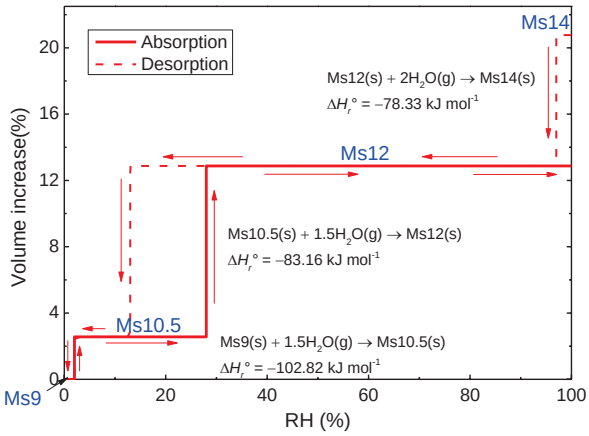
Strength. Performance. Passion.

Impact of water activity on the stability of cement hydrates

Thomas Matschei, Luis Baquerizo

GEMS workshop 2014



Outline

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

Introduction

- **Relative Humidity**

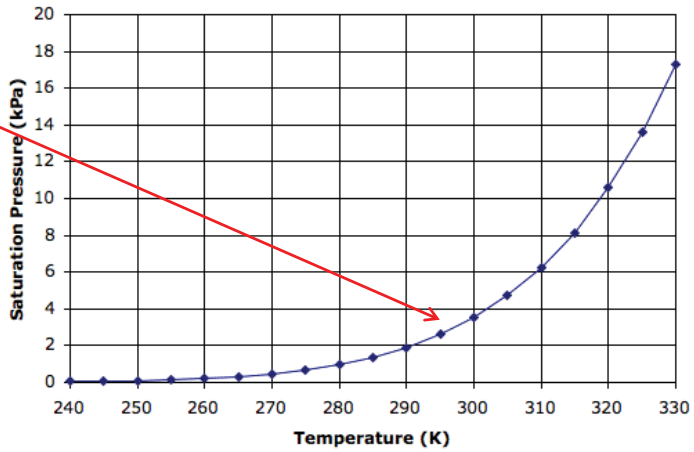
  RH = V/Vs = P/Ps

  V = vapor content

  P = vapor pressure

  Vs= saturation vapor content

  Ps = saturation vapor pressure



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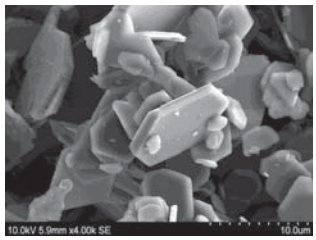
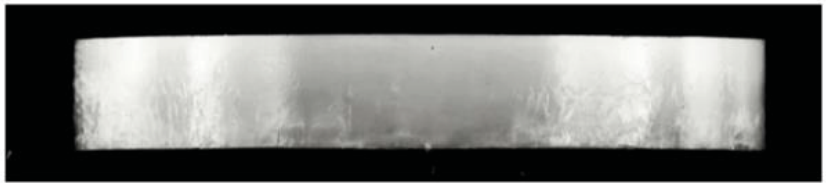
Introduction

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

- Example: Monosulfoaluminate (Ms)
  - Normal exposure conditions $[Ca_4(Al)_2(OH)_{12}]^{2+}$ $[SO_4 \cdot \mathbf{6}H_2O]^{2-}$ → **Ms12**
  - At 8% RH $[Ca_4(Al)_2(OH)_{12}]^{2+}$ $[SO_4 \cdot \mathbf{4.5}H_2O]^{2-}$ → **Ms10.5**



- 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?



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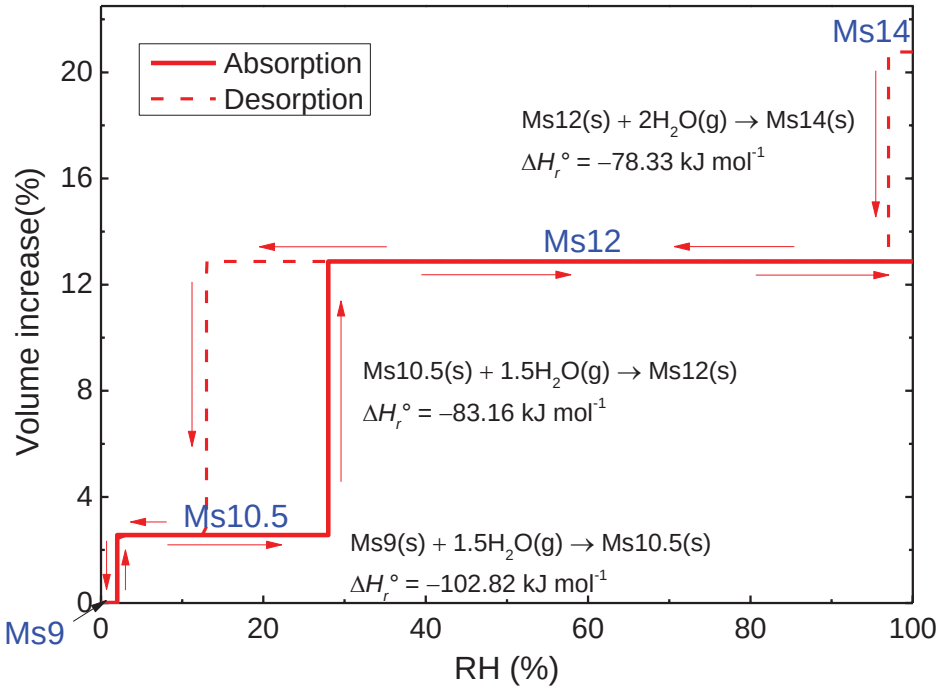
Monosulfoaluminate isotherm

- **A summary of input data we had to obtain**



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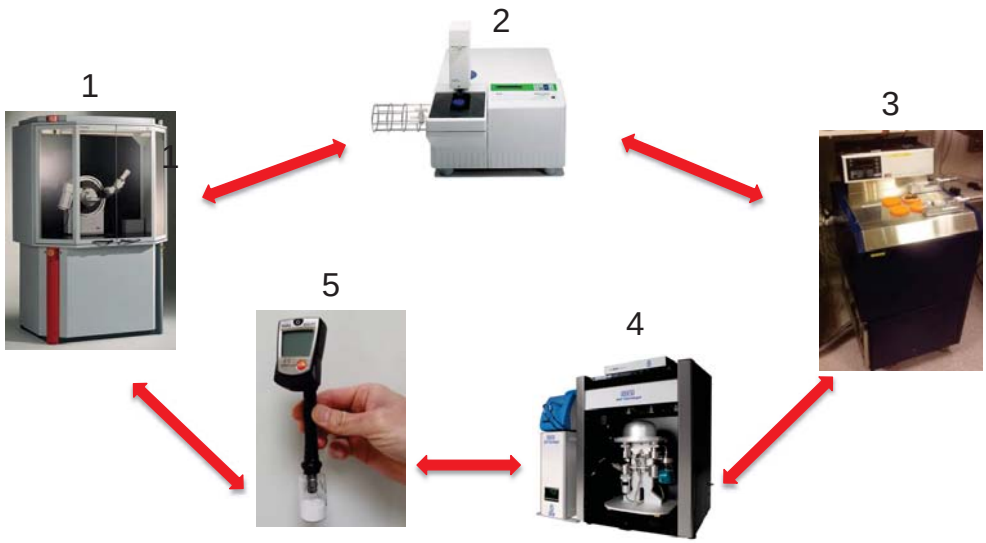
Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

Methodology. Answering the questions

1. **X-Ray diffraction (XRD)**
2. **Thermogravimetric analysis (TGA)**
3. **Sorption calorimeter**: collaboration Transcend Project 6: Lund University
4. **Sorption balance**: collaboration Transcend Project 6: Lund University
5. **Hydrate pair - humidity buffer method**



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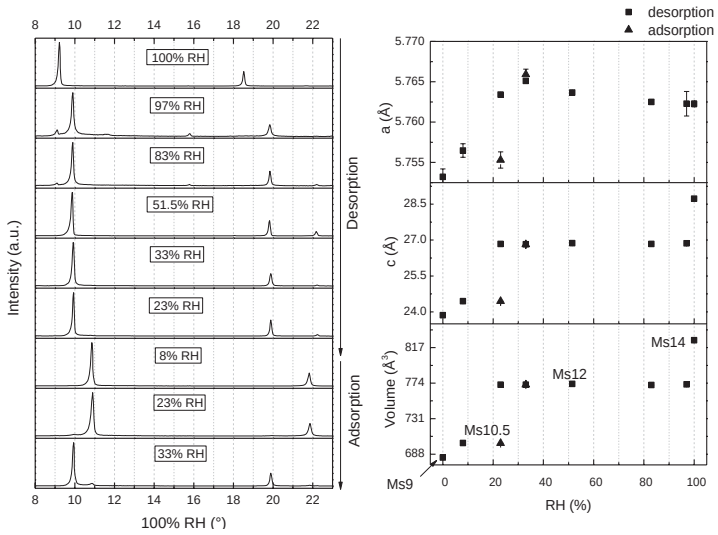
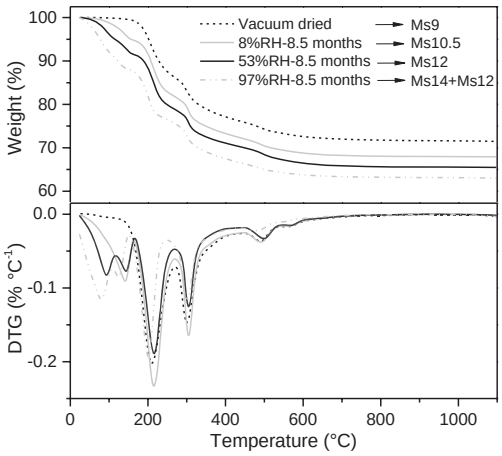
Methodology

- XRD/ TGA



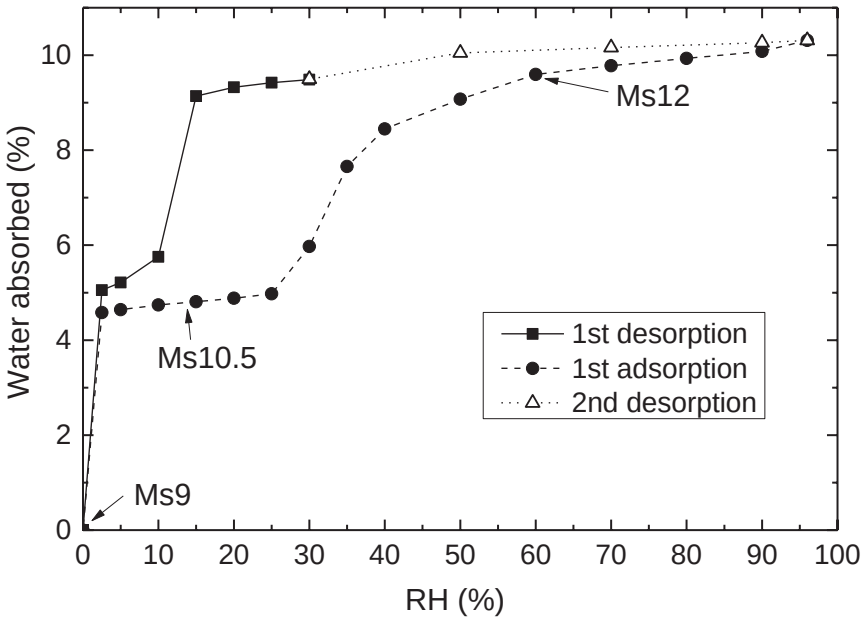


- Limitations: Lattice parameters refinement assuming that the space group did not change

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

Methodology

- Sorption balance



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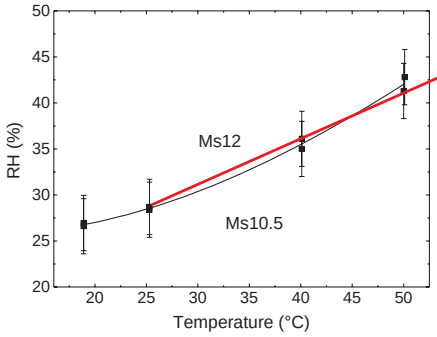
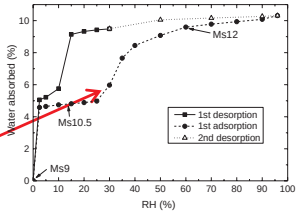
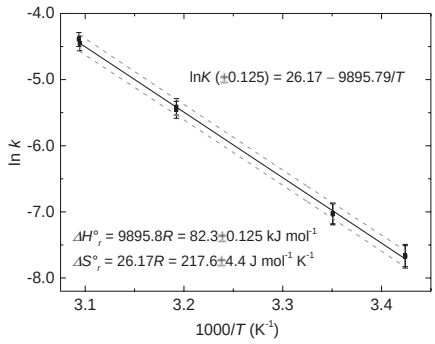
Methodology

- Hydrate pair – humidity buffer method







$$Ms12(s) \rightarrow Ms10.5(s) + 1.5H_2O(g)$$

$$\Delta G_r^o = -RT\ln K = -RT\ln[f(H_2O)^{1.5}] = -1.5RT\ln\frac{f^*(H_2O)RH}{100}$$

$$\frac{\partial(lnK)}{\partial(1/T)} = -\frac{\Delta H_r^o}{R} \qquad \Delta G_r^o = \Delta H_r^o - T\Delta S_r^o$$

$\Delta G_r°$ [kJ mol^{-1}]	$\Delta H_r°$ [kJ mol^{-1}]	$\Delta S_r°$ [J mol^{-1} K^{-1}]
17.4 ± 0.3	82.3 ± 1.0	217.6 ± 4.4

