



NATURAL RESOURCES

Sustainable Targets, Technologies, Lifestyles and Governance

Christian Ludwig | Cecilia Matasci | Xaver Edelmann | Editors
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43. Recovery of metals from waste, an example for the resource cycle

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Abstract

Bottom ash from municipal solid waste incineration (MSWI) consists of elemental metals in considerable amounts. The fine fraction < 4 mm additionally contains chemically bound metals (oxides, carbonates, silicates). Separation prospects with techniques as in ore processing (flotation, density separation, bioleaching, hydrothermal solution) are discussed. During alteration after wet extraction mineral material with hydraulic properties form coatings on almost all particles of the bottom ash and complicate separation procedures. In addition bottom ash from MSWI is a heterogeneous material. For sufficient enrichment different concerted treatment steps seemed to be essential associated with an uncertainty of economic viability. The utilisation of metal compounds present in bottom ash as secondary raw material depends on the energy- and resource-efficiency of the enrichment processes. Therefore energy and material flow considerations are presented.

Keywords: recyclable material, recycling technology, environmental technology, waste management.

Introduction

Municipal solid waste (MSW) consists of elemental metals in considerable amounts. After waste incineration these metals are contained in the solid residues of the process. The largest residual fraction is bottom ash which comprises approximately 25 % by weight (10 % by volume) of the total. Almost 10 % of the bottom ash consists of elemental metals which can be easily separated with magnets (scrap iron) and eddy current separators (non-ferrous metals, primarily aluminium, copper, brass, etc.). To increase the efficiency of these techniques and thereby the recovery rate in numerous treatment plants nowadays three or four sieve fractions are processed in parallel. However, the fraction of approximately < 4 mm is of minor interest and is normally deposited. This is due to the lack of recycling prospects but also since established techniques are not yet suitable for fine grain sizes. Despite this, the fine mineral fraction of the bottom ash contains heavy metal compounds in concentrations which are in some cases higher than those of the respective ores. Prior to recovery of the chemical bound metals a treatment for enrichment of these compounds has to be performed. Here the same processes as in mineral processing can be applied (flotation, density separation, bioleaching, hydrothermal solution).

The total amount of metals in the bottom ash is frequently evaluated and thereby well known. Several elemental contents are independent of the grain size. For other elements per smaller grain sizes the concentrations are increasing but enrichment factors achieved by sizing would not be sufficient for economic recovery. On the other hand the proportion of elemental, oxidised and otherwise bound metals along with their speciation is not well known so far. However selection of the treatment technique as well as the terms and conditions should be based on this knowledge.

This paper evaluates some opportunities and limits of metal recovery from waste. Energy and material flow considerations will also be discussed.

Composition of MSWI bottom ash

Bottom ash is the largest residual fraction in the process of municipal solid waste incineration (MSWI). It consists of 1.) solid phases already contained in MSW such as glass cullet, ceramics, cinder and metals (iron and non-ferrous metals) and 2.) new phases formed during the incineration process (Bayuseno and Schmahl, 2010). Since bottom ash amounts to 20-25 % by weight MSWI is a substance concentrating process with an enrichment factor of 4-5 with regard to the metals (Rechberger and Brunner, 2002). The 5 most common elements in MSWI bottom ash are Silicon, Calcium, Iron, Aluminium and Sodium. Si and Ca appear as oxides, Al and Fe in both their elemental form and as oxides and Na as chloride (Chandler et al., 1997). Scrap iron and non-ferrous scrap amounts to 9 % and 1 %, respectively (Zwahr, 2006). In contact with water bottom ash (usually bottom ash is extracted by wet ash discharge systems) exhibits alkaline pH values of 12 and above due to the formation of $\text{Ca}(\text{OH})_2$. Subsequent storage leads to carbonisation of the ash and lower pH values. These aging reactions are accompanied by hardening and hydraulic cementation reactions resulting in mineral attachments on elemental metals. Aluminium is partly oxidised under alkaline conditions forming $\text{Al}(\text{OH})_3$ and hydrogen. Copper is present in elemental form and as chemical compound. Different to zinc it shows a uniform grain size distribution as displayed in *Figure 1*. However, bottom ash is an extremely inhomogeneous material which makes general statements difficult.

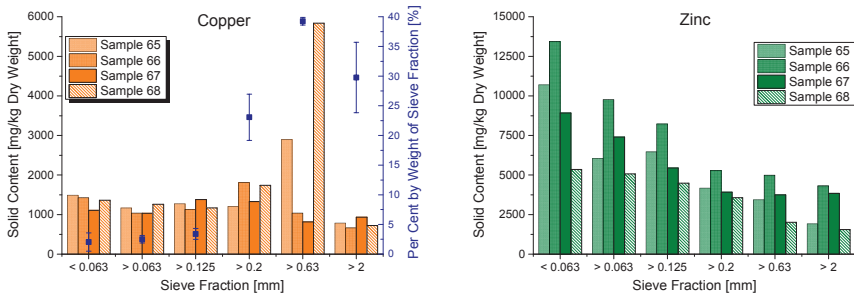


Figure 1. Grain size distribution of copper (left) and zinc in MSWI bottom ash. The mass fractions of the grain size distribution are displayed on the left side (second y-axis).

