from the acidic scrubber stage, sulfate water from the SO_2-scrubber stage, and condensate water from the flue gas condensing scrubber.

The temperatures of the HCl and sulfate solutions were around 60 °C, while the temperature of the condensate water was about 40 °C. In campaign K, sulfuric acid (25 wt% H_2SO_4, technical quality) was used as leaching agent together with condensate water. Concentrations of selected ions (Cl, Na, K, Ca, Fe, Mg, Mn, Al, Sb, As, Ba, Be, Pb, B, P, Cd, Si, Co, Cu, Cr, Li, Mo, Ni, Se, Ag, Sr, S, Tl, Sn, Ti, U, V, and Zn) in the scrubber liquids were analysed throughout the project. Representative analyses of the liquids used in campaign D are also provided in Table 1.

A drawback of using the HCl liquid as leaching agent is the presence of Hg in the liquid, as the Hg is partially adsorbed on the fly ash particles during leaching (Karlfeldt Fedje et al., 2015, Karlfeldt Fedje and Strömvall, 2016). However, Hg can be separated from the HCl using a Hg selective ion exchange resin (e.g. Lewatit TP 214), which has been tested on this HCl liquid with good results (Karlfeldt Fedje and Strömvall, 2019). In this study, no Hg ion exchanger was used, however this would be necessary in a full-scale process, in order to avoid Hg accumulation in the system if the fly ash is re-incinerated.

The pilot plant for leaching of Zn from ESP ash with HCl, consisting of ash dosage system, stirred vessel and leachate collection. The fly ash was added continuously to the stirred vessel by means of a big bag discharger using a frequency controlled multi screw feeder (75–150 kg ash/h), and transported by a screw conveyor, while the leaching agents were pumped directly from the pressure side of the scrubber circulation pumps to the 0.2 m^3 stirred vessel (d = 0.52 m, h = 1 m). To enhance the Zn leaching from the ash-acid-slurry, an impeller was used to ensure efficient mixing and avoid sedimentation. The pH was kept constant by controlling the flow of acids added. By varying the slurry throughput and liquid level, the residence time in the stirred vessel was varied between 9 and 17 min. Additional details about the leaching (fly ash and leaching agent flow rates, average leaching time (τ), L/S, and pH) are provided in Table 2**.** Leaching parameters (fly ash and leaching agent flow rates, L/S, pH and average leaching time, τ) and % Zn released from the fly ash during campaign # A-K. In addition, the Zn concentrations [mg/L] in the corresponding leachates are given. The slurry was pumped by a hose pump to a pilot scale vacuum belt filter with two dewatering zones, where the leachate was separated from the ash and collected in 1 m^3 Cipax tanks. The solid ash residue was washed with water in a counter-current operation, using condensate from the scrubber or tap water. The wash water was collected in the same Cipax tanks as the leachates, while the leached, filtered and washed ash residue was collected in small containers until the re-incineration experiments.

Previous laboratory studies show that about 30 wt% of the solid ash is dissolved during acidic leaching (Karlfeldt Fedje et al., 2014). The amount of ash dissolved during leaching was calculated by mass balance, based on the assumption that Si is not dissolved during leaching and washing. The Si concentration in the leachates was low (0.01–2 g/kg ash), which supports this assumption. This includes ash particles following the leachates, i.e. the actual Si release from the ash is lower.

2.2. Pilot tests: Zinc precipitation

The Zn precipitation pilot tests were conducted using the same stirred vessel as in the leaching experiments, together with a pilot scale membrane filter press. NaOH (25%, technical quality) was gradually added to selected leachates from campaigns A-K in batch wise experiments to increase the pH and precipitate $Zn(OH)_2$ crystals. Once the desired pH was reached, the mixture was agitated for about 60 min to favour precipitation and growth of the $Zn(OH)_2$ crystals, which would facilitate filtration. Thereafter the slurry was pumped to a membrane filter press, where the Zn cakes were filtered, washed, dewatered, and dried using pressurized air. All leachates contained small amounts of solids originating from the fly ash, i.e. ash particles following the leachate though the filter cloth. During storage, these solids sedimented to the bottom of the Cipax tanks, and to produce representative filter cake compositions, the filtrates were agitated using compressed air in experiments 3, 6–9, 11–14, and 18–19 (marked "Mixing" in Table 3)

Table 1
Average composition [mg/kg DS] of ash samples A-K together with the standard deviations (SD) in brackets. Concentrations [mg/L] of HCl, sulfate and condensation scrubber liquids used in campaign D for leaching and/or washing of ash samples. Beryllium, Se, Ag, Sr, Tl and U were also analysed but they were all <0.5 mg/L.

