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GEMS workshop 2014

Impact of water activity on the stability of cement hydrates

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Innovation – PT
Holcim Technology Ltd.

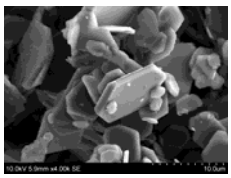
EMPA, Dübendorf, May 8, 2014

Outline

- Introduction
- Methodology used and results
  - Multi-method Approach
- Application example
  - Thermodynamic modelling of monosulfoaluminate – H2O interactions

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 $[Ca_4(Al)_2(OH)_{12}]^{2+}$ $[CO_3 \cdot \mathbf{4.5}H_2O]^{2-}$ → **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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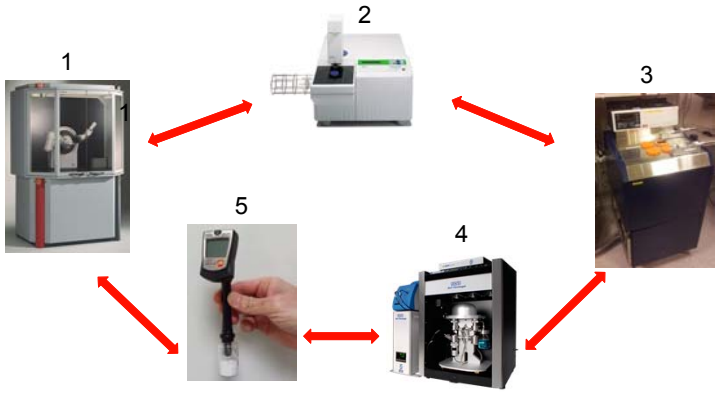
Methodology. Answering the questions

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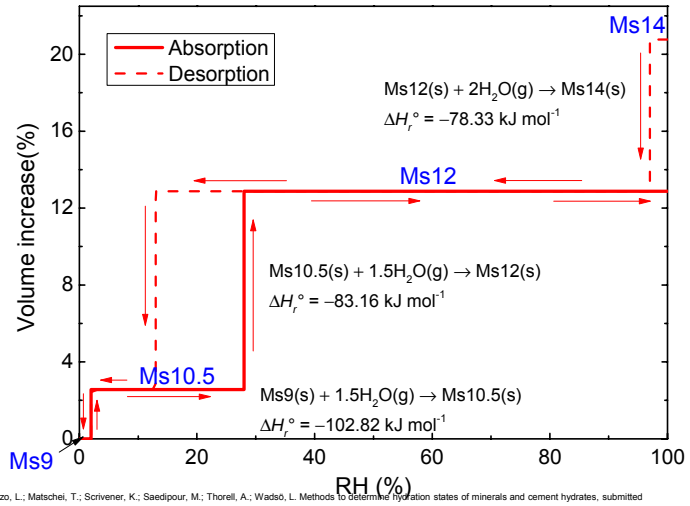
Baquerizo, L.; Matschei, T.; Scrivener, K.; Saedipour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

 4

Monosulfoaluminate – H_2O isotherm

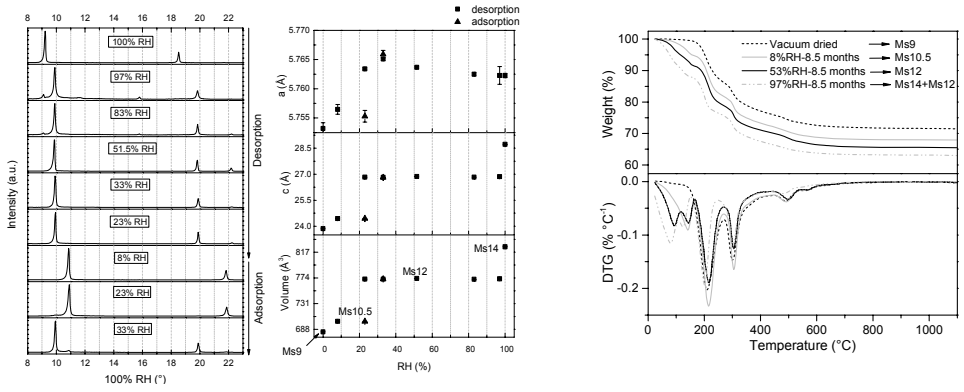
- **A first look at what we need to derive**



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

Methodology

- XRD/ TGA



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

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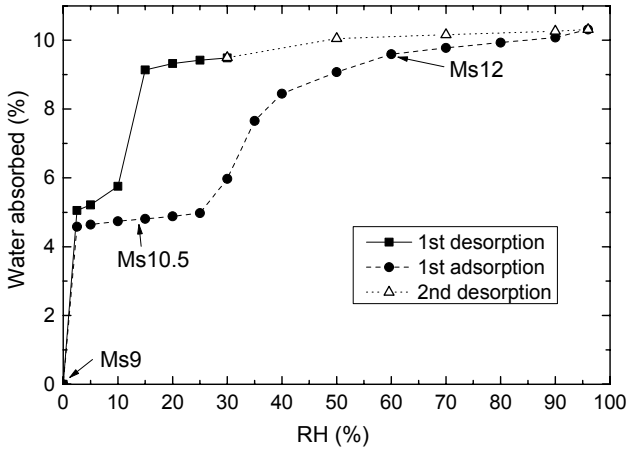
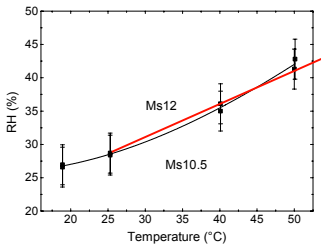
Methodology

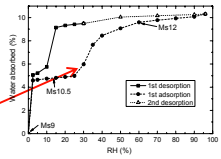
- Sorption balance

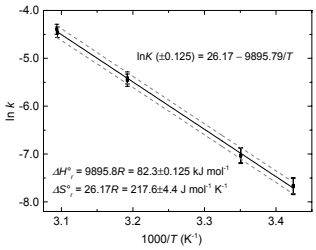


Methodology

- Hydrate pair – humidity buffer method







Ms12(s) → Ms10.5(s) + 1.5H_2O(g)

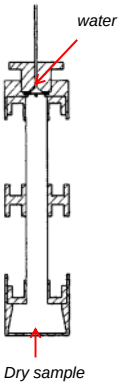
$$\Delta G_r^o = -RT\ln K = -RT\ln[f(\mathrm{H_2O})^{1.5}] = -1.5RT\ln\frac{f^*(\mathrm{H_2O})RH}{100}$$

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

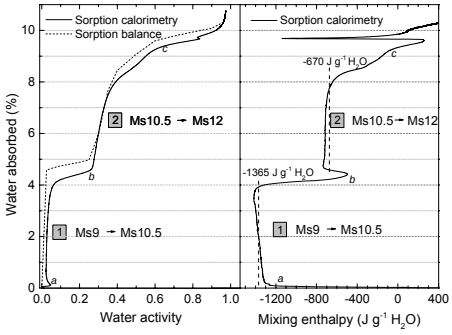
ΔG_r° [kJ mol^{-1}]	ΔH_r° [kJ mol^{-1}]	ΔS_r° [J mol^{-1} K^{-1}]
17.4 ± 0.3	82.3 ± 1.0	217.6 ± 4.4

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

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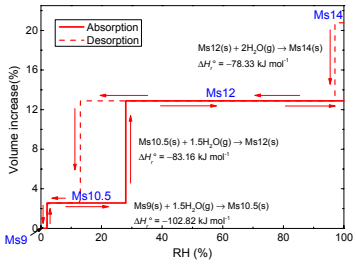
Methodology

- 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
  - 25 °C → 85% RH
  - 25 °C → 78% RH