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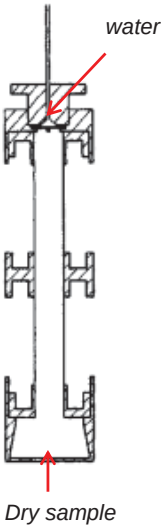
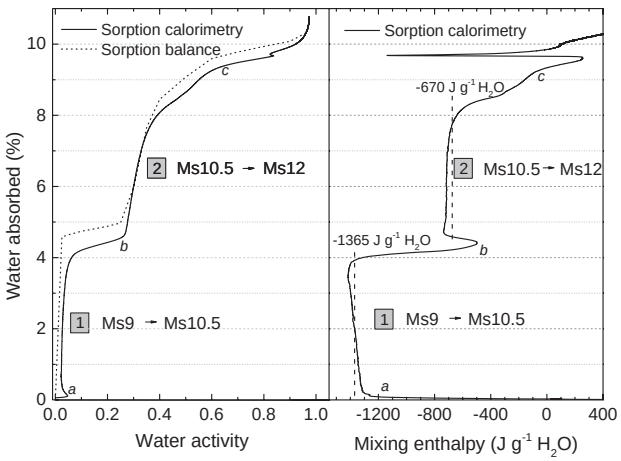
Methodology

- Sorption calorimetry





Sorption Vessel

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

	$\Delta G_r°$ [kJ mol^{-1}]	$\Delta H_r°$ [kJ mol^{-1}]	$\Delta S_r°$ [J mol^{-1} K^{-1}]
Ms9→Ms10.5	27.3	102.8	253.2
Ms10.5→Ms12	17.4	84.04	223.5

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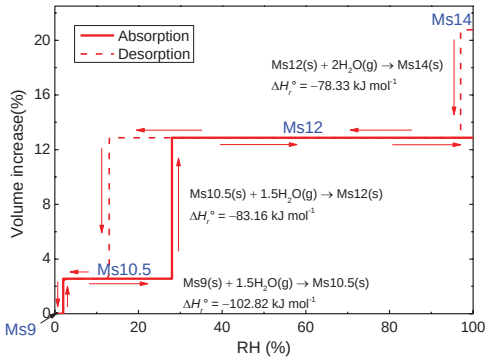
Methodology

- For the reaction

  Ms14 → Ms12 + 2H_2O



- 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:

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

$$\frac{\partial(lnK)}{\partial(1/T)} = -\frac{\Delta H_r^o}{R}$$

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

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Methodology

- Derived thermodynamic properties

Reaction	Change of hyd. state (% RH)	$\Delta G_r°$ (kJ mol^{-1})	$\Delta H_r°$ (kJ mol^{-1})	$\Delta S_r°$ (J mol^{-1} K^{-1})
Ms14(s)→Ms12(s)+2H_2O(g)	97	17.15	78.33 [a]	205.20
Ms12(s)→Ms10.5(s)+1.5H_2O(g)	28.5 [b]	17.42	83.16 [c]	220.51
Ms10.5(s)→Ms9(s)+1.5H_2O(g)	2 [d]	27.29	102.82 [e]	253.32

[a]Calculated considering a change of hydration state at 97, 90, 85 and 78% RH at 25, 50, 65 and 75 °C, respectively [b]From hydrate pair - humidity buffer method [c]Average value from sorption calorimetry and hydrate pair –humidity buffer method [d] From sorption balance [e]From sorption calorimetry

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Thermodynamic modelling

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

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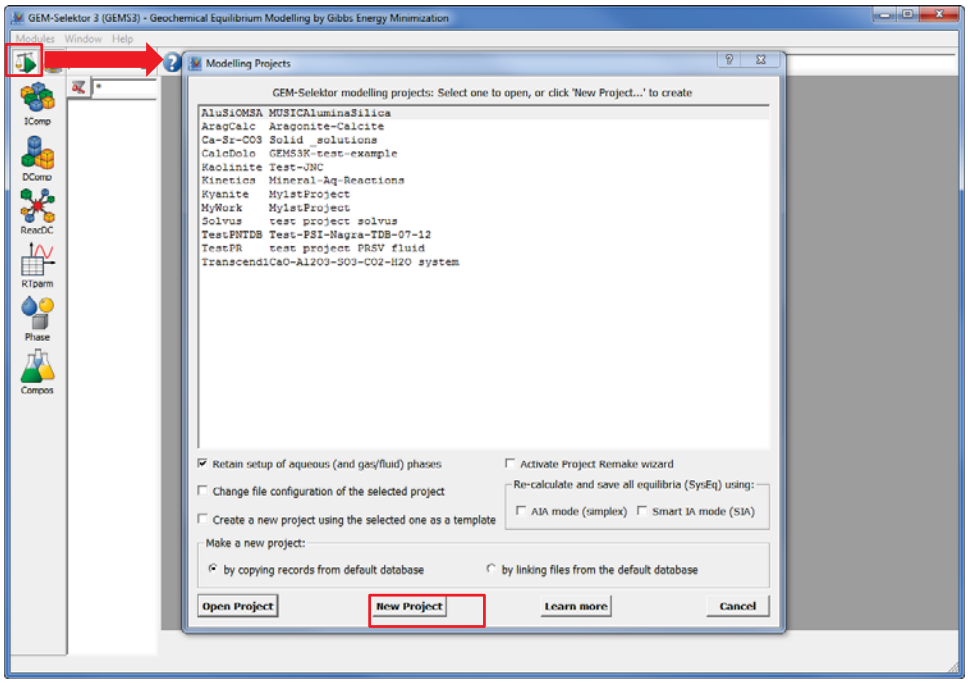
Create new project



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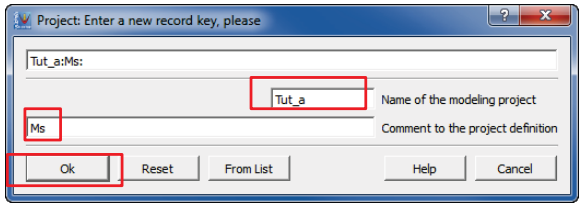

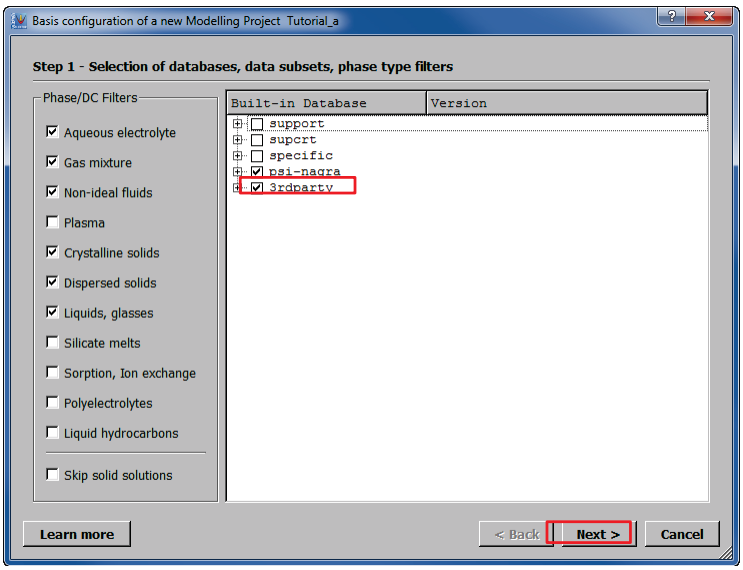

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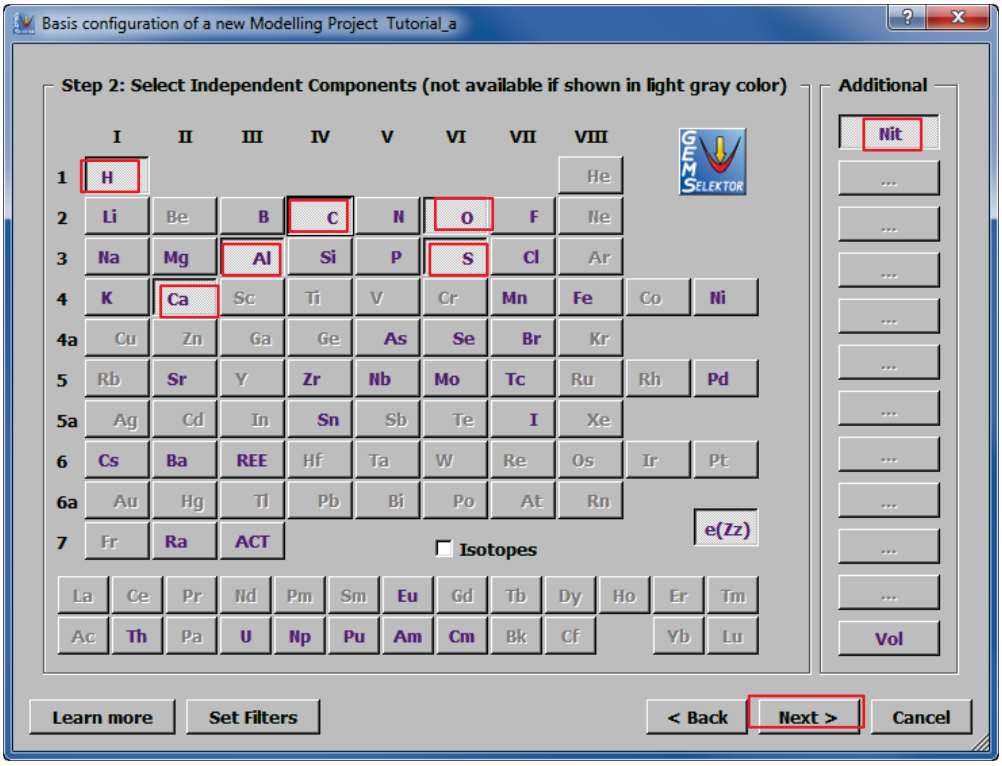

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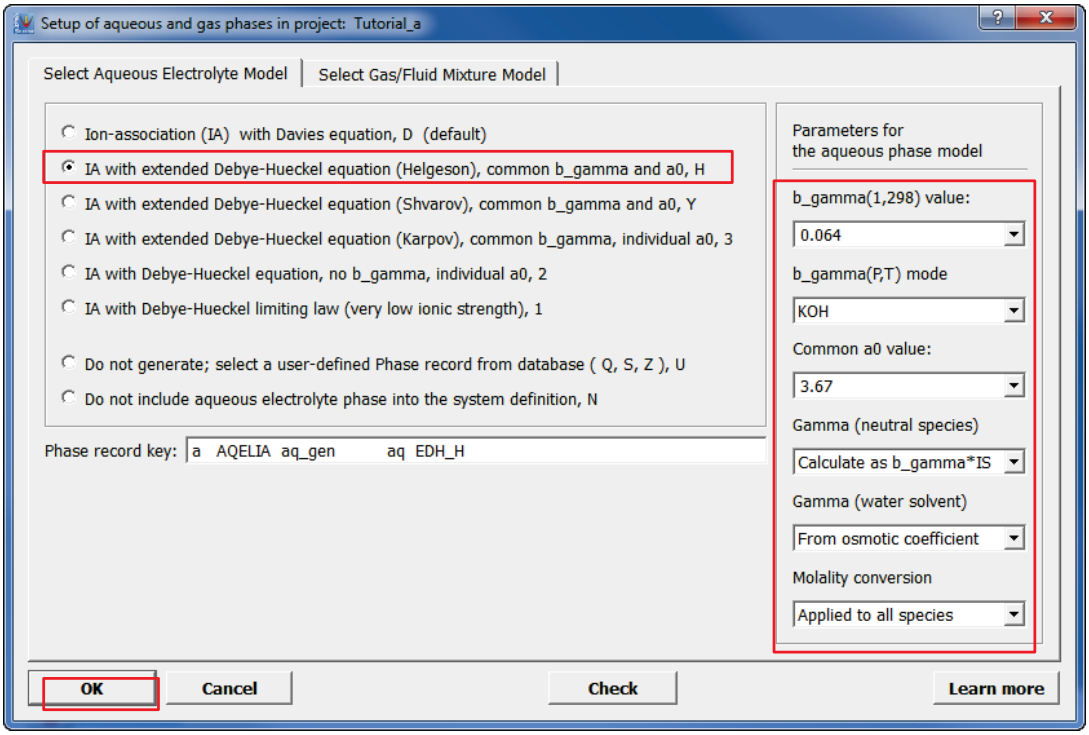
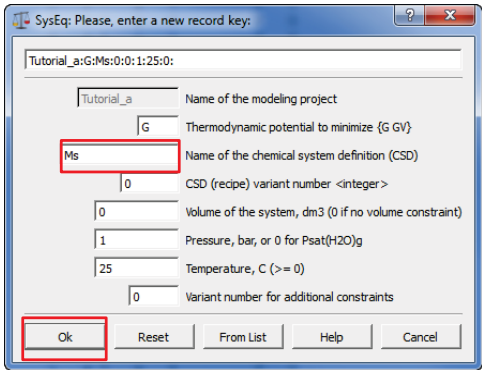
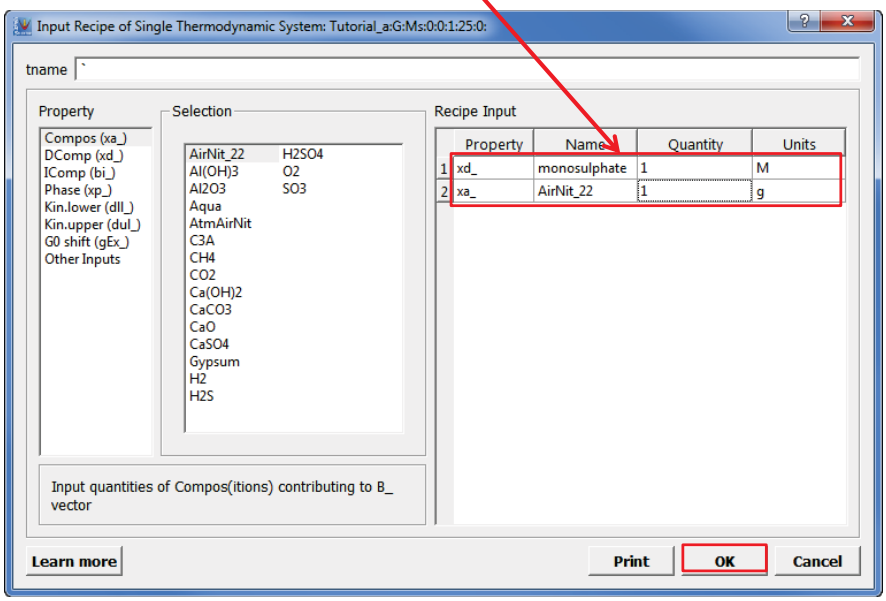


