GEMS-workshop 2010

Introduction

Thomas Matschei

(Holcim Group support, CH)

Program for the morning session

1. General introduction to GEMS
2. How to get started – 1st hands on example
3. Database management in GEMS
4. Introduction to more complex calculation of Multi-Equilibria-Process-Simulations

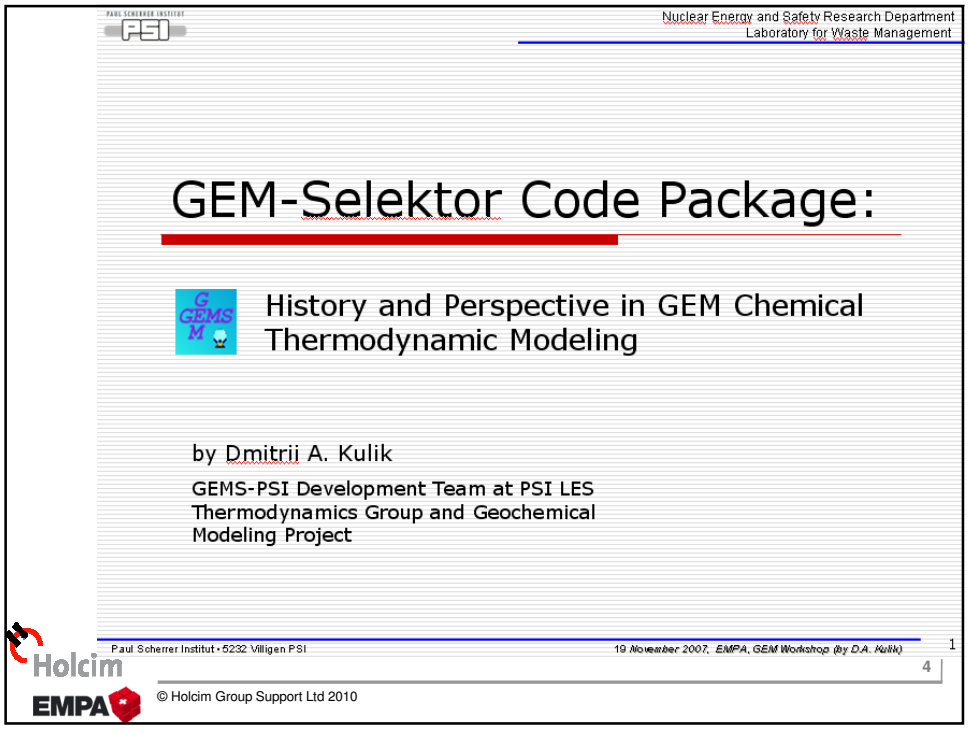
Application of Thermodynamics

Thermodynamics can be used as tool in many research areas:

Application mainly depends on the contents of the built-in thermodynamic data base (a lot of work to compile!)

- speciation in aquatic chemistry (e.g. environmental chemistry)
- high temperature processes (e.g. metallurgy, ceramics; cement clinkering)
- Geochemistry (e.g. interactions between different types of rocks; reactive transport modelling, etc.)
- hydration processes (e.g. cement chemistry)
- nuclear waste treatment (e.g. stability of radioactive species, etc

Holcim EMPA



4

Holcim EMPA

Thermodynamic Modeling:

- computes **chemical speciation** from the mass balance and thermodynamic data at *T,P* of interest
- assumes **partial/local equilibrium** in complex systems with phases-solutions
- works in **"forward" and "inverse"** modes
- **two main approaches** (and code types) exist:

• LMA (Law of Mass Action):

minimizes the mass balance residuals (master species are taken directly, product species - through their LMA expressions)

Codes: Phreeqc; Chess; Mineql; wateq4f, …

• GEM (Gibbs Energy *G*(*n*) Minimization):

finds amounts of components in all phases that minimize total *G*(*n*) of the system while maintaining the mass balance

Codes: GEMS, HSC; Fact(Chem)-Sage, …

Holcim EMPA

LMA & GEM Complementarity

LMA

- very fast and accurate
- aqueous speciation, diagrams
- only limited capabilities how to treat solid solutions
- surface complexation based on site balances
- redox can be set in the input
- pH can be set in the input
- thermod. data: not needed for master species; *K*(*T*) for product species

GEM

- fast; accuracy depends on consistency of input data
- aqueous speciation, diagrams
- many (non)ideal solution phases; phase diagrams
- surface complexation without site balances
- intrinsic redox state (pe) & pH
- thermod. data: $G^o(T)$ for all components in all phases; non-ideal mixing parameters

By application of the correct boundary conditions, both approaches give similar results. Only GEM solves redox-sensitive systems with many solution phases!

