Use of ChemSheet and Kilnsimu for Material and Energy Saving Processes

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Outline of presentation

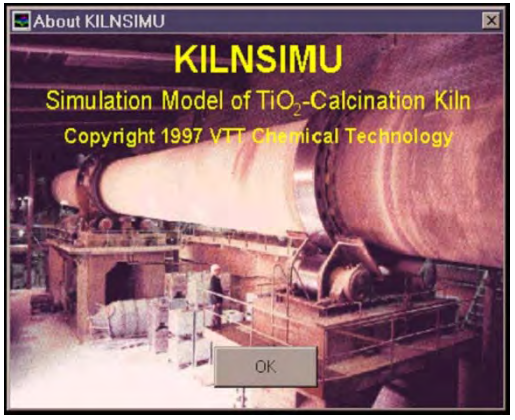
- Recent progress with ChemSheet and Kilnsimu
- ChemSheet and Kilnsimu using full equilibrium models
  - SteaMax for mixed and biofuel boilers
  - Zinc recovery in the Waelz kiln (news from 2011)
  - ChemSheet modelling of acid mine drainage
- Use of additional constraints – CFE method
- Selected examples with CFE
  - surface energies of alloys and mixtures
  - back diffusion and paraequilibria in solidification
  - simulation of rotary kilns as non-equilibrium reactors
- Summary
- Acknowledgements

Thermochemical process modeling at VTT

- Development of advanced multi-phase methods and algorithms with Gibbs energy minimization
- Constrained Gibbs free energy techniques for forced equilibria and rate-controlled multi-phase processes
- Robust and practice-oriented simulation based on many years of industrial experience
- VTT software:
  - ChemSheet – Gibbs'ian models in Excel™ spreadsheets
  - BALAS – Flowsheet simulation of pulp & papermaking
  - KilnSimu – Multi-phase chemistry for rotary drums
  - Ratemix - Reaction rate-controlled Gibbs'ian systems
  - ChemApp – Thermodynamic multi-phase applications

ChemSheet™

BALAS® Process Simulation Software



- ChemSheet & KilnSimu licenced & jointly developed with GTT

Recent progress with ChemSheet and KilnSimu models

Application	Program	Type	CFE-use*	Problem solved	Advantage
SteaMax for bio & mixed fuel boilers	ChemSheet	EQ	-	Material corrosivity in heat exchangers	Competitive edge of several M€ (boiler design)
TiO2 burner	ChemSheet	Non-EQ	Kinetic	Scale-up, location secondary feed	Resource intensity without extra investment
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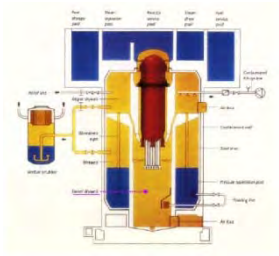
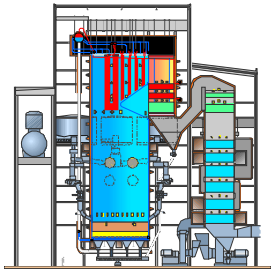
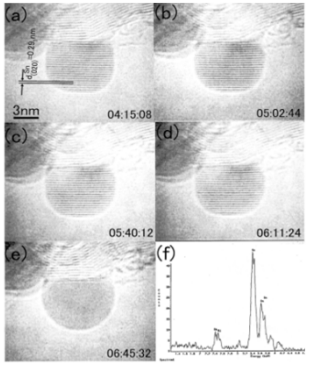
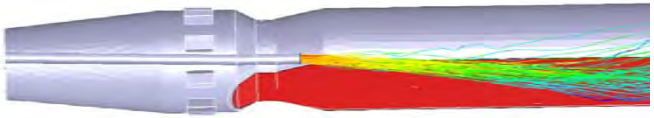
Paper machine neutral conversion	ChemSheet	Partial EQ	Donnan	Ion exchange and pH of fibrous pulp	Control of hemical dosage for stable operation
ChemPool for nuclear safety	ChemSheet (extended)	EQ	-	pH buffering of drywell/wetwell safety systems	Design & scale-up e.g. by U.S. NRC-standards
Alloy nanoparticles	ChemSheet	Partial EQ	Surface	Phase behaviour and melting	Design of functional nanomaterials
Surface properties of alloys	ChemSheet	Partial EQ	Surface	Surface tension and melting	Design of functional composite matrixes
Rotary kilns for cement, pigment, pig iron etc.	KilnSimu	Non-EQ	Kinetic	ChemEner profiles in kilns with variable feed	Scale-up and sustainable operation of rotary kilns
Flame structure in rotary kilns	Fluent-KilnSimu	Non-EQ	(kinetic)	2-way coupling of kiln bed and gas	Reduce kiln carbon footprint
ProMine to recover metal values from AMD	ChemSheet	EQ	-	Interpretation of mine drainage titration	Recovery of value-added nanoparticles from mine waters
Paraequilibria	ChemSheet	P-EQ	Paraeq.	Phase formation in solidification	Improved steel / alloy property control
Magnetic eq.	ChemSheet		To be	published	



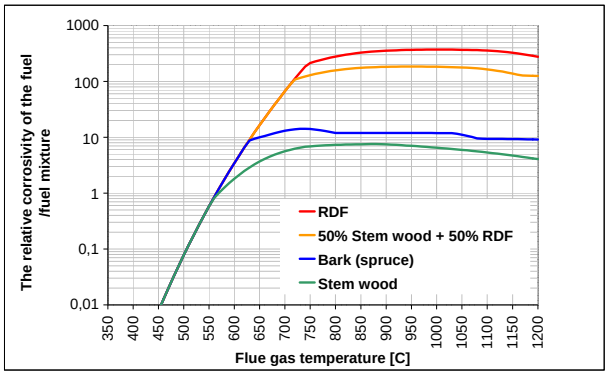


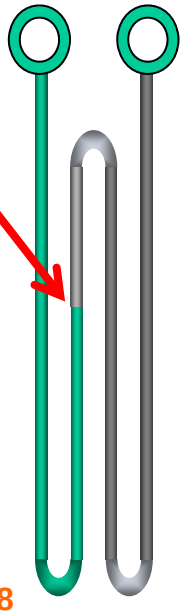



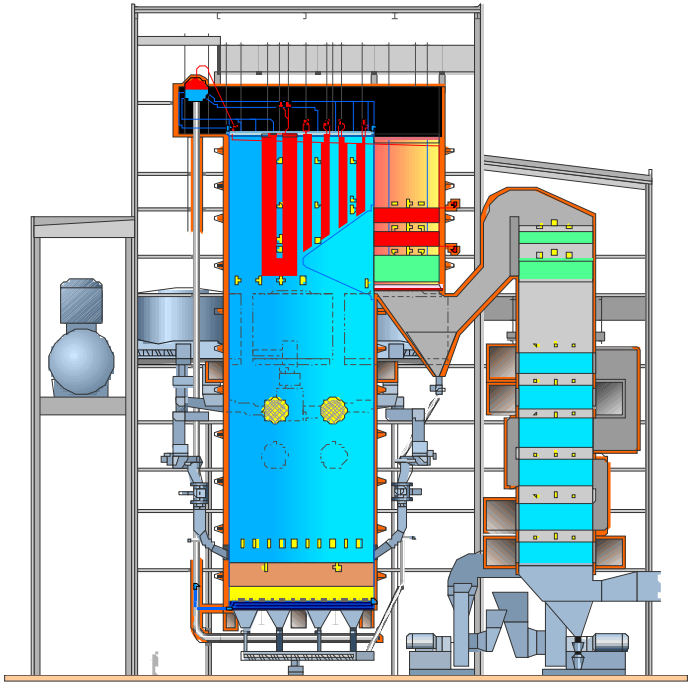
*CFE = 'Constrained Free Energy' applies additional immaterial constraints in Gibbs energy minimisation

SteaMax expert system for biofuel boilers

- ChemSheet expert system for boiler design by ash and flue gas chemistry
- Steam capacity of bio- and waste fuel boilers
- Exact switch position from stainless to carbon steel in the superheater
- Maximum material temperatures for low-alloy and stainless steels
- Total amount of steel in the heat exchanger may exceed 500 t / unit, giving a significant competitive advance to SteaMax designs







