Shortened online version – for further information contact sander.arnout@inspyro.be

# Applications of thermodynamics in rare earth recycling research

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InsPyro

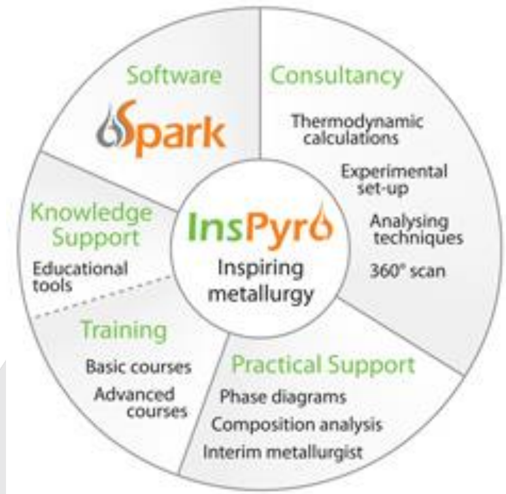
# Introduction: InsPyro

B2B consultancy company

KU Leuven spin-off (2009)

Founded and run by PhD's

- Process development & improvement through:
  - Modelling and literature
  - Experiments
  - Characterization
  - Industrial experience
- Industries:
  - Recycling incl. batteries and residues
  - Non-ferrous metallurgy (lead-zinc)
  - Steel, cast iron and ferro-alloys
- www.inspyro.be

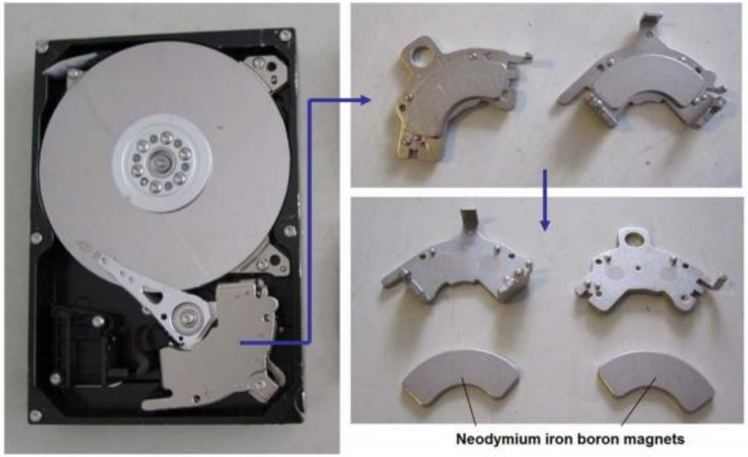



# Rare earth recycling and thermodynamics

- Thermodynamic approach highly successful in understanding and predicting high temperature processes
- Several high temperature processes under investigation for rare earths
- Requirement: databases of relevant phases (Gibbs free energy of solids, solutions,...)

# Example: EREAN project

- Focus on magnets
  - Electric motors
    - Windmills
    - Cars
  - Hard disk drives
- Balance problem
  - Nd and Dy highly wanted




