



Strength. Performance. Passion.

GEMS workshop 2014



Impact of water activity on the stability of cement hydrates

Thomas Matschei, Luis Baquerizo
Innovation – PT
Holcim Technology Ltd.

EMPA, Dübendorf, May 8, 2014

© 2014 Holcim Ltd

Outline

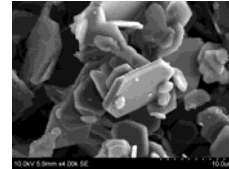
- Introduction
- Methodology used and results
 - ▶ Multi-method Approach
- Application example
 - ▶ Thermodynamic modelling of monosulfoaluminate – H₂O interactions



© 2014 Holcim Ltd 2

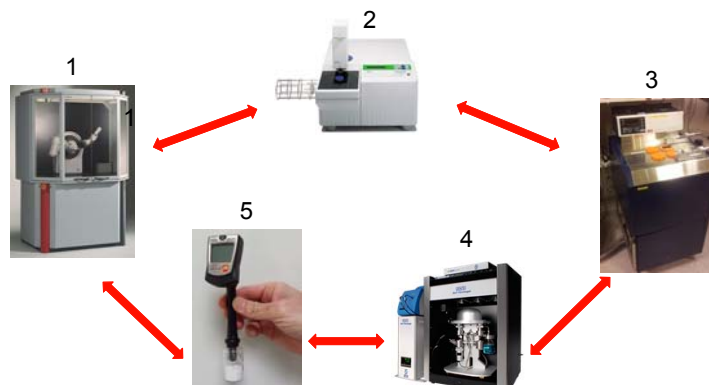
Introduction

- **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 $[\text{Ca}_4(\text{Al})_2(\text{OH})_{12}]^{2+} [\text{CO}_3 \cdot 4.5\text{H}_2\text{O}]^{2-} \rightarrow \text{Ms}_{10.5}$
- 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?



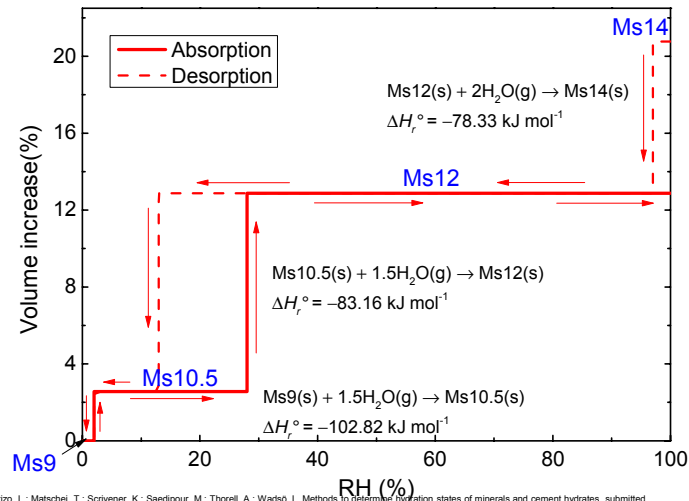
Methodology. Answering the questions

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



Monosulfoaluminate – H₂O isotherm

- A first look at what we need to derive

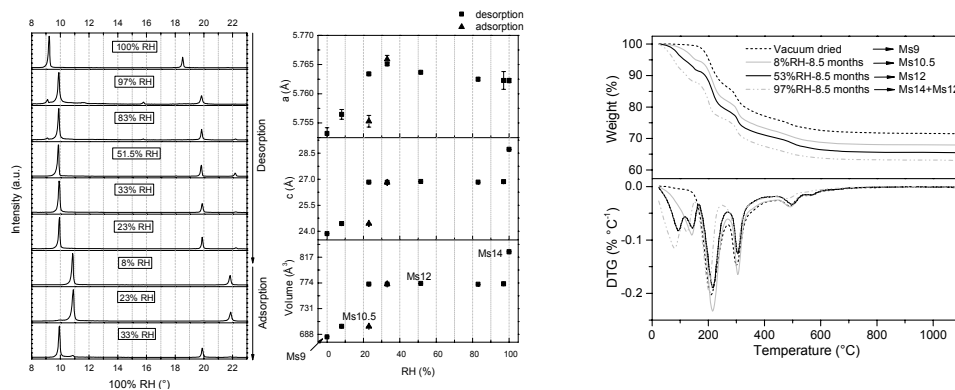


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saediour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

© 2014 Holcim Ltd 5

Methodology

- XRD/ TGA



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

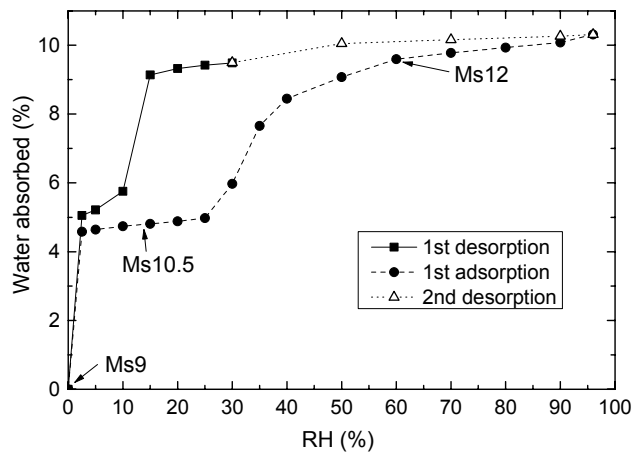


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saediour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

© 2014 Holcim Ltd 6

Methodology

- Sorption balance

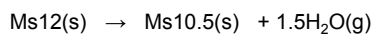
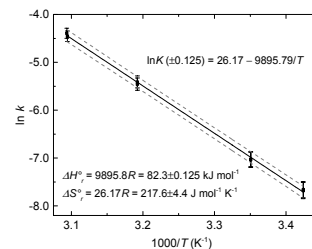
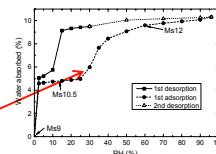
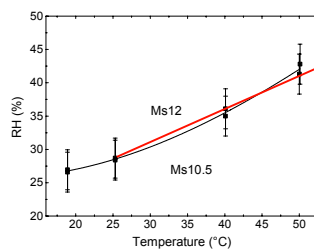


