High Temperature Processing of Secondary Metallurgical Resources

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Overview

- Introduction
- Research overview (TU Delft)
  - Municipal solid waste incineration (MSWI) bottom ash
  - Zinc bearing residues
  - Vanadium containing fly ashes
- Resource recovery from MSWI bottom ash
- Conclusions
Secondary metallurgical resources

- **Scrap (metallic)**
  - New (prompt) scrap; old scrap

- **Metal bearing waste (non-metallic)**
  - Solid waste generated during (metallurgical) processing
    - Slags
    - Flue dust
    - Solid residues and ashes
  - Concentration tailings
  - Urban mines/landfill mines
Mine tailings

Open pit mining

Mineral processing plant

Nickel Tailings No. 34, Sudbury, Ontario 1996
Metallurgical smelters
Global flow of metals

- Where the metals go?
  - Production of 1 ton of refined zinc: 420 kg of zinc loss

- Where are the loses?
  - Tailings 34%; slags/solid residues 11%; landfill 55%

### Table: Global Flow of Metals

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Mine metal (ore, kt)</td>
<td>7.800</td>
<td>9.490</td>
<td>20.200 t</td>
<td>1.338</td>
<td>5.140</td>
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<tr>
<td>Refined metal (kt)</td>
<td>7.210</td>
<td>11.800</td>
<td>24.600 t</td>
<td>1.120</td>
<td>3.900</td>
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<tr>
<td>Total metal loss (kt)</td>
<td>3.033</td>
<td>3.350</td>
<td>9.400 t</td>
<td>509</td>
<td>1.910</td>
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<tr>
<td>Metal loss/Refined metal</td>
<td>0.42</td>
<td>0.28</td>
<td>0.38</td>
<td>0.45</td>
<td>0.49</td>
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<tr>
<td>Tailings (kt)</td>
<td>1.030 (34%)</td>
<td>1.400 (42%)</td>
<td>4.000 t (42.5%)</td>
<td>167 (32.8)</td>
<td>740 (39%)</td>
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<tr>
<td>Slag (kt)</td>
<td>330 (11%)</td>
<td>150 (4%)</td>
<td>1.400 t (15%)</td>
<td>74 (14.5%)</td>
<td>590 (31%)</td>
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<tr>
<td>Metal to landfill (kt)</td>
<td>1.673 (55%)</td>
<td>1.800 (54%)</td>
<td>4.000 t (42.5%)</td>
<td>268 (52.7%)*</td>
<td>580 (30%)</td>
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<tr>
<td>Reference</td>
<td>Gordon et al., 2004</td>
<td>Lifset et al., 2002</td>
<td>Johnson et al., 2006</td>
<td>Reck &amp; Gordon, 2008</td>
<td>Reck &amp; Gordon, 2008</td>
</tr>
</tbody>
</table>

**Metal loss during Concentration-smelting**

- ~17%
- ~16%
- ~27%
- ~18%
- ~26%

Prompt scrap is recycled back to refined metal!
Other potential sources of metals

- Residues from non-metallurgical industry
  - Power generation industry
    - Fly ashes
  - Thermal waste processing industry
    - Fly ashes
    - Bottom ashes
  - Petrochemical/chemical industry
    - Spent catalysts

- Not all metals are feasible for recovery.
  - Reactive and light metals such as Al, Mg, Si, Ca etc. in the slags or ashes
Am I forgetting any other sources of metals?
Metal recovery from secondary resources

- **Ash utilisation:** metal recovery, vitrification
  - MSWI bottom ash: vitrification
  - Metal recovery and refining
  - Slag formation and slag chemistry

- **Residue treatment:** metal recovery
  - **Zinc recovery:** from various solid residues
    - Galvanising (HDG) bottom dross
    - Brass recycling flue dust
    - Industrial Zn-bearing residues (similar to EAF dust)
  - **Smart processing:** waste + waste = product
    - Fe-V production (using BOF dust + power plant fly ash)
From solid residues to zinc metal

