Valorization of zinc smelter leach products

PROMETIA scientific seminar 28-29/11/2017

Nyrstar / X Constant Group Manager Projects

Nyrstar at glance

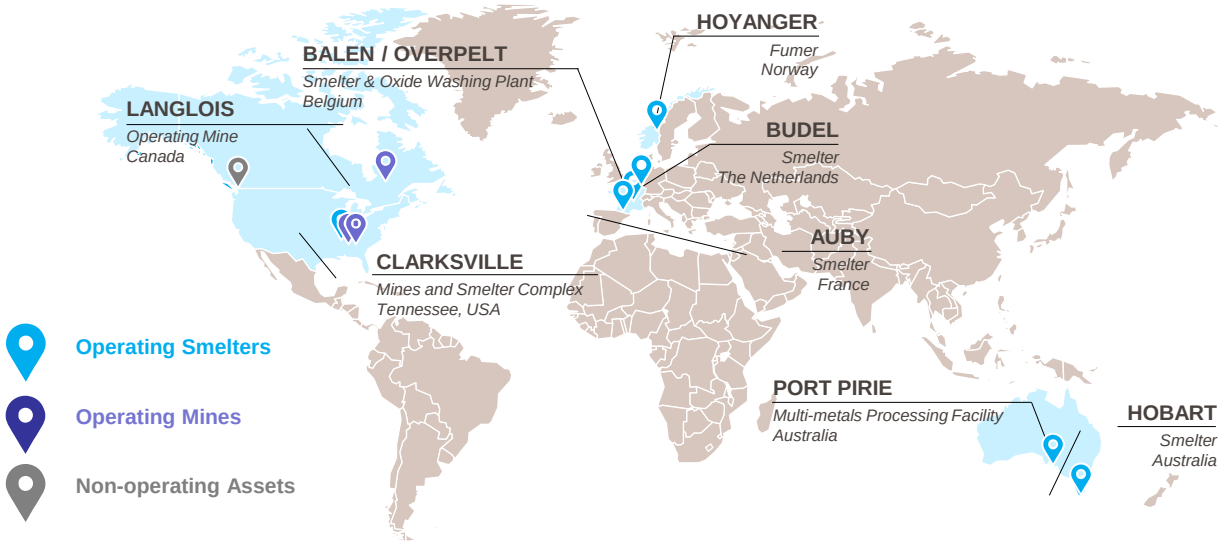
Geographically diverse smelters operating in OECD countries[1]

2016 revenue:

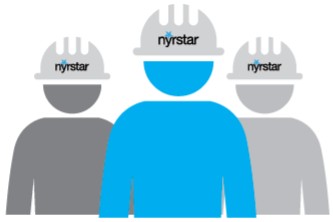
EUR 2.8bn

2016 production:

1,015kt zinc metal
96kt zinc in conc.