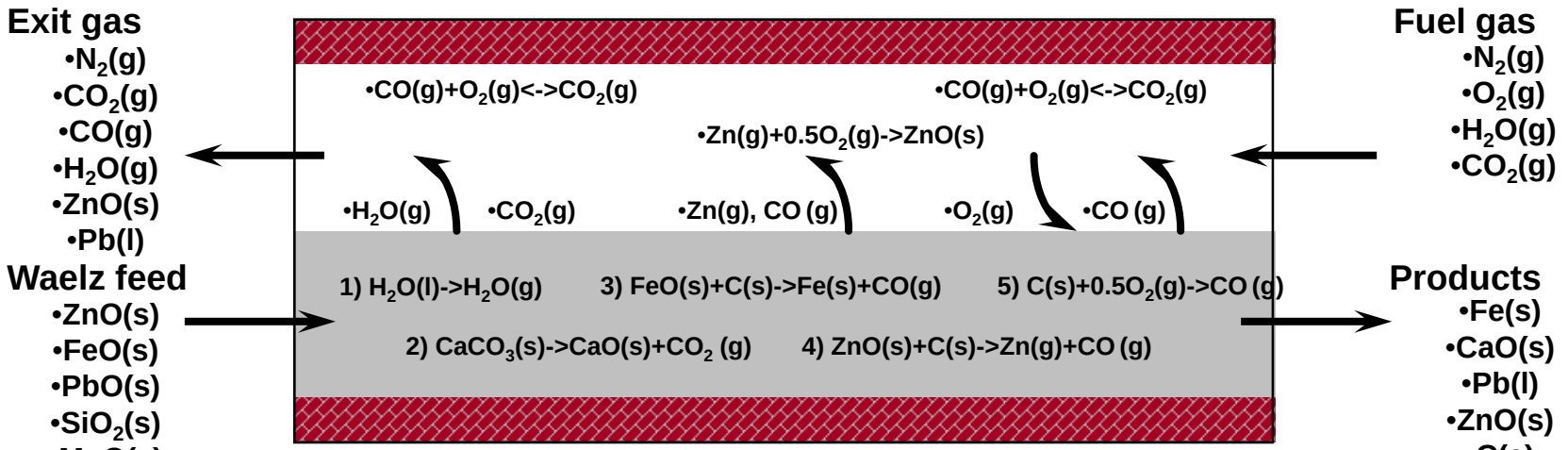
Enestam, S., Niemi, J. and Mäkelä, K.: STEAMAX – A novel approach for corrosion prediction, material selection and optimization of steam parameters for boilers firing fuel and fuel mixtures derived from biomass and waste The Clearwater Coal Conference, Clearwater, Florida, June 2008

Enestam, S., Koukkari, P.: SteaMax expert system for superheater design, in VTT Research Notes 2506, Espoo 2009

Enestam S.: Corrosivity of hot flue gases in the fluidized bed combustion of recovered waste wood, Report 11-04, (2011), Åbo Akademi, Department of Chemical Engineering (thesis).

Recycling zinc from steel production

- 40 % of steel produced in Europe is recycled from scrap in electric arc furnaces (EAF)
- in EAF Zn evaporates and is later collected as ZnO dust (35 % Zn)
- Zn is then recovered in the Waelz process
- EU27 Zn recovery is ca 250 000 t/yr

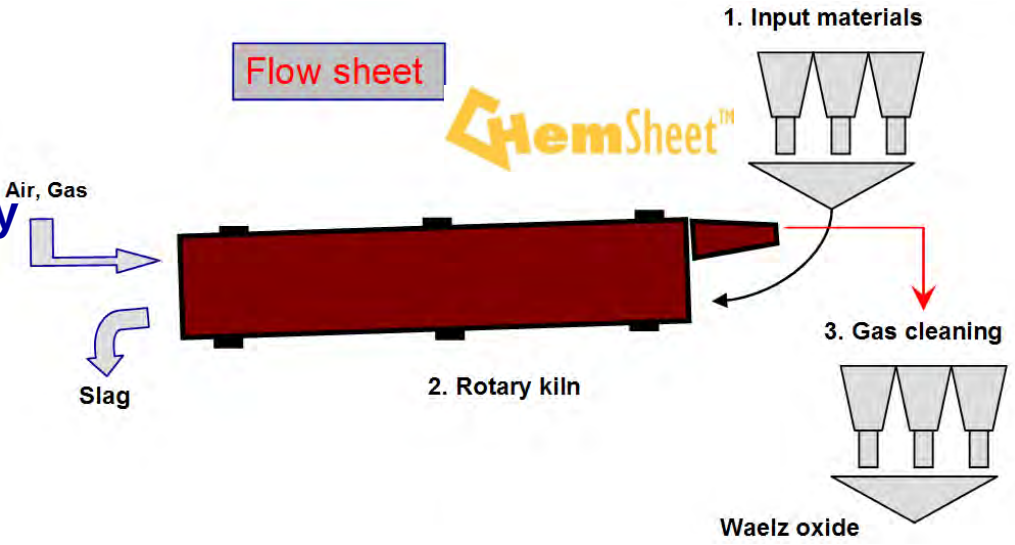


Schematic view of the Waelz kiln chemistry

ChemSheet model of the SDHL Waelz kiln*

A 4-stage ChemSheet model:

- **Zn-oxide reduction**
- **the oxidation of Waelz-slag (including autogenic oxidation of reduced iron by additional air-blasting)**
- **oxidation of reduced Zn-vapour to Zn-oxide dust**
- **finally, model for the offgas cooling and cleaning.**



The model is used to find adequate operating temperatures for the reduction and oxidation stages in the bed.

Furthermore, the composition of the gas and the yield of both zinc and lead in the vapour phase become calculated.

*Jürgen Korb GTT-Technologies, Freiberg/Sachsen at GTT Workshop, Herzogenrath 2003

Contribution to development of BAT

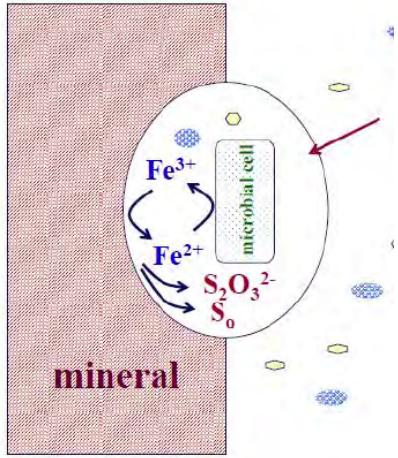
For the development of the so-called SDHL technology that allows about 40 % savings of CO_2-emissions, the Waelz-process has been awarded already in 2003 the Environmental Award of Saxony, a federal state in Germany.

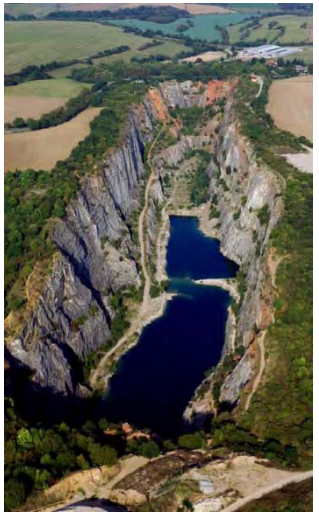
"Since then, the Waelz-process has been improved permanently. Today it is regarded as the best available technology for recycling EAF dusts", says Dipl.-Ing. Andeas Ruh, Befesa Steel Services GmbH.

'Zinc meets steel: a strong team in climate protection and resource efficiency', Leoben 10.05.2011;
www.foundry-planet.com/pt/detailview-corporate/9710.html.