- Rotterdam Harbour: 5000 tons Zn residues stored for 17+ years without solutions.
- Dutch brass recycling industry generates a few thousands tons of filter dust and slag rich in zinc.
- Dutch steel industry: over 5000 tons of Zn metal lost as flue dust (EAF, BOF, BF)
  - 30 mt/year flue dust (worldwide)
- Galvanising industry: 500 tons almost pure zinc lost as dross
- Zinc ferrites and Gahnite spinels in flue dust: difficult to recover!
From solid residues to zinc metal

- TU Delft: Pyro- and Hydrometallurgical processes

Product: Zinc metal

- Na$_2$CO$_3$ Roasting
- NaOH leaching
- Electrowinning
- Carbothermic reduction
- Brass recycling flue dust
- ZnO or Zn metal
Smart processing of multi-wastes

- **Waste + Waste = Products!**
- **Example: FeV alloy production**
  - Fly ash from oil-fired power plant: source of V and C
  - Flue dust from BOS steelmaking: source of Fe

(V+C)-bearing power plant fly ash + BOF steelmaking Flue dust → Product: Fe-V alloy
MSW Incineration bottom ash

- Metal recovery and slag utilisation
  - MSW incineration (Waste-to-Energy)
  - European Union
    - 60 million tons annual processing
    - Generation of more than 10-20 million tons of bottom ash
  - Netherlands (2008)
    - Processing over 6 million tons of MSW in 11 MSWI
    - 3000 GWh electricity, 3000 TH thermal energy
    - 11% sustainable energy
    - 1,321 kt bottom ash, 85 kt fly ash
    - 115 kt ferrous scrap, 21,5 kt non-ferrous scrap (from bottom ash)

European policy
“Stimulating recycling & energy recovery”!

Dutch national policy
“Stimulating materials recycling”!
MSW Incineration bottom ash

- EU MSW processing: recycling, combustion, landfill (2008)

(http://www.verenigingafvalbedrijven.nl/)
MSWI and the bottom ash

- MSW Incineration
  - MSW (4-10 MJ/kg)
  - Combustion (~900°C)
  - Power plant

- Bottom ash (BA)
  - 20-25% of the MSW
  - Valuable resource of metal
  - 15 -20% metal in the BA
  - Only 60% metal recovered

- Bottom ash and metal separation plant
Bottom ash treatment

- **Current practice**
  - Physical separation of metal (partial)
    - Magnetic separation
    - Dry or wet eddy current separation
  - Construction material (low grade)
  - Unstable and leaching problems (Cu, Mo, Sb)

- **Vitrification: safer option**
  - Melting the ash at above 1400°C
  - 2 useful products: **metal + slag**
  - Option for safe ash disposal/utilisation
  - Conversion of ash to stable glassy slag
  - Metals recovered as an alloy
Bottom ash treatment

- **Vitrification product – recovered alloy** (*AVR case*)
  - ~ 8% of total bottom ash
  - Chemical composition:
    - Fe–Cu based
    - 82% Fe – 12% Cu – 2% P – 1.5% S – 1.5% C + 1% other impurities
  - Market for the alloy?
    - Direct applications?
    - Steel scrap?
    - Copper scrap?
- **Purification necessary!**
Bottom ash treatment: Fe-Cu separation

- **Copper removal** from steel and Fe-based alloys
  - Cu as a harmful impurity in steelmaking
    - Steel scrap tolerance: 0.5-1.0% Cu
  - Fe-Cu alloy from MSWI ash vitrification: high in Cu
    - Over 10% Cu, no commercial or any research results available

- **Possibilities**
  - Vacuum refining, chlorination, filtration
  - Sulfide treatment: FeS-based sulphide mixture

- **Current research Objective**: sulphide treatment
  - Cu recovered as a matte: Cu$_2$S-FeS --> copper smelter
  - Steel scrap: low in Cu (market in steelmaking industry)
Fe-Cu separation: sulphide treatment

**Principles**

\[
2[Cu]_{alloy} + MeS = [Me]_{alloy} + (Cu_2S)_{matte}
\]

\( (Fe, Zn, Al, Na, Ni, etc.) \)

\[
2[Cu]_{alloy} + FeS = [Fe]_{alloy} + (Cu_2S)_{matte}
\]

\[
2[Cu]_{alloy} + ZnS = Zn_{gas} \uparrow + (Cu_2S)_{matte}
\]