- Then the thermodynamic properties were calculated with the equations:

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

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

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

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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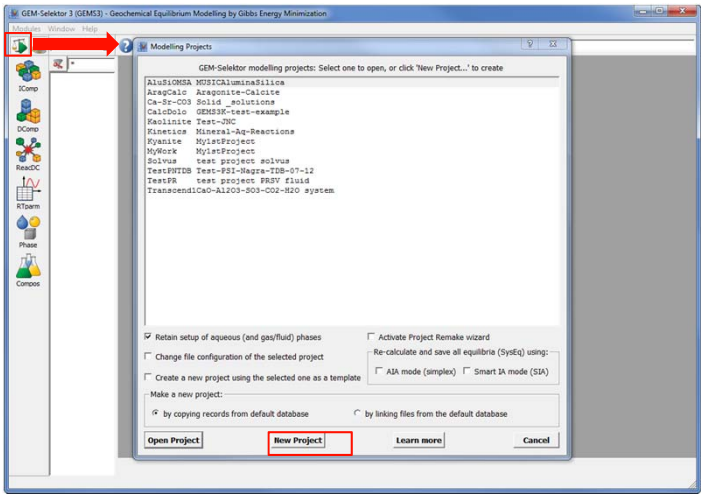
Create new project



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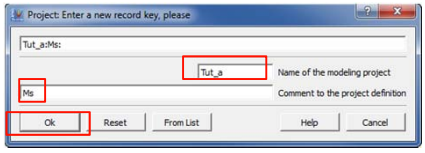

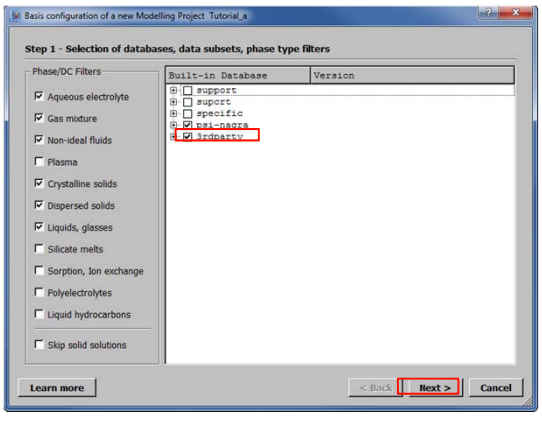

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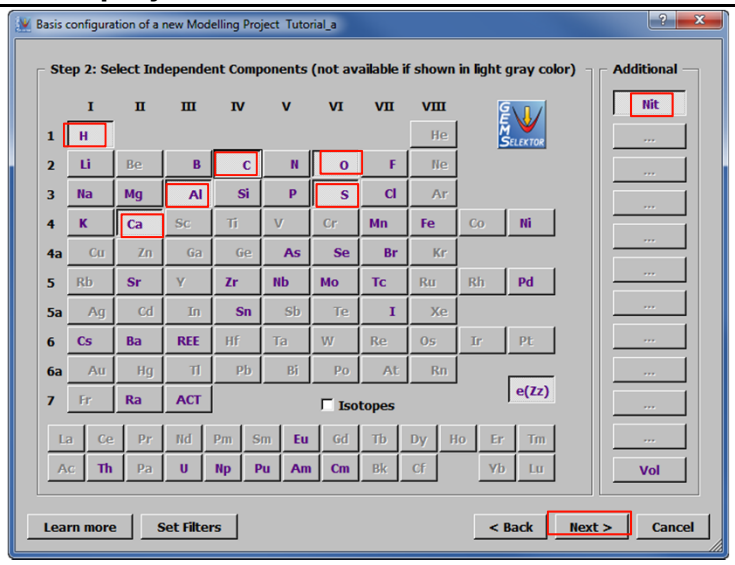

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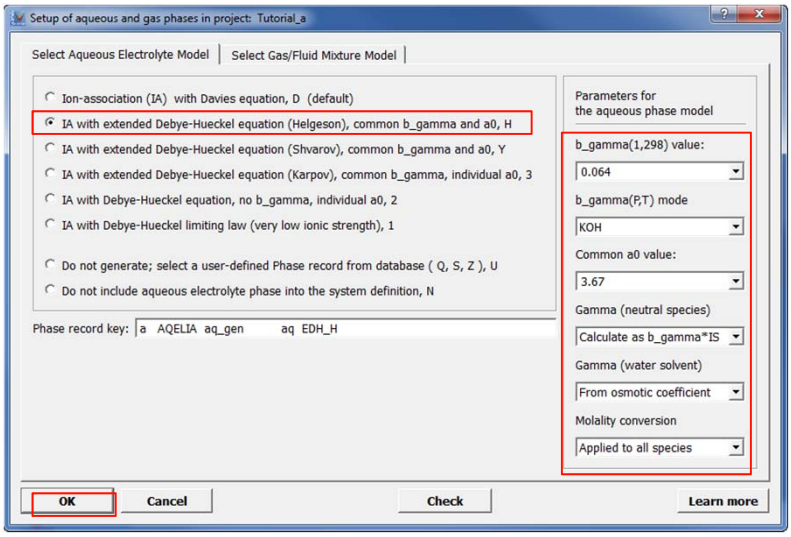
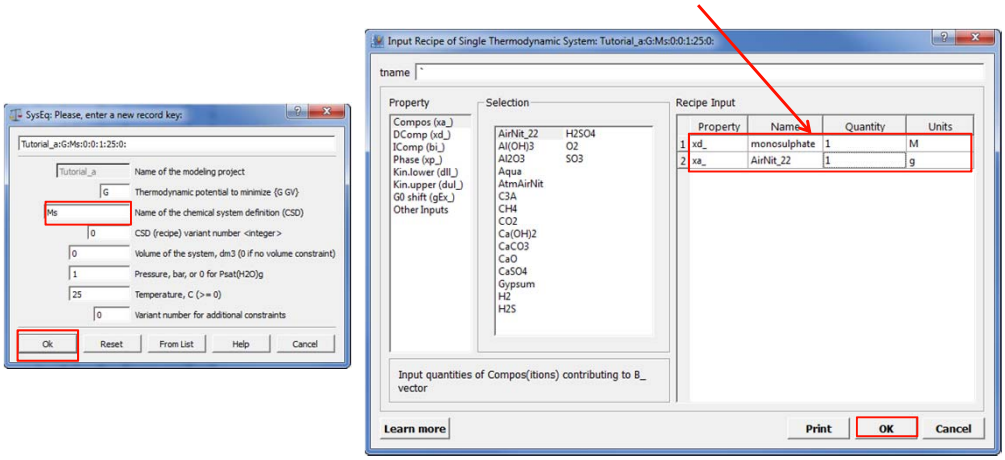


