

Lecture 07

Interaction with the environment



Klaartje De Weerd, NTNU
Barbara Lothenbach, EMPA
Alisa Machner, TUM

Software development/fitting
tools/kinetic:
Dmitrii Kulik
Dan Miron

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Comparing chloride ingress from seawater and NaCl solution in Portland cement mortar

K. De Weerd^{a,*}, B. Lothenbach^{b,c}, M.R. Gierke^a

^aDepartment of Structural Engineering, NTNU, Norway
^bEmpa, Dübendorf, Switzerland

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ABSTRACT

This study investigates whether chloride ingress testing can be done using NaCl solution instead of seawater when assessing the performance of concrete in marine conditions. However, concrete binding, sulfate and chloride additional elements such as sulfate and magnesium, which can change the phase assemblage in the concrete and thereby affect chloride ingress. Hence, concrete prepared with Portland cement was exposed to seawater or NaCl solution with a similar chloride concentration. After 180 days of exposure to seawater, only the outer 1 mm was enriched in sulfate and magnesium, which had with a limited impact on the chloride ingress. In contrast, in the water 10–15 mm both for NaCl and for seawater exposure had a much stronger influence on the chloride ingress. Hence, chloride ingress in marine exposed concrete can be assessed using NaCl solution. To assess the binding in field exposure, the volume of exposure solution needs to be high.

1. Introduction

Reinforced concrete is an important construction material for marine exposed structures such as bridges, docks, harbours and off-shore piles. Due to its ability to withstand the harsh marine environment, however, the service life of reinforced concrete structures can be limited by several deterioration mechanisms. In marine environment, one of the major deterioration mechanisms is chloride induced corrosion of the reinforcement steel. When chlorides reach the reinforcement steel and accumulate to critical concentrations they can initiate corrosion. Hence, to ensure sufficient service life, such concrete used to be designed and constructed with concrete compositions with high chloride ingress resistance, as well as an appropriate concrete cover depth in order to prevent the reinforcement from the damaged concrete [1].

Laboratory testing of concrete compositions for marine applications is generally performed with NaCl solution to assess the marine environment. Commonly used diffusion tests either prescribe exposure to 3% NaCl solution (e.g., [2]), which gives a similar chloride ion concentration as the Atlantic (ASTM C1543 [3]), EN 12390 [4], CEN/TS 12390-1 [5]) or about 1.5 times higher concentration (340 g/L NaCl solution, ASTM C1208 [6] and BS EN 12390-2 [7]). However, seawater contains, in addition to sulfate and chloride, other ions, for example magnesium, sodium, and sulfates, which potentially can influence the chloride ingress [8]. The effect of seawater on the phase assemblage of concrete is complex. The differences in the solubility of the ions and in the solubility of the reaction products results in elemental migration in the concrete near the surface [9–11].

In this study, we investigated whether the presence of ions other than sulfate and chloride in seawater will affect the chloride ingress. The chloride ingress by NaCl diffusion in Portland cement mortars exposed to seawater is compared with ingress in mortars exposed to NaCl solution with a similar chloride concentration. Selected samples were exposed to seawater and NaCl solution 7 days after casting. Elemental profiles were determined after 25, 50 and 180 days of exposure at 20 °C.

2. Experimental

2.1. Materials

Mortars with ordinary Portland cement (OPC) type CEM I 42.5 R according to EN197-1 [12] with 6% silica fume (SF) were investigated. The fine composition of the mortars is given in Table 1.

The chemical composition of the different mortars is given in Table 2. Table 2 gives the mineral composition of the Portland cement determined by XRD (Brenntag, about 90.2% of the silica fume is SiO₂ amorphous). The PC mortar was prepared with a water-to-binder mass ratio of 0.45 and the sand-to-binder mass ratio of 0.53. A polycarboxylate based superplasticizer (SP) was included to obtain good

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Chloride resistance of concrete and its binding capacity – Comparison between experimental results and thermodynamic modeling

Roman Loeiser^a, Barbara Lothenbach, Andreas Leemann, Martin Tuchschnig

^aEmpa, Swiss Federal Laboratories for Materials Testing and Research, Switzerland

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Keywords:
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Chloride binding
Thermodynamic modeling
Moisture adsorption

ABSTRACT

The chloride resistance of concrete structures produced with different binders and water-to-binder ratios is determined by three different methods (natural chloride diffusion, accelerated chloride migration and conductivity measurement). The influence of pore structure and type of binder are evaluated and related to porosity. The effect of chloride binding on chloride resistance is assessed by thermodynamic modeling and compared with chloride content measured with acid and water extraction.

Chloride resistance depends on the type of binder and on water-to-binder ratio. Chloride content measurements and thermodynamic modeling both show that chloride binding is strongly related to the hydration degree of the cement and of the mineral admixtures. However, the decisive parameter for chloride resistance is not the water to binder ratio but the permeability of the concrete. Chloride binding is less important, if the concrete is more permeable.

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1. Introduction

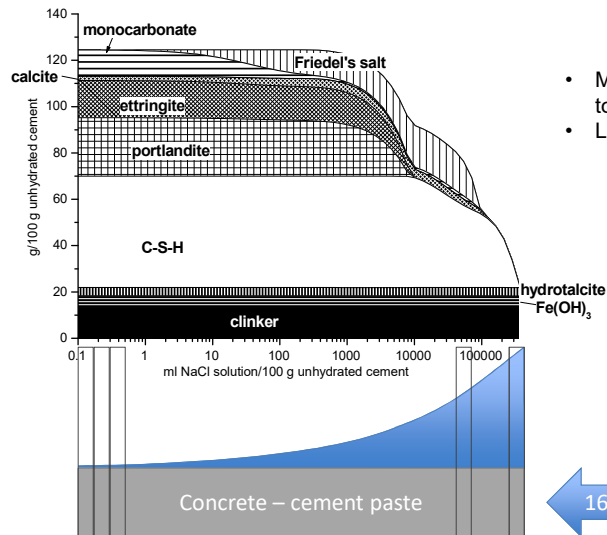
Resistance of concrete to chloride ingress is a key property for the durability of reinforced concrete structures exposed to the sea water or sea water. If chloride penetrates into concrete, it can cause fast and severe corrosion of the reinforcement [1] which reduces the cross section of the reinforcement and thus leads to the loss of its load carrying capacity. Chloride-induced corrosion of the reinforcement is one of the main causes of structural concrete deterioration and therefore responsible for a large share of the cost of the rehabilitation of concrete structures [2]. The thickness of concrete cover over the reinforcement and the permeability of the concrete are used to control the ingress of chloride to prevent corrosion in reinforced concrete structures.

For this reason, chloride penetration into concrete has been investigated for many years. It is known that concrete has the ability to bind chlorides, dependent on its chemical composition. Therefore, chloride binding capacity can be affected by chloride binding as well as bound to cement hydration products in the form of Friedel's salt (Ca₂Cl₂·F₂·H₂O) or sulfate salts (Ca₂Cl₂·SO₄·H₂O) [3–5]. In only "free" chloride ions in the pore solution can move, which both tend to reduce the amount of bound chlorides. Therefore, non-steady-state migration tests with strong external electric field and a short test duration than non-steady-state diffusion tests, which both tend to reduce the amount of bound chlorides. Therefore, non-steady-state migration tests with strong external electric field and a short test duration than non-steady-state diffusion tests, which both tend to reduce the amount of bound chlorides. Therefore, non-steady-state migration tests with strong external electric field and a short test duration than non-steady-state diffusion tests, which both tend to reduce the amount of bound chlorides.

The aim of this study is to investigate the influence of permeability and chloride binding on chloride resistance of concrete by combining experimental techniques with thermodynamic modeling.

Simple modelling approach

Loser ea 2010, CCC 32



- Monocarbonate transforms to Friedel's salt
- Leaching at surface

165 g/L NaCl

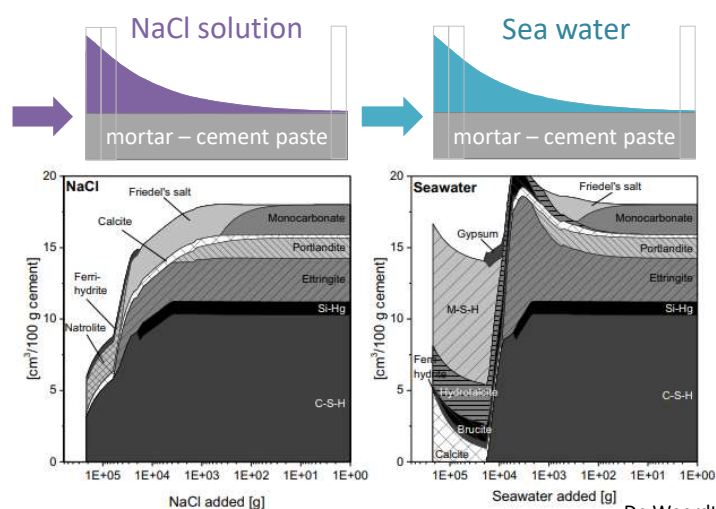
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GOAL:

Predict phase changes when adding an increasing amount of ..



De Weerd et al 2010, CCR

Fig. 10. Predicted volume of the phases in the PC paste upon exposure to increasing amounts of NaCl solution (left) or seawater (right) in [cm³/100 g cement].

Learning goals

GEMS-skills:

- Building a SysEq file from scratch
- Editing a Proces file
- Insert predefined compositions (OPC)

Content

Example: calculate the phase changes in PC paste exposed to NaCl solution

1. Create Single System – SysEq ☺
2. Make predefined composition of PC
3. Make Process

Task: calculate the phase changes in PC paste exposed to sea water

Content

Example: calculate the phase changes in PC paste exposed to NaCl solution

1. Create Single System – SysEq ☺
2. Make predefined composition of PC
3. Make Process

Task: calculate the phase changes in PC paste exposed to sea water

Modelling Projects

GEM-Selektor modelling projects: Select one to open, or click 'New Project...' to create

AluSiOMSA MUSICALuminaSilica
AragCalc Aragonite-Calcite
BermanMSS TestsMultiSiteSolidSolutions
CASHNK CASHNK-SS-modelling-2
Ca-Sr-CO3 Solid_solutions
CalDo1Co12GEM2MT-test
CalDo1Co12GEM3K-test-example
CarbSea CarbonatesAndSeawater

☒ Retain setup of aqueous (and gas/fluid) phase: Re-calculate and save all equilibria (SysEq) using

☐ Change file configuration of the selected proje ☐ GEMStest export ☒ Without speciation

☐ Activate Project Remake wizard ☐ Recalculate all eq ☐ Dump results into a

☐ Create a new project using the selected one as Use a mode of GEM initial approximation (gu

☒ Automatic cold-st ☐ Smart warm-start (p

Make a new project:

☒ by copying records from default databases ☐ by linking files from the default database