	Fly ash mg/kg DS	HCl mg/L	Sulfate mg/L	Condensate mg/L
Al	34 000 (4400)	3.9	0.17	0.06
As	1000 (560)	<0.5	<0.5	<0.5
B	210 (14)	14	0.9	1.2
Ba	14 000 (200)	0.60	<0.1	<0.1
Ca	190 000 (11 000)	17	<80	<0.8
Cd	240 (29)	0.60	0.14	0.05
Cl	110 000 (12 000)	40 000	–	100
Co	27 (4)	<0.5	<0.5	<0.5
Cr	520 (74)	<0.5	<0.5	<0.5
Cu	2200 (430)	3.1	0.82	0.21
Fe	16 000 (720)	6.6	0.21	0.07
Hg	0.68 (0.17)	–	–	–
K	55 000 (7000)	120	430	18
Mg	13 000 (1100)	<2.0	<200	<2.0
Mn	710 (32)	0.50	0.04	0.01
Mo	28 (3.5)	<0.5	<0.5	<0.5
Na	61 000 (5300)	730	23 000	14
Ni	92 (7.0)	<0.5	<0.5	<0.5
P	7000 (360)	1.9	<120	<1.2
Pb	4800 (1500)	11	1.7	0.40
S	47 000 (7000)	490	15 000	12
Sb	1700 (170)	2.9	0.60	0.07
Si	57 000 (6600)	19	<200	<2.0
Sn	960 (66)	1.6	0.10	0.03
Ti	12 000 (950)	1400	<20 000	<200
V	58 (14)	<0.0020	<0.0020	<0.0020
Zn	25 000 (2000)	68	23	5.5

– Not analysed.

Table 2
Leaching parameters (fly ash and leaching agent flow rates, L/S, pH, and average leaching time, τ) and % Zn released from the fly ash during campaign # A-K. In addition, the Zn concentrations [mg/L] in the corresponding leachates are shown.

#	Ash kg/h	HCl L/h	Cond. L/h	Sulfate L/h	H_2SO_4 L/h	Wash L/h	L/S –	pH	τ min	Zn leached %	Zn in leachate mg/L
A	100	310	–[1]	–	–	100	3.1	3.6	13	57	5400
B	150	470	–	–	–	80	3.1	3.6	10	61	4500
C	100	340	–	–	–	80	3.4	3.3	11	58	4700
D	75	220	–	250	–	80	6.2	3.5	10	74	3200
E	125	–	490	–	–	80	3.9	10.2	9	<1	12
F	100	330	–	200	–	80	5.3	3.6	9	57	2800
G	100	380	–	–	–	80	3.8	3.3	10	62	3500
H	100	430	–	–	–	80	4.3	3.2	17	65	4000
I	75	240	220	–	–	80	6.2	3.5	10	47	2300
J	80	330	–	–	–	80	4.1	3.4	13	55	4800
K	100	–	320	–	70	80	3.9	3.6	10	63	4300

[1] No addition.

prior to precipitation experiments. To increase the potential effect from a higher concentration of ash particles in the filtrates (simulating a coarser filter cloth), washed ash was added to the filtrates in three tests; 8–9, and 12 (marked "Precoat" in Table 3). In some experiments, 1–5, and 10, (marked "Flocking" in Table 3) flocculating agents (Magnafloc 110L and Zetag 9016) were used to potentially enhance the filtration properties of the $Zn(OH)_2(s)$ slurry.

2.3. Full-scale tests: Detoxification through re-incineration

Two full scale tests were carried out to study the effects of re-incineration of leached and washed fly ash. The tests were made to ensure that only a small fraction of the re-incinerated fly ash is released as fly ash, and most of it is thermally treated on the grate together with the waste, ending up in the bottom ash without lowering the bottom ash quality. In the first test, residues from ash A-D were used, and in the second test the residues from ash E-K were re-incinerated. The leached fly ash was tipped into the bunker and thoroughly mixed with ordinary waste using the crane in proportions equal to a situation where all the fly ash had been leached and re-incinerated continuously. The waste-ash-mixture was continuously added to the furnace for 4 h in each test. To account for the time period when the waste remains in the hopper and on the grate, the starting time for sampling the fly ash was two hours after the time when the ash addition started. The delay in slag sampling was three hours, as the wet slag ejection takes approximately one additional hour. 10-litre wet slag samples were taken manually every 30 min: 4 or 5 samples before, and 5 samples during, the ash addition.

The fly ash was isokinetically sampled from the flue gas channel before the electrostatic filter for 30 min, in accordance with EN 13284-1. Two samples were taken before the ash addition, four

Table 3
Zinc hydroxide concentrations [wt%] and amounts of Zn cake produced [kg/m^3] (100% DS) during each precipitation experiment. In addition, the treatment options used in each test are shown.