Multicomponent modelling of acid mine drainage

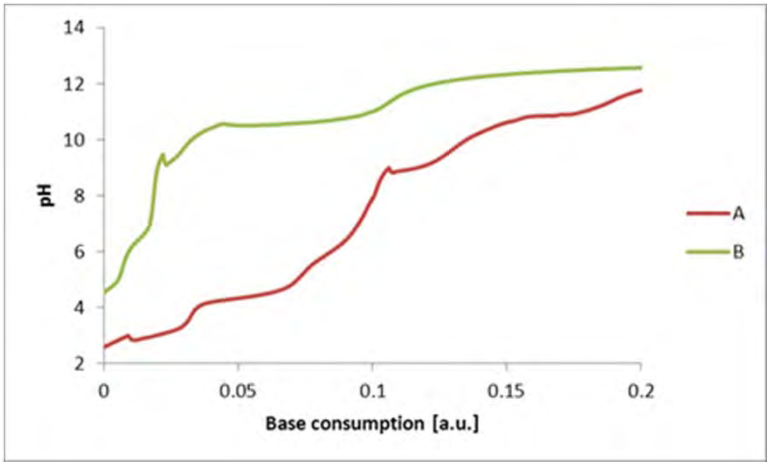
- acid mine water drainage (AMD) is a major challenge at both operating and closed mining and mineral processing sites
- slow oxidation of exposed sulphide minerals leads to formation of (tio)sulphates and eventually sulphuric acid
- dissolution of sulphates to ground water and/or rain leads to acidic leakage to environment => ecological problems

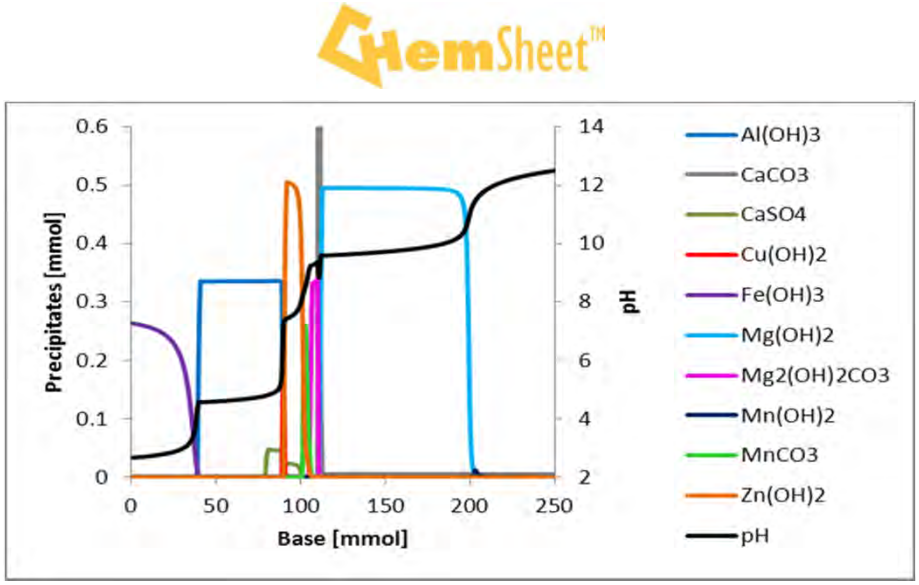




Selective precipitation of metals from mine waters

- neutralisation of AMD leads to multicomponent precipitation with little practical value
- selective precipitation could provide re-usable fractions
- mine water titration curves will give valuable information for selective precipitations
- dilute solutions give a fair performance of Pitzer G^E-models





- Most metal ions form specific stoichiometric compounds that begin to form once the pH of the solution exceeds a compound-specific threshold
- => possible to selectively recover metals by model-based pH control

Recovery of metal fractions from mine water samples

Values are percentages of total amount of each metal

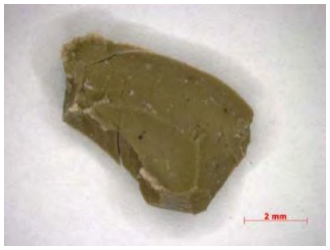
Element	pH 2.6-3.6	pH 3.6-5	pH 5-8	pH 8-10	pH 10-11
Magnesium		2%	2%	6%	90%
Iron	97%	3%			
Calcium	4%	9%	7%	1%	79%
Aluminum	2%	94%	4%		
Zinc	1%	2%	97%	1%	
Sodium	7%	50%		8%	35%
Manganese	2%	4%	37%	52%	5%
Copper	3%	18%	79%		

- The aim was to recover Zn and Cu from the waste water at high yield.
- Initial concentrations of Zn and Cu were 350 and 14 mg/L
- Titration yields 97% Zn and 79% Cu (pH fraction 4.9 to 8)
- Exclusion of CO_2 will enable recovery of Mn and Mg as separate fractions

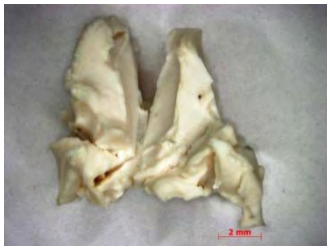
Images from stereomicroscope

pH∠5

pH∠8



pH∠11



Räsänen, L., Blomberg, P., Mäki, T. , Koukkari P.: Quantitative Analysis of Multi-Component Acid-Base Titration and Selective Recovery of Metals from Acidic Mine Waters (to be published at ISSP 2012, Xining, China)

... there were a number of applications with 'CFE-use'

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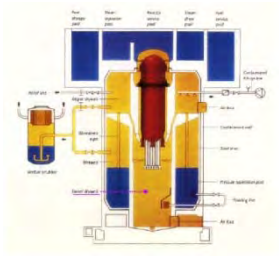
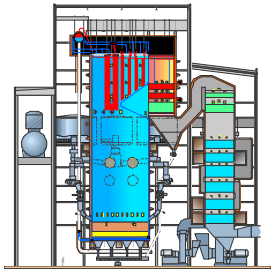



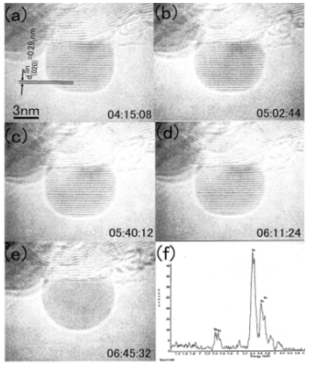


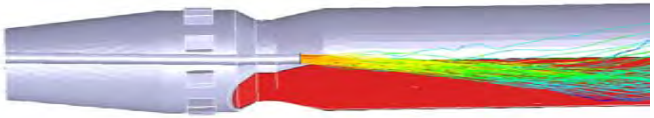

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Background for constrained Gibbs energy models

- multi-phase Gibbs free energy methods well established for mass-balance based equilibrium calculations (phase diagrams & multi-phase equilibria)
- conventional mass-balance constrained techniques are not sufficient for
  - ✓ systems with immaterial entities and work effects
    - surface energy problems
    - material chemistry of fibre suspensions and membrane systems
    - other force/field -related conditions
  - ✓ paraequilibrium systems constrained by transport phenomena
  - ✓ multi-phase problems which include extent of reaction or reaction rates
- the constrained (Gibbs) Free Energy method (CFE) was developed to extend the availability of traditional multi-phase techniques to such ‘dynamic’ problems

The constrained Gibbs free energy method

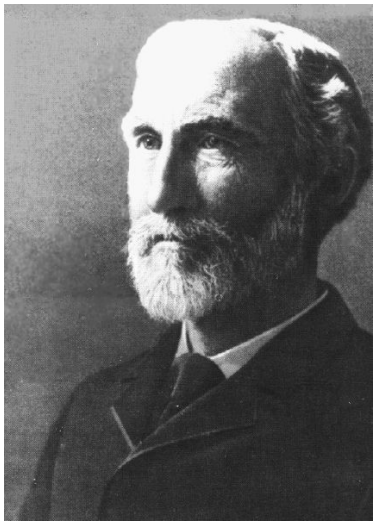
The general Gibbs energy equation is:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum \mu_{k'}\mathrm{d}n_{k'} - \sum A_r\,\mathrm{d}\xi_r + \sum z_k\,F\varphi_k\mathrm{d}n_k + \sigma\sum A_k\,\mathrm{d}n_k + \cdots$$

With appropriate constraining the *min(G)* problem

can include:

- reaction kinetics via extents of reaction [(ξ_r) with affinity (A_r)]
- surface energy [(σ) with molar area (A_k)]
- Donnan (membrane) equilibria
- electrochemical & surface charge problems
- paraequilibrium systems
- magnetic field effects
- etc.



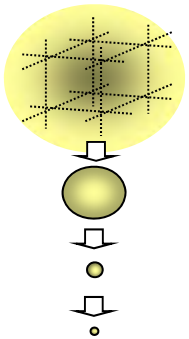
J.W. Gibbs

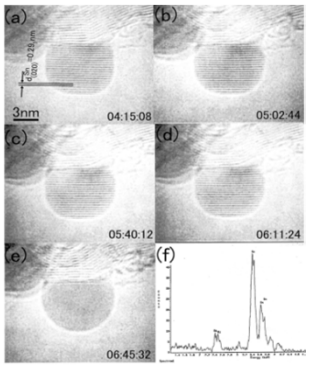
1839 - 1903

The novel constrained free energy method (CFE) brings the additional right hand terms into the Gibbs energy minimisation.

