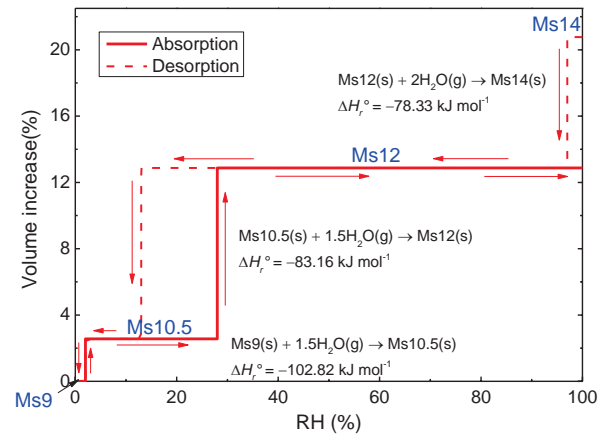


Impact of water activity on the stability of cement hydrates

Thomas Matschei, Luis Baquerizo

GEMS workshop 2014



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Outline

- Introduction
- Methodology used and results
 - Multi-method Approach
- Thermodynamic modelling

Introduction

- **Relative Humidity**

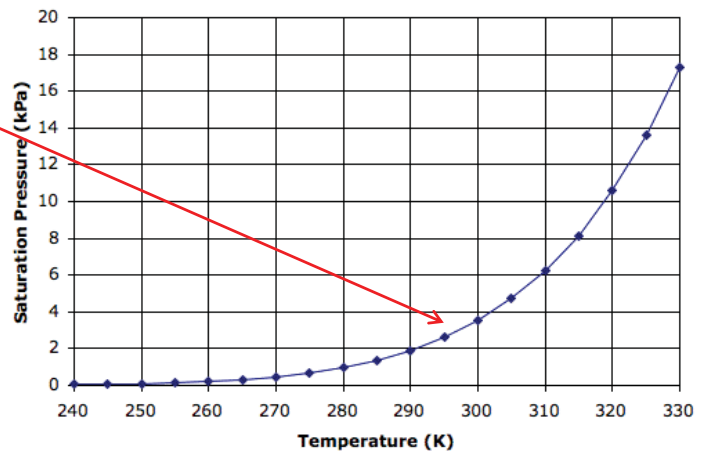
$$RH = V/V_s = P/P_s$$

V = vapor content

P = vapor pressure

V_s = saturation vapor content

P_s = saturation vapor pressure

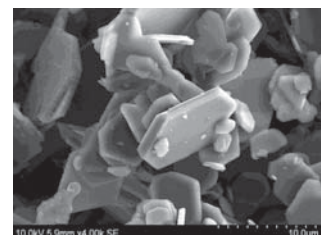


Introduction

- **Hydration states:** Varying water content of a hydrated phase

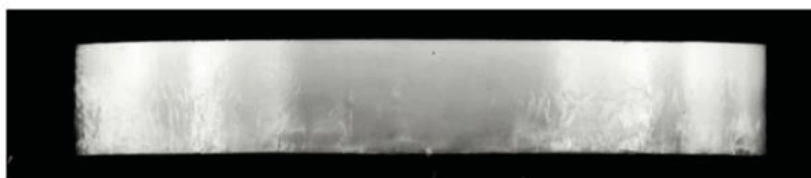
- Example: Monosulfoaluminate (Ms)

- ▶ Normal exposure conditions $[\text{Ca}_4(\text{Al})_2(\text{OH})_{12}]^{2+} [\text{SO}_4 \cdot 6\text{H}_2\text{O}]^{2-} \rightarrow \text{Ms}_{12}$
- ▶ At 8% RH $[\text{Ca}_4(\text{Al})_2(\text{OH})_{12}]^{2+} [\text{SO}_4 \cdot 4.5\text{H}_2\text{O}]^{2-} \rightarrow \text{Ms}_{10.5}$



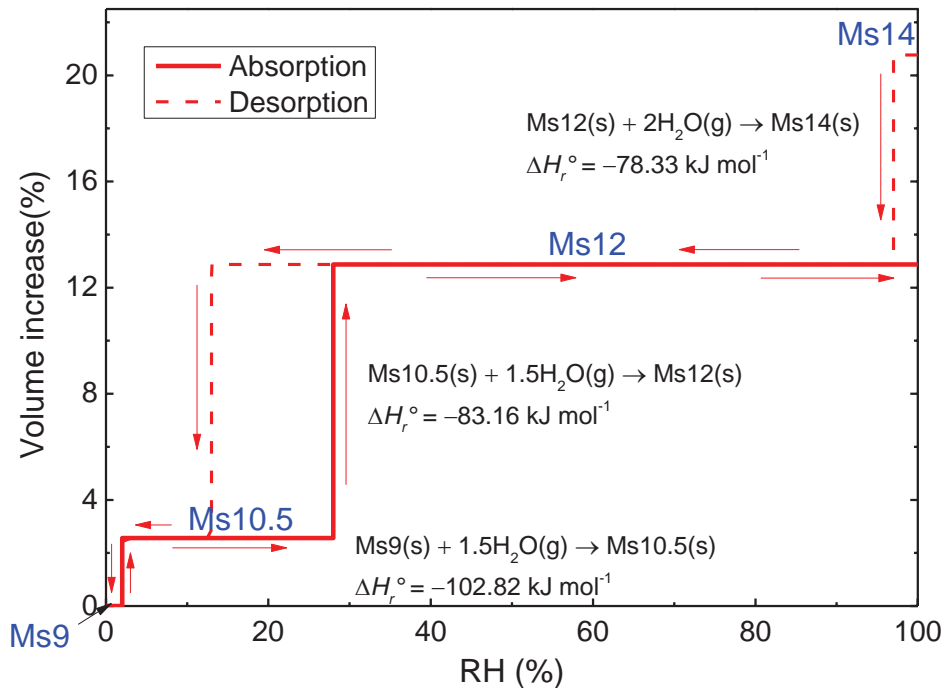
- Questions?

- ▶ At which conditions (RH and temperature) a change of hydration state takes place?
- ▶ What are the thermodynamic properties associated to these changes?
- ▶ How are the physical parameters (volume and density) affected?
- ▶ How these changes affect porosity and volume stability?



Monosulfoaluminate isotherm

- A summary of input data we had to obtain

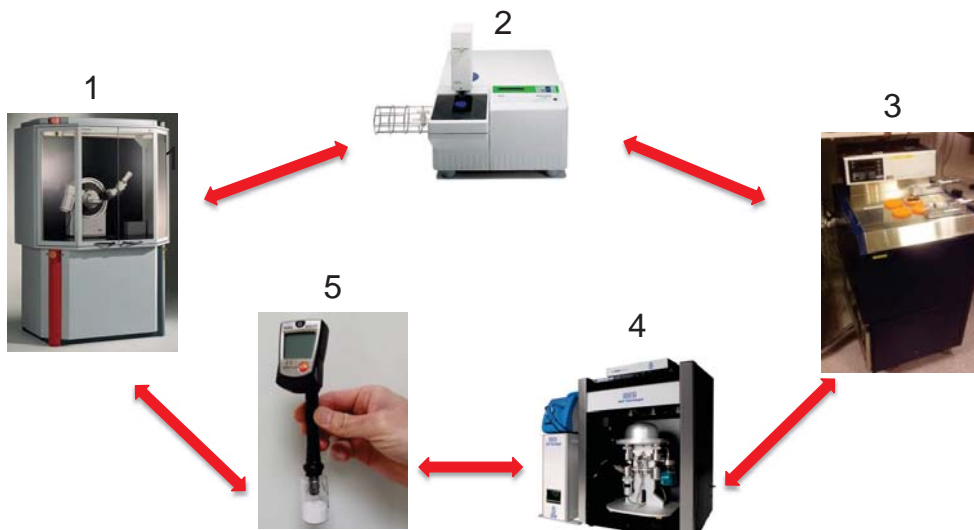


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

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Methodology. Answering the questions

- X-Ray diffraction (XRD)
- Thermogravimetric analysis (TGA)
- Sorption calorimeter: collaboration Transcend Project 6: Lund University
- Sorption balance: collaboration Transcend Project 6: Lund University
- Hydrate pair - humidity buffer method

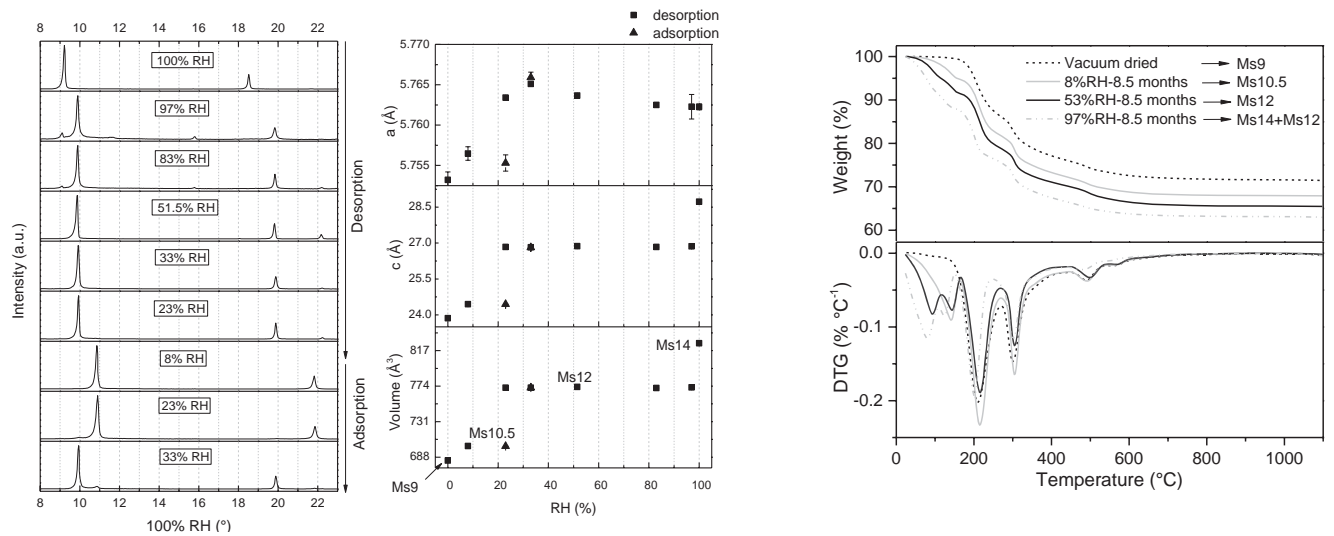


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

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Methodology

- XRD/ TGA



- Limitations: Lattice parameters refinement assuming that the space group did not change