6 Smelters ▪ 1 Fumer
4 Mining Operations



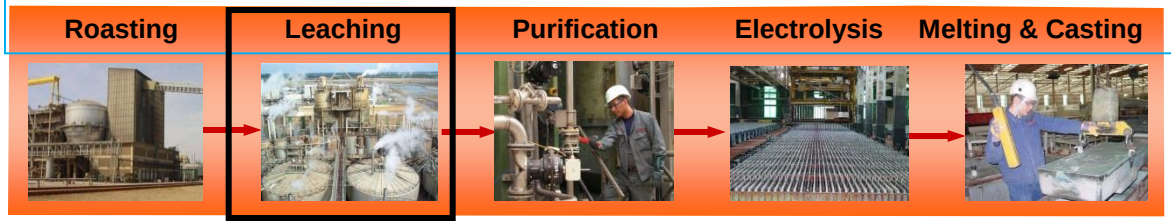
4,300 EMPLOYEES
across 4 continents

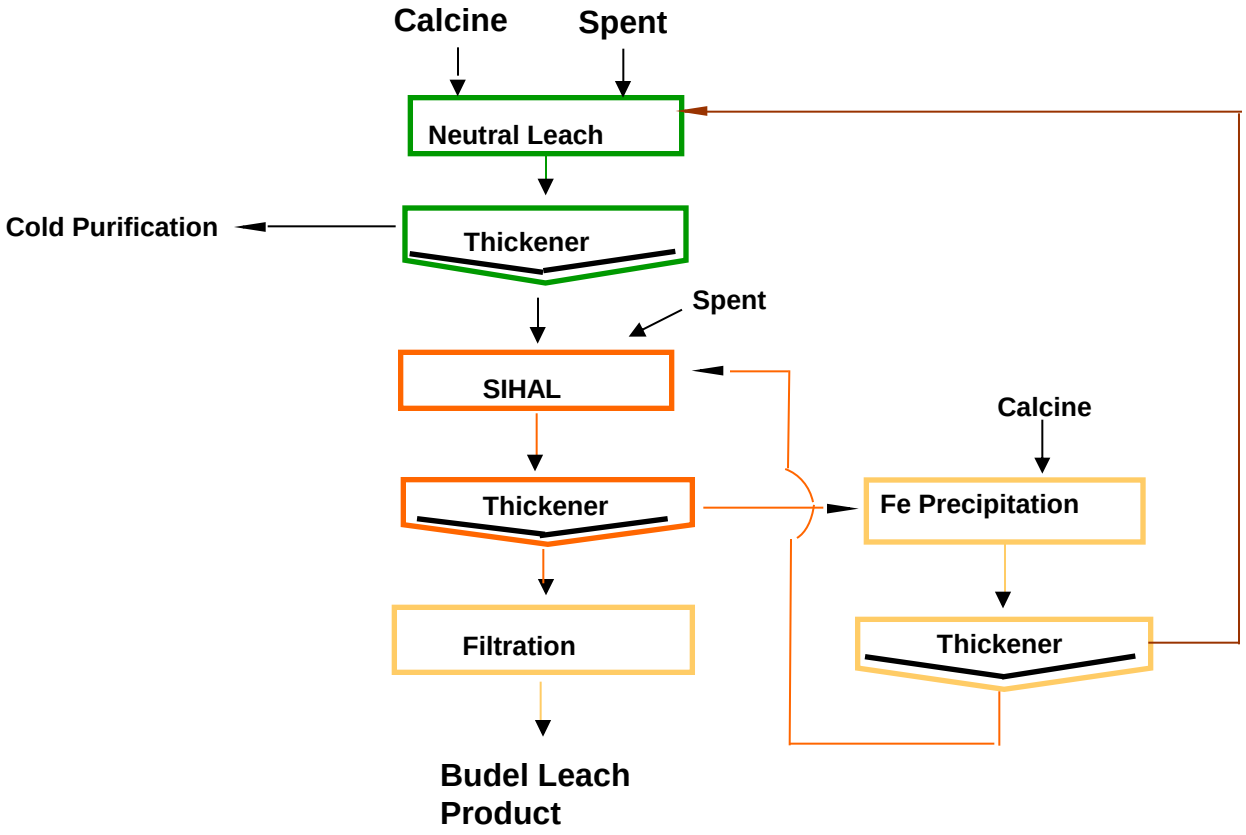
2ND LARGEST ZINC
metal producer

Listed on
EURONEXT BRUSSELS

[1] *Excludes corporate offices and mining assets where sale has been agreed or completed*
Source: Wood Mackenzie; Nyrstar company information

Origin of zinc smelter leach products : The Nyrstar Budel case





Composition of Budel leach product (BuLP)

- Main or relevant Elements

Zn%	Pb%	Cu%	Ag ppm	Fe%	Si%	Al%	Ca%	Stot %	As%	Hg ppm
3,5-4,5	7-10	0,4-0,8	500-700	17-21	3-5	0,8-1,2	2,5-3,5	11-13	0,2-0,4	10-20

- Main Species

PbSO4	ZnFe204	Zn2SiO4	CaSO4,2H20	SiO2	Jarosites (K,Na,H3O+…)	alunites
10-15	2,5-3,5	4-6	10,5-15	5-7	45-55	4-6

- 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 :
  - $M^+,Fe_3(SO_4)_2(OH)_6$
  - Cation M^+ being either : K^+, Na^+, H_3O^+ 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 ?

