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Fine fraction of municipal solid waste incinerator : zinc and copper urban mine

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Introduction

Fine fraction (< 2 mm) of bottom ashes from municipal solid waste incineration (MSWI) represent 30% wt. of the total produced bottom ashes amount. The objective of the Refina project is to recover the most valuables metals based on the environmental, economic and geopolitical criteria. The zinc and the copper have been identified as the priority elements (Fig. 2). Their mean concentrations are close to actual mining grades (Fig 1); 3000-3500 mg/kg, corresponding to around 18 000 Mt of each metal landfilled each year in Europe. With the decrease of mining grades and increase of metal demand (Fig 1), MSWI could become a new secondary resource of copper and zinc (Fig.2).

Geopolitics :
- Criteria : critical element according to EU or not
- Limit : yes/not

Economy :
- Economic potential (product of concentration by market value)
- Limit : S$/t BA

Environment :
- Element submitted to environmental limits in leachates *(NF EN 12457-2)*
- Limit : yes/not

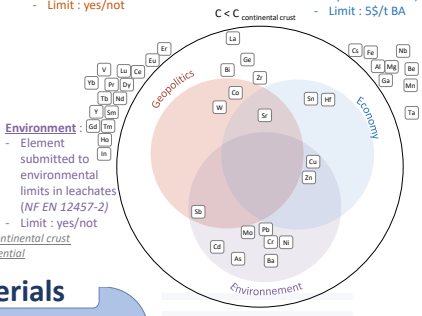
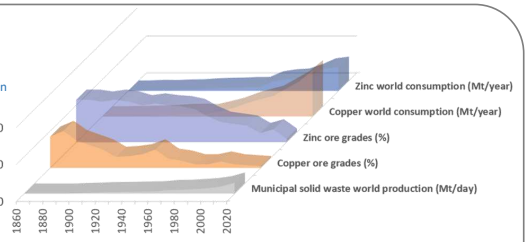


Fig. 2 : Classification of elements in MSWI according to their enrichment factor (compared with continental crust concentration), environmental regulation (French), criticality according to EU and economical potential



The objective of the current work is to develop a low-cost process to recover Cu and Zn. Heap leaching technology is envisaged here to recover metals from MSWI via laboratory column leaching experiments.

Fig. 1: Evolution of world municipal solid waste production, compared with zinc and copper ore grades evolution and copper and zinc world consumption since 1860

Materials



Origin of samples: Indaver incineration plant - Belgium
Pretreatments: quenching – wet screening
Particle size fraction used: **0.063-2 mm**
Homogenizing and sampling: by wet quartering on large plastic tarpaulin

Characterizations: Elementary analysis - SARM Nancy, XRD, SEM-EDS

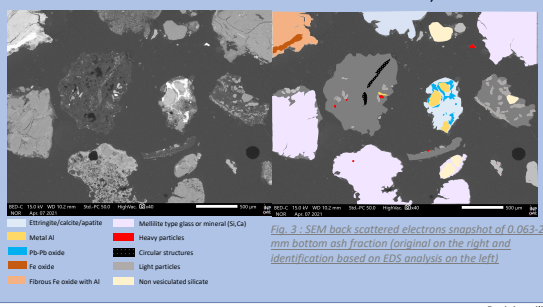


Fig. 3 : SEM back scattered electrons snapshot of 0.063-2 mm bottom ash fraction (original on the right and identification based on EDS analysis on the left)

Washing

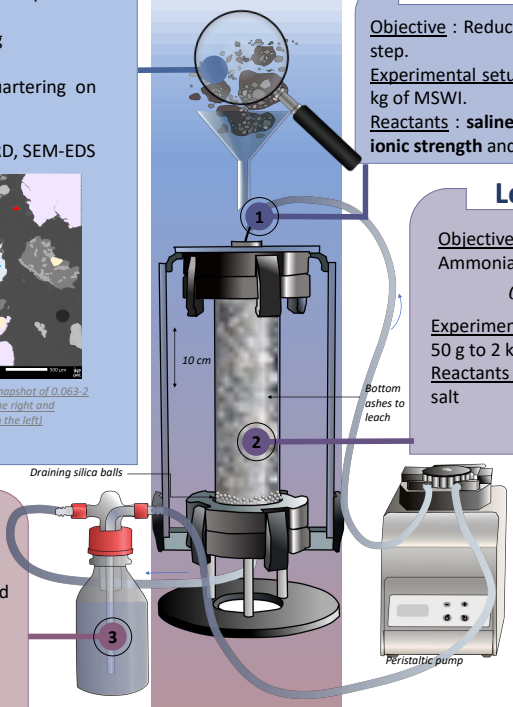
Objective : Reduction of leachable sulfates content prior to the leaching step.
Experimental setup : **down-flow** percolating column filled with 50 g to 2 kg of MSWI.
Reactants : **saline solutions** to enhance sulfate solubilization (increasing **ionic strength** and **cationic exchange capacity**) – NaCl 1M

