

Urban mining: Metal recovery from fly and filter ash in Waste to Energy plants

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Abstract

About half of waste-to-energy (WTE) plants with wet flue gas cleaning process in Switzerland are using the FLUWA process to separate heavy metals from filter ash. The processed heavy-metal-free filter ash cake is recycled together with the bottom ash. The downstream FLUREC process extracts high-purity zinc from the heavy-metal-filtrate out of the FLUWA process - direct on site: The Swiss form of urban mining.

The FLUWA process uses the acid in the scrub water, mobilizes and extracts the heavy metals contained in the filter ash. At the same time, the excess acidic content of the scrub water is neutralized by the alkalinity of the filter ash. The downstream FLUREC process separates cadmium, lead and copper, and recovers zinc, a valuable metal that is present in high concentrations in the filter ash, as a high-purity metal (Zn > 99.99 %). Organic substances remaining in the low-metal content filter ash cake (especially dioxins) can be returned to the combustion process for thermal destruction.

Keywords: Filter ash extraction, zinc recovery, recycling, electrowinning, urban mining

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1. Introduction

Volatile heavy metals such as zinc, cadmium and lead and organic substances (polychlorinated dibenzo-p-dioxins and furans, PCDD/F) are enriched in the filter ash produced in the thermal treatment of municipal solid waste. Due to the high level of contamination with these organic and inorganic pollutants, filter ash must be landfilled under close regulation and at great cost, or must be hydrochemically processed.

These processes can be subdivided into a neutral and an acidic filter ash leaching process. The former permits only a reduction in the soluble chloride loads and therefore solidification with cement. Urban mining with neutral leaching is very limited therefore.

Acidic filter ash leaching (FLUWA process) permits the targeted separation and recovery of the heavy metals present as recyclables and primary enables the urban mining of filter ash. Using further process steps downstream, it is possible to win high-purity metals out of filter ash (FLUREC process).

Additionally, this process can be followed by thermal destruction of the remaining organic substances, PCDD/F in particular. This combination of processes to mobilize recyclables, render pollutants inert, and destroy organic substances opens up excellent ecological and economic perspectives.

The option of recovering heavy metals from filter ash and also thermally destroying organic compounds was investigated for the first time in the "3R" process [1], and was implemented on a pilot scale. However, selective and efficient recovery of specific heavy metals from the ash extract has 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 filter ash leaching (FLUWA process) with the addition of the extracted filter ash cake to the bottom ash is already practised in Switzerland on an industrial scale in several waste-to-energy (WTE) plants. It therefore represents the state of the art.

2. Acidic filter ash leaching

Filter ash produced in the thermal treatment of municipal solid waste poses a serious ecological problem due to the high heavy metal load and the associated PCDD/F burden in the ash. The FLUWA process for the sustainable treatment of the filter ash and acidic scrub water has been established by further developing and optimizing acidic filter ash leaching.

The filter ash is leached using both acidic and alkaline scrub water – the residues of wet flue gas cleaning – in a multistage extraction cascade without the application of heat. Prior to filter ash leaching, mercury dissolved in the acidic scrub water is separated by means of a selective ion exchanger [2]. By adding hydrogen peroxide to the filter ash leaching process, dissolved

iron (II) is converted into its trivalent form and precipitated. After sufficient residence time in the extraction cascade, solids and liquids are separated by means of vacuum belt filtration into a compact, low-metal filter ash cake and a metalliferous filtrate (Table 1).