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saediour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

© 2014 Holcim Ltd 7

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

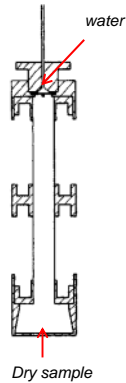


Baquerizo, L.; Matschei, T.; Scrivener, K.; Saediour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, submitted

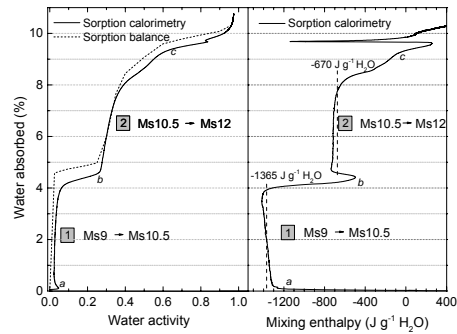
© 2014 Holcim Ltd 8

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



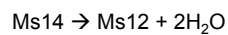
Holcim

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

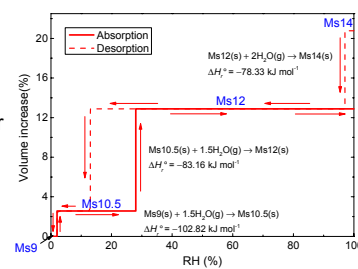
© 2014 Holcim Ltd 9

Methodology

- For the reaction



- 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:

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

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

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



Holcim

© 2014 Holcim Ltd 10

Methodology

- Derived thermodynamic properties

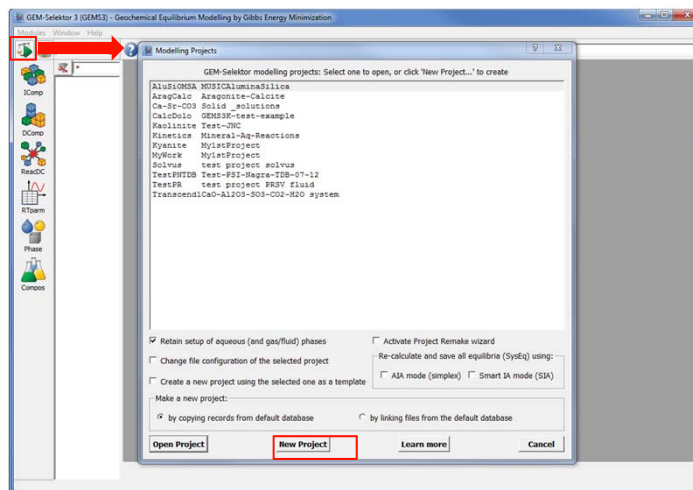
Reaction	Change of hyd. state (% RH)	ΔG_r° (kJ mol ⁻¹)	ΔH_r° (kJ mol ⁻¹)	ΔS_r° (J mol ⁻¹ K ⁻¹)
Ms14(s)→Ms12(s)+2H ₂ O(g)	97	17.15	78.33 ^a	205.20
Ms12(s)→Ms10.5(s)+1.5H ₂ O(g)	28.5 ^b	17.42	83.16 ^c	220.51
Ms10.5(s)→Ms9(s)+1.5H ₂ O(g)	2 ^d	27.29	102.82 ^e	253.32

^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

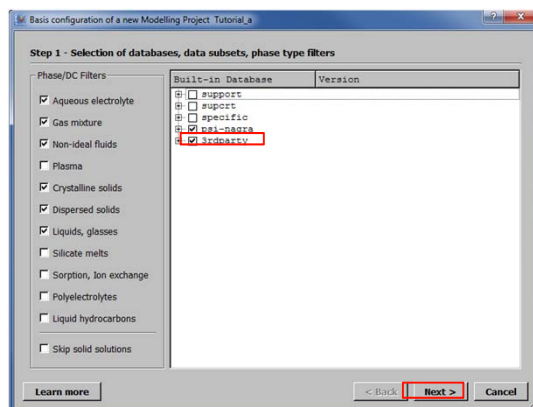
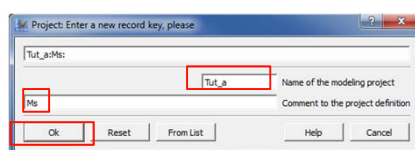
Thermodynamic modelling

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



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)

Additional

	I	II	III	IV	V	VI	VII	VIII
1	H							He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe
4a	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru
5a	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	REE	Hf	Ta	W	Re	Os
6a	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	ACT					

Isotopes

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm
Ac Th Pa U Np Pu Am Cm Bk Cf Yb Lu

Additional: Mit

Learn more Set Filters < Back Next > Cancel

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 a_0 , H
☐ IA with extended Debye-Hueckel equation (Shvarov), common b_{gamma} and a_0 , Y
☐ IA with extended Debye-Hueckel equation (Karpov), common b_{gamma} , individual a_0 , 3
☐ IA with Debye-Hueckel equation, no b_{gamma} , individual a_0 , 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

$b_{\text{gamma}}(1,298)$ value: 0.064
 $b_{\text{gamma}}(P,T)$ mode: KOH
 Common a_0 value: 3.67
 Gamma (neutral species): Calculate as $b_{\text{gamma}} \cdot I^S$
 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(120)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 (x_a)
DComp (x_d)
AI(OH)₃
Al₂O₃
Phase (x_p)
KinLower (dl_L)
KinUpper (du_L)
G0 shift (gEx_L)
Other Inputs

H2SO4
O2
SO3
Aqua
AtmAirNit
C3A
CH4
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



© 2014 Holcim Ltd 17

Create new project

GEM-Selector 3 (GEM3) - Geochemical Equilibrium Modeling by Gibbs Energy Minimization - [Eq2] State: Single Thermodynamic System in Project Tutorial_a