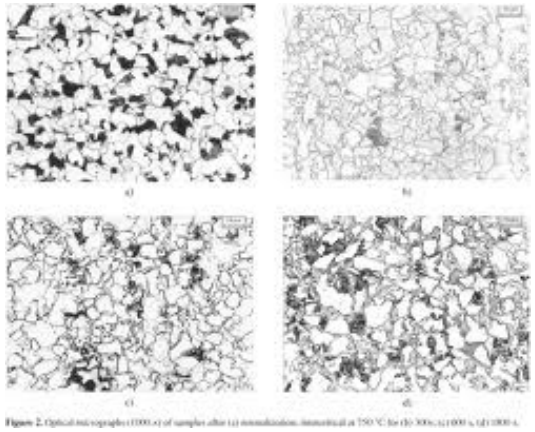
Examples of 'constrained' thermochemical systems

Phase behaviour of (alloy) nano-particles





Composition of solidifying alloys and steel



Process chemistry &
fuel consumption in high-temperature furnaces (rotary kilns as example)

Conditions for the thermochemical modelling of constrained systems

Rotary drums (as many other chemical reactors) are non-equilibrium systems. For one or several reactions there is:

$$0 < \xi < \xi_{eq} \; ; \quad \Leftrightarrow \quad G = G[T, P, n_k(\xi)]$$

Alloy or steel solidification is a diffusion-limited partial (or para) –equilibrium system:

$$D_k \in R \; ; \quad \Leftrightarrow \quad G = G[T, P, n_k(D_k)]$$

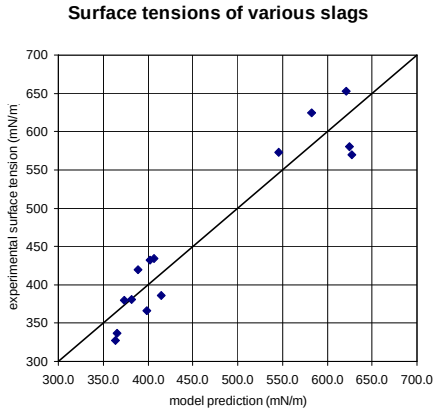
Phase stability of (alloy) nanoparticles is affected by the surface energy of the material:

$$\sigma \in R \; ; \quad \Leftrightarrow \quad G = G(T, P, n_k, \sigma)$$

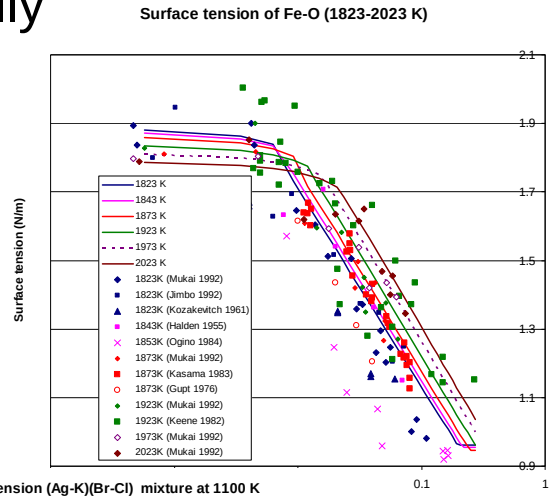
The common feature is to bring the respective constraints into $min(G)$

Surface Tension and Sorption over a Wide Temperature Range

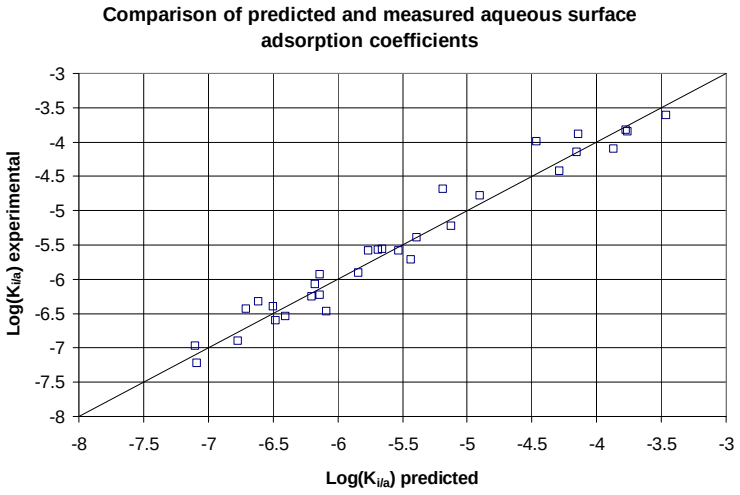
- Surface tension and adsorption can be calculated for a variety of systems
- The model requires an excess Gibbs energy (activity coefficient) model for both the bulk & surface layers
- The G^E model for the surface layer is typically a modified version of the bulk model



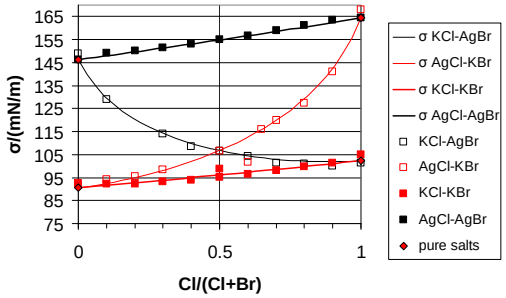
Molten slags > 1500 C



Oxygen adsorption on metals and alloys 1100 C



Aqueous -organic adsorption 25 C



Salt melts 200-1000 C

R. Pajarre, P. Koukkari *J.Colloid & Interface Sci.* 2009

Applications for surface / interfacial energies

- physical properties of alloys and mixtures
- castability of (light metal) alloys
- development of casting powders for steelmaking
- models for slag foaming (when connected with viscosity data)
- developing new (Pb-free) solder components
- development of functional composite materials
- microstructure modelling (dendrite formation in solidification)
- …

Back diffusion and paraequilibria

In steel solidification and phase transformations in addition to thermodynamics also diffusion and convection control the phase formation.

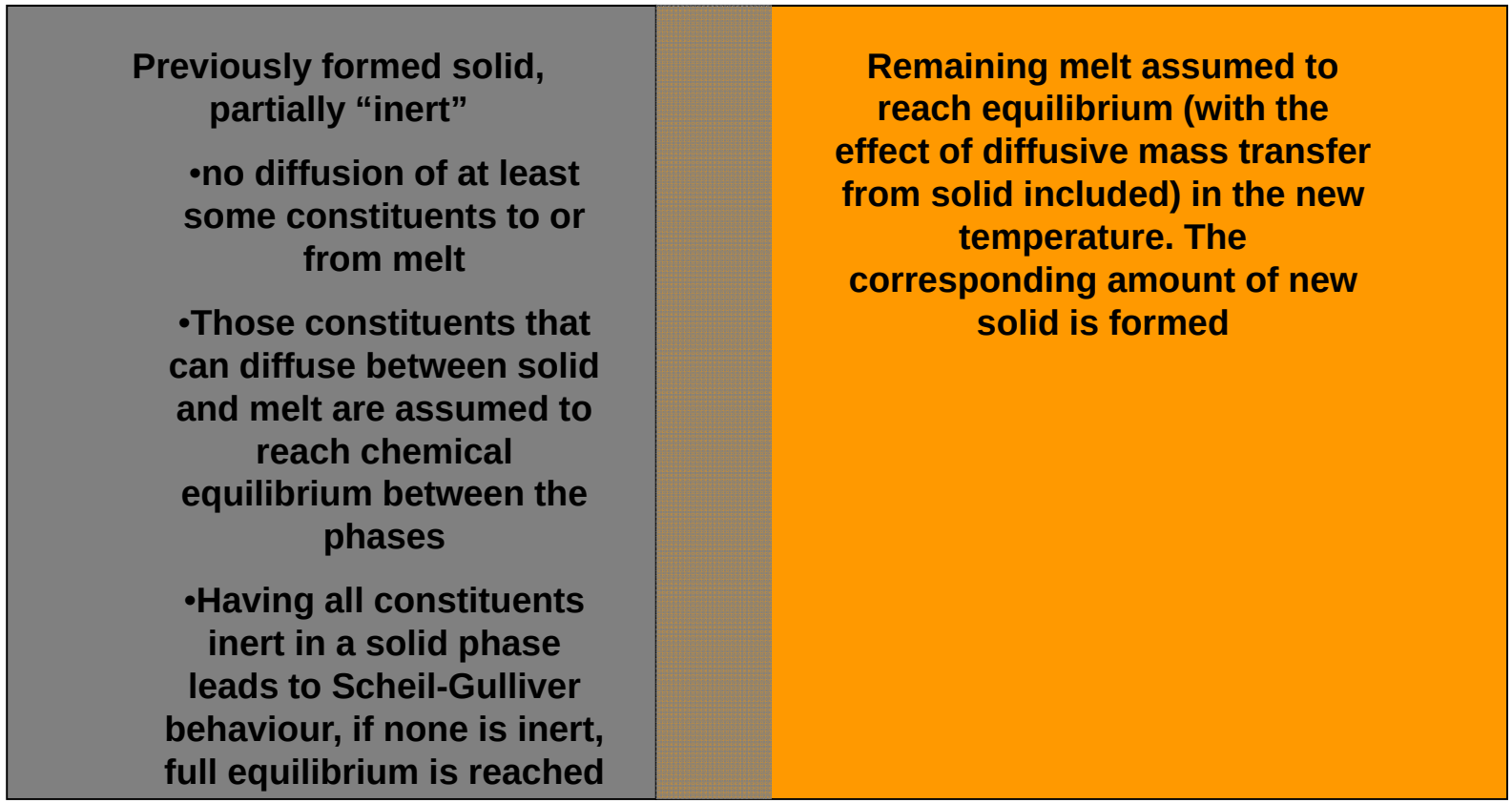
To avoid computationally intensive diffusion calculations, the problems are often solved using approximate solutions based on some simplifying assumption such as:

- Full equilibrium (diffusion is assumed to be fast enough that equilibrium between solid and liquid is always maintained
- Scheil cooling, where once formed solid is assumed to be effectively inert. Liquid is assumed to completely mixed and local chemical equilibrium is assumed on the advancing solidification front.

The ability in ChemSheet calculations to set constraints on arbitrary constituents or reactions or phase transformations allows also equally easy use of more sophisticated assumptions such as:

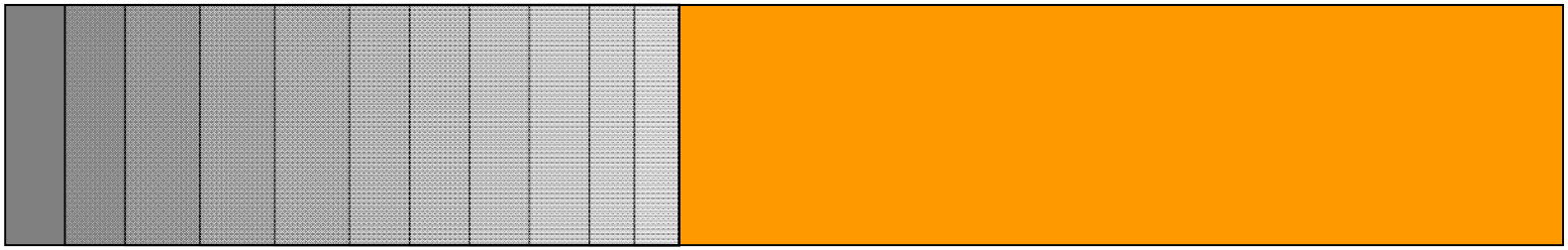
- Backdiffusion, where the small interstitial solutes in solid iron are assumed to be able to move between solid and liquid, while the larger metal atoms in solid are assumed immobile.
- Paraequilibrium, where new phases form with the same ratio of iron and alloying elements than in the parent pahse.

Solidification with back diffusion calculation schema



Calculation schema

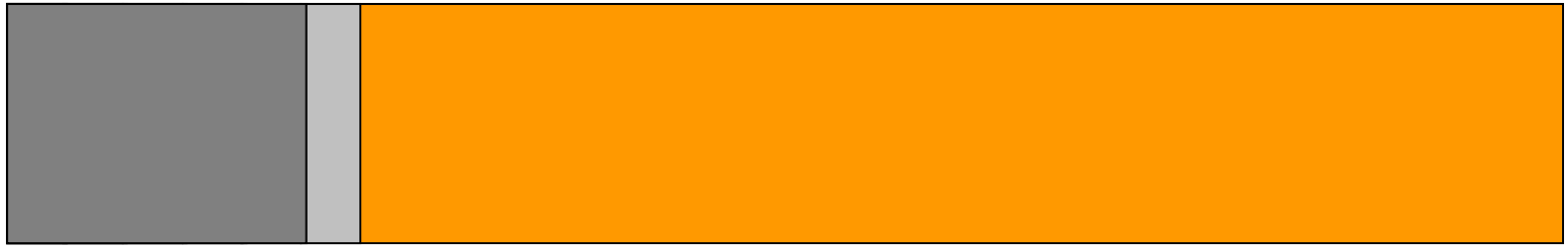
Applying the outlined calculation procedure directly leads to system with one new solid layer (which has depending on the composition, temperature and thermochemistry one or more solid phases) for each cooling step.



This is initially cumbersome to implement, and becomes impossible after a while using ChemApp because of the number of components required.