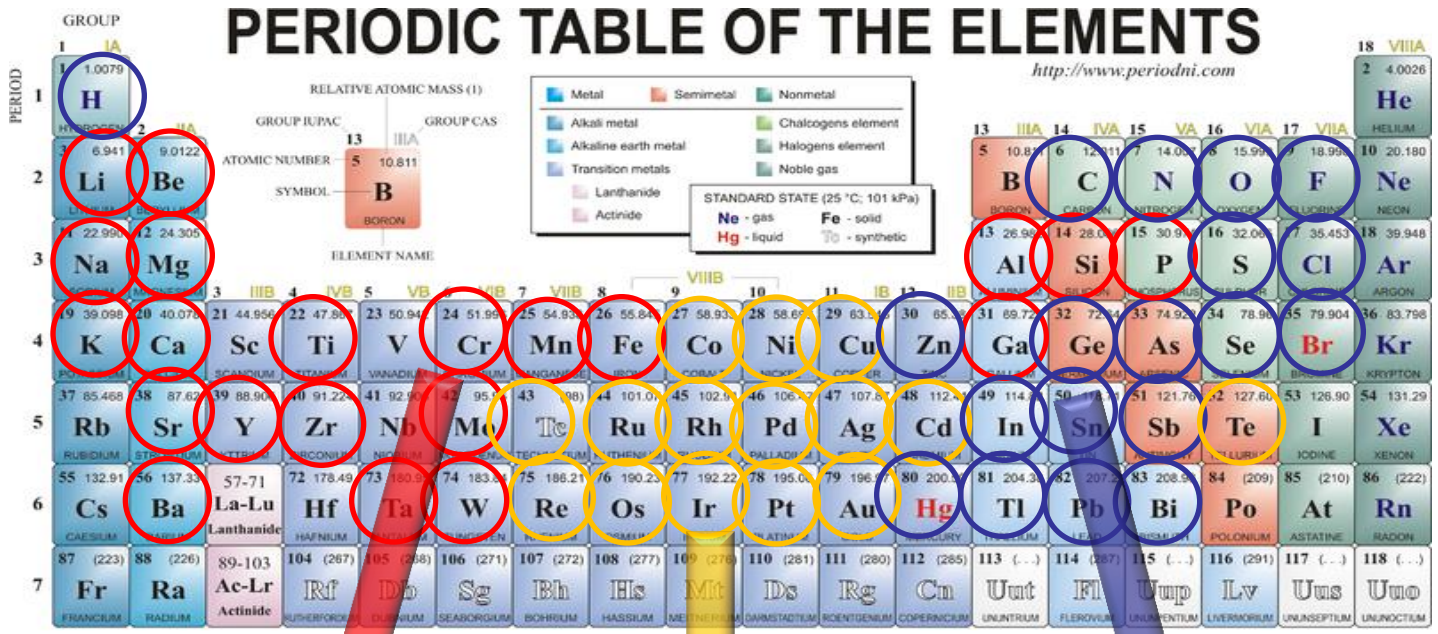
- *Fuming is about heating a material in a furnace at typically 1100-1300 °C (even higher) in order to volatilize compounds with a high vapor pressure at operating temperature : PbO, Zn, etc…*

- *Typically a reductant is used for reducing oxides into more volatile metals eg :*
  - *ZnO +CO(g) ➔ Zn (g) + CO2(g)*

- *Fuming process separates the raw material treated in 2 or possibly 3 phases :*
  - *Slag where non volatile compounds collect : Fe0,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*



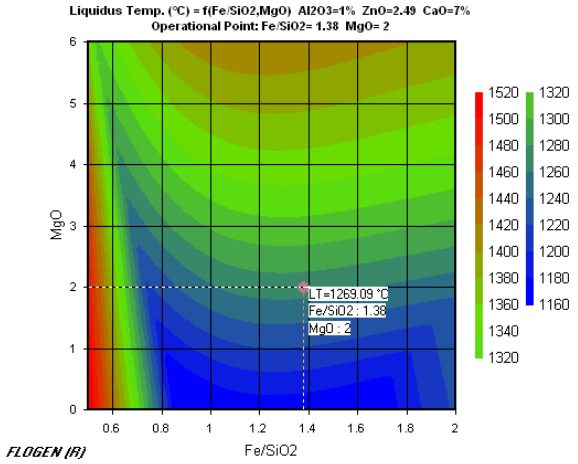
Elements collected essentially into slag