**Challenges**

- New impurities?
  - FeS best option
- Phase separation
  - Fluxing agent needed
  - Carbon saturation: critical
Experiments

- **Furnace:** vertical tube furnace
- **Synthetic Fe-Cu alloy**
  - 87.2% Fe + 12.8% Cu
- **Temperature:** 1500°C
- **Atmosphere:** N₂ flow (100 l/h)
- **Reaction time:** 2-4 hours
- **Reaction system:**
  - Graphite crucible; C-saturation
- **S/Cu ratio:** 2-8 stoichiometric
- **Analysis:** XRF, SEM, EMPA

Lab-scale furnace
Fe-Cu separation: sulphide treatment

- If no C-saturation, no phase separation
  - Matte (FeS-Cu$_2$S) – alloy (Fe-Cu) fully mixed
- Under C-saturation, separate matte layer
- Cu in the alloy: reduced (pushing out by carbon)

Resin
Cu (1.9%)
Fe (93.6%)
C (4.5%)

Entrapped matte
Cu (2.8%)
Fe (96.8%)
C (0.4%)

Matte
S/Cu=4.0 at 1500°C
Fe-Cu separation: sulphide treatment

- FeS alone is ineffective
- Effect of S/Cu ratio

![Graph showing Cu removal efficiency using FeS vs S/Cu ratio.](image-url)
Fe-Cu separation: sulphide treatment

- **Effect of sulphide additives**
  - Lowering the melting point of sulphides
  - Decreasing the activities of Cu$_2$S
  - Possibly participating the reaction.

- **Use of Na$_2$S and Al$_2$S$_3$ additives**
  - Na$_2$S (72.5 mol%) – FeS (27.5 mol%) system
    - Pre-melting (1200°C) or non pre-melting
  - Al$_2$S$_3$ (70 mol%) – FeS (30 mol%) system
  - S/Cu= 2.0 Stoichiometric ratio (based on FeS only)

- **Problem**: impurity pick-up in the alloy
  - Al: 2.8% (wt)
  - Na: 10 – 15%
Effect of additives on Cu removal

- Increased Cu-removal efficiency

![Graph showing efficiency of Cu removal for different sulfide mixtures.](image-url)
Pyrite treatment: Fe-Cu separation

- **Pyrite concentrate**
  - 89.3% Fe$_2$S

- **Reactions**
  \[
  FeS_2 + 4[Cu] = [Fe] + 2(Cu_2S)
  \]
  \[
  K = \frac{a_{[Fe]} \cdot a_{(Cu_2S)}^2}{a_{(FeS_2)} \cdot a_{[Cu]}^4} = 1.60 \cdot 10^6
  \]

- **Efficiency**: 92%

- **Phase separation**
  - Good!
Pyrite treatment: Fe-Cu separation

Cu remaining in the alloy by using pyrite

1500°C for 4.0 hours
Cu removal with zinc sludge (ZnS)

- **Zinc sludge**
  - Waste from zinc smelter
  - 80% ZnS

- **Reactions**
  
  \[(ZnS) + 2[Cu] = Zn_{(g)} + (Cu_2S)\]

  \[K = \frac{p_{Zn} \cdot a_{[Cu_2S]}}{a_{(ZnS)} \cdot a_{[Cu]}^2} = 20.46\]

- **Results**
  - High efficiency
  - Zn to vapour phase
  - No contamination to alloy

![Graph showing Cu removal efficiency using zinc sludge (80% ZnS)]
From waste to metals

- Comparison of different sulphide treatment

![Graph showing Copper removal efficiency vs S/Cu ratio for FeS, Pyrite, and Zinc sludge]
Thermodynamic study of MSWI slag

- MSWI bottom ash: vitrified slag (~1500°C)
  - $\text{SiO}_2$ (52.1 %), $\text{CaO}$ (16.2 %), $\text{Al}_2\text{O}_3$ (12.2 %), $\text{Fe}_2\text{O}_3$ (7.7 %), $\text{Na}_2\text{O}$ (4.2 %) and $\text{MgO}$ (2.3 %)