Create a new file

Project: Enter a new record key, please

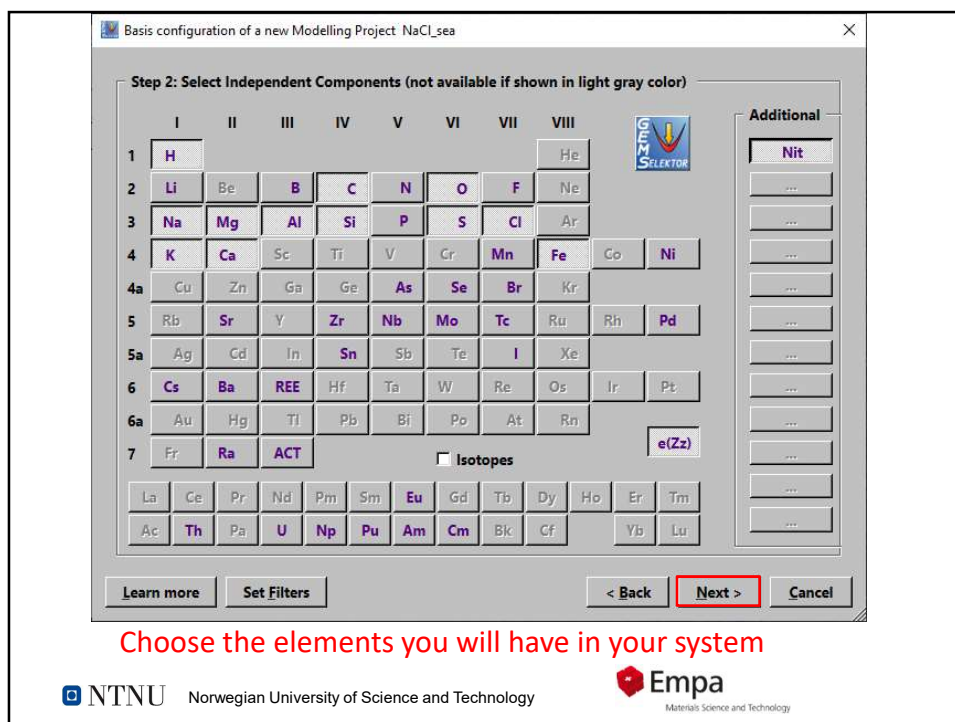
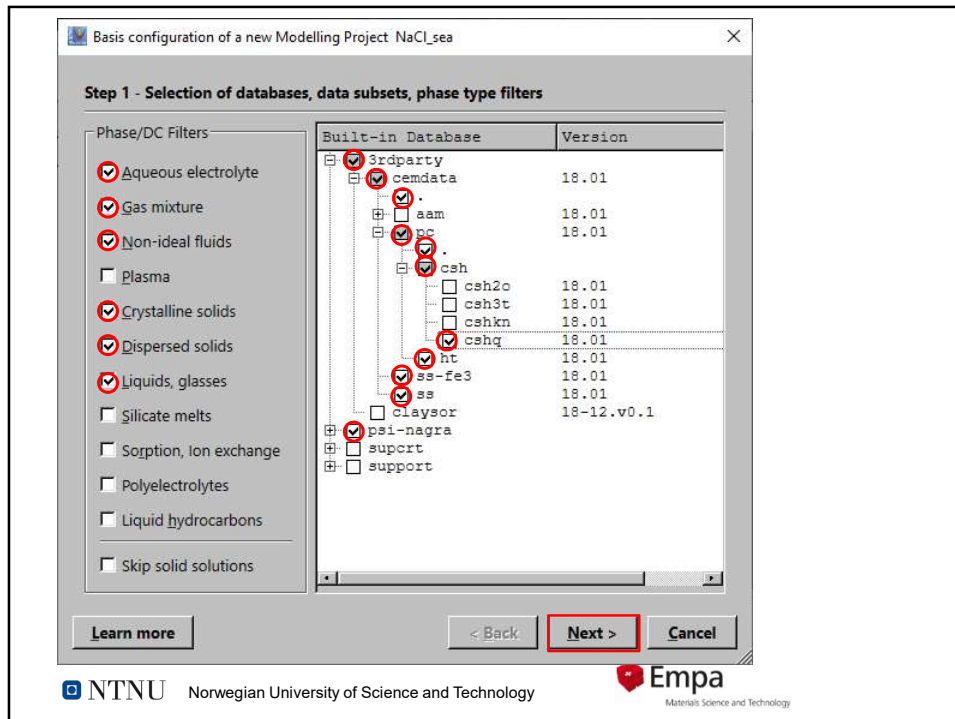
NaCl_sea:My1stProject:

NaCl_sea Name of the modeling project

course Comment to the project definition

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Setup of aqueous and gas phases in project: NaCl_sea

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

1

- ☐ 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, Z
- ☐ 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

2

b_gamma(1,298) value: 0.064

b_gamma(P,T) mode: NaCl

Common a0 value: 3.72

Gamma (neutral species): Calculate as b_gamma

Gamma (water solvent): From osmotic coefficient

Molality conversion: Applied to all species

4

3

OK Cancel Check Learn more

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SysEq: Please, enter a new record key:

NaCl_sea:G:NaCl-PC:0:0:1:20:0:

Name of the modeling project: NaCl_sea

Thermodynamic potential to minimize {G GV}: G

Name of the chemical system definition (CSD): NaCl-PC

CSD (recipe) variant number <integer>: 0

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

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

Temperature, C (>= 0): 20

Variant number for additional constraints: 0

OK Reset From List Help Cancel

Name your single file

Temperature

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Input Recipe of Single Thermodynamic System: NaCl_sea:G:NaCl-PC:0:0:1:20:0:

Title:

Comment:

Property

Compos (xa_)

DComp (xd_)

IComp (bi_)

Phase (xp_)

Kin.lower (dll_)

Kin.upper (dul_)

G0 shift (gEx_)

Other Inputs

Selection

NaCl

NaClO4

NaOH

O2

PC

SO3

SWsaltSimp

SiO2

Input quantities of Compos(itions) contributing to B_ vector

	Property	Name	Quantity	Units
1	xa_	Aqua	50	g
2	xa_	NaCl	0.001	M
3	xa_	O2	0.1	g
4	xa_	PC	80	g

We make a dummy system; we will add a new PC to the database

Learn more

Print

OK

Cancel

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermod...]

SingleSystem

Input: System Definition

Results: Equilibrium State

SysEq

Process

GtDemo

GEM2MT

UnSpace

Project

Phase/species	L	T	On	UC	Add to BC	UG	G0 corr.	U
Anhydrite	1	s	+	g	0	J	0	
Gypsum	1	s	+	g	0	J	0	
Hemihydrate	1	s	+	g	0	J	0	
Chaunite	1	s	+	g	0	J	0	
Iron	1	s	+	g	0	J	0	
Fe-carbonate	1	s	+	g	0	J	0	
Siderite	1	s	+	g	0	J	0	
Hematite	1	s	+	g	0	J	0	
Magnetite	1	s	+	g	0	J	0	
Ferrihydrite-am	1	s	+	g	0	J	0	
Ferrihydrite-mc	1	s	+	g	0	J	0	
Goethite	1	s	+	g	0	J	0	
Pyrite	1	s	+	g	0	J	0	
Troilite	1	s	+	g	0	J	0	
Melanterite	1	s	+	g	0	J	0	
arcanite	1	s	+	g	0	J	0	
syngenite	1	s	+	g	0	J	0	
K-oxide	1	s	+	g	0	J	0	
OH-hydroxalcalite	1	s	+	g	0	J	0	
Magnesite	1	s	+	g	0	J	0	
Brucite	1	s	+	g	0	J	0	
chenardite	1	s	+	g	0	J	0	
Natroilite	1	s	+	g	0	J	0	
ZeoliteX	1	s	+	g	0	J	0	
ZeoliteY	1	s	+	g	0	J	0	
Na-oxide	1	s	+	g	0	J	0	
Sulphur	1	s	+	g	0	J	0	
Quartz	1	s	+	g	0	J	0	
SiO2-amorph	1	s	+	g	0	J	0	

Title:

Comment:

Block phases you want to prevent from forming

Check the system

NaCl_sea:G:NaCl-PC:0:0:1:20:0:

Missing ICs: ☒ Nit

CONFLICT WARNING!

Mole amounts of some Independent Components (IC) are missing in the calculated bulk composition vector (B_i) ($P_{a,DB}$):

POSSIBLE ACTIONS:

- * EXCLUDE ALL these ICs together with DCs that contain them and some Phases made of those DCs;
- * RETAIN ALL missing ICs by inserting a default mole amount (below) into b_i vector cells;
- * CHECK some boxes to keep these ICs in the system by inserting a default mole amount into b_i ; unchecked ICs will be turned off together with all DCs that contain them.

Buttons: EXCLUDE ALL, RETAIN ALL, CHECK/Qk

Default amount, mol (editable): 1e-09

Buttons: Learn more..., Cancel

Title: Please, enter here a title explaining what this chemical system is

Comment: Please, enter here a comment about the purpose of this system defini

fname: Comment line for full identification of this CSD

15

Calculate equilibrium

Converged at $DK=9.99999e-06$

GEM IPM calculation (run time: 0.016 s).

System: NaCl_sea:G:NaCl-PC:0:0:1:20:0:

Iter: 1: 5: 259

Gaseous: 0.10048

Aqueous: 20.9414

Liquid: 0

Solid: 109.117

pH: 13.4911

pe: 7.65407

IS: 0.346178

Buttons: Accept, Dismiss

Title: Please, enter here a title explaining what this chemical system is

Comment: Please, enter here a comment about the purpose of this system defini

Accept to see the results

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Safe file

You have created a single file 😊

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Content

Example: calculate the phase changes in PC paste exposed to NaCl solution

1. Create Single System – SysEq 😊
2. Make predefined composition of PC
3. Make Process

Task: calculate the phase changes in PC paste exposed to sea water

GEM-Selektor (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Compos : Predefined composition objects (PCO)

Page 1 Settings 16/05/2023, 13:03

PC with limestone
Composition from Lothenbach_ea_b:2008:pap:

0.0600843 0 0 0 0

symIC PCO symIC CIO1

0 Al e 0.05907926 0 Al e M

1 C e 0.003631367 1 C e M

2 Ca e 0.7004179 2 Ca e M

3 Fe e 0.02463493 3 Fe e M

4 K e 0.01017973 4 K e M

5 Mg e 0.02745139 5 Mg e M

6 Na e 0.008330652 6 Na e M

7 O o 1.336 7 O o M

8 S e 0.01758069 8 S e M

1 Open the database

2 Select Compos

3 Select the standard PC in GEMS

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Compos : Predefined composition objects (PCO)

Page 1 Settings 16/05/2023, 13:03

PC with limestone
Composition from Lothenbach_ea_b:2008:pap:

0 0

symIC CIO1

0 Al e M

1 C e M

2 Ca e M

3 Fe e M

4 K e M

5 Mg e M

6 Na e 0.008330652

7 O o 1.336

8 S e 0.01758069 8 S e M

Clone 1

Compos: Please, set a new record key

PC:MIN:Portland_cement_

PC_2

MIN

Portland_cement_

Ok Reset From List Help Cancel

Name the substance
Add comment

GEM-Selektor Compos Setup: PC_2-MIN-Portland_cement_

Step 1 - Predefined Composition Object (PCO) configuration

Compos record contains data for a Predefined Composition Object (PCO), which describes a salt, the air, a mineral, a rock, a natural water, etc., treated as a single named entity in the chemical system recipe.

