

Recovery of high purity zinc from filter ash produced during the thermal treatment of waste and inerting of residual materials

The method described below recovers zinc, a valuable metal that is present in high concentrations in filter ash from the thermal treatment of waste, and returns the filter ash stripped of heavy metals to the combustion process in order to destroy organic substances. On an industrial scale, the heavy metals in the filter ash were mobilized by means of hydrochloric acid in the acidic fluids produced in the flue-gas scrubbing process without the addition of further chemicals. A pilot plant for implementing the selective reactive extraction (SRE) method on the ash extracts, using a highly selective complexant, was operated over a period of several months in order to obtain a concentrated, high-purity zinc salt solution (mono metal solution). A zinc depletion rate of 99.8% in the aqueous extract was achieved using mixer–settler units. The residual zinc concentration in the waste water was then $< 2 \text{ mg L}^{-1}$. By stripping the loaded organic phase, a concentrated, high-purity mono metal solution with 190 g L^{-1} zinc was obtained. Zinc metal with a purity $> 99.99\%$ is then separated by means of electrolysis. To destroy organic substances present in the filter ash, particularly dioxins and furans, the extracted filter ash cake was returned to the combustion process together with household waste. Plant operation, raw and pure gas parameters, and quality of the bottom ash produced were not impacted by such recirculation. The profitability of the overall process is attributable both to the recovery of valuable zinc metal and to the cost savings made in waste water treatment and in the disposal of the waste combustion residues because the remaining mixture of filter ash and bottom ash can be reused in a combined form. This method therefore supports the sustainable and economically viable reuse of filter ash.

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Introduction

During the combustion of household waste, volatile heavy metals such as zinc, cadmium and lead as well as organic sub-

stances such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are consolidated in the filter ash produced.

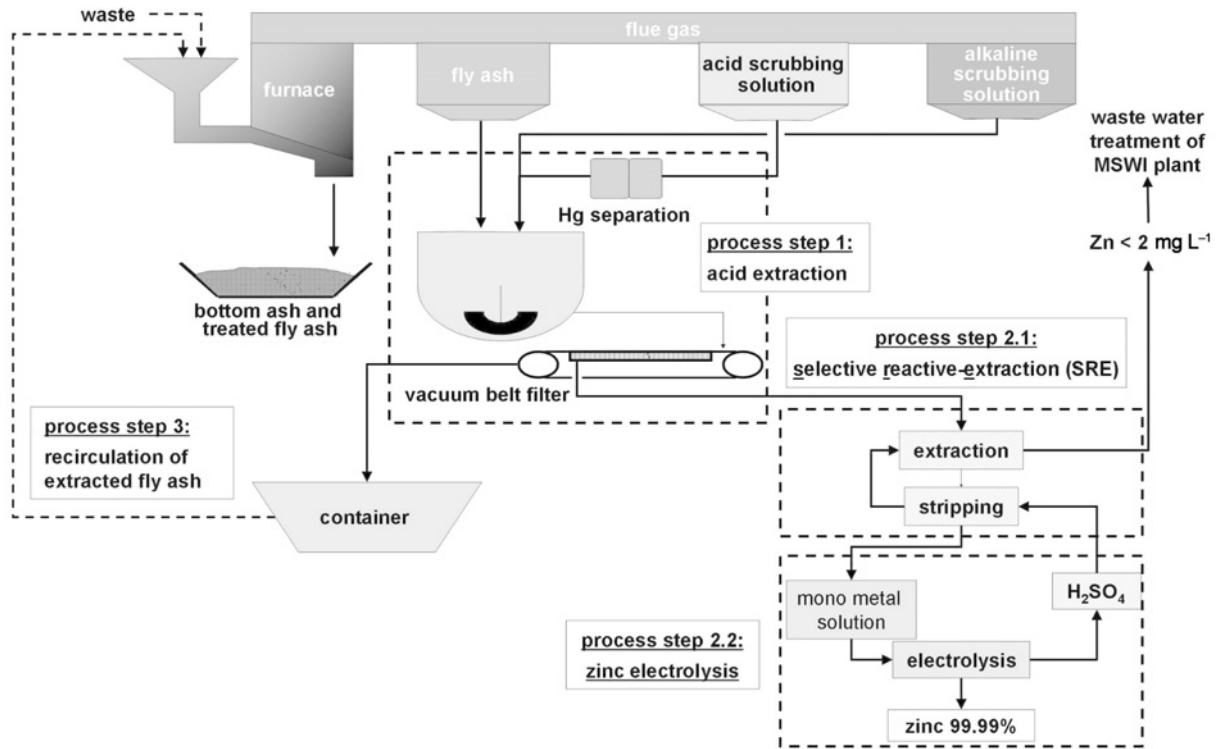


Fig. 1: Process overview.

Due to this contamination with organic and inorganic pollutants, regulated disposal of this filter ash is essential. As an alternative, new methods of making the filter ash inert have been developed over the last few years; for example, chemical stabilization (Cheng & Bishop 1992), solidification (Derie 1996), sintering (Wang *et al.* 1998, Mangialardi 2001) and vitrification (Oden & O'Connor 1994, Tadashi 1996). These methods unfortunately do not support the recovery of recyclables in filter ash, but a combined method comprising the mobilization of recyclables, the inerting of pollutants, and the destruction of organic substances opens up promising ecological and economic perspectives. The option of recovering heavy metals from electrostatic precipitator ash and also thermally destroying organic compounds was investigated for the first time in the '3R' process (Vehlow *et al.* 1990) and was implemented on a pilot scale. Selective and efficient recovery of specific heavy metals from ash extract has, however, proved to be impossible or can only be achieved with very high investment in equipment and control facilities. Ash treatment in the form of 'acidic scrubbing' with addition of the extracted filter ash to the bottom ash is already practised on an industrial scale in several plants that combust household waste in Switzerland (Figure 1, process step 1).