#	Filtrate	Treatment	End pH	Zn as $Zn(OH)_2$ wt%	Zn cake kg DS/m^3
1	A	Flocking	9.1	64	8.3
2	A	Flocking	9.2	40	18.7
3	A	Mixing+Flocking	10.5	46	13.4
4	B	Flocking	9.0	49	11.5
5	B	Flocking	9.0	47	14.8
6	C	Mixing	9.0	73	7.6
7	C	Mixing	9.2	64	9.7
8	C	Mixing+Precoat	9.3	56	12.2
9	C	Mixing+Precoat	8.5	58	10.7
10	D	Flocking	9.1	52	9.5
11	D	Mixing	9.3	61	5.4
12	D	Mixing+Precoat	9.3	68	5.4
13	D	Mixing	6.9	76	4.9
14	D	Mixing	7.9	70	5.5
15	I	–[1]	9.3	58	6.6
16	K	–	9.0	49	9.6
17	K	–	9.0	55	9.2
18	K	Mixing	10.5	67	6.8
19	K	Mixing	9.6	64	7.9
20	Re-pulp 10D		7.8	79	

[1] No treatment.

during the addition, and finally two samples after the addition. Due to problems during sampling only the fly ash samples from the first re-incineration test could be evaluated.

All analyses were performed according to standardized methods. Total amounts in solid samples were analysed using ICP-AES/ICP-MS, according to EN 13656, with the exception of B (SS 028150-2), SiO_2 (EN 14385), Hg (SS 28150-2, AFS), and Cl (SS 187185 using IC-EC). Ions in liquids were analysed without further filtration, according to EN ISO 15587, EN ISO 15587-2, EN ISO 11885, EN ISO 17294, except for chlorine (NE ISO 10304) and Hg (EN ISO 17852). Dust measurements during ash re-incineration were performed according to SS-EN-13284-1. Moisture content in solids was analysed using EN 14774-1,2,3:2009 mod/15414-1,2,3:2011 mod/SS18.

All enrichment factors are calculated according to:

$$\text{Enrichment factor} = (C_{\text{residue}} - C_{\text{original}})/C_{\text{original}}$$

giving that a value >0 means a higher content in the residue than in the original ash.

3. Results and discussion

3.1. Ash leaching

The Zn releases (Table 2) show good correlation with similar experiments in earlier laboratory studies (Karlfeldt Fedje et al., 2014). Except in test E (water), the Zn release varies between 47 and 74%, irrespective of the leaching parameters used. Both low pH values and high L/S ratios are known to favour Zn leaching in laboratory experiments (Liu et al., 2005, Karlfeldt Fedje et al., 2010, Karlfeldt Fedje et al., 2014) and were identified as the most important leaching parameters in the present study. Leaching time was of less importance. Both HCl and H_2SO_4 give similar Zn leaching efficiencies in the best cases (test H and K, respectively) but the best Zn leaching is achieved using a combination of HCl and sulfate solution from the SO_2 scrubber i.e. in test D as described by Schlumberger et al. (2007). This cannot be explained by the higher L/S ratio used in this test compared to tests H (HCl) and K (H_2SO_4), as test I has the same leaching parameters, except that water is added instead of sulfate solution to increase the L/S ratio. Consequently, the addition of sulfate solution is favourable for Zn leaching.

Zinc can form soluble hydroxides at high pH values e.g. (Reichle et al., 1975) but <1% of the Zn was released during water washing (Table 2). This is significantly lower than for acid leaching and consequently alkaline leaching is not a favourable option if Zn is to be recovered from the ash. A more alkaline pH would most likely increase the leachability, however this was not tested. Water leaching, i.e. campaign E, also gives low releases of most other elements, except water-soluble compounds like chlorides of Na, K, and Ca, which are released in large proportions. Concentrations of other elements in leachates C, D, E and K are shown in Table S1.

A recent review report on speciation of Zn in MSWI fly ashes shows that oxides and halides are the most frequently reported Zn compounds, however silicates and phosphates have also been identified (Jones et al., 2018). The number of scientific papers on this subject is limited and a high variety of Zn compounds are reported in the literature, indicating that more research is needed before general conclusions can be drawn. However, the Zn speciation in ash cannot be described by a single Zn compound; instead a mix of different compounds is present, which explains the non-complete leaching. This has also been shown in several leaching studies at low pH, where about 60–80% of the Zn is released at pH < 2, see e.g. (Hong et al., 2000). Consequently, if all Zn is to be recovered, more or less the whole ash matrix must be dissolved, which is not desirable, as a lot of unwanted elements would then be released.