PCO can be configured according to the source data: as IC or DC amounts/concentrations; as user-defined formula (UDF) units; or as a large UDF entered into a text field.

Upon re-calculation, all given quantities will be added into a single IC mole amounts PCO vector, optionally scaled to a given total mass (in kg) or total number of moles.

PCO input data configuration:

☒ Use amounts of Independent Components (IComp) in this PCO definition (default)?

☐ Use formulae of Dependent Components (from DComp/ReacDC records) in this PCO?

9 Set number of user-defined formula units for this PCO definition (0 by default)

Optional: Input user-defined formula (UDF) text

☐ Use a user-defined formula text input field for this PCO definition?

M moles Select units of measurement for this UDF quantity (default: M)

0 Enter here the UDF quantity or amount in selected units (default: 1)

Learn more < Back **Next>** Cancel

Step 2 - Additional settings and next actions

Optional

8 Set here the number of links to SDref bibliography records (default 0)

☐ Use a vector of data uncertainties in this PCO definition

What will happen after you click "Finish"

- (1) For a PCO definition using IComp amounts, a list of available IComp records will be shown, asking you to mark the desired ones.
- (2) In a PCO definition using DC formulae, a list of available ReacDC/DComp records will be shown, asking you to mark the desired ones.
- (3) Page 1 of the 'Compos' window appears. Fill out Bcname field and (optionally) Bcname lines. Then enter data and formulae wherever needed, check units of amount/concentration.
- (4) Click on 'Calculate' toolbar button to compute the PCO vector. Check or enter the normalization values in MasVol[0] and MasVol[6] fields and calculate again, if needed. Setting both fields to zero disables the normalization of PCO to the total mass or total amount of moles, respectively.

Learn more < Back **Finish** Cancel

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Please, mark IComp keys for PCO definition

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

Al	e	Aluminum
C	e	Carbon
Ca	e	Calcium
Cl	e	Chlorine
Fe	e	Iron
H	h	Hydrogen
K	e	Potassium
Mg	e	Magnesium
Na	e	Sodium
Nit	a	Nitrogen atm
O	o	Oxygen
S	e	Sulfur
Si	e	Silicon
Zz	z	Electric_charge

Ok Set Filter Select All Clear All Help Cancel

Choose the elements for PC

GEM-Selektor 3 (GEM53) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Compos

3 Calculate the composition

4 Save

Compos: Remake of the new record finished OK. It is recommended to re-calculate the...

Page 1 Settings 16/05/2023, 13:03

+ - + - - M 10 0 9 0 10 0

	formU	AUol	CA
0	CaO	g	61.6
1	SiO2	g	19.6
2	Al2O3	g	4.5
3	Fe2O3	g	3.5
4	MgO	g	1
5	K2O	g	1
6	Na2O	g	0.5
7	CO2	g	2.4
8	SO3	g	2.5

2

61.6
19.6
4.5
3.5
1
1
0.5
2.4
2.5

Add the composition in g/100g for the different oxides.

CA [0.0] : Quantity/concentration of user-defined formula units C(AC)

GEM-Selektor 3 (GEM53) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Compos

Compos: Calculation finished OK (elapsed time: 0 s).

Page 1 Settings 16/05/2023, 13:03

PC with limestone

Composition used at GEMS course

0.0600843 0

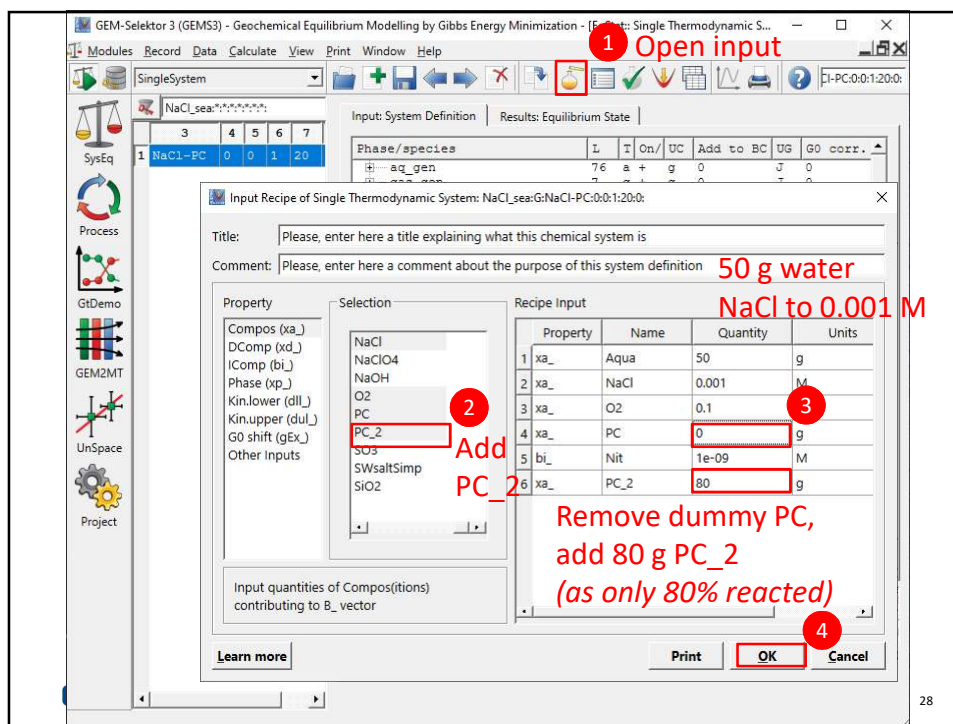
Add description here

	symIC	PCO		symIC	CicI		
0	Al	e	0.05490237	0	Al	e	M
1	C	e	0.03391936	1	C	e	M
2	Ca	e	0.6832454	2	Ca	e	M
3	Fe	e	0.02726523	3	Fe	e	M
4	K	e	0.01320631	4	K	e	M
5	Mg	e	0.01543233	5	Mg	e	M
6	Na	e	0.01003551	6	Na	e	M
7	O	o	1.36545	7	O	o	M
8	S	e	0.01942135	8	S	e	M

You created a new PC 😊

Molar composition cement [mol/100g]

BCnote: Input comment to BCname (optional)



GEM-Selektor 3 (GEM53) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic S...

Modules Record Data Calculate View Print Window Help

SingleSystem

NaCl_sea:*****

Input: System Definition Results: Equilibrium State

3 4 5 6 7

1 NaCl-PC 0 0 1 20

Phase/species L T On/ UC Add to BC US G0 corr.

aq_gen 76 a + g 0 J 0

g 7 g + g 0 J 0

C3 (AF) SO.84H 2 s 0.03216066 -2.278e-08

CSHQ 6 s 0.3534916 -1.09e-08

ettringite-AlFe 2 s 0 -0.08293

ettringite-FeAl 2 s 0 -0.08293

monosulph-AlFe 2 s 0 -1

monosulph-FeAl 2 s 0 -1

straetlingite 2 s 0 -2.908

ettringite 2 s 0 -0.07466

SO4 OH AFm 2 s 0 -1

OH SO4 AFm 2 s 0 -1

SO4 CO3 AFt 2 s 0.02899997 -1.56e-09

CO3 SO4 AFt 2 s 3.686141e-07 -1.56e-09

hydrotalc-pyro 2 s 0 -8.642

MSH 2 s 0 -3.711

Al(OH)3am 1 s 0 -4.064

Al(OH)3mic 1 s 0 -3.201

Gibbsite 1 s 0 -2.678

Kaolinite 1 s 0 -15.29

Graphite 1 s 0 -83.74

Mayenite 1 s 0 -92.94

Belite 1 s 0 -1.945

Aluminate 1 s 0 -38.95

Alite 1 s 0 -14.21

Ferrite 1 s 0 -37.49

C 1 s 0 -13.03

Converged at DK=9.99999e-06

GEM IPM calculation (run time: 0.01 s).

100%

System:

NaCl_sea:G:NaCl-PC:0:0:1:20:0:

Iter 1: 5: 150

Gaseous 0.100455

Aqueous 21.7947

Liquid 0

Solid 108.263

pH 13.5908

pe 7.5551

IS 0.429885

Accept Dismiss

explaining what this chemical system :
about the purpose of this system de:
Aqueous: built-in EDH(H); pH = 0.000; pe = 0.000

29

GEM-Selektor 3 (GEM53) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic S...

Modules Record Data Calculate View Print Window Help

SingleSystem

NaCl_sea:*****

Input: System Definition Results: Equilibrium State

3 4 5 6 7

1 NaCl-PC 0 0 1 20

Phase/species L T Amount (mol) LogSI/Activity

aq_gen 76 a 1.200042 -1.569e-09

gas_gen 7 g 0.003172179 -8.58e-10

C3 (AF) SO.84H 2 s 0.03216066 -2.278e-08

CSHQ 6 s 0.3534916 -1.09e-08

ettringite-AlFe 2 s 0 -0.08293

ettringite-FeAl 2 s 0 -0.08293

monosulph-AlFe 2 s 0 -1

monosulph-FeAl 2 s 0 -1

straetlingite 2 s 0 -2.908

ettringite 2 s 0 -0.07466

SO4 OH AFm 2 s 0 -1

OH SO4 AFm 2 s 0 -1

SO4 CO3 AFt 2 s 0.02899997 -1.56e-09

CO3 SO4 AFt 2 s 3.686141e-07 -1.56e-09

hydrotalc-pyro 2 s 0 -8.642

MSH 2 s 0 -3.711

Al(OH)3am 1 s 0 -4.064

Al(OH)3mic 1 s 0 -3.201

Gibbsite 1 s 0 -2.678

Kaolinite 1 s 0 -15.29

Graphite 1 s 0 -83.74

Mayenite 1 s 0 -92.94

Belite 1 s 0 -1.945

Aluminate 1 s 0 -38.95

Alite 1 s 0 -14.21

Ferrite 1 s 0 -37.49

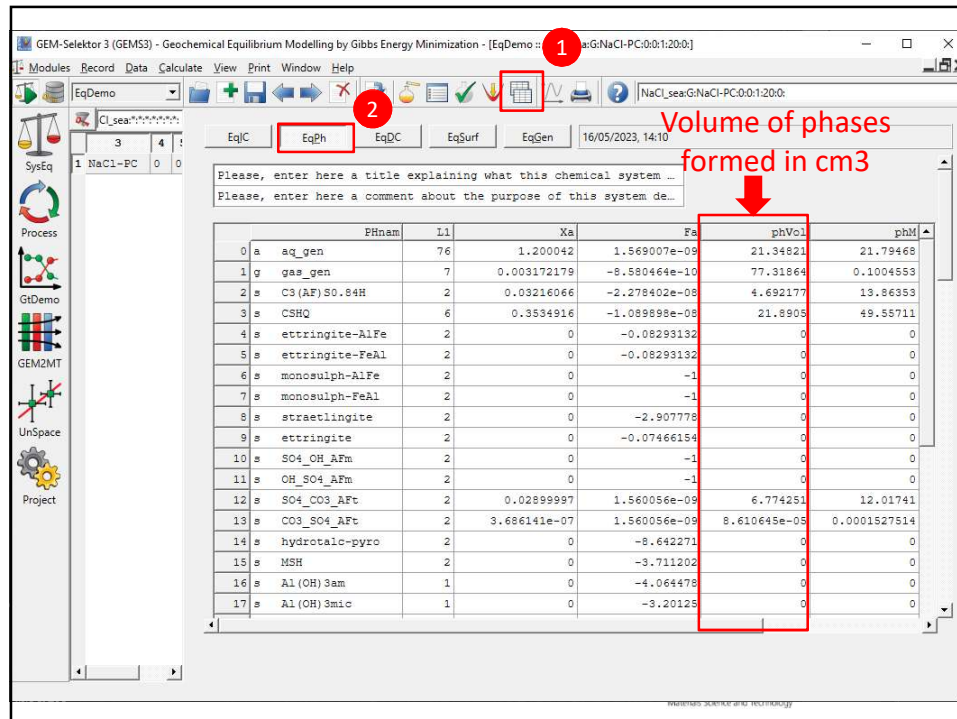
C 1 s 0 -13.03

Title: Please, enter here a title explaining what this chemical system :

Comment: Please, enter here a comment about the purpose of this system de:

System: T = 293.15 K; P = 1.00 bar; V = 0.1466 L; Aqueous: built-in EDH(H); pH = 13.591; pe = 7.