Table 1
Typical chemical composition of the metalliferous filtrate

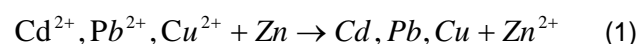
| Element | Unit | Concentration |
|-----------|------|---------------|
| Chloride | mg/L | 30000 – 70000 |
| Fluoride | mg/L | 200 – 600 |
| Sulphate | mg/L | 1000 – 5000 |
| Aluminium | mg/L | 100 – 800 |
| Lead | mg/L | 500 – 2000 |
| Cadmium | mg/L | 40 – 200 |
| Calcium | mg/L | 3000 – 12000 |
| Iron | mg/L | < 5 |
| Copper | mg/L | 20 – 300 |
| Magnesium | mg/L | 500 – 2000 |
| Nickel | mg/L | < 1 |
| Mercury | mg/L | 0.003 – 0.01 |
| Zinc | mg/L | 4000 – 12000 |

Due to the composition of the waste at Swiss WTE plants (that might be alike to the Scandinavian composition), the hydrochloric acid load in the scrub water at each plant is greater than the alkalinity of the filter ash. Up to present, excess acid is neutralized by adding lime slurry. The co-processing of additional filter ash for the stoichiometric management of residues offers not only economic benefits but also potential savings in neutralization chemicals and the possibility of recovering higher metal loads. The necessary individual process steps are described below with reference to industrial piloting trials conducted so far.

3. Process concepts for the recovery of heavy metals

3.1. Cementation

During cementation, cadmium, lead and copper are reductively separated from the metalliferous filtrate of the FLUWA process. For this purpose, zinc powder is added to the filtrate as a reducing agent. The reaction is as shown in equation (1).



Metals comparatively more noble than zinc are separated as a metallic cementate and filtered out. The reducing agent zinc dissolves. In this way, the heavy metals cadmium, copper and lead can be reduced to concentrations of less than 3 mg/L in the filtrate (Figure 1).

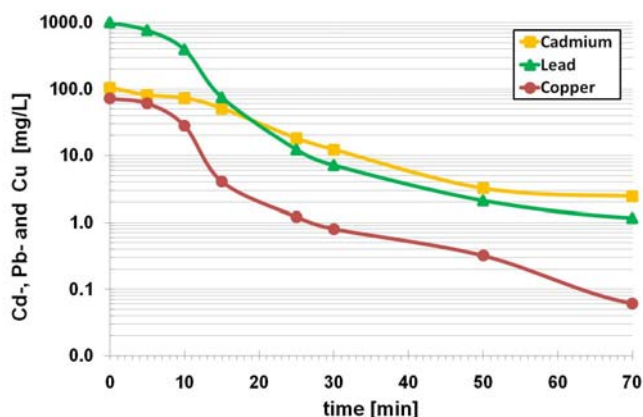


Figure 1: Course of cementation during separation of lead, cadmium and copper from the filtrate

The metallically stripped impurities are separated out as "cementate" in a filtration unit. The cementate has a dry matter content of > 60 %. Due to the high lead load of approx. 50 – 70 % by weight (Table 2), the cementate can be sent directly to a lead smelter for use there. The remaining heavy metals present are recovered in the lead production process at the smelter and are returned to the substance cycle.

Table 2
Chemical composition of the cementate

| Element | Unit | Concentration |
|---------|-------------|---------------|
| Lead | % by weight | 50 – 70 |
| Cadmium | % by weight | 5 – 15 |
| Copper | % by weight | 3 – 15 |
| Zinc | % by weight | 10 – 20 |

3.2. Solvent extraction

In solvent extraction (SX) the target metal zinc is separated selectively from the pre-cleaned filtrate, and is then cleaned and enriched. The solvent extraction process is characterized by the selective transfer of zinc ions from the aqueous filtrate phase into a non-water-soluble, organic extractant phase.

Solvent extraction can be subdivided into three individual steps (Figure 2):

1. Extraction
2. Scrubbing
3. Stripping

These steps are described in more detail below.

Mixer/settlers are used for solvent extraction. The two non-mixable liquid phases are mixed homogeneously in a mixing chamber to increase the mass transfer surface area. The two phases are then separated to recover the solvent phase in the settler unit. Optimal mixing conditions are critical for efficient mass transfer. Very small droplets have a very large specific mass transfer surface area but can result in stable emulsions that either take a long time to separate or cannot be separated at all. The goal of efficient metal extraction

can therefore only be achieved by optimizing the emulsion and coalescing processes.

