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Norwegian University of Science and Technology

Precipitation of iron oxides in zinc and nickel production

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Main objectives

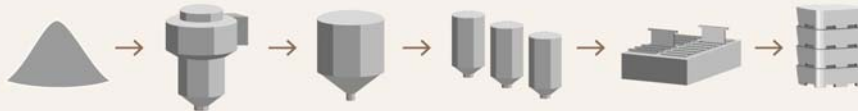
- Better understanding of iron precipitation
- Remove impurities – Boliden Odda
- Better filterability – Glencore Nikkelverk



Zinc production

Zinc smelters

The zinc process comprises five main stages including roasting, leaching, purification and electrowinning, before the finished zinc is smelted and cast into ingots. Zinc smelters are extremely energy-intensive.



Metal concentrate
Metal concentrate from mines usually comprises approximately 50 per cent zinc.

Roasting
The concentrate is roasted in a furnace in order to remove the sulphur. The result is what is known as calcine, which comprises approximately 60 per cent zinc. The so-called direct leaching method enables the roasting stage to be eliminated.

Leaching
The calcine is leached with sulphuric acid in order to precipitate out and filter off the iron content. The result is a zinc sulphate solution with small amounts of impurities.

Purification
The zinc sulphate solution is purified in three stages to remove any copper, cobalt, nickel and cadmium, after which it contains approximately 150 grams of zinc per litre of solution.

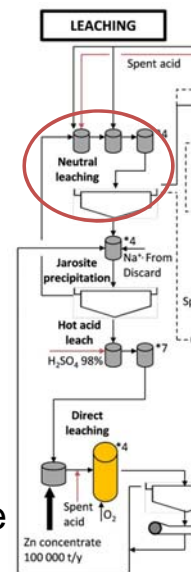
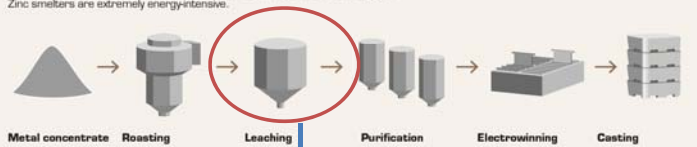
Electrowinning
The zinc is precipitated out of the solution by means of electrowinning. The result is zinc cathodes with a zinc content of 99.995 per cent.

Casting
The zinc is then cast to form zinc ingots and sold as pure zinc or alloyed to form zinc alloys in line with specific customer requirements.



Zinc smelters

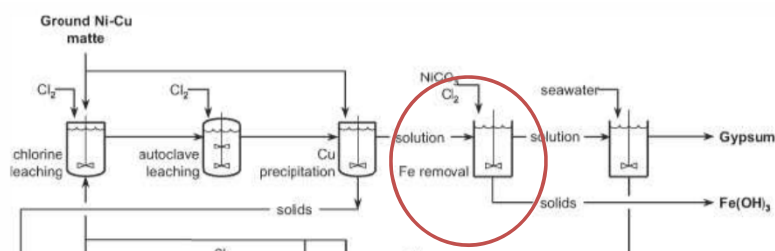
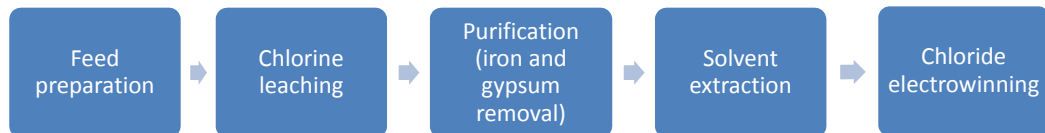
The zinc process comprises five main stages including roasting, leaching, purification and electrowinning, before the finished zinc is smelted and cast into ingots. Zinc smelters are extremely energy-intensive.



- Cathode sticking problem
 - Corrosion of cathodes
- Desirable to improve removal of fluoride and increase cathode lifetime
- Removal of fluoride with iron precipitate in the neutral leaching



Nickel production



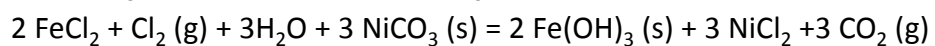
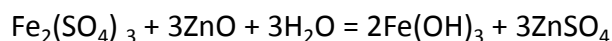
- Better filterability is desirable

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Precipitation of iron oxides

- Complex
- Many different iron oxides
 - Fe(II) and Fe(III)
 - Crystalline, amorphous, nanocrystalline
- Typical iron oxides in zinc and nickel production?