At the Technical University of Munich, methods for separating heavy metals from waste water and process solutions using highly selective complexants have been developed on a laboratory and pilot scale (Nitsch *et al.* 1992, 1997, Schus-

ter *et al.* 1997, Rether & Schuster 2003). A new method that can be implemented on an industrial scale was developed on the basis of university research and industry experience. This method is described below. The goal of this method is to remove heavy metals from filter ash by extraction using the acidic scrubber water from the flue-gas scrubbing process and to recover the zinc contained in high concentrations in the extract by means of selective reactive extraction (SRE). The reactive extraction process is characterized by the fact that selective transfer of zinc ions takes place from the aqueous ash extraction phase into a non-water-soluble complexant phase. This phase is regenerated with diluted sulphuric acid, the zinc present is concentrated in a high-purity solution, and afterwards recovered by electrolysis.

The ash that has been largely stripped of its heavy metals is returned to the combustion process in order to destroy organic substances. The results of research carried out so far indicate that the bottom ash produced contains no higher levels of organic or inorganic substances of environmental relevance than is the case for conventional bottom ash.

Materials and methods

The method comprises three main process steps and Figure 1 shows an overview of the process. Step 1 has already been integrated on an industrial scale in nine Swiss thermal waste treat-

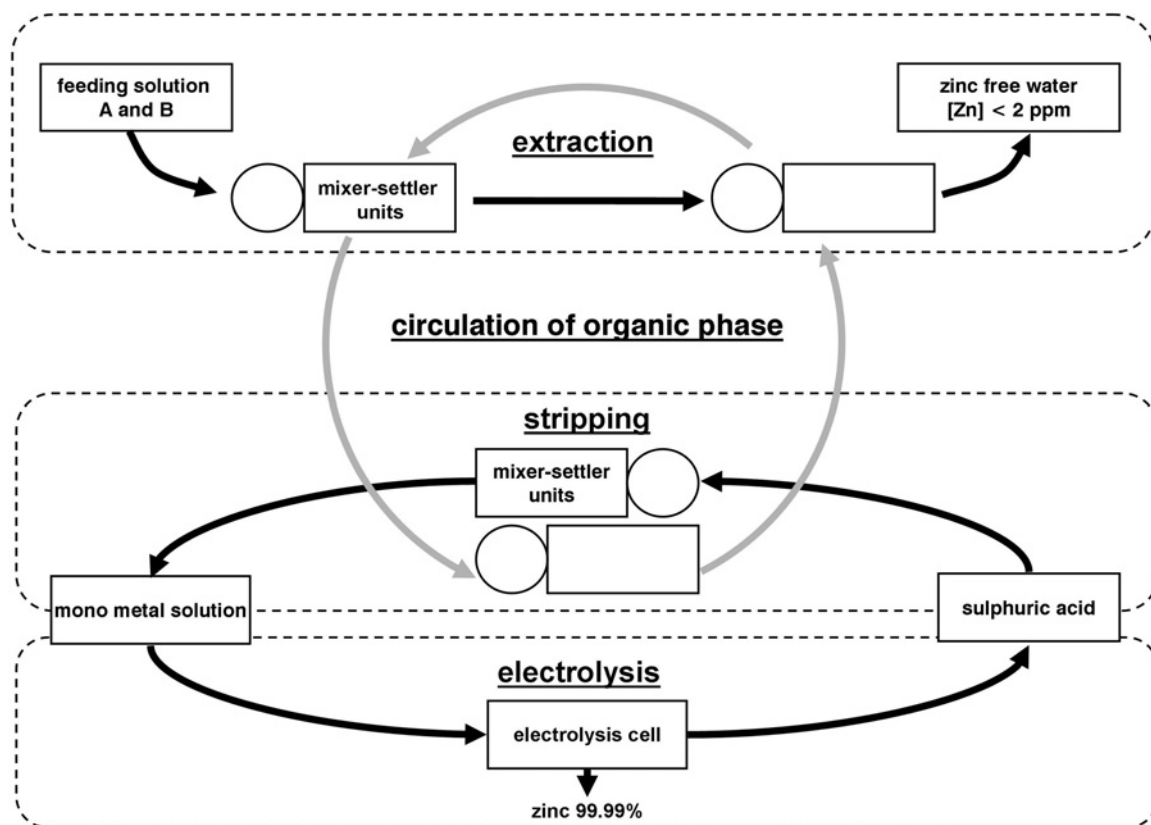


Fig. 2: Diagram of selective reactive extraction (SRE) and integrated zinc electrolysis.

ment plants. Steps 2 and 3 have been piloted on an industrial scale.