Create new project

Introduce monosulphate and AirNit_22



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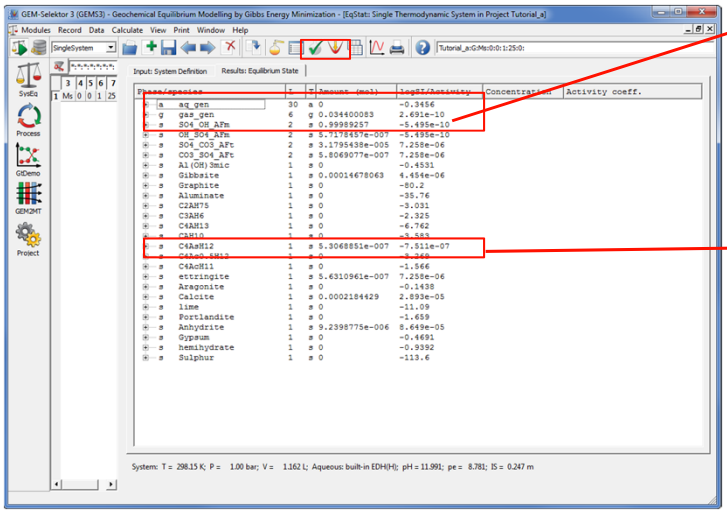
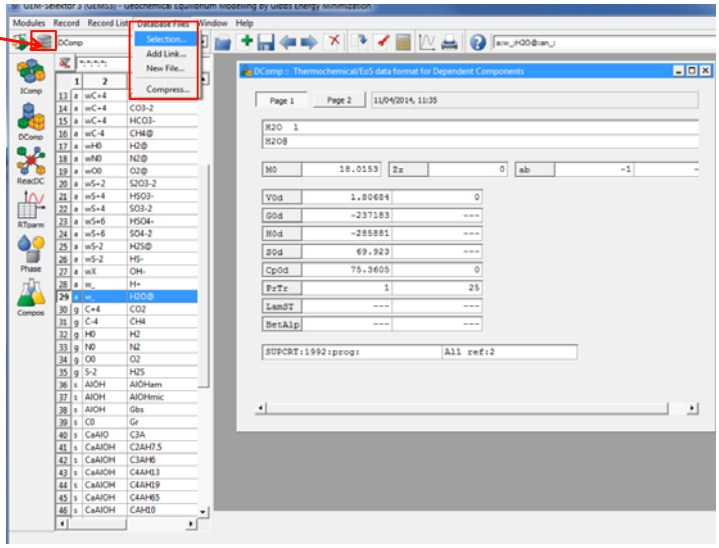


SO4_OH_AFm more stable than C4AsH12 (Ms12): for the moment we sip solid solution formation

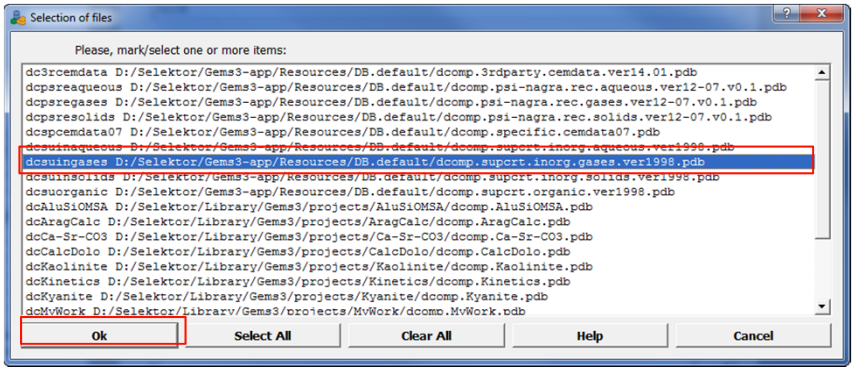
Just C4AsH12 (Ms12) appears. The other hydration states are not introduced

Introduce water vapor

Go to Database management mode to introduce water vapor

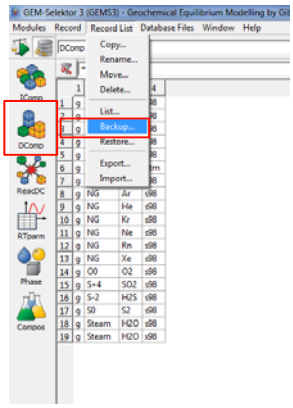


Introduce water vapor

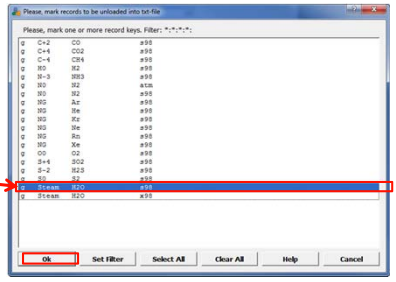


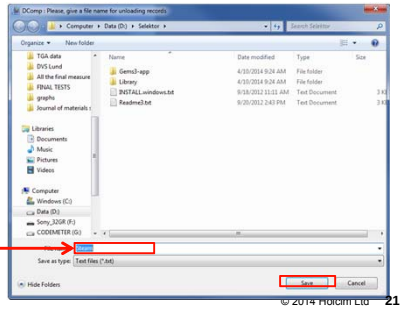
Introduce water vapor

Backup Steam s98



Choose Steam s98





Save as Steam.txt

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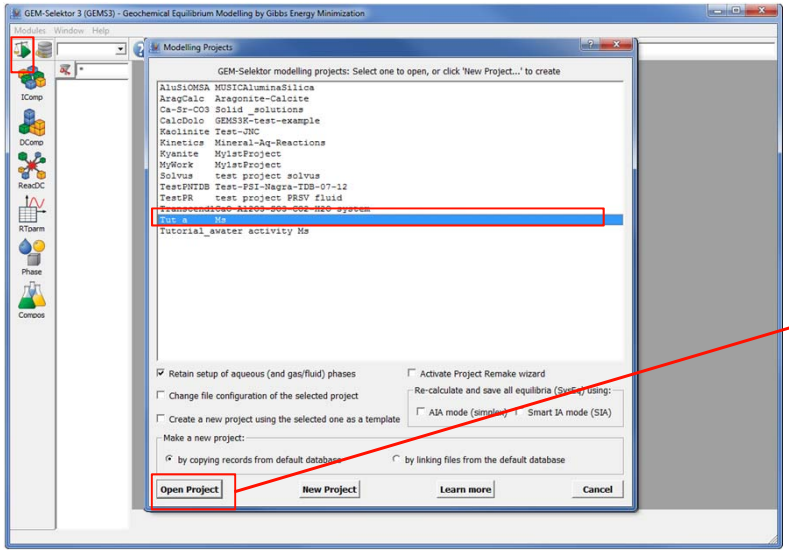
Introduce water vapor



Open the project

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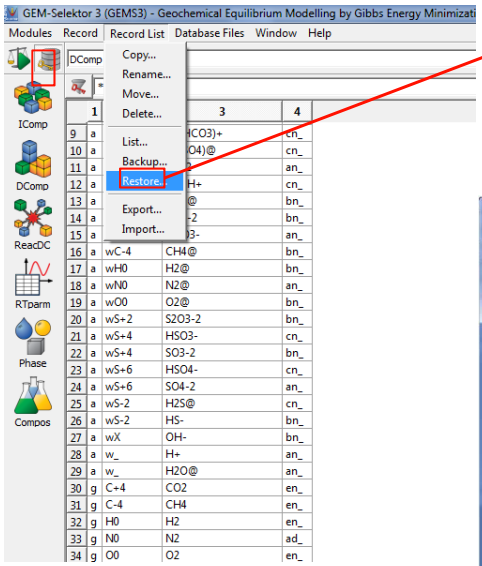
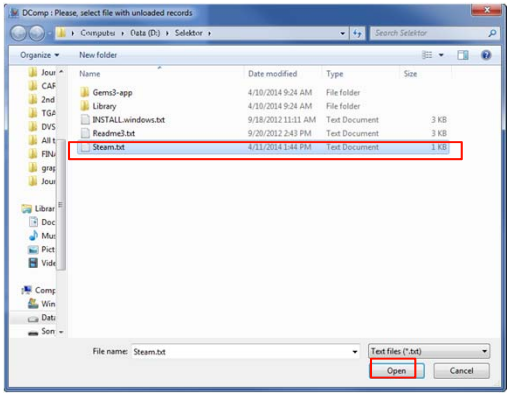
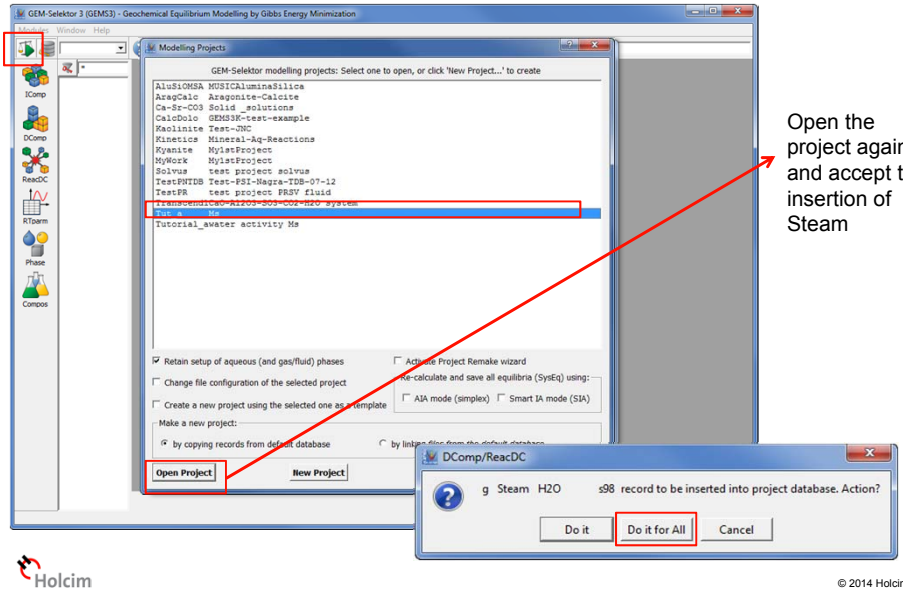
Introduce water vapor