3.2. Zinc precipitation

Leachates with the highest Zn releases in combination with the lowest HCl consumption were chosen for the precipitation tests and included HCl (A, B, C,) HCl + sulfate solution (D) and H_2SO_4 (K) as leaching agents (Table 3). In addition, leachate I, with lower Zn leaching, was studied to investigate the Zn precipitation efficiency in case of low Zn concentrations. A special test where the Zn cake from experiment 10D was re-suspended in tap water to wash out chlorides and generate a cleaner Zn product was also carried out. The literature gives that the maximum precipitation for pure $Zn(OH)_2$ in a water solution occurs at around pH 9, e.g. (Industrial Environmental Research Laboratory, 1980), and therefore most experiments were performed at this pH, but lower and higher pH values were studied as well. However, the results do not show peak precipitation efficiencies at pH 9; there is instead a tendency for lower pH values to enhance the Zn content in the final product (Table 3). This is due to the complexity of real ash leachates compared to pure Zn hydroxide solutions, which also influences the precipitation of other elements. In addition, other Zn compounds than pure $Zn(OH)_2$ e.g. $Zn_5(OH)_5Cl_2{\cdot}H_2O$ can precipitate at these pH ranges, as Cl is present in significant concentrations.

A low precipitation pH is also favourable as the consumption of NaOH is reduced, which decreases both the need for chemicals and the cost. However, it is not only pH that affects the Zn precipitation but also the crystallization process. Mixing of the leachate before precipitation, to resuspend ash particles present in the leachate, on which the $Zn(OH)_2$ crystals can grow, seems to be an important factor, as the best results use mixing as a treatment method. Neither the addition of extra ash particles nor flocking media contributes to higher Zn precipitation efficiencies.

The overall compositions for two representative Zn products are similar, but there are some interesting differences (Fig. 1a and b). In product 6C, the total content of Cl and Mg is about 7% of the product weight, while in product 13D, Si alone contributes with 8 wt%. For Mg, this is probably due to the higher precipitation pH as discussed above. The Si probably stems from the ash particles in the leachate, and the more efficiently the filtrate is mixed before precipitation, the more Si and other ash matrix elements are present in the final Zn product. Consequently, although mixing favours Zn precipitation, too vigorous mixing can result in more impurities in the Zn products, as described for Si. There is also a weak trend that increased thickness of the Zn filter cake leads to lower Zn content, which may be due to less efficient removal of impurities during washing.

The highest Zn content was found in the new cake produced when the product from experiment 10D was resuspended in water (Fig. 1c). The Zn content increased from 52 to 79 wt% $Zn(OH)_2$ and the Cl content decreased from 8 to 3 wt%, which shows that leaching the product with water may be a way to produce more concentrated and purer Zn products. To achieve this in full-scale continuous operation, the complexity of the plant would have to increase significantly.

The aim of this work is to produce a $Zn(OH)_2$ product, which can be refined to pure zinc in a zinc production plant. Normally, these plants have processes for removing Pb, Cd and other contaminants present in the raw materials, while Cl, Mg and Sb can be problematic, depending on which process is used and where in the process