Species	Formula
Magnetite	Fe_3O_4
Hematite	$\alpha\text{-Fe}_2\text{O}_3$
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Goethite	$\alpha\text{-FeOOH}$
Akageneite	$\beta\text{-FeOOH}$
Lepidocrocite	$\gamma\text{-FeOOH}$
Bernalite	$\text{Fe}(\text{OH})_3$
Wustite	FeO
Feroxyhyte	$\delta\text{-FeOOH}$
Ferrihydrite	

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Fluoride adsorption

- Results from SINTEF – even distribution of fluoride on the precipitate
 - Adsorption?
- Literature research
 - Iron hydroxides as adsorbent for fluoride in water treatment*
- Mechanism
 - Adsorption (chemisorption) $\equiv\text{FeOH}^{-1/2} + \text{F}^{-1}(\text{aq}) + \text{H}^{+}(\text{aq}) \rightleftharpoons \text{FeF}^{-1/2} + \text{H}_2\text{O}(\text{l})$
 - Ligand exchange** $\equiv\text{Fe}_2\text{OH}^0 + \text{F}^{-1}(\text{aq}) + \text{H}^{+}(\text{aq}) \rightleftharpoons \text{Fe}_2\text{F}^0 + \text{H}_2\text{O}(\text{l})$
- Important factors
 - pH
 - Surface area
 - Type of iron oxide
 - Competing anions

*Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E., & Singh, P. (2009). Review of fluoride removal from drinking water. *Journal of Environmental Management*, 91(1), 67-77.

**Ding, X. (2012). Identity of Fluoride and Phosphate-Binding Sites at FeOOH Surfaces.

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Fluoride adsorption

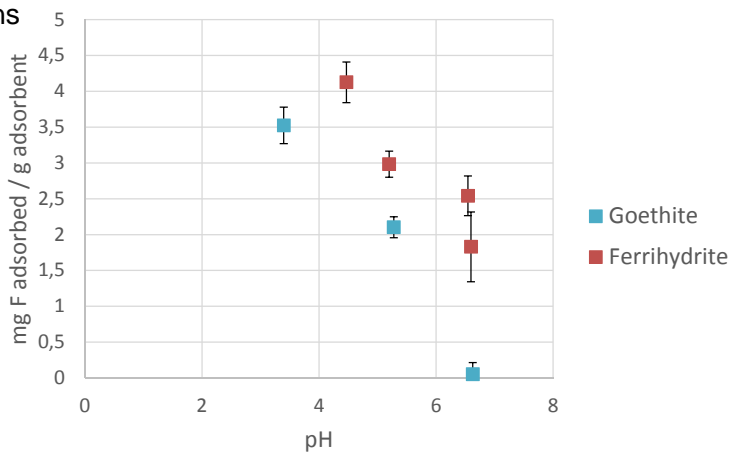
- Two different synthetic iron oxides
 - Goethite
 - Crystalline
 - Low surface area (35 m²/g)
 - Ferrihydrite
 - Amorphous/nanocrystalline
 - High surface area (272 m²/g)

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Fluoride adsorption

- Effect of pH and adsorbent
- Surface area **not** taken into account
- Experimental conditions
 - T=25 °C
 - 10 g/L fluoride
 - 2 g/L adsorbent



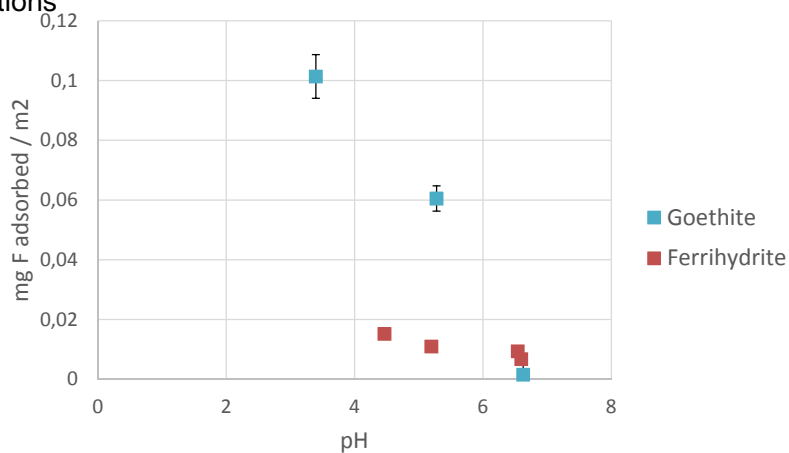
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Fluoride adsorption

- Effect of pH and adsorbent
- Surface area **taken** into account
- Experimental conditions
 - T=25 °C
 - 10 g/L fluoride
 - 2 g/L adsorbent