Holcim EMPA

Fundamentals of GEM (Gibbs Energy Minimisation)

Input → **Output**

Given:

- Temperature *T*, pressure *P*
- elemental bulk composition $n^{(b)}$
- list of chemical species *L* grouped into (non)ideal phases *F*
- molar $G(T,P)$ for *L* species
- optional mixing parameters
- specific surfaces, etc.

Finds:

- Speciation $n^{(x)}$ (primal solution)
- amounts of phases $n^{(\phi)}$
- activity coefficients $\gamma^{(x)}$
- chemical potentials of elements $u^{(b)}$ (dual solution)
- that all correspond to a global minimum of $G(n^{(x)})$ function

Holcim EMPA

Background
Principle of minimisation of free energy:

1. Mass balance $Ax = b$ (A…matrix as a function of stoichiometry coefficients of the input phases; b…input vector defining initial system composition; x…output vector defining final system composition)

2. Function to be minimised

$G(x) \Rightarrow \min;$

$$G(x) = \sum_i \sum_k x_i \upsilon_i$$

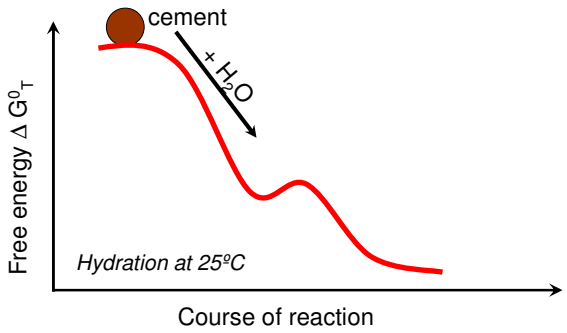
υi … chem. Potential of comp i

$$\upsilon_i = \frac{G^0_{i,T}}{RT} + \ln C_i + \ln \gamma_i$$

Standard molar Gibbs energy — Concentration — Activity coefficient

Holcim EMPA

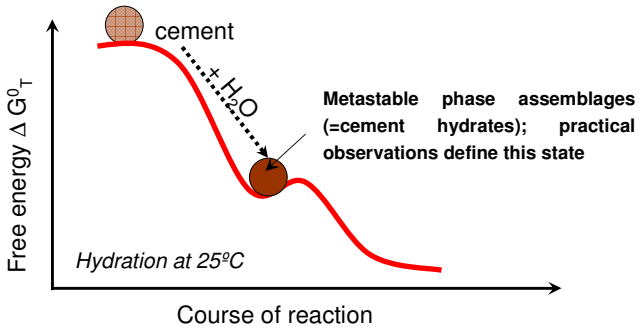
Background
Principle of minimisation of free energy:



Every system tends to move towards its lowest state of free energy

Holcim
EMPA

Background
Principle of minimisation of free energy:

