Art of metal making: science or alchemy?

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Outotec
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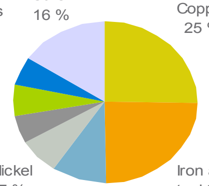
Outline

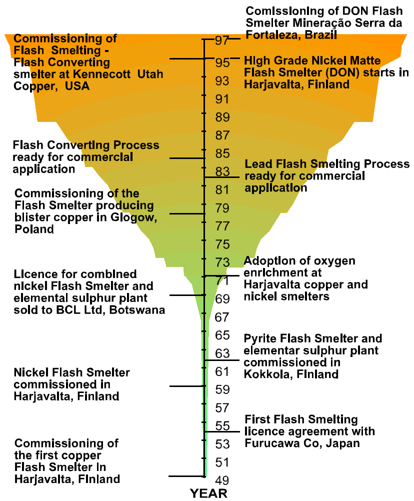
- Outotec Oyj
- Outotec Research Oy
- Metals as a natural resource
- Some key skills in technology development
  - chemical equilibria and reactions
  - reactor dynamics
  - properties of construction materials in use

Outotec Oyj

- A new listed company – former technology division of Outokumpu Oyj
- 1800 persons in 18 countries
- Turnover >1 b€ (est. 2007)



OT: Technology sales by metal 2007



Milestones of Flash Smelting: 'the invention of 20th century in metallurgy' (American Society for Metals)

Outotec Research Oy

- Location: Pori – 'sister R&D unit' in Frankfurt
- 165 employees (25 PhD level scientists)
- Research facilities:
  - 8 laboratories
  - 2 bench scale pilots
  - Pyro- and hydrometallurgical pilot plants
  - HydroCopper® demonstration plant
- Expertise area:
  - process and equipment development (low & high temperature)

ORC: Core and generic competencies

Core competencies

- **Mineral technology**
- **Extractive metallurgy of base metals and precious metals**
- **Ferrous technology**
- **Materials technology**
- **Environmental technology**
- **Experimentation**

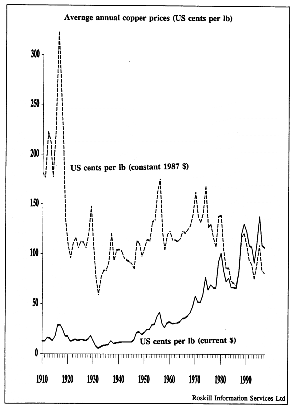
Generic competencies

Mineralogy	**Thermodynamics**	**Fluid dynamics**
Minerals processing	Analytical chemistry	Reactor techniques
Material science	**Electrochemistry**	Solvent extraction
Structure analysis	Process chemistry	Process control
Modeling and simulation	Information management	Piloting (scale up/down)

Metals as a natural resource

- Fully recyclable, without any degradation of props
- Availability secured to the next century – at least
- General trends & facts:
  - unit price lower each year
  - leaner deposits in use every year
  - increasing energy price
  - most metals are commodities – the prices are determined by daily 'auctions' (LME)

Copper

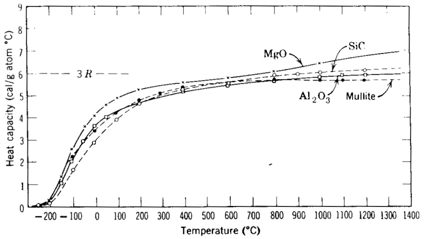


Some key skills in our technology development

- As technology and equipment developer, we must be well aware of the advancement of science in our key areas, as typically today:
  - computational methods in materials properties (thermodynamics) – modelling of fundamental materials properties (i.e. c_p, G(T,P,n), G^{ex}(T,P,x) …)
  - computational and experimental fluid dynamics
  - performance of construction materials (metals, organics, ceramics…) in demanding conditions – wear, surface scales, coatings etc. – cost vs. life
- Knowledge management and dissemination within the group is the responsibility of the R&D unit

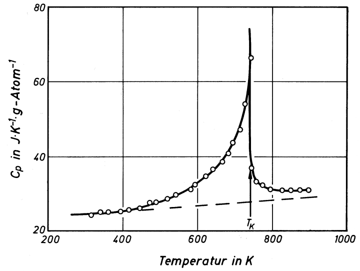
Thermodynamics-stability of substances

- Large number of thermo-dynamic stability criteria (G, F, A…)
- Only two fundamental properties can be measured:
  - heat content or enthalpy
    - heat capacity is $(\partial H/\partial T)_{p \text{ or } V}$
    - lim c = 0 as T → 0K (all crystalline substances in eq.)
  - changes in Gibbs energy in various 'transformations'