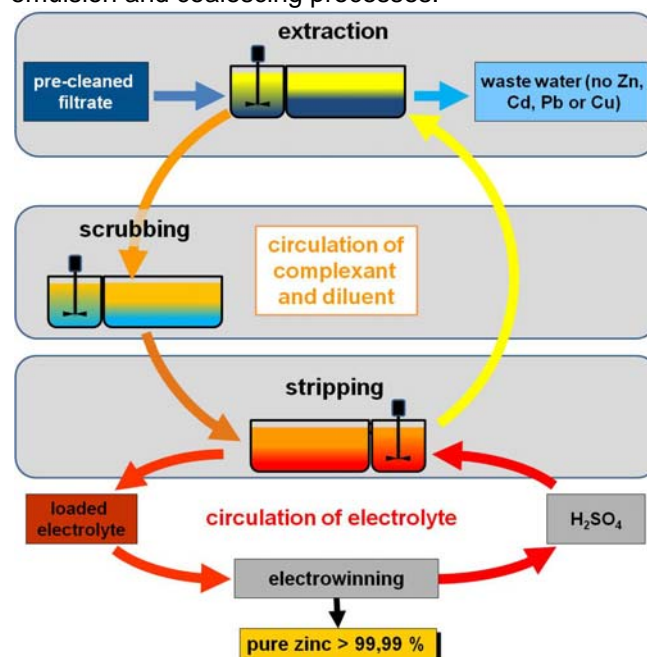
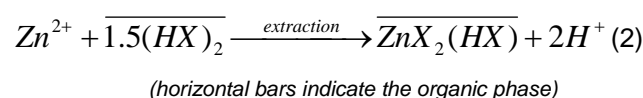


Figure 2: Schematic diagram of the solvent extraction and zinc electrowinning cycles

3.2.1. Extraction

In the extraction stage, heavy metals (e.g. zinc) are extracted from an aqueous solution and transferred to the organic phase using a selective extractant (HX). An aliphatic solvent with a high flash point (> 70°C) that does not mix with water is used to dissolve the extractant. The resulting reaction is illustrated by reference to an example of zinc extraction.



Complexation of the metals with the extractant HX depends primarily on the pH value of the filtrate. By a suitable choice of pH value, the target metal zinc can be selectively separated from the remaining metals, from calcium in particular (Figure 3).

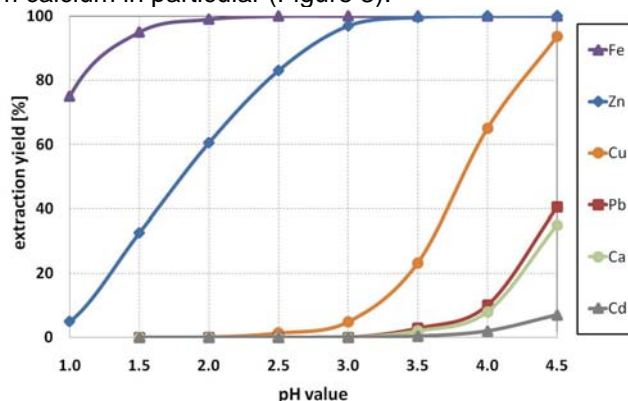


Figure 3: pH dependence and extraction yields of solvent extraction for selected metals in the form M²⁺