30

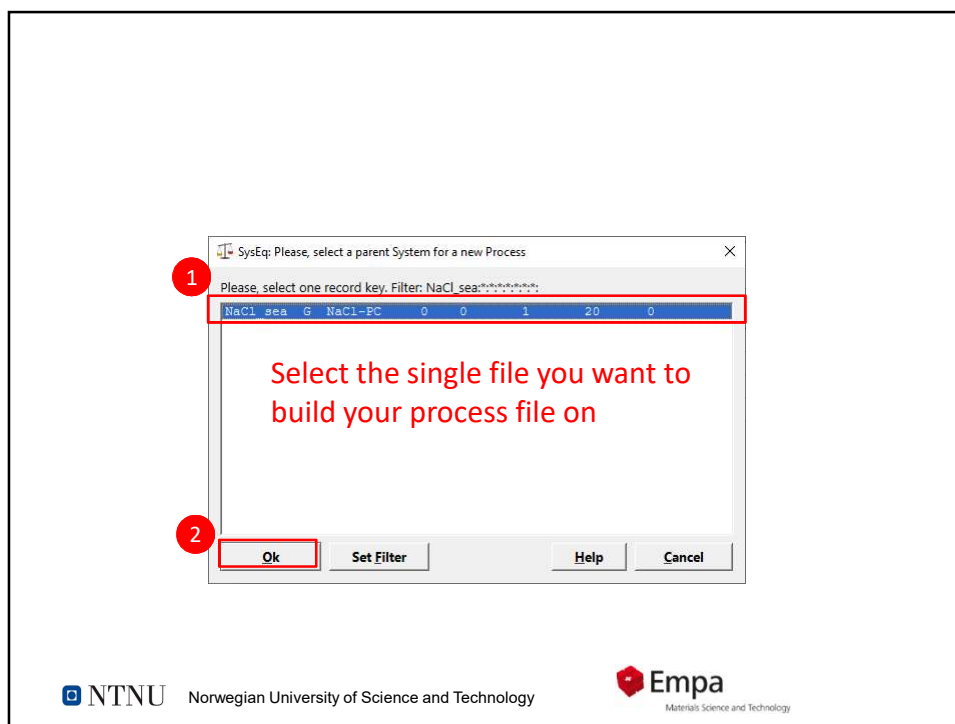
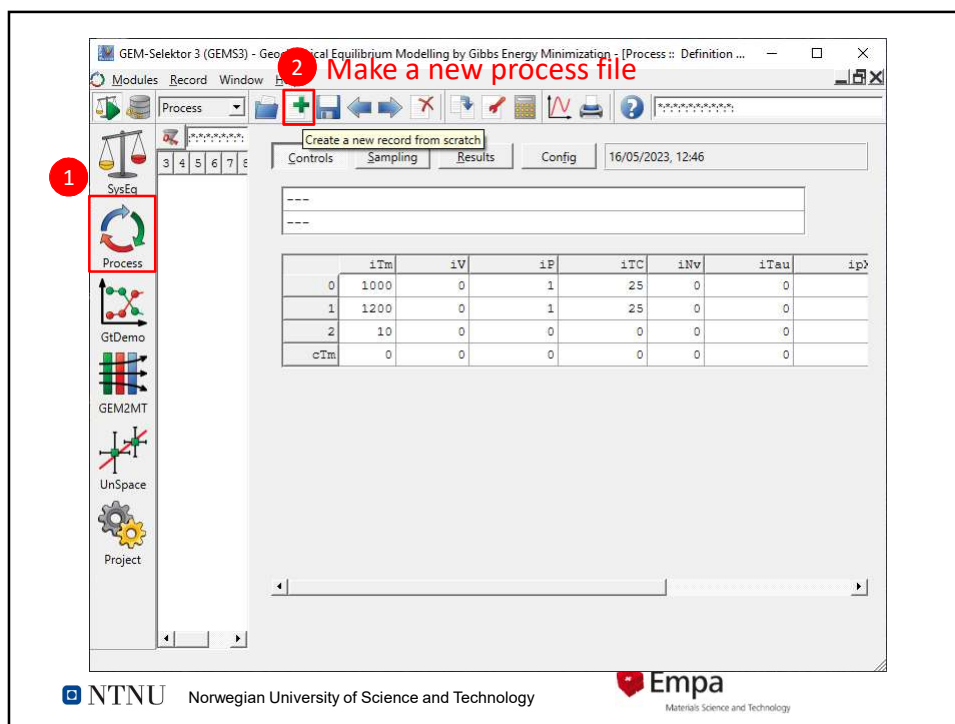


Content

Example: calculate the phase changes in PC paste exposed to NaCl solution

1. Create Single System – SysEq ☺
2. Make predefined composition of PC
3. Make Process

Task: calculate the phase changes in PC paste exposed to sea water



Process: Please, set a new record key

NaCl_sea:G:NaCl-PC:0:1:20:0:NaCl:S

NaCl_sea Name of the modeling project

G Thermodynamic potential to minimize (G)

NaCl-PC 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

20 Temperature, C

0 Variant number for additional constraints

NaCl Name of this process simulation task

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

Ok Reset From List Help Cancel

Name your process file
S → sequential changes

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GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:1:20:0:NaCl: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 outputs (e.g. composition of phases) from the 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.

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

☐ R - Single flow-through reactor (SFTR) simulation using equilibrium compositions of phases

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

Learn more

< Back Next> Cancel

We are going to make sequential changes in the composition

GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl: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	1200	0	1	25	0	0	0	0	0	0
Step	10	0	0	0	0	0	0	0	0	0

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

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

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

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

K2CO3
K2O
K2SO4
KCl
KOH
Mg(OH)2
Mg3Si2O5(OH)4
MgCO3
MgCl2
MgO
MgSO4
Na2CO3
Na2O
Na2SO4
NaCl
NaClO4
NaOH
O2
PC
PC_2
SO3
SWsaltSimp
SiO2

modC[] := cNu;
xa_[(Aqua)] := cNu * 1;
xa_[(NaCl)] := cNu * 1;

We will change the coding later

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

GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S

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

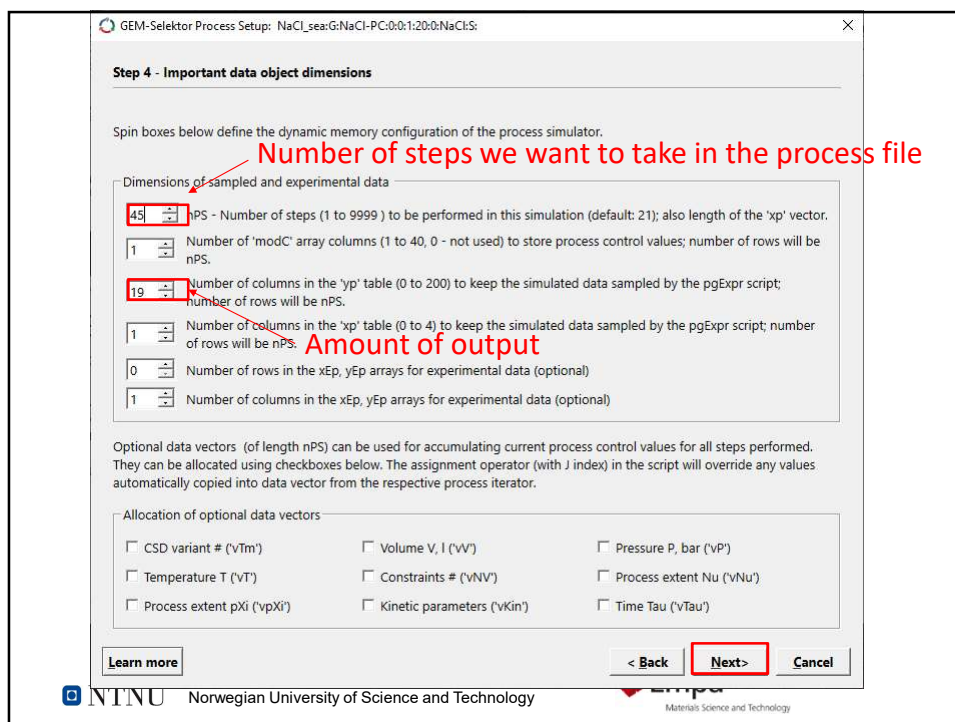
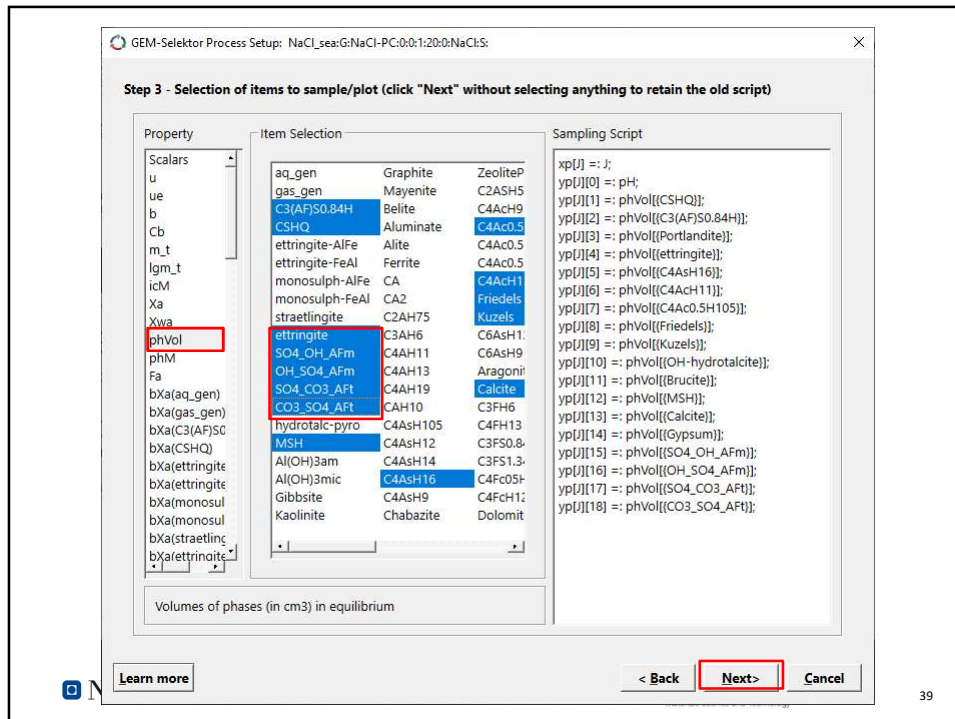
Property
Scalars
u
ue
b
Cb
m_t
lgm_t
icM
Xa
Xwa
phVol
phM
Fa
bXa(aq_gen)
bXa(gas_gen)
bXa(C3(AP)SC
bXa(CSHQ)
bXa(ettringite
bXa(ettringite
bXa(monosul
bXa(monosul
bXa(straetling
bXa(ettringite