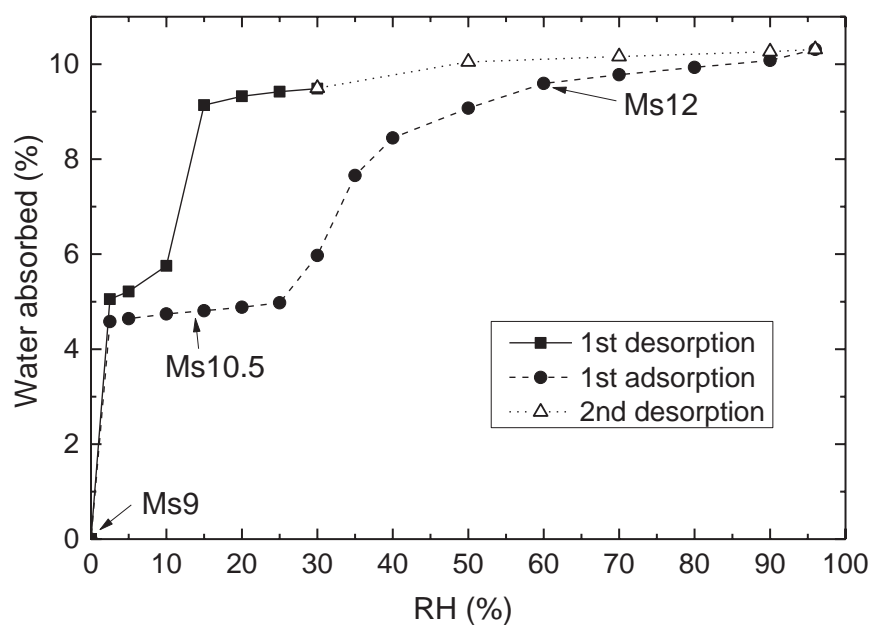


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

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Methodology

- Sorption balance

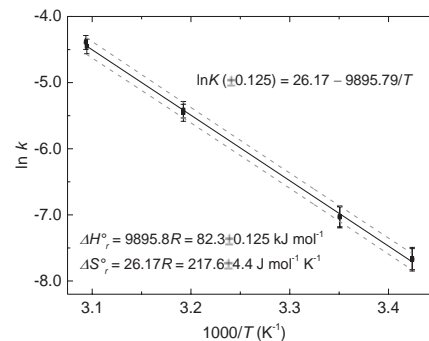
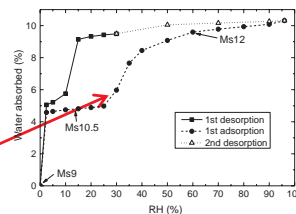
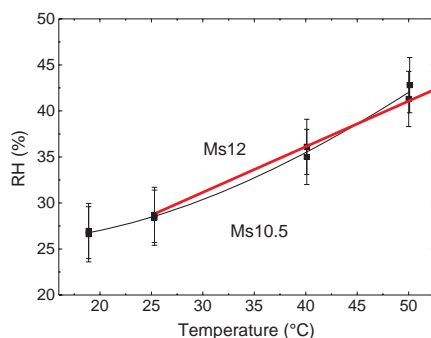


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

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Methodology

- Hydrate pair – humidity buffer method



$$\Delta G_r^\circ = -RT \ln K = -RT \ln [f(\text{H}_2\text{O})^{1.5}] = -1.5RT \ln \frac{f^*(\text{H}_2\text{O})RH}{100}$$

$$\frac{\partial(\ln K)}{\partial(1/T)} = -\frac{\Delta H_r^\circ}{R}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

ΔG_r° [kJ mol ⁻¹]	ΔH_r° [kJ mol ⁻¹]	ΔS_r° [J mol ⁻¹ K ⁻¹]
17.4 ± 0.3	82.3 ± 1.0	217.6 ± 4.4

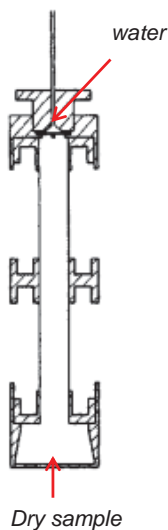


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedi-pour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

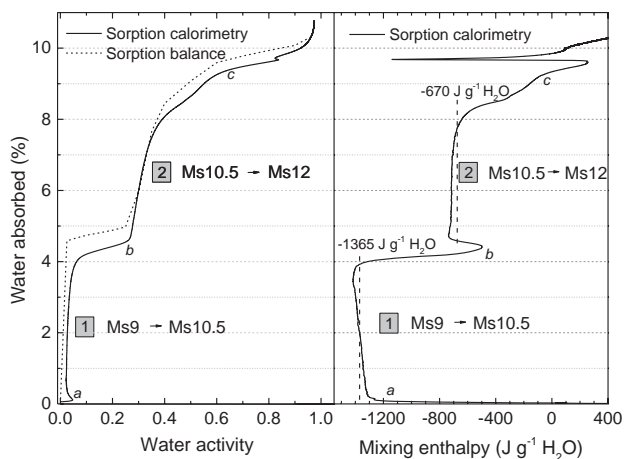
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Methodology

- Sorption calorimetry



Sorption Vessel



- Data so far:
 - Ms9→Ms10.5: 2% RH
 - Ms10.5→Ms12: 28.5% RH

	ΔG_r° [kJ mol ⁻¹]	ΔH_r° [kJ mol ⁻¹]	ΔS_r° [J mol ⁻¹ K ⁻¹]
Ms9→Ms10.5	27.3	102.8	253.2
Ms10.5→Ms12	17.4	84.04	223.5



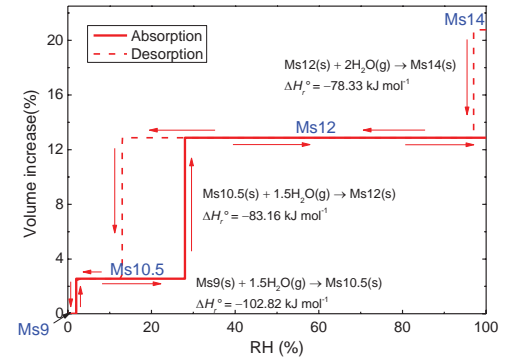
Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedi-pour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

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Methodology

- For the reaction

$$\text{Ms14} \rightarrow \text{Ms12} + 2\text{H}_2\text{O}$$
- In situ XRD testing was carried out using a humidity chamber
- The change of hydration state takes place at around:
 - 25 °C → 97% RH
 - 50 °C → 90% RH
 - 65 °C → 85% RH
 - 75 °C → 78% RH



- Then the thermodynamic properties were calculated with the equations:

$$\Delta G_r^\circ = -RT \ln K$$

$$\frac{\partial(\ln K)}{\partial(1/T)} = -\frac{\Delta H_r^\circ}{R}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T \Delta S_r^\circ$$



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Methodology

- Derived thermodynamic properties

Reaction	Change of hyd. state (% RH)	ΔG_r° (kJ mol ⁻¹)	ΔH_r° (kJ mol ⁻¹)	ΔS_r° (J mol ⁻¹ K ⁻¹)
$\text{Ms14(s)} \rightarrow \text{Ms12(s)} + 2\text{H}_2\text{O(g)}$	97	17.15	78.33 ^a	205.20
$\text{Ms12(s)} \rightarrow \text{Ms10.5(s)} + 1.5\text{H}_2\text{O(g)}$	28.5 ^b	17.42	83.16 ^c	220.51
$\text{Ms10.5(s)} \rightarrow \text{Ms9(s)} + 1.5\text{H}_2\text{O(g)}$	2 ^d	27.29	102.82 ^e	253.32

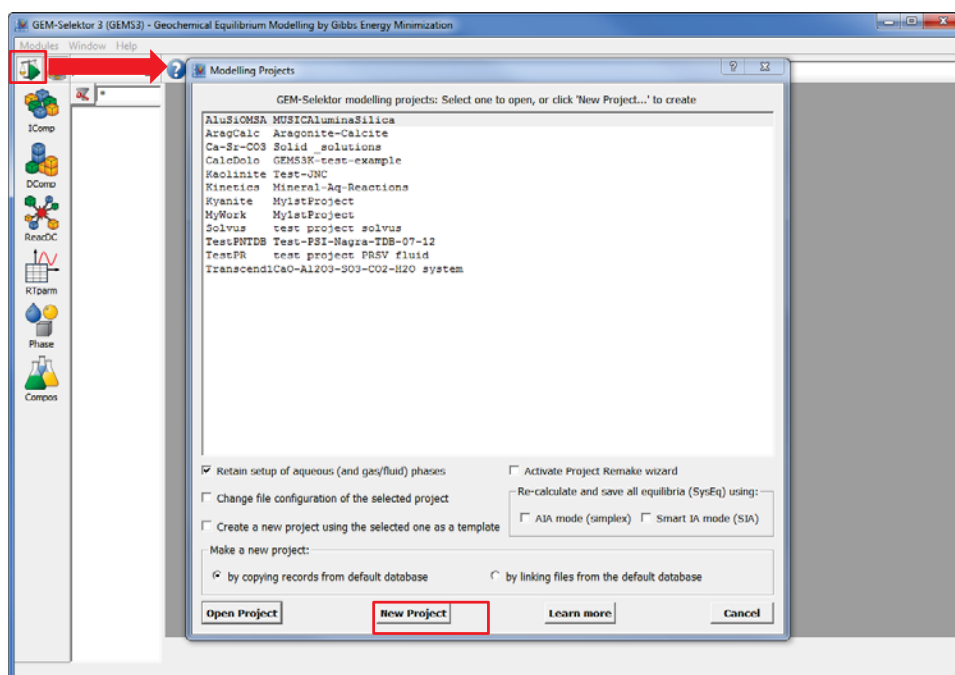
^aCalculated considering a change of hydration state at 97, 90, 85 and 78% RH at 25, 50, 65 and 75 °C, respectively ^bFrom hydrate pair - humidity buffer method ^cAverage value from sorption calorimetry and hydrate pair –humidity buffer method ^dFrom sorption balance ^eFrom sorption calorimetry



Thermodynamic modelling

1. Create Monosulphate14 in DComp
2. Introduce Monosulphate12, Monosulphate10.5 and Monosulphate9 in ReacDC
3. Model drying of Monosulphate14

Create new project



Create new project

Project: Enter a new record key, please

Tut_a:Ms:

Name of the modeling project

Comment to the project definition

Basis configuration of a new Modelling Project Tutorial_a

Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

- ☒ Aqueous electrolyte
- ☒ Gas mixture
- ☒ Non-ideal fluids
- ☐ Plasma
- ☒ Crystalline solids
- ☒ Dispersed solids
- ☒ Liquids, glasses
- ☐ Silicate melts
- ☐ Sorption, Ion exchange
- ☐ Polyelectrolytes
- ☐ Liquid hydrocarbons
- ☐ Skip solid solutions

Built-in Database

Built-in Database	Version
<input type="checkbox"/> support	
<input type="checkbox"/> support	
<input type="checkbox"/> specific	
<input checked="" type="checkbox"/> psi-nagra	
<input checked="" type="checkbox"/> 3rdparty	

Create new project

Basis configuration of a new Modelling Project Tutorial_a

Step 2: Select Independent Components (not available if shown in light gray color)

	I	II	III	IV	V	VI	VII	VIII	
1	<input checked="" type="checkbox"/> H								He
2	Li	Be	<input checked="" type="checkbox"/> B	<input checked="" type="checkbox"/> C	<input checked="" type="checkbox"/> N	<input checked="" type="checkbox"/> O	<input checked="" type="checkbox"/> F		Ne
3	Na	Mg	<input checked="" type="checkbox"/> Al	Si	P	<input checked="" type="checkbox"/> S	Cl		Ar
4	K	<input checked="" type="checkbox"/> Ca	Sc	Ti	V	Cr	Mn	Fe	Co
4a	Cu	Zn	Ga	Ge	As	Se	Br		Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh
5a	Ag	Cd	In	Sn	Sb	Te	I		Xe
6	Cs	Ba	REE	Hf	Ta	W	Re	Os	Ir
6a	Au	Hg	Tl	Pb	Bi	Po	At		Rn
7	Fr	Ra	ACT						
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk

☐ Isotopes

Additional

☒ Nit

Create new project

Setup of aqueous and gas phases in project: Tutorial_a

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

☐ Ion-association (IA) with Davies equation, D (default)

☒ IA with extended Debye-Hueckel equation (Helgeson), common b_gamma and a0, H

☐ IA with extended Debye-Hueckel equation (Shvarov), common b_gamma and a0, Y

☐ IA with extended Debye-Hueckel equation (Karpov), common b_gamma, individual a0, 3

☐ IA with Debye-Hueckel equation, no b_gamma, individual a0, 2

☐ IA with Debye-Hueckel limiting law (very low ionic strength), 1

☐ Do not generate; select a user-defined Phase record from database (Q, S, Z), U

☐ Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq_gen aq EDH_H

Parameters for the aqueous phase model

b_gamma(1,298) value: 0.064

b_gamma(P,T) mode: KOH

Common a0 value: 3.67

Gamma (neutral species): Calculate as b_gamma*IS

Gamma (water solvent): From osmotic coefficient

Molality conversion: Applied to all species

OK Cancel Check Learn more

Create new project

Introduce monosulphate and AirNit_22

SysEq: Please, enter a new record key:

Tutorial_a:G:Ms:0:0:1:25:0:

Tutorial_a Name of the modeling project

G Thermodynamic potential to minimize {G GV}

Ms Name of the chemical system definition (CSD)

0 CSD (recipe) variant number <integer>

0 Volume of the system, dm3 (0 if no volume constraint)

1 Pressure, bar, or 0 for Psat(H2O)g

25 Temperature, C (>= 0)

0 Variant number for additional constraints

Ok Reset From List Help Cancel

Input Recipe of Single Thermodynamic System: Tutorial_a:G:Ms:0:0:1:25:0:

tname

Property Selection

Compos (xa_) AirNit_22 H2SO4

DComp (xd_) Al(OH)3 O2

IComp (bi_) Al2O3 SO3

Phase (xp_) Aqua

Kin.lower (dll_) AtmAirNit

Kin.upper (dul_) C3A

G0 shift (gEx_) CH4

Other Inputs CO2

Ca(OH)2

CaCO3

CaO

CaSO4

Gypsum

H2

H2S

Recipe Input

Property	Name	Quantity	Units
1	xd_ monosulphate	1	M
2	xa_ AirNit_22	1	g

Input quantities of Compos(itions) contributing to B_ vector

Learn more Print OK Cancel

Create new project

Input: System Definition Results: Equilibrium State

Phase/Species	T	Amount (mol)	log10(Activity)	Concentration	Activity coeff.
aq_gen	30	a 0	-0.3456		
gas_gen	6	g 0.034400083	2.691e-10		
SO4_OH_AFm	2	s 0.99999257	-5.495e-10		
OH_SO4_AFm	2	s 5.7178457e-007	-5.495e-10		
SO4_CO3_Af	2	s 3.1795438e-005	7.258e-06		
CO3_SO4_Af	2	s 5.8069077e-007	7.258e-06		
Al(OH)3mic	1	s 0	-0.4531		
Gibbsite	1	s 0.00014678063	4.454e-06		
Graphite	1	s 0	-80.2		
Aluminate	1	s 0	-35.76		
C2AH7.5	1	s 0	-3.031		
C3AH6	1	s 0	-2.325		
C4AH13	1	s 0	-6.762		
CAH10	1	s 0	-3.583		
C4AsH12	1	s 5.3068851e-007	-7.511e-07		
C4AsH11	1	s 0	-1.566		
ettringite	1	s 5.6310961e-007	7.258e-06		
Arasgonite	1	s 0	-0.1438		
Calcite	1	s 0.0002184429	2.893e-05		
lime	1	s 0	-11.09		
Portlandite	1	s 0	-1.659		
Anhydrite	1	s 9.2398775e-006	8.649e-05		
Gypsum	1	s 0	-0.4691		
hemihydrate	1	s 0	-0.9392		
Sulphur	1	s 0	-113.6		

System: T = 298.15 K; P = 1.00 bar; V = 1.162 L; Aqueous: built-in EDH(H); pH = 11.991; pe = 8.781; IS = 0.247 m

SO4_OH_AFm
more stable than
C4AsH12 (Ms12):
its formation has to
be skipped

Just C4AsH12
(Ms12) appears.
The other hydration
states are not
introduced



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Introduce water vapor

Go to Database
management
mode to introduce
water vapor

Modules Record Record List Database Files Window Help

DComp Selection... Add Link... New File... Compress...

DComp :: Thermochemical/EoS data format for Dependent Components

Page 1 Page 2 11/04/2014, 11:35

H2O 1
H2O@

M0 18.0153 Zz 0 ab -1 -

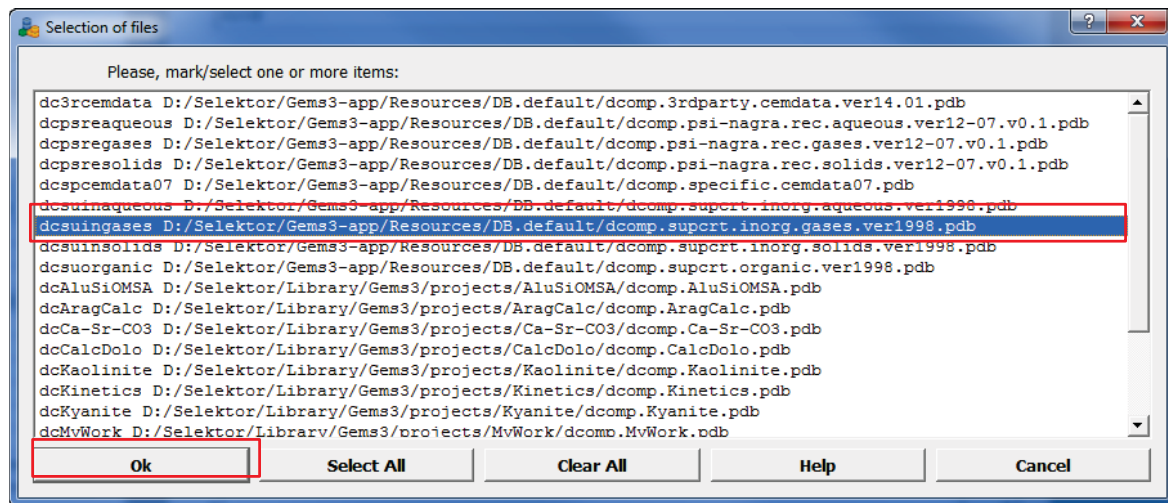
V0d 1.80684 0
G0d -237183 ---
H0d -285881 ---
S0d 69.923 ---
Cp0d 75.3605 0
PrTr 1 25
LamST --- ---
BetAlp --- ---