Create new project

Introduce monosulphate and AirNit_22





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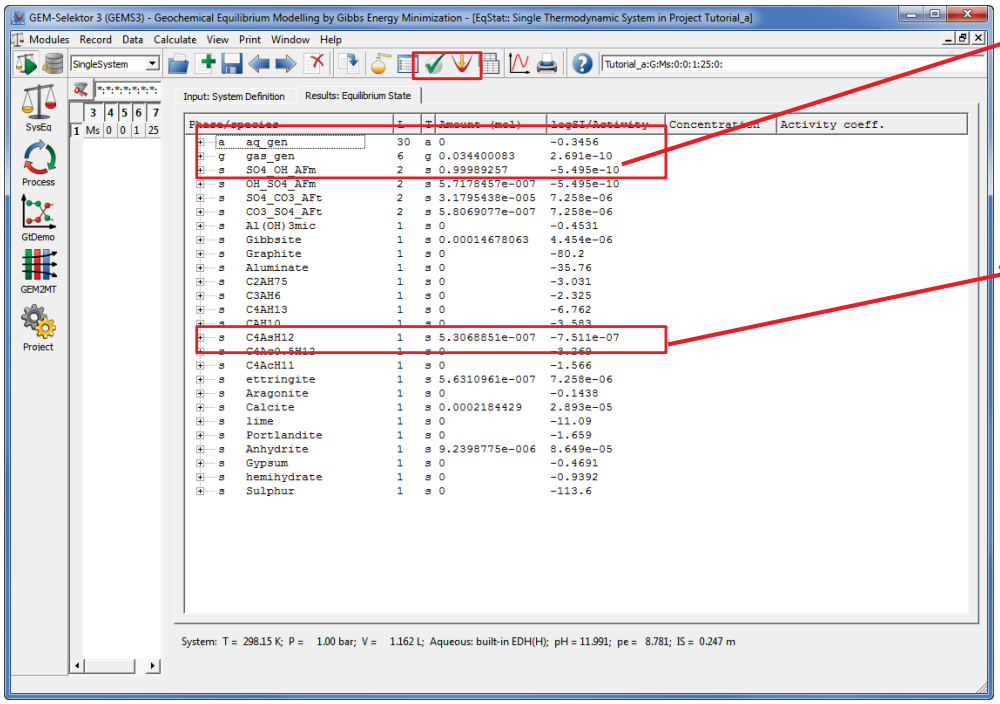
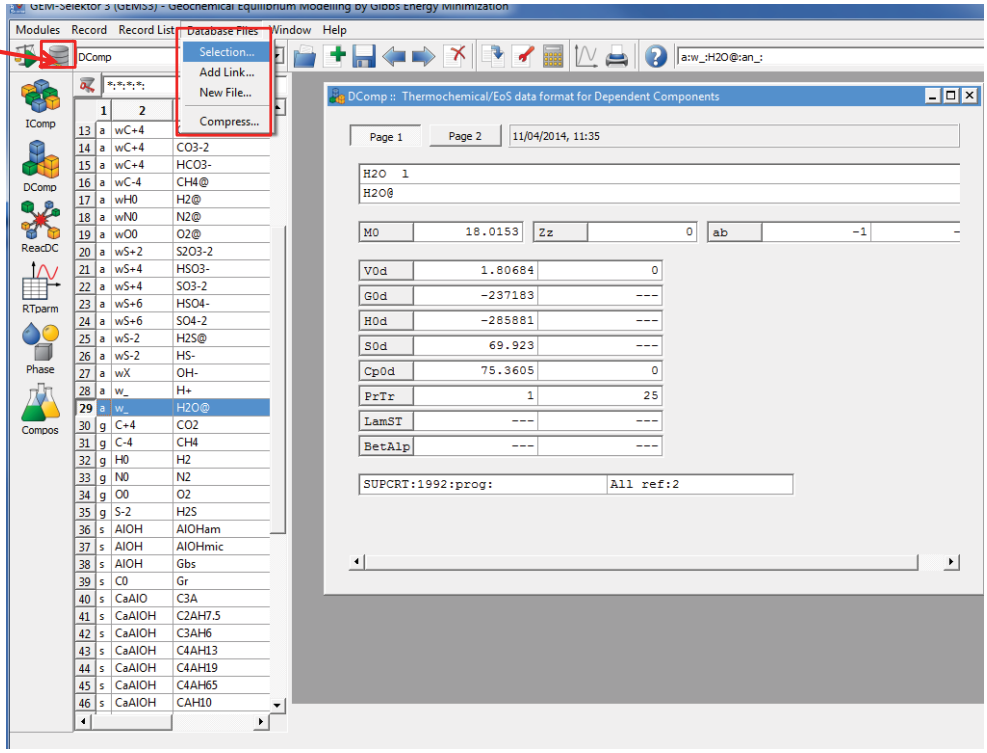


SO4_OH_AFm more stable than C4AsH12 (Ms12): its formation has to be skipped

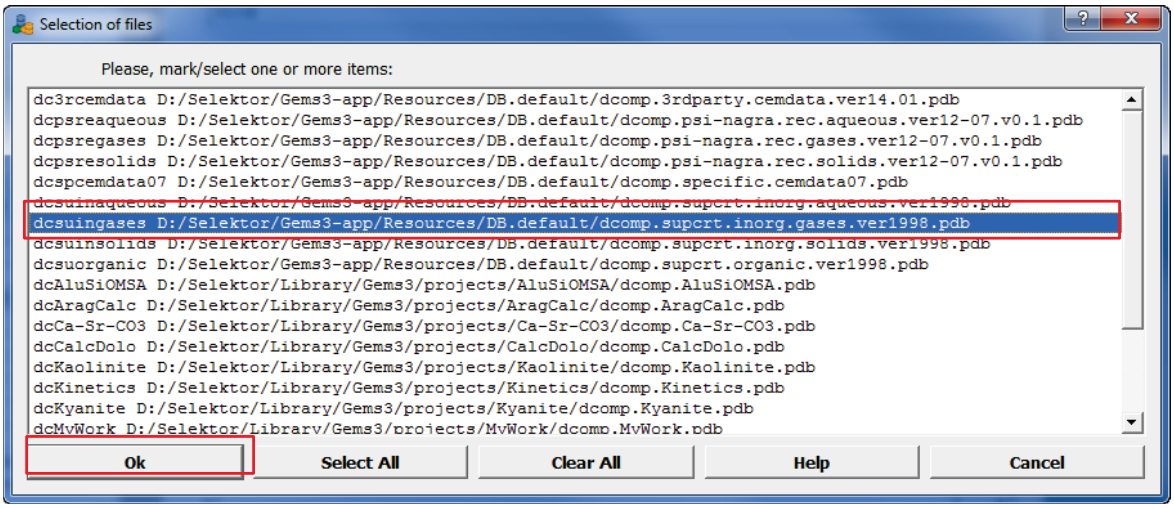
Just C4AsH12 (Ms12) appears. The other hydration states are not introduced

Introduce water vapor

Go to Database management mode to introduce water vapor

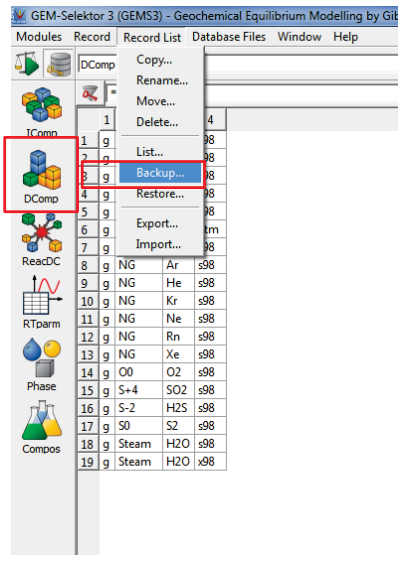


Introduce water vapor

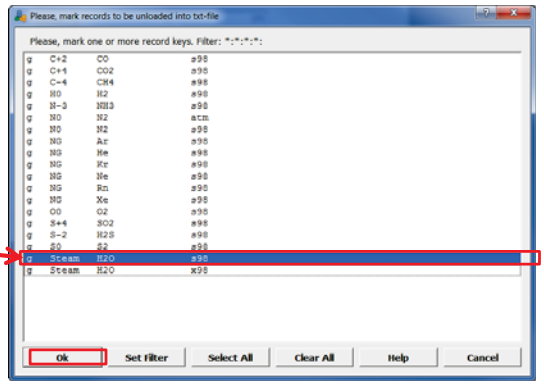


Introduce water vapor

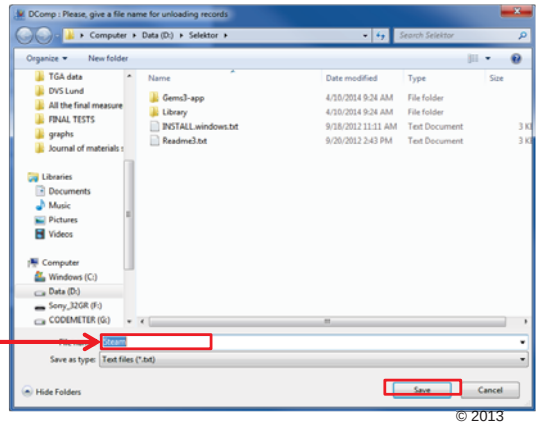
Backup Steam s98



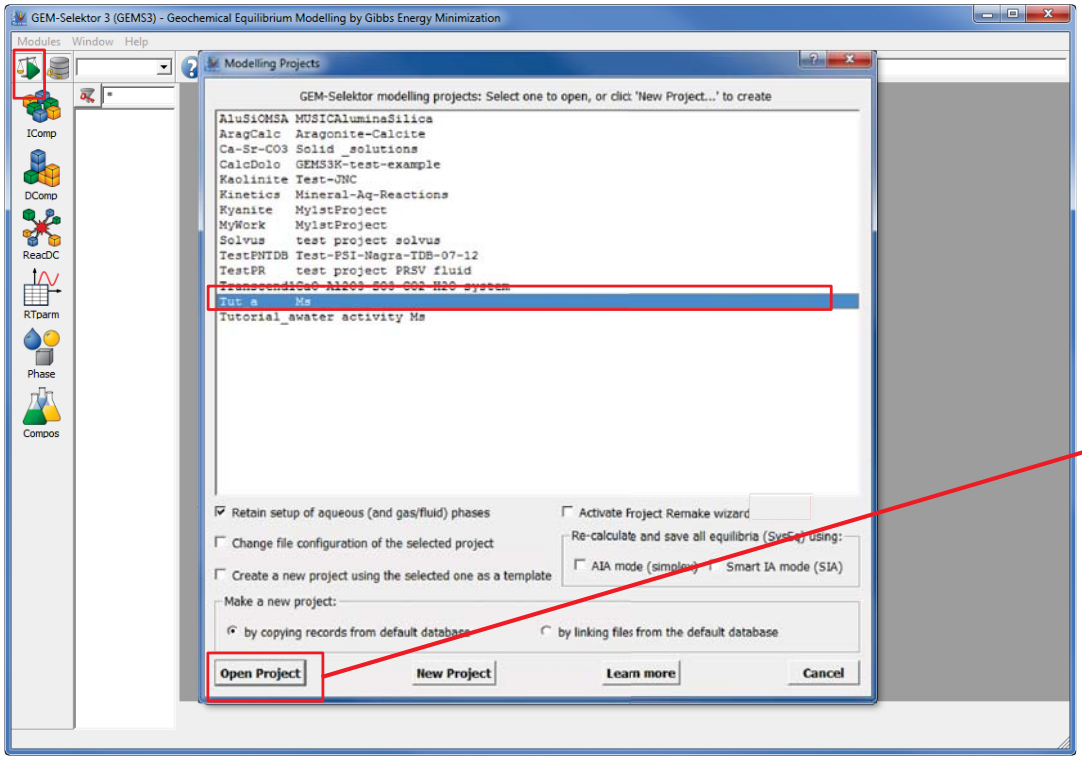
Choose Steam s98



Save as Steam.txt



Introduce water vapor



Open the project

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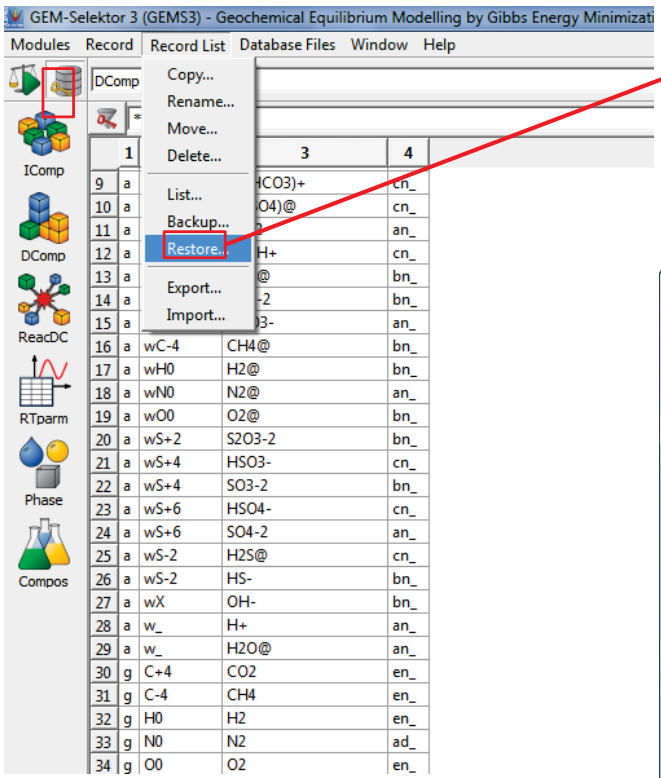
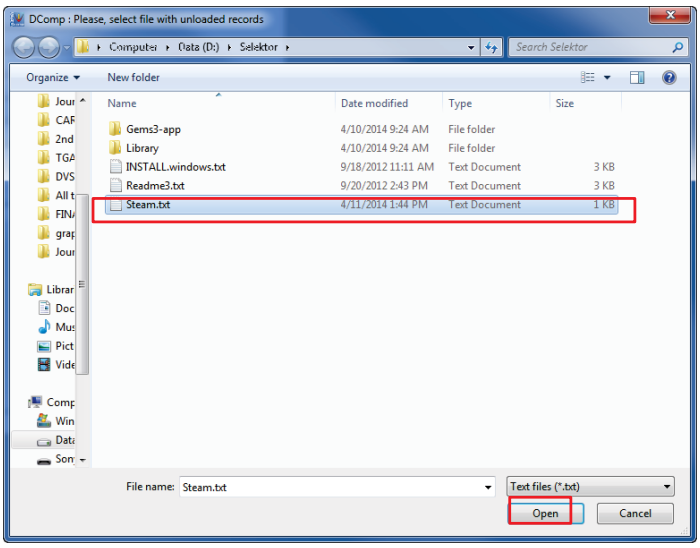
Introduce water vapor