In accordance with reaction equation (2), two mole protons (H^+) are released for each mole of extracted metal M^{2+} . The associated pH reduction must be compensated by adding diluted sodium hydroxide as this is the only way of achieving a sufficiently high extraction yield with a small number of separation stages. Under the conditions described, almost quantitative separation of zinc can be achieved from the pre-cleaned filtrate at a pH value between 2.7 – 3.0 in a two-stage extraction cascade with an extraction yield of greater than 99.5 %. The remaining waste water has a zinc content of less than 25 mg/L. In addition to zinc, of the original heavy metal fractions only traces of cadmium, copper and lead (< 3 mg/L) are present and these give rise to no appreciable heavy metal hydroxide sludge in waste water treatment. The hydroxide sludge produced during waste water treatment is reduced by 80 - 90 % as compared to the normal load. As a result of the very low water solubility of the organic diluent and extractant, no appreciable organic content is discharged via this waste water material flow. However, for safety reasons, an activated carbon filter is integrated upstream of the waste water treatment facility in order to reduce the total organic carbon concentration (TOC).

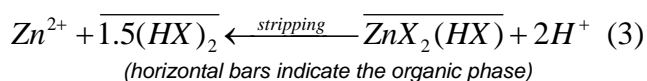
3.2.2. Scrubbing stage

Due to the use of dispersive solvent extraction, some very fine droplets of the dispersed phase are always discharged with the continuous phase. In addition to the chemically co-extracted heavy metals, these droplets constitute the main impurities of the organic phase.

In the scrubbing stage, these impurities are separated from the loaded organic phase by means of suitable scrubbing steps. Consequently, the number of complications that can occur in the subsequent electrolytic zinc recovery process as a result of impurities can be reduced.

3.2.3. Stripping

Enrichment of the zinc concentration as well as the necessary regeneration of the extractant are achieved in the stripping stage, the latter so that the extractant can be used in a new load cycle. The scrubbed, zinc-loaded organic phase is regenerated using diluted sulphuric acid. This is done by reversing equation (2) and adding acid. This shifts the reaction balance in favour of the free zinc cation Zn^{2+} and the regenerated extractant HX.



Enrichment takes place in the stripping process by selecting suitable phase ratios between organic phase and aqueous acid phase. This enables zinc to be enriched up to concentrations of greater than 200 g/L.

The high-purity zinc sulphate solution obtained in this way (also referred to as loaded electrolyte below) acts as the source solution for subsequent electrochemical zinc recovery (Table 3).

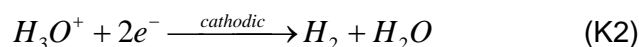
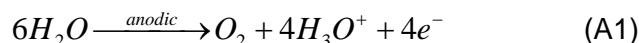
Table 3
Chemical composition of the electrolyte solution

| Element | Unit | Concentration |
|----------------|------|-----------------|
| Chloride | mg/L | 30 – 100 |
| Fluoride | mg/L | < 5 |
| Free H_2SO_4 | mg/L | 20000 – 150000 |
| Lead | mg/L | < 1 |
| Cadmium | mg/L | < 1 |
| Copper | mg/L | < 1 |
| Zinc | mg/L | 100000 – 200000 |

3.3. Zinc electrowinning

3.3.1. General

By applying an electrical DC voltage, zinc can be separated from the loaded electrolyte and deposited electrochemically on an aluminium cathode. Zinc reduction takes place in a continuous process at the cathode in the electrolyte (K1). The anodic counter-reaction is the formation of oxygen (A1) at the noble metal coated titan anode. Given the standard potential of zinc (-0.763 V referred to a normal hydrogen electrode NHE), removal should not be possible from a thermodynamic perspective because zinc is less noble than hydrogen (0 V vs. NHE). That removal is nevertheless possible is due to the hydrogen overvoltage in zinc electrowinning. The more negative the standard potential of the metal, the greater is the hydrogen evolution (K2) during metal stripping from aqueous acid solutions and therefore the smaller is the current yield for metal recovery.



Anode and cathode reactions in zinc electrowinning from acidic solutions

Because the zinc concentration depletes continuously as a result of electrowinning, new loaded electrolyte from the stripping stage of solvent extraction must be added continuously. The acid required for stripping is recovered to a very large extent by the anode reaction (A1). As a result of the hydrogen overvoltage, a small amount of the available acid (< 5 %) is lost in zinc electrowinning due to hydrogen evolution. This loss is compensated by the conductivity-controlled addition of fresh sulphuric acid.