SUPCRT:1992:prog: All ref:2



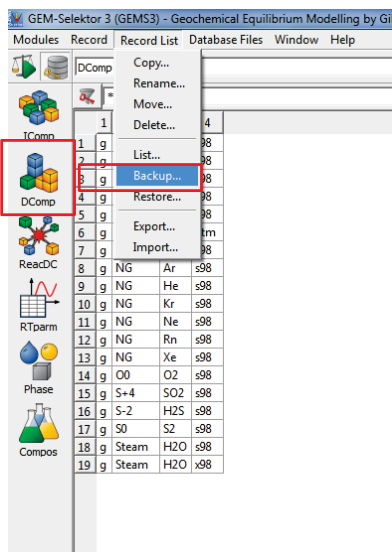
© 2013

© 2013

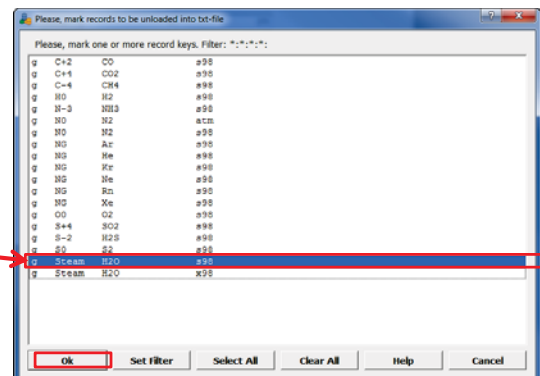


© 2013

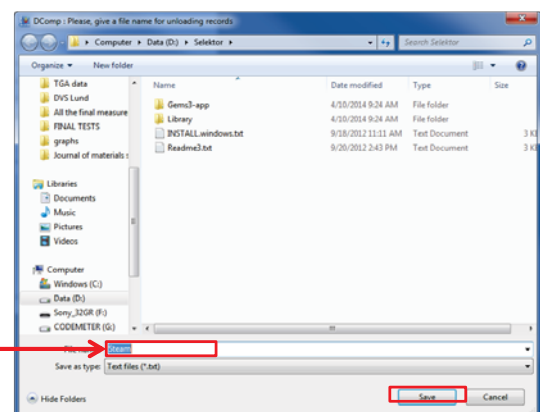
Backup Steam s98



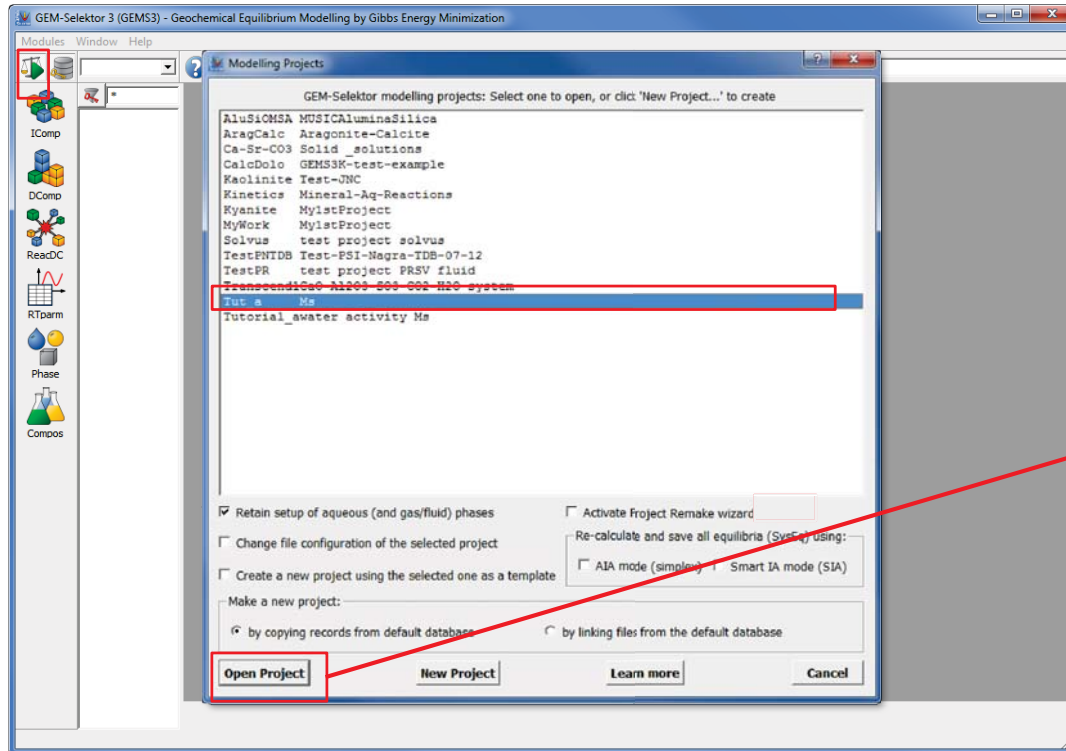
Choose Steam s98



Save as Steam.txt



Introduce water vapor

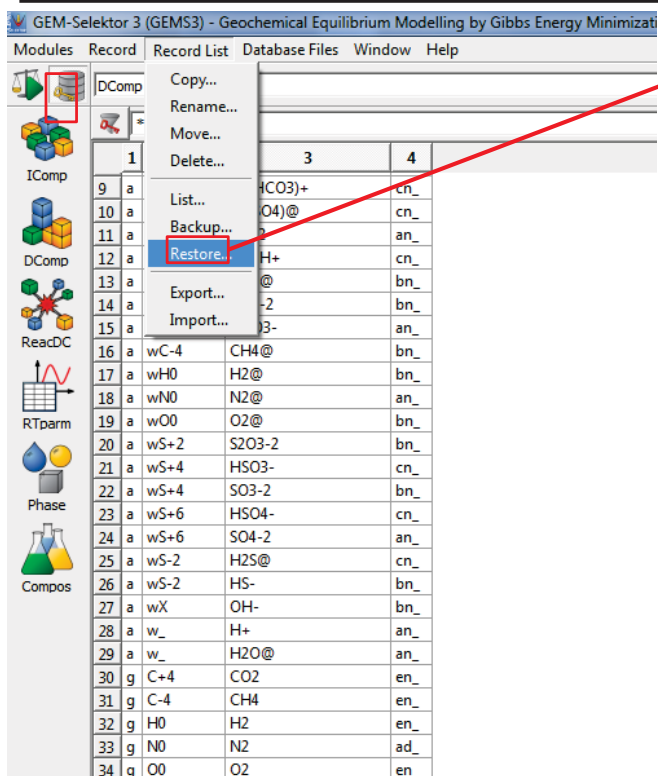


Open the project

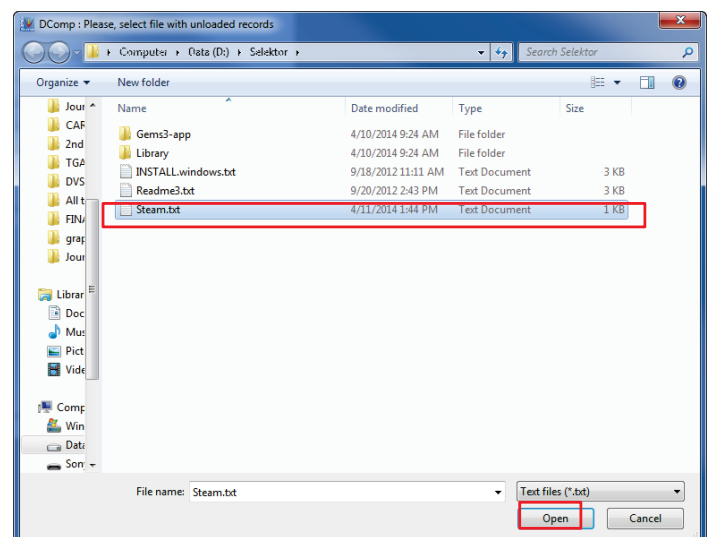


© 2013

Introduce water vapor



Restore Steam.txt into the project database



© 2013

Introduce water vapor

Open the project again and accept the insertion of Steam

© 2013

Introduce water vapor: checking the equilibrium RH

Calculate equilibrium → H₂O appears as a component of the gas_gen

Equilibrium RH of the system can be calculated as follows:

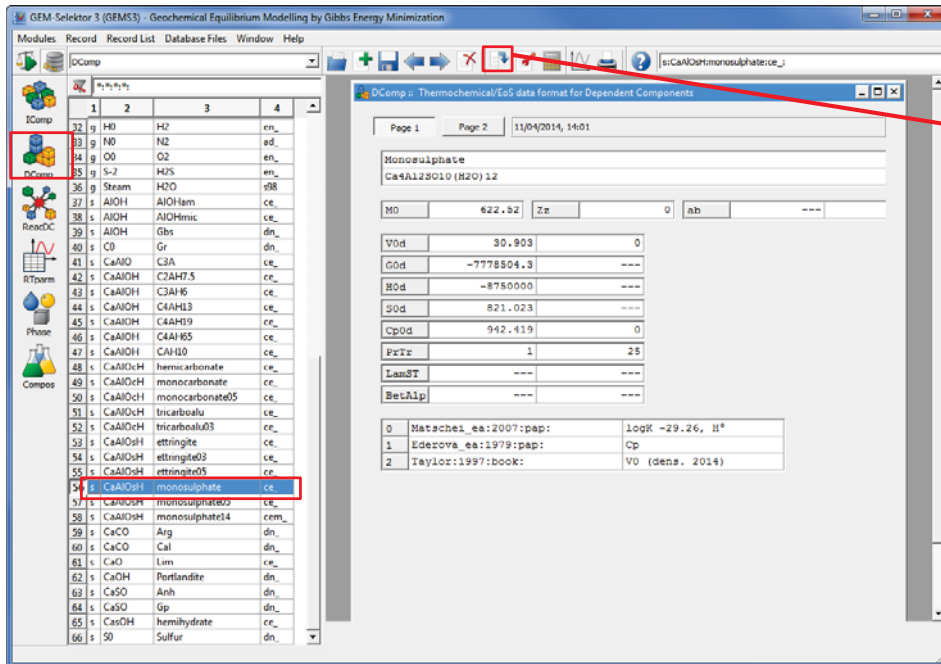
$$RH = \frac{a\{H_2O\}}{0.0324456} \times 100$$

$a\{H_2O\}]_{\text{sat at } 25^\circ\text{C}}$

System: T = 298.15 K; P = 1.00 bar; V = 1.174 L; Aqueous: built-in EDHS; pH = 0.000; pe = 0.000; IS = 0.278 m

Introduce Ms14 in DComp

Monosulphate14 (Ms14) is the stable hydration state at saturated conditions
Ms14 has to be introduced starting from monosulphate

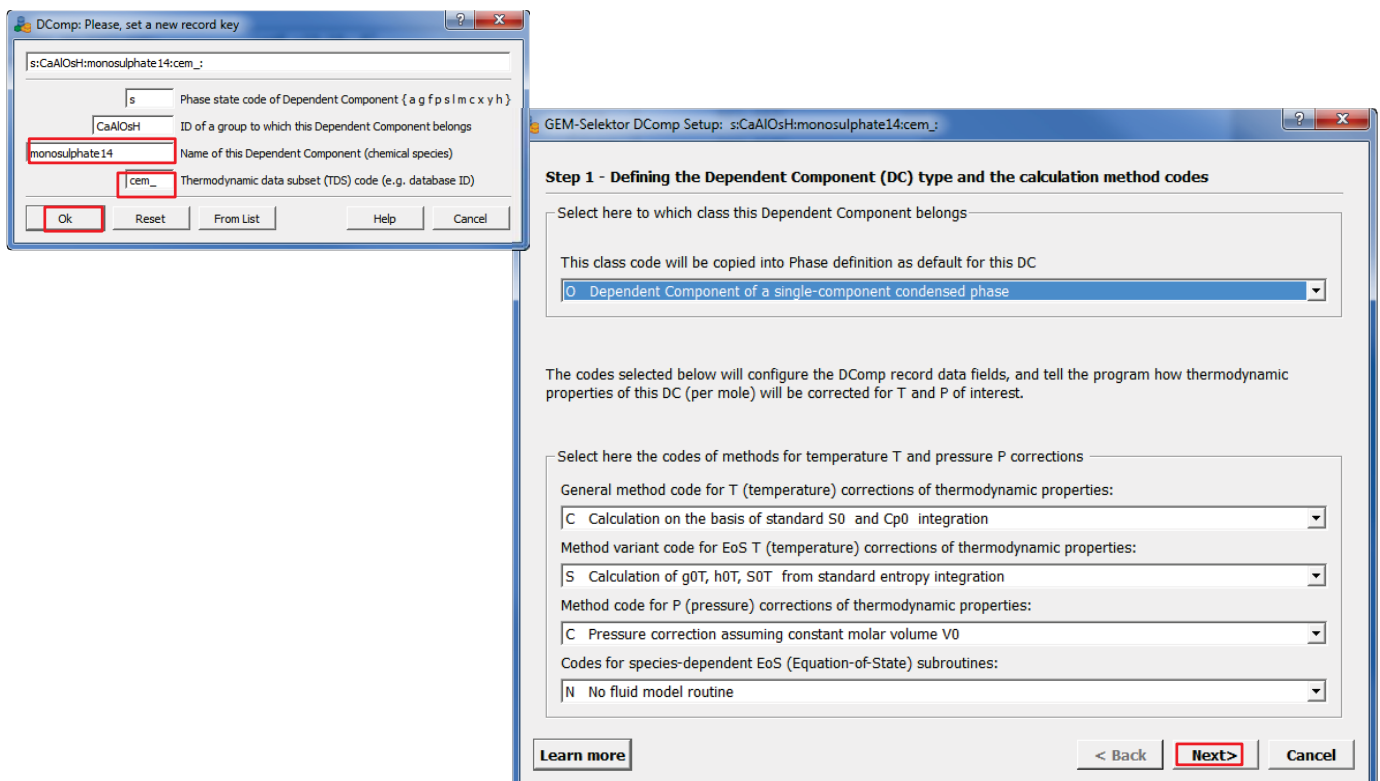


Clone monosulphate



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Introduce Ms14 in DComp



© 2013

Introduce Ms14 in DComp

GEM-Selektor DComp Setup: s:CaAlO₃Hmonosulphate14.cem_

Step 2 - Specific dimensions and settings

Dimensions to change only in special cases

1 Number of sets of coefficients of $C_p=f(T)$ equation can be changed here, if available for several temperature intervals. Default is 1, maximum 5 sets (intervals).

0 Number of phase transitions can be changed here, if necessary (usually one less than the number of sets of $C_p=f(T)$ coefficients). Default is 0, maximum 4.

0 Number of EoS coefficients can be set here for certain EoS models of fluids (default: 0). Coefficients will be collected automatically into Phase record, if this DC is included.

☐ Check here to allocate the $V_m = f(P, T)$ vector of coefficients (reserved)

Units of measurement (cannot be changed in this version of GEMS)

J J/mol(K) Units of energy (default: J)

J J/bar = 0.1 cm³/mol Units of volume (default: J)

b bar = 10⁵ Pa Units of pressure (default: b)

C Celsius Units of temperature (default: C)

Learn more < Back **Next>** Cancel

GEM-Selektor DComp Setup: s:CaAlO₃Hmonosulphate14.cem_

Step 3 - Useful hints

Optional

3 Set here the number of links to bibliography Sdref records (default 0)

What will happen after you click "Finish"

(1) Page 1 of "DComp" window appears. Fill out the DCname field, and (essential!) enter DC formula into DCform field.

