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Norwegian University of Science and Technology

Precipitation of iron oxides in zinc and nickel production

HYDROMET seminar, Lillestrøm 07.03.17
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Main objectives

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

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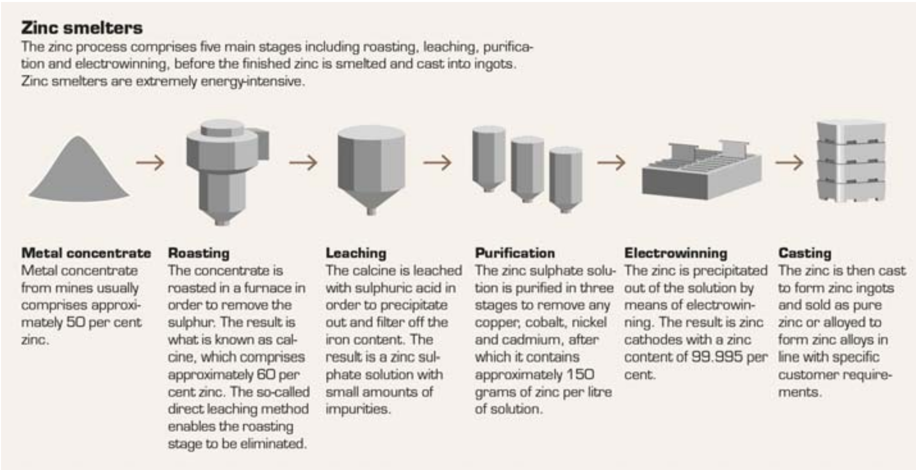
Zinc production



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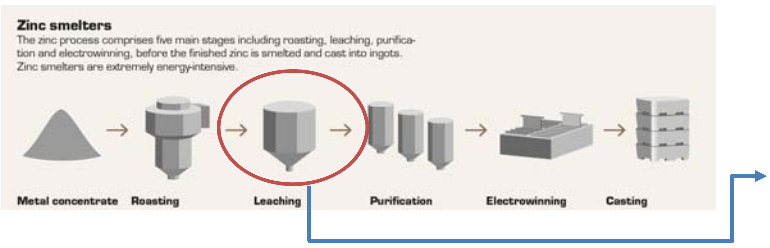

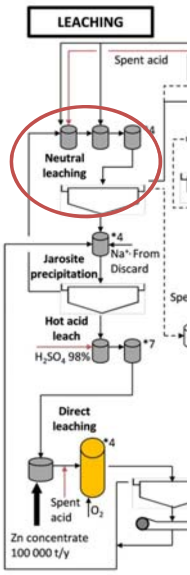

- Cathode sticking problem
  - Corrosion of cathodes
- Desirable to improve removal of fluoride and increase cathode lifetime
- Removal of fluoride with iron precipitate in the neutral leaching

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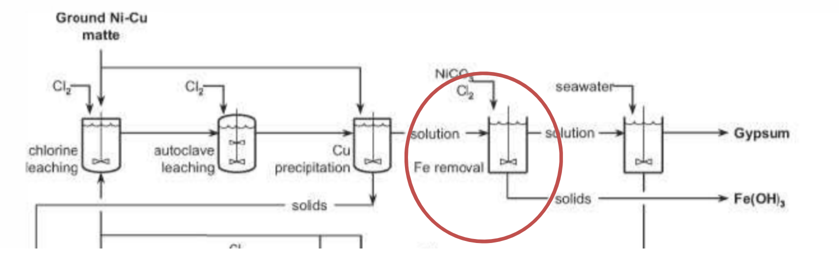
Nickel production

Feed preparation → Chlorine leaching → Purification (iron and gypsum removal) → Solvent extraction → Chloride electrowinning



- 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	α-Fe_2O_3
Maghemite	γ-Fe_2O_3
Goethite	α-FeOOH
Akageneite	β-FeOOH
Lepidocrocite	γ-FeOOH
Bernalite	$Fe(OH)_3$
Wustite	FeO
Feroxyhyte	δ-FeOOH
Ferrihydrite	