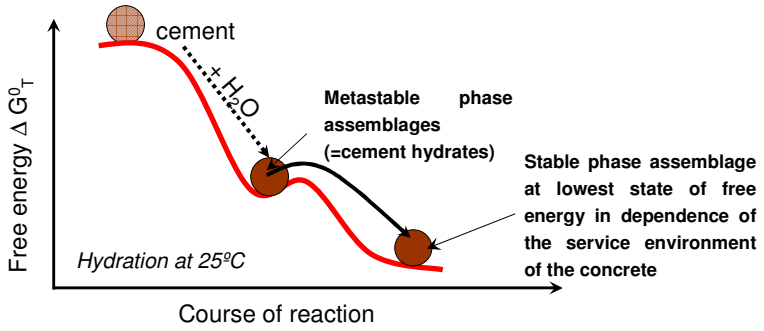


Every system tends to move towards lower states of free energy

Holcim
EMPA

Background

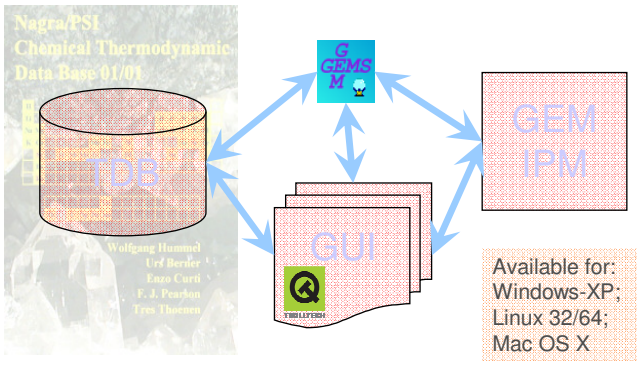
Principle of minimisation of free energy:



kinetic information, if available, can be included to focus and apply the calculations

Holcim
EMPA

GEMS-PSI Package



- Integrated
- Interactive
- User-friendly
- User scripts
- Runtime help
- Graphics
- Written in C/C++
- Built on Qt v.3
- Modular code
- Modular database

Official web page: http://gems.web.psi.ch/ (download, docs, screenshot tutorial)

Holcim
EMPA

Advantages of GEMS-PSI

1. *Chemical plausibility* of models
2. *Quality* & internal *consistency* of results
3. *Robustness & sensitivity* evaluation
4. Modeling *flexibility & performance*

Chemical Plausibility

- **intrinsic redox state** (f_{O2}, pe, Eh) and pH (aqueous)
- non-ideal aqueous solutions (various models)
- (non)ideal gas (fluid) mixtures
- **(non)ideal solid solutions**, partitioning easy to compute
- solid phase surfaces, **dispersity effects on solubility**
- **multi-surface sorption phases** & various EDL models
- **multi-site surface complexation** without site balances
- simulation of irreversible mass transfer processes (local and partial equilibrium principles) and plotting phase **diagrams**
- automatic *T,P* corrections of thermodynamic data
- isotopic equilibria (complete or partial)

Quality & Consistency

- GEM IPM2 solver: stable, fast, and accurate (uses JAMA C++)
- Is made available also as a standalone program GEMIPM2K
- Inbuilt phase- and species stability criteria
- *DComp* module (thermochemical data base format)
- *ReacDC* module (reaction-defined data base format)
- *RTparm* module for checking thermodynamic data vs *T,P*

Holcim
EMPA

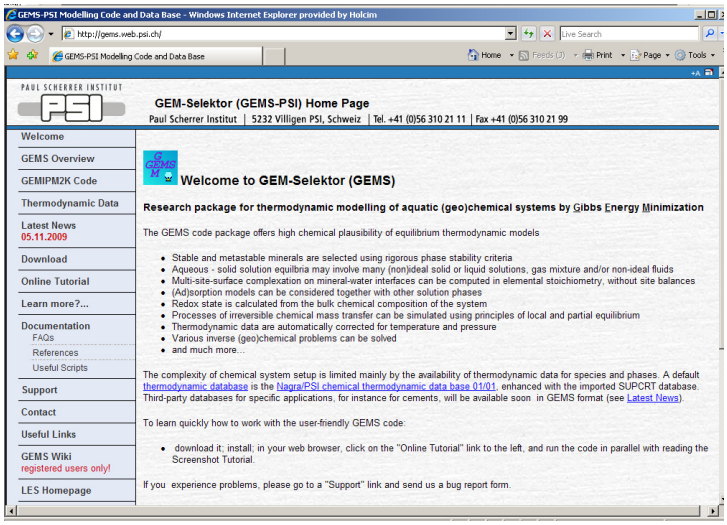
Flexibility & Performance

- very flexible system definition and setup within “modelling projects” that can be exchanged between users
- built-in thermodynamic and composition data bases (incl. plug-in third party data bases, e.g. CEMDATA)
- process simulators, run-, demo- & print scripts
- GtDemo samplers for export and plotting data; graphical presentation (in 3 modes)
- GUI, dialogs, record configuration wizards
- Runtime and online HTML help
- Tutorials, test projects (your help incl. setting up relevant tutorials and benchmark test projects is highly welcome)