Input: System Definition Result: Equilibrium State

Phase/Species	S	Z	Amounts (moles)	log10(Activity)	Concentration	Activity coeff.
aq_gh	30	0	-0.2486			
gas_gh	6	0	0.034400083	2.691e-10		
SO4_OH_Afm	2	0	0.9998257	-5.495e-10		
SO4_OH_Afm	2	0	3.1795439e-005	7.258e-06		
CO3_SO4_Afm	2	0	5.8069077e-007	7.258e-06		
Al(OH) ₃ imc	1	0	-0.4531			
Gibbsite	1	0	0.00014678063	4.454e-06		
Graphite	1	0	-80.2			
Aluminate	1	0	-95.76			
C2AHT5	1	0	-3.031			
C3A6	1	0	-2.925			
C4A113	1	0	-6.762			
C4A112	1	0	9.3068851e-007	-7.511e-07		
C4A112	1	0	-3.266			
C4A111	1	0	-1.566			
ettringite	1	0	5.6310961e-007	7.258e-06		
Aragonite	1	0	-0.1438			
Calcite	1	0	0.0002184429	2.993e-05		
lime	1	0	-11.09			
Portlandite	1	0	-1.459			
Anhydrite	1	0	9.2398775e-006	6.649e-05		
Gypsum	1	0	-0.4691			
hemihydrate	1	0	-0.9392			
Sulphur	1	0	-113.6			

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

SO4_OH_Afm
more stable than
C4AsH12 (Ms12):
for the moment we
skip solid solution
formation

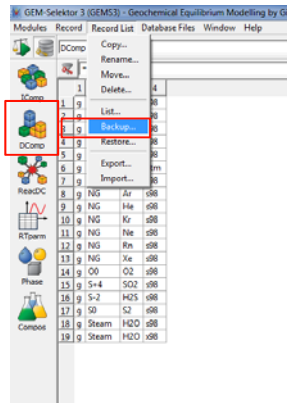
Just C4AsH12
(Ms12) appears.
The other hydration
states are not
introduced



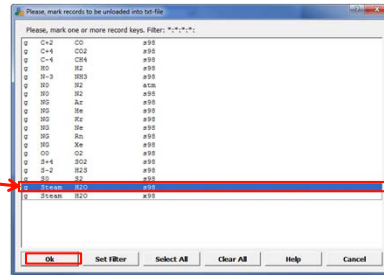
© 2014 Holcim Ltd 18

Introduce water vapor

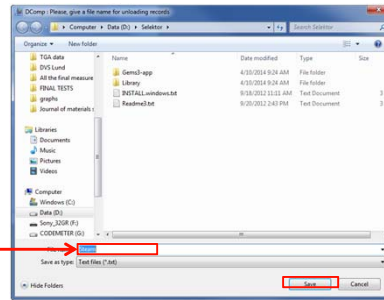
Backup Steam s98



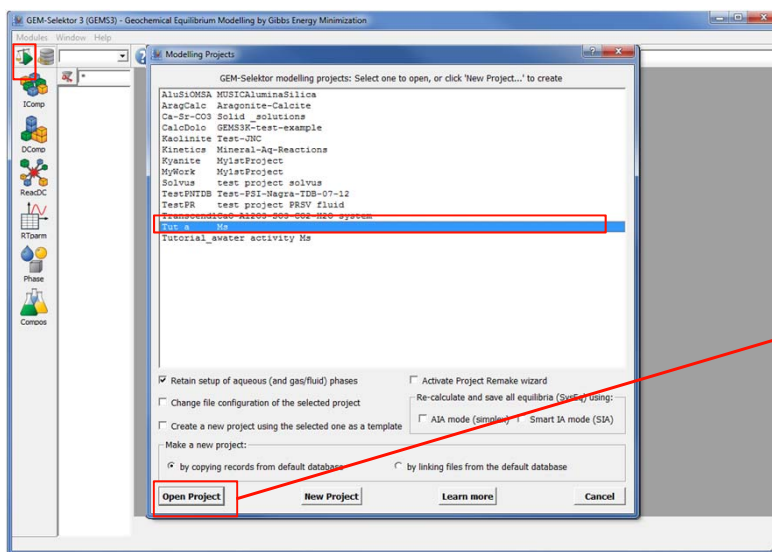
Choose Steam s98



Save as Steam.txt



Introduce water vapor



Open the project

Introduce water vapor

The screenshot shows the GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization interface. The 'Record List' menu is open, and the 'Restore' option is highlighted. A red arrow points from this option to a file selection dialog titled 'DComp: Please, select file with unloaded records'. The dialog shows a list of files in the 'C:\Program Files\GEMS3' directory, with 'Steam.txt' selected. The 'Open' button is highlighted.

Restore Steam.txt into the project database

© 2014 Holcim Ltd 23

Introduce water vapor

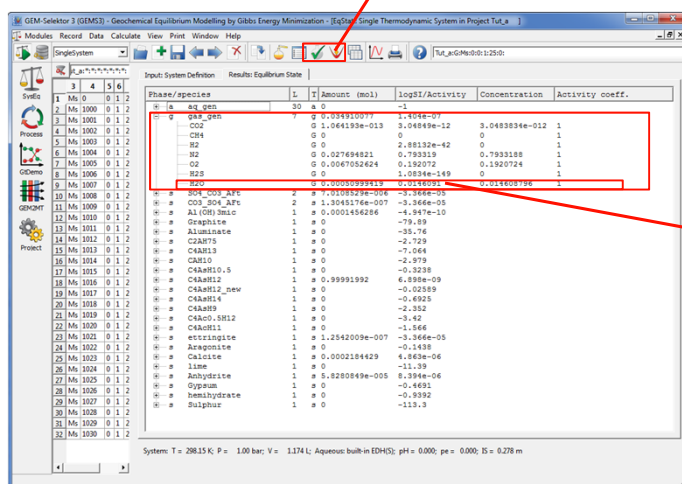
The screenshot shows the GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization interface. The 'Modeling Projects' dialog is open, showing a list of projects. The 'Tutorial_ewater activity 1a' project is selected. The 'Open Project' button is highlighted. A red arrow points from this button to a confirmation dialog titled 'DComp/ReacDC'. The dialog asks: 'g Steam H2O s98 record to be inserted into project database. Action?'. The 'Do it for All' button is highlighted.