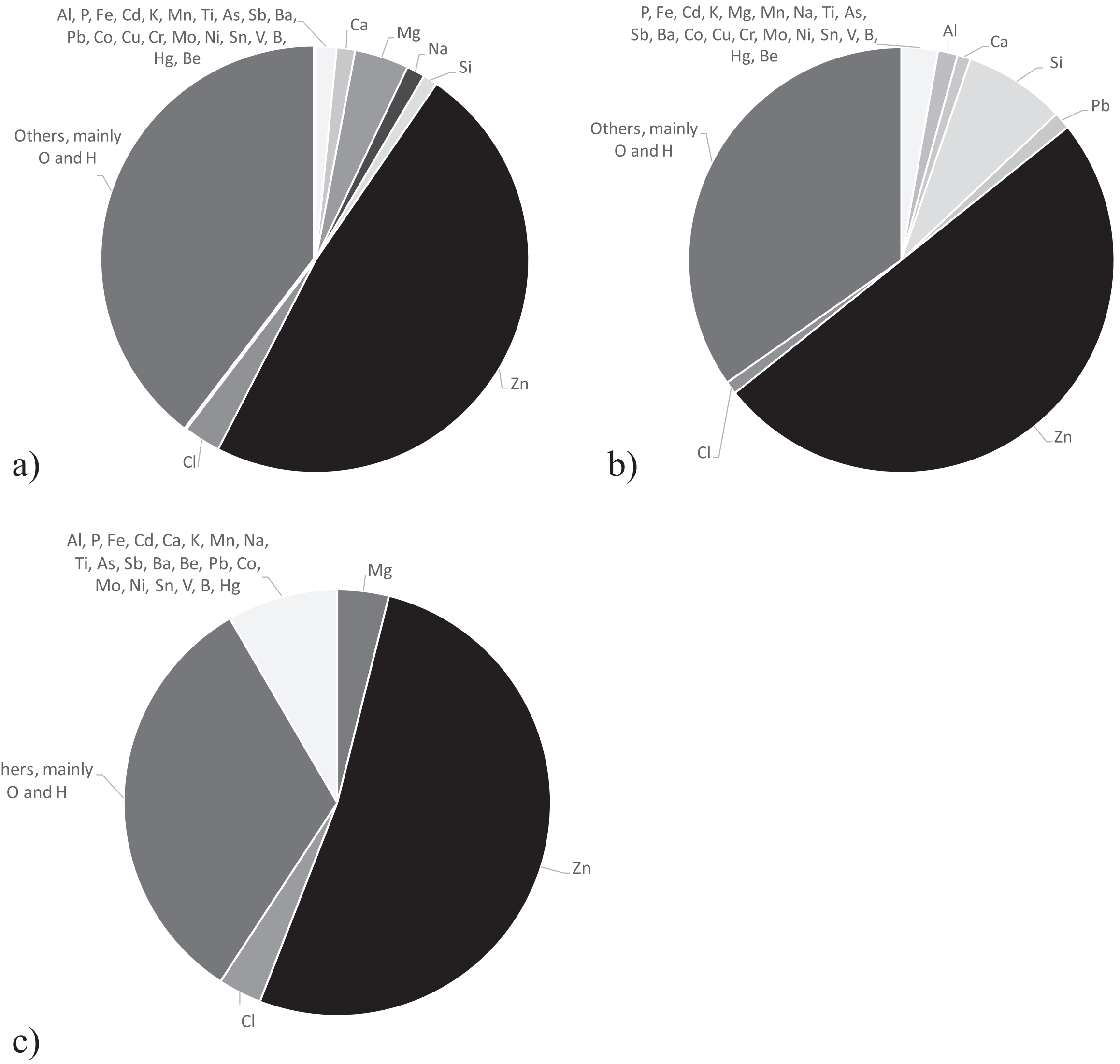

Fig. 1. Composition of representative Zn cake products a) 6C (HCl), 13D (HCl and sulfate solution) and c) re-pulp of 10D. All values are given as weight % of dry substance.

this product would be added. Chlorine is generally present as water soluble compounds and originates not only from the leaching agent but also from the ash itself (Table 1). The Cl concentration can be decreased by washing of the final product. However, despite the fact that similar washing procedures were used in all experiments, the Cl content in the final products varied. This could not be explained by the initial chloride concentrations in the leachates. Instead, the mass of the Zn precipitation products shows a stronger correlation, where the Cl content decreases with the decreased mass of the Zn precipitation product (Fig. S1). A potential reason is that a thinner solid cake leads to more evenly distributed water washing. Chloride is present in all Zn products, including the re-pulped product 10D, which may indicate that Cl is not only adsorbed or present as e.g. easy soluble NaCl or $ZnCl_2$, but also bound into the Zn crystals, potentially as e.g. $Zn_5(OH)_5Cl_2{\cdot}H_2O$.

Except for elements that form easily soluble salts, such as Cl, K, Na and Ca, the precipitation efficiencies from the suspensions, i.e. leaching filtrate and washing water, are in general >90% (Table 4). This is especially clear in filtrate C, with a final pH of 9, compared to filtrate D, with a pH of 6.9. However, as the Zn precipitation is similar for the two samples, the lower pH value generates cleaner precipitation products, and decreases the need to use NaOH for pH adjustment.

3.3. Ash residue characterization and handling

All analysed elements except the alkali metals, Cl, B, Ba, Cd, and Zn have a higher occurrence in the fly ash residues than in the original ashes (Table S2). This is mainly due to the loss of ash mass from leaching of easily soluble salts. As expected, however, B, Ba, Cd, and Zn have a higher occurrence in the water-leached ash residue E, as leaching at the resulting high pH value is less efficient than acid leaching. Although both the initial compositions of the ashes and the leaching parameters vary between the experiments, the enrichment factors are comparable, which shows that all ashes contain compounds that are not mobile unless stronger leaching parameters are used. This is especially clear for As, Cu, and Pb, which were originally present in higher amounts in ashes A-E than in F-K, but have similar enrichment patterns (Tables 1 and S2).