3.3.2. Electrowinning systems

An important aspect when choosing a suitable electrowinning system for the industrial recovery of zinc in WTE plants is the planned annual amount of zinc. A basic distinction can be made between continuous and discontinuous electrowinning systems. In smaller operations with less than 100 t/a of zinc metal, it is advantageous to use continuous electrowinning systems. If the annual amount of zinc exceeds 100 tonnes, it is essential to use conventional discontinuous systems. In both cases, pure aluminium is used as the cathode material. Zinc is removed electrochemically at the cathode and can be separated with little effort as compact metal foil.

3.3.2.1. Continuous electrowinning system:

The almost fully in electrolyte immersed aluminium cathode is in the form of a slowly rotating hollow drum. This drum deposits the zinc metal onto the aluminium surface. A scraper is affixed on the non-immersed drum area. This exerts pressure against the direction of rotation of the cathode and continuously separates the deposited zinc foil from the cathode (Figure 4). The zinc foil can be rolled or cut for further processing.

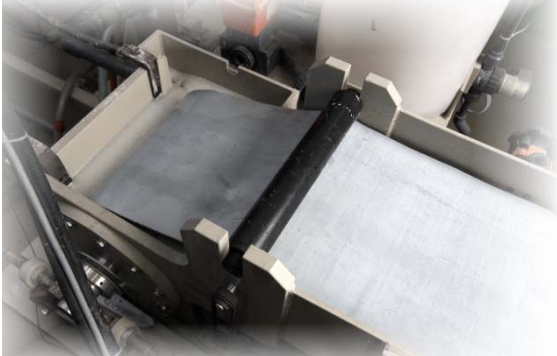


Figure 4: Continuous zinc foil production with rotating aluminium cathode

3.3.2.2. Discontinuous electrowinning system:

Plate electrowinning cells are used on an industrial scale as discontinuous systems in primary zinc recovery. Here, aluminium plates immersed in the electrolytes act as cathodes (Figure 5).



Figure 5: Zinc plate electrowinning, harvesting zinc from cathode

In this case, the zinc metal is harvested using an automated process in which the cathodes are raised from the cell and the zinc is stripped at a stripping station (Figure 6).

The individual zinc-loaded cathodes are handled by a robot. The stripping operation is carried out by mechanical scrapers in a two-part vertical stripping process. The removed zinc plates are automatically palletized and sent to zinc-processing companies.

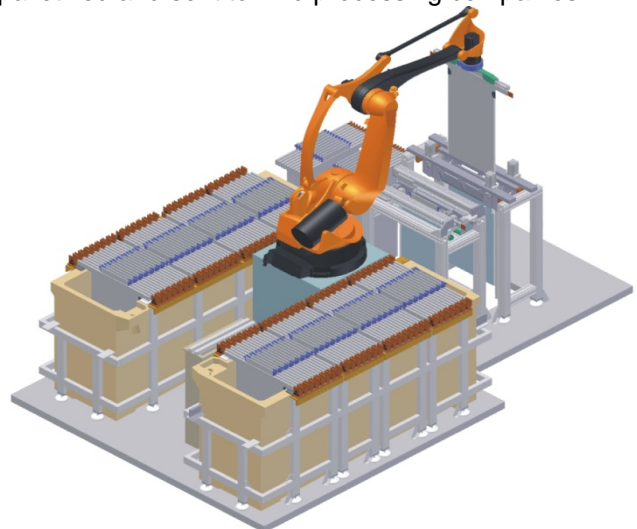


Figure 6: Zinc electrowinning with robot and automatic stripping system

3.3.3. Characteristics of zinc electrowinning

Due to the fact, that installations in WTE plants normally more than 100 tonnes per year zinc could be produced, the discontinuous electrowinning system is more relevant. The needed specific energy of approximately 2.9 – 3.5 kWh/t of zinc is generally produced on site by the waste to energy plants itself. In plate electrowinning systems, the maximum current density for trouble-free operation is 600 A/m². The longer separation cycles of 24 - 48 hours support operation at lower current densities. As the cathodic area is much easier to extend in plate electrowinning systems by adding further cathode plates, it is normal practice to use lower current densities and larger cathodic areas.

