Metals in MSWI ash –problems or opportunities?

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Abstract
Incineration of municipal solid waste (MSW) is a commonly used management method to take care of our waste. The solid residues i.e. the ash often contain significant amounts of metals and therefore these ashes represent a possible metal source. Recovery of metals from waste combustion residues would thus give an opportunity to turn a waste into a valuable resource.

In this paper a method to recover Cu from MSW incineration fly ash developed and tested in laboratory scale is shortly discussed. The leaching of metal compounds from the ash is a very important step in the recovery process and in some cases more or less all Cu was leached from the ash. The results obtained showed that about 90% of the Cu in the ash leachates could be selectively recovered using solvent extraction.

In addition, the potential of recovering other valuable metals from ash is discussed.

Keywords: MSWI ash, metals, leaching, extraction, recovery

Introduction and background

Approximately 4 700 000 tonnes, more than 500 kg/capita, of municipal solid waste (MSW) was generated in Sweden in 2008 [1]. This is an increase of more than 100 kg/capita since 1995 [2]. A similar increase in amounts of MSW has been observed in the countries included in EU-27: from 474kg/capita in 1995 to 517kg/capita in 2006 [2,3]. Somewhat older statistics for the USA show a similar development: an increase in MSW from 450kg/capita in 1960 to 760kg/capita in 1999 [4]. As the definition of MSW differs between countries, the numbers given here are not exactly comparable. The trend of increased waste production is evident, however.

While landfilling is the most commonly used management method, incineration is increasing both in Sweden and in other countries in Europe [1, 2]. This leads to the production of significant amounts of ashes which, in turn, must be handled in ways that ensure that there are no negative effects on the environment or human health. Today this mainly means landfilling in appropriate landfilling sites. However, as society strives towards more sustainable material cycles, a larger fraction of the materials currently classified as waste will be recycled in the near future. Since the ashes produced from waste incineration contain significant amounts of metal compounds they represent a possible source of metals. Recovery of metals from waste combustion residues would thus give an opportunity to turn a waste into a valuable resource.

While mechanical metal recovery only extracts metals in metallic form, wet chemical leaching offers an opportunity to recover not only pure metals but also metals present in various chemical compounds like oxides and chlorides. The principle is based on enhanced leaching to produce a metal rich leachate from which the metals can be recovered using e.g. solvent extraction and electrolysis (Figure 1). After characterization the solid residue could be used as e.g. construction material or landfilled. In this paper a method to recover Cu from MSW incineration fly ash developed and tested in laboratory scale is shortly discussed.

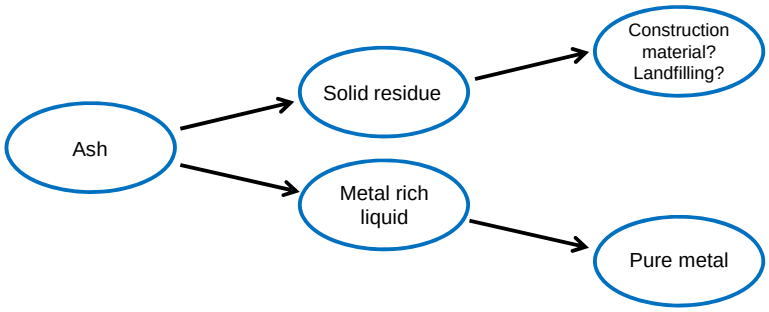

Figure 1. Principal for metal recovery from MSW incineration ash using wet chemical treatment.

Results and discussion

Sample characterization

This work included fly ash samples from fluidised bed combustion (FB) and grate fired (MB) combustion units mainly incinerating MSW. Details on the ash samples are given in Table 1.

Table 1. Details on the MSW incineration ash samples used in this work.

Ash	1	2	3	4	5
Boiler type	FB	FB	FB	MB	MB
Ash collection device	textile filter	textile filter	textile filter	textile filter	electric precipitator filter
Addition for flue gas treatment	CaO	$Ca(OH)_2$	$Ca(OH)_2$	$CaCO_3$	No addition

Taken from reference [5].