3.4. Detoxification of washed fly ash through re-incineration

The detoxification tests, i.e. re-incineration of the washed fly ash residue, showed that the average content of most elements was higher in the fly ash collected during re-incineration compared to the normal conditions right before and after the re-incineration (Table 5 and Fig. S2). In general, the calculated enrichment factors can be explained by the natural variation in the waste used for the re-incineration tests. Arsenic, Cr, Sn, and Pb show the highest enrichment factors, however for all elements except Cr, their occurrence in the re-incinerated ash residues is significantly higher than in the fly ash from normal incineration, which explains some of the enrichment. Chromium shows the opposite i.e. lower content in the ash residues than in the normal fly ash during the re-incineration test. Variations between ash samples can also be observed for other elements, such as Ni, Sb, and Zn, which shows the complexity of studying ash in full-scale experiments, as the composition of the ash is directly correlated to what is incinerated (Fig. S2). This is of course known, but is worth mentioning, as it must be taken into account when the results are evaluated. The dust concentration in the flue gas downstream of the boiler increased from 3200 ± 900 to 3500 ± 2400 mg/Nm^3 dry gas, during the re-incineration test compared to normal incineration. This means that on average, only 8% of the re-incinerated fly ash entered the flue gas, while the major part is found in the slag. The dust emission to atmosphere was <0.1 mg/Nm^3 d.g. @ 11% O_2 before, during and after the test (the emission limit is 10 mg/Nm^3 d.g. @ 11% O_2). This has also been found in previous studies (Schlumberger et al., 2012). For comparison, it has been calculated that if all re-incinerated fly ash was new fly ash, the amounts would have increased by 70%. To summarize, the contents of most elements are higher in the fly ash collected during re-incineration of washed fly ash compared to the normal incineration periods. However, there are natural differences in fly ash composition dur-

Table 4
Concentrations [mg/L] in two representative leachates before and after alkaline precipitation and filtration. In addition, final pH and precipitation efficiencies in % are shown.

Element Final pH	Leachate C – mg/L	Filtrate 6C 9.0 mg/L	Prec. eff. – %	Leachate D – mg/L	Filtrate 13D 6.9 mg/L	Prec. eff. – %
Al	3.1	0.01	100	31	0.1	100
As	1.2	<0.01	100	2.3	<0.01	100
B	44	38	14	29	28	3
Ba	3.6	1.2	67	0.10	0.30	−123
Ca	7300	6800	7	920	840	9
Cd	53	33	38	39	31	21
Cl	61 000	59 000	3	39 000	32 000	18
Co	0.55	<0.01	100	0.4	0.2	56
Cr	0.07	<0.01	97	0.09	<0.01	98
Cu	3.7	0.18	95	12.0	0.10	99
Fe	1.6	0.01	99	0.10	<0.01	>94
K	15 000	14 000	7	9800	9900	−1
Mg	930	550	41	540	530	2
Mn	31	0.37	99	19	13	32
Mo	0.07	0.02	68	0.03	0.04	−34
Na	22 000	20 000	9	25 000	24 000	4
Ni	0.34	<0.01	98	0.60	0.30	45
P	<1.5	<1.5	–	<1.5	<1.5	–
Pb	28	0.51	98	25.0	8.4	66
Sb	3.5	0.07	98	1.9	0.1	94
Si	34	<2.5	93	77	18	77
Sn	0.31	<0.01	99	0.01	<0.01	86
Ti	0.58	<0.25	>57	<250	<250	–
V	0.03	0.01	97	0.10	<0.01	97
Zn	3800	68	98	2600	130	95

Table 5
Average and maximum amounts in fly ash during normal incineration and during re-incineration of washed fly ash, test 1. The values are shown as average values [mg/kg dry ash] of four samples with SDs in brackets. The potential enrichment in % is also provided.