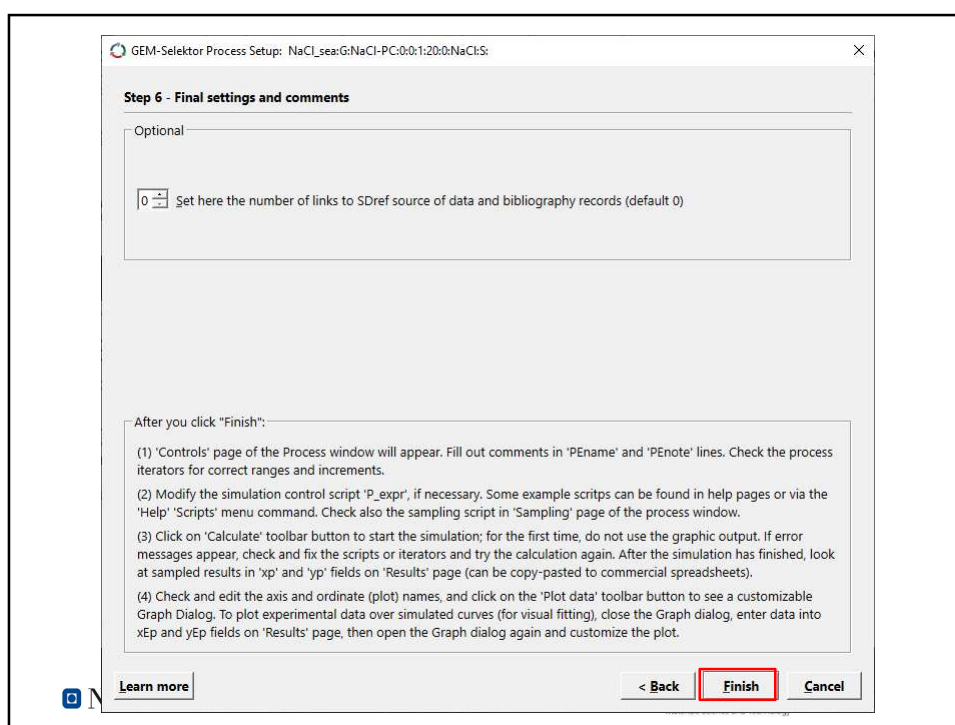
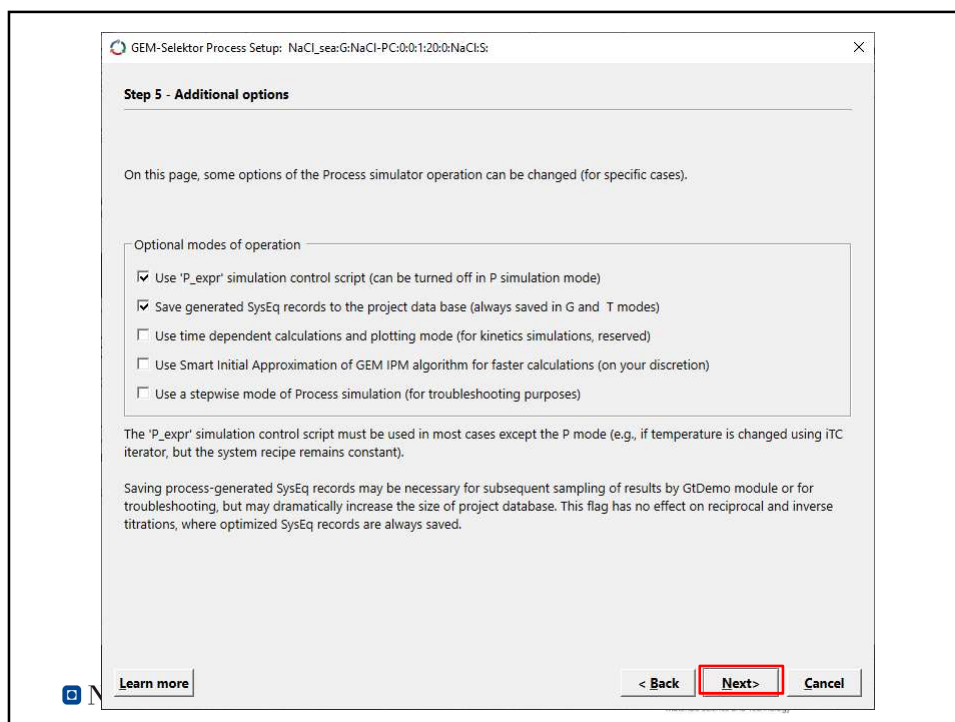
Item Selection
Mbx _nnr[0] F_RT Fi_3]
pmXs _nnr[1] Xw T
GX L[0] Masses[0] P
IS L[1] Masses[1] RTf[0]
pH L[2] Masses[2] RTf[1]
pe L[3] Masses[3] RoW[0][0]
Eh L[4] Masses[4] EpsW[0][0]
TC[0] L[5] Masses[5] VisW[0]
TC[1] Fi[0] Volumes[0] iTm[0]
TK[0] Fi[1] Volumes[1] iTm[1]
TK[1] Fi[2] N_ iTm[2]
PG[0] Fi[0] L_0] cTm
PG[1] Fi[1] L_1] iV[0]
Vx[0] Fi[2] L_2] iV[1]
Vx[1] denW[0][0] L_3] iV[2]
It denW[1][0] L_4] cv
ItEfd epsW[0][0] L_5] iP[0]
Itipm epsW[1][0] Fi_1] iP[1]
Psi_DK[0] InP Fi_1] iP[2]
Psi_DK[1] RT Fi_2] cP

Sampling Script
xp[] := ;
yp[] := pH;

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

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





1

2

NaCl-PC

The process file is created 😊

	iTm	iV	iP	iTC	iNv	iTau
0	1000	0	1	25	0	0
1	1031	0	1	25	0	0
2	1	0	0	0	0	0
cTm	1000	0	1	25	0	0

```

modC[J] =: cNu;
xa_[{Aqua}] =: cNu * 1;
xa_[{NaCl}] =: cNu * 1;

```

Now we start editing the code ..
(next slide)

PC in contact with more and more NaCl water

Brief description

	iTm	iV	iP	iTC	iNv	iTau
0	1000	0	1	25	0	0
1	1031	0	1	25	0	0
2	1	0	0	0	0	0
cTm	1000	0	1	25	0	0

```

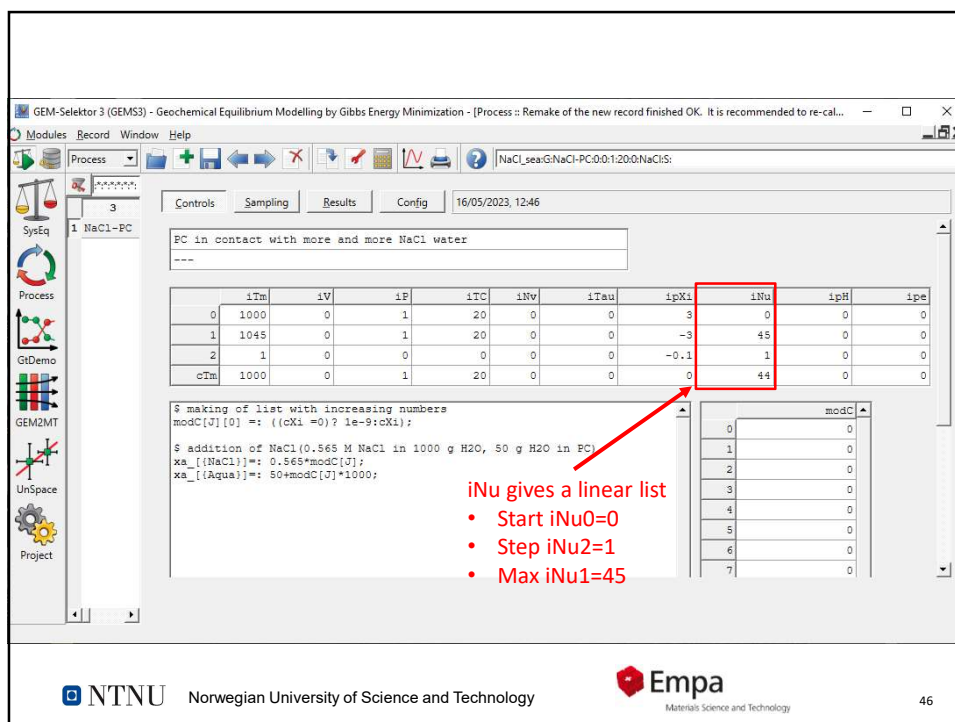
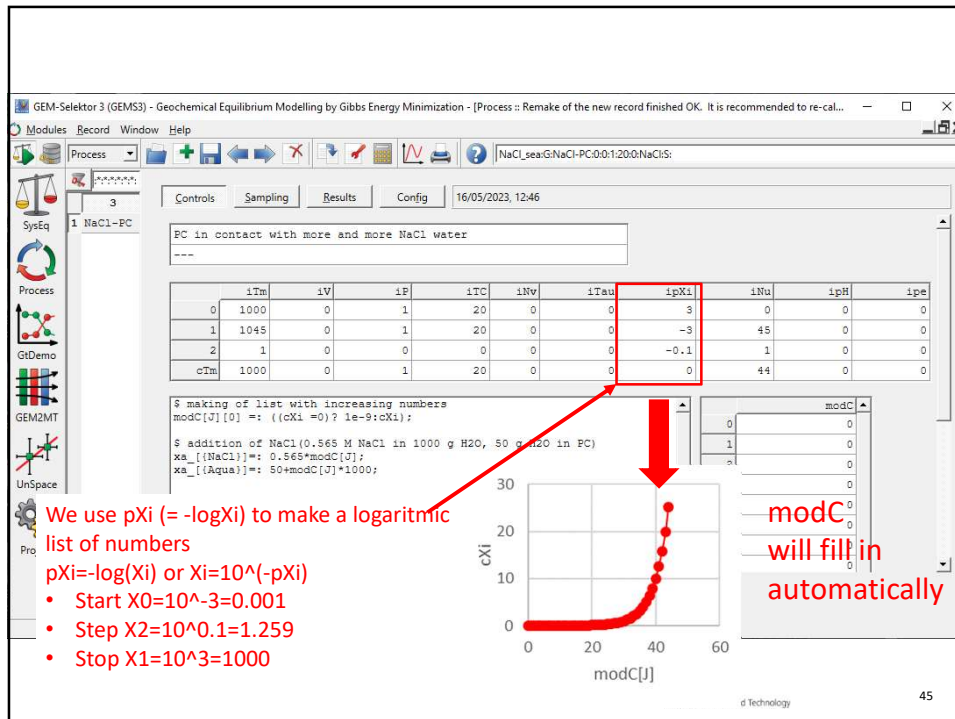
$ making of list with increasing numbers
modC[J][0] =: ((cXi = 0)? 1e-9:cXi);

$ addition of NaCl(0.565 M NaCl in 1000 g H2O, 50 g H2O in PC)
xa_[{NaCl}] =: 0.565*modC[J];
xa_[{Aqua}] =: 50+modC[J]*1000;

```

\$ making of list with increasing numbers
modC[J][0] =: ((cXi = 0)? 1e-9:cXi); => this means (IF (...) ? THEN.. : ELSE)

\$ addition of NaCl(0.565 M NaCl in 1000 g H2O, 50 g H2O in PC)
xa_[{NaCl}] =: 0.565*modC[J];
xa_[{Aqua}] =: 50+modC[J]*1000;



GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Remake of the new record finished OK. It is recommended to re-cal...