(2) Enter standard molar properties of DC into V0d, G0d, H0d, S0d, Cp0d cells. If unknown, enter the 'empty' value ('---'). Any two of three values G0, H0 and S0 must be known; the third one (if given as 'empty') will be retrieved upon re-calculation.

(3) Switch to Page 2 and enter values into TCint, then a1Cp or aiHKF arrays, whatever appropriate. In some cases, fluid EoS coefficients, critical parameters, or V(T,P) coefficients may need to be entered.

(4) Go back to Page 1 and click the 'Calculate' toolbar button. Missing DC properties will appear. If $C_p=f(T)$ (or HKF) coefficients were entered, Cp0 (and V0) values will also be calculated. Save the record. To test T,P corrections, create a RTParm tabulator for this DComp record.

Learn more < Back **Finish** Cancel



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Introduce Ms14 in DComp

Introduce Ms14 properties and then calculate



DComp :: Thermodynamic/EoS data format

Page 1 Page 2 11/04/2014

Monosulphate

Ca4Al2S010 (H2O) 14

M0 658.55 Zz ---

V0d 33.16

G0d -8252870.3

H0d -9321762

S0d 960.854

Cp0d 1028.53 0

PrTr 1 25

LamST --- ---

BetAlp --- ---

0 Matschei_ea:2007:pap: God and Hod adding 2H2O

1 Ms14+2Cs->Ms12+2CsH Cp calculation

2 Baquerizo et al 2014 Vo

DComp :: Calculation...

Page 1 Page 2 11/04

C S C N O J J b

TCint

0 0

1 80

a1CpT

0 619

1 1.387

2 0

3 0

4 0

5 0

6 0

7 0

8 0

9 0

10 0

11 0

* $C_p^o = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{-0.5}$

*Matschei T (2007) Thermodynamics of Cement Hydration. PhD Dissertation, University of Aberdeen.

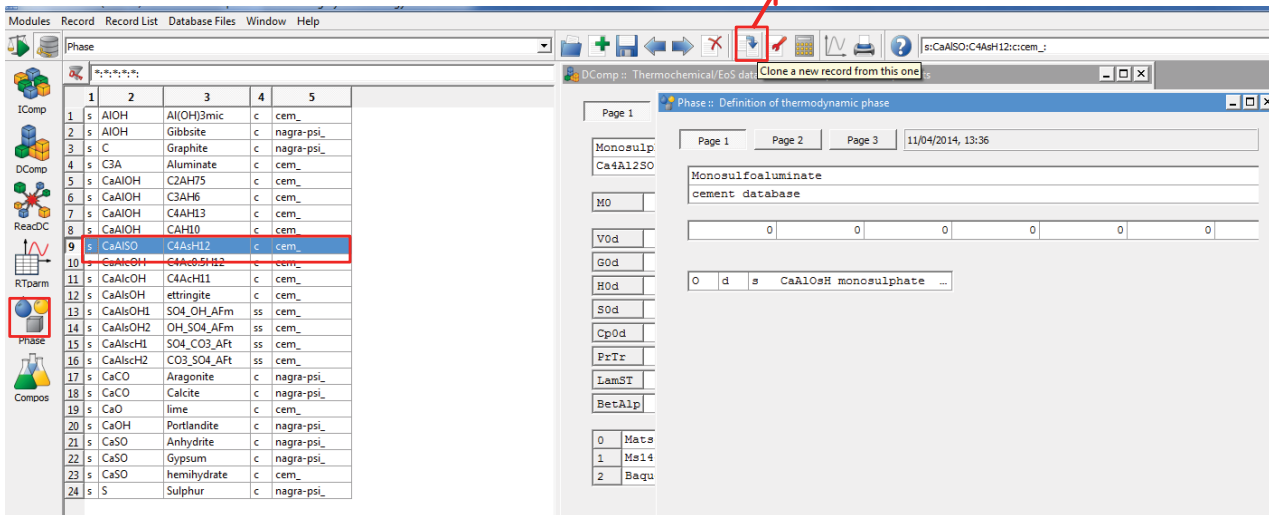


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Create the Phase Ms14

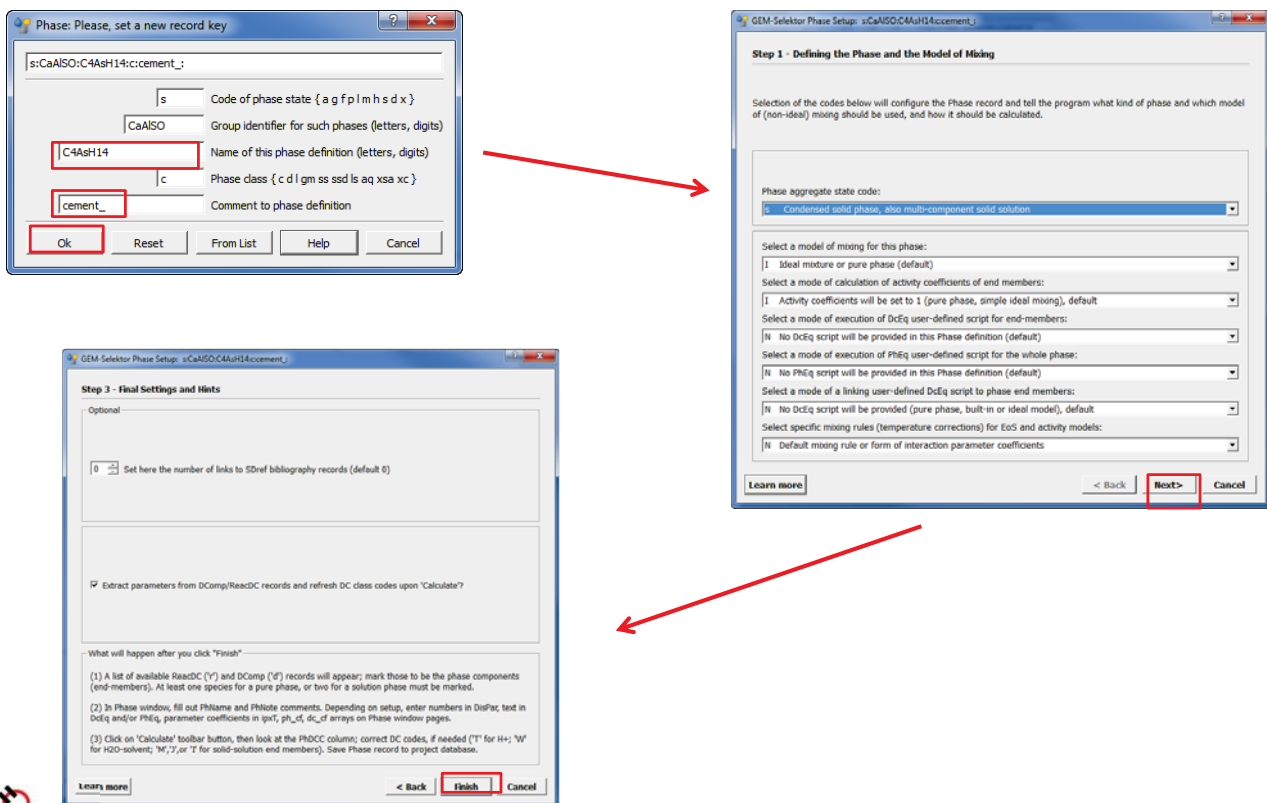
Ms14 has to be added as a Phase
We can start cloning monosulphate (C4AsH12)

Clone C4AsH12



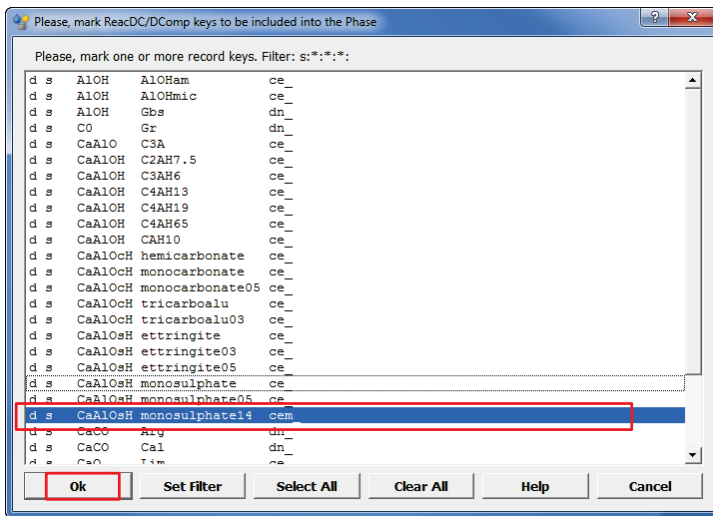
© 2013

Create the Phase Ms14



© 2013

Create the Phase Ms14



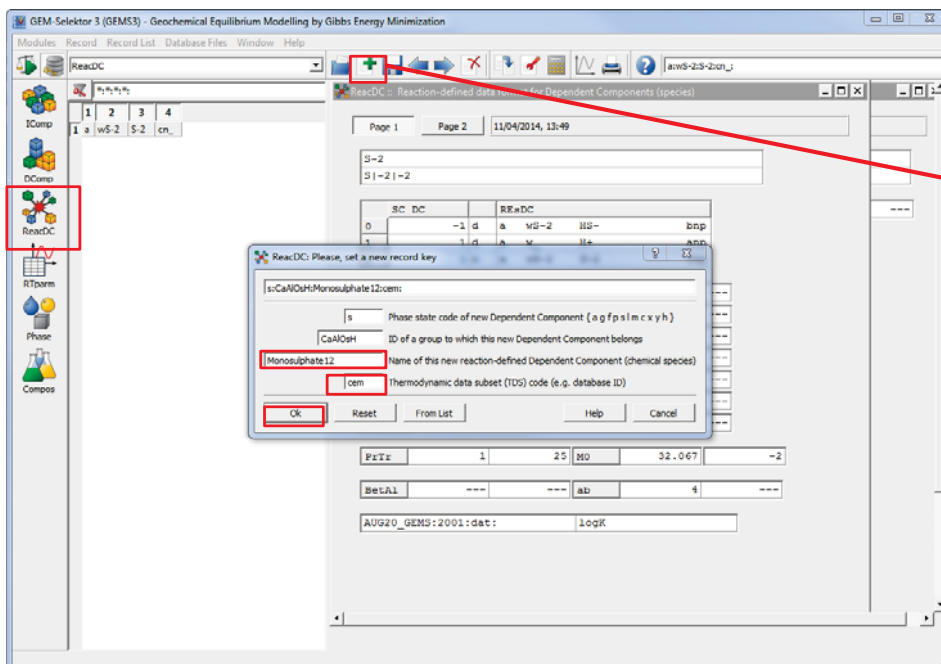
1	2	3	4	5
1	s	AlOH	Al(OH)3mic	c
2	s	AlOH	Gibbsite	c
3	s	C	Graphite	c
4	s	C3A	Aluminate	c
5	s	CaAlOH	C2AH75	c
6	s	CaAlOH	C3AH6	c
7	s	CaAlOH	C4AH13	c
8	s	CaAlOH	CAH10	c
9	s	CaAlSO	C4AsH12	c
10	s	CaAlSO	C4AsH14	c
11	s	CaAlcOH	C4Ac0.5H12	c
12	s	CaAlcOH	C4AcH11	c
13	s	CaAlSOH	ettringite	c
14	s	CaAlSOH1	SO4_OH_AFm	ss
15	s	CaAlSOH2	OH_SO4_AFm	ss
16	s	CaAlscH1	SO4_CO3_Aft	ss
17	s	CaAlscH2	CO3_SO4_Aft	ss
18	s	CaCO	Aragonite	c
19	s	CaCO	Calcite	c
20	s	CaO	lime	c
21	s	CaOH	Portlandite	c
22	s	CaSO	Anhydrite	c
23	s	CaSO	Gypsum	c
24	s	CaSO	hemihydrate	c
25	s	S	Sulphur	c