The upstream scrubbing processes of cementation and solvent extraction ensure that high-purity zinc is separated from the electrolyte solution. The achieved purity of 99.995 % is equal to that of *special high grade* (SHG) zinc. Direct use in hot-dip galvanizing and electroplating plants is therefore possible.

Table 4
Key zinc electrowinning data for the rotating electrowinning system (A) and for plate electrowinning (B)

| Element | Unit | System A | System B |
|--------------------------|------------------|-----------|-----------|
| Current density | A/m ² | 1500 | 600 |
| Cell voltage | V | 4.0 – 5.0 | 3.4 – 3.9 |
| Temperature | °C | 30 – 40 | 30 – 40 |
| Current yield | % | 92 – 95 | 90 – 95 |
| Spec. energy consumption | kWh/t zinc | 3.5 – 4.8 | 2.9 – 3.5 |

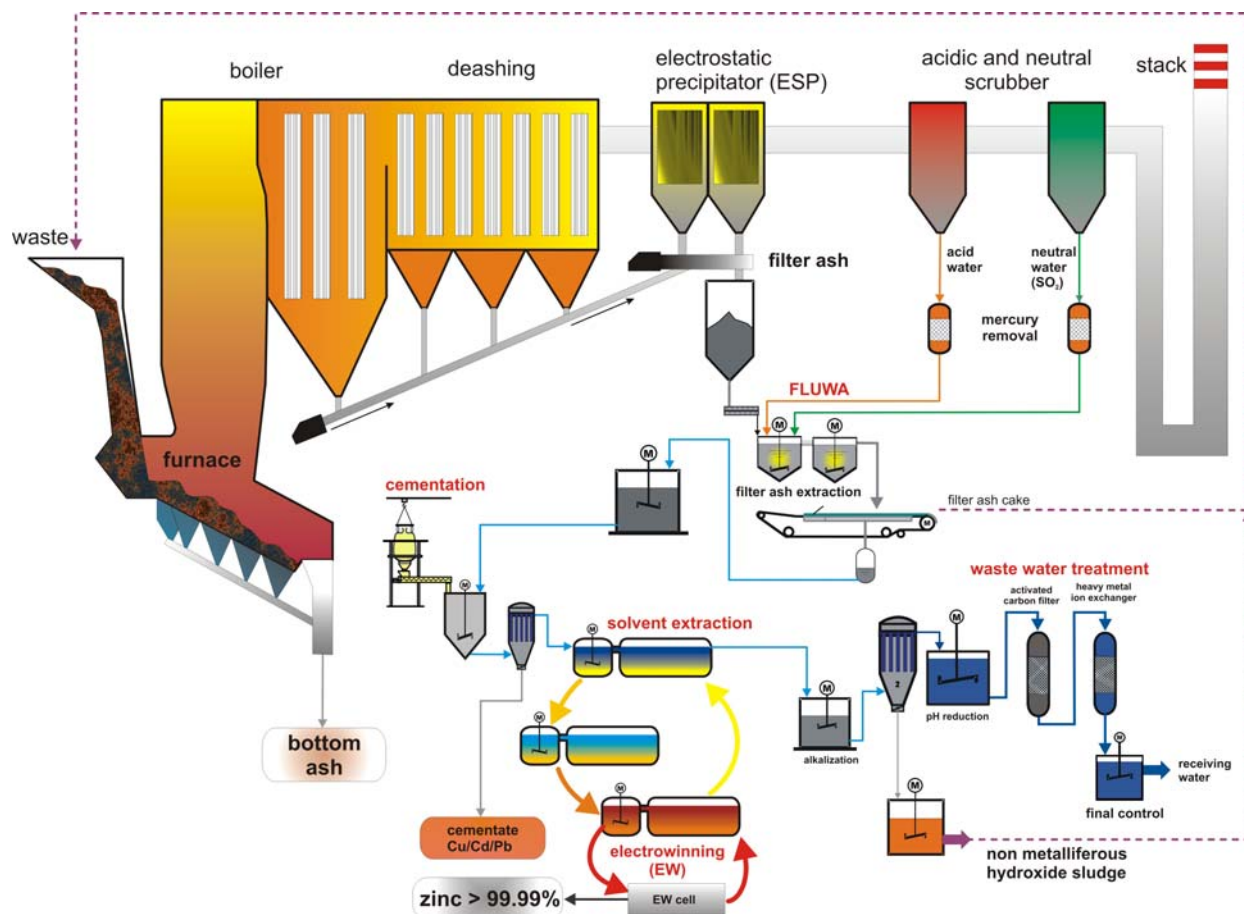


Figure 7: Process diagram for waste incineration with sustainable residues management and recovery of recyclable materials (FLUREC)

4. Ecological and economic sustainability

The process described here combines the benefits of recyclables recovery from secondary raw materials such as purest zinc, lead, cadmium and copper cementate with the sustainable inerting of the remaining filter ash cake (FLUREC process, Figure 7).

Due to the recovery of metals, this process gives rise to a significant reduction of residues in thermal waste treatment plants. In addition, it is now possible to close the substance cycles for secondary raw materials and to implement recycling of the recovered metals locally on WTE sites where the necessary energy also is produced. This supports ecologically sustainable recycling as an alternative to landfilling.

Figure 8: Diagram of the recovered substance cycle for zinc: the conventional acidic FLUWA process with hydroxide sludge and the new materials recycling process (FLUREC)