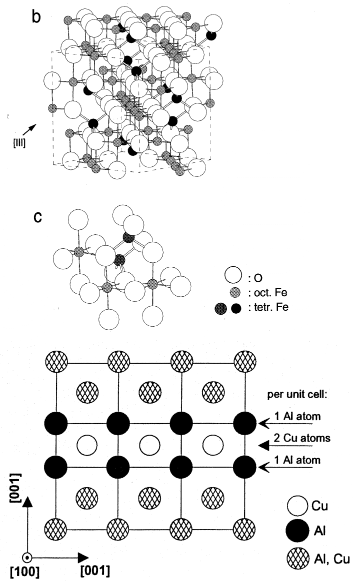
Computational methods in materials properties – thermodynamic simulation (I)

- Industrial processes are chemically complicated:
  - several components
  - a lot of phases ('substances')
- Metal making reactors - often involve hostile or dangerous environments:
  - high temperature, explosive
  - toxic, closed, etc.
- High-temperatures allow fast material transport-equilibrium
  - the approach used since '30s with success
  - phase diagrams as practical tool



PROPS INFLUENCING THE THERMODYNAMICS TO BE MODELLED TODAY

- Compositional and temperature dependency
  - miscibility gaps
  - congruent melting
  - azeotropic points
- Magnetic transformations
  - λ–transformations
- Pressure contribution
- Crystallographic structures
  - sublattices
  - interstitial phases
  - electronic defects
- Short range ordering
- Chemical ordering



Computational methods in materials properties – thermodynamic simulation (II)

- Advanced property databases developed in cooperation with NPL
- Areas of application:
  - Smelting and refining processes in metal making (high temperature and aqueous)
  - Hot-corrosion, joining, coating and other features in use and fabrication

1. *terminen tasap aino* eli kaikissa sen faaseissa on sama lämpötila:

$$_{\alpha}T = {}_{\beta}T = \ldots = T. \quad (4)$$

2. *mekaaninen tasapaino* eli kaikissa sen faaseissa vallitsee sama paine:

$$_{\alpha}P = {}_{\beta}P = \ldots = P. \quad (5)$$

3. *kemiallinen tasapaino* eli kullakin sen komponentill a i on sama kemiallinen potentiaali eli moolinen Gibbsin energia kaikissa systeemin faaseissa:

$$\begin{aligned} {}_{\alpha}G_1 &= {}_{\beta}G_1 = \ldots = G_1 \\ {}_{\alpha}G_2 &= {}_{\beta}G_2 = \ldots = G_2 \\ &\vdots \\ {}_{\alpha}G_N &= {}_{\beta}G_N = \ldots = G_N. \end{aligned} \quad (6)$$

JW Gibbs, On the equilibria of heterogeneous substances, 1873

THE SOLUTION MODELS USED

- The database Mtox and its analytical formalisms:
  - The Gibbs energies of stoichio-metric compounds and species within solution phases are expressed in the $G-H_{SER}$ form
  - The liquid oxide ('slag') phase is modelled in terms of a series of non-ideally interacting species
  - Crystalline solution phases, such as the spinel, halite, olivine and pyroxene structures are represented using the compound energy model ('sub-lattice treatment')

- Uniformal definition of the reference state:

- for any stable form of the elements:

$$\Delta H(298.15\ \mathrm{K},\ 1\ \mathrm{bar}) \equiv 0$$

- Molar Gibbs energy of a phase is:

$$G = G^{id} + {}^{Ex}G$$

$$\text{where } {}^{Ex}G = \Phi(P, T, {}^{\alpha}x_i)$$

- substitutional solution:

$$G = \Sigma x_i\, {}^{\circ}\mu_i + RT\, \Sigma x_i \ln x_i + {}^{Ex}G,\ i = 1..N$$

- interstitial solution (two sub-lattices):

$$G = y_M y_{Va}\, {}^{\circ}G_{MVa} + y_N y_{Va}\, {}^{\circ}G_{NV} + y_M y_C\, {}^{\circ}G_{MC} + y_N y_C\, {}^{\circ}G_{NC} + RT[y_M \ln y_M + y_N \ln y_N + y_C \ln y_C + y_{Va} \ln y_{Va}] + G^{Ex}$$