Leaching

Objectives : Copper and zinc selective leaching
Ammonia based complexing leaching applied

$$Cu^{2+} + 4NH_4^+ + 4H_2O \leftrightarrow Cu(NH_3)_4^{2+} + 4H_3O^+$$

Experimental setup : **down-flow** percolating column filled with 50 g to 2 kg of previously washed MSWI.
Reactants : Ammonia chemical grade and ammonium chloride salt



Factors improving leaching efficiency
- Optimized concentration and ratio of reactants
- Oxygen access
- Time
- Promoted galvanic corrosion of zinc

Leaching efficiency

Factors limiting leaching efficiency
- **Copper cementation**
- **Occurrence of galvanic protection of copper**
- **Presence of others complexing agents forming less soluble complexes**
- **Limited accessibility and liberation of metallic particles in column**

Zn Recovery

Objectives
- Recover the maximum of Zn
- Recirculate the leaching solution (no changes in pH and reactants concentrations)

Precipitation has been chosen to satisfy theses objectives

Zn precipitation

Maximum precipitation achieved at :
- Temperature of approx. 40°C
- Precisely 2 moles of $AlNO_3.9H_2O$ /1 mole of Zn
- Best at 1.5 M total ammonia

$$Zn^{2+} + AlNO_3.9H_2O + NH_3 \rightarrow Zn(OH)_2.2Al(OH)_3$$

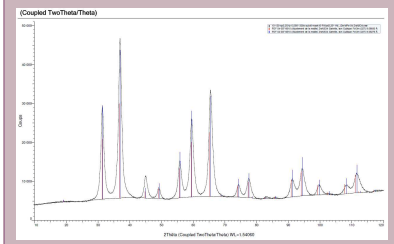
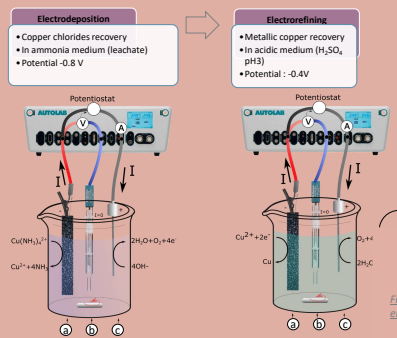


Fig. 4 : XRD spectrum of calcinated zinc precipitate corresponding to a pure $ZnAl_2O_4$ phase.

Precipitation by aluminum nitrate allows to reach a **zinc recovery of 92%** and it's a **selective operation** because the copper concentration remains constant during the precipitation step. No pH change is necessary or observed.

Cu Recovery

Electrodeposition in two steps (Fig. 5).



- a • *Graphite foam cathode*
- b • *Reference electrode Ag/AgCl (E=0.176 V/ESH)*
- c • *Dimensional stable anode (DSA)*

Fig. 5: schematic representation of electrodeposition and electrorefining steps

After copper electrodeposition, leachate is **recirculated** to leach again the column. Also, the cathodic deposit is redissolved in acidic media to perform to the electrowinning step.

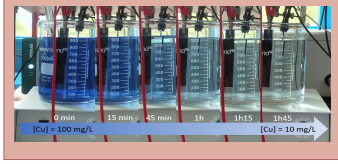


Fig. 6: Leachate color evolution during electrodeposition step

Copper removal efficiency : **up to 85 %**

Conclusions

Up to **70% of copper and 60% of zinc** are now recovered *via* the **four steps process** based on column leaching with less than 0.1% of iron co-solubilized.

The leaching step is a key step to improve efficiencies. By identifying leaching limiting and improving factors it's possible to drastically improve total recovery for both metals.

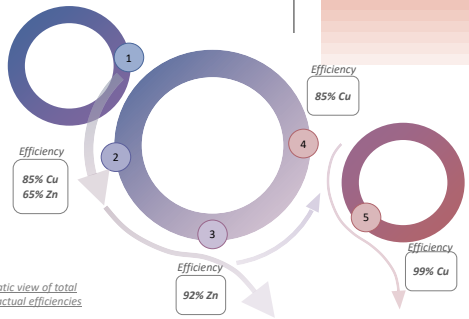


Fig. 7: Schematic view of total process with actual efficiencies

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