The treatment of waste water that is free of heavy metals produces no appreciable amount of hydroxide sludge that would otherwise have to be landfilled at great cost or processed expensive. Due to its low metal load, a residual alkaline earth metal sludge consisting mainly of gypsum (gypsum slurry) can be added to the bottom ash via the combustion process. The chemical composition of the slurry is largely identical to the residual metal sludge described here. In addition to separation of the heavy metal loads, the organic substances are thermally destroyed by returning the acid-leached filter ash cake to the combustion process. The filter ash cake is no longer produced as an individual residue but is recycled together with the bottom ash. As a result, the organic load can also be described as similar to the bottom ash along with the inorganic residue of the acid-leached filter ash cake.

Due to the combination of process steps described here, no additional residue is produced when the residues of flue gas cleaning products are treated.

The only remaining residue is the bottom ash whose quality is not impacted by the technologies described here.

This combination of processes is also very interesting from an economic point of view. In addition to the benefits of marketing the recovered metal fractions, there are no disposal costs for the hydroxide metal sludge that would otherwise be produced (Figure 8).

The option of co-processing external ash gives WTE plant operators the opportunity to save on neutralization chemicals and fully exploit the raw-material potential of the heavy metal fractions.

5. Outlook

The process steps described here have proven their value in long-term piloting projects at various industrial sites. Heavy metal recovery will be implemented on a large scale (FLUREC) during process technology replacement at the Zuchwil WTE plant in Switzerland and will go into operation in 2012. It is planned to recover approx. 350 tonnes of zinc per annum.

Figure 9: FLUWA and FLUREC technology enables Urban mining and closes substance cycle.

- [1] Vehlow, J., Braun, H., Horch, K., Merz, A., Schneider, J., Stieglitz, L., Vogg, H., Waste Management & Research, 8, 461-472, 1990.
- [2] Braun, H., Metzger, H., Vogg, H. Müll & Abfall, 18, 89 – 95, 1986.