Source: Öko-Institut

# The balance problem

| | REE | Bastnasite Mountain Pass, USA | Bastnasite Bayan Obo, China | Monazite Mt. Weld, Australia | Xenotime Lehat, Malaysia | High Y RE laterite Longnan, China | Low Y RE laterite Xunwu, China | Loparite Kola Peninsula Russia |
|---|---|---|---|---|---|---|---|---|
| Light REE | La | 33.8 | 23.0 | 25.5 | 1.2 | 1.8 | 43.4 | 25.0 |
| | Ce | 49.6 | 50.0 | 46.7 | 3.1 | 0.4 | 2.4 | 50.5 |
| | Pr | 4.1 | 6.2 | 5.3 | 0.5 | 0.7 | 9.0 | 5.0 |
| | Nd | 11.2 | 18.5 | 18.5 | 1.6 | 3.0 | 31.7 | 15.0 |
| | Sm | 0.9 | 0.8 | 2.3 | 1.1 | 2.8 | 3.9 | 0.7 |
| HeavyREE | Eu | 0.1 | 0.2 | 0.4 | Trace | 0.1 | 0.5 | 0.1 |
| | Gd | 0.2 | 0.7 | <0.1 | 3.5 | 6.9 | 3.0 | 0.6 |
| | Tb | 0.01 | 0.1 | <0.1 | 0.9 | 1.3 | Trace | Trace |
| | Dy | 0.03 | 0.1 | 0.1 | 8.3 | 6.7 | Trace | 0.6 |
| | Ho | 0.01 | Trace | Trace | 2.0 | 1.6 | Trace | 0.7 |
| | Er | 0.01 | Trace | Trace | 6.4 | 4.9 | Trace | 0.8 |
| | Tm | 0.01 | Trace | --- | 1.1 | 0.7 | Trace | 0.1 |
