Valorization of zinc smelter leach products

PROMETIA scientific seminar 28-29/11/2017
Nyrstar at glance

Geographically diverse smelters operating in OECD countries

2016 revenue: EUR 2.8bn
2016 production: 1,015kt zinc metal, 96kt zinc in conc.

Operating Smelters
Operating Mines
Non-operating Assets

4,300 employees across 4 continents

2nd largest zinc metal producer

Listed on Euronext Brussels

1 Excludes corporate offices and mining assets where sale has been agreed or completed
Source: Wood Mackenzie; Nyrstar company information
Composition of Budel leach product (BuLP)

- **Main or relevant Elements**

<table>
<thead>
<tr>
<th>Zn%</th>
<th>Pb%</th>
<th>Cu%</th>
<th>Ag ppm</th>
<th>Fe%</th>
<th>Si%</th>
<th>Al%</th>
<th>Ca%</th>
<th>Stot %</th>
<th>As%</th>
<th>Hg ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-4.5</td>
<td>7-10</td>
<td>0,4-0,8</td>
<td>500-700</td>
<td>17-21</td>
<td>3-5</td>
<td>0,8-1,2</td>
<td>2,5-3,5</td>
<td>11-13</td>
<td>0,2-0,4</td>
<td>10-20</td>
</tr>
</tbody>
</table>

- **Main Species**

<table>
<thead>
<tr>
<th>PbSO4</th>
<th>ZnFe204</th>
<th>Zn2SiO4</th>
<th>CaSO4,2H2O</th>
<th>SiO2</th>
<th>Jarosites (K,Na,H3O+)</th>
<th>alunites</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-15</td>
<td>2,5-3,5</td>
<td>4-6</td>
<td>10,5-15</td>
<td>5-7</td>
<td>45-55</td>
<td>4-6</td>
</tr>
</tbody>
</table>

- BuLP combines solid residue obtained after hot acid leaching of zinc calcine (lead sulfate, gypsum, silica..) together with iron precipitate.
- Budel smelter precipitates iron as Jarosite:
  - $\text{M}^+\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
  - Cation M+ being either: K+, Na+, H3O+ etc…
- The production of a single solid residue outlet from its leaching plant makes Budel flowsheet very lean and efficient and allows excellent zinc recoveries.
- However the resulting dilution of valuables (Pb, Ag) by jarosites makes BuLP less attractive for lead & silver refiners who are traditional customers for zinc leach products.
- The treatment of BuLP in a fuming process is an alternative that offers better returns than external sales.
Why treating Budel leach product in a fumer?

- **Fuming is about** heating a material in a furnace at typically 1100-1300 °C (even higher) in order to volatilize compounds with a high vapor pressure at operating temperature: PbO, Zn, etc...

- **Typically a reductant is used for reducing oxides into more volatile metals eg:**
  - \[ \text{ZnO} + \text{CO(g)} \rightarrow \text{Zn (g)} + \text{CO}_2(g) \]

- **Fuming process separates the raw material treated in 2 or possibly 3 phases:**
  - **Slag** where non volatile compounds collect: FeO, SiO2, CaO, MgO, Al2O3
  - **Off gas** to which volatile elements report (PbO, Zn, etc…) and are collected as fume after post combustion.
  - **In case** sulfur is available in raw material, a matte phase (Cu2S-FeS) can be produced where copper together with nickel, silver and precious metals collect

- **BuLP contains large proportions of slag forming elements**: Fe, Si, Ca which dilute the contained valuable elements: Zn, Pb, Ag, In, Ge

- **Fuming process offers the capability to separate non valuable elements from valuables and collect the latter in higher concentration products, more suitable for downstream refiners**
Elements collected essentially into slag

Elements collected essentially in Matte phase

Elements collected essentially into fume
Basis principles

- **Operating Temperature**
  - Kinetics (vapor pressure of volatile components)
  - Refractory / slag freeze lining

- **Slag chemistry**
  - Melting point
  - Content FeII; Fe°:
    - \(2 \text{FeO} + \text{ZnO} \rightarrow \text{Zn(g)} + \text{Fe}_2\text{O}_3\)
    - \(\text{Fe} + \text{ZnO} \rightarrow \text{Zn(g)} + \text{FeO}\)
  - Basicity: facilitates fuming by increasing activity of ZnO

- **Furnace atmosphere:** \(\text{PO}_2, \text{PS}_2\) …
  - Low \(\text{PO}_2\) required for Zinc fuming
  - \(\text{PS}_2\) for production of matte