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Introduce Ms12: ReacDC

The lower hydration states (Ms12, Ms10.5 and Ms9) have to be introduced as a reaction



Create a new record



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Introduce Ms12: ReacDC

GEM-Selektor ReacDC Setup: s:CaAlO₂H:Monosulphate12:cm:

Step 1 - Selection of reaction-defined DC type and codes of methods of T,P correction

Select here the class code for the reaction-defined Dependent Component (DC)

This DC class code will be copied to Phase definition (can be changed there too):

Dependent Component of a single-component condensed phase

The codes set below will configure the ReacDC record and define how to compute T,P corrections for the reaction and the new DC it defines.

Select here method codes of T,P correction for molar properties of the reaction-defined DC

General method code for temperature corrections:

Calculation through the logK of reaction TP dependency

Method variant code for temperature EoS corrections:

Three-term extrapolation of logK (T) at dCpr (T) = const

Method code for pressure corrections:

Molar volume of new DC calculated from constant dVr of reaction

Codes for species-dependent EoS subroutines

No fluid model routine

[Learn more](#) [< Back](#) [Next >](#) [Cancel](#)

GEM-Selektor ReacDC Setup: s:CaAlO₂H:Monosulphate12:cm:

Step 2 - Specific dimensions and settings

Dimension to change only in special cases (e.g. to find properties of reaction between existing DCs)

Number of DCs in the reaction (usually set automatically after selecting the DCs)

Dimensions to set only for the logK array for T,P corrections by interpolation (KZZ method codes)

Number of interpolation points along T (> 2, < 20)

Number of interpolation points along P (> 1, < 10)

Units of measurement (cannot be changed in this version of GEMS)

J/mol(K) Units of energy (default: j)

J/bar = 0.1 cm³/mol Units of volume (default: j)

bar = 10⁵ Pa Units of pressure (default: b)

Celsius Units of temperature (default: C)

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Introduce Ms12: ReacDC

Introduce the components taking part of the reaction

Please, mark ReacDC/DComp keys to be included

Please, mark one or more record keys. Filter: *.*.*.*:

d	g	Steam	H2O	s98
d	s	AlOH	AlOHam	ce_
d	s	AlOH	AlOHmic	ce_
d	s	AlOH	Gbs	dn_
d	s	CO	Gr	dn_
d	s	CaAlO	C3A	ce_
d	s	CaAlOH	C2AH7.5	ce_
d	s	CaAlOH	C3AH6	ce_
d	s	CaAlOH	C4AH13	ce_
d	s	CaAlOH	C4AH19	ce_
d	s	CaAlOH	C4AH65	ce_
d	s	CaAlOH	CAH10	ce_
d	s	CaAlOCH	hemcarbonate	ce_
d	s	CaAlOCH	monocarbonate	ce_
d	s	CaAlOCH	monocarbonate05	ce_
d	s	CaAlOCH	tricarboalu	ce_
d	s	CaAlOCH	tricarboalu03	ce_
d	s	CaAlOsH	ettringite	ce_
d	s	CaAlOsH	ettringite03	ce_
d	s	CaAlOsH	ettringite05	ce_
d	s	CaAlOsH	monosulphate	ce_
d	s	CaAlOsH	monosulphate05	ce_
d	s	CaAlOsH	monosulphate14	cem
d	s	CaCO	Arg	dn_
d	s	CaCO	Ca1	dn_

[Ok](#) [Set Filter](#) [Select All](#) [Clear All](#) [Help](#) [Cancel](#)

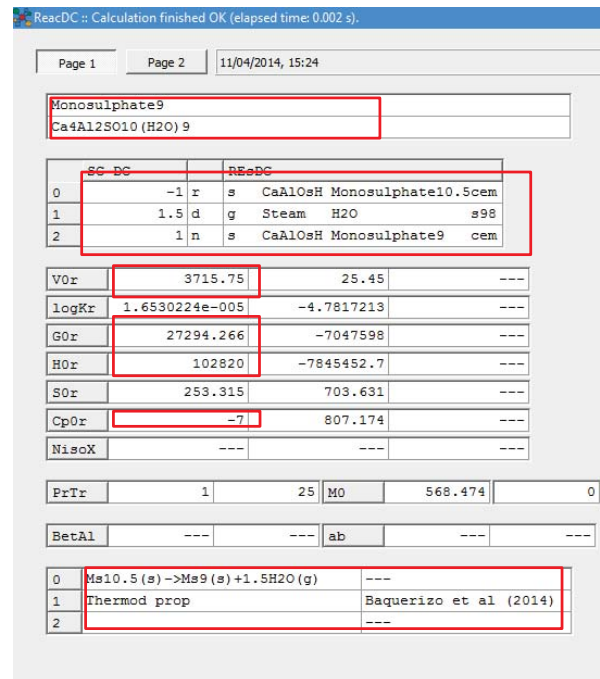
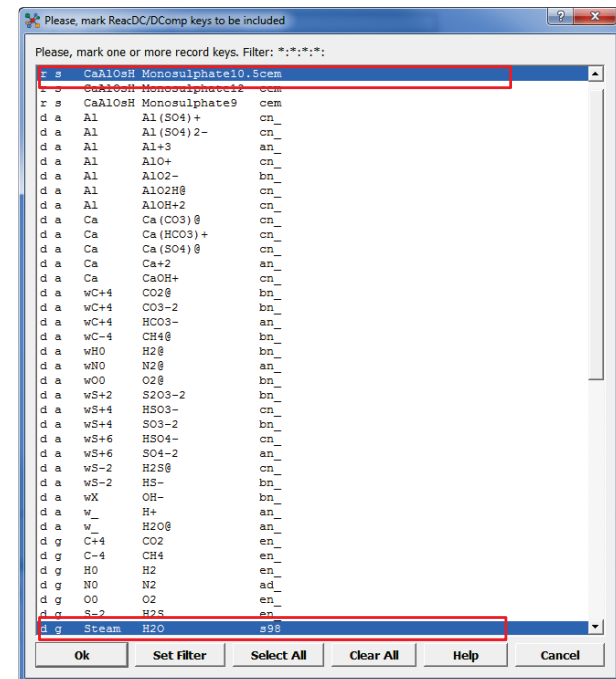


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Introduce Ms9: ReacDC

The same procedure done with Ms10.5 is repeated to introduce Ms10.5



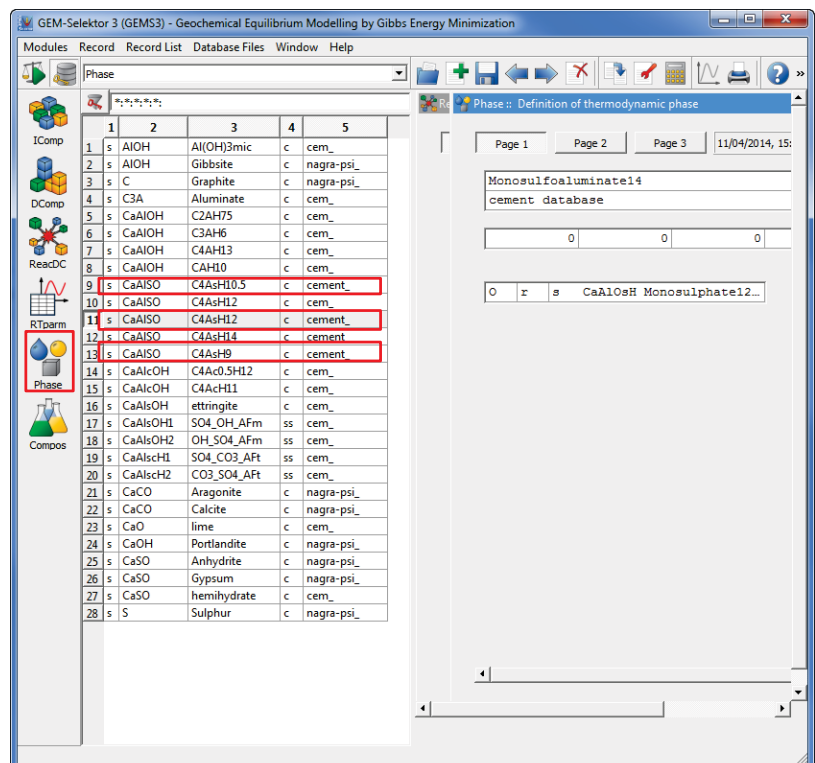
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Introduce Ms12, Ms10.5 and Ms9 as phases

Introduce all the hydration states as Phases as previously done with Ms14.