| | Yb | 0.01 | Trace | --- | 6.8 | 2.5 | 0.3 | 0.2 |
| | Lu | Trace | Trace | --- | 1.0 | 0.4 | 0.1 | 0.2 |
| | Y | 0.1 | Trace | <0.1 | 61.0 | 65.0 | 8.0 | 1.3 |

Source: K. Binnemans, KU Leuven

# Rare earth alloys

- Application of rare earths in alloys
  - Database for aluminium alloys containing rare earths
  - Database for magnesium alloys containing rare earths

| Al Alloys |
|---|
| Ag, Al, As, Au, B, Ba, Be, Bi, C, Ca, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, H, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, N, Na, Nb, Nd, Ni, O, P, Pb, Pr, S, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Ti, Tm, V, W, Y, Yb, Zn, Zr |
| **Mg Alloys** |
| Ag, Al, B, Ba, Be, Bi, C, Ca, Ce, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ge, H, Ho, In, K, La, Li, Lu, Mg, Mn, Na, Nd, Ni, Pb, Pr, Sb, Sc, Si, Sm, Sn, Sr, Tb, Ti, Tm, V, Y, Yb, Zn, Zr |

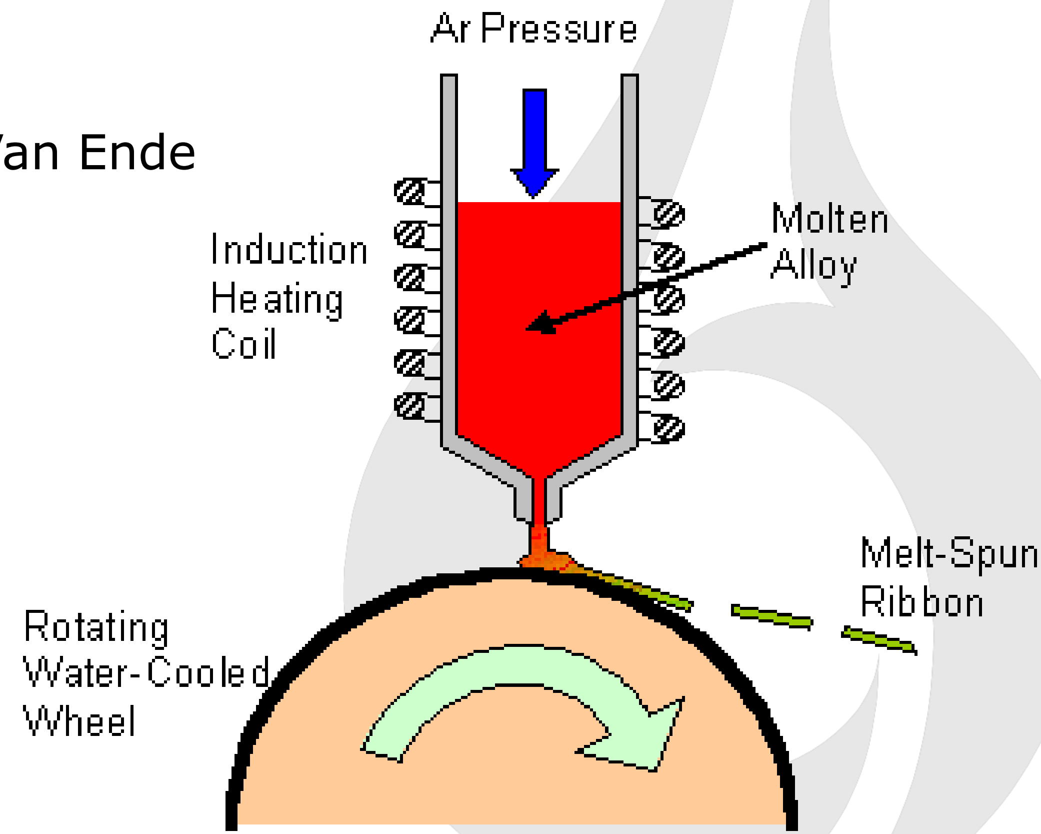
  - Limited interactions in iron and zinc based systems
    - E.g. Fe-Dy-Tb
    - E.g. Fe-Nd-B