Process step 1 (acid extraction)

Filter ash resulting from the thermal treatment of household waste was extracted with a throughput of 3.5 t h^{-1} using the acidic and alkaline fluids produced by the wet flue-gas scrubbing process in a three-stage stirred tank cascade without the application of heat (liquid to solid wt. ratio, 3 : 1). The pH value was kept constant in the range 3.8 – 4.2 during extraction. Prior to ash extraction, mercury dissolved in the acidic scrubber water has to be separated (Braun *et al.* 1986) by means of a selective ion exchanger, using the Mercury-Ion 10 resin (BSH Umweltservice AG, Sursee, Switzerland). The mercury concentration of the acidic wash water was reduced from an initial 10 mg L^{-1} to $< 15 \text{ } \mu\text{g L}^{-1}$ as a result. The completely loaded resin is then sent to the resin supplier for recovery. After 60 min of residence time in the extraction cascade, solids and liquids were separated by means of vacuum belt filtration into a compact, low-metal ash fraction and a metalliferous filtrate (ash extract). Air was added to the metalliferous filtrate to oxidize dissolved iron (II) into its trivalent form. The iron was precipitated as hydroxide in the weakly acidic pH range (3.5–4.5) and separated by means of

candle filtration. For pilot steps 2 and 3, the filtration water and the extracted ash cake were taken directly from the industrial process of the Swiss plant for combusting household waste and further treated at the research site.

Process step 2 (selective zinc reactive extraction and zinc electrolysis)

Zinc was separated from the filtrate discharge of the vacuum belt filter (ash extract) by means of selective reactive extraction (SRE). The aqueous phase containing heavy metals with a flow of 150 L h^{-1} was brought into contact with an organic, non-water-soluble complexant phase in mixer-settler units. The dissolved metals were extracted depending on the pH value. The complexant used was bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA, Cytec Canada Inc.) dissolved in a Shellsol D 70 aliphatic solvent (Shell Chemicals). The BTMPPA concentration in the organic phase was 30% by weight. Zinc was extracted using two counter-current mixer-settler units MSU-40 (Metal Extracting AB, Aachen, Germany).

A pilot system based on the process diagram shown in Figure 2 was built for selective reactive extraction. Table 1 lists the operating parameters of the SRE pilot plant. The extraction and stripping unit residence time was 2 min per mixing chamber or 10 min per settler. Diluted sulphuric acid

Table 1: Operating parameters of the SRE pilot plant.

Flow rate aqueous filtrate	150 L h ⁻¹
Flow rate organic phase	75 L h ⁻¹
Flow rate stripping acid	7.5 L h ⁻¹
pH of extraction	2.5–3.0
Temperature	293 K

Table 2: Operating parameters of the zinc electrolysis pilot plant.

Cathodic surface	1753 cm ²
Current density	0.12 A cm ⁻²
Cell voltage	6.0 V
pH value	2.0
Current efficiency	94.8%
Energy consumption per kg of Zn	5.6 kWh kg ⁻¹
Temperature	318 K

($c_{\text{H}_2\text{SO}_4} = 2.5 \text{ mol L}^{-1}$) and a sulphuric zinc concentrate (mono metal solution) were obtained for stripping of the loaded organic phase.

No further precleaning took place before the zinc was separated electrolytically from the mono metal solution. Zinc was continuously separated and removed in batches as zinc foil on a rotating aluminium cathode. The stripped electrolyte solution was returned to the stripping process to be re-enriched with zinc. Noble metal coated titanium was used as the anode material. The operating parameters of the electrolytic cell are specified in Table 2. The gaseous by-products produced by electrolysis (H₂, O₂ and small traces of Cl₂) were drawn off and sent to the combustion plant's extraction system.

Process step 3 (recirculation)

In the third process step the filter ash cake stripped of heavy metals was returned to the combustion process to destroy organic substances (above all PCDD/F). In a programme of measurements lasting 2 weeks, comparative analyses between normal and test operation were carried out on a household waste combustion plant with a MARTIN[®] reverse-acting grate using 41 Mg of a mixture of wet, acid-scrubbed boiler ash and electrostatic precipitator ash (filter ash cake). In the test operation, a filter ash cake proportion of 4.4% by weight was recirculated as part of the hourly waste flow of 9.1 Mg h⁻¹. This corresponds to a continuous supply of approximately 400 kg h⁻¹ fed together with the waste to the combustion process. Mechanical compaction (pelletization) of the acid-scrubbed filter ash cake was not necessary. The treated ash was adequately compacted during several days of storage in the containers without any hydraulic binding. The filter ash cake poured well as a material and was tipped directly from

the containers into the refuse pit. The accumulated material under the bunker gates was then mixed with the waste by means of a crane grapple and some of the mixture was then stored temporarily in a small, previously emptied ancillary bunker. The waste grapple fed the treated ash to the chute with the household waste. Stable combustion and uniform distribution of the material on the grate were ensured by feeding filter ash cake 2 days before measurements were started with extracted filter ash recirculation.

Analytical methods

Aqua regia extraction of dry residues was performed in accordance with DIN 38 414 (Part 7) to determine the element content of the solid samples. Metal content was determined by means of mass spectrometry with inductively coupled plasma (ICP-MS) using an Elan 6000 mass spectrometer (Perkin Elmer GmbH, Überlingen, Germany). Mercury was determined after aqua regia digestion (DIN 38 414, Part 7) of dry residues by means of cold-steam atomic absorption spectrometry using an FIMS FIAS400 mercury analyser (Perkin Elmer GmbH). Chlorine, phosphorus, sulphur and silicon were measured by means of energy-dispersive X-ray fluorescence analysis (RFA) using an X-Lab 2000 X-ray fluorescence spectrometer (Spectro Analytical Instruments GmbH & Co. KG, Kleve, Germany).