Restore Steam.txt into the project database



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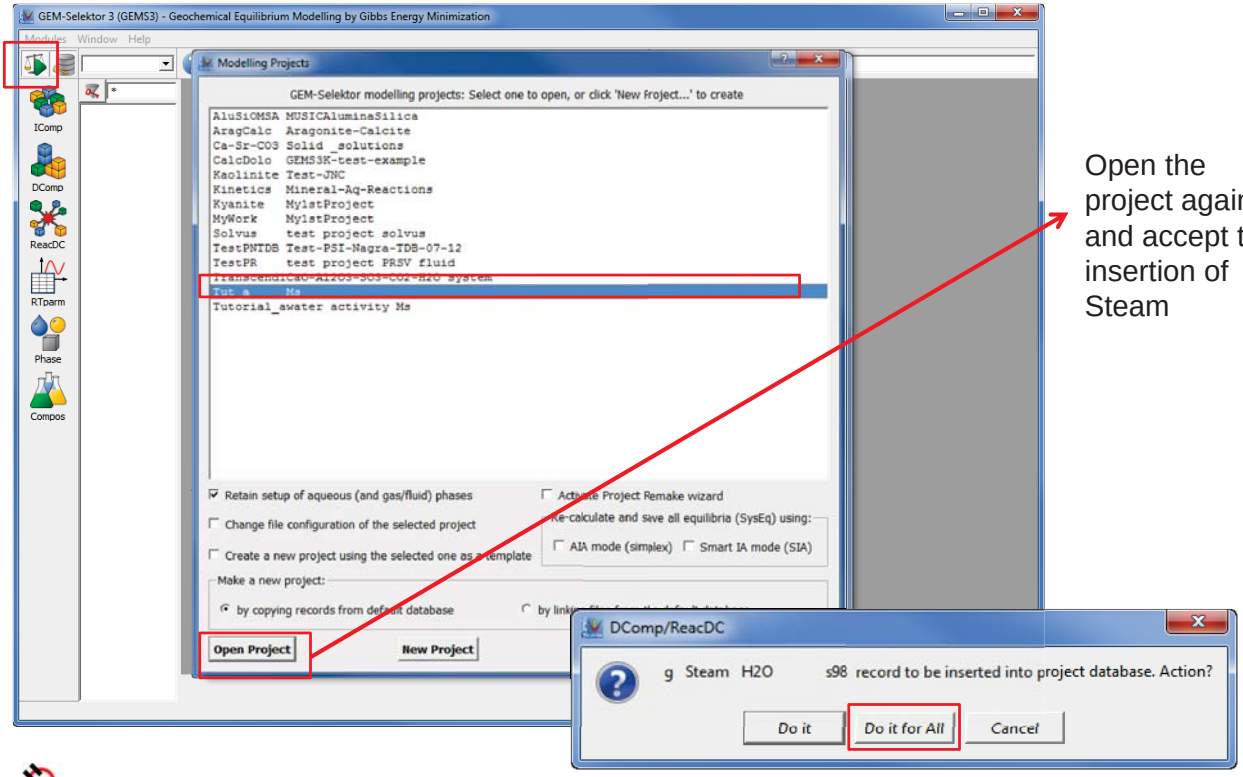
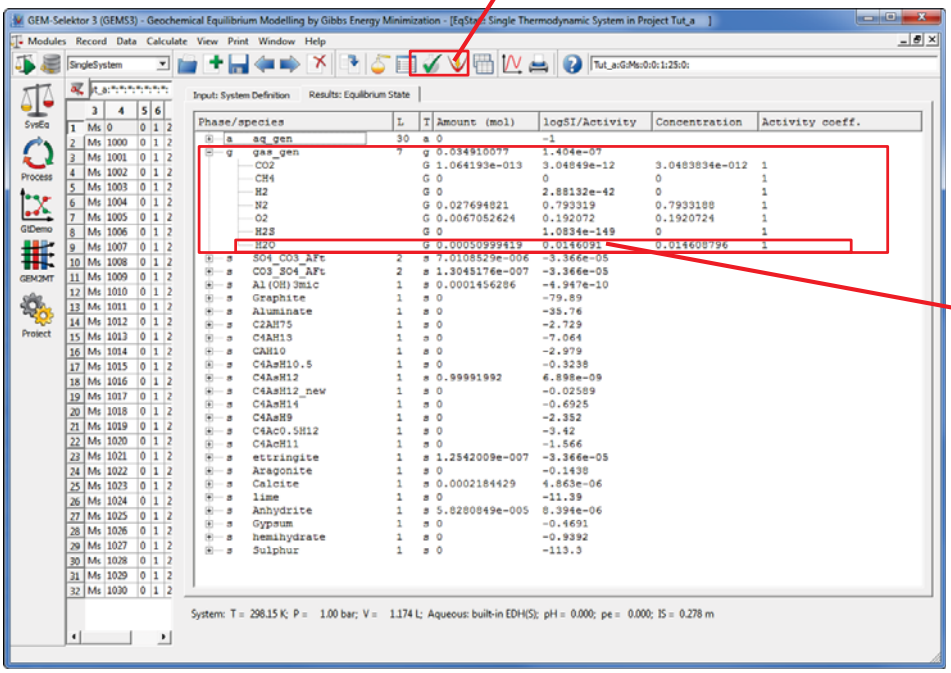
Introduce water vapor



Open the project again and accept the insertion of Steam

Introduce water vapor: checking the equilibrium RH

Calculate equilibrium→ H2O appears as a component of the gas_gen



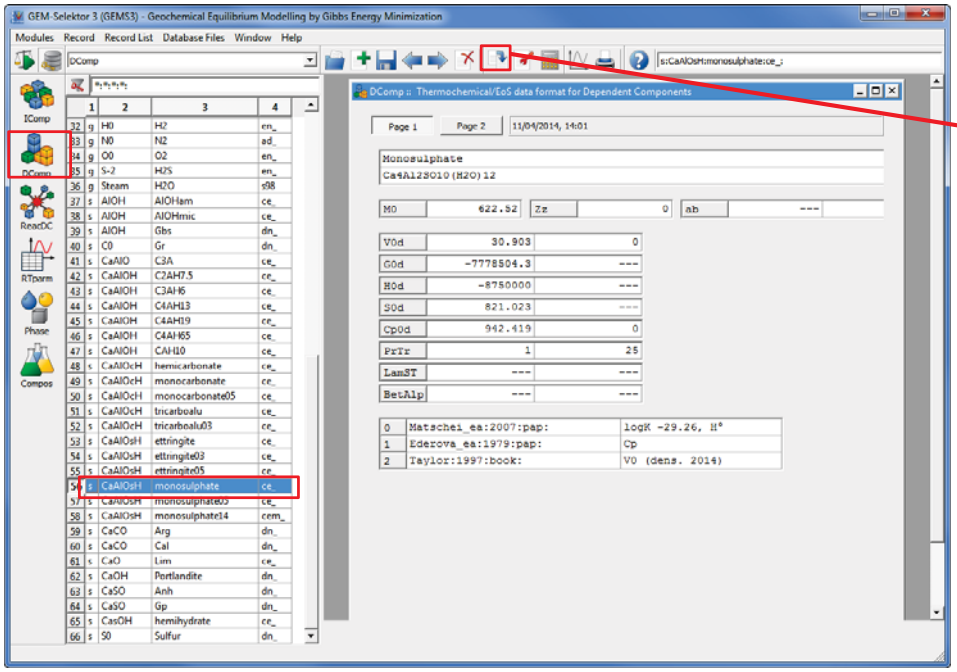
Equilibrium RH of the system can be calculated as follows:

$$RH = \frac{a[\{H2O\}])}{0.0324456} \times 100$$

$a[\{H2O\}])$sat at 25 °C

Introduce Ms14 in DComp

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



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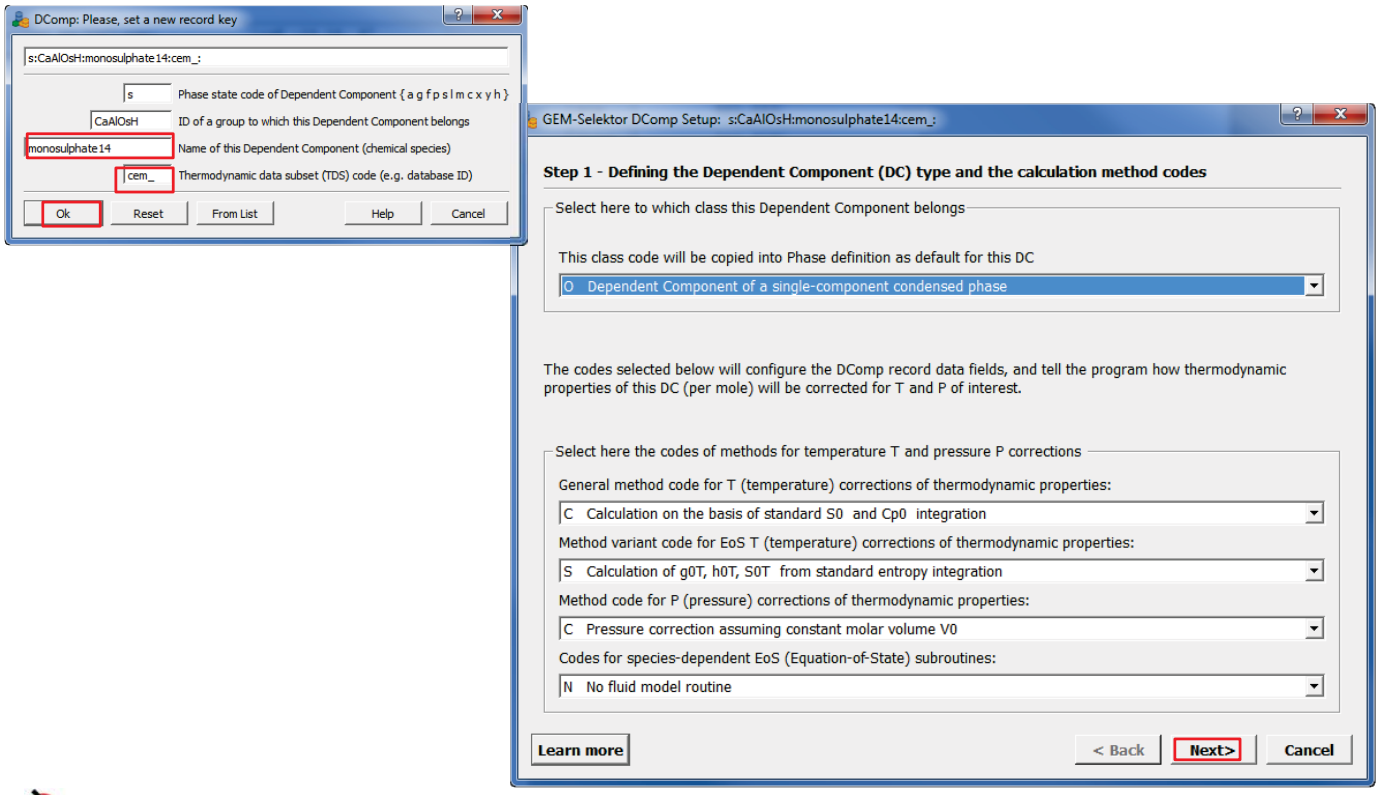
Introduce Ms14 in DComp