Restore Steam.txt into the project database



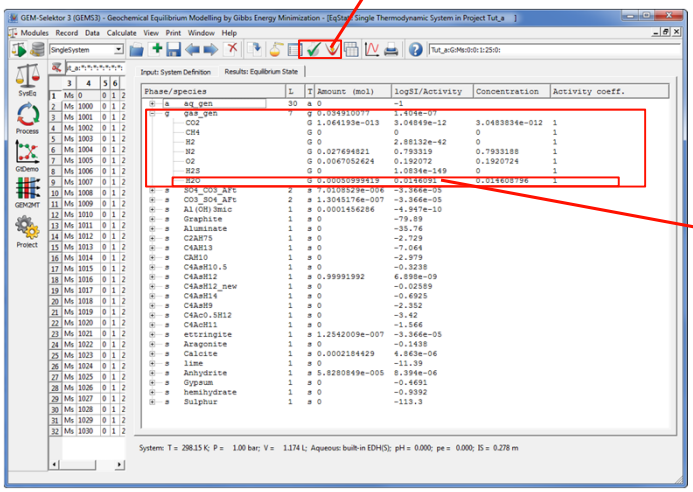
Introduce water vapor



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

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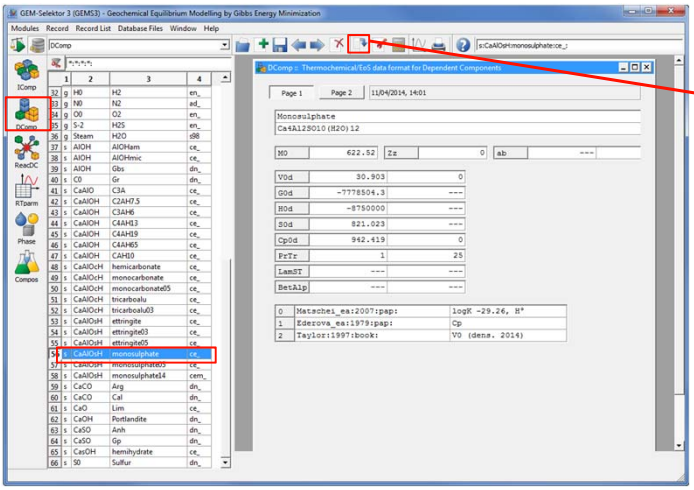
Introduce Ms14 in DComp

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



Clone monosulphate

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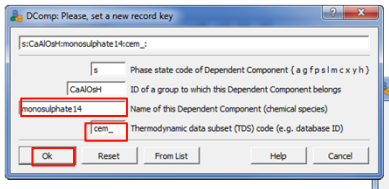
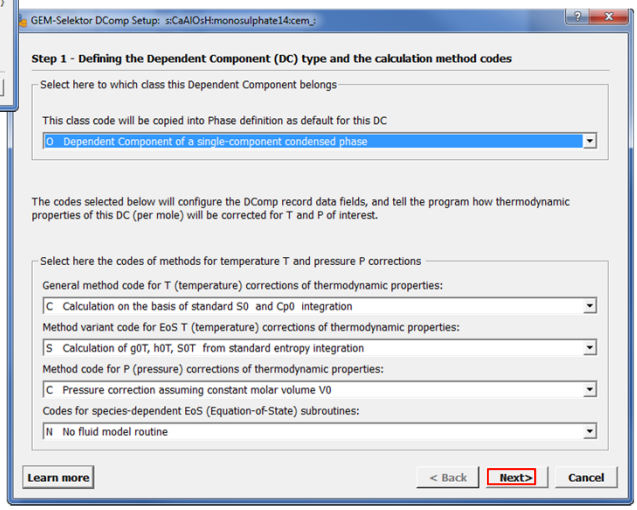
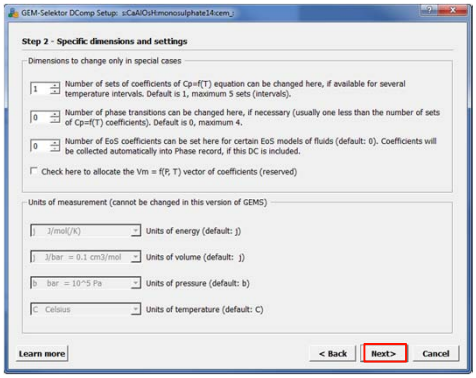
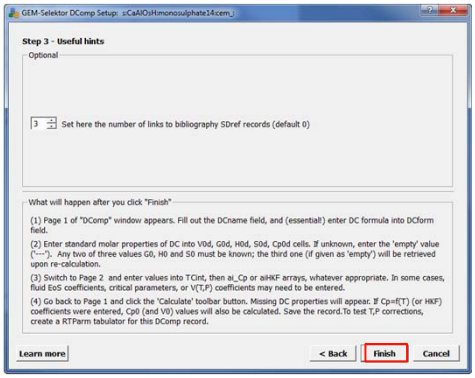
Introduce Ms14 in DComp