Sample	BET surface area (m ² /g)
Goethite	35
Ferrihydrite	272



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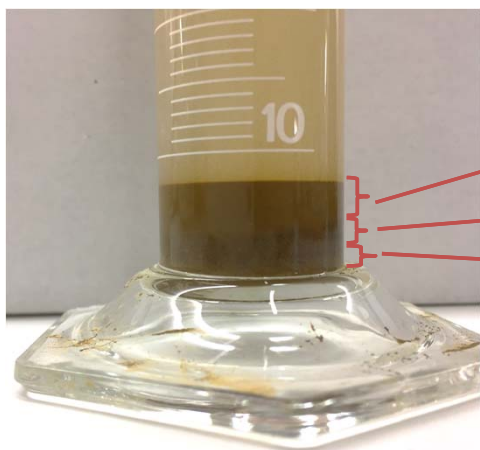
Characterisation of industrial samples – Boliden

- Samples from the neutral leaching
 - NLT2
 - NLT5
 - Settler

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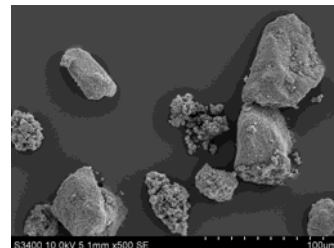
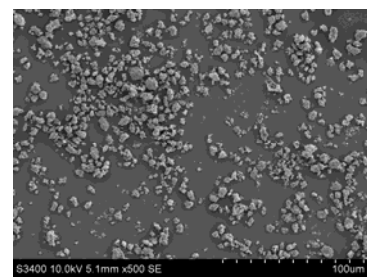
Characterisation of industrial samples – Boliden



Top layer

Middle layer

Bottom layer

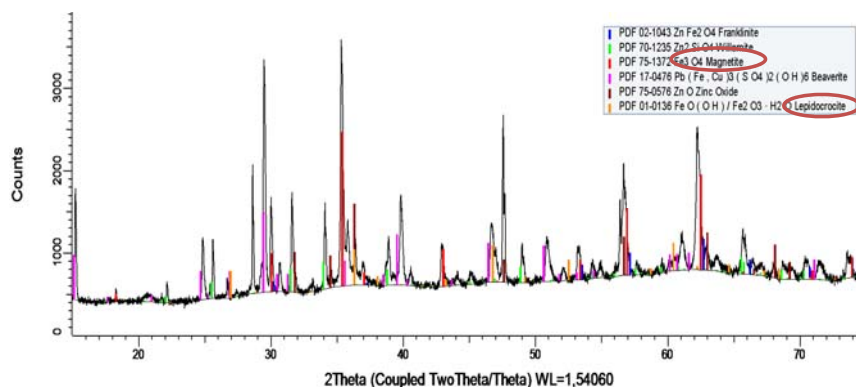


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Characterisation of industrial samples – Boliden

- XRD - Top and middle layer

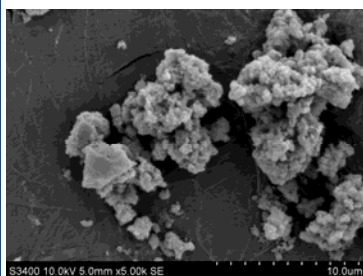


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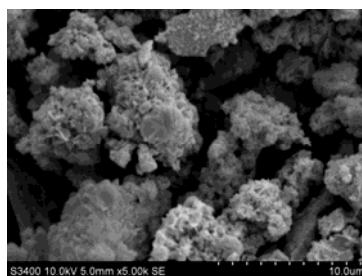


Characterisation of industrial samples – Boliden

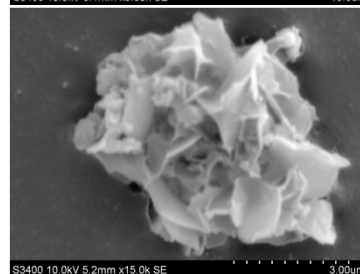
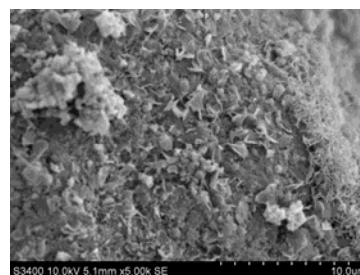
- SEM – Top and middle layer