$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = 2Fe(OH)_3 + 3ZnSO_4$$

$$2\ FeCl_2 + Cl_2\ (g) + 3H_2O + 3\ NiCO_3\ (s) = 2\ Fe(OH)_3\ (s) + 3\ NiCl_2 + 3\ CO_2\ (g)$$

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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)
  - Ligand exchange**

$$\equiv FeOH^{-1/2} + F^{-1}(aq) + H^{+}(aq) \rightleftharpoons FeF^{-1/2} + H_2O(l)$$

$$\equiv Fe_2OH^{0} + F^{-1}(aq) + H^{+}(aq) \rightleftharpoons Fe_2F^{0} + H_2O(l)$$

- 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 m^2/g)
  - Ferrihydrite
    - Amorphous/nanocrystalline
    - High surface area (272 m^2/g)

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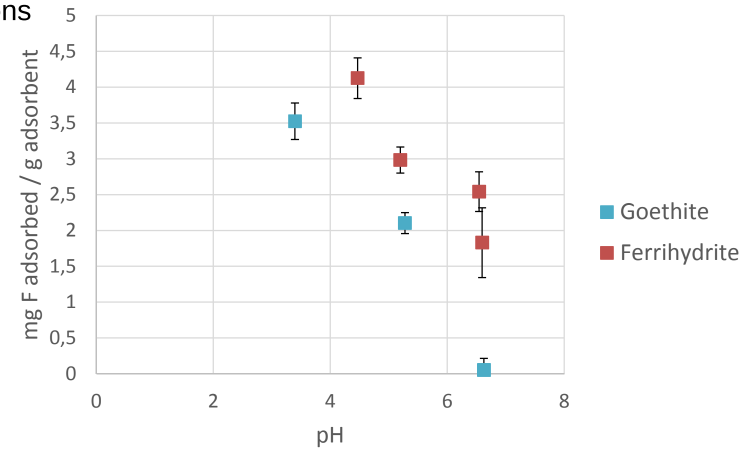
Fluoride adsorption

- 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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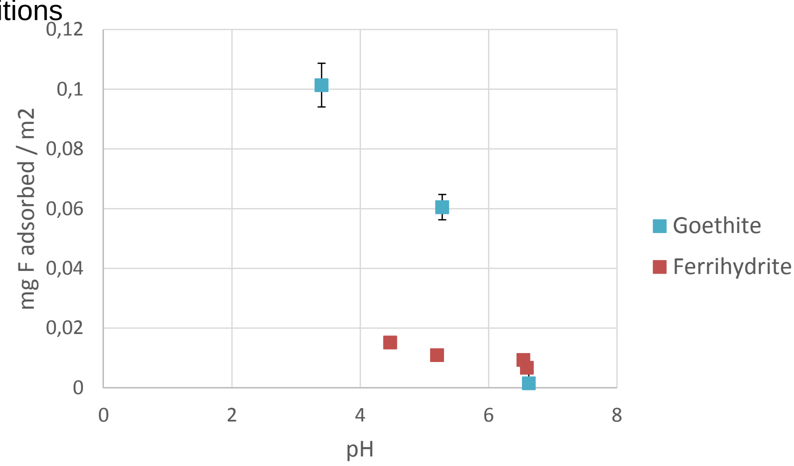
Fluoride adsorption

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

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



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Characterisation of industrial samples – Boliden

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

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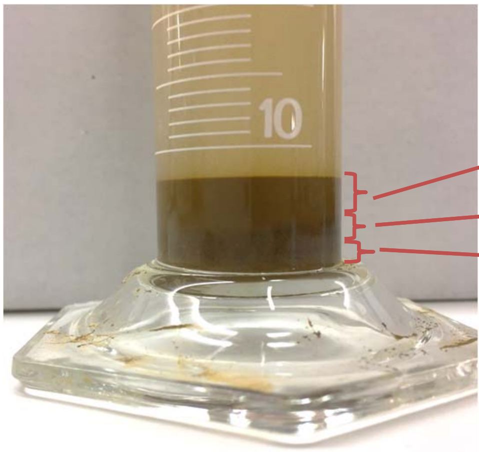
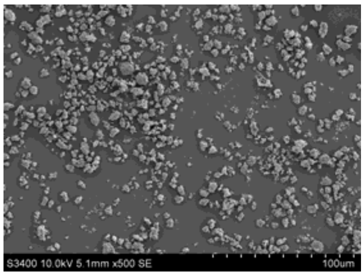
Characterisation of industrial samples – Boliden