Leaching tests were conducted in accordance with DIN 38 414, Part 4, DEV S4, by means of leaching in an end-over-end shaker (speed: 1 rpm). Once leaching was completed, the leachates were decanted and filtered under pressure using a glass-wadding prefilter and a 0.45 µm membrane filter.

Al, Ag, As, Ba, Ca, Cr, Co, Cu, Hg, Mg, Mn, Mo, Na, Ni, Sb, Se, Sr and Ti were determined in the ash leachates by means of mass spectrometry with inductively coupled plasma (ICP-MS) using an Elan 6000 mass spectrometer (Perkin Elmer GmbH). Ca, Fe and K were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-OES) using an axial ICP-OES Optima 3200 XL spectrometer (Perkin Elmer GmbH). Chloride, fluoride, nitrate, phosphate and sulphate were determined ion chromatographically using a DX-120 ion chromatograph (Dionex GmbH, Idstein, Germany).

Metal concentrations in the aqueous and organic phase were measured by means of ICP-OES (Plasma 400, Perkin Elmer GmbH). Metals complexed in the organic phase were first stripped with sulphuric acid and then analysed.

Results and discussion

Acidic filter ash leaching

The acidic filter ash extraction process strips almost all heavy metals from the filter ash. Table 3 illustrates the com-

Table 3: Solid and leachate analysis of filter ash and of the acid-extracted filter cake.

Element	Solids		Leachates		
	Filter ash (mg kg ⁻¹)	Filter cake (mg kg ⁻¹)	Filter ash (µg L ⁻¹)	Filter cake (µg L ⁻¹)	
Ag	52.9 ± 6.9	67.9 ± 13.8	14.0 ± 13.7	< 0.5	
As	59.0 ± 2.2	58.0 ± 9.2	< 20.0	< 20.0	
Ba	104.8 ± 5.1	69.6 ± 2.7	376.1 ± 69.8	202.9 ± 14.8	
Ca	125385.8 ± 126.5	140679.1 ± 4482.2	936825.3 ± 56101.9	688154.5 ± 33493.4	
Cd	379.4 ± 5.9	133.3 ± 9.7	25901.2 ± 3393.9	5.7 ± 3.5	
Co	41.1 ± 0.8	42.5 ± 2.3	< 1.0	< 1.0	
Cr	359.0 ± 24.6	461.9 ± 30.9	< 50.0	< 50.0	
Cu	2362.7 ± 365.1	2929.7 ± 411.9	48.7 ± 14.7	< 10.0	
Fe	23969.0 ± 875.5	28524.2 ± 1342.2	< 500.0	< 500.0	
Hg	1.0 ± 0.1	7.5 ± 0.9	< 80.0	< 80.0	
K	44658.7 ± 292.1	11352.2 ± 410.1	3766139.7 ± 13730.8	105532.0 ± 29568.0	
Mg	10678.5 ± 311.8	10538.4 ± 120.5	87599.4 ± 7026.7	810.9 ± 234.3	
Mn	624.3 ± 17.4	682.4 ± 16.1	3571.8 ± 459.2	< 10.0	
Na	32587.7 ± 808.5	7668.9 ± 917.0	3346338.2 ± 168381.2	240537.2 ± 99784.4	
Ni	202.7 ± 43.7	232.9 ± 10.8	< 20.0	< 20.0	
Pb	18853.7 ± 468.1	21974.4 ± 1868.8	5613.5 ± 794.1	34.3 ± 3.7	
Se	–	–	1208.0 ± 4.8	69.2 ± 8.7	
Si	53400.0 ± 4808.3	65066.7 ± 3594.9	–	–	
Sn	1352.3 ± 80.9	1682.3 ± 81.7	< 50.0	< 50.0	
Sr	272.8 ± 1.0	292.0 ± 9.0	3459.4 ± 126.2	1423.8 ± 36.6	
Ti	3248.4 ± 97.0	2957.4 ± 119.0	56.0 ± 0.4	< 50.0	
Zn	46381.9 ± 1931.8	22359.6 ± 1724.1	74822.6 ± 4006.7	154.6 ± 75.0	
Zr	7.9 ± 0.5	8.5 ± 0.8	< 5.0	< 5.0	
	Non-metals (mg kg ⁻¹)		Anions (mg L ⁻¹)		
F	–	–	F ⁻	< 14.0	< 14.0
Cl	109700.0 ± 2828.4	4534.0 ± 1633.8	Cl ⁻	6789.5 ± 328.8	474.3 ± 159.2
N	–	–	NO ₃ ⁻	< 19.0	< 19.0
P	1965.5 ± 354.3	1136.7 ± 359.9	PO ₄ ³⁻	< 15.0	< 15.0
S	54145.0 ± 1817.3	114700.0 ± 2227.1	SO ₄ ²⁻	3246.0 ± 41.0	1563.3 ± 179.7

Detection limits are given where measured values fall below these limits.

position of filter ash and of the extracted filter ash cake. A comparison of the leaching values before and after ash treatment shows that the toxicologically and environmentally relevant heavy metals Cd and Pb in the leachate of the filter ash cake could be significantly reduced by 99.98 and 99.34%, respectively. The leachates complied with the limit values of the TVA ordinance (Technical Ordinance on Waste, Switzerland), Appendix 1, Section 2. The heavy metals were separated from the filter ash in accordance with the TVA ordinance, article 38 c. Consequently, the filter ash cake may be disposed of together with bottom ash on reactor landfill sites in Switzerland.