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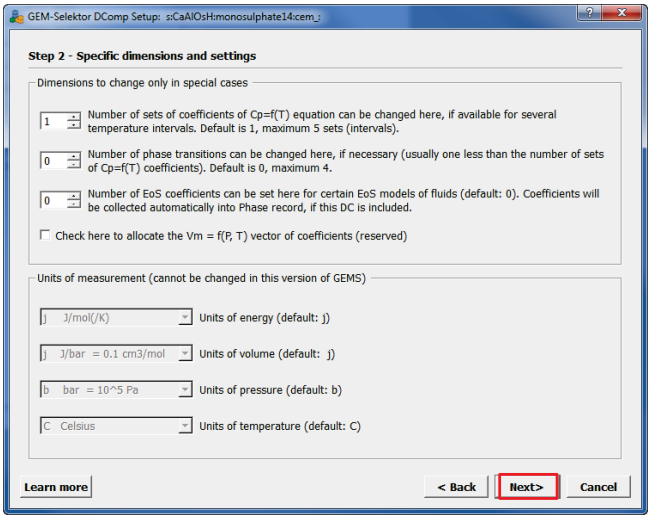
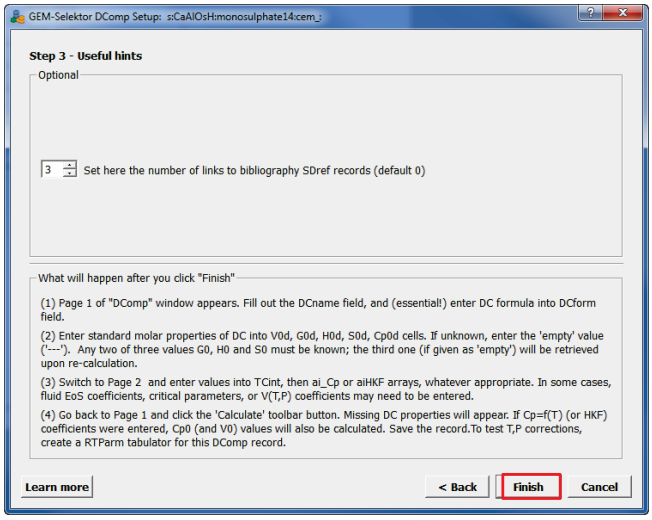
Introduce Ms14 in DComp





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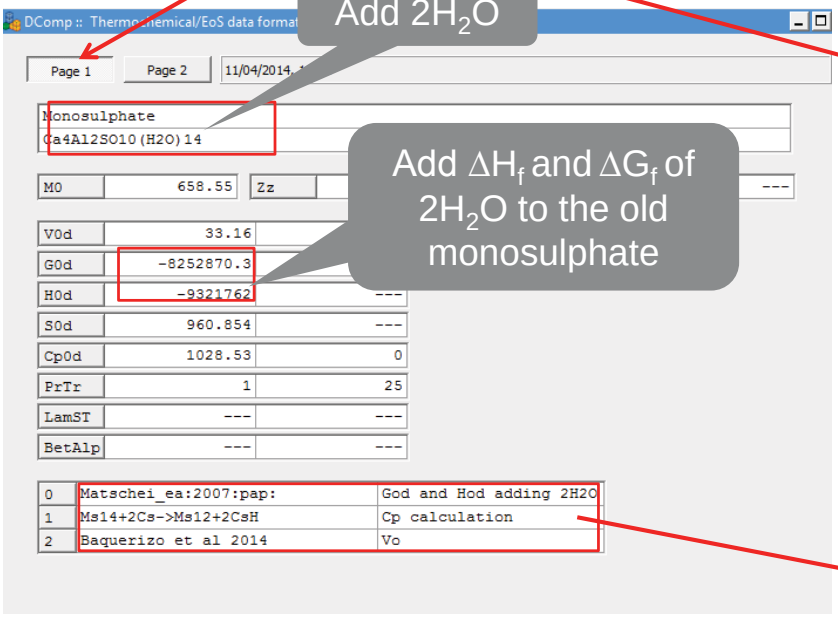
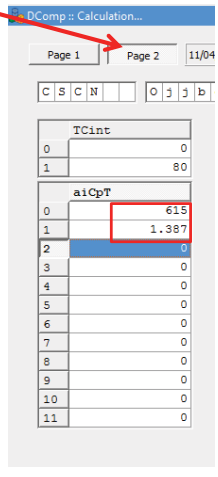
Introduce Ms14 in DComp

Introduce Ms14 properties and then calculate

Add $2H_2O$

Add ΔH_f and ΔG_f of $2H_2O$ to the old monosulphate





$*Cp° = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5}$

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

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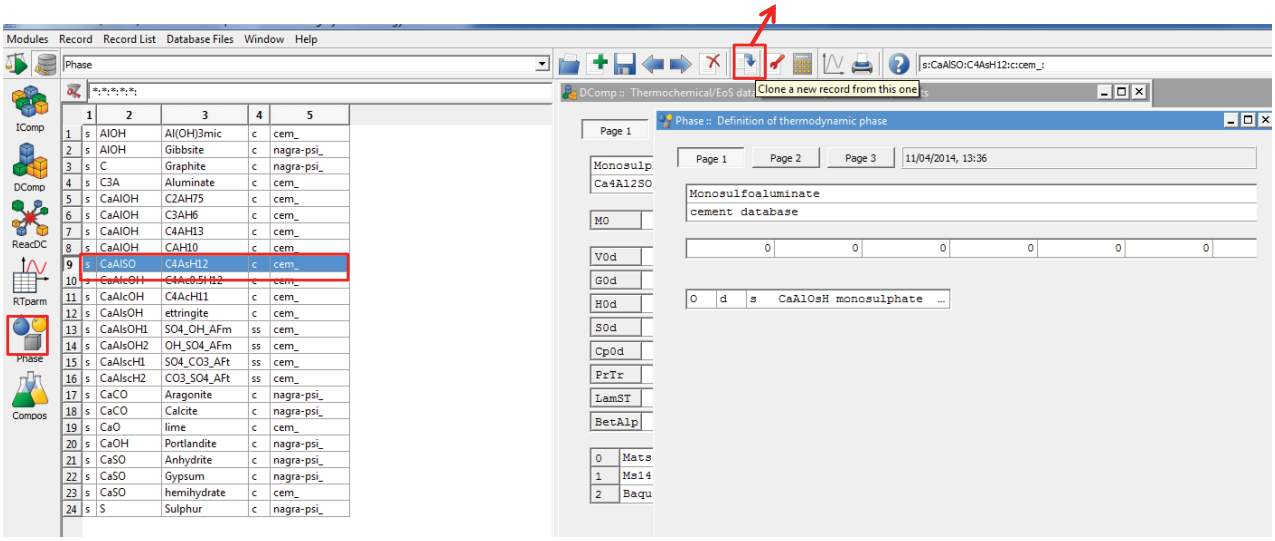
Create the Phase Ms14

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

Clone C4AsH12



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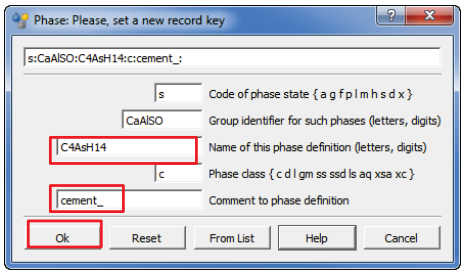
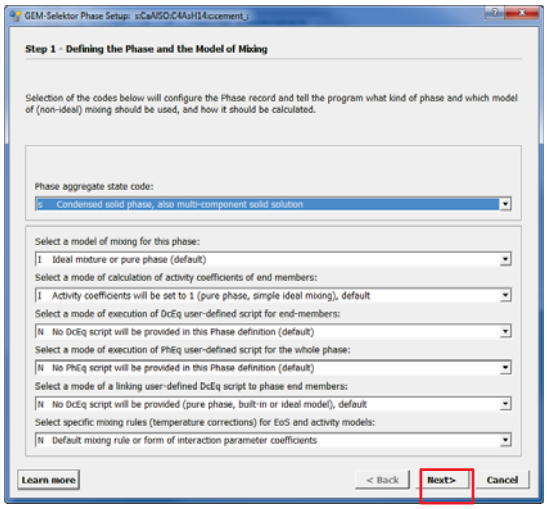
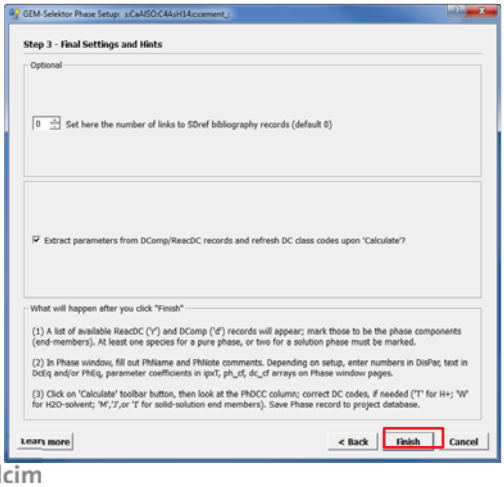
Create the Phase Ms14







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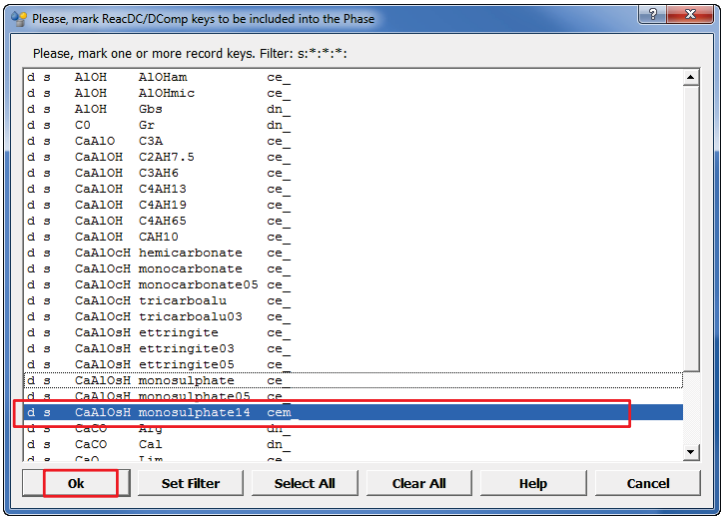
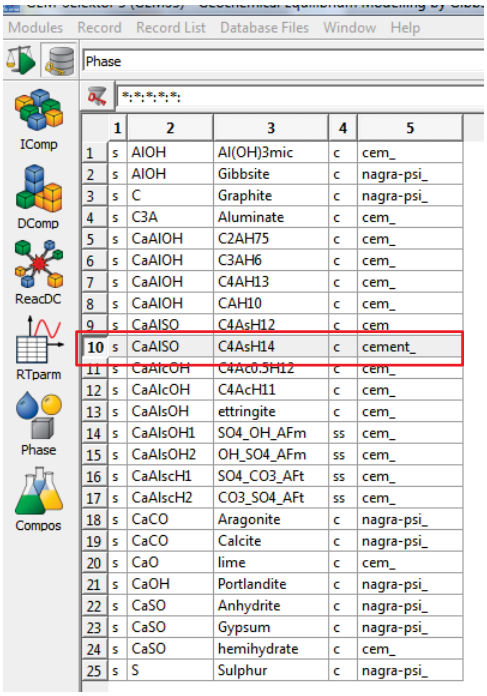
Create the Phase Ms14

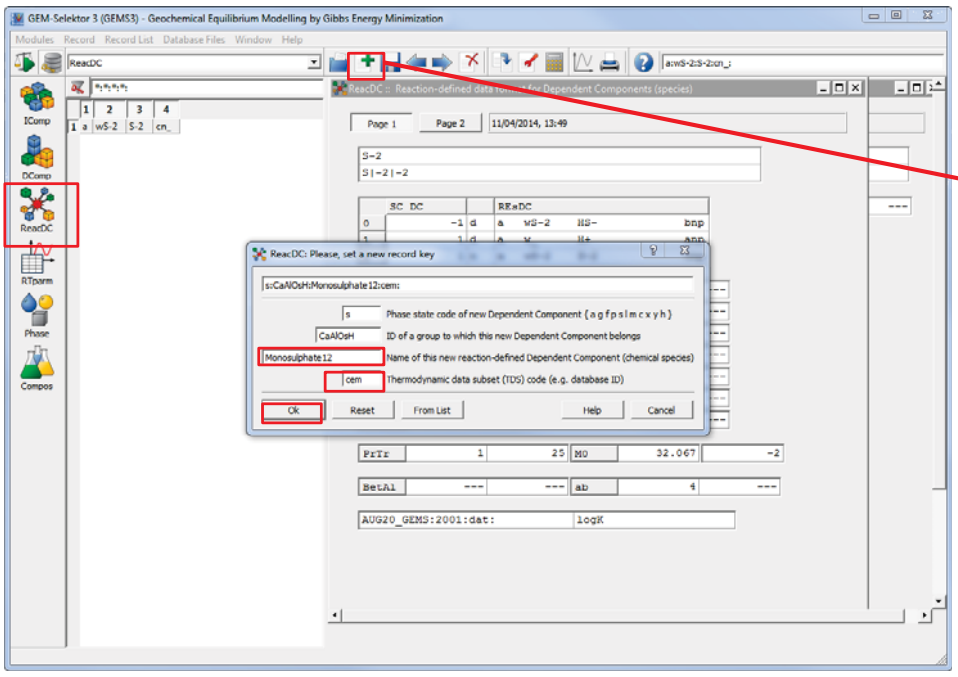




Holcim

Introduce Ms12: ReacDC

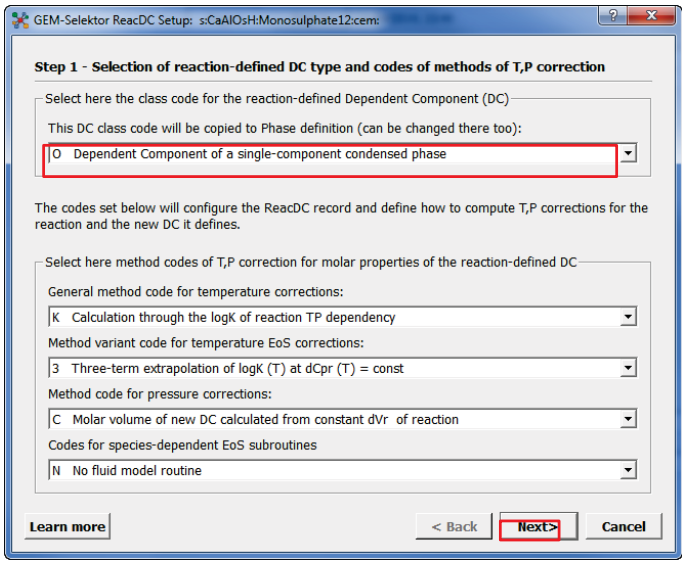
The lower hydration states (Ms12, Ms10.5 and Ms9) have to be introduced as a reaction