NLT2



NLT5



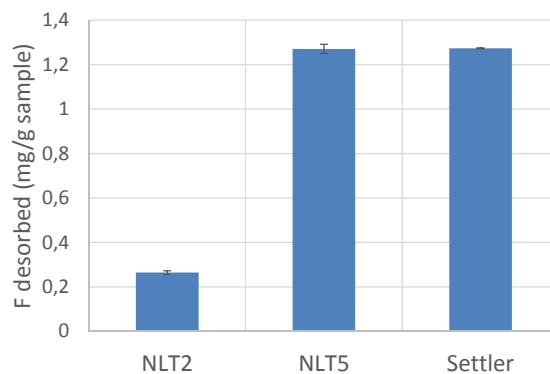
Settler

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Characterisation of industrial samples – Boliden

- Fluoride desorption



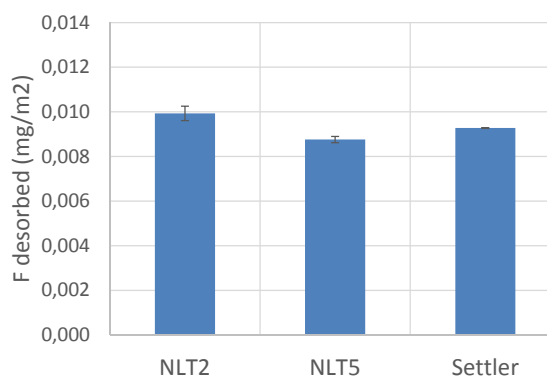
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Characterisation of industrial samples – Boliden

- Fluoride desorption – surface area taken into account

Sample	BET surface area (m ² /g)
NLT2	27
NLT5	145
Settler	137

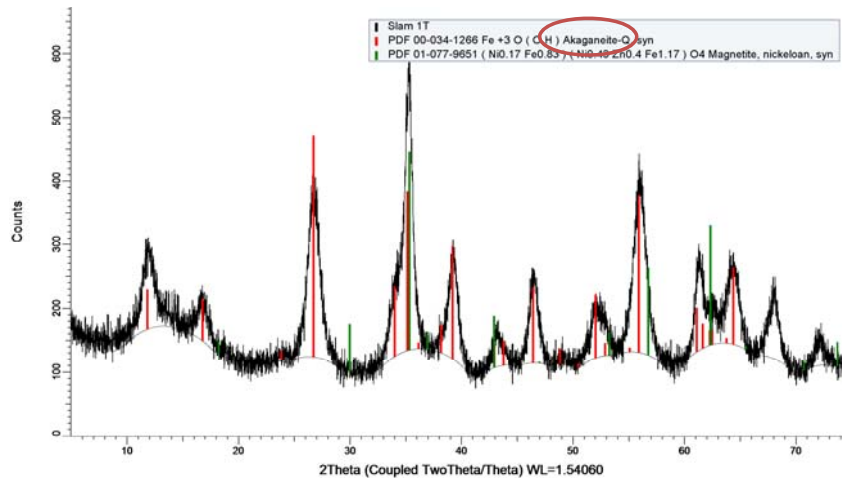


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Characterisation of industrial samples – Glencore

- XRD



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Iron precipitation in nickel production

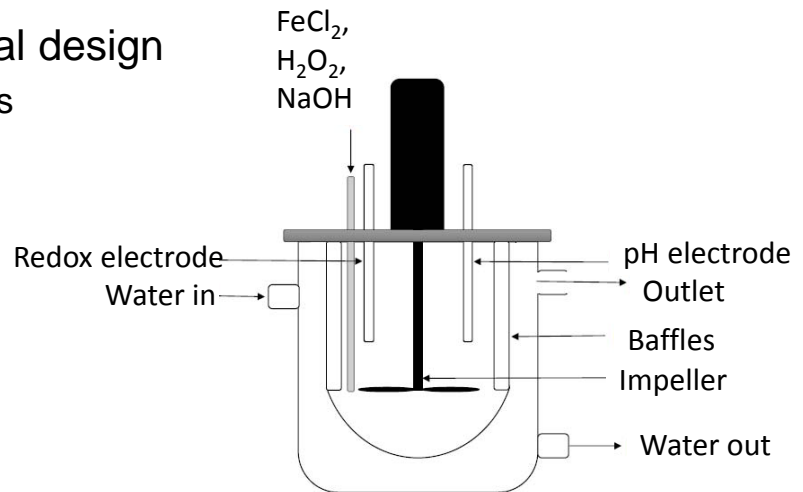
- Filterability
- Particle size
- Important factors
 - Temperature
 - Supersaturation
 - Oxidation from Fe(II) to Fe(III)

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Iron precipitation in nickel production

- Experimental design
 - Continuous



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Thank you!
Questions?

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