Element	Normal, average mg/L	Normal, max mg/L	Re-incin, average mg/L	Re-incin, max mg/L	Enrichment, average %	Enrichment, max %
Al	36 000 (6100)	45 000	36 000 (6700)	42 000	0	−7
As	340 (150)	480	1600 (520)	2500	390	420
Ba	1100 (210	1400	1300 (280)	1600	19	14
Ca	190 000 (30 000	220 000	170 000 (32 000)	210 000	−11	−5
Cd	36 (7.0)	43	49 (18)	78	35	81
Co	30 (10)	47	45 (11)	61	51	30
Cr	1700 (1300)	3800	3200 (1600)	5400	89	42
Cu	4300 (1800)	6000	4400 (1400)	6100	1	2
Fe	17 000 (5000)	25 000	23 000 (3800)	29 000	38	16
K	18 000 (1100)	19 000	17 000 (2000)	20 000	−4	5
Mg	14 000 (2100)	16 000	14 000 (1900)	16 000	2	0
Mn	690 (74)	780	910 (36)	960	33	23
Mo	120 (68)	230	190 (110)	350	51	52
Na	22 000 (2300)	25 000	19 000 (3300)	24 000	−12	−4
Ni	1100 (1000)	2900	1700 (1200)	3300	49	14
P	6300 (970)	7800	6500 (1000)	7400	2	−5
Pb	960 (240)	1300	1900 (470)	2700	100	110
Sb	710 (150)	870	940 (71)	1000	32	15
Sn	310 (41)	380	600 (48)	680	93	79
Ti	12 000 (2800)	16 000	11 000 (2600)	14 000	−6	−13
V	37 (3)	41	53 (7)	64	44	56
Zn	11 000 (2700)	16 000	14 000 (3300)	19 000	18	19

ing normal incineration due to variations in waste composition that influence the results.

The bottom ash is also impacted by re-incineration of fly ash residues, although the trends are less clear. There are variations in the enrichment factors for the two re-incineration tests, where an element is enriched in one test but not in the other, e.g. Pb, Table S3. As a limited number of elements were analysed during normal incineration in re-incineration test 1, these analyses were complemented with other total amount analyses, carried out during normal incineration. These also show the natural variation in the total contents, e.g. for Ni, for which the content varies between 100 and 1200 mg/kg DS during normal incineration. This is not only due to the fact that the samples relate to a longer time period (months or years) with varying waste compositions, as even samples taken within a short time period (30 min) can show large variations, both during normal incineration and during re-incineration tests, Fig. S3. This highlight both the heterogeneity of the slag itself and the complexities of slag sampling. However, when all analyses from normal incineration are compared to all analyses from re-incineration, the trend becomes stronger. The Cd content is significantly lower in slag with re-incinerated fly ash, while the amounts of Sn and Zn are higher (Table 6).

Re-incineration of washed fly ash does not have a significant impact on the slag composition, and no significant effects on the incineration process itself as a result of the fly ash addition were identified. Similar results are found in a WtE-plant, where return of washed fly ash has been in operation for several years (Schlumberger et al., 2012). It has also been shown that the particle size distribution in the bottom ash is not affected by fly ash addition (Schlumberger et al., 2007). As discussed above, our study shows that >90% of the re-incinerated fly ash is transformed to slag, which corresponds to <15% of the total slag amount. However, there is a risk of enrichment of some elements in both fly ash and slag if all washed fly ash is returned to the furnace.

Table 6
Average contents (mg/kg DS) and corresponding SDs in brackets in slag during normal incineration and during re-incineration tests as well as enrichment (%).

Element	Normal, average, 4–18 analyzes mg/L	Re-incin, average, 10 analyzes mg/L	Enrichment, all normal vs all re-incin. %
Al	56 000 (28 000)	54 000 (7700)	−9
As	27 (14)	22 (9.4)	−18
B	180 (37)	210 (28)	17
Ba	2400 (1300)	1500 (350)	−36
Ca	150 000 (22 000)	150 000 (12 000)	−5
Cd	3.2 (3.5)	1.0 (0.50)	−70
Cl	5800 (2300)	6100 (570)	5
Co	70 (160)	38 (28)	−45
Cr	460 (160)	670 (400)	48
Cu	3600 (2700)	4200 (1800)	15
Fe	74 000 (20 000)	66 000 (16 000)	−10
K	12 000 (1900)	16 000 (2100)	32
Mg	13 000 (860)	14 000 (1000)	7
Mn	1100 (400)	1000 (160)	−10
Mo	20 (14)	27 (3.1)	33
Na	31 000 (9300)	24 000 (2300)	−23
Ni	640 (1600)	660 (330)	4
P	5100 (1600)	6900 (1300)	35
Pb	1200 (2400)	880 (930)	−26
S	9300 (4400)	11 000 (2200)	19
Sb	82 (42)	84 (24)	3
Si	170 000 (35 000)	160 000 (25 000)	−3
Sn	96 (41)	220 (250)	130
Ti	9700 (2000)	9800 (1500)	0
V	58 (15)	61 (16)	6
Zn	3600 (1400)	6200 (5100)	75