# Rare earth alloys

- Fe-Nd-B system relevant to magnets

E.g. Assessment by M.A. Van Ende

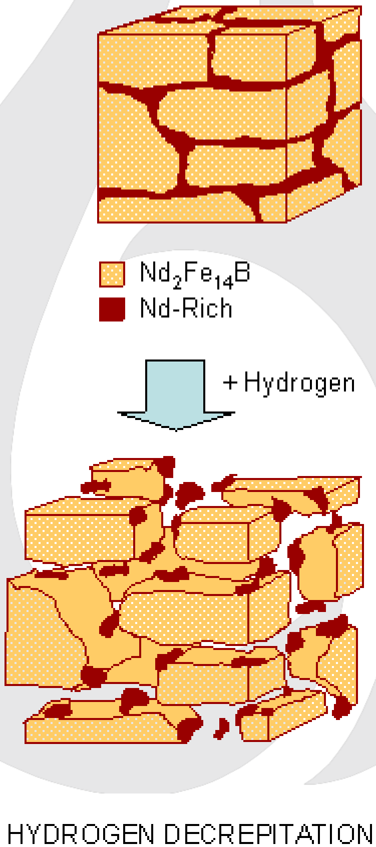
Solidification trajectory
Scheil / equilibrium



# Solidification of Fe-Nd-B alloy

Equilibrium cooling

Scheil cooling



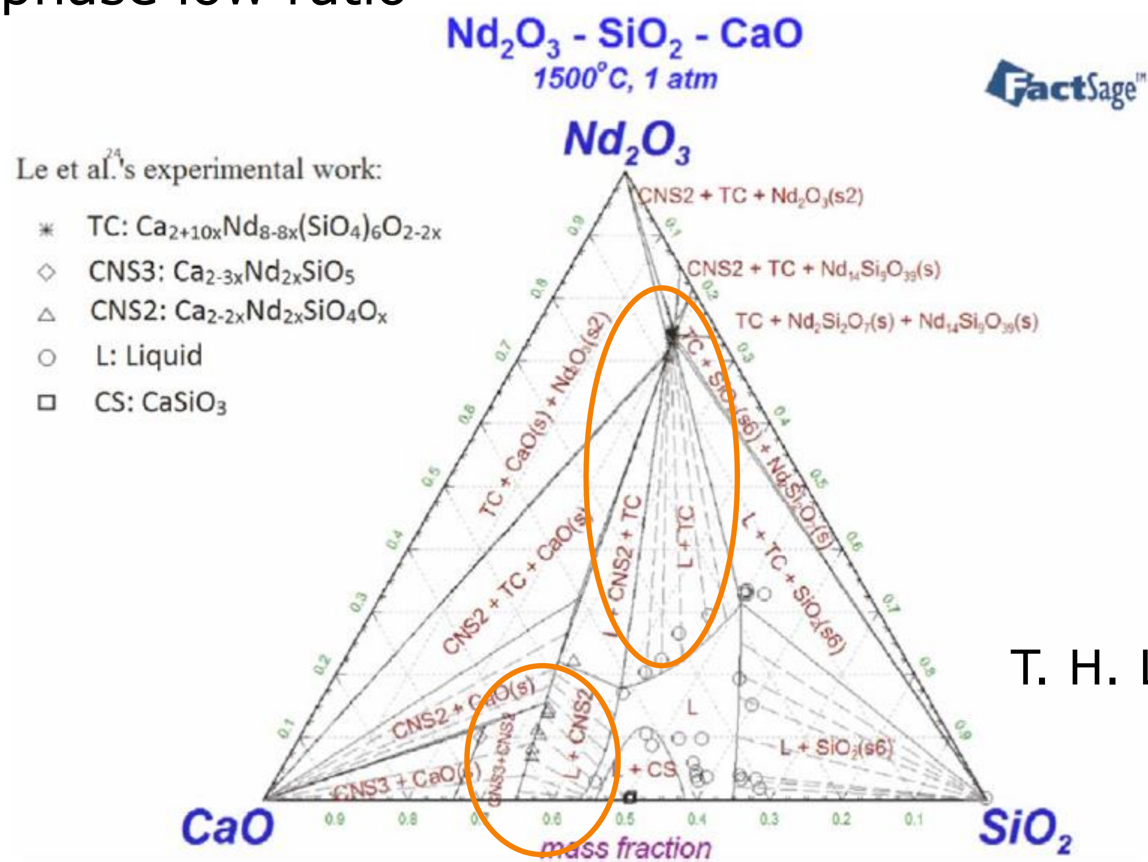

Substitution, hydrogen decripitation:
Database has no Ce, no H

# Rare earths in slag

- Limited databases available
  - $Al_2O_3$-REO
- Behaviour in silicate slags: focus on Nd
  - T.H. Le:
  - Phase Relations of the CaO-SiO2-Nd2O3 System and the Implication for Rare Earths Recycling, Met Trans B
  - Thermodynamic assessment of the Nd2O3-CaO-SiO2 ternary system, Calphad