Open the project again and accept the insertion of Steam

© 2014 Holcim Ltd 24

Introduce water vapor: checking the equilibrium RH

Calculate equilibrium → H₂O appears as a component of the gas_gen



Phase/species	Amount (mol)	logP/Activity	Concentration	Activity coeff.
gas_gen	30	-1		
H2O	0.0000000000000000	0.014603796	0.0324456	1
CO2	0.004195e-013	3.04849e-12	3.0483834e-012	1
CH4	0	0	0	1
N2	0	2.8132e-42	0	1
O2	0.027494821	0.793319	0.7933189	1
CO	0.0047052424	0.192072	0.1920724	1
H2	0	1.0834e-149	0	1

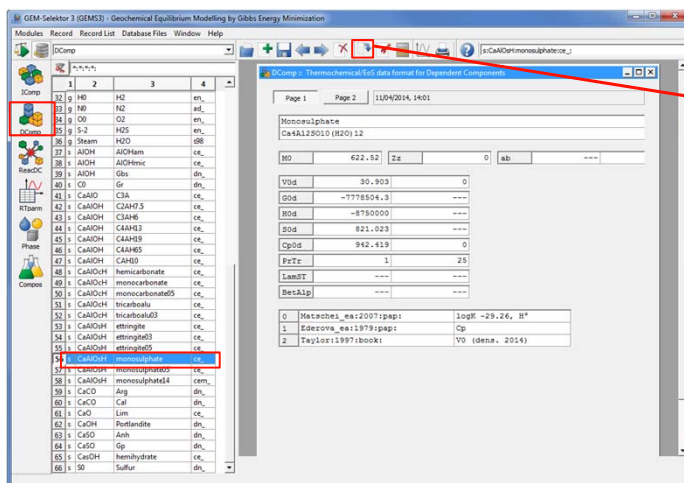
Equilibrium RH of the system can be calculated as follows:

$$RH = \frac{a[\text{H}_2\text{O}]}{0.0324456} \times 100$$

↑
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



Phase/species	Amount (mol)	logP/Activity	Concentration	Activity coeff.
Monosulphate	1	0	0	1
Ms14	0.0000000000000000	0.014603796	0.0324456	1

Clone monosulphate

Introduce Ms14 in DComp

DComp: Please, set a new record key

File Edit View Help

s:CaAlO₉Hmonosulphate14:cm_

Phase state code of Dependent Component (a g f p s l m c x y h)

CaAlO₉H ID of a group to which this Dependent Component belongs

monosulphate14 Name of this Dependent Component (chemical species)

cm_ Thermodynamic data subset (TDS) code (e.g. database ID)

OK Reset From List Help Cancel

GEM-Selektor DComp Setup: s:CaAlO₉Hmonosulphate14:cm_

Step 1 - Defining the Dependent Component (DC) type and the calculation method codes

Select here to which class this Dependent Component belongs

This class code will be copied into Phase definition as default for this DC

0 Dependent Component of a single-component condensed phase

The codes selected below will configure the DComp record data fields, and tell the program how thermodynamic properties of this DC (per mole) will be corrected for T and P of interest.

Select here the codes of methods for temperature T and pressure P corrections

General method code for T (temperature) corrections of thermodynamic properties:

C Calculation on the basis of standard S₀ and Cp₀ integration

Method variant code for EoS T (temperature) corrections of thermodynamic properties:

S Calculation of g⁰T, h⁰T, S⁰T from standard entropy integration

Method code for P (pressure) corrections of thermodynamic properties:

C Pressure correction assuming constant molar volume V⁰

Codes for species-dependent EoS (Equation-of-State) subroutines:

N No fluid model routine

Learn more < Back Next > Cancel

Holcim © 2014 Holcim Ltd 27

Introduce Ms14 in DComp

GEM-Selektor DComp Setup: s:CaAlO₉Hmonosulphate14:cm_

Step 2 - Specific dimensions and settings

Dimensions to change only in special cases

1 Number of sets of coefficients of Cp=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 Cp=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 Vm = f(P, T) vector of coefficients (reserved)

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

J Units of energy (default: J)

3 Units of volume (default: l)

bar Units of pressure (default: b)

C Units of temperature (default: C)

Learn more < Back Next > Cancel

GEM-Selektor DComp Setup: s:CaAlO₉Hmonosulphate14:cm_

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 V06, G06, H06, S06, Cp06 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 Tcrit, then at_Cp or aHkf 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 Cp=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 RTerm tabulator for this DComp record.

Learn more < Back Finish > Cancel

Holcim © 2014 Holcim Ltd 28

Introduce Ms14 in DComp

Introduce Ms14 properties and then calculate

The screenshot shows the DComp software interface. On the left, the 'Monosulphate' phase is defined with the formula Ca4Al2SO10(H2O)14. Below this, a table lists properties: V_0d (33.16), G_0d (-8252870.0), H_0d (-9321762), S_0d (960.854), Cp_0d (1028.53), $PrTr$ (1), $LamST$ (---), and $BetaAlp$ (---). At the bottom, a table shows the calculation steps:

0	Matschei et al 2007: ipap1	cod and h0s adding 2H2O
1	Ms14+2Cs->Ms12+2CsH	Cp calculation
2	Baquerizo et al 2014	Vo

On the right, the 'DComp: Calculation...' window shows the calculated properties: $TClnt$ (0), a_1CpT (1.387), and a_2CpT (0).

Below the screenshot, the equation for Cp is given: $*Cp = a_0 + a_1T + a_2T^2 + a_3T^{0.5}$.