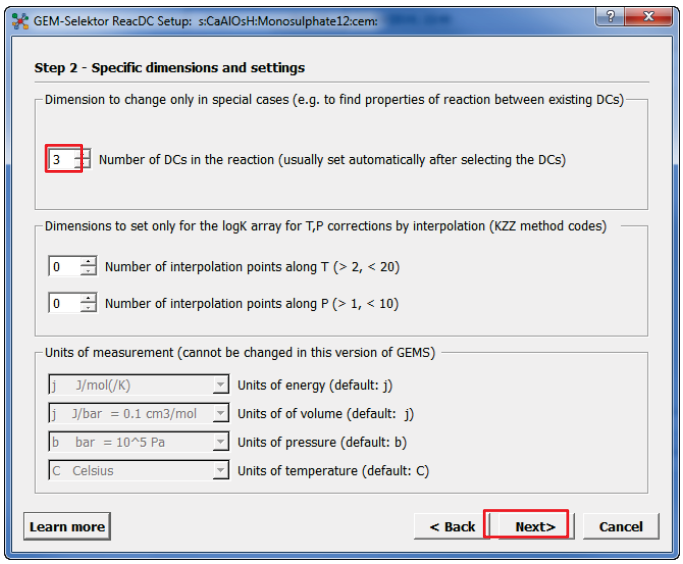


Create a new record

Holcim

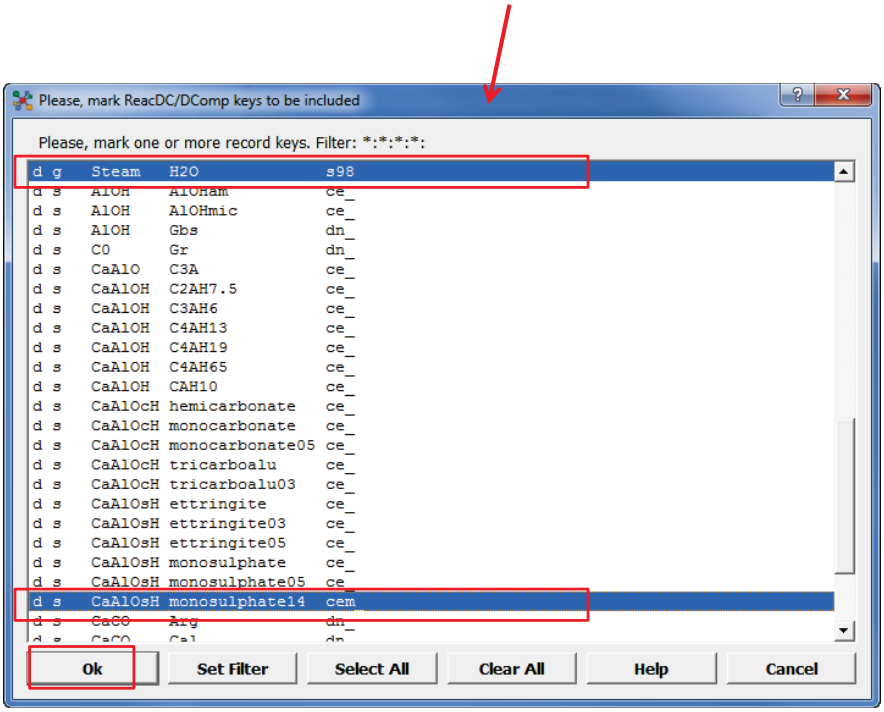
Introduce Ms12: ReacDC





Introduce Ms12: ReacDC

Introduce the components taking part of the reaction



Introduce Ms12: ReacDC

ReacDC :: Reaction-defined data format for Dependent Components (species)

Page 1 | Page 2 | 11/04/2014, 15:03

Monosulphate12
Ca4Al2SO10(H2O)12

	SC DC		REsDC			
0	2	d	g	Steam	H2O	s98
1	-1	d	s	CaAlOsH	monosulphate14	ce…
2	1	n	s	CaAlOsH	Monosulphate12	cem

V0r	4955.78	30.9998	---	
logKr	0.00099050355	-3.004144	---	
G0r	17147.78	-7778356.5	---	
H0r	78329.34	-8758632.7	---	
S0r	205.204	791.558	---	
Cp0r	-6	942.39	---	
NisoX	---	---	---	

PrTr	1	25	M0	622.52	0
BetAl	---	---	ab	---	---

0	Ms14(s)->Ms12(s)+2H2O(g)	50°C - 90% RH
1	25°C - 97% RH	65°C - 85% RH
2		75°C - 78% RH

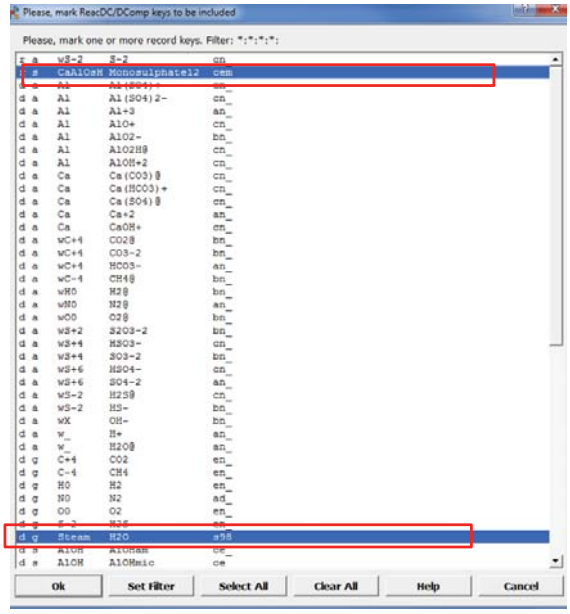
Introduce reaction and thermodynamic properties and then calculate

Reaction	Change of hyd. state (% RH)	ΔG_r° (kJ mol^{-1})	$\Delta H_{r_1}^\circ$ (kJ mol^{-1})	ΔS_r° (J mol^{-1} K^{-1})
Ms14(s)→Ms12(s)+2H_2O(g)	97	17.15	78.33 [a]	205.20
Ms12(s)→Ms10.5(s)+1.5H_2O(g)	28.5 [b]	17.42	83.16 [c]	220.51
Ms10.5(s)→Ms9(s)+1.5H_2O(g)	2 [d]	27.29	102.82 [e]	253.32

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

Introduce Ms10.5: ReacDC

The same procedure done with Ms12 is repeated to introduce Ms10.5



ReacDC :: Reaction-defined data format for Dependent Components (species)

Page 1 | Page 2 | 11/04/2014, 15:24

Monosulphate10.5
Ca4Al2SO10(H2O)10.5

	SC DC		REsDC			
0	-1	r	s	CaAlOsH	Monosulphate12	cem
1	1.5	d	g	Steam	H2O	s98
2	1	n	s	CaAlOsH	Monosulphate10.5	cem

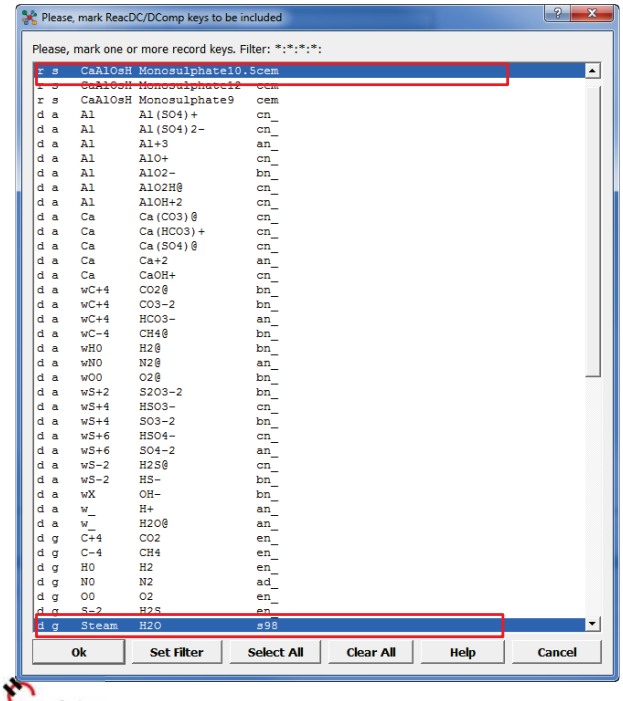
V0r	3715.61	28.155	---
logKr	0.00088920335	-3.0509989	---
G0r	17415.23	-7417916.8	---
H0r	83160	-8311872.7	---
S0r	220.509	731.192	---
Cp0r	-8	874.282	---
NisoX	---	---	---

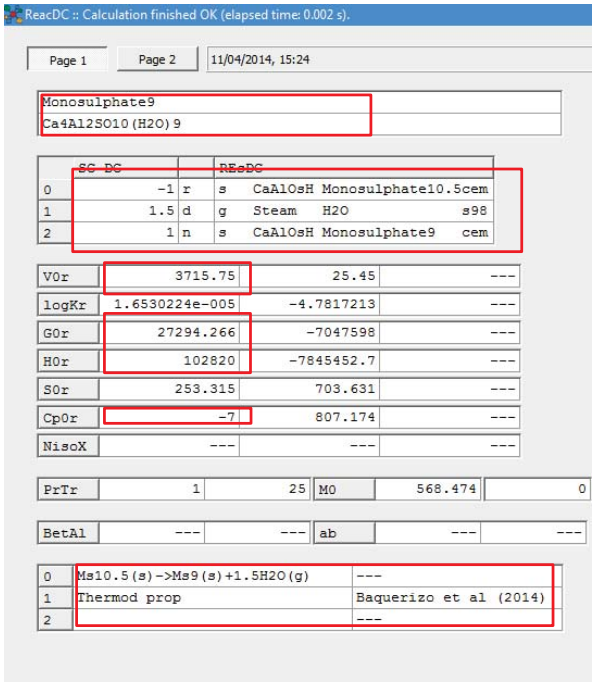
PrTr	1	25	M0	595.497	0
BetAl	---	---	ab	---	---

0	Ms12(s)->Ms10.5(s)+1.5H2O(g)	---
1	Thermod prop	Baquerizo et al (2014)
2		---

Introduce Ms9: ReacDC

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





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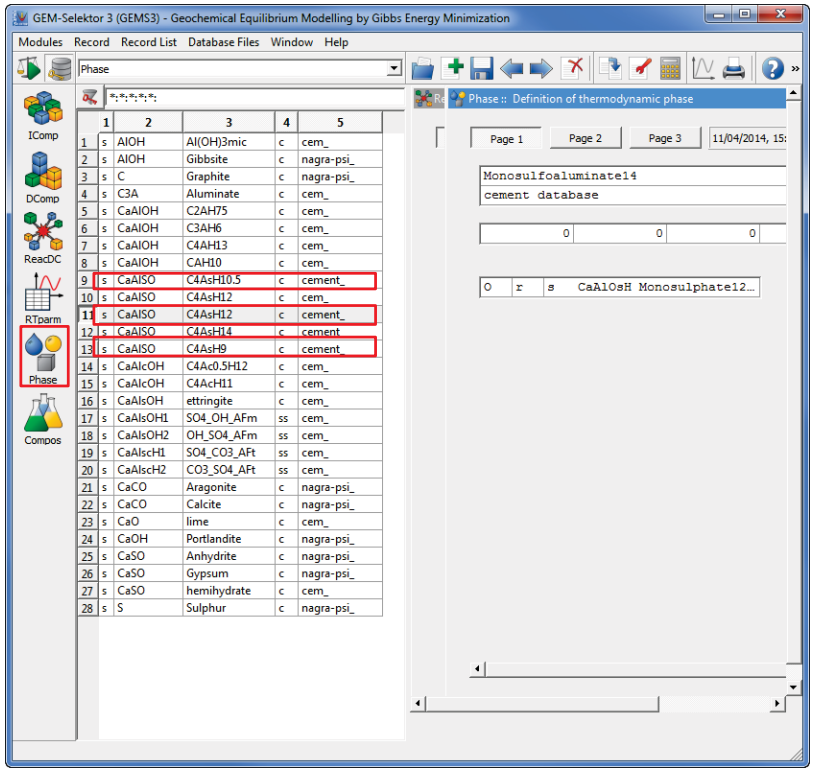
Introduce Ms12, Ms10.5 and Ms9 as phases

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

Phases to be introduced

- Ms12
- Ms10.5
- Ms9



Holcim

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 $2H_2O$
- Introduce Ms12, Ms10.5, Ms9 with help of the experimentally derived thermodynamic properties of the different hydration states