Phases to be introduced

- Ms12
- Ms10.5
- Ms9



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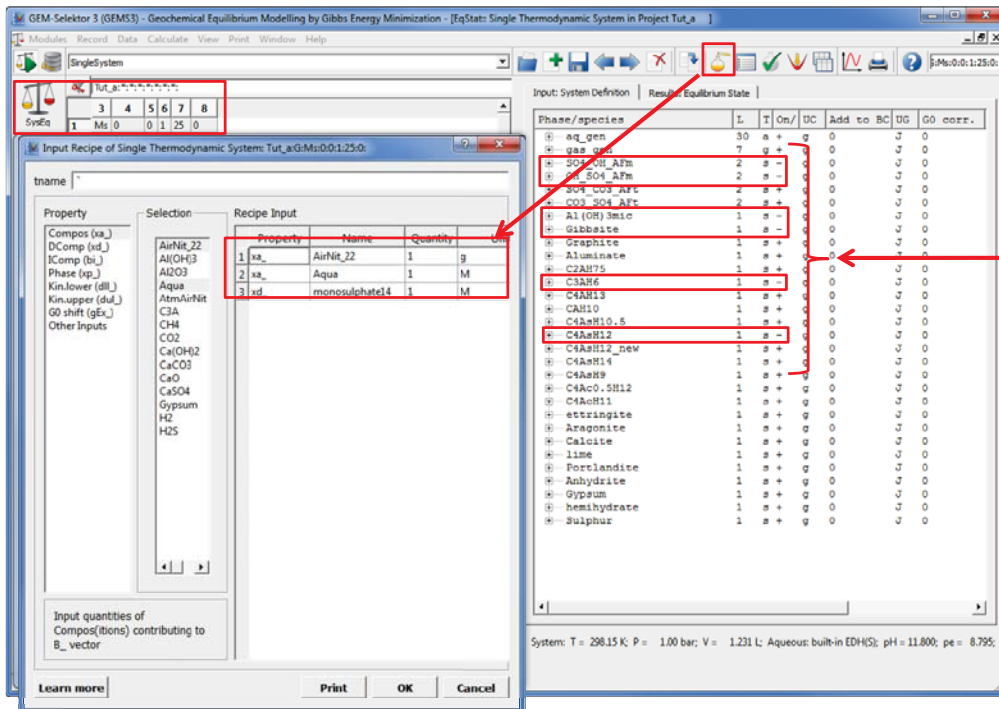
What we have done so far

- Create project
- Introduce water vapor (steam phase) from the supcrt database
- Introduce Ms14 starting from the “old” Ms12 (monosulphate) by addition of $2\text{H}_2\text{O}$
- Introduce Ms12, Ms10.5, Ms9 with help of the experimentally derived thermodynamic properties of the different hydration states

-
- **Modelling the drying behavior of Monosulfoaluminate**

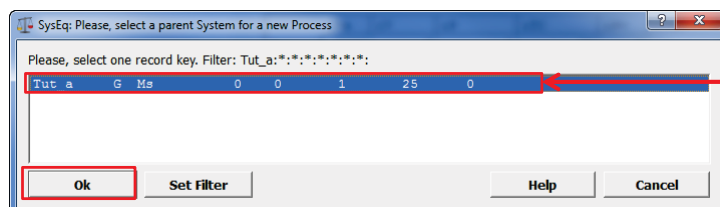
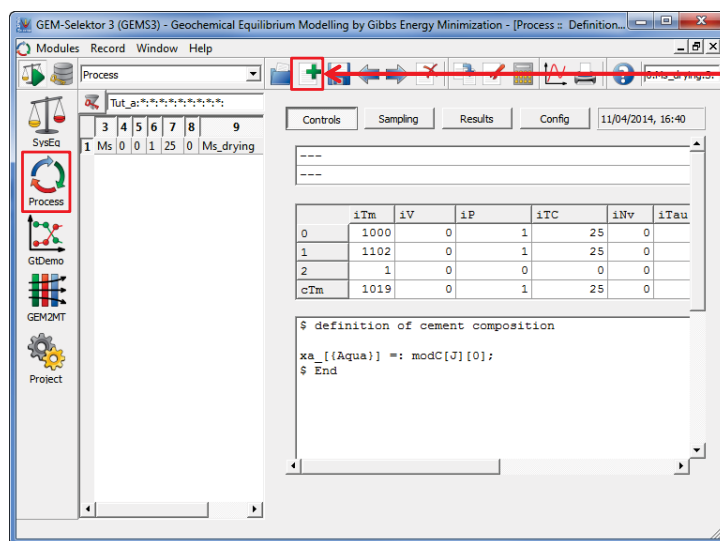
Modelling drying: Process simulation

Modify the initial single system created: the system should contain AirNit_22, Aqua and monosulphate14



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Modelling drying: Process simulation



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Modelling drying: Process simulation

Process: Please, set a new record key

Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S:

Tut_a Name of the modeling project

G Thermodynamic potential to minimize {G}

Ms Name of the parent chemical system definition (CSD)

0 CSD (recipe) variant number <integer>

0 Volume of the system, dm3

1 Pressure, bar, or 0 for Psat(H2O)g

25 Temperature, C

0 Variant number for additional constraints

Ms_drying Name of this process simulation task

1 S Process simulation mode code { P, S, L, G, T, R }

Ok Reset From List Help Cancel

To simulate drying, water will be removed from the system

GEM-Selektor Process Setup: Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, irreversible geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) can be simulated.

The Process record can be configured in several modes to perform specific simulation scenarios by execution of process control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be easily produced using this wizard.

Any process simulator belongs to one of three types:

1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from previous step (mode R);
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; modes G, T).

Please, choose a process simulation mode:

☒ P Sequential temperature and/or pressure change at fixed bulk composition

☒ S Direct sequential change of bulk composition and/or constraints (default)

☐ G Batch inverse titration sequence for incremented pH values etc.

☐ T One arbitrary inverse titration calculation as defined in Process control script

☐ R Sequential reactor scheme, uses equilibrium bulk compositions of phases

☐ L Lippmann diagram (transposed) for a binary solid solution

Learn more

< Back Next> Cancel



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Modelling drying: Process simulation

GEM-Selektor Process Setup: Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S:

Step 2 - Process Simulation Controls (click 'Next' to retain the old script)

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	25	0	0	0	0	0	0
Until	1102	0	1	25	0	0	0	0	0	0
Step	1	0	0	0	0	0	0	0	0	0

☒ Titration cNu (linear) ☐ Diagram logD vs linear x ☐ Titration cpXi logarithmic ☐ Diagram logKd vs log(m)

Linear titration and logD diagram use iNu; logarithmic titration and logKd diagram use ipXi. Titrations: select items from 'Compos', 'DComp', 'IComp' or 'Phase' lists to act as titrants, optionally also from 'DC-lower' or 'DC-upper' to change metastability constraints.

To plot logD vs linear x scale, (i) select minor then host end member from the 'DComp' list, then trace then host ions from the 'Molality' list. To plot logKd and isotherms vs log(molality) scale, select trace and host compositions from the 'Compos' list, then trace and host elements from the 'Sorbed' list. In both cases, skip the next wizard page.

Compos: AirNit_22, Al(OH)3, Al2O3, Aqua, AtmAirNit, C3A, CH4, CO2, Ca(OH)2, CaCO3, CaO, CaSO4, Gypsum, H2

DComp:
IComp:
Phases:
DC-lower:
DC-upper:
Molality:
Sorbed:

\$ definition of cement composition
xa_[{Aqua}] =: modC[]][0];
\$ End

Learn more

< Back Next> Cancel

To simulate drying water will be removed from the system



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Modelling drying: Process simulation

GEM-Selektor Process Setup: Tut_ar\Gis\0:0:1:25:0:Ms_drying\S:

Step 3 - Selection of items to sample/plot (click "Next" without selecting anything to retain the old script)

Property

Scalars

- u
- ue
- b
- Cb
- m_t
- lgm_t
- icM
- Xa
- Xwa
- phVol
- phM
- Fa
- bXa(aq_gen)
- bXa(gas_gen)
- bXa(SO4_CO3)
- bXa(CO3_SO4)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x
- Wxx
- my
- v
- vEx

Item Selection

Mbx	L[3]	Volumes[1]	iV[1]	cXi	vpXi
GX	L[4]	N_	iV[2]	iNu[0]	vNu
IS	L[5]	L[0]	cV	iNu[1]	vKin
pH	Fi[0]	L[1]	iP[0]	iNu[2]	moc
pe	Fi[1]	L[2]	iP[1]	cNu	xp
Eh	Fi[2]	L[3]	iP[2]	ipH[0]	yp
TC[0]	Fi[0]	L[4]	cP	ipH[1]	xEp
TC[1]	Fi[1]	L[5]	iTC[0]	ipH[2]	yEp
TK[0]	Fi[2]	Fi[0]	iTC[1]	cpH	
TK[1]	denW[0][0]	Fi[1]	iTC[2]	ipe[0]	
PG[0]	denW[1][0]	Fi[2]	cTC	ipe[1]	
PG[1]	epsW[0][0]	Fi[3]	cT	ipe[2]	
Vx[0]	epsW[1][0]	T	iNv[0]	cpe	
Vx[1]	lnP	P	iNv[1]	cEh	
It	RT	RTf[0]	iNv[2]	Next	
ItEfd	F_RT	RTf[1]	cNV	I	
Itlpm	Xw	RoW[0][0]	iTau[0]	J	
Psi_DK[0]	Masses[0]	EpsW[0][0]	iTau[1]	Jp	
Psi_DK[1]	Masses[1]	VisW[0]	iTau[2]	vTm	
_nnr[0]	Masses[2]	iTm[0]	cTau	vNV	
_nnr[1]	Masses[3]	iTm[1]	ipXi[0]	vP	
L[0]	Masses[4]	iTm[2]	ipXi[1]	vV	
L[1]	Masses[5]	cTm	ipXi[2]	vT	
L[2]	Volumes[0]	iV[0]	cpXi	vTau	

Sampling Script

```
$ x-axis  
xp[J] =: xa_{Aqua};  
$ y-axis  
yp[J][0] =: phVol[{C4Ash14}];  
yp[J][1] =: phVol[{C4Ash12_new}];  
yp[J][2] =: phVol[{C4Ash10.5}];  
yp[J][3] =: phVol[{C4Ash9}];  
yp[J][4] =: (10^-Iga[{H2O}])/0.0324456*100;  
$ End
```

List of static data objects (see tooltip on each object name)

[Learn more](#) [Back](#) [Next>](#) [Cancel](#)

yp[J][4] corresponds to the RH at 25 °C



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Modelling drying: Process simulation

GEM-Selektor Process Setup: Tut_ar\Gis\0:0:1:25:0:Ms_drying\S:

Step 4 - Important data object dimensions

Spin boxes below define the dynamic memory configuration of the process simulator.

Dimensions of sampled and experimental data

103	nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' ve
1	Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be nPS.
5	Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
1	Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
0	Number of rows in the xEp, yEp arrays for experimental data (optional)
0	Number of columns in the xEp, yEp arrays for experimental data (optional)

Optional data vectors (of length nPS) can be used for accumulating current process control values for all steps performed. They can be allocated using checkboxes below. The assignment operator (with J index) in the script will override any values automatically copied into data vector from the respective process iterator.

Allocation of optional data vectors

<input type="checkbox"/> CSD variant # ('vTm')	<input type="checkbox"/> Volume V, I ('vV')	<input type="checkbox"/> Pressure P, bar ('vP')
<input type="checkbox"/> Temperature T ('vT')	<input type="checkbox"/> Constraints # ('vNV')	<input type="checkbox"/> Process extent Nu ('vNu')
<input type="checkbox"/> Process extent pXi ('vpXi')	<input type="checkbox"/> Kinetic parameters ('vKin')	<input type="checkbox"/> Time Tau ('vTau')

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Modelling drying: Process simulation

GEM-Selektor Process Setup: Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S

Step 5 - Additional options

On this page, some options of the Process simulator operation can be changed (for specific cases).

Optional modes of operation

- ☒ Use 'P_expr' simulation control script (can be turned off in P simulation mode)
- ☒ Save generated SysEq records to the project data base (always saved in G and T modes)
- ☐ Use time dependent calculations and plotting mode (for kinetics simulations, reserved)
- ☐ Use Smart Initial Approximation of GEM IFM algorithm for faster calculations (on your discretion)
- ☐ Use a stepwise mode of Process simulation (for troubleshooting purposes)

The 'P_expr' simulation control script must be used in most cases except the P mode (e.g., if temperature is changed using ITC iterator, but the system recipe remains constant).

Saving process-generated SysEq records may be necessary for subsequent sampling of results by GtDemo module or for troubleshooting, but may dramatically increase the size of project database. This flag has no effect on reciprocal and inverse titrations, where optimized SysEq records are always saved.