Not only separation of the ecologically relevant heavy metals but also a good extraction yield is essential if zinc is to be recovered economically. Given the conditions described above, 80% of the zinc in the ash could be mobilized and recovered in a separate process.

Selective reactive extraction of zinc and zinc electrolysis

Different batches of ash extracts were used for zinc recovery. Table 4 shows the heavy metal content of the filtrates analysed. The widely varying composition of the ash extracts reflects fluctuations in the waste composition and therefore in the ash composition.

Table 4: Heavy metal contents of the ash extracts analysed.

Heavy metal	Concentration range (mg L ⁻¹)
Lead	60–100
Cadmium	120–180
Calcium	1500–4000
Iron	0.1–1
Copper	0.5–2
Zinc	4000–11 000

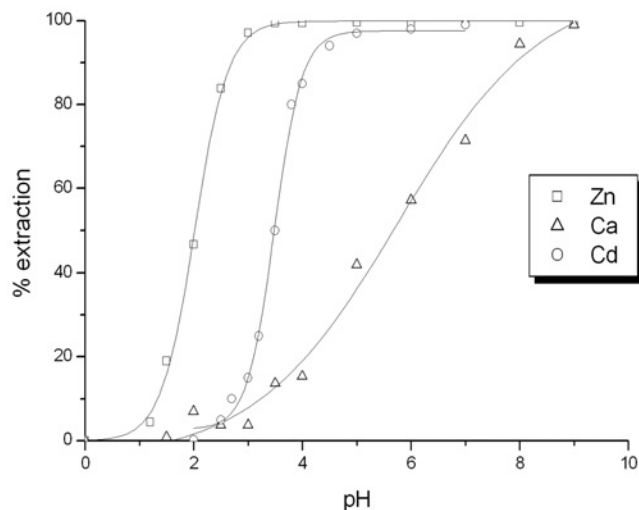
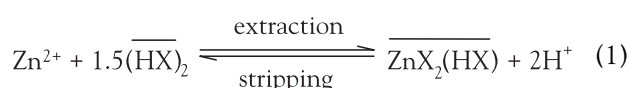


Fig. 3: Zn/Ca/Cd selectivity of the BTMPPA complexant as a function of pH value.

BTMPPA was identified as a very selective complexant for the extraction of zinc from chloride-containing acidic ash extracts. BTMPPA had already been successfully used for zinc calcium separation (Jha *et al.* 2005, Ali *et al.* 2006) and zinc cadmium separation (Cox *et al.* 2002, Qiong *et al.* 2002; Dakhil & Pincovski 2003). It is particularly sensitive to zinc as opposed to calcium and cadmium (Figure 3), thereby allowing efficient separation of the ash extract's main components, namely zinc and calcium. As hardly any cadmium is extracted under the given circumstances, the electrolytically separated zinc is minimally contaminated with cadmium and a marketable resource is produced. The chemical reaction that takes place during reactive extraction of zinc with BTMPPA (present here as dimer $(HX)_2$ (Paatero *et al.* 1990) is shown in equation (1). Horizontal bars indicate the organic phase.



Selective zinc recovery is subdivided into three steps.

Step 1: Solvent extraction in two counter-current mixer-settler units at constant pH value.

Table 5: Zinc extraction in the mixer-settler units (MS); filtrate volume flow 150 L h^{-1} , organic phase volume flow: 75 L h^{-1} .

Feed (mg L^{-1})	Discharge (mg L^{-1})	
	First mixer-settler	Second mixer-settler
Feed A MS	11 000	890
Feed B MS	4000	< 2
		< 0.1

Step 2: Stripping in two counter-current mixer-settler units.
Step 3: Electrolytic production of purest zinc from the mono metal solution of step 2.

Table 5 shows the zinc concentrations in the water-side feed and effluent of the extraction units. The feed concentration of the mixer-settler unit varied between 4 and 11 g L^{-1} (feed B, feed A) during pilot operation, depending on the varying zinc content of the filter ash and/or the incinerated waste. Extraction of zinc below the discharge limit concentration of 2 mg L^{-1} (Ministry of Environment 2004) was achieved by two counter-current mixer-settler units. In the water phase, an increase in TOC content by a mere 4 mg L^{-1} was determined after extraction. The complexant/organic phase losses in the solvent extraction process are consequently very low.

Two counter-current mixer-settler units with a phase ratio (A/O) of 10/1 were used to strip the loaded organic phase. Table 6 shows an overview of the metal contents in the mono metal solution and in the stripped organic phase. The values listed provide a general picture of the metal contents obtained during piloting. The chemical composition of the process solutions analysed was always within the specified concentration ranges.

Starting with a loaded organic phase with $10\text{--}18 \text{ g L}^{-1}$ zinc, it was possible to concentrate zinc to 190 g L^{-1} by means of stripping. This equates with a maximum 48-fold concentration as referred to the feed value of $4\text{--}11 \text{ g L}^{-1}$ zinc. Also of note is the outstanding selectivity vis-à-vis calcium that is present in the ash extract in a similar concentration to zinc. In the mono metal solution, the maximum calcium concentration was 150 mg L^{-1} . The specific selectivity for zinc in relation to calcium is therefore 1300 : 1. The cadmium concentration of the mono metal solutions obtained was always $< 1 \text{ mg L}^{-1}$.