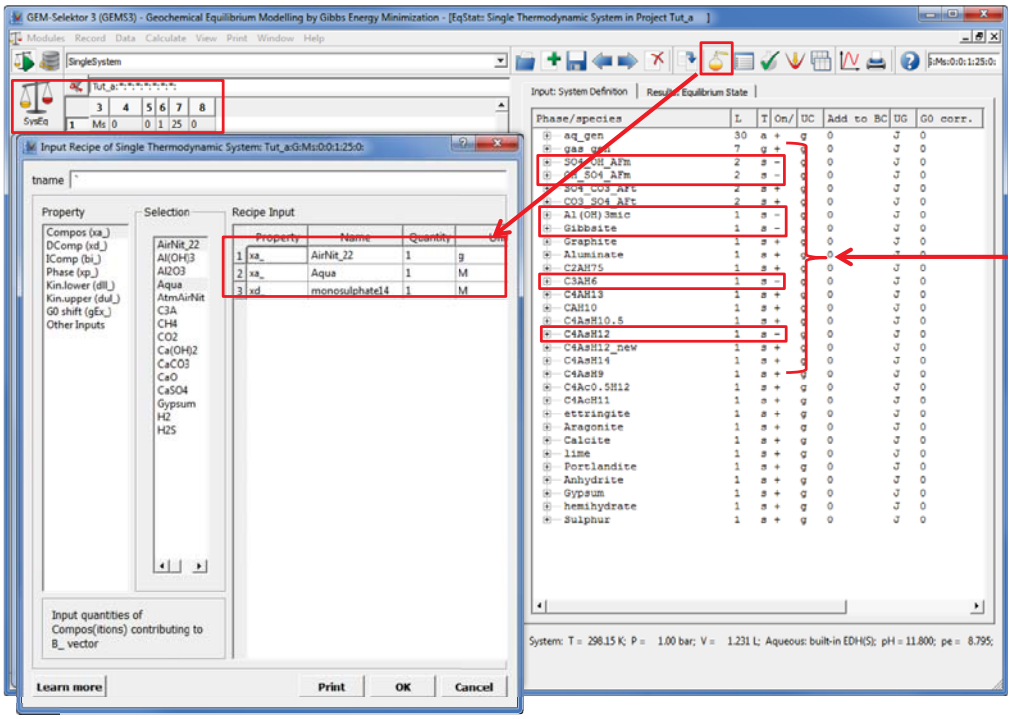
Holcim

- **Modelling the drying behavior of Monosulfoaluminate**

Holcim

Modelling drying: Process simulation

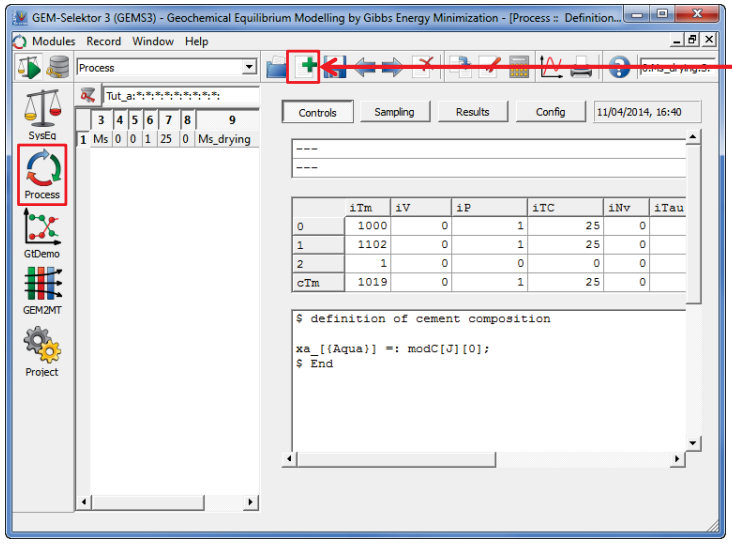
Modify the initial single system created: the system should contain AirNit_22, Aqua and monosulphate14



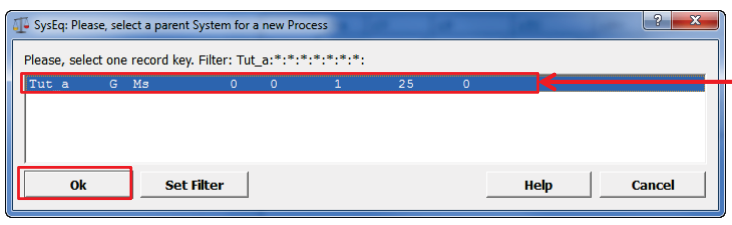
Deactivate the formation of SO4_OH and OH_SO4 solid solutions, Al(OH)3mic, Gibbsite and C3AH6

Holcim

Modelling drying: Process simulation



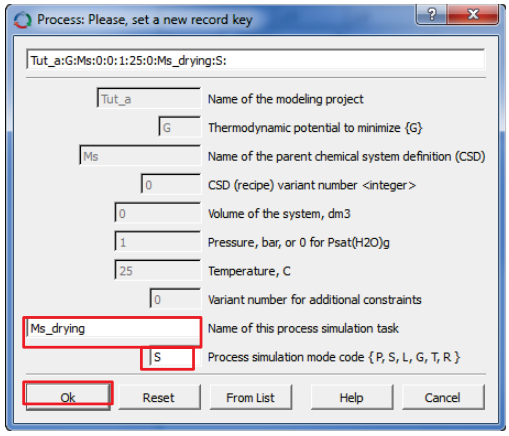
Create a new process



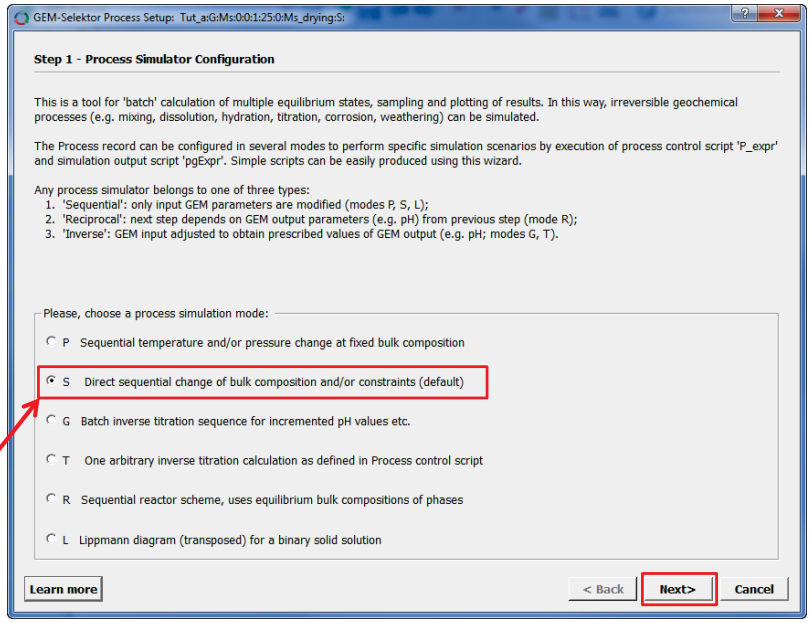
Select as parent file the single system containing AirNit_22, Aqua and monosulphate14