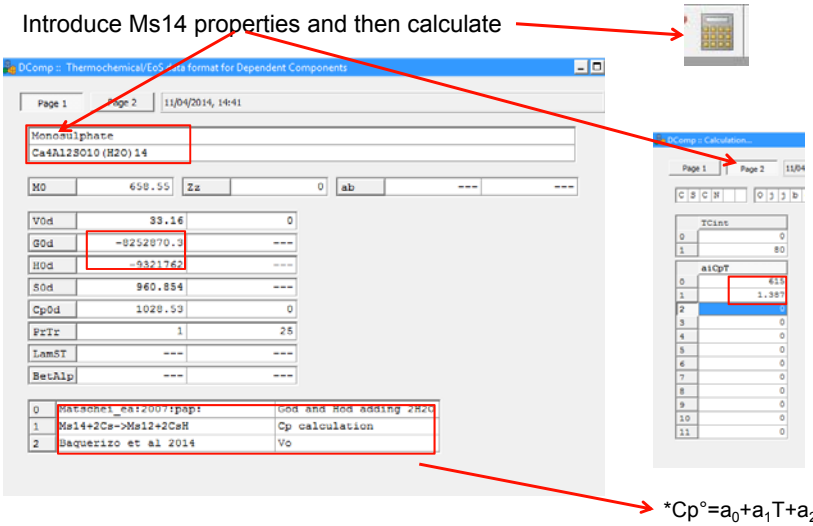
Introduce Ms14 in DComp





Introduce Ms14 in DComp

Introduce Ms14 properties and then calculate



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

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

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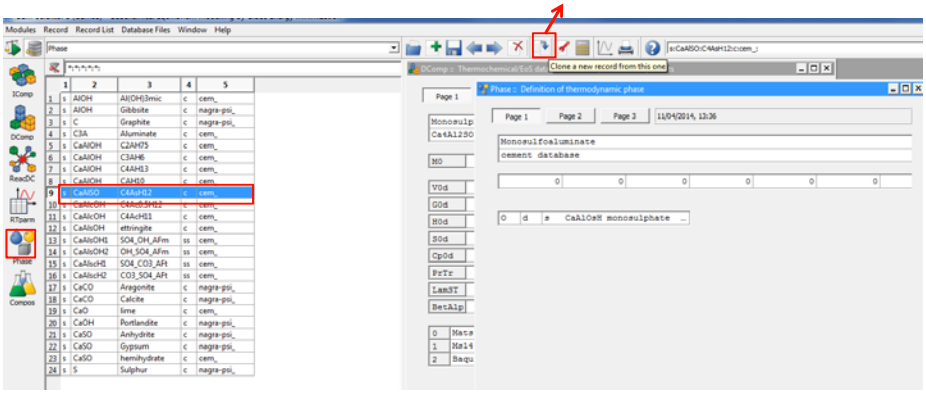
Create the Phase Ms14

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

Clone C4AsH12



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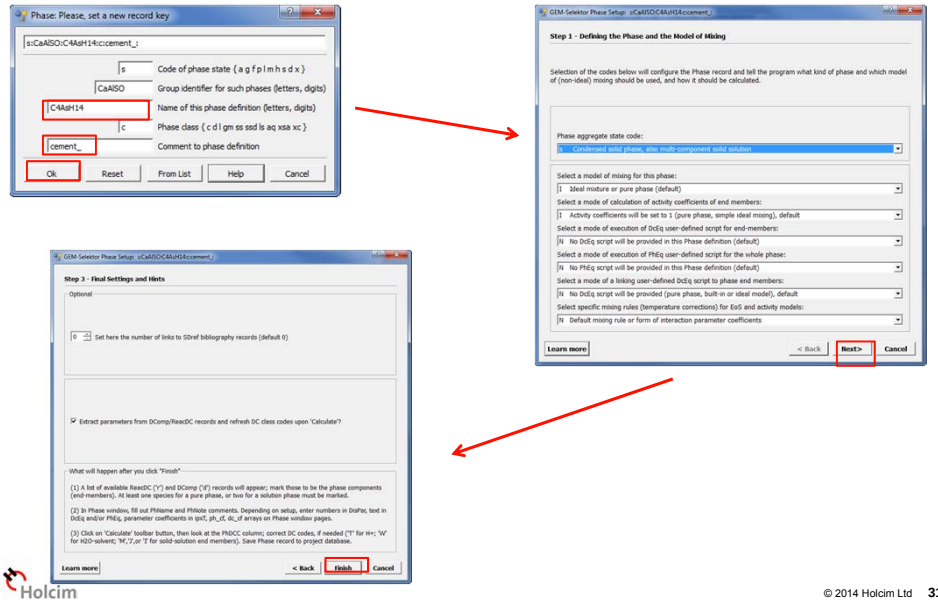
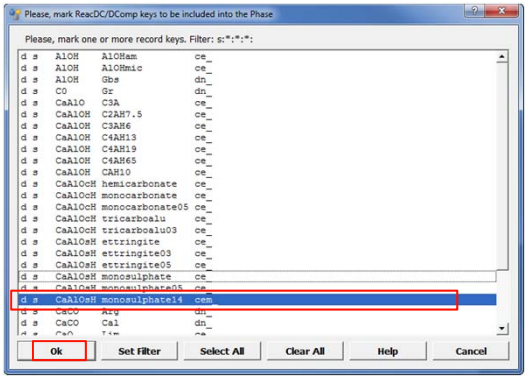
Create the Phase Ms14



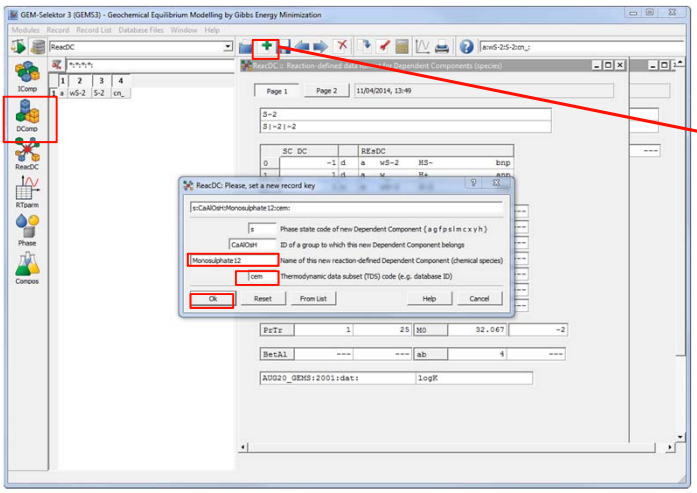
Create the Phase Ms14



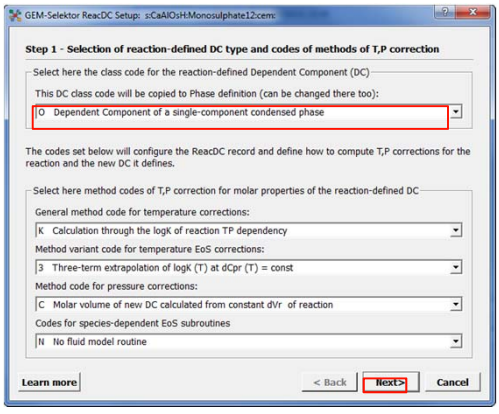
	1	2	3	4	5
1	s	AlOH	Al(OH)3mic	c	cem_
2	s	AlOH	Gibbsite	c	nagra-psi_
3	s	C	Graphite	c	nagra-psi_
4	s	C3A	Aluminate	c	cem_
5	s	CaAlOH	C2AH75	c	cem_
6	s	CaAlOH	C3AH6	c	cem_
7	s	CaAlOH	C4AH13	c	cem_
8	s	CaAlOH	CAH10	c	cem_
9	s	CaAlSO	C4AsH12	c	cem
10	s	CaAlSO	C4AsH14	c	cement_
11	s	CaAlcOH	C4Ac0.5H12	c	cem_
12	s	CaAlcOH	C4AcH11	c	cem_
13	s	CaAlsOH	ettringite	c	cem_
14	s	CaAlsOH1	SO4_OH_AFm	ss	cem_
15	s	CaAlsOH2	OH_SO4_AFm	ss	cem_
16	s	CaAlscH1	SO4_CO3_AFt	ss	cem_
17	s	CaAlscH2	CO3_SO4_AFt	ss	cem_
18	s	CaCO	Aragonite	c	nagra-psi_
19	s	CaCO	Calcite	c	nagra-psi_
20	s	CaO	lime	c	cem_
21	s	CaOH	Portlandite	c	nagra-psi_
22	s	CaSO	Anhydrite	c	nagra-psi_
23	s	CaSO	Gypsum	c	nagra-psi_
24	s	CaSO	hemihydrate	c	cem_
25	s	S	Sulphur	c	nagra-psi_