- **Feed preparation:**
  - Fluxes: \(\text{CaO, MgO, SiO}_2\) for adjustment of slag melting point and basicity
  - Mixing
  - Control of solid carry over to off gas: pelletisation, granulation etc…
  - Optionally: pre drying of feed mix to optimize energy consumption.
BuLP fuming at Nyrstar Hoyanger

- Acquisition by Nyrstar in December 2013.
- 3X2.5 MW submerged plasma fumer.
- Treatment of EAF dust until 2014 – adaptation of plant to the treatment of BuLP as from 2015
- Production of:
  - Fume with Pb,Zn,(Ag) & minor metals for further treatment in Nyrstar Europe facilities
  - Matte for sale
  - Clean slag
Why choosing submerged plasma technology?

- Plasma is about transformation of electric energy into energy carried by a hot gas (LNG, air)…

- Submerged plasma technology offers key benefits:
  - High fuming kinetics linked to high agitation of molten bath an high temperatures in the neighborhood of plasma torches.
  - Ability to recover gold silver and copper in a matte phase, next to volatile metals recovered in fume.
  - Possibility to produce a very stable slag suitable for commercial applications.
  - Relatively low footprint thank to smaller off gas generation than other fuming technologies using fossil energies. (*)
  - Low CO2 footprint if electricity is obtained from non fossil sources (which is the case in Norway)

- As every molten bath technology, submerged plasma remains energy intensive
  - Opex highly influenced by electricity prices

(*) Off gas treatment is a capital intensive aspect of pyrometallurgical plants. Capex is highly correlated to off gas volumes to be treated
Treating BuLP in a plasma furnace

**Raw materials**
- Budel Leach Product
- Pet Coke (limited quantity)

**Fumes**
- Zinc
- Lead
- Germanium
- Indium
- Silver
- + As, Sb, Sn, Bi, Hf, Cl, F ...

**Plasma generators**
- Gas
- Electricity

**Leach stable slag**
- (FeO, SiO2, CaO etc...)

- Matte
  - Copper
  - Silver
  - Gold

- The (non-dried) feed is mixed with pet coke and dropped directly into the furnace, and melted into a liquid slag.

- The energy for smelting is transferred to the slag from the plasma generators.

- The fuming reaction is controlled through the air/coal ratio.

- Zinc, lead, germanium, indium, some silver are fumed out as reduced metal or volatile oxides, re-oxidated or re-sulfated and captured in a bag house as a metal rich fume.

- The copper matte and slag that remain in the furnace are tapped in pots and recovered after settling and cooling.
Treating BuLP in a plasma furnace: off gas cooling

1. Post combustion of fumer off gas: burn CO, H2, oxidize metals and radiation cooling
2. Adiabatic cooling in a spray tower down to 160°

- BuLP contains 11-13% Sulfur,
- Its fuming generates high amounts of SO2 that requires further treatment,
- Attention is to be paid on acid dew point in furnace and off gas cooling
BuLP is a complex material with a high content of sulfur and presence of contaminants: As (0,2-0,4%, Hg (5-20 ppm) that require a dedicated off gas treatment. Nyrstar Hoyanger off gas treatment was designed with BAT techniques:

- After quenching the gas down to 160°C, fumes are collected in a baghouse filter.
- A second baghouse filter was implemented downstream to capture mercury by means of an absorbant.
- A wet acid scrubber collects the last traces of metals.
- Effluent produced from WAS are treated in a wastewater treatment plant (iron chloride, NaHS, S/L separation).
- Finally, SO2 is absorbed in two sea water scrubbers.

Levels of emissions at Nyrstar Hoyanger plant are among the lowest of metal industry:

- SO2 < 20 ppm in tail gas
- Hg < 0,02 µg/l in effluent
Conclusion

- Nyrstar Budel leach product (BuLP) is the main byproducts from Budel zinc smelter, that collects iron as jarosites together with lead sulfate and residual unleached zinc from RLE refining process,
- A suitable treatment for BuLP, based on submerged plasma fuming technology was developed at Nyrstar Hoyanger (No)
- Fuming process allows to valorize valuable metals contained in BuLP as:
  - Copper iron matte sold to copper refiners
  - PbZn fume further refined by Nyrstar European plants to recover lead and silver, zinc and minor metals
- Non valuables: Fe, Si, Ca … are disposed as clean slag, suitable for usage as road filler etc..
- BuLP composition required the implementation of a highly performing off gas and effluent treatment that allow to meet very low emissions of contaminant to air and water.
- Nyrstar Hoyanger plant has the capability to treat a wide range of raw materials, in particular sulfur bearing leach products from zinc industry.