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

© 2014 Holcim Ltd 29

Create the Phase Ms14

Ms14 has to be added as a Phase

We can start cloning monosulphate (C4AsH12)

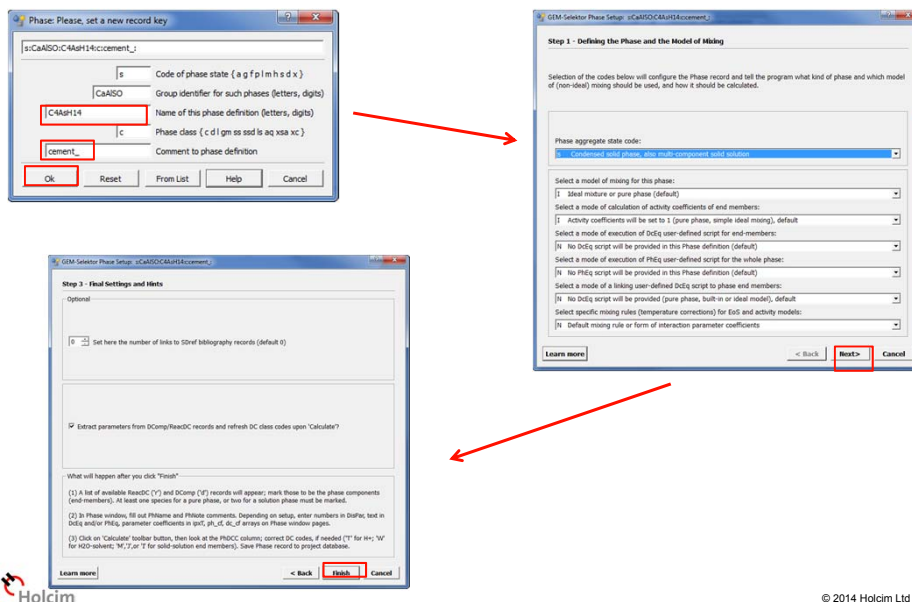
Clone C4AsH12

The screenshot shows the DComp software interface. On the left, a list of phases is shown, with 'C4AsH12' highlighted. On the right, the 'Phase: Definition of thermodynamic phase' window is open, showing the 'Monosulphate' phase with the formula Ca4Al2SO10(H2O)14. The 'Monosulphate' phase is defined with the formula Ca4Al2SO10(H2O)14. The 'Monosulphate' phase is defined with the formula Ca4Al2SO10(H2O)14.