Maximized leaching

Several leaching media were tested to achieve high release of Cu from the studied ash samples (HNO_3, HCl, H_2SO_4, acidic process water, formic acid, acetic acid, lactic acid, oxalic acid, EDTA, NH_4Cl and NH_4NO_3). Mineral acids and complex forming agents gave the highest Cu leaching and release data for Cu using HNO3 or NH_4NO_3 as leaching media are shown in Table 2. Details about the leaching experiments and the release of other metals are given in references [5, 6].

Table 2. Amounts of Cu leached from ashes 1-5 using HNO_3 at initial pH=2.2 or 3M NH_4NO_3 after 24 hours of leaching. All results are given as % released of total amount in the dry ash.

Element	Ash 1	Ash 2	Ash 3	Ash 4	Ash 5
NHO_3	95	42	100	100	58
NH_4NO_3	98	73	100	81	57

Taken from reference [5].

Variations in Cu leaching efficiency between ash samples and leaching media are not directly correlated to the total amounts of Cu in each ash [5]. Instead factors like the speciation of Cu, the release of alkaline compounds and the particle size distribution are important. Thus, thorough investigations of different kinds of ashes are needed to find optimal leaching conditions in each specific case.

Extraction

Extraction experiments were done on both HNO_3 and NH_4NO_3 leachates using four chemically different and commercially available extraction reagents (LIX 54-100, LIX 84, LIX 860N-I and Cyanex 272). The most selective Cu extraction was reached using LIX 860N-I for extraction and 2M H_2SO_4 for stripping. About 90% or more of the Cu ions in the ash leachates were extracted using LIX 860N-I independently of initial Cu concentration (200 mg/L to 1500 mg/L) and leaching media used. The final Cu solutions were qualitatively analysed using ICP-MS (inductively coupled plasma mass spectrometry). Only trace amounts ($<10^{-6}$mmol/L; <1mg/L) of Zn^{2+} and Pb^{2+} (only in the cases when

acid leaching was applied) were found indicating that high purity Cu metal can be produced using electrolysis.

The overall recovery efficiencies (i.e. leaching and extraction) calculated based on the total Cu amounts in each ash sample varied between 40% and 90%, compared to about 90% recovery efficiency during the extraction, as discussed before. This shows that the leaching is the single most important step to reach an effective Cu recovery from ash. Details about the extraction experiments are given in references [5, 7].

Electrolysis

About 20% of the world's copper mine production is supplied using leaching and solvent extraction followed by electrowinning [8]. The last step, electrowinning, consumes a lot of energy and makes the process vulnerable to increased energy prices. Ash leachates typically contain lower Cu concentrations compared to ore leachates (0.2-1.5 g/L and 1-6 g/L, respectively) [5,9]. This makes electrolytic Cu recovery from ashes even more sensitive to energy prices than electrowinning from ore leachates.

Therefore the use of microbial bioelectrochemical system (BES) is a very interesting alternative. Recently Ter Heijne et al. reduced Cu at the cathode of a BES and suggested that this process could be used for recovery of Cu from e.g. mine wastewaters [10]. Our experiments done on simulated purified ash leachates containing 1 g/L Cu showed that a biological anode lowered the energy consumption required for Cu electrolysis from 1.46 to 0.23 kWh/kg Cu for a titanium cathode poised at -0.3 V [11]. When the cathode was operated at 0.1 V, electrical energy could be recovered from the system in combination with copper [11].

This far no tests on authentic ash leachates have been done but BES experiments on simulated ash leachates containing a mixture of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} (1g/L) show that Cu metal of high purity could be generated. This opens up for the opportunity to do electrowinning directly on unpurified ash leachate. This would reduce the need for the purification step using solvent extraction in addition to the decreased energy consumption. Further studies on real ash leachates are in progress and the results will soon be published in a scientific journal.

The potential

In the work by Karlsson et al. the suggested Cu recovery process i.e. leaching, solvent extraction and conventional electro winning was investigated and discussed to address the economic viability and environmental impact compared to current handling i.e. landfilling [12]. The results show that it is possible to achieve a profitable process but a crucial factor is that the recycling rate of the organic solvent is around 99% [12]. However, if taking into account that the method is not optimized and that there is a potential of recover further metals from the leachate the opportunities of making a profitable method is good.