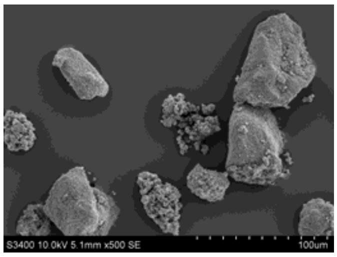


Top layer

Middle layer

Bottom layer





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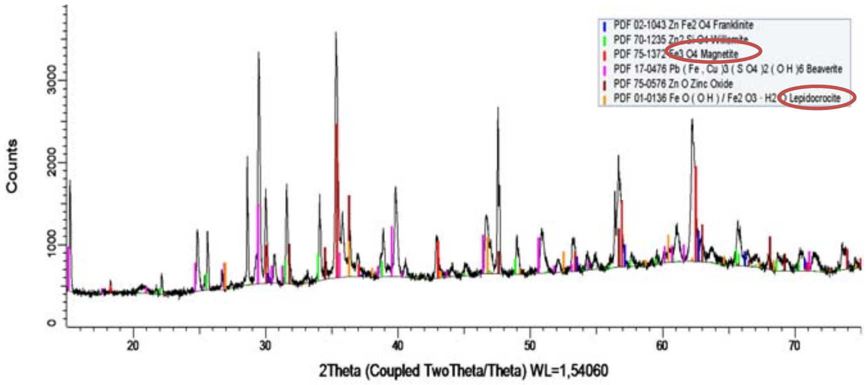
Characterisation of industrial samples – Boliden

- XRD - Top and middle layer



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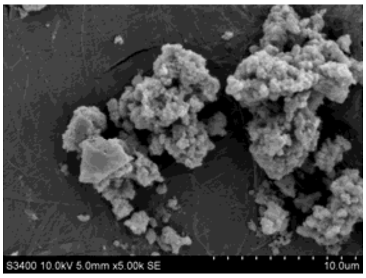
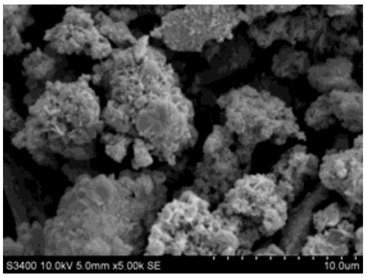
Characterisation of industrial samples – Boliden

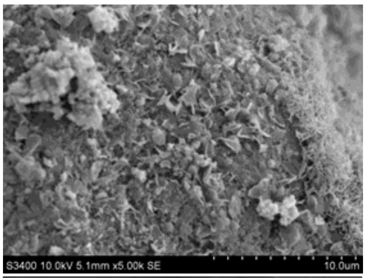
- SEM – Top and middle layer

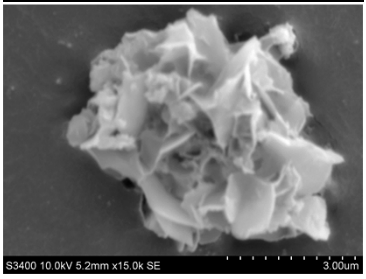


NLT2



NLT5





Settler

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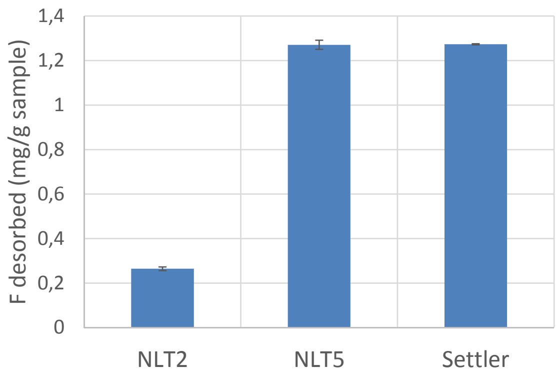
Characterisation of industrial samples – Boliden