Recovery processes

Applications and publications concerning the treatment of bottom ash with techniques like flotation, density separation, bioleaching and hydrothermal solutions are scarce. Fly ash is more often investigated using these techniques. Typically, the techniques are applied to fly ash to extract or immobilize undesirable contents like heavy metals, dioxins and furanes or un-burnt carbon for subsequent disposal (Bosshard et al., 1996, Huang et al., 2003, Jing et al., 2010). In contrast to this for bottom ash recovery of valuables is the major objective.

Pretreatment of bottom ash

It has to be considered that bottom ash from MSWI is a heterogeneous material strongly dependent on the composition of the treated waste. In addition, during the alteration after wet extraction from the incineration mineral material with hydraulic properties form coatings on almost all particles and complicate separation procedures. Hence a pre-treatment like milling

and sieving seems to be essential to establish the aforementioned techniques. Techniques such as breaking up clustered materials with impact mills could be promising.

Recovery processes for elemental metals and metal compounds

Flotation

Froth flotation is a widely used technique for the selective enrichment of valuable contents especially in ore mining. The main challenge here is the prior mechanical separation of ore and gangue, which leads to a high energy consumption. Flotation as a three phase interaction process is affected by numerous factors such as the flotation reagents, pH-value, grain sizes, pulp density etc. and is still not completely understood (Shean and Cilliers, 2011). In ore mining flotation targets usually only a single or a few ingredients of the miscellaneous pulp. Due to this, it is comparatively easy to identify the most adequate chemicals and find out the best process conditions, which then results in high recovery rates.

Flotation of bottom ash is another unique issue. As pointed out bottom ash is an extremely inhomogeneous material. On the other hand the relative uniform mineral attachments on the bulk of the particles hinder the selective impact of flotation surfactants. The coatings should be detached and the grain size distribution constricted for a better performance, equivalent to a high preparation effort. For the flotation process it should be considered that there is not only a single target to be separated. At the expense of high recovery rates a more general approach is required to establish a favourable flotation process.

Density separation

In principle the densities of elemental, alloyed and chemical bound copper should enable a separation. However a proportion of copper in bottom ash is mineral bound (e.g. in cuprite or tenorite (Arickx et al., 2008)) and is particularly associated with other ash components. Also mineral attachments reduce the density of such particles. As is the case in flotation, a prior treatment of the bottom ash might be necessary to achieve sufficient enrichment e.g. in a jig.

Bioleaching

In primary production of copper bioleaching is by now widely used for the low grade ores but similar to flotation mainly to process sulphide ores. Microorganism enhances then the oxidation of the sulphides and the copper is merged into the solution. In bottom ash copper mainly exists in elemental or in oxidised form. This is why applying enzymes may be more effective. Despite this, bioleaching is very slow procedure and the mineral coatings of the bottom ash hinder the reactions additionally.

Hydrothermal Solution

Under hydrothermal and alkaline conditions in bottom ash the formation of zeolite, tobermorite and other minerals with high potential for immobilisation were observed (Penilla et al., 2003, Jing et al., 2007). The hydrothermal treatment therefore should be applied in acid solutions. Different acids have been developed for the leaching of heavy metals from fly ash (Zhang and Itoh, 2006). According to the results hydrochloric acid is able to degrade chemical structures and thus enhance the leaching process of heavy metals accompanied with a decrease in acid consumption. However, the released heavy metals precipitate again and the concentrations in the solution decreases with time.

Energy and material flows

Recovered metals replace metals from primary production. For the production of the non-ferrous metals copper and aluminium from natural resources very large masses have to be processed. Furthermore reduction to the elemental form is highly energy-consuming. In Figure 2 the mass and energy flows for the production of 1 Mg of Aluminium and Copper is displayed in Sankey diagrams. In the case of Al 7.8 Mg of material have to be handled for the production of 1 Mg elemental Al, in the case of Cu even 204 Mg. Whereas bauxite, the raw material for Al contains between 55 and 65 % Al_2O_3 , copper ores have today metal contents below 1 % (for the data in Figure 2 a concentration of 0.6 % was assumed). In the lower section of the figure the exergy flows are displayed. The input flow of the copper production has a considerable share of exergy. The reason is that roasting of sulfidic copper ores is an exothermic process (therefore CuS has high value of chemical exergy (Bakshi et al., 2011)) and the final product, sulphuric acid has a high value for chemical exergy. Exergy in the input flow of Al production arises almost completely from coke, which is consumed as electrode material in the electrolysis. Note the high value of chemical exergy of elemental Al in the output flow. Exergy accounting for primary Al and Cu is described in detail elsewhere (Ayres et al., 2006).