Holcim

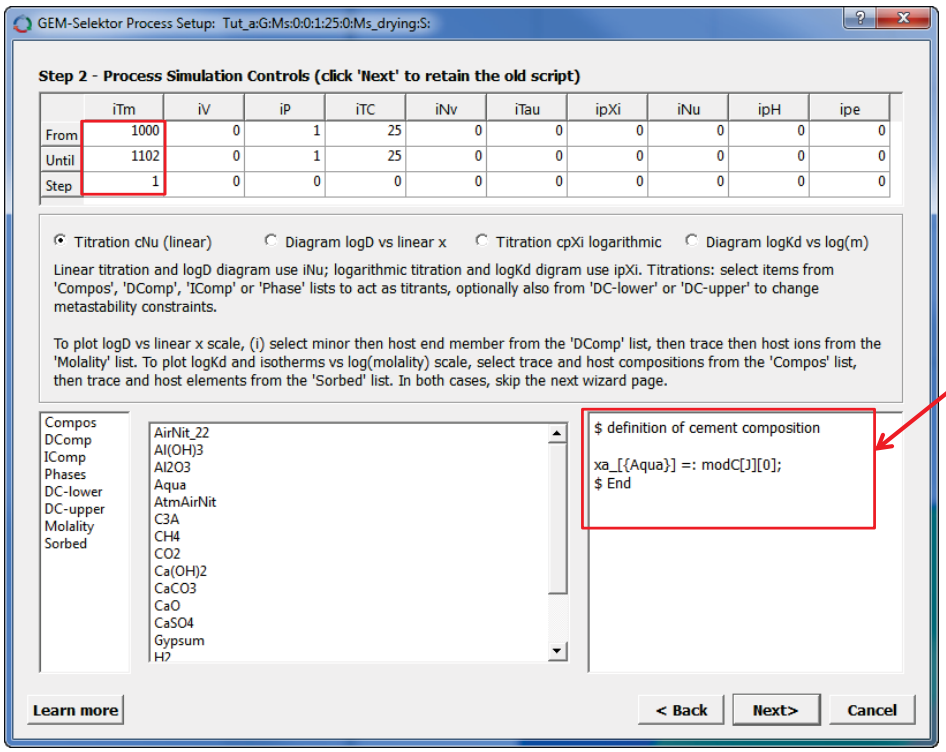
Modelling drying: Process simulation



To simulate drying, water will be removed from the system

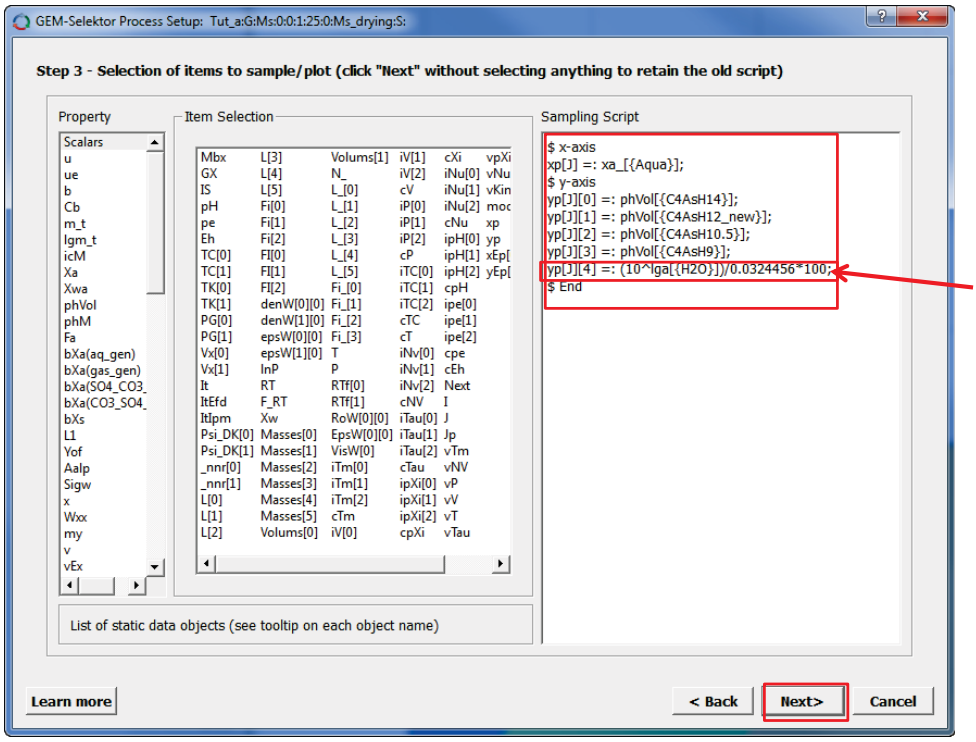


Modelling drying: Process simulation



To simulate drying water will be removed from the system

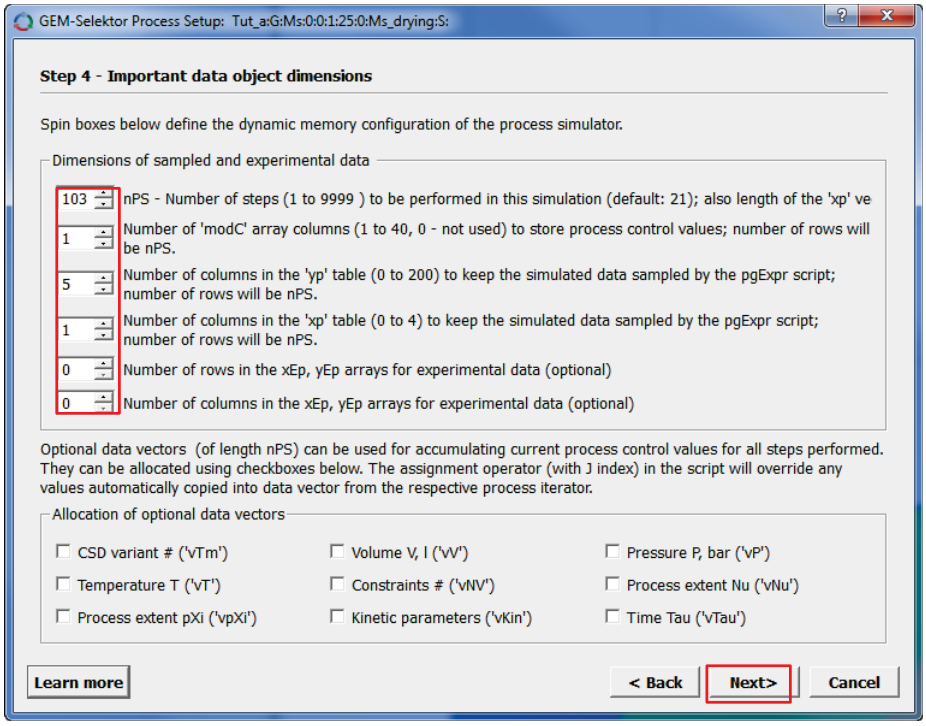
Modelling drying: Process simulation



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

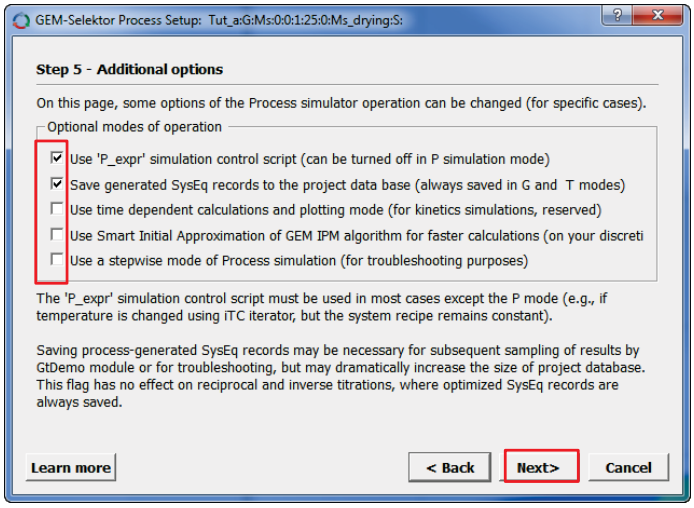
Holcim

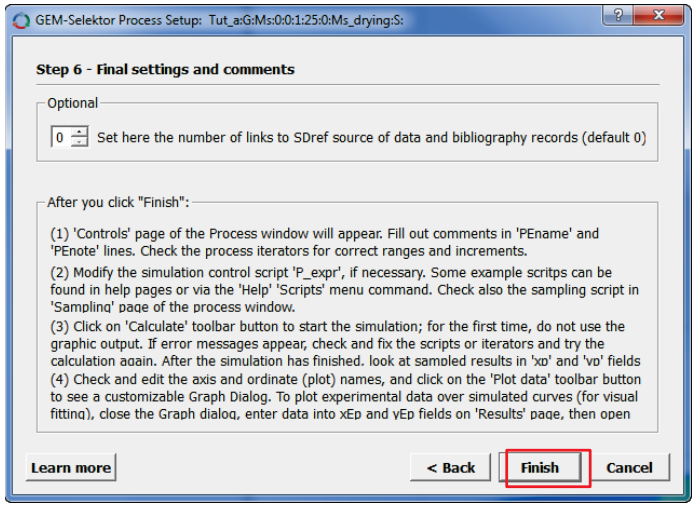
Modelling drying: Process simulation



Holcim

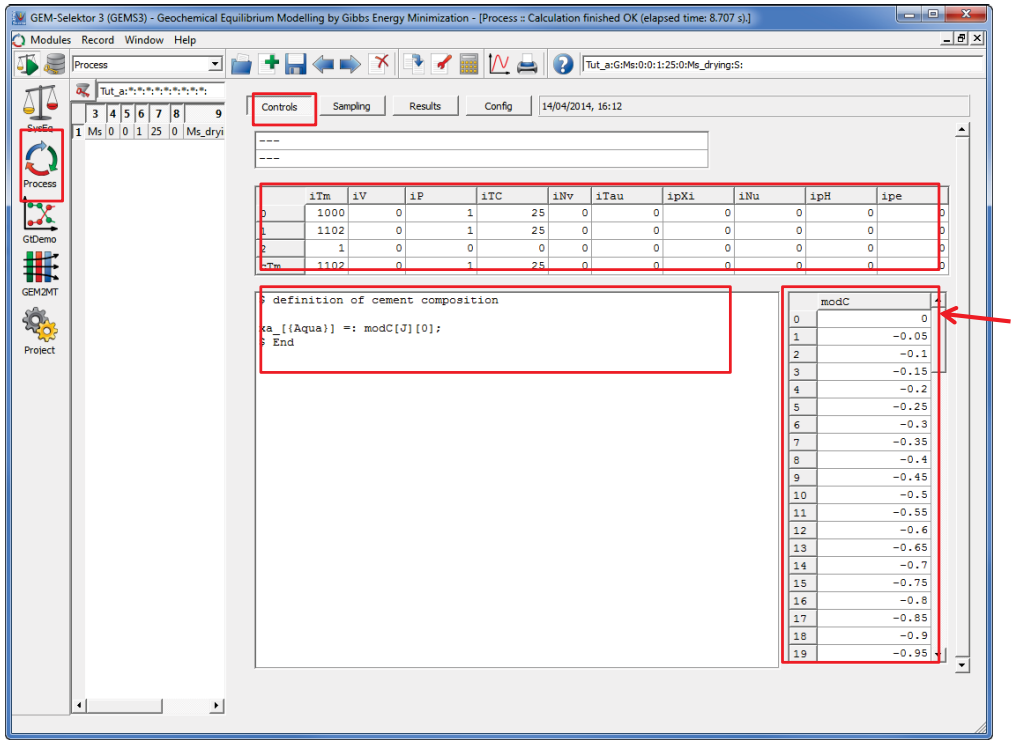
Modelling drying: Process simulation





Holcim

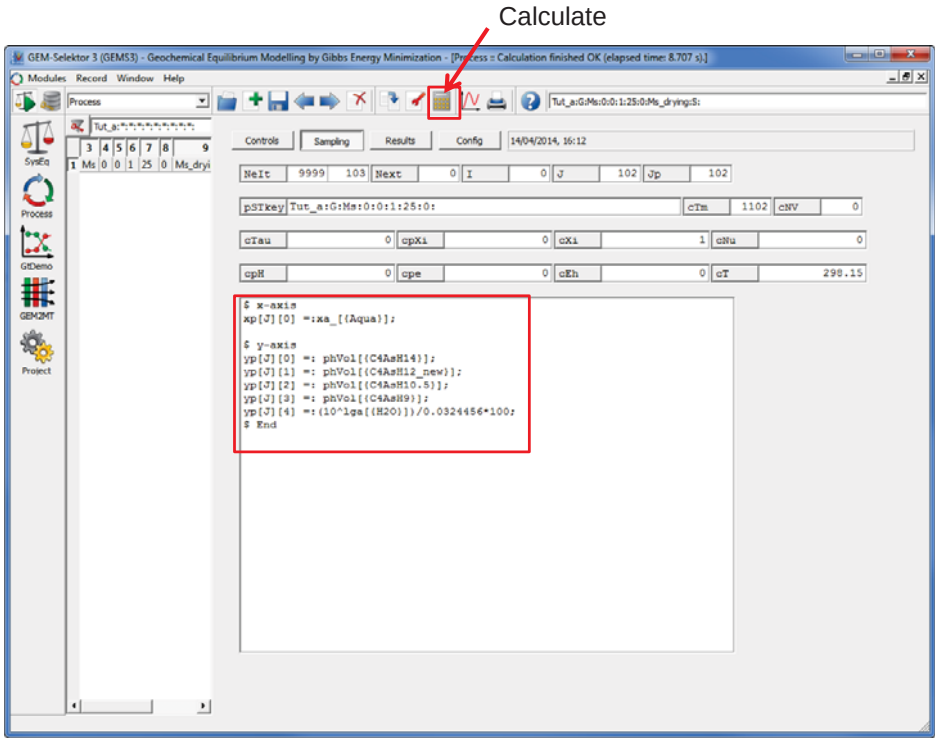
Modelling drying: Process simulation



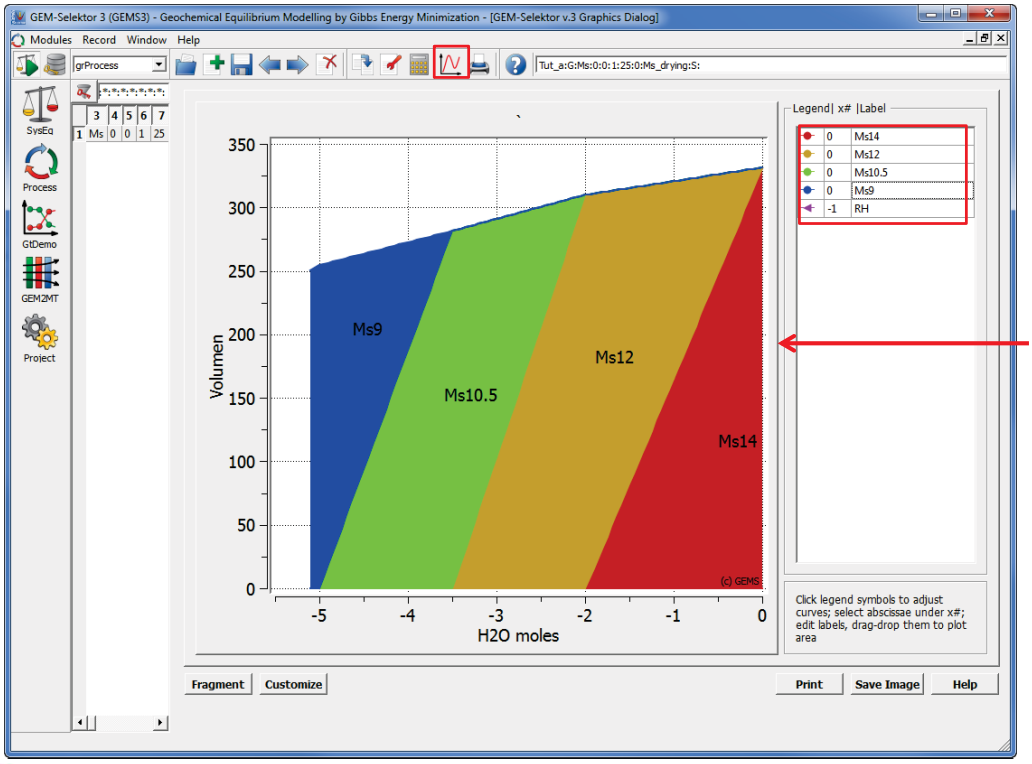
Water quantity to be introduced must be negative: removal of water

Holcim

Modelling drying: Process simulation



Modelling drying: Process simulation

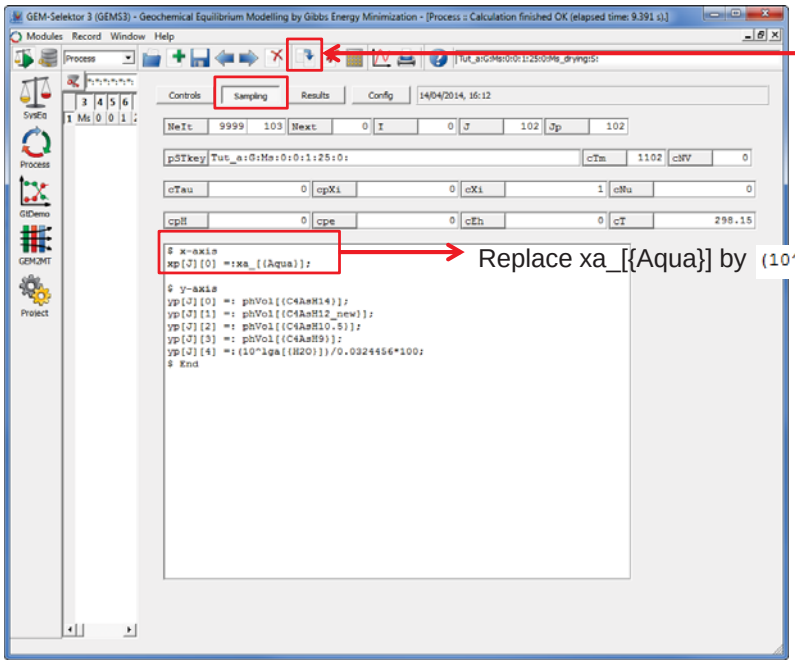


Phase assemblage upon removal of water

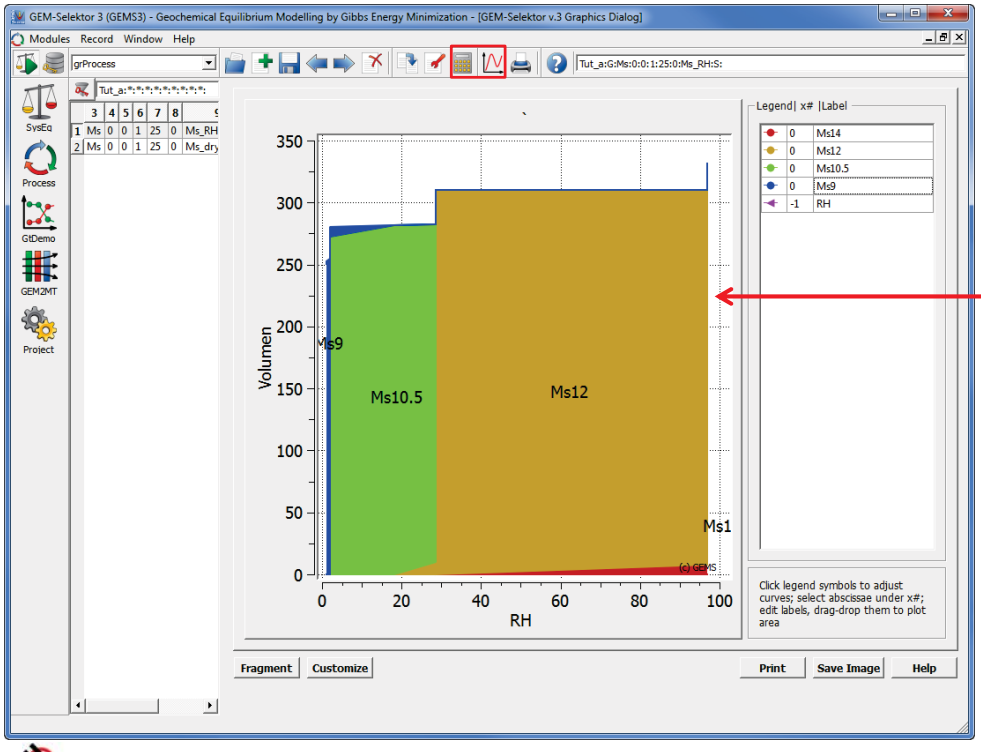
Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

Modelling drying: 2nd Process simulation

Now we will plot the volume changes as function of RH



Modelling drying: 2nd Process simulation



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

Thank you for your attention

nanocem

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