Holcim
EMPA

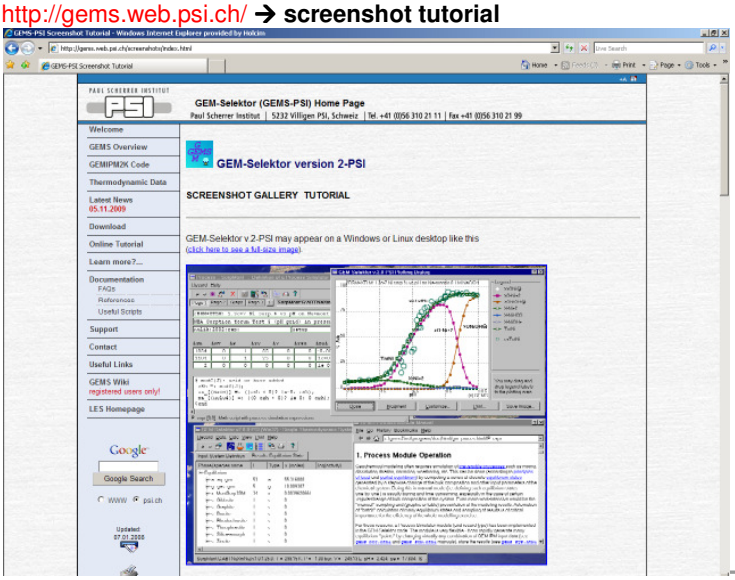
GEMS – How to get started

http://gems.web.psi.ch/



GEMS – How to get started

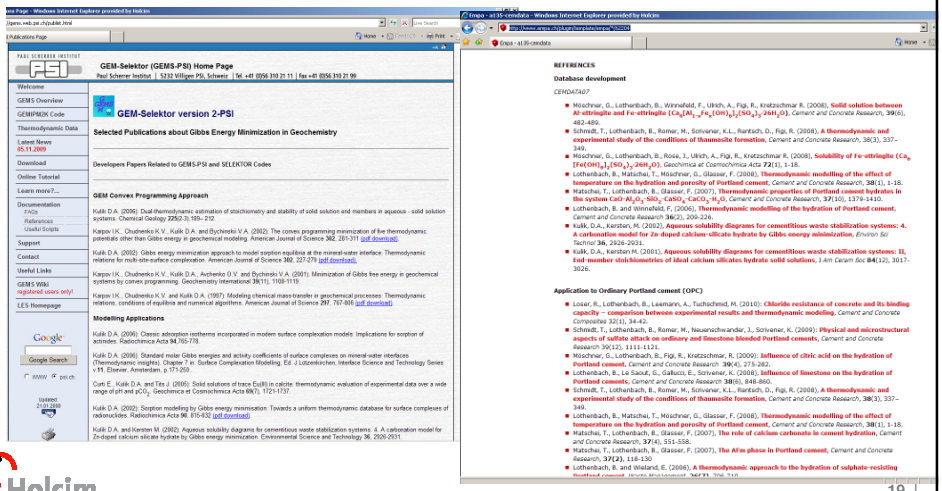
http://gems.web.psi.ch/ → **screenshot tutorial**



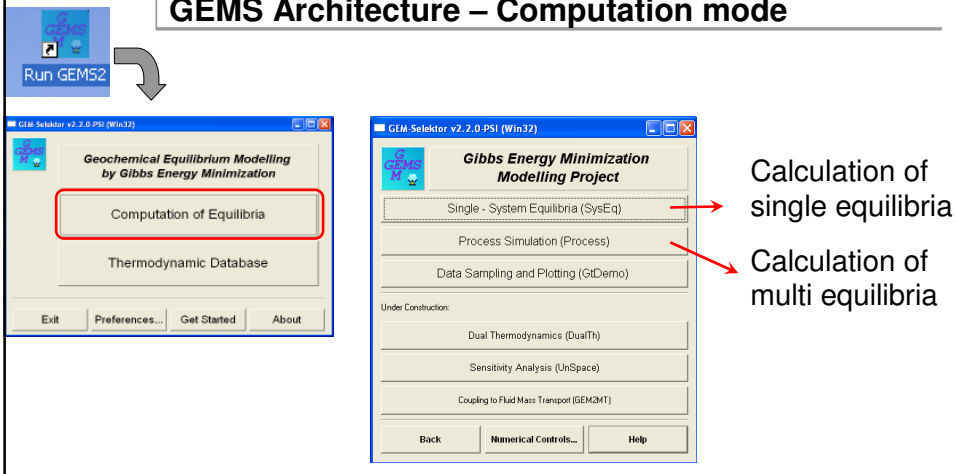
GEMS – How to get started

http://gems.web.psi.ch/;