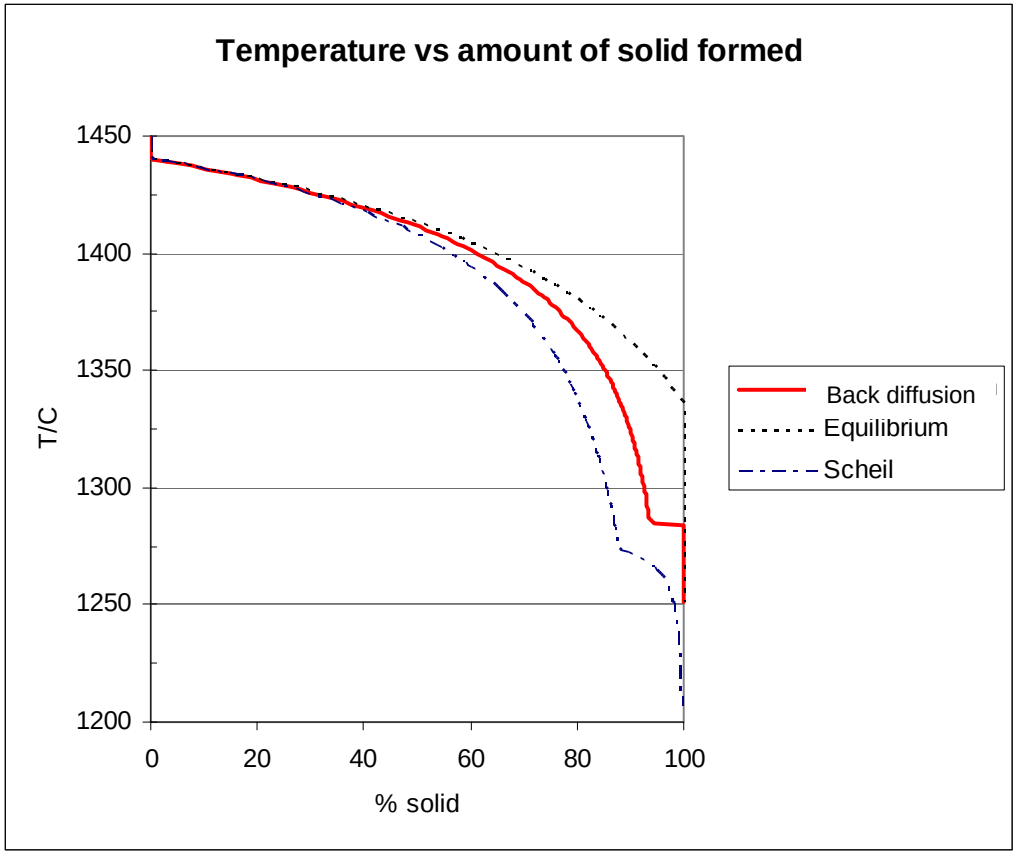
Calculation schema

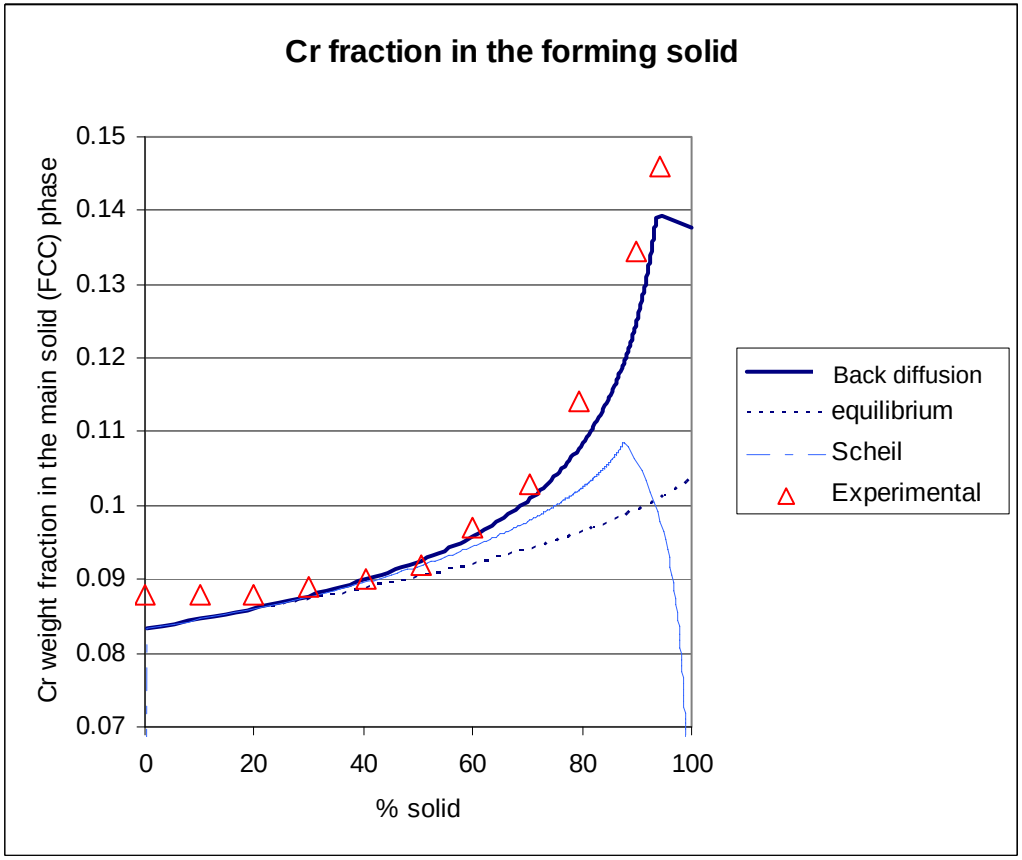
As a simplification, in the calculations it has been assumed that to calculate the chemical potential for the diffusive species in the solid, the layered structure can be replaced by one layer where the solid phases have a weighted average composition of those they have in the individual layers



It is still possible to keep track on the composition of the individual layers as they are formed

Back diffusion vs. Scheil cooling: result comparison





Composition: 10.84% Cr, 0.95% C. Cooling rate in experiment 0.167K/s

Paraequilibrium

In paraequilibrium the metallic composition of the new growing phase is the same as in the parent phase while carbon is able to equilibrate between the phases

For a system with two metallic components, if initially all the metallic components are in the parent phase, the constraint of equal relative amounts of components in the two phases is the same as requiring that the relative changes in the amounts of metallic components in one of the phases equals their relative amounts in the system.

For example:

$$dn_{Fe}^{FCC} / dn_{Ni}^{FCC} = n_{Fe} / n_{Ni} \Leftrightarrow n_{Fe} / (n_{Fe} + n_{Ni}) \cdot dn_{Ni}^{FCC} - n_{Ni} / (n_{Fe} + n_{Ni}) \cdot dn_{Fe}^{FCC} = 0$$

$$\equiv u_{Fe} \cdot dn_{Ni}^{FCC} - u_{Ni} \cdot dn_{Fe}^{FCC} = 0$$

The latter form is mathematically identical to a mass balance relation indicating that the required constraint can be included in the stoichiometric matrix with coefficients that match the (relative) molar feed amounts

(stoichiometric description for a paraequilibrium between FCC and BCC phases)

		Fe	Ni	C	*Ni-FCC
FCC	Fe:C	1		1	$-u_{Ni}$
	Fe	1			$-u_{Ni}$
	Ni:C		1	1	u_{Fe}
	Ni		1		u_{Fe}
BCC	Fe:C	1		1	
	Fe	1			
	Ni:C		1	1	
	Ni		1		

Paraequilibrium

		Fe	Ni	C	*Ni-FCC
FCC	Fe:C	1		1	$-u_{Ni}$
	Fe	1			$-u_{Ni}$
	Ni:C		1	1	u_{Fe}
	Ni		1		u_{Fe}
BCC	Fe:C	1		1	
	Fe	1			
	Ni:C		1	1	
	Ni		1		

From the stoichiometric matrix it follows that in the calculated paraequilibrium state

- $\mu_C^{FCC} = \mu_C^{BCC}$ (Carbon is in equilibrium between the phases)
- $u_{Fe}\mu_{Fe}^{FCC} + u_{Ni}\mu_{Ni}^{FCC} = u_{Fe}\mu_{Fe}^{BCC} + u_{Ni}\mu_{Ni}^{BCC}$

(Weighted average of chemical potentials of iron and alloying metals are the same, cf M. Hillert: Thermodynamics and phase transformations, EDP Sciences, 2006 Chpt. 14.5)

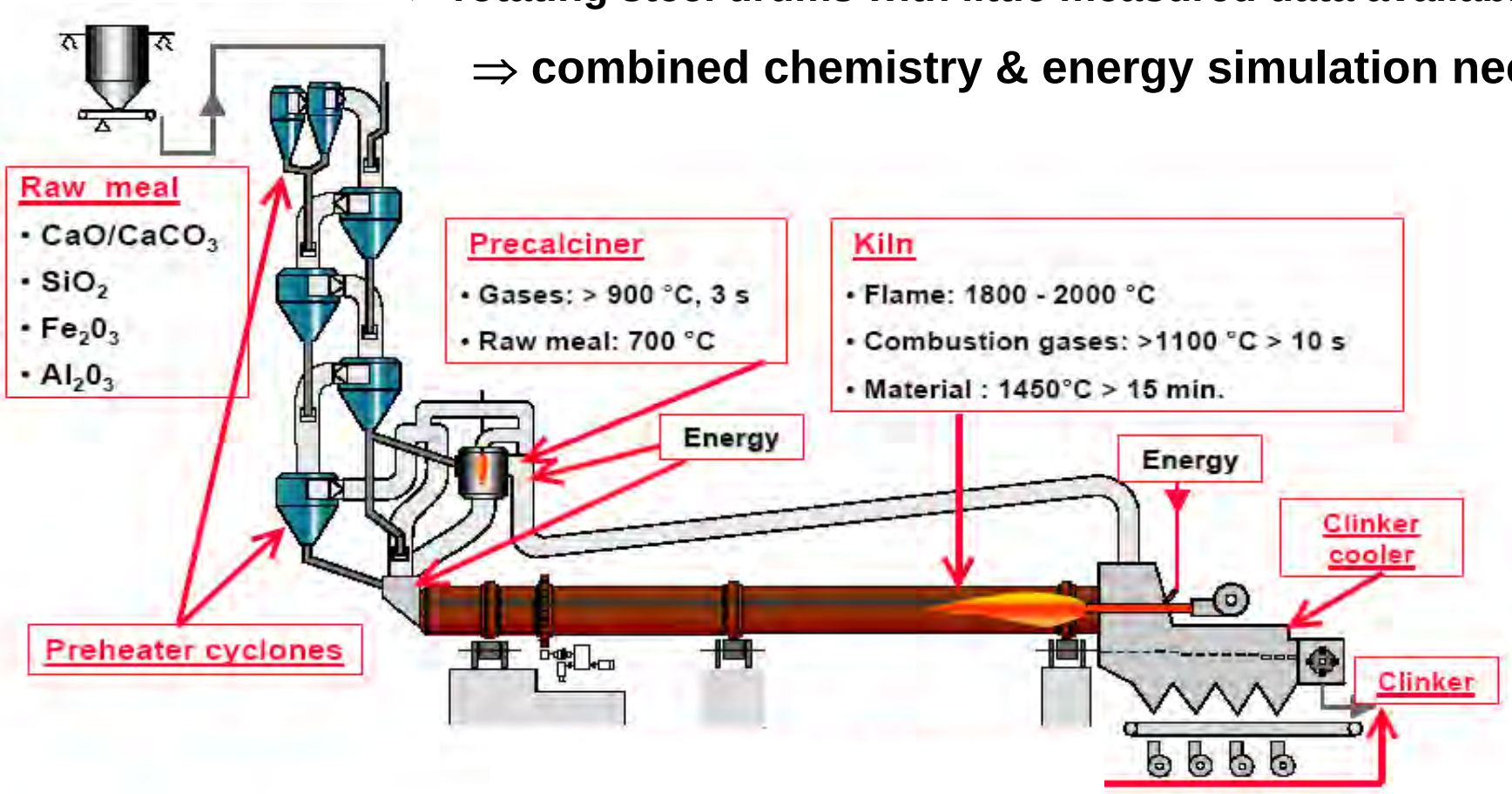
When the number of phases *N* or the number of metallic components *M* is larger than two the number of required constraint components is given by (N-1)*(M-1)