In the production of secondary metals much less material has to be handled and less energy is needed. Usually the scrap metals have to be remelted only. Energy consumption in secondary copper production is 4.45 GJ/Mg for scrap of excellent quality, for scrap of lower quality 20.15 GJ/Mg and for scrap of the lowest quality 49.16 GJ/Mg with only 25-35 % Cu present are quoted (Ayres et al., 2002). Secondary Al production requires around 25 GJ/Mg (Frischenschlager et al., 2010). Alloying elements cannot be removed easily. Therefore the application of secondary metals might be limited (Weber, 1990).

Production of secondary metals from metal compounds is of course more energy consuming. Although the Al_2O_3 concentration in bottom ash is in the order of magnitude of bauxite, utilisation of bottom ash as feedstock for Al production is neither economically nor ecologically feasible. The concentration of copper in bottom ash (see *Figure 1*) is in the region of copper ores (Mudd, 2007, Mudd, 2010). Thus, copper could be recovered from MSWI bottom ash with methods applied already in copper ore mining. For oxidised copper present in bottom ash (Wei et al., 2011, Yao et al., 2013) enrichment by flotation or application of the solvent extraction/electrowinning (SX/EW) process might be suitable. With the SX/EW process route considerably less energy is needed (app. -40 %), however, the resource utilisation efficiency (kg copper/ton of feedstock) is smaller (Marsden, 2008). Energy consumption in copper production is strongly dependent on the ore grade or concentration in the feedstock. Marsden showed that energy consumption is increased by

more than 60 % in both SX/EW and flotation/roasting/electrorefining routes when the ore grade decreases from 0.5 to 0.25 %. Exergetic considerations on the recovery of metals from waste are discussed in detail elsewhere (Simon and Holm, 2015).

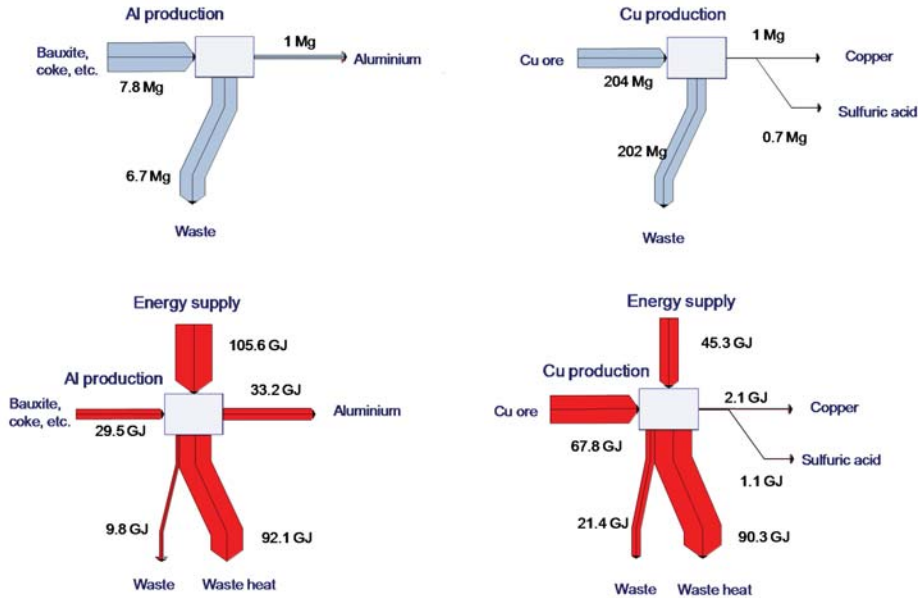


Figure 2. Mass and exergy flows for the production of Al and Cu from natural resources (Ayres et al., 2006).

Conclusions

The resource cycle starts with mining of ores and preparation of (raw) materials which are used for the fabrication of products and goods. After the use phase the products are disposed of in the end-of-life phase. In all phases of this cycle waste is generated. Established recycling strategies already exist for most of production waste, e.g. scrap utilisation in metal working. The utilisation of mixed wastes in the end-of-life phase is more difficult. Although bottom ash from MSWI is a mixture of different materials the recovery of elemental metals is technically feasible and helps to close the resource cycle. To implement the fine fraction < 4 mm in the resource cycle several development works have to be done. It is expected that no stand-alone technique could handle this complex scope of work rather successions of concerted treatment steps are needed for sufficient enrichment. Doubling the yield of metals recovered from MSWI bottom ash seems to be possible (Simon and Holm, 2013) associated with an uncertainty of economic viability.

Substitution by secondary metals saves enormous quantities of energy because chemical reduction is not needed rather than in primary production from ores. The utilisation of metal compounds present in bottom ash as secondary raw material depends on the energy- and resource-efficiency of the enrichment processes.