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GEM-Selektor Process Setup: Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S

Step 6 - Final settings and comments

Optional

0 [+](#) [-](#) Set here the number of links to SDref source of data and bibliography records (default 0)

After you click "Finish":

- (1) 'Controls' page of the Process window will appear. Fill out comments in 'PName' and 'PNote' lines. Check the process iterators for correct ranges and increments.
- (2) Modify the simulation control script 'P_expr', if necessary. Some example scripts can be found in help pages or via the 'Help' 'Scripts' menu command. Check also the sampling script in 'Sampling' page of the process window.
- (3) Click on 'Calculate' toolbar button to start the simulation; for the first time, do not use the graphic output. If error messages appear, check and fix the scripts or iterators and try the calculation again. After the simulation has finished, look at sampled results in 'xo' and 'vo' fields
- (4) Check and edit the axis and ordinate (plot) names, and click on the 'Plot data' toolbar button to see a customizable Graph Dialog. To plot experimental data over simulated curves (for visual fitting), close the Graph dialog, enter data into xEp and vEp fields on 'Results' page, then open

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Modelling drying: Process simulation

GEM-Selektor 3 (GEM3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process - Calculation finished OK (elapsed time: 8.707 s)]

Modules Record Window Help

Process

Tut_a:G:Ms:0:0:1:25:0:Ms_drying:S

14/04/2014, 16:12

	iTm	iV	iP	ITC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	25	0	0	0	0	0	0
1	1102	0	1	25	0	0	0	0	0	0
2	1	0	0	0	0	0	0	0	0	0
ITm	1102	0	1	25	0	0	0	0	0	0

definition of cement composition

```
ka_{{Aqua}} =: modC[J] [0];  
End
```

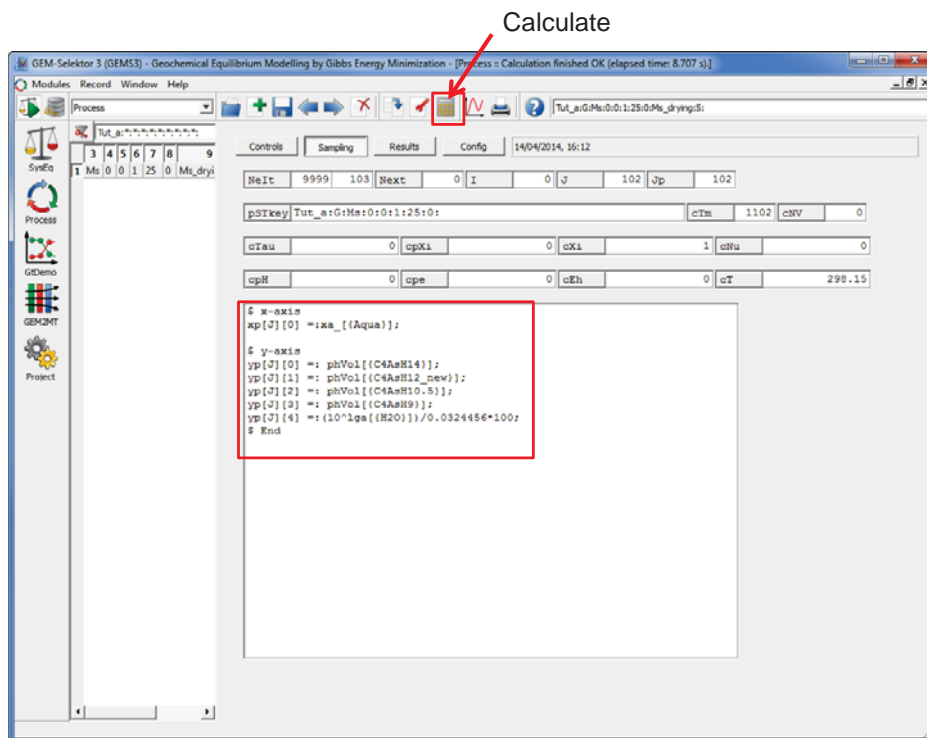
modC	
0	0
1	-0.05
2	-0.1
3	-0.15
4	-0.2
5	-0.25
6	-0.3
7	-0.35
8	-0.4
9	-0.45
10	-0.5
11	-0.55
12	-0.6
13	-0.65
14	-0.7
15	-0.75
16	-0.8
17	-0.85
18	-0.9
19	-0.95

Water quantity to be introduced must be negative: removal of water



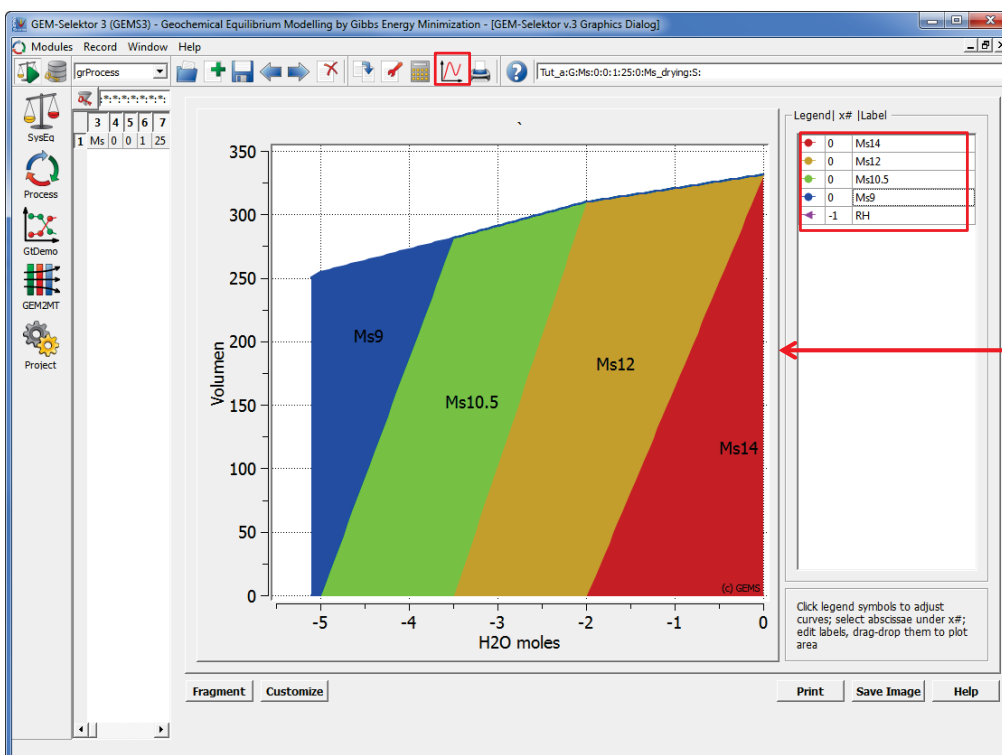
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Modelling drying: Process simulation



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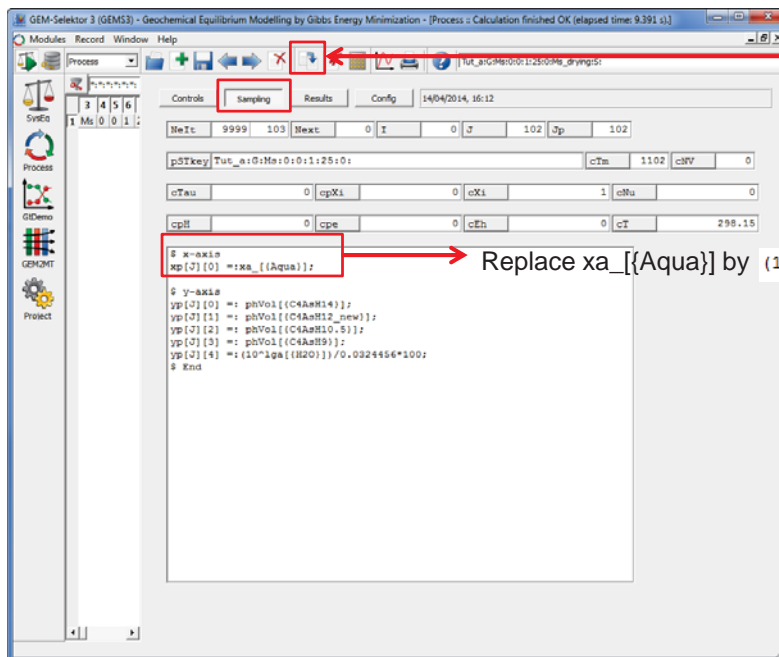
Modelling drying: Process simulation



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Modelling drying: 2nd Process simulation

Now we will plot the volume changes as function of RH



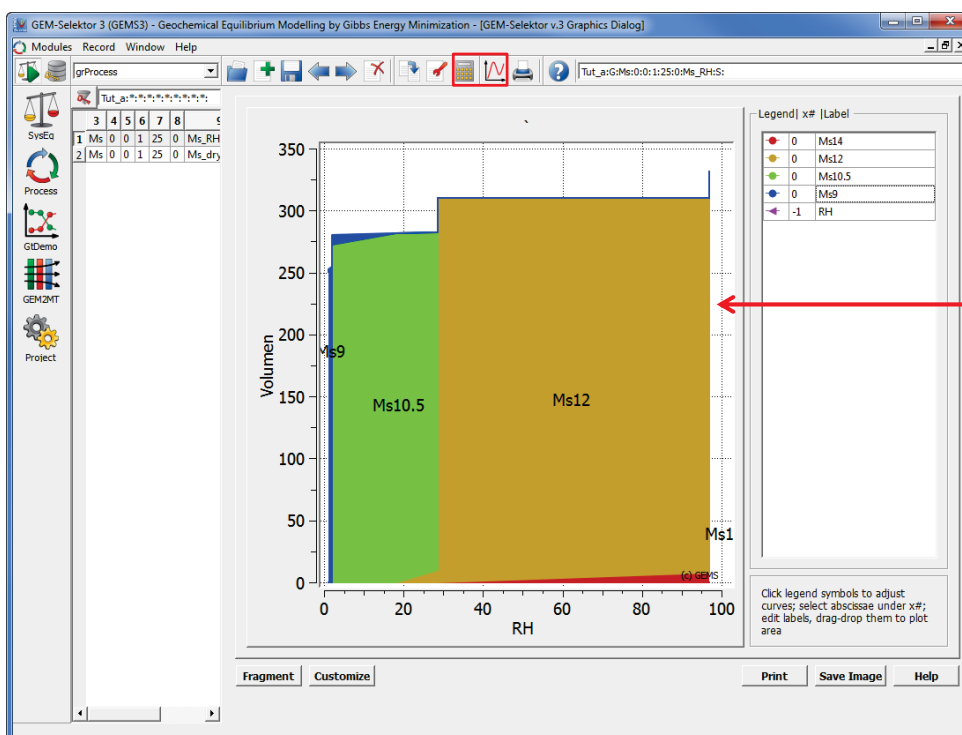
Clone the previous process

Replace $x_{a_{{Aqua}}}$ by $(10^{\lg a[{{H2O}}]})/0.0324456*100;$



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Modelling drying: 2nd Process simulation



From 100 to 97% RH
no phase is plotted
because the first
calculated system is
already at 97% RH



Thank you for your attention



nanocem

ACKNOWLEDGMENTS: The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under grant agreement n°264448.



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