Approximate calculations show that the potential Cu metal value in MSW incineration fly ash annually generated in Sweden is around 6 million Euros based on an average Cu content of 0.4 w% and 200 000 tonnes of fly ash. Other examples are the potential metal values for Zn (2.5 w%) and V (0.00 5w%) of about 8 million Euros/year and 3 million Euros/year. On a European level approximately 2 million tonnes of MSW incineration fly ash is generated each year giving corresponding potential metal values for Cu, Zn and V of 60 million Euros/year, 80 million Euros/year and 30 million Euros/year, respectively. If also taking sorted bottom ash into consideration the potential values will increase drastically. In addition to the potential metal values from the well-known metals like Cu, Zn, Al and Ti there are several other valuable and rare metals like In and Zr present in ash. These kinds of metals will most certainly become more important in the future with increasing metal prices as a consequence. Even though some of the potential metal values present in fly and bottom ash are already recovered today most part of it is literally buried into the ground.

CONCLUSIONS

- A method to recover Cu from MSW incineration fly ash based on leaching, extraction and electrolysis has been developed and tested in laboratory scale.

- Initial studies show that this recovery process could be profitable, both economically and environmentally, compared to land filling and the potential of improving the method is large.
- About 90% or more of all Cu in the ash leachates could be selectively recovered using solvent extraction.
- Effective leaching is a most important step in Cu recovery from ash and the Cu concentration in a specific leachate is not directly correlated to the total Cu amount present in the corresponding ash.
- The energy consumption during Cu electro winning can be reduced >80% using advanced electrolysis systems like BES.
- The metal contents in MSW incineration ash are relatively high and for several metals like Cu and Zn the amounts are comparable to those in ores.
- The potential metal value in MSW incineration ash generated in Europe is hundreds of million Euros each year.

REFERENCES

[1] W. Wiqvist, *Svensk Avfallshantering 2009 (Swedish Waste Treatment 2009)*, The Swedish Association of Waste Management, Malmö, Sweden, 2009

[2] Eurostat, *Key figures on Europe, 2009 edition*, Office for Official Publications of the European Communities, Luxembourg, 2009

[3] W. Kloek and K. Blumenthal, *Eurostat, Statistics in focus 30/2009, Generation and treatment of waste*, Eurostat, Luxembourg, ISSN 1977-0316, 2009

[4] N.P. Cheremisinoff, *Handbook of solid waste management and waste minimization technologies*, Elsevier Science, 2003

[5] K. Karlfeldt Fedje, *Metals in MSWI fly ash – problems or opportunities?,* PhD Thesis, Department of Chemical and Biological Engineering, Chalmers University of Technology. ISBN 978-91-7385-386-6, 2010.

[6] K. Karlfeldt Fedje, C. Ekberg, G. Skarnemark and B.-M. Steenari, *Removal of hazardous metals from MSW fly ash - An evaluation of ash leaching method,* Journal of Hazardous Materials, 2010, 310-317

[7] K. Karlfeldt Fedje, C. Ekberg, G. Skarnemark, I. Pires and B.-M. Steenari**,** *Initial studies of the recovery of Cu from MSWI fly ash leachates using solvent extraction*, accepted for publication in Waste Management and Research

[8] International Copper Study Group, *World Copper Fact Book,* International Copper Study Group, 2010

[9] J. Jenkins, P. Dodge, and A. Morenci*, Solvent extraction transfer of Cu from leach solution to electrolyte. Extractive metallurgy of copper*, 4th edition, 2002, 307-325

[10] A. Ter Heijne, F. Liu, R. Van Der Weijden, J. Weijma, C.J.N. Buisman and H.V.M. Hamelers, *Copper recovery combined with electricity production in a microbial fuel cell,* Environmental Science & Technology, 2010, 4376-4381

[11] O. Modin and K. Karlfeldt Fedje, *Combined wastewater treatment and recovery of copper from ash leachates,* Submitted to IWA World Water Congress, Busan, Korea, Sept 16-21, 2012

[12] S. Karlsson, P. Carlsson, D. Åberg, K. Karlfeldt Fedje, J. Krook and B.-M. Steenari, *What is required for the viability of metal recovery from municipal solid waste incineration fly ash? – Design and assessment of a process plant for copper extraction,* Presented at the conference Linnaeus ECO-TECH ´10, Kalmar, Sweden, November 22-24, 2010