- Fluoride desorption



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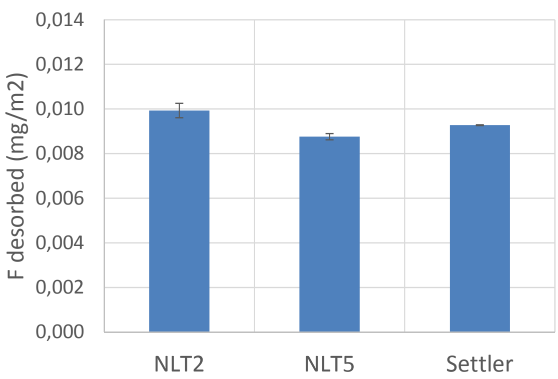
Characterisation of industrial samples – Boliden

- Fluoride desorption – surface area taken into account

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



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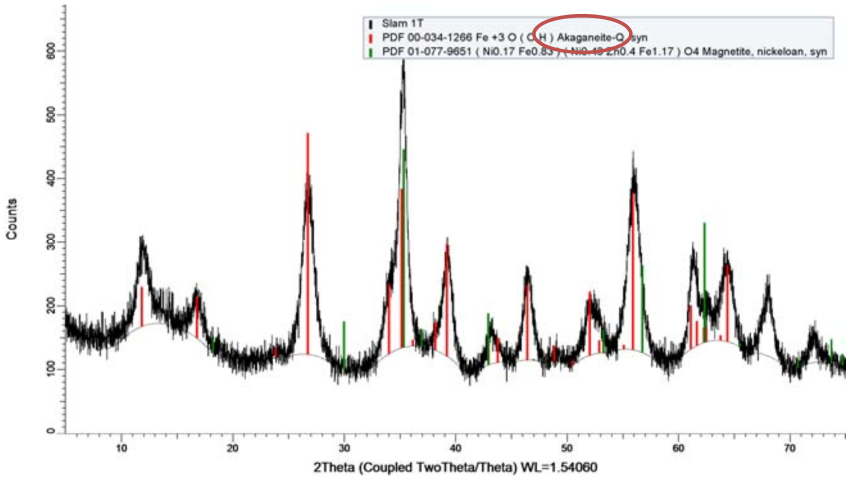
Characterisation of industrial samples – Glencore

- XRD



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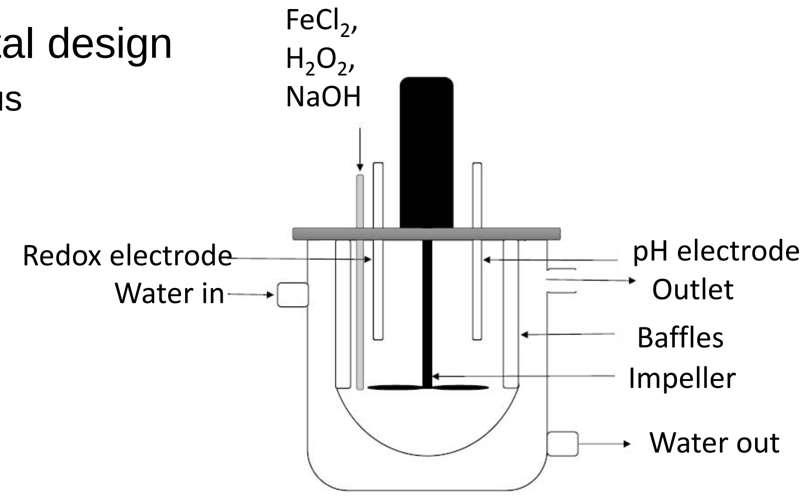
Iron precipitation in nickel production

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

Iron precipitation in nickel production

- Experimental design
  - Continuous



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Thank you!

Questions?

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