Elements collected essentially in Matte phase

Elements collected essentially into fume

Basis principles

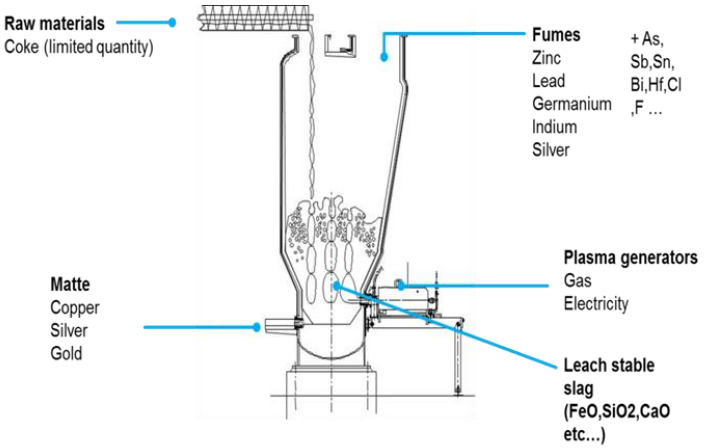
- *Operating Temperature*
  - *Kinetics (vapor pressure of volatile components)*
  - *Refractory / slag freeze lining*
- *Slag chemistry*
  - *Melting point*
  - *Content FeII ; Fe° :*
    - *2 FeO+ZnO ➔ Zn(g) + Fe_2O_3*
    - *Fe + ZnO ➔ Zn(g) + Fe0*
  - *Basicity : facilitates fuming by increasing activity of ZnO*



- *Furnace atmosphere : PO_2, PS_2 …*
  - *Low PO_2 required for Zinc fuming*
  - *PS_2 for production of matte*

- *Feed preparation:*
  - *Fluxes : CaO, MgO, SiO2 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.*

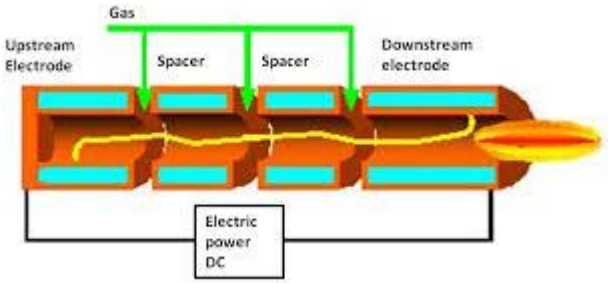
BuLP fuming at Nyrstar Hoyanger

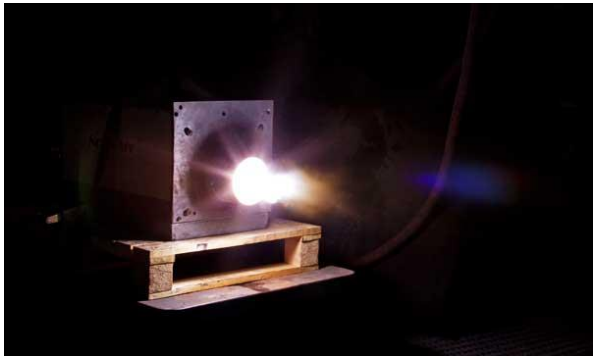


- Acquisition by Nyrstar in December 2013.
- 3X2,5 MW submerged plasma fumer.
- Treatment of EAF dust until 2014 – adaptation of plant to the treatment of BuLP as from 2015
- Production of :
  - Fume with Pb,Zn,(Ag) & minor metals for further treatment in Nyrstar Europe facilities
  - Matte for sale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

Why choosing submerged plasma technology ?