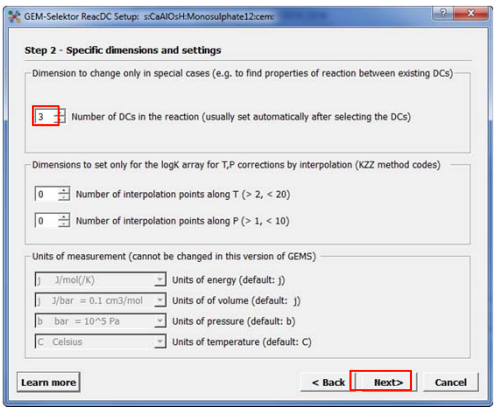
Introduce Ms12: ReacDC

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



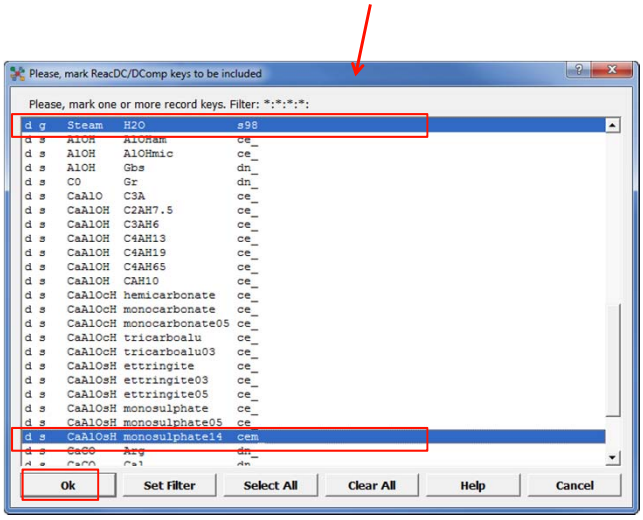
Introduce Ms12: ReacDC



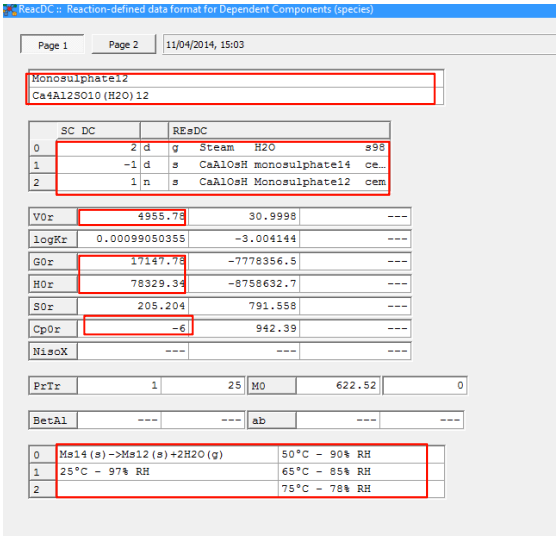


Introduce Ms12: ReacDC

Introduce the components taking part of the reaction



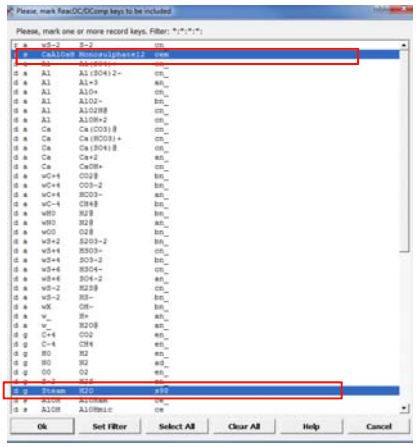
Introduce Ms12: ReacDC

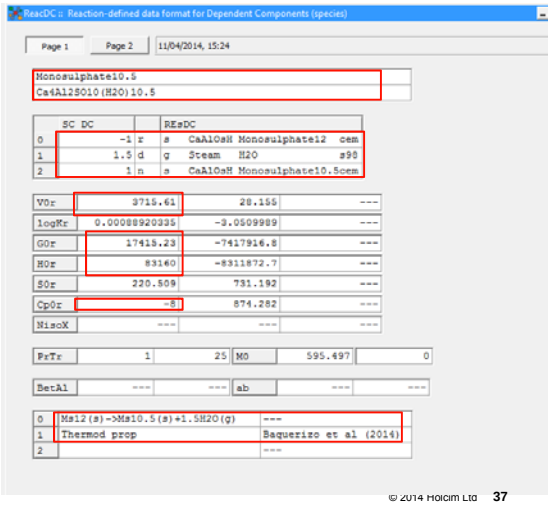


Introduce reaction and thermodynamic properties and then calculate 

Introduce Ms10.5: ReacDC

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

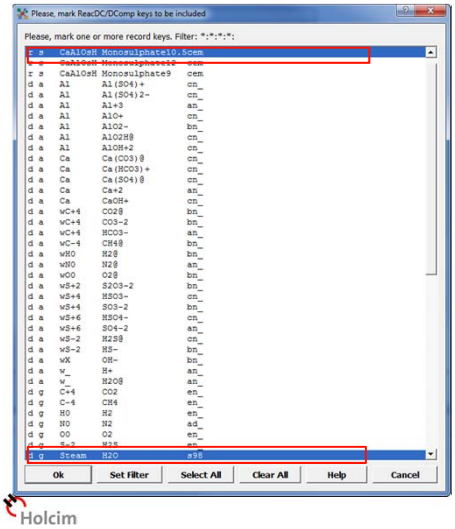


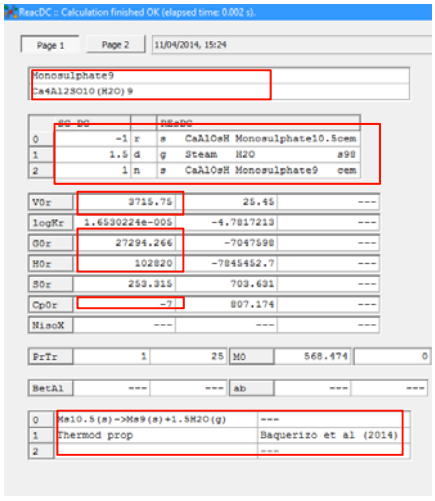


Holcim

Introduce Ms9: ReacDC

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



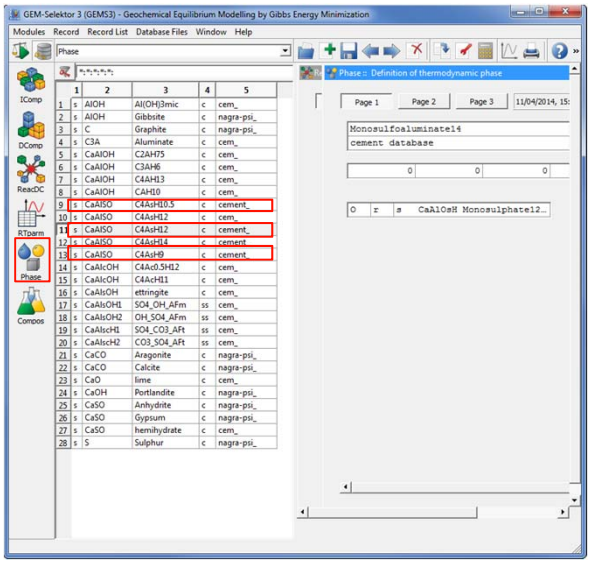


Holcim

Introduce Ms12, Ms10.5 and Ms9 as phases

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

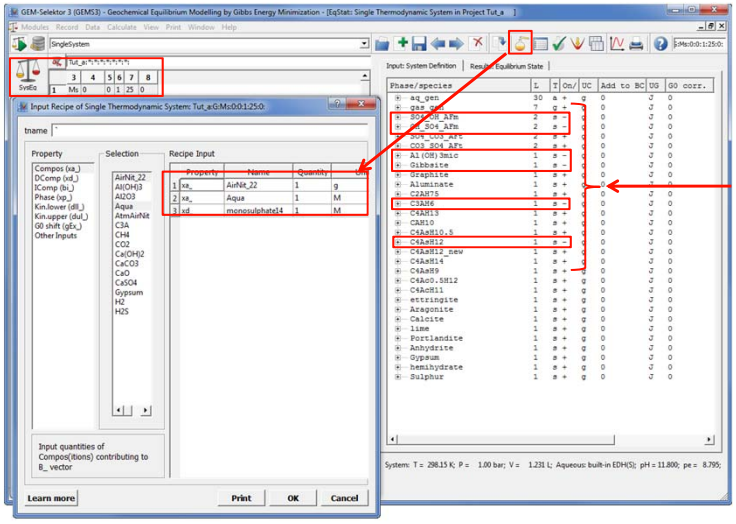
Phases to be introduced
- Ms12
- Ms10.5
- Ms9