Modules Record Window Help

Process 3 NaCl-PC

Controls Sampling Results Config 16/05/2023, 12:46

PC in contact with more and more NaCl water

	iTm	iV	iP	ITC	iNv	iTau	ipX1	iNu	ipH	ipe
0	1000	0	1	20	0	0	3	0	0	0
1	1045	0	1	20	0	0	-3	45	0	0
2	1	0	0	0	0	0	-0.1	1	0	0
cTm	1000	0	1	20	0	0	0	44	0	0

\$ making of list with increasing numbers
modC[J][0] = ((cX1 = 0) ? 1e-9 : cX1);

\$ addition of NaCl(0.565 M NaCl in 1000 g H2O, 50 g H2O in PC)
xa_([NaCl]) = 0.565*modC[J];
xa_([Aqua]) = 50*modC[J]*1000;

modC

0	0
1	0
2	0
3	0
4	0
5	0
6	0
7	0

Numbering of the single files

- Start: iTm = 1000
- Step: iTm2 = 1
- Max: iTm1=1045

Calculation stops as soon as any max is reached

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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Remake of the new record finished OK. It is recommended to re-cal...

Modules Record Window Help

Process 3 NaCl-PC

Controls Sampling Results Config 16/05/2023, 12:46

PC in contact with more and more NaCl water

	iTm	iV	iP	ITC	iNv	iTau	ipX1	iNu	ipH	ipe
0	1000	0	1	20	0	0	3	0	0	0
1	1045	0	1	20	0	0	-3	45	0	0
2	1	0	0	0	0	0	-0.1	1	0	0
cTm	1000	0	1	20	0	0	0	44	0	0

\$ making of list with increasing numbers
modC[J][0] = ((cX1 = 0) ? 1e-9 : cX1);

\$ addition of NaCl(0.565 M NaCl in 1000 g H2O, 50 g H2O in PC)
xa_([NaCl]) = 0.565*modC[J];
xa_([Aqua]) = 50*modC[J]*1000;

modC

0	0
1	0
2	0
3	0
4	0
5	0
6	0
7	0

Varying the temperature

- Start: iTC = 20
- Step: iTC2 = 0
- Max: iTC1=20

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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Remake of ...]

Modules Record Window Help

Process: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaClS:

Controls Sampling Results Config 16/05/2023, 12:46

NaIt 9999 0 Next 1 I 0 J 0 Up

pStke

$x_p[J] = ((c_{Nu} = 0) ? 0 - 3 : \lg((x_{a_}[Aqua] - 50)/1000));$

cTau 0 cpX1 0 cX1 1

cpH 0 cpe 0 cEh 0

\$ Abscissa in L seawater per 100 g cement (+ 50 ml H2O in cement)

\$ Ordinate (in cm3/100g cement)

\$ Unreacted OPC 20g with 3.15g/cm3 density

yp[J][0] = 20/3.15;

yp[J][1] = phVol[{CSHQ}];

yp[J][2] = phVol[{C3(AF)S0.84H}];

yp[J][3] = phVol[{Portlandite}];

yp[J][4] = phVol[{ettringite}] + phVol[{SO4_CO3_Aft}] + phVol[{CO3_SO4_Aft}];

yp[J][5] = phVol[{C4AsH16}] + phVol[{OH_SO4_Afm}] + phVol[{SO4_OH_Afm}];

yp[J][6] = phVol[{C4AcH11}];

yp[J][7] = phVol[{C4Ac0.5H105}];

yp[J][8] = phVol[{Friedels}];

yp[J][9] = phVol[{Kuzels}];

yp[J][10] = phVol[{OH-hydratocalcite}];

yp[J][11] = phVol[{Brucite}];

yp[J][12] = phVol[{MSH}];

yp[J][13] = phVol[{Calcite}];

yp[J][14] = phVol[{Gypsum}];

yp[J][15] = 0;

yp[J][16] = 0;

(If ? Then : else)

0-3: Gems needs an operator first

We plot the volumes in [cm3] of the different hydration phases

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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Calculation...]

Modules Record Window Help

Process: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaClS:

Controls Sampling Results Config 16/05/2023, 15:49

NaIt 9999 0 Next 1 I 0 J 0 Up

pStke

$x_p[J] = ((c_{Nu} = 0) ? 0 - 3 : \lg((x_{a_}[Aqua] - 50)/1000));$

cTau 0 cpX1 -1.4 cX1 25.11886

cpH 0 cpe 0 cEh 0

\$ Abscissa in L seawater per 100 g cement (+ 50 ml H2O in cement)

\$ Ordinate (in cm3/100g cement)

\$ Unreacted OPC 20g with 3.15g/cm3 density

yp[J][0] = 20/3.15;

yp[J][1] = phVol[{CSHQ}];

yp[J][2] = phVol[{C3(AF)S0.84H}];

yp[J][3] = phVol[{Portlandite}];

yp[J][4] = phVol[{ettringite}] + phVol[{SO4_CO3_Aft}] + phVol[{CO3_SO4_Aft}];

yp[J][5] = phVol[{C4AsH16}] + phVol[{OH_SO4_Afm}] + phVol[{SO4_OH_Afm}];

yp[J][6] = phVol[{C4AcH11}];

yp[J][7] = phVol[{C4Ac0.5H105}];

yp[J][8] = phVol[{Friedels}];

yp[J][9] = phVol[{Kuzels}];

yp[J][10] = phVol[{OH-hydratocalcite}];

yp[J][11] = phVol[{Brucite}];

yp[J][12] = phVol[{MSH}];

yp[J][13] = phVol[{Calcite}];

yp[J][14] = phVol[{Gypsum}];

yp[J][15] = 0;

yp[J][16] = 0;

yp[J][17] = 0;

yp[J][18] = 0;

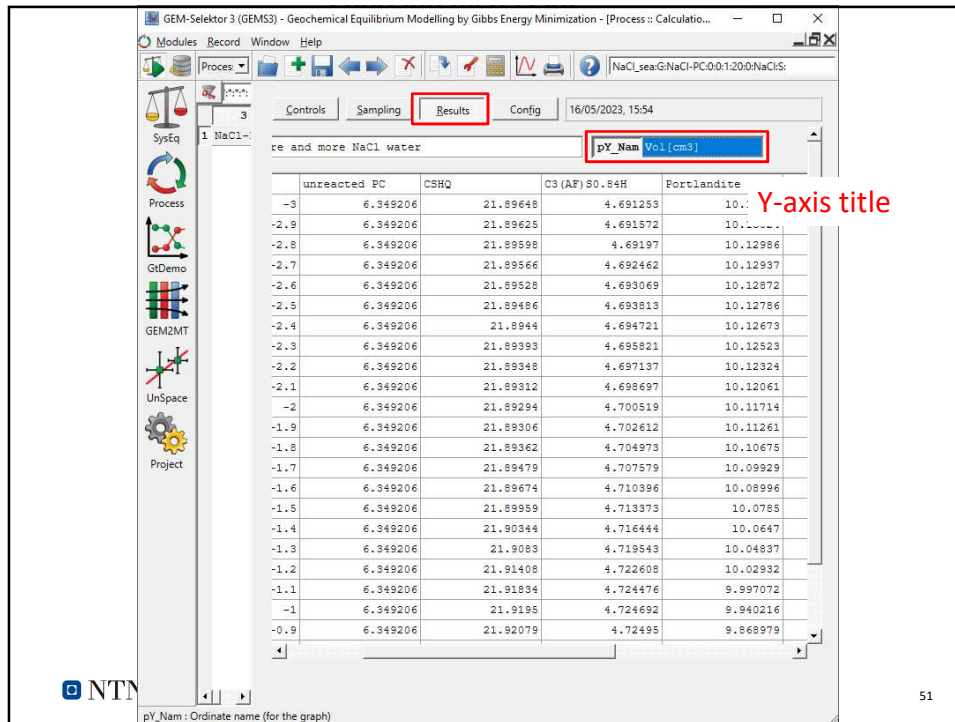
pX_Nam vol NaCl

pLnam unreacted PC CSHQ C3(AF)S0.84H Portlandite

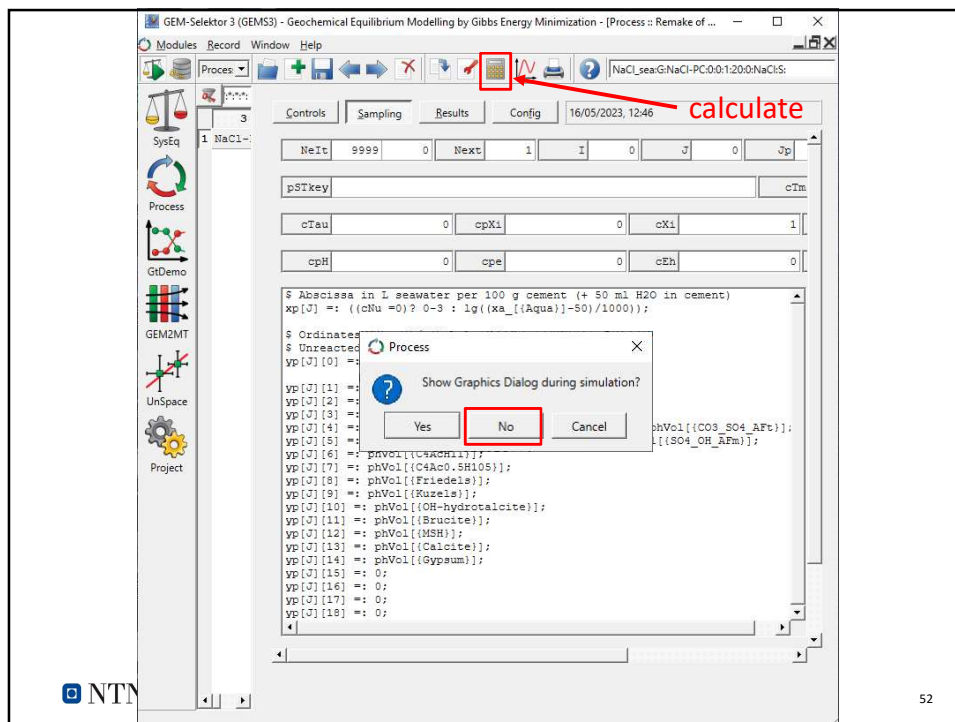
pLnam [0,0] : List of names of curves (columns in the yp array)