http://www.empa.ch/plugin/template/empa/*/62204 **→references**

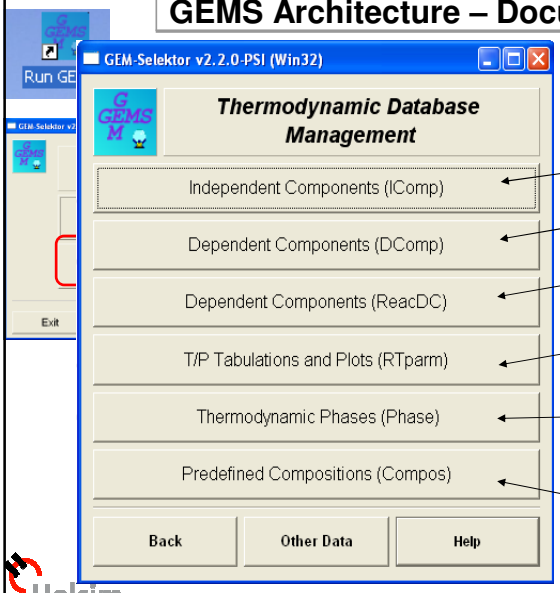


GEMS Architecture – Computation mode



GEMS – How to get started

GEMS Architecture – Documentation mode



Basic data (chemical elements)

Standard state properties

Standard state data defined via reaction with another species e.g. if only Ksp of reaction is known

Calculation and plot of thermodynamic data for dependent components

Definition of single- and multicomponent phases included in the corresponding project

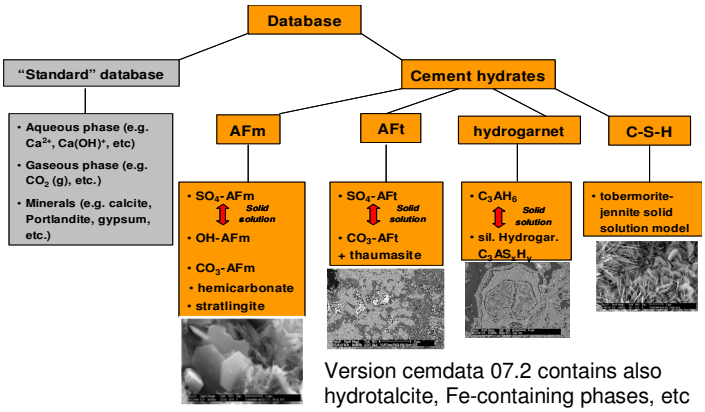
Predefined stoichiometric compositions independent from thermodynamic data

Holcim EMPA

21

Background

Thermodynamic database for cement hydrates



Version cemdata 07.2 contains also hydrotalcite, Fe-containing phases, etc

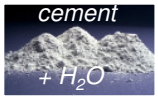
For original data source see: Matschei et al CCR 2007 (37) 1379-1410
Lothenbach et al CCR 2008 (38) 1-18

Qualitative and quantitative calculation of phase assemblages in the range 1 – 99°C are possible with the updated cement database (for database cemdata 07.2 see http://www.empa.ch/plugin/template/empa/*/62204)

Holcim EMPA

22

Summary
Thermodynamic modelling with GEMS



Ca^{2+} $CaOH^{+}$ $HSiO_3^{-}$ SO_4^{2-} CO_3^{2-}

Solids + aq. species

- GEMS-PSI, a geochemical modelling code, developed by Kulik, et al.
- Is based on the principle of the minimisation of the Gibbs energy of a complex chemical system

  $G(x) \Rightarrow$ *min. at given T, P*

- Computes mass balances, based on equilibrium phase assemblages and speciation in the aqueous phase, from total bulk composition $\Rightarrow$ *possibility of quantification*
- A comprehensive database involving all relevant phases has to be included

Holcim
EMPA