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





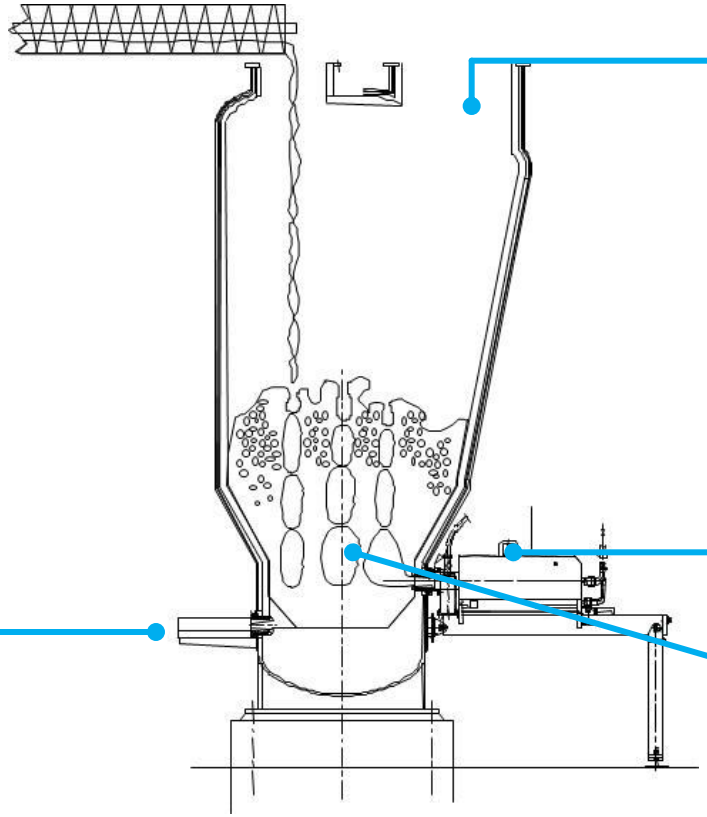
- Submerged plasma technology offers key benefits :
  - High fuming kinetics linked to high agitation of molten bath an high temperatures in the neighborhood of plasma torches.
  - Ability to recover gold silver and copper in a matte phase, next to volatile metals recovered in fume.
  - Possibility to 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