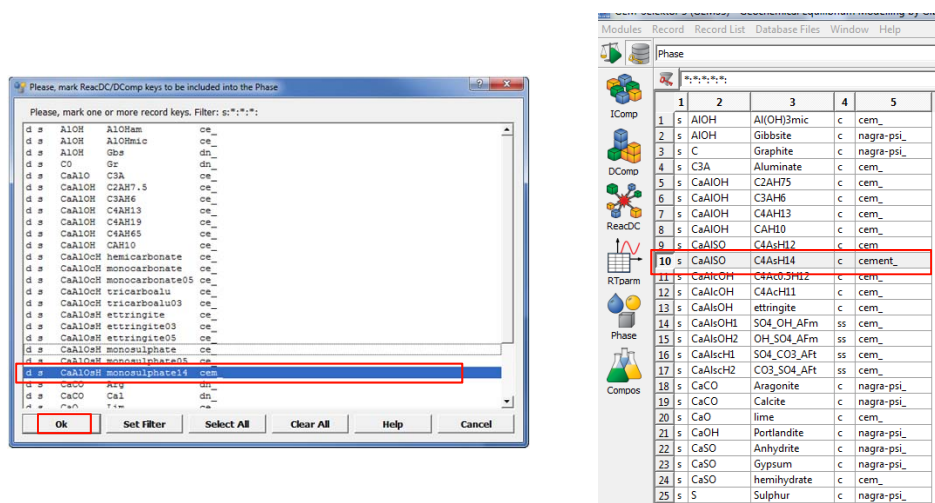
© 2014 Holcim Ltd 30

Create the Phase Ms14



© 2014 Holcim Ltd 31

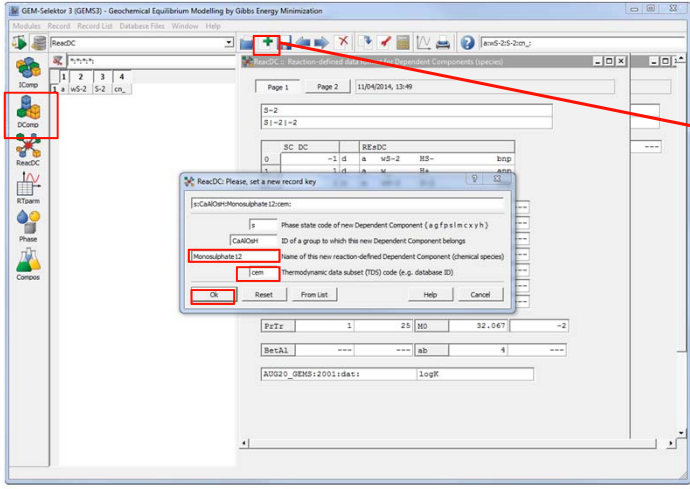
Create the Phase Ms14



© 2014 Holcim Ltd 32

Introduce Ms12: ReacDC

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

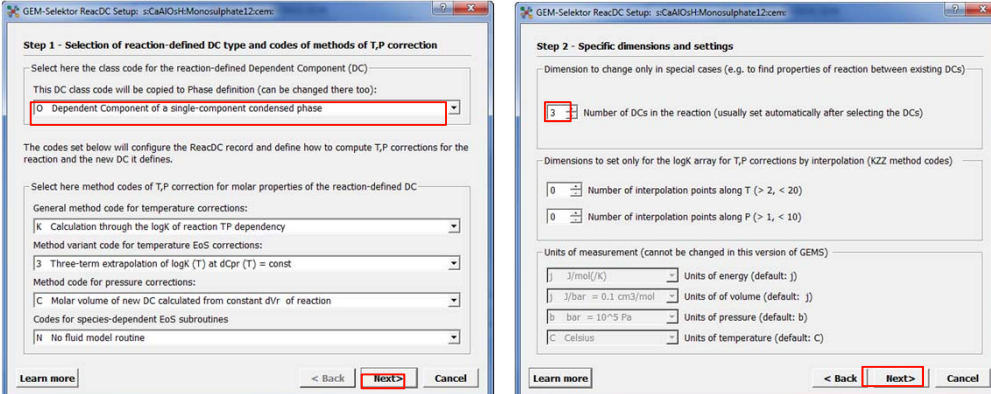


Create a new record

Holcim

© 2014 Holcim Ltd 33

Introduce Ms12: ReacDC

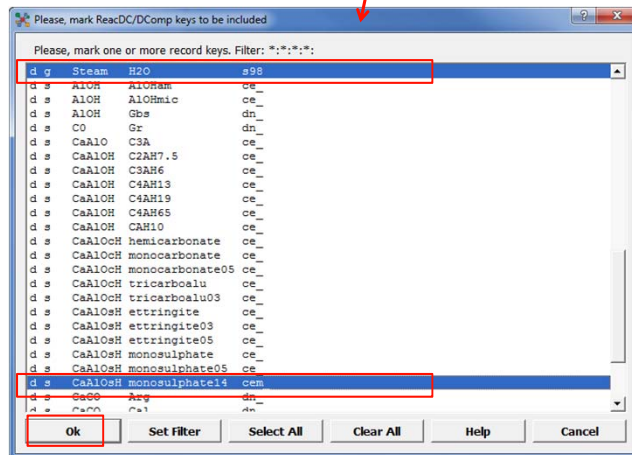


Holcim

© 2014 Holcim Ltd 34

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	REDC
0	2 d g	Steam H2O s98
1	-1 d s	CaAlO2H Monosulphate14 cem
2	1 n s	CaAlO2H 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	---	---	---

FrTr	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



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
Ca4Al2S010 (H2O) 10.5

SC DC	REDC
0	-1 s CaAlO6H Monosulphate12 cem
1	1.5 d g Steam H2O s90
2	1 n CaAlO6H Monosulphate10.5cem

V0r 3715.61 28.155 ---
logKf 0.0088920325 -3.0509989 ---
G0r 17415.23 -7417916.8 ---
H0r 83140 -8311872.7 ---
S0r 220.509 731.192 ---
Cp0r -3 874.282 ---
NiacX --- --- ---

PrTr 1 25 M0 595.497 0

BetAl --- ab --- ---

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

© 2014 Holcim Ltd 37

Introduce Ms9: ReacDC

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

ReacDC: Calculation finished OK (elapsed time: 0.002 s)

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

Monosulphate9
Ca4Al2S010 (H2O) 9

SC DC	REDC
0	-1 s CaAlO6H Monosulphate10.5cem
1	1.5 d g Steam H2O s90
2	1 n CaAlO6H Monosulphate9 cem

V0r 3715.75 28.46 ---
logKf 1.6530224e-005 -4.7817213 ---
G0r 27294.266 -7047598 ---
H0r 102820 -7845452.7 ---
S0r 220.315 703.431 ---
Cp0r -7 807.174 ---
NiacX --- --- ---

PrTr 1 25 M0 568.474 0

BetAl --- ab --- ---

0	Ms10.5(s) -> Ms9(s) + 1.5H2O(g)	---
1	Thermodyn prop	Baquerizo et al (2014)
2		---

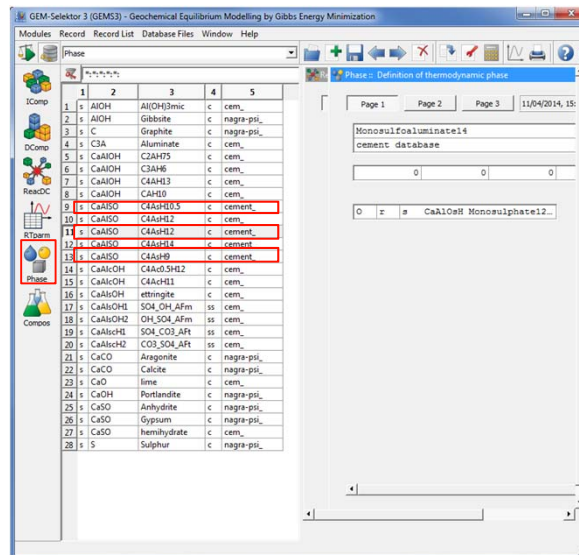
© 2014 Holcim Ltd 38

Introduce Ms12, Ms10.5 and Ms9 as phases

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

Phases to be introduced

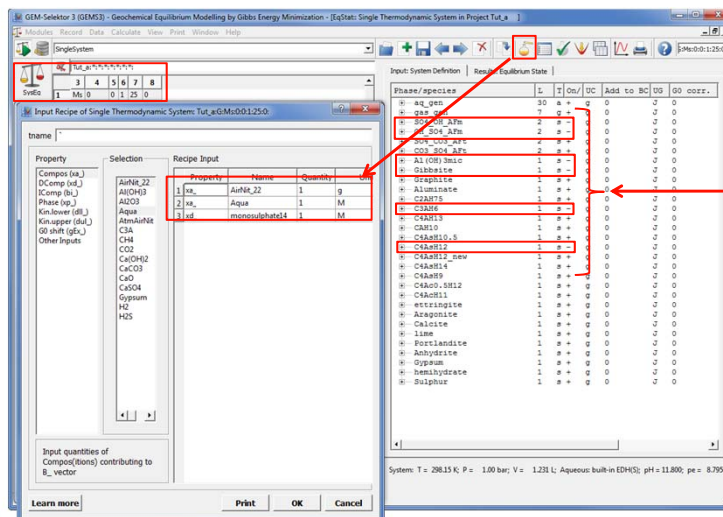
- Ms12
- Ms10.5
- Ms9



- **Modelling the drying behavior of Monosulfoaluminate**

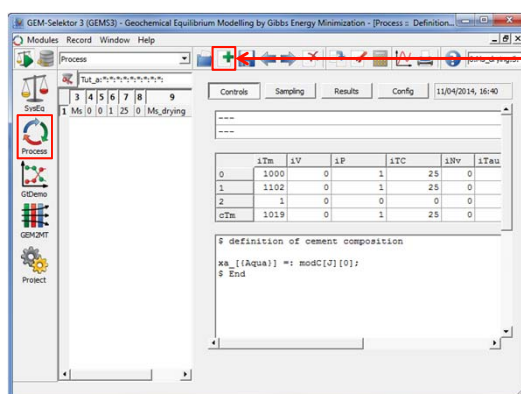
Modelling drying: Process simulation

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

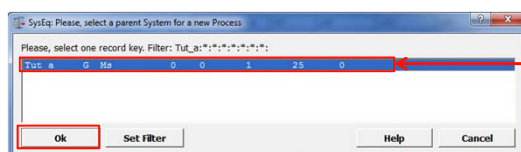


Skip the formation of SO4_OH and OH_SO4 solid solutions, Al(OH)3mic, Gibbsite and C3AH6