- **Modelling the drying behavior of Monosulfoaluminate**

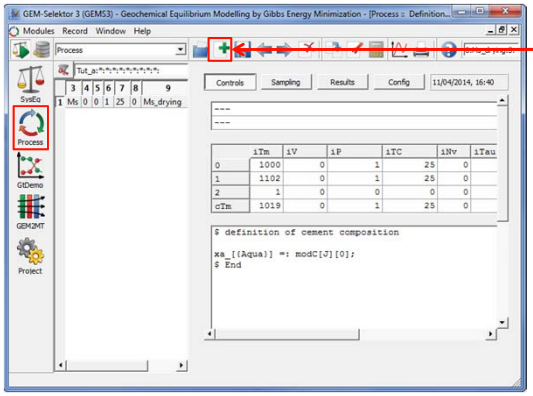
Modelling drying: Process simulation

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

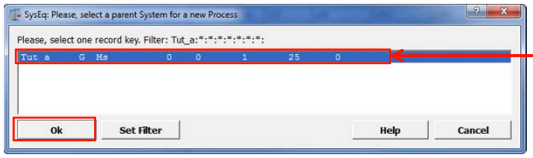


Skip the formation of SO4_OH and OH_SO4 solid solutions, Al(OH)3mic, Gibbsite and C3AH6

Modelling drying: Process simulation

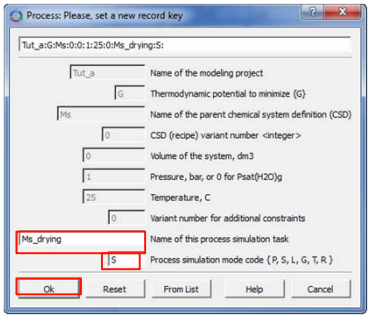


Create a new process

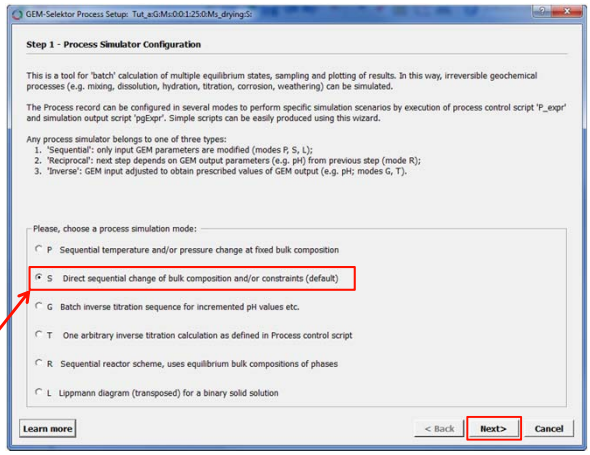


Select as parent file the single system containing AirNit_22, Aqua and monosulphate14

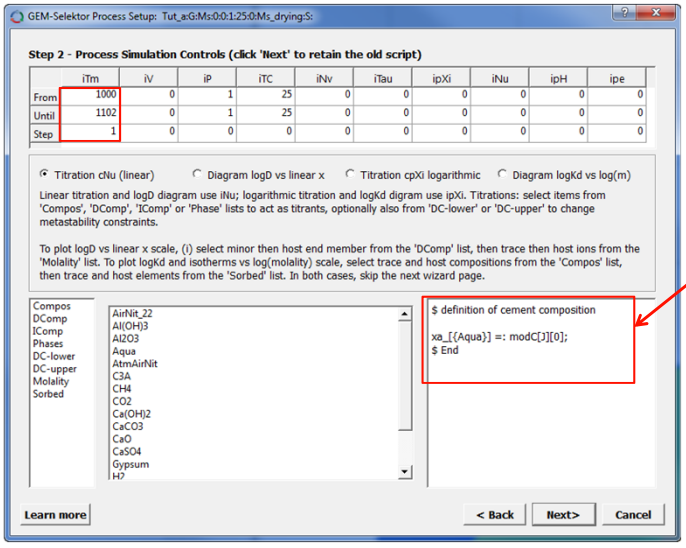
Modelling drying: Process simulation



To simulate drying, water will be removed from the system

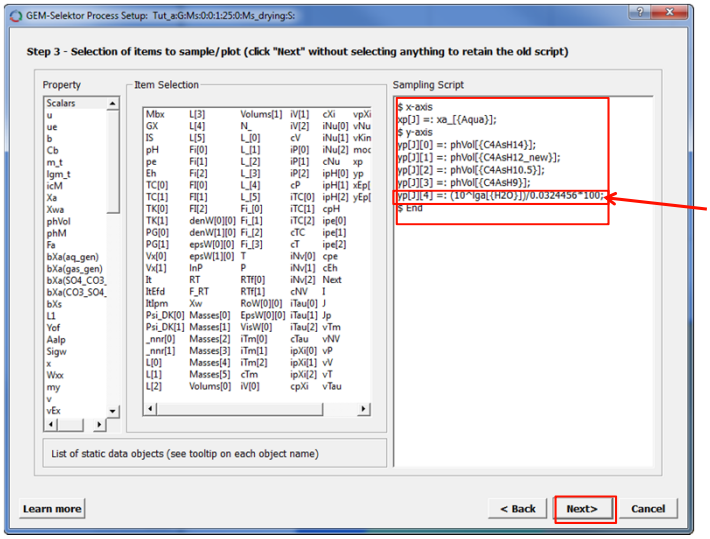


Modelling drying: Process simulation



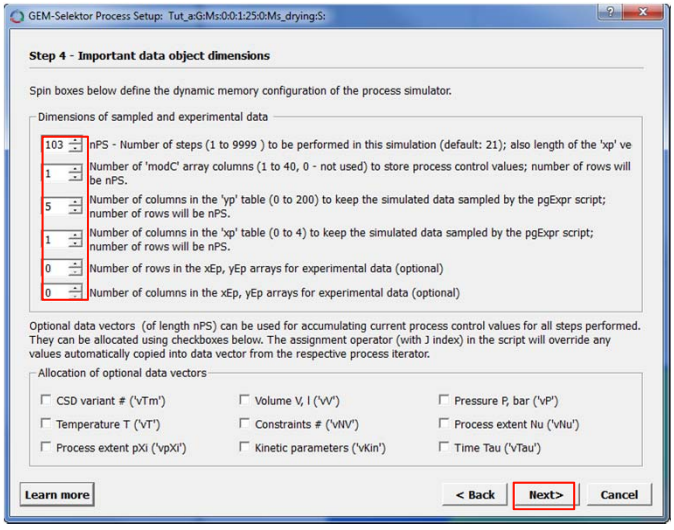
To simulate drying water will be removed from the system