Table 6: Metal contents of the loaded organic phase, the stripped organic phase and the re-extracted organic phase (mono metal solution).

	Loaded organic phase	Stripped organic phase	H_2SO_4 extract of organic phase
Cadmium (mg L^{-1})	0.05–0.1	< 1	< 1
Calcium (mg L^{-1})	10–25	1–10	40–150
Iron (mg L^{-1})	0.5–2	0.1–3	2–10
Lead (mg L^{-1})	0.5–1	0.05–0.1	< 1
Zinc (g L^{-1})	10–18	0.3–0.5	100–190

Table 7: Purity of zinc metal obtained by electrolysis.

Zinc (%)	> 99.99
Aluminium (ppm)	< 5
Cadmium (ppm)	84
Copper (ppm)	< 3
Iron (ppm)	6
Lead (ppm)	< 3
Magnesium (ppm)	4

In the third step, the zinc is electrolytically separated from the previously produced mono metal solution. In combination with the SRE process, a zinc recovery rate of 99.8% could be achieved from the acidic ash extracts. Continuous production of a homogenous zinc foil was made possible by using a rotating aluminium cathode. This ensures almost fully automatic operation of the electrolysis unit. The purity of the recovered zinc was > 99.99% (Table 7), meaning that it can be used directly in electro-plating shops or hot-dip galvanizing plants (Marti 2002). The gaseous by-products produced by electrolysis (H_2 , O_2 and traces of Cl_2) do not constitute a safety risk, as chlorine was removed in the form of a hypochlorite solution with an alkaline scrubber and the remaining exhaust air was supplied to the combustion plant's extraction system.

In a thermal waste treatment plant with a waste throughput of 100 000 t year⁻¹, approximately 60 t zinc can be recovered annually and returned to the recovered substance cycle. Given the increasing demand for valuable metals, processes for recovering these secondary raw materials will become more and more important in the future and will, in addition to having positive ecological benefits, contribute to the increased efficiency of waste treatment plants.

Ash recirculation

The filter ash cake fed back to combustion still contained approximately 30% residual moisture. The residual moisture had a positive effect in that no dust was thrown up when tipping or mixing the fuel in the refuse pit. Co-combustion of the wet filter ash cake resulted in an insignificant reduction in the heating value of the waste. There is no negative impact on the combustion process because of the low proportion of filter ash cake. The ash recirculation process used functioned smoothly and can be implemented in all waste-to-energy plants given appropriate bunker management.

When key process measurements were compared, no significant differences were found between normal and test operation. In summary, the quality of the un-aged bottom ash and of the boiler ash/electrostatic precipitator ash may be regarded as equivalent in terms of composition of solids and leaching properties, taking waste-input-related and process-

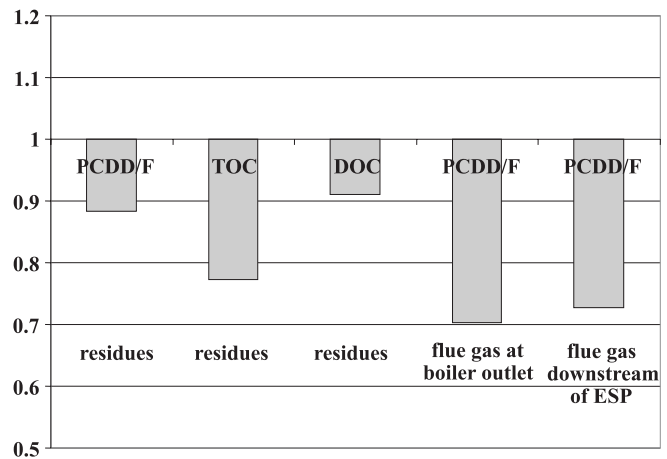


Fig. 4: Comparison of the PCDD/F / TOC / DOC contents in the residues and the PCDD/F contents in the flue gas for test operation as compared to normal operation.

specific fluctuations during test operation into consideration. No significant change in the residue flows was detected during test operation. In addition, the screening curves behaved almost identically in both normal and test operation, indicating that the fine-grain material introduced as a result of returning the filter ash cake to the combustion process did not cause the proportion of fine grain in the bottom ash to increase. The continuously recorded flue gas parameters also remained at the same level or lay within the process-specific fluctuation ranges. The key parameters used to evaluate the destruction of organic components with ash recirculation are the PCDD/F content in the residues and flue gas, the total organic carbon content in solids, and the dissolved organic carbon content in the leachates of the residues. Figure 4 shows these parameters for test operation as compared to normal operation. Within waste-input-related and process-specific fluctuation margins, a slight decrease in organic substances was detected in test operation. This documents the fact that the re-circulated organic substances were reliably destroyed.

PCDD/Fs are lipophilic by nature and are therefore not extracted when leached in acidic scrubber water (polar solvent). Instead, they remain in the filter ash cake. Measurements confirmed that even the mother filtrate used to recover zinc had only a PCDD/F content of 0.3 pg I-TEQ L⁻¹.

Feasibility study

The industrial feasibility and efficiency of the process presented here are linked to three fundamental conditions.

- The combustion plant must have a wet flue gas cleaning system.
- Certain limit values must be complied with if salts from waste water treatment are to be introduced to watercourses.