Modelling drying: Process simulation

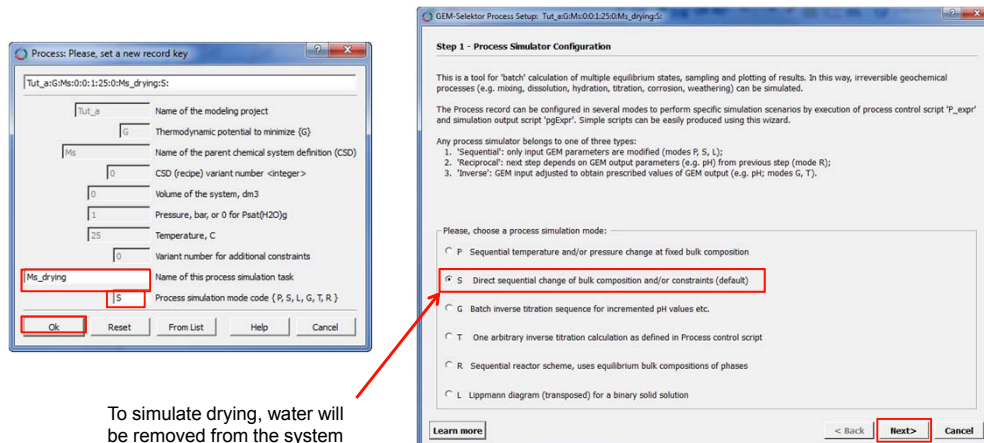


Create a new process



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

Modelling drying: Process simulation



Process: Please, set a new record key

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

Name of the modeling project: Tut_a

Thermodynamic potential to minimize (G): 0

Name of the parent chemical system definition (CSD): Ms

CSD (recipe) variant number <integer>: 0

Volume of the system, dm3: 0

Pressure, bar, or 0 for Psat(120)g: 1

Temperature, C: 25

Variant number for additional constraints: 0

Name of this process simulation task: Ms_drying

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

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

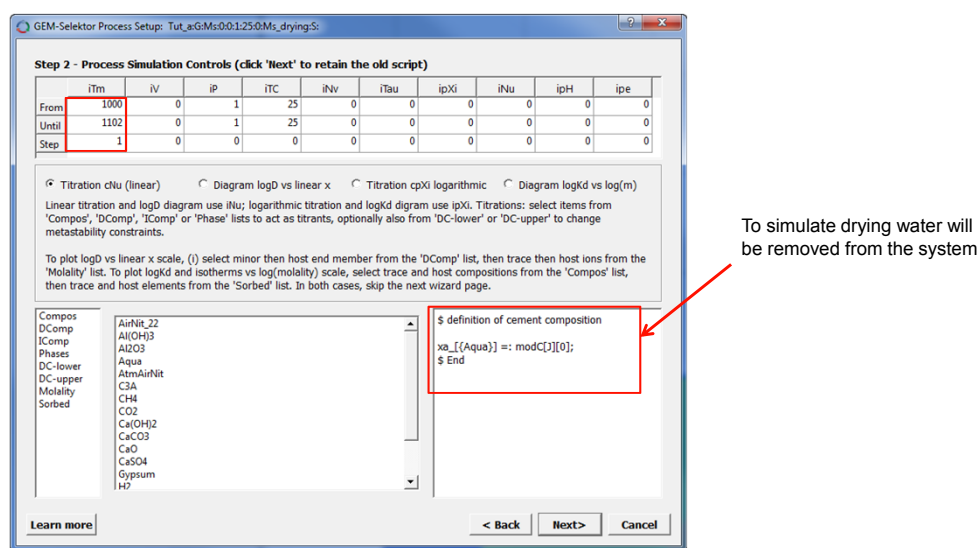
Learn more < Back Next> Cancel

To simulate drying, water will be removed from the system

Holcim

© 2014 Holcim Ltd 43

Modelling drying: Process simulation



GEM-Selector 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, AtmAir/Nit, 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[1][0];
\$ End