3.5. Landfilling

Due to the presence of several metals in the ash residues, the potential for using them as e.g. construction material in countries like Sweden is limited. Instead, landfilling is an alternative to re-incineration, which makes it important to consider leaching in general. Both the studied ash residues, i.e. C and D, show low leachability and could according to the European landfill directive be deposited in a landfill for non-hazardous waste (Swedish Environmental Protection Acency 2004), with one exception; Sb in residue C (Table 7). The Sb release was about 4 times higher from the residues than from the original ashes, and mobilization of Sb from acid-leached ashes like the ones used in this project has been reported previously (Karlfeldt Fedje et al., 2014). This phenomenon has also been reported for water washed fly ashes (Staffas et al., 2016). Antimony can be present in redox states III

Table 7
Total amounts of selected elements in ash residues C and D after acid leaching and washing, and corresponding release according to the EN-12457-3 test. The latter is compared to the limits for acceptance by landfills for non-hazardous waste (Swedish Environmental Protection Acency, 2004). Values exceeding the limit are marked in bold. All values are given as mg/kg DS.

	Total amount		Leaching		
Element	Ash residue C mg/kg DS	Ash residue D mg/kg DS	Ash residue C mg/kg DS	Ash residue D mg/kg DS	Non hazardous mg/kg DS
As	2300	1900	1.5	1.8	2
B	150	140	–[1]	–	–
Ba	410	1600	–	–	–
Be	<2.8	<2.8	–	–	–
Cd	100	58	<0.01	<0.01	1
Co	29	24	–	–	–
Cr	730	890	4.5	5.0	10
Cu	3700	3300	<0.20	<0.20	50
Hg	0.13	4.2	<0.001	<0.001	0.2
Mo	43	36	8.6	6.0	10
Ni	120	90	<0.04	<0.04	10
Pb	8700	7000	0.10	<0.05	10
Sb	2400	2100	**1.1**	0.50	0.7
Se	–	–	0.07	0.06	0.5
Sn	1400	1300	–	–	–
V	64	52	–	–	–
Zn	19 000	14 000	<0.40	<0.40	50
Ions and DOC[2]					
Cl^-	–	–	6400	2600	15 000
F^-	–	–	12	9.0	150
SO_4^{2-}	–	–	14 000	15 000	20 000
DOC	–	–	150	120	800

[1] Not analysed or no limit exists.
[2] Dissolved organic carbon.

and V, in addition to its elemental state, and preferably forms (hydr)oxides in alkaline media with positive redox potential, i.e. ash leachates (Vink 1996, Cornelis et al., 2008). At alkaline pH both Sb redox states are present, while Sb(III) is the dominating specie at acidic pH values. The presence of iron hydroxides or manganese oxides can also affect the redox state of Sb (Cornelis et al., 2008). As Sb(V) is more soluble than Sb(III) (Cornelis et al., 2008) this explains the higher leachability of Sb when ash is leached or washed in water compared to acid. In addition, Sb could be encapsulated in ash particles in the original ashes, which then dissolve during leaching and thus expose the Sb compound to the leaching media. Antimony can for instance appear as a solid solution with Ca (Cornelis et al., 2008). Consequently, from a Sb leaching point of view it would be preferable not to water-wash the ash after acid leaching, however this is not a good option for other elements, like Cl. Instead it seems that improved water washing steps may decrease the Sb leaching, as loosely adsorbed Sb is released (Staffas et al., 2016).

4. Conclusions

The aim of this study was to recover Zn from MSWI fly ash at pilot scale, and to re-incinerate the washed fly ash in the furnace, thereby producing less toxic bottom ash.

In total, 70% of the Zn in the fly ash could be recovered. The leaching is the limiting factor and more or less all released Zn was found in the final product. The choice of leaching media, pH value, and L/S ratio influences the Zn leaching efficiency and by using pH values between 3 and 4, an L/S ratio around 4 or higher, and a leaching time of approximately 10 min, about 70% of the Zn was released from the ash. The final Zn cake product contained up to 80 wt% $Zn(OH)_2$ in dry solids, calculated from Zn(tot). The precipitation pH is important for the purity of the product. The full-scale re-incineration tests showed that >90% of the re-incinerated fly ash is transformed to bottom ash. No significant effects on the incineration process connected to the re-incineration could be identified during the short-term tests made. In cases where re-incineration is not possible, landfilling is an option. This study showed that the leaching from the fly ash residue met the limits for landfilling in a deposit for non-hazardous waste, except for Sb in one case.

The process parameters used and the results from the pilot tests are comparable to previous laboratory studies, indicating that upscaling of the recovery process from pilot to full scale is likely to be successful. There are several advantages with such a process. For instance, the need for landfill and transportation of toxic materials is decreased, which benefits both the economy and the environment. In addition, the ash residue is less reactive, which offers more treatment options. However, the most important advantage is that this opens for sustainable and circular treatment of MSWI fly ash, where waste from society is refined to create new usable products.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2020.07.017.

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