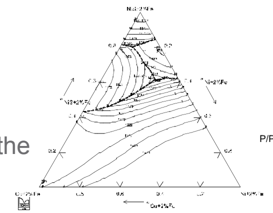
THERMODYNAMIC SOLVER AND AN EXTENSIVE OXIDE DATABASE

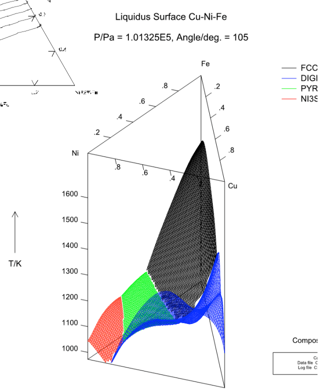
- The phase equilibrium calculations carried out using a thermochemical modelling package MTDATA
- The content of an extensive oxide-sulphide database Mtox is described in table I
- Model coefficients appropriate to large multicomponent systems are build up gradually, from smaller subsystems, in a careful validation work
- The focus of Mtox is in smelting and refining slags and their equilibria:
  - thus the thermodynamic components of the database are typically slag-forming oxides, such as CaO and SiO_2, and not their elements

Systems	Current Database
Oxide base system	Na_2O-K_2O-CaO-Fe-O-MgO-Al_2O_3-SiO_2
Sulphur in slags	Dilute solution of S
Cu-O	CaO-Cu-Fe-O-MgO-Al_2O_3-SiO_2
PbO and ZnO	CaO-Fe-O-PbO-ZnO-Al_2O_3-SiO_2
Matte/metal base system	Cu-Fe-Ni-S-O
ZrO_2 and oxides of V	CaO-MgO-Al_2O_3-SiO_2-ZrO_2
B_2O_3 and Li_2O	Li_2O-Na_2O-B_2O_3-SiO_2 Na_2O-CaO-Fe-O-MgO-Al_2O_3-B_2O_3-SiO_2
MnO	CaO-Fe-O-MgO-MnO-Al_2O_3-SiO_2
Cr-O	CaO-Cr-Fe-O-MgO-Al_2O_3-SiO_2
NiO	CaO-Fe-O-MgO-NiO-Al_2O_3-SiO_2
Trace anion database	Dilute solution of S^{2-}, OH^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, F^- in parts of oxide base liquid

Examples: melting points of industrial 'substances'

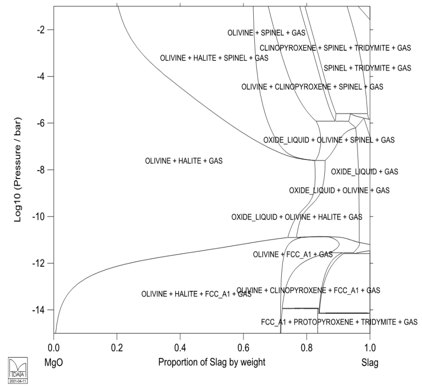
- (I) Low temperature fluidity of nickel mattes is known in the literature, but a CT-approach allows us to study this phenomenon in detail and in the very conditions of a smelting vessel
  - unexpected matte leakages
  - refractory failures and
  - problems in tapping during the operation
- DON technology challenges the smelting furnace design and puts new requirements to molten nickel matte handling, when smelting low-Cu raw materials





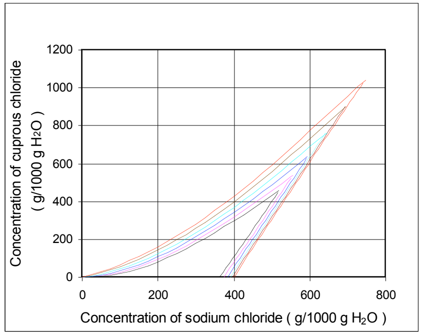
Examples: (II) Refractory wear in copper smelting

- An essential part of furnace integrity is control of the refractory wear
- Wear is complex phenomenon of mechanical erosion and chemical factors, depending on the type of the smelting vessel and the stage of processing
- Figure shows the crucial phase equilibria of refractory wear in a copper smelting or converting furnace
- Appearance of molten phases indicates dissolution of the autogeneous (protective) layer from the refractory lining



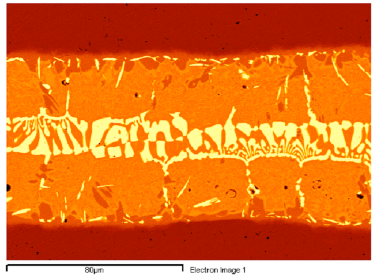
Examples: (III) Solubility of CuCl in strong brine

- Aqueous systems
  - can be approximated as ideal solutions at very low concentrations only, <<1 mol/kg H_2O
  - the Pitzer model has gained popularity and databases are available
  - a large number of electrolytes have been modelled in the literature
  - the calculated solubility of cupric chloride in water at 25-100 °C
- Boundary conditions of a novel Cu-process by OT