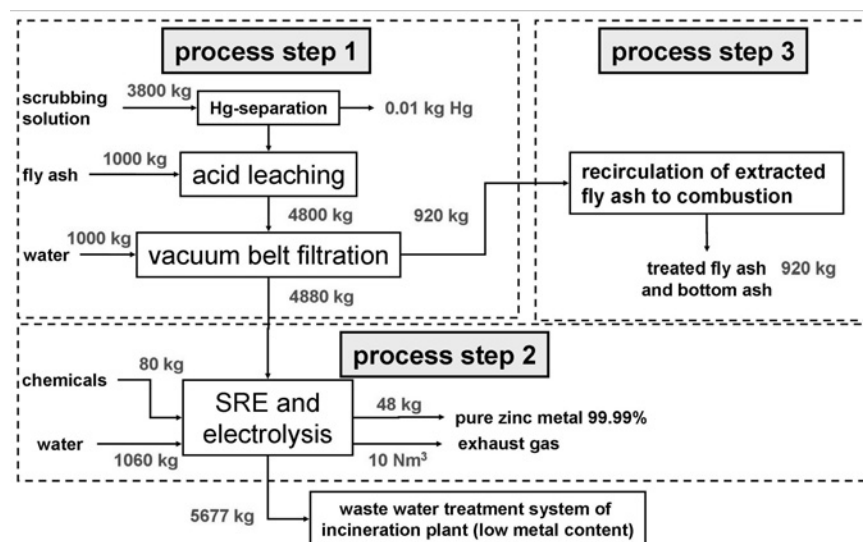


Fig. 5: Mass balance calculated for the zinc recovery process, based on 1000 kg of filter ash/50 000 kg of treated waste.

Table 8: Profitability calculation for a waste treatment plant (waste throughput: 100 000 Mg year⁻¹; 60 g zinc kg⁻¹ filter ash; annual amount of filter ash: 2000 Mg) with zinc recovery and inerting of residues.

Investment costs	3 000 000 €
Cost of utilities (chemicals, energy, etc.)	45 000 €
Personnel costs	50 000 €
Returns:	
Savings related to filter ash	330 000 €
Sale of zinc	245 000 €
Savings related to hydroxide sludge	37 000 €
Annual profit	517 000 €
Amortization	5.8 years

- Proof of compliance with leachate limit values must be provided before extracted filter ash is recycled together with bottom ash.

If these conditions are met, as is the case in Switzerland, the process can easily be implemented on an industrial scale.

Figure 5 shows the mass balance based on 1000 kg of filter ash/50 000 kg of waste for the total zinc recovery process and the subsequent thermal destruction of the organic substances.

Using a Swiss waste-to-energy plant (waste input 100 000 Mg year⁻¹) as the basis for examining the economic aspects of the process, it can be seen that reduction of the amount of residues to be disposed of, a costly matter, contributes to efficiency (Table 8). After treatment as described here, the filter ash is subject to in-process recycling with the bottom ash.

60% of the total return is obtained in this way. Sale of the zinc produced contributes to 35% of the return (sales price: 2500 € Mg⁻¹). The zinc price is linked to the market trend on the London Metal Exchange and shows a clear price increase in recent years due to the increasing demand for valuable metals, above all in the up-and-coming Eastern and Asian economies (Figure 6). A clear drop in the zinc price due to limited reserves of raw materials is consequently not to be expected and will not affect the efficiency of this process.

Conclusions

With the method described here and assuming a typical filter ash zinc content of 60 mg kg⁻¹, 48 kg of zinc can be recovered from each tonne of filter ash and returned to the recovered substance cycle. Re-circulating ash to the furnace resulted in the complete destruction of organic substances and, within waste-input-related and process-specific fluctuation margins, had no significant impact on the operating parameters of the household waste combustion plant or on residue quality.

The profitability of the overall process is attributable to the recovery of high-purity zinc and to the cost savings in the treatment of waste water and in the disposal of the residues produced because the remaining mixture of filter ash and bottom ash can be reused jointly. The investment and operating costs for the method described here can be recouped within a few years through the savings made in the waste water segment.