List names of output

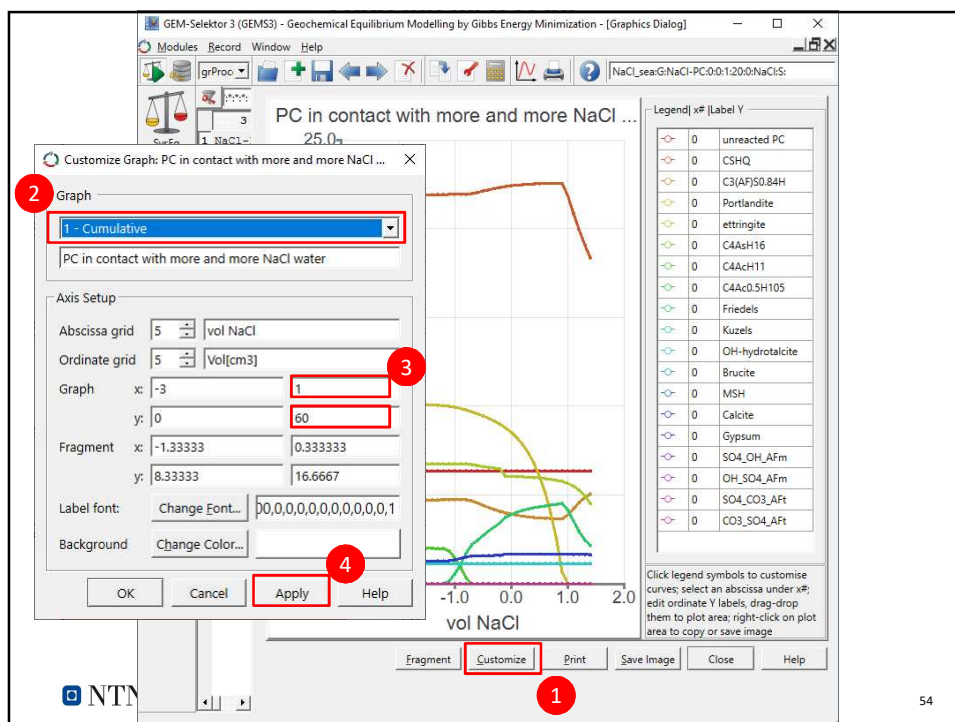
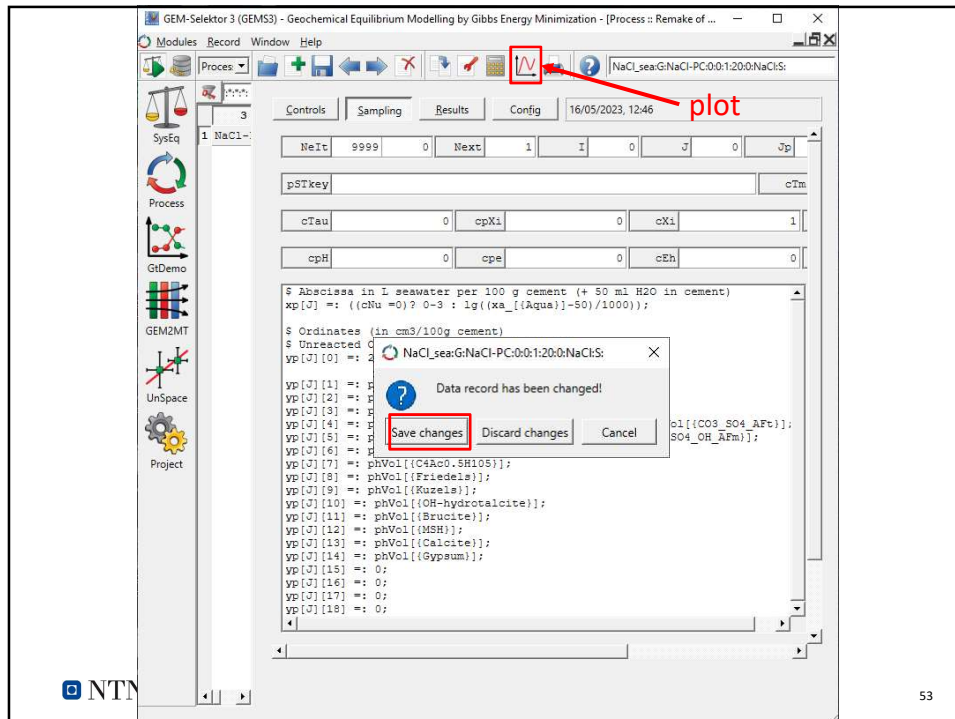
50

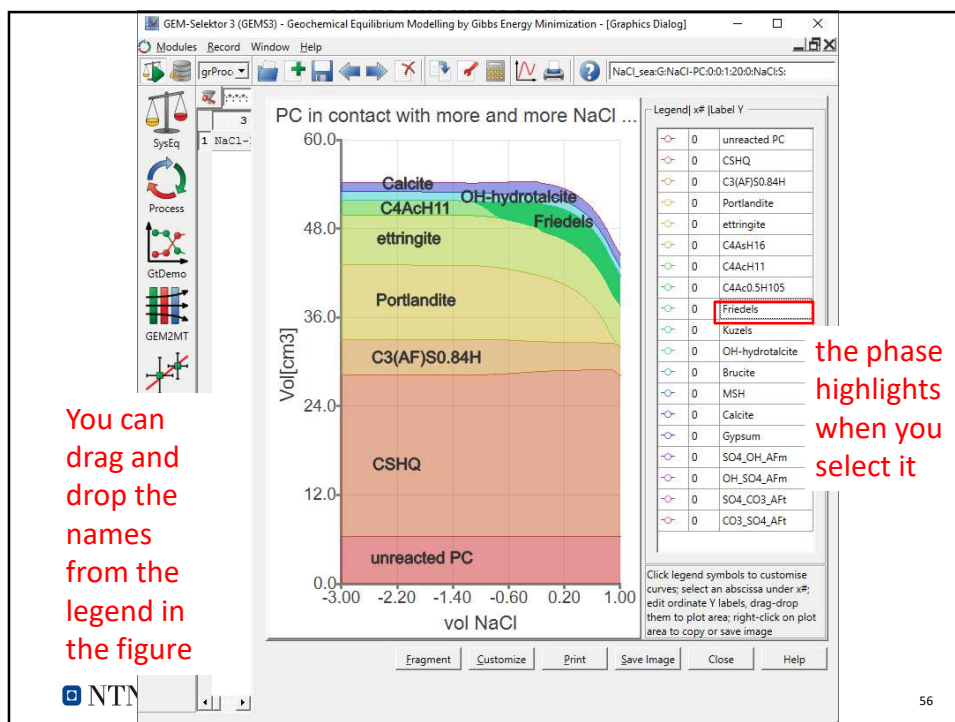
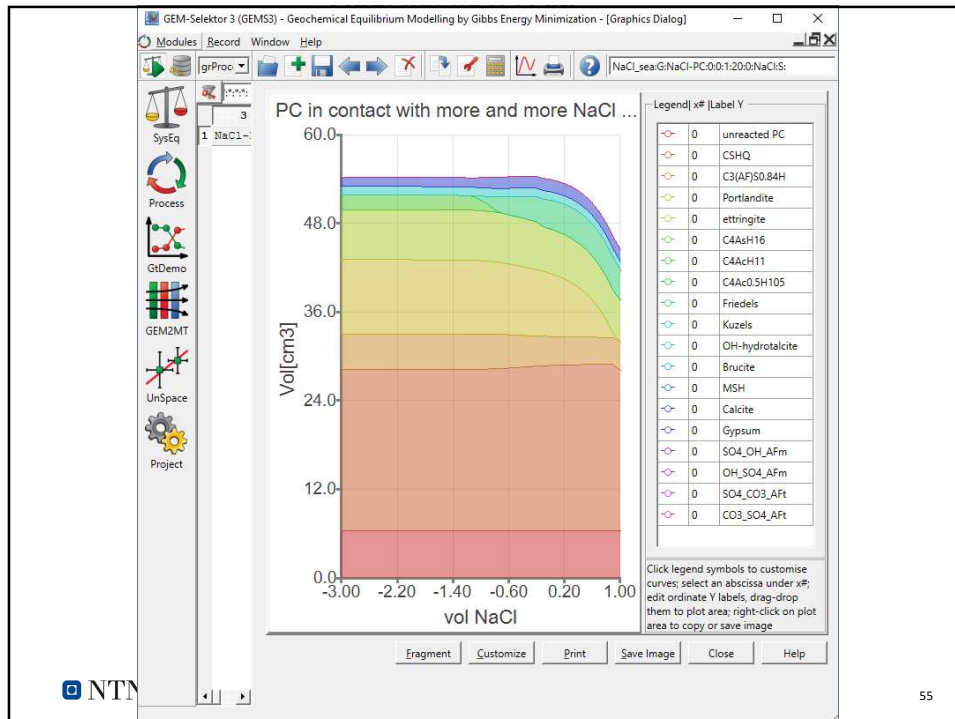


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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic System in Pr...

Modules Record Data Calculate View Print Window Help

SingleSystem

NaCl_sea:*****

Each step of the process file is a single (SysEq) file

Input: System Definition Results: Equilibrium State

Phase/species	L	T	On/UC	Add to BC
aq_gen	76	a	g	0
gas_gen	7	g	g	0
C3(AF)SO.84H	2	s	g	0
CSHQ	6	s	g	0
ettringite-AlFe	2	s	g	0
ettringite-FeAl	2	s	g	0
monosulph-AlFe	2	s	g	0
Al(OH)3am	1	s	g	0
Al(OH)3mic	1	s	g	0
Gibbsite	1	s	g	0
Kaolinite	1	s	g	0
Graphite	1	s	g	0
Mayenite	1	s	g	0
Belite	1	s	g	0
Aluminate	1	s	g	0
Alite	1	s	g	0
Ferrite	1	s	g	0
CA	1	s	g	0

Title: Please, enter here a title explaining what this chem...

Comment: Please, enter here a comment about the purpose of th...

System: T = 293.15 K; P = 1.00 bar; V = 0.1466 L; Aqueous: built-in EDH(H); pH

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqDemo: NaCl_sea:GNaCl-PC

Modules Record Data Calculate View Print Window Help

EqDemo

NaCl_sea:*****

Look up the results for each step

Volume Mass

EqC EqPh EqDC EqSurf EqGen 16/05/2023, 15:53

Please, enter here a title explaining what this chemical system ...