Modelling drying: Process simulation

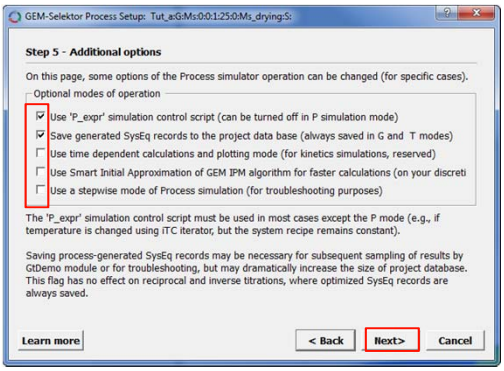


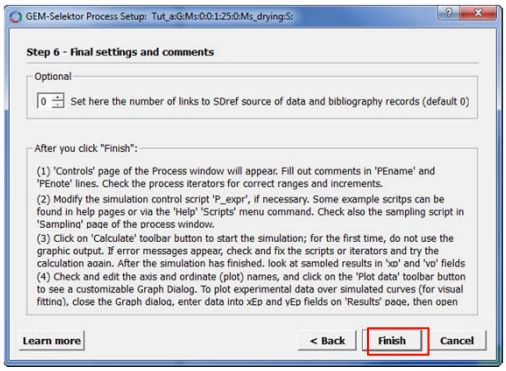
yp[J][4] corresponds to the RH at 25 °C

Modelling drying: Process simulation

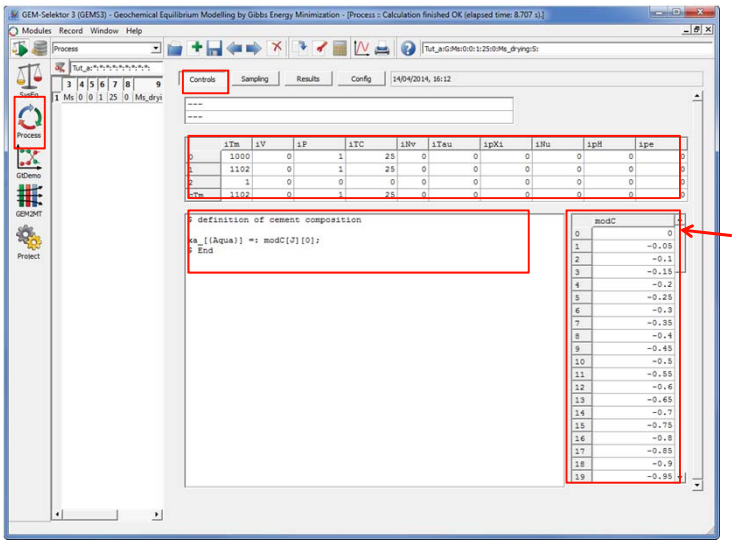


Modelling drying: Process simulation



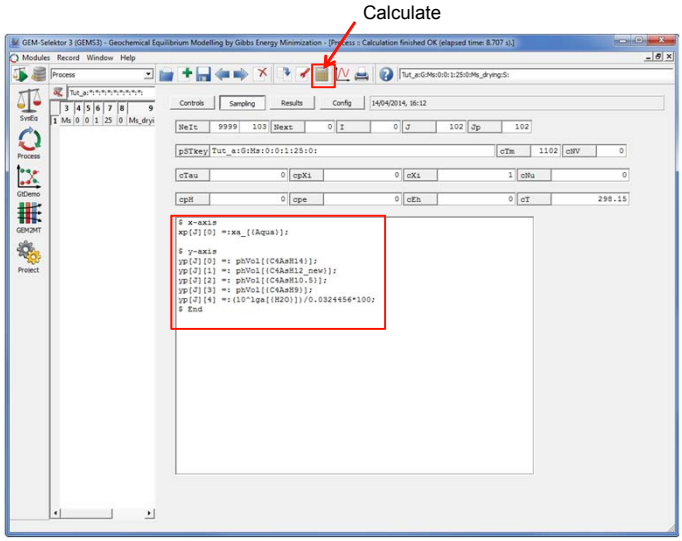


Modelling drying: Process simulation



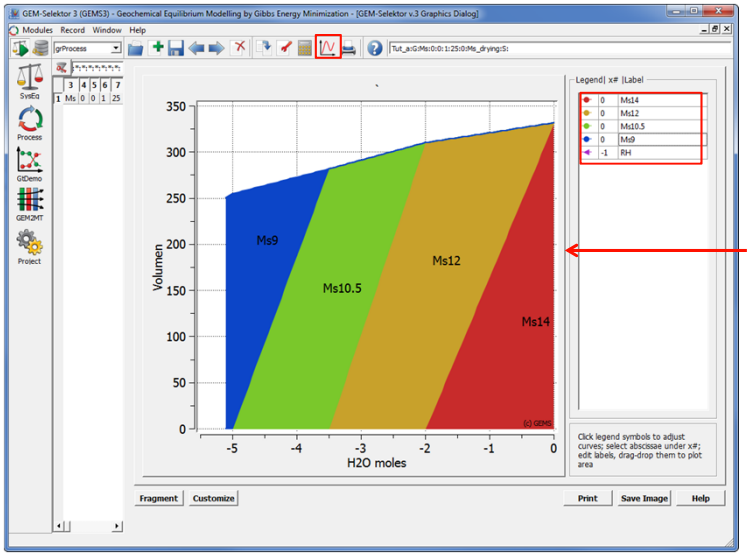
Water quantity to be introduced must be negative: removal of water

Modelling drying: Process simulation



Holcim

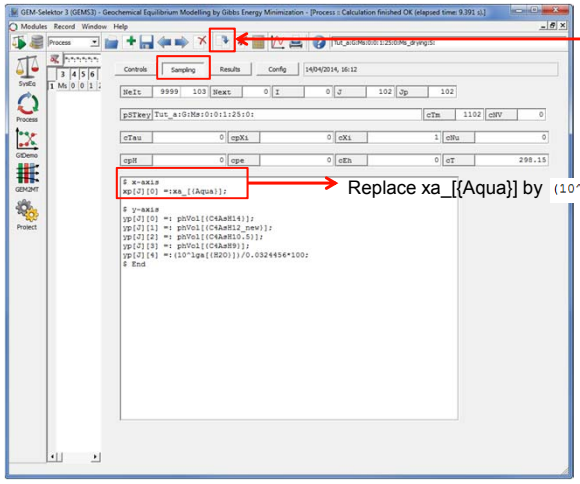
Modelling drying: Process simulation



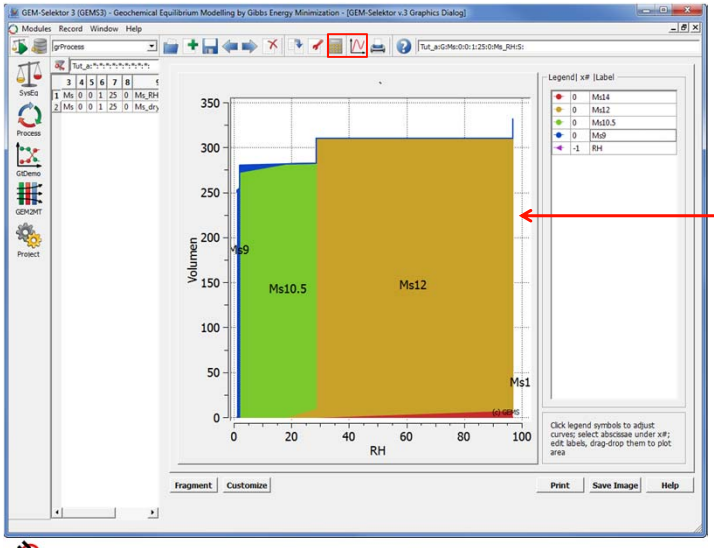
Holcim

Modelling drying: 2nd Process simulation

Now we will plot the volume changes as function of RH



Modelling drying: 2nd Process simulation



Thank you for your attention

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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.