- High in alkali: $\text{Na}_2\text{O} + \text{K}_2\text{O}$
  - Lack of information on thermodynamic data and phase relations

- Phase relations in $\text{SiO}_2$-$\text{CaO}$-$\text{N}_2\text{O}$ slag system
  - Phase diagram: Liquidus temperatures
  - Experimental: thermal analysis (DSC) + phase equilibrium
  - Modelling: FactSage
  - A PhD project
Primary phase fields and liquidus surface projection: Na$_2$O-CaO-SiO$_2$ containing (0 - 40 wt%Na$_2$O and 30 - 70 wt%SiO$_2$).

The primary phase fields: Ca$_2$SiO$_4$, Ca$_3$Si$_2$O$_7$, CaSiO$_3$, Na$_2$Ca$_2$Si$_2$O$_7$, Na$_2$Ca$_2$Si$_3$O$_9$, and Na$_2$CaSiO$_4$ I, II, III, IV, V and VI).

(C=CaO; N=Na$_2$O; S=SiO$_2$).
Conclusions

- Carbon is essential in sulfide treatment
- High S/Cu ratio is beneficial for Cu removal
- Reaction rate: fast (first 10 min. completed)
- Sulphide additives (Na$_2$S and Al$_2$S$_3$) improve Cu-removal but bring new impurities (Na, Al).
- Pyrite and zinc sludge are good alternatives with high Cu removal efficiency & no pollution to the alloy
- Cu removal below 1-2% in the alloy is more difficult and multi-step treatment is an option.
Thank you!
MSW Incineration bottom ash

MSW processing in EU (2005)

Current disposal/utilisation alternatives

- **Landfill** (after possible partial metal recovery (>10 mm))
- **Construction materials**
  - Partial recovery of metals (>10 mm))
  - Deep dry metal recovery (>4 mm)
  - Wet separation metal recovery (0.1 mm)
- **Metal recovery**
  - Magnetic and eddy current separation
  - Ferrous and non-ferrous scrap
The role of carbon saturation

Carbon promote Cu – Fe separation

- In the absence of sulphide
  - C-saturation forming Fe-Cu-C ternary alloy
  - Solubility of copper in iron: decreased
  - Copper was precipitated to certain extent
  - Phase separation: still difficult!
## Raw materials

- **Petroleum fly ash (PFA)**
  - Main constituents (%): V (27.56), C (36.5), S (12.3), Ni (5.9)
  - Main phase: $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{NiS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (XRD)

- **BOF steelmaking flue dust**
  - Coarse fraction and fine fraction (BOF-CF; BOF-FF)
  - Fe/FeOx, CaO, MgO

## Chemical analysis

<table>
<thead>
<tr>
<th>Element, wt%</th>
<th>Fe</th>
<th>V</th>
<th>Ni</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Mg</th>
<th>S</th>
<th>P</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA</td>
<td>0.767</td>
<td>27.56</td>
<td>5.925</td>
<td>0.269</td>
<td>0.788</td>
<td>0.058</td>
<td>2.645</td>
<td>12.75</td>
<td>0.023</td>
<td>1.386</td>
<td>0.080</td>
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<tr>
<td>BOF-CF</td>
<td>36.03</td>
<td>0.033</td>
<td>0.008</td>
<td>0.705</td>
<td>42.55</td>
<td>0.222</td>
<td>7.400</td>
<td>0.049</td>
<td>0.008</td>
<td>0.053</td>
<td>0.045</td>
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<tr>
<td>BOF-FF</td>
<td>82.95</td>
<td>0.026</td>
<td>0.000</td>
<td>0.740</td>
<td>8.535</td>
<td>0.043</td>
<td>1.247</td>
<td>0.053</td>
<td>0.050</td>
<td>0.203</td>
<td>0.033</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Element, wt%</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Cd</th>
<th>Cl</th>
<th>C (LECO)</th>
<th>SUM</th>
<th>S (LECO)</th>
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<tbody>
<tr>
<td>PFA</td>
<td>0.133</td>
<td>0.000</td>
<td>0.022</td>
<td>0.052</td>
<td>0.059</td>
<td>0.049</td>
<td>0.000</td>
<td>0.000</td>
<td>36.5</td>
<td>89.1</td>
<td>12.3</td>
</tr>
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<td>BOF-CF</td>
<td>0.070</td>
<td>0.015</td>
<td>0.625</td>
<td>0.193</td>
<td>0.011</td>
<td>0.010</td>
<td>0.000</td>
<td>0.027</td>
<td>0.570</td>
<td>88.6</td>
<td>0.002</td>
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<td>BOF-FF</td>
<td>0.024</td>
<td>0.028</td>
<td>1.429</td>
<td>0.370</td>
<td>0.065</td>
<td>0.000</td>
<td>0.012</td>
<td>0.012</td>
<td>1.650</td>
<td>97.5</td>
<td>0.039</td>
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</tbody>
</table>
Results of smelting tests