Multiphase models for rotary kilns

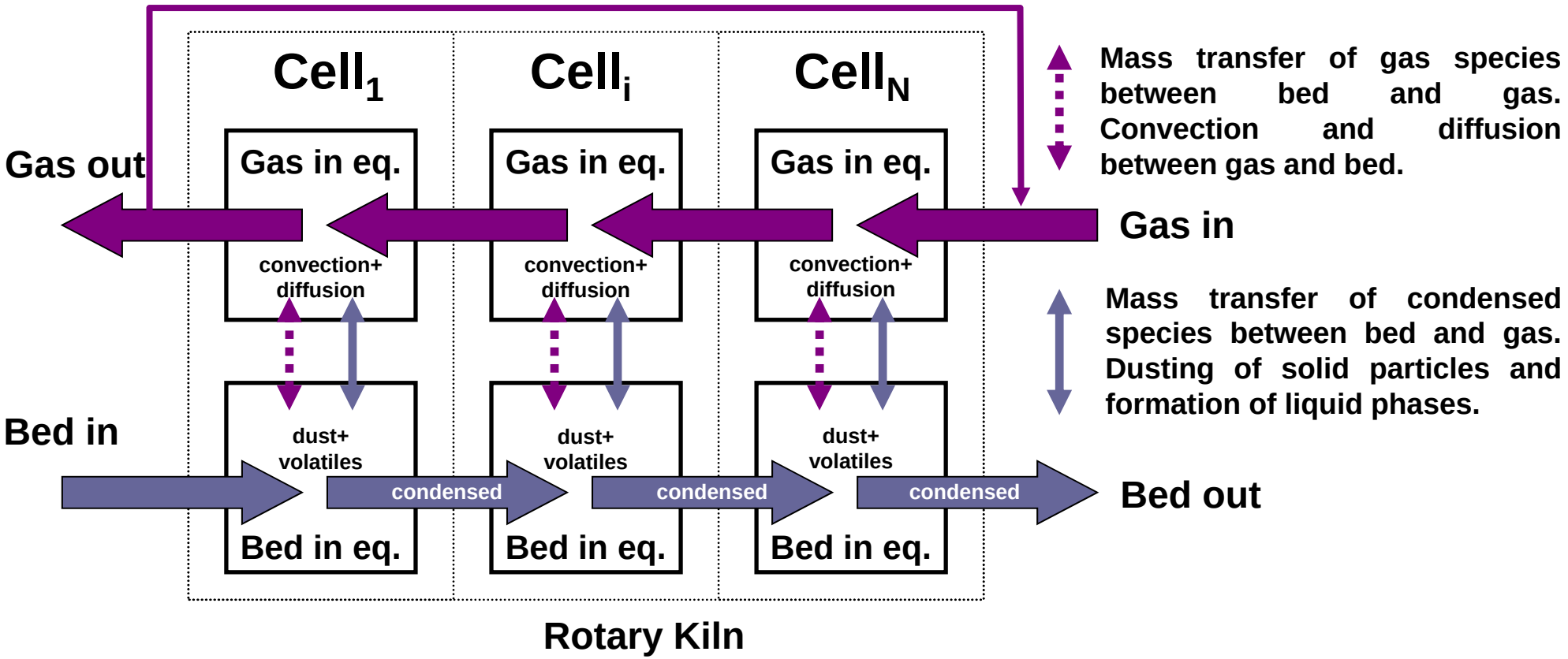
Counter-current rotary drums:

- **BAT for clinkering, calcination, chemical recovery etc.**
- **rotating steel drums with little measured data available**

⇒ combined chemistry & energy simulation needed !



Rotary kiln model (KilnSimu)



- Axial plug flow model is used for both the bed and the gas in each cell.
- The variables in each cell are the temperature of bed, gas, inner and outer wall and the mass flows of species in bed and gas.
- The bed and gas output from each cell is in thermodynamic equilibrium but they may contain non-reactive parts that are calculated with kinetics.

Cement kiln – a multiphase system with several kinetic restrictions

The thermodynamic system contains elements Fe-Ca-K-Cl-S-Si-Al-Mg-Na-O-N-C-H consisting of gas, slag and pure condensed phases with altogether 78 species

Kinetic restrictions are combined e.g. for 5 species including carbon (used as fuel), CaCO3, CaO, SiO2, Ca2SiO2 and Ca3SiO5 phases.

System Fe-Ca-K-Cl-S-Si-Al-Mg-Na-O-N-C-H
18 2 32 8 43

Fe	**Ca**	**K**
Cl	**S**	**Si**
Al	**Mg**	**Na**
O	**N**	**C**
H	**R_C**	**R_CaCO3**
R_CaO	**R_Ca3SiO5**	**R_SiO2**

Component listing from the cement kiln FactSage file

Components in red are virtual and control 5 kinetically slow reactions

$$C + O_2 \rightarrow CO_2$$
$$CaCO_3 \rightarrow CaO + CO_2$$
$$2CaO + SiO_2 \rightarrow Ca_2SiO_4$$
$$CaO + Ca_2SiO_4 \rightarrow Ca_3SiO_5$$
$$SiO_2 + Ca_xSiyO_z \rightarrow Ca_xSi_{y+1}O_{z+2}$$

Kinetically constrained reactions

Kinetics with the virtual components

	C	Ca	O	R_CaCO3
CO2	1	0	2	0
CaO	0	1	1	0
CaCO3	1	1	3	1
ξ+	0	0	0	1
ξ-	0	0	0	-1

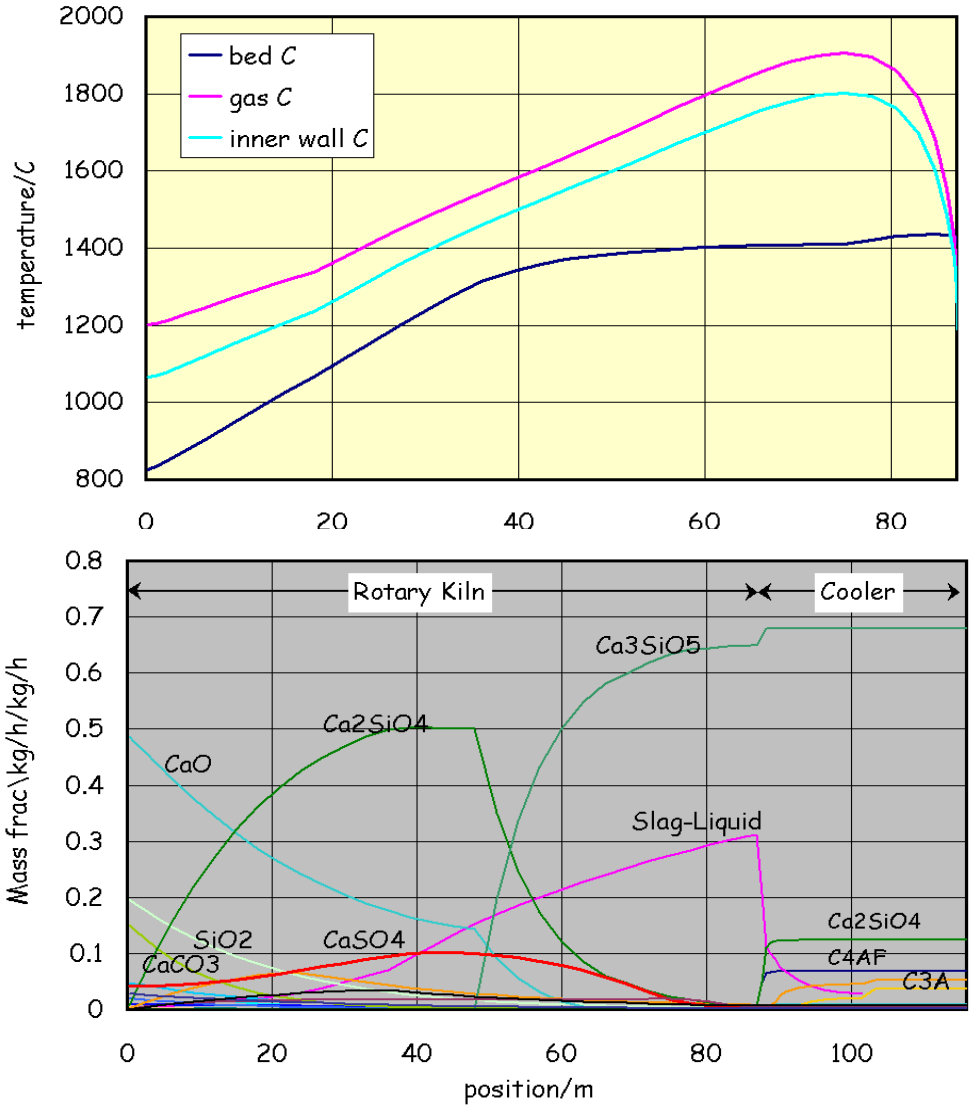
Kinetically constrained decomposition of calcite:

$CaCO_3 \rightarrow CaO + CO_2$

- virtual component R is introduced to control the extent of reaction
- virtual phases ξ+ and ξ- used to feed rates of forward or reverse reactions
- the extent of reaction [$\xi = \xi(t)$] is calculated from the known reaction rate [$\frac{d\xi}{dt} = Ae^{-Ea/RT} \cdot f(n_j, T)$] $\Rightarrow$ $\Delta n_{CaCO3} = \Delta n_{\xi-} = \Delta\xi(t)$ [mol]
- partial chemical equilibrium assumed for other reactions in the system
- min(*G*) performed for the constrained system until equilibrium is reached

Simulated temperature and phase profiles

- the kiln is divided into 100-150 cells in axial direction
- the cell volume elements of the material bed and gas described as open systems
- simulation by min(*G*) combined with the mass and heat transfer between the volume elements and their surroundings.
- 1-Dimensional profiles received for:
  - ✓ temperatures
  - ✓ bed & gas composition
  - ✓ radial heat fluxes
  - ✓ kiln holdup
  - ✓ etc.



Courtesy of Ube Industries Dr. Morihisa Yokota

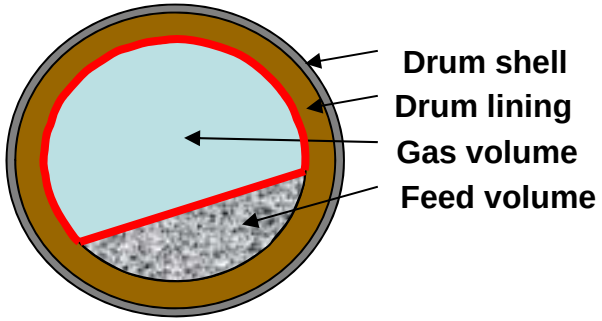
Illustration of the coupling: KilnSimu → Fluent

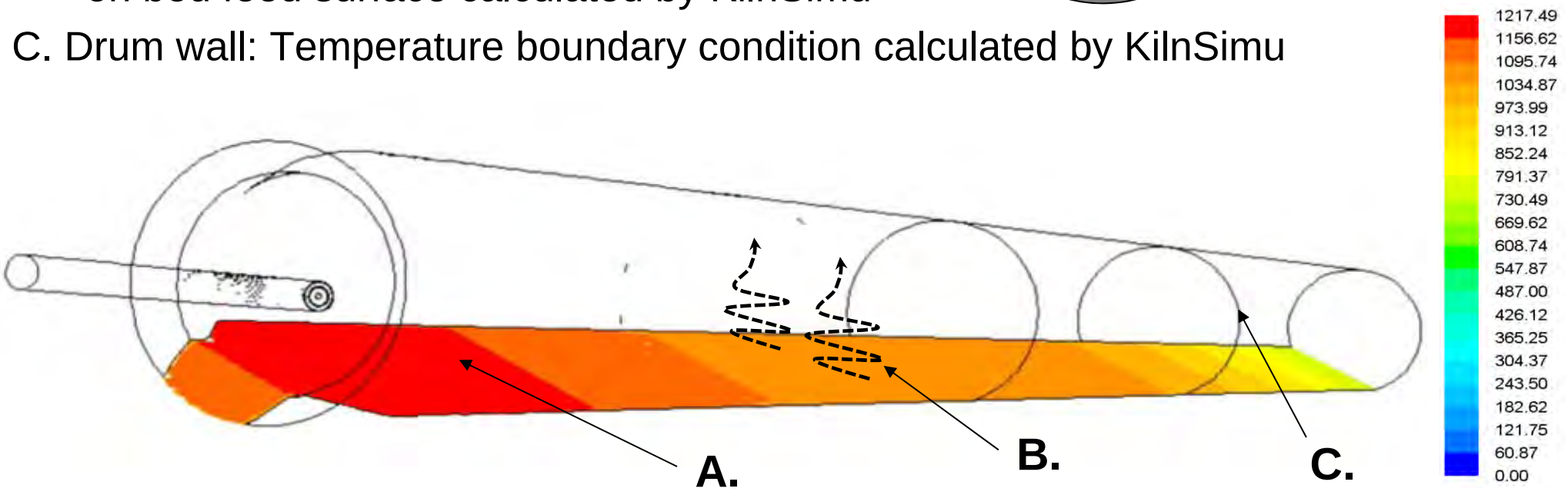
Data calculated by KilnSimu are transferred to Fluent by FKS

A. Bed feed surface: Temperature boundary condition calculated by KilnSimu

B. Gas volume: Mass flow (e.g. CO_2) sources on bed feed surface calculated by KilnSimu

C. Drum wall: Temperature boundary condition calculated by KilnSimu





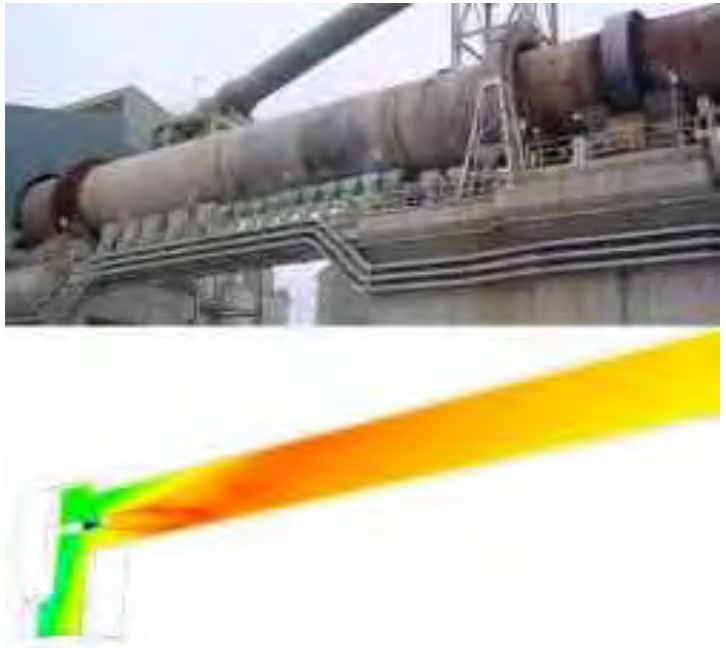
Benefits of the coupled simulation

Accurate 3 D description of the entire kiln

- Flame position and gas phase phenomena: Fluent
- Bed multiphase phenomena: KilnSimu
- Coupled solution for global convergence: FKS

Improved resource efficiency for BAT rotary kilns

- Control of emissions
- Lower carbon impact (by use of biofuel etc.)
- Reduced energy consumption



www.kilnsimu-fks.com

Uses of rotary kiln simulations

- Demand of combustion air
- Study of various fuels
- Optimization of fuel consumption
- Optimization of gas circulation
- Optimization of energy efficiency
- Phase formation studies (material bed and gas composition)
- Exit bed composition
- Exit gas composition
- Kiln scale-up

Summary

- ChemApp has been used for various intricate problems leading to material and energy saving solutions
- ChemSheet and Kilnsimu used as major platforms
- Methods are yet generic & applicable in any other min(*G*) software
- Process simulation based on both global equilibrium and constrained techniques
- CFE can be applied in any ChemApp procedure by using the program *CSFAP* for the necessary datafile manipulation

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