# Slag upgrading using solubility

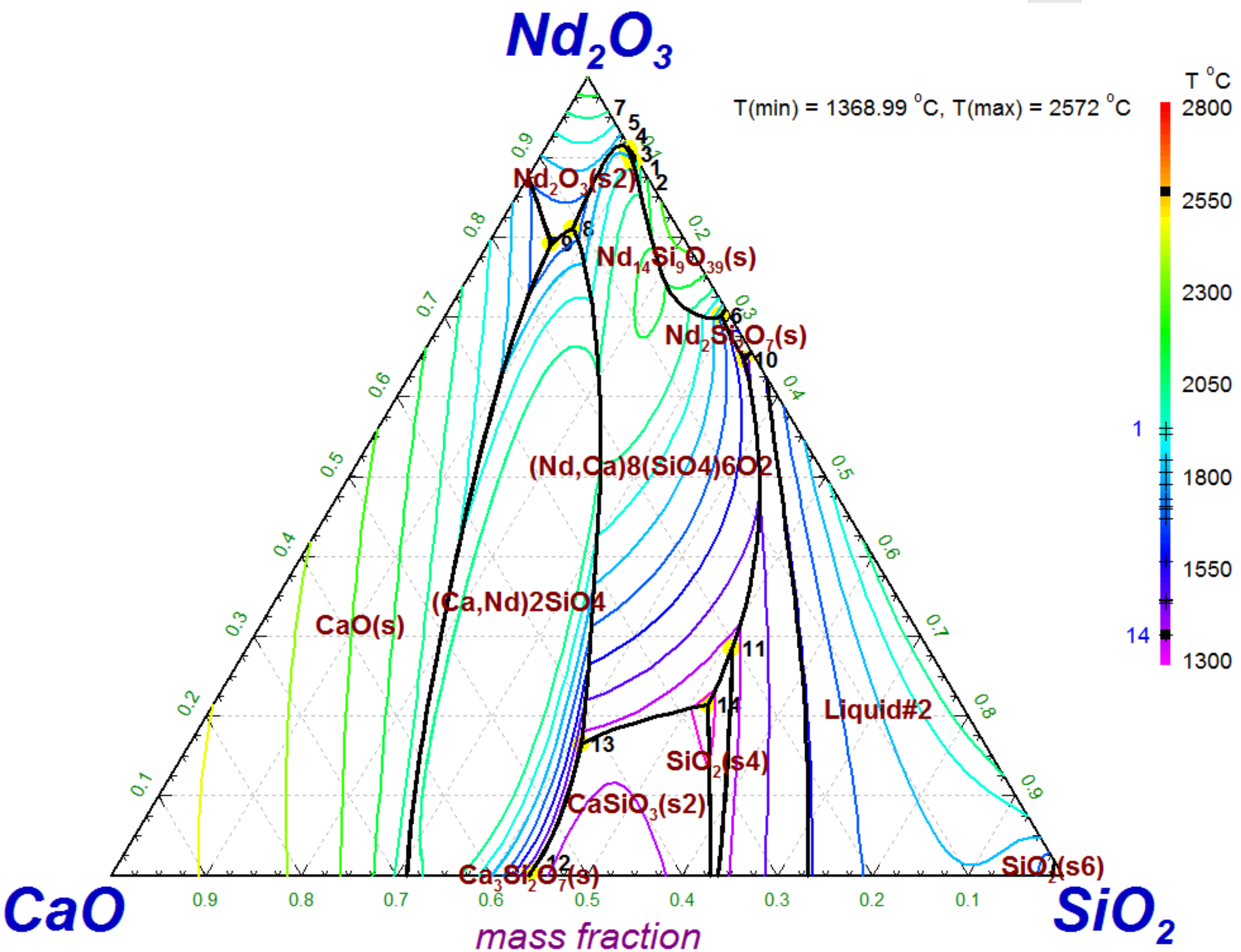
- Ideal: L+S domain with large ratio of Nd
- Real:
  - High Nd phase, but high solubility
  - $C_2S$ phase low ratio




T. H. Le, Calphad paper

# Rare earths in slag

- Behaviour in silicate slags: focus on Nd (T.H. Le)