- Conditions: 1550°C for 2 hours in Ar
- Metal yield: 27-32%
- Weight loss (off-gas + dust): 32-42%
- Slag yield (balance): 29-37%

<table>
<thead>
<tr>
<th>Test</th>
<th>Charge, g</th>
<th>BOO FA to BOF-CF ratio</th>
<th>Total weight, g</th>
<th>Weight loss, %</th>
<th>Metal yield, %</th>
<th>Remarks</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>BOO FA</td>
<td>BOF-CF</td>
<td>SiO₂</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-1</td>
<td>1.28</td>
<td>1.59</td>
<td>0.96</td>
<td>---</td>
<td>0.8</td>
<td>3.83</td>
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<tr>
<td></td>
<td>B-2</td>
<td>1.07</td>
<td>1.33</td>
<td>0.81-0.07</td>
<td>0.8</td>
<td>3.28</td>
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<tr>
<td>B-3</td>
<td>0.95</td>
<td>1.59</td>
<td>0.95</td>
<td>---</td>
<td>0.6</td>
<td>3.49</td>
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<tr>
<td>B-4</td>
<td>16.0</td>
<td>20.0</td>
<td>12.0</td>
<td>---</td>
<td>0.8</td>
<td>48.0</td>
</tr>
</tbody>
</table>
Results of smelting tests

- Major compositions of slag and metal
  - Metal: 62-63% Fe, 18-22% V, 1-2% Ni
  - Slag: CaO-SiO$_2$-MgO-VO-NiO

<table>
<thead>
<tr>
<th>Test</th>
<th>Slag, wt%</th>
<th>Metal, wt%</th>
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<td></td>
<td>CaO</td>
<td>SiO$_2$</td>
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<td>B-1</td>
<td>28.3</td>
<td>35.6</td>
</tr>
<tr>
<td>B-3</td>
<td>26.0</td>
<td>44.8</td>
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<tr>
<td>B-4</td>
<td>33.6</td>
<td>38.6</td>
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</table>
## Experimental results

### Element distribution (test B-4 during smelting)

<table>
<thead>
<tr>
<th>Elemental distribution, %</th>
<th>Slag</th>
<th>Metal</th>
<th>Off-gas/flue dust</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>12.4</td>
<td>83.5</td>
<td>4.1</td>
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<tr>
<td>V</td>
<td>4.2</td>
<td>50.1</td>
<td>45.7</td>
</tr>
<tr>
<td>Ni</td>
<td>2.0</td>
<td>19.5</td>
<td>78.5</td>
</tr>
<tr>
<td>Si</td>
<td>79.8</td>
<td>14.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Ca</td>
<td>71.1</td>
<td>0.4</td>
<td>28.5</td>
</tr>
<tr>
<td>S</td>
<td>77.3</td>
<td>3.1</td>
<td>19.6</td>
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<tr>
<td>Na</td>
<td>63.1</td>
<td>0.6</td>
<td>36.4</td>
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<tr>
<td>Zn</td>
<td>0.0</td>
<td>1.8</td>
<td>98.2</td>
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<tr>
<td>Pb</td>
<td>0.0</td>
<td>10.7</td>
<td>89.3</td>
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<tr>
<td>Cu</td>
<td>26.8</td>
<td>31.6</td>
<td>41.6</td>
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