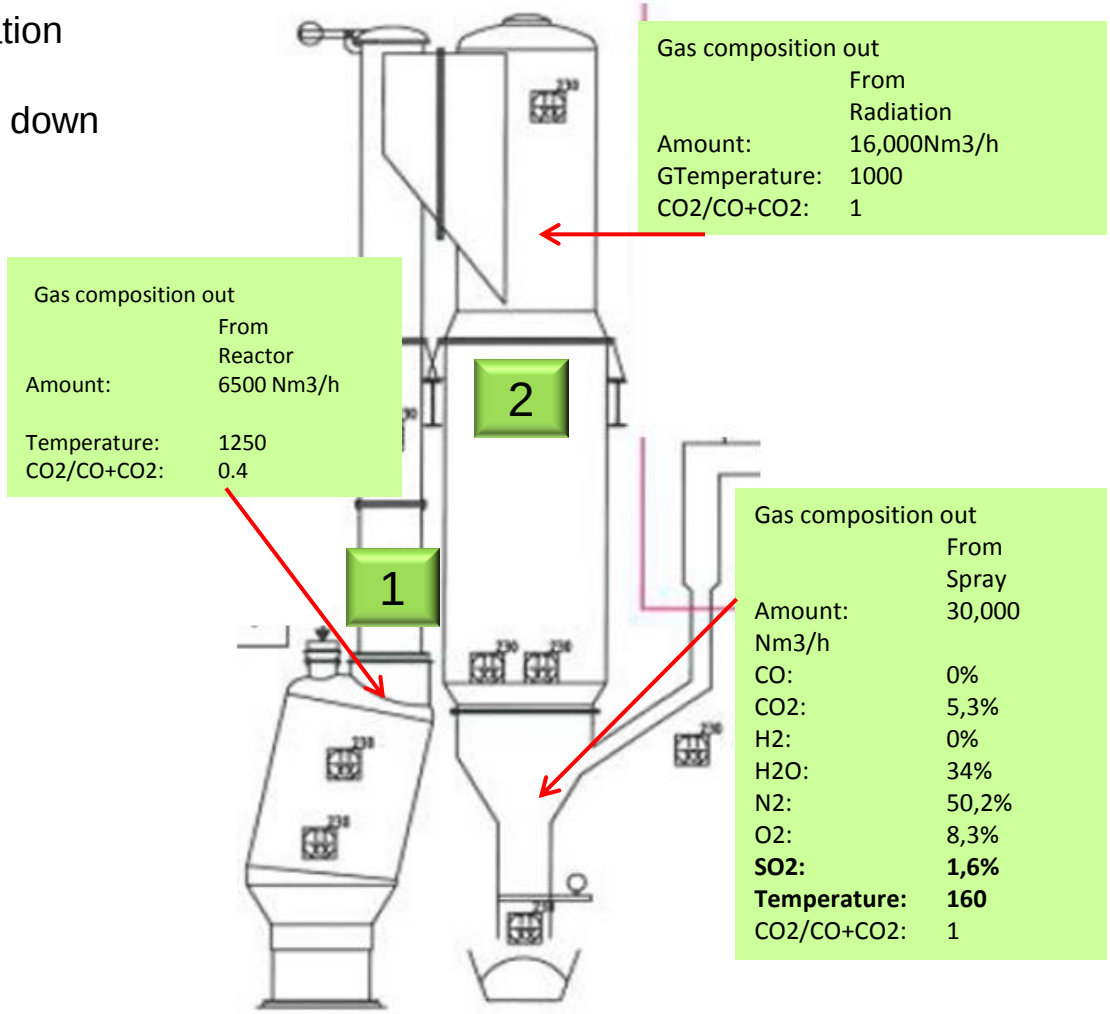
Matte
Copper
Silver
Gold

Leach stable slag (FeO,SiO2,CaO etc…)

- 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.

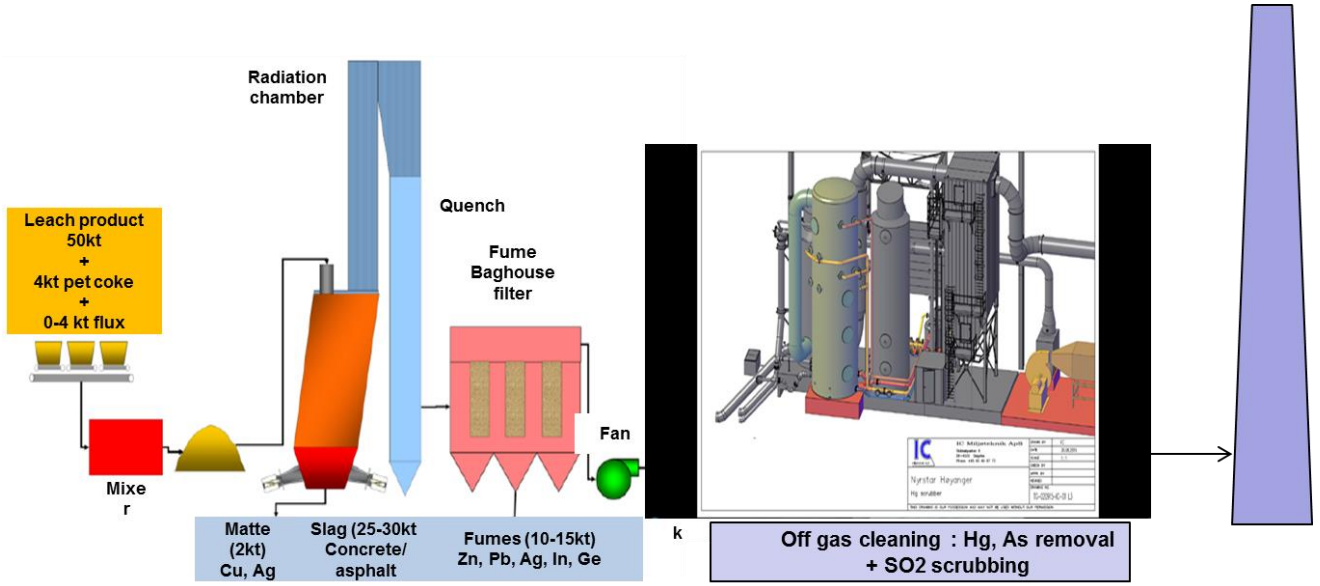
Treating BuLP in a plasma furnace : off gas cooling

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

Treating BuLP in a plasma furnace : BAT off gas treatment



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 wwtp designed for it (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 by products 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.