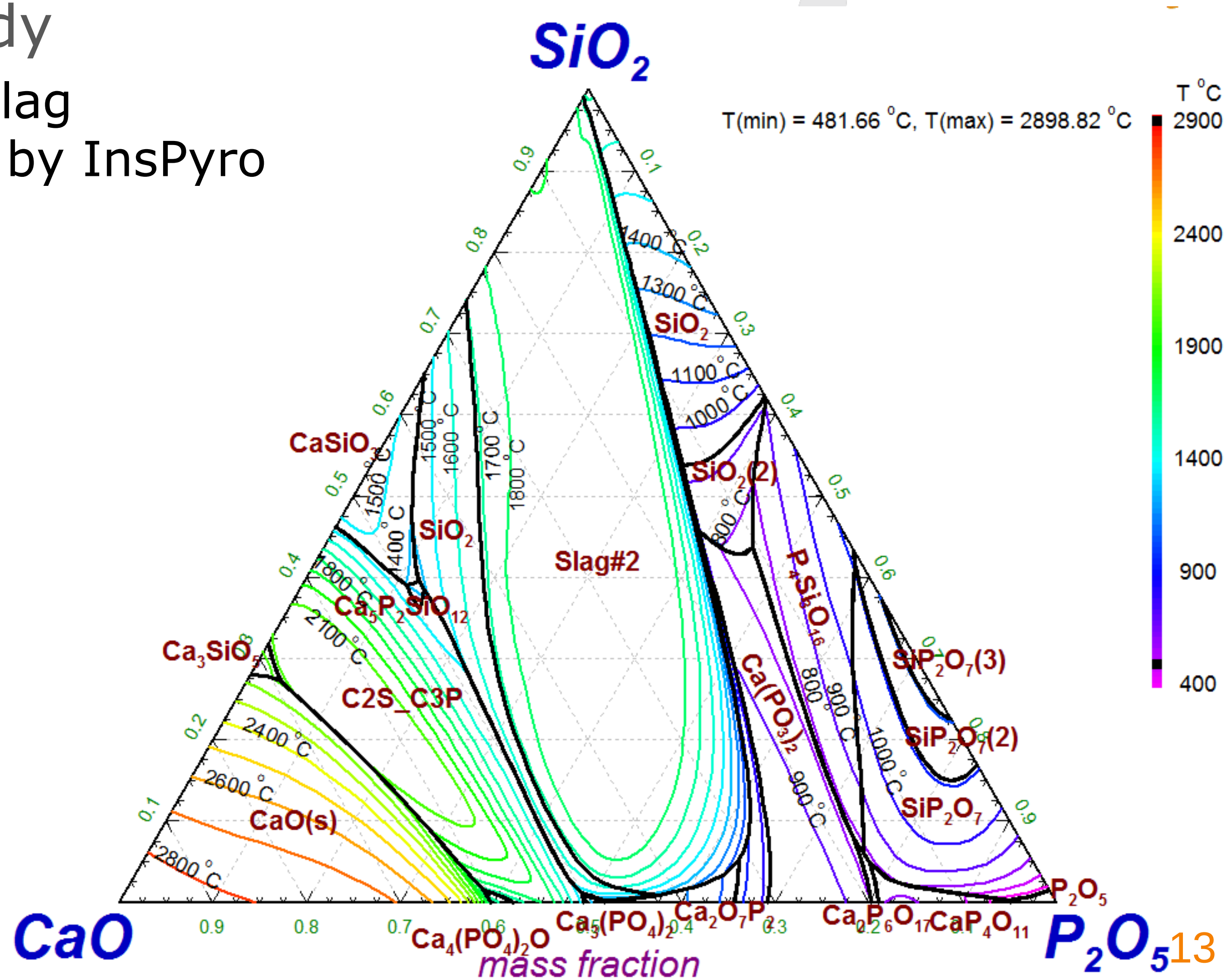


# NTNU work on apatite concentrate

- Apatite concentrate
- REE content not so large, but left in slag after removal of P, and possibly $CaC_2$
- Thermodynamic estimation of process
- M.W. Kennedy et al. Pyrometallurgical Treatment of Apatite Concentrate with the Objective of Rare Earth Element Recover, J. Sustainable Metallurgy

# Rare earth concentration in slags

- Apatite smelting process proposed by T. Sun and M.W. Kennedy
  - Phosphate slag calculations by InsPyro



# Other processes

- Roasting + leaching processes (e.g. M.R. Onal):
  - Sulphates: some solids are available
  - Chlorides: some solids are available
  - Nitrates: ?
  - To be checked whether all is consistent
  - Aqueous database (Thereda) focus on actinides (heavy REE)

- High-temperature electrolysis
  - RE oxides and salts in liquid salt systems
  - System Li,Mg,Ca,La,Ce,Nd//F: mainly binary systems
  - System Li,Mg,Ca,La,Ce,Nd//Cl: mainly binary systems
  - ReCl3-ReF3 (Re = La,Ce,Nd): approximately optimized

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