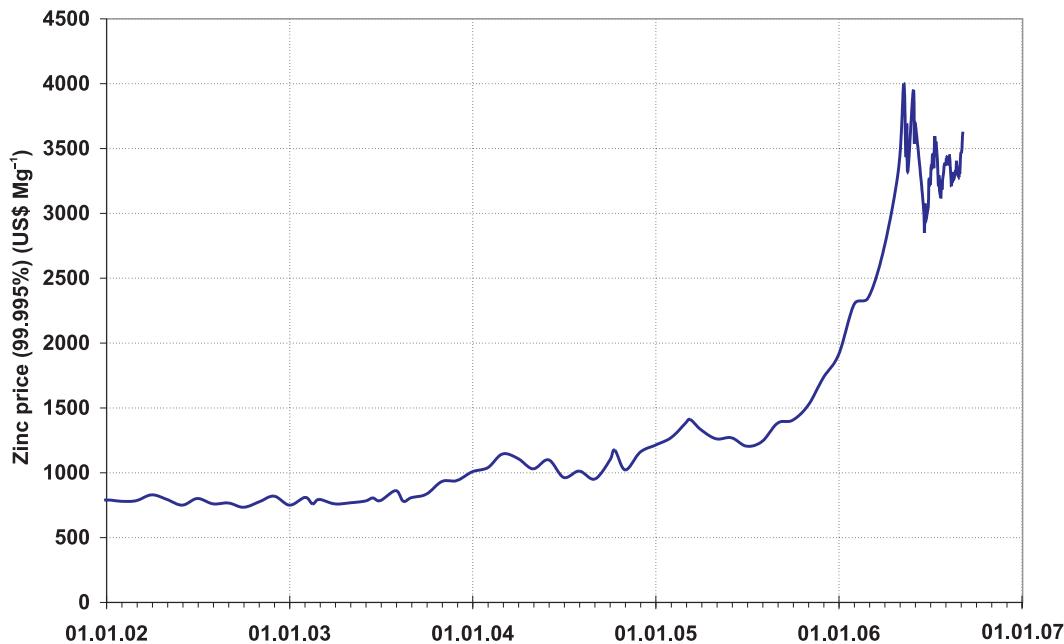


Fig. 6: Price development of special high grade zinc (99.995%), based on London Metal Exchange values.

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References

- Ali, A.M., Ahmad, I.M. & Daoud, J.A. (2006) Cyanex 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit. *Separation and Purification Technology*, **47**, 135–140.
- Braun, H., Metzger, H., & Vogg, H. (1986) Zur Problematik der Quecksilberabscheidung aus Rauchgasen von Müllverbrennungsanlagen (On the problems of mercury separation from flue gases of municipal solid waste incinerators). *Müll & Abfall*, **18**, 89–95.
- Cheng, K.Y. & Bishop, P.L. (1992) Sorption, important in stabilized/solidified waste forms. *Hazardous Wastes & Hazardous Materials*, **9**, 289–296.
- Cox, M., Flett, D.S., & Gotfryd, L. (2002) The extraction of copper, zinc, cadmium and lead from waste streams in the zinc-lead industry. In: Proc. of the International Solvent Extraction Conference, Cape Town, pp. 879–883. South African Institute of Mining and Metallurgy, South Africa.
- Dakhil, R.M. & Pincovschi, E. (2003) Equilibrium solvent extraction of zinc, copper and cadmium. *Science and Technology of Environmental Protection*, **10**, 97–105.
- Derie, R. (1996) A new way to stabilize filter ash from municipal incinerators. *Waste Management (Oxford)*, **16**, 711.
- Jha, M.K., Kumar, V., Maharaj, L., & Singh, R.J. (2005) Extraction and separation of Zn and Ca from solution using thiophosphinic extractant. *Journal of Metallurgy and Materials Science*, **47**, 71–83.
- Mangialardi, T. (2001) Sintering of MSW fly ash for reuse as a concrete aggregate. *Journal of Hazardous Materials*, **87**, 225–239.
- Marti, J. (2003): Cadmium in zinc. *Umweltmaterialien*, **168**, 1–22.
- Nitsch, W., Michel, T., Plucinski, P., Geist, A., & Daiminger, U. (1992) Heavy metal separation from waste waters by liquid-liquid extraction. In: Wilderer, P.A. & Potzel, J.U. (eds), pp. 225–232. Garching, Germany.
- Nitsch, W., Plucinski, K., Geist, A., Kremm, M., & Schöner, P. (1997) Process engineering of heavy metal extraction in hollow fiber modules. In Wilderer, P.A., Tartler, D.C., & Gilch, G. (eds), pp. 203–212. Garching, Germany.
- Oden, L. & O'Connor, W. (1994) *Vitrification of Residues (ash) from Municipal Waste Combustion Systems*. The American Society of Mechanical Engineers, New York.
- Paatero, E., Lantto, T., & Ernola, P. (1990) The effect of trioctylphosphine oxide on phase and extraction equilibria in systems containing bis(2,4,4-trimethylpentyl)phosphinic acid. *Solvent Extraction and Ion Exchange*, **8**, 371–388.
- Qiong, J., Dequian, L., & Chunji, N. (2002) Synergistic extraction of Zinc(II) by mixtures of primary Amine N193 and Cyanex 272. *Solvent Extraction and Ion Exchange*, **20**, 751–764.
- Rether, A. & Schuster, M. (2003) Selective separation and recovery of heavy metal ions using water-soluble *N*-benzoylthiourea modified PAMAM polymers. *Reactive & Functional Polymers*, **57**, 13–21.
- Schuster, M., Rether, A., & Vilsmeier, F. (1997) Selective separation and recovery of heavy metals from waste water by use of *N*-acylthiourea. In Wilderer, P.A., Tartler, D.C., & Gilch, G. (eds), pp. 243–254. Garching, Germany.
- Tadashi, I. (1996) Vitrification of fly ash by swirling-flow furnace. *Waste Management*, **16**, 453–460.
- Ministry of Environment (Umweltministerium) (2004) Ordinance about demands on the disposal of waste water into rivers and lakes, AbWV-German waste water ordinance June 17, 2004 BGBI. I Nr. 28 from June 22, 2004), appendix 33, washing of exhaust gases resulting from the combustion waste, as of June 22, 2004.
- Vehlow, J., Braun, H., Horch, K., Merz, A., Schneider, J., Stieglitz, L., & Vogg, H. (1990) Semi-technical demonstration of the 3R process. *Waste Management & Research*, **8**, 461–472.
- Wang, K., Chiang, K., Perng, J., & Sun, C. (1998) The characteristics study on sintering of municipal solid waste incinerator ashes. *Journal of Hazardous Materials*, **59**, 201–210.