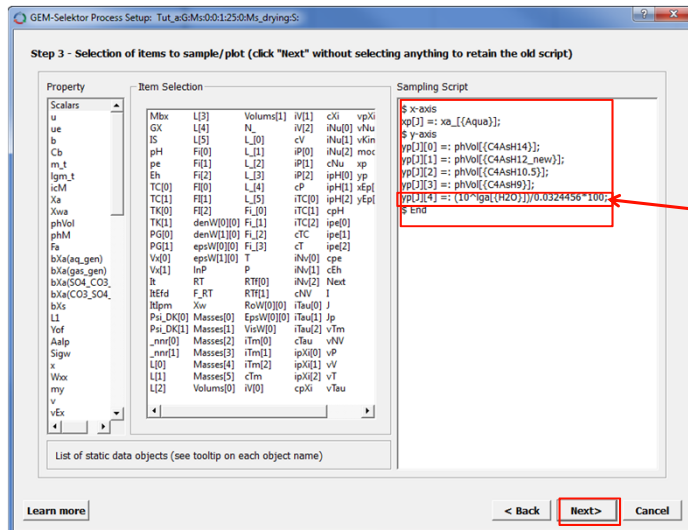
Learn more < Back Next> Cancel

To simulate drying water will be removed from the system

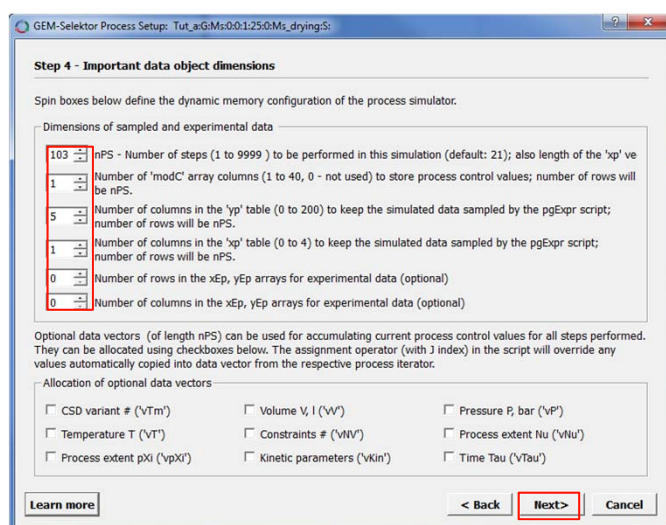
Holcim

© 2014 Holcim Ltd 44

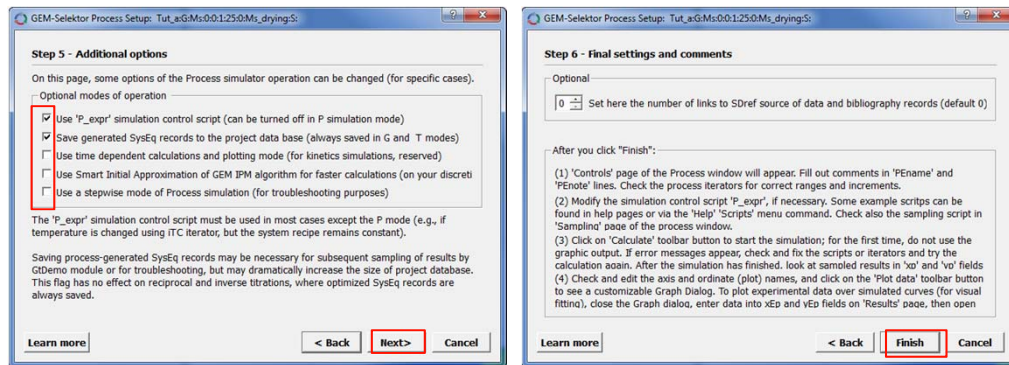
Modelling drying: Process simulation



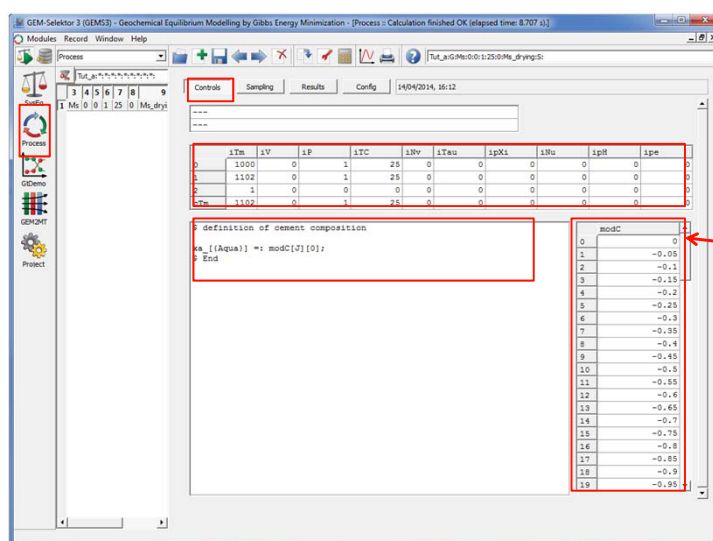
Modelling drying: Process simulation



Modelling drying: Process simulation



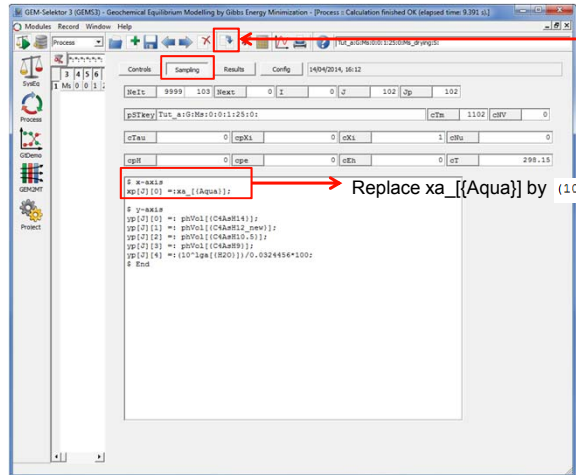
Modelling drying: Process simulation



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

Modelling drying: 2nd Process simulation

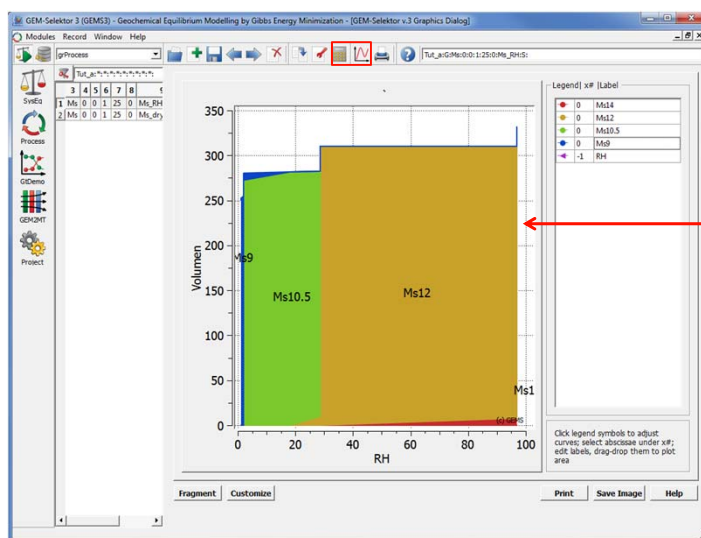
Now we will plot the volume changes as function of RH



Clone the previous process

Replace $xa_{\{Aqua\}}$ by $(10 \cdot \lg\{H_2O\}) / 0.0324456 \cdot 100$;

Modelling drying: 2nd Process simulation



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.



© 2014 Holcim Ltd 53