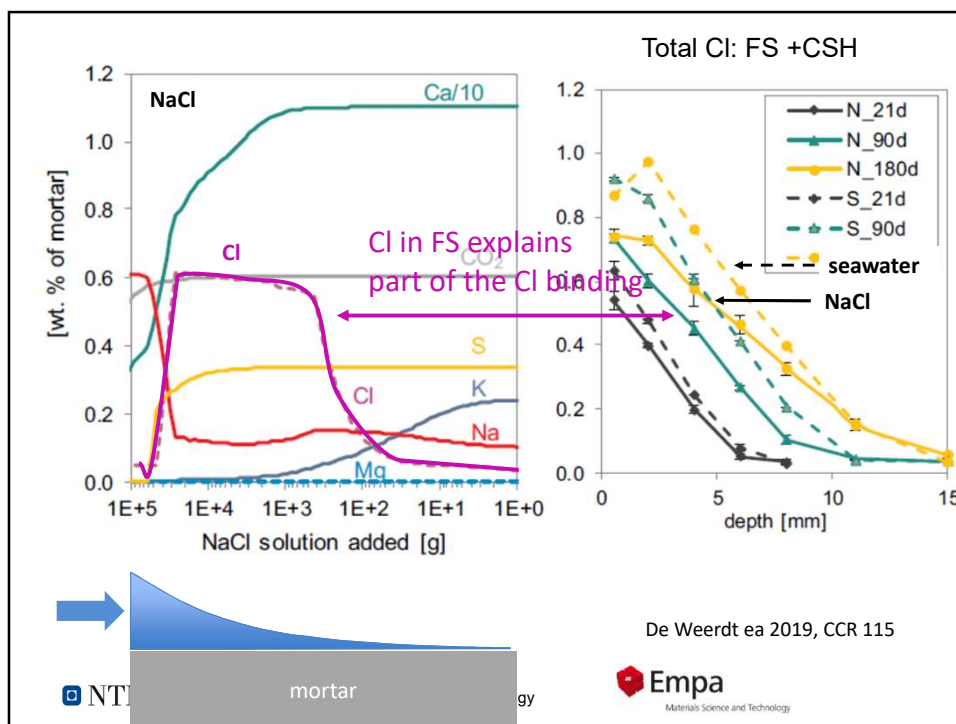
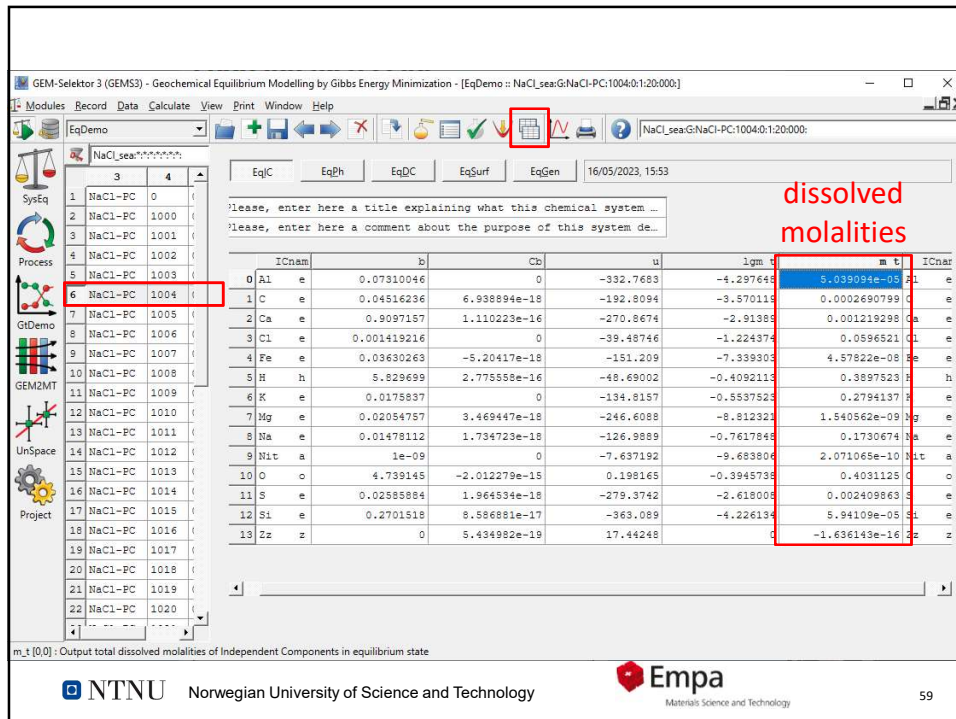
Please, enter here a comment about the purpose of this system de...

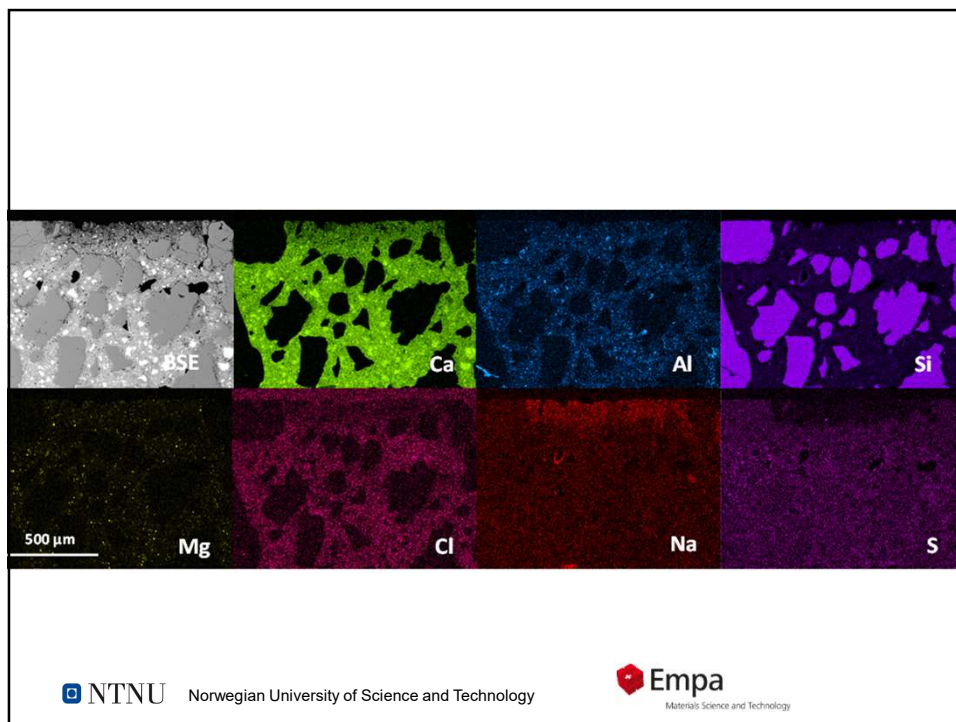
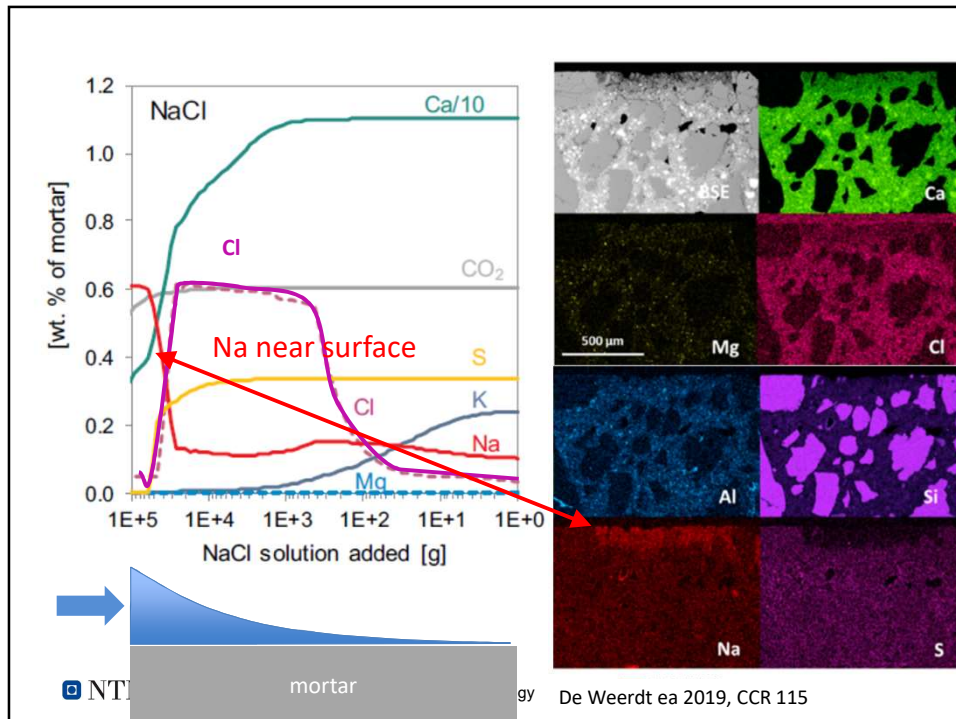
	Phnam	L1	Xa	Fa	phVol	phM
0 a	aq_gen	76	1.341441	-5.728505e-09	23.87291	24.36238
1 g	gas_gen	7	0.003168777	9.466632e-10	77.23572	0.1003474
2 s	C3(AF)SO.84H	2	0.03216692	-1.267402e-08	4.693069	13.86603
3 s	CSHQ	6	0.3526	1.380564e-08	21.89528	49.55067
4 s	ettringite-AlFe	2	0	-1	0	0
5 s	ettringite-FeAl	2	0	-1	0	0
6 s	monosulph-AlFe	2	0	-1	0	0
7 s	monosulph-FeAl	2	0	-1	0	0
8 s	straetlingite	2	0	-2.906141	0	0
9 s	ettringite	2	0	-0.07491623	0	0
10 s	SO4_OH_AfM	2	0	-1	0	0
11 s	OH_SO4_AfM	2	0	-1	0	0
12 s	SO4_CO3_AfT	2	0.02900384	1.243994e-08	6.775082	12.01887
13 s	CO3_SO4_AfT	2	3.828567e-07	1.243994e-08	8.943248e-05	0.0001586516
14 s	hydrotalc-pyro	2	0	-8.642145	0	0
15 s	MSH	2	0	-3.709231	0	0

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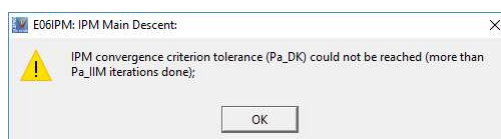




We might encounter some instability problems on the way.
Please adapt the project controls 😊

GEMS – Convergence problem

This error message might occur :



The reason is the current solid solution model, e.g. for Al-Fe-Aft.

As a workaround there are two possible solutions:

- 1) Do not use this solid solution. Use the single phases instead.
- 2) Modify the some of the settings of GEMS as shown on the next slide.
In most cases this should work.

Convergence problem - workaround

2. Coverage tolerance parameter:
use higher value, e.g. 1e-004,
maximum seems to be 5e-003

3. Minimum amount of stable phases:
use lower value, e.g. 1e-023

1. Smoothing parameter:
use low positive value, e.g. 0.01
E => 0.01 works

Do not touch the other values !!!

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