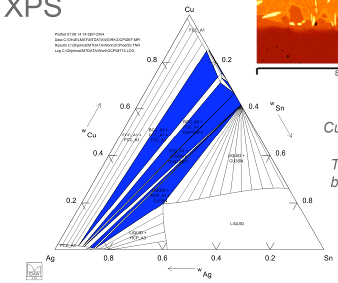


(VI) Performance of construction materials in demanding conditions

- Failure analysis
- New manufacturing methods
- Trouble shooting – SEM, EDS/WDS, XPS



Cu-Cu brazing / microstructure



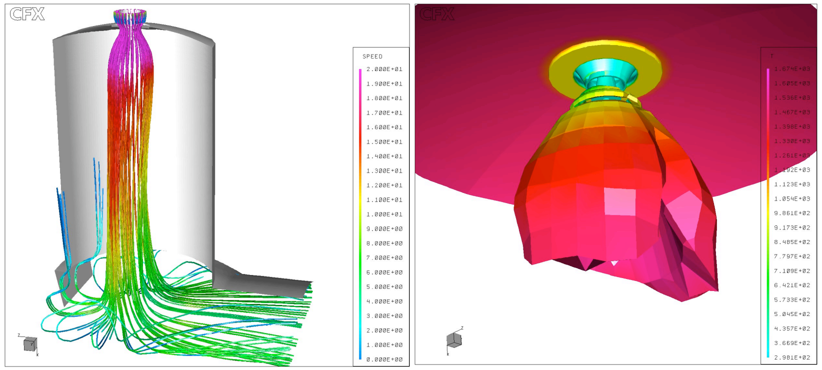
Ternary phase diagram Cu-Sn-Ag in brazing conditions (MTDATA)

Computational Fluid Dynamics

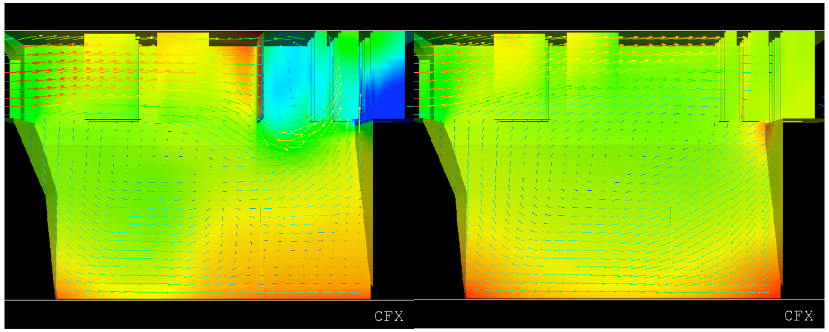
A very useful tool for studying mass, heat and momentum transfer in metallurgical/chemical processes

- High & low temperature phenomena
- Large (true) geometrical scales
- Real physical properties of phases
- Intensive chemical reactions (coming, submodels upon request)

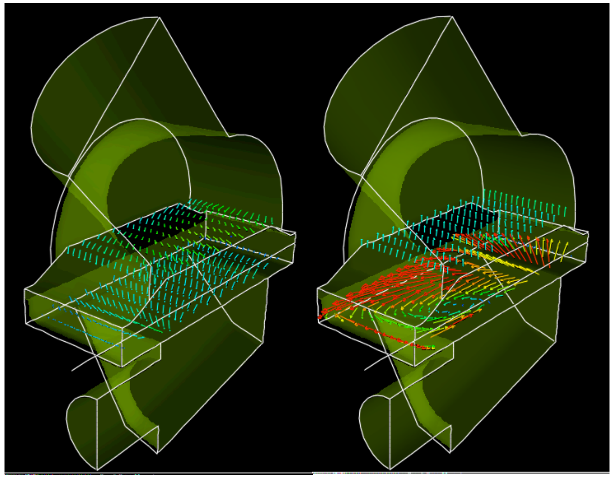
Examples: (I) stream lines and the combustion zone of a flash smelting furnace



(II) Influence of a cross sectional baffle on the wall pressure distribution and flow field in a Zn-roaster heat recovery boiler



(III) Gas flow distribution in the zones of a belt sintering furnace (FeCr-production – feed preparation for smelting)



Conclusions

- High educational level necessary
- Strong basic knowledge in physics & chemistry – and their applications in industrial challenges needed
- International and multinational working environment – engineering subsidiaries in Sweden & Germany, sales offices in 18 countries
- Good language and presentation skills preferred