Lecture 06
Interaction with the environment

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Slides developed by K. De Weerdt, NTNU

NTNU Norwegian University of Science and Technology

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

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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. Seawater contains besides sodium and chlorine additional elements such as sulfur and magnesium, which can change the phase assemblage in the concrete and thereby affect chloride ingress. Mortar samples prepared with Portland cement were 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 sulfur and magnesium, which had only a limited impact on the chloride ingress. Leaching, observed in the outer 10–20 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 solutions. To mirror the leaching 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 platforms 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 and accumulate to critical concentrations they can initiate corrosion. Hence, to ensure sufficient service life, such structures need to be designed and constructed with concrete compositions with high chloride ingress resistance, as well as an appropriate concrete cover depth in order to protect the reinforcement during the designed service life.

Laboratory testing of concrete compositions for marine applications is generally performed with NaCl solutions to mimic the marine conditions. Commonly used diffusion tests either prescribe exposure to 3% NaCl solution (approx. 30 g/l), which yields a similar chloride concentration as in the Atlantic, (ASTM C1543 [1], EN 13396 [2], CEN/TS 12390-11 [3]) or about 5.5 times higher concentration (165 g/l NaCl solution), (ASTM C1556 [4] and NT BUILD 443 [5]).

However, seawater contains, in addition to sodium and chloride, other ions, for example magnesium, sulfate, and carbonates, which potentially can influence the chloride ingress [6]. The effect of seawater on the phase assemblage of concrete is complex. The differences in the mobility of the ions and in the solubility of the reaction products results in elemental zonation in the concrete near the surface [7–11].

In this study, we investigated whether the presence of ions other than sodium and chloride in seawater will affect the chloride ingress. The chloride ingress by bulk diffusion in Portland cement mortars exposed to seawater is compared with ingress in mortars exposed to NaCl solution with a similar chloride concentration. Saturated samples were exposed to seawater and NaCl solution 7 days after casting. Elemental profiles were determined after 21, 90 and 180 days of exposure at 20 °C.

2. Experimental

2.1. Materials

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

The chemical composition of the different materials is given in Table 2. Table 3 gives the mineral composition of the Portland cement determined by XRD-Rietveld. About 99.2% of the silica fume is X-ray amorphous. The PC mortar was proportioned with a water-to-binder mass ratio of 0.40 and the sand-to-binder mass ratio of 2.5:1. A polycarboxylate based superplastisizer (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

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ABSTRACT

The chloride resistance of concrete mixtures 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 mix design 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 in all the tests is the permeability while the influence of chloride binding is less important.

1. Introduction

Resistance of concrete to chloride ingress is a key property for the durability of reinforced concrete structures exposed to de-icing salts 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 for 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 cement has the ability to bind chlorides, dependent on its chemical composition. Therefore, chloride is present in concrete both as ion in the pore solution as well as bound to cement hydration products in the form of Friedel's salt ($Ca_4Al_2Cl_2(OH)_{12}{\cdot}4H_2O$) or sorbed to C–S–H [3–5]. Since only "free" chloride ions in the pore solution can move, chloride binding can affect resistance of concrete to chloride ingress by delaying the penetration process. So far, chloride binding has been mainly studied using experimental techniques. Few attempts have been made to investigate the subject by thermodynamic modeling [6,7]. Additionally, the chloride resistance of a cement based material is known to increase with decreasing porosity [8,9] since the mobility of water and thus of the chloride ions is reduced.

To characterize the resistance of concrete against chloride ingress numerous tests have been developed. An overview of such test methods is given e.g. in [10,11]. These methods can mainly be categorized into three categories: diffusion tests, migration tests and indirect tests based on resistivity or conductivity.

In diffusion tests, chloride penetrates slowly into the saturated concrete due to a gradient in chloride concentration, while in the migration and indirect tests, the chloride transport is accelerated by an externally applied electrical field. Furthermore, the difference between steady-state and non-steady-state testing conditions have to be distinguished.

Under steady-state testing conditions (e.g. conductivity tests), the extent of chloride binding has no influence on the results. However, non-steady-state transport can be affected by chloride binding, dependent on the method used. Non-steady-state migration tests are working with a strong external electrical field and a shorter test duration than non-steady-state diffusion tests, which both tend to reduce the amount of bound chlorides. Therefore, non-steady-state migration coefficient describes chloride transport under reduced chloride binding conditions [12]. As a result, the different test methods may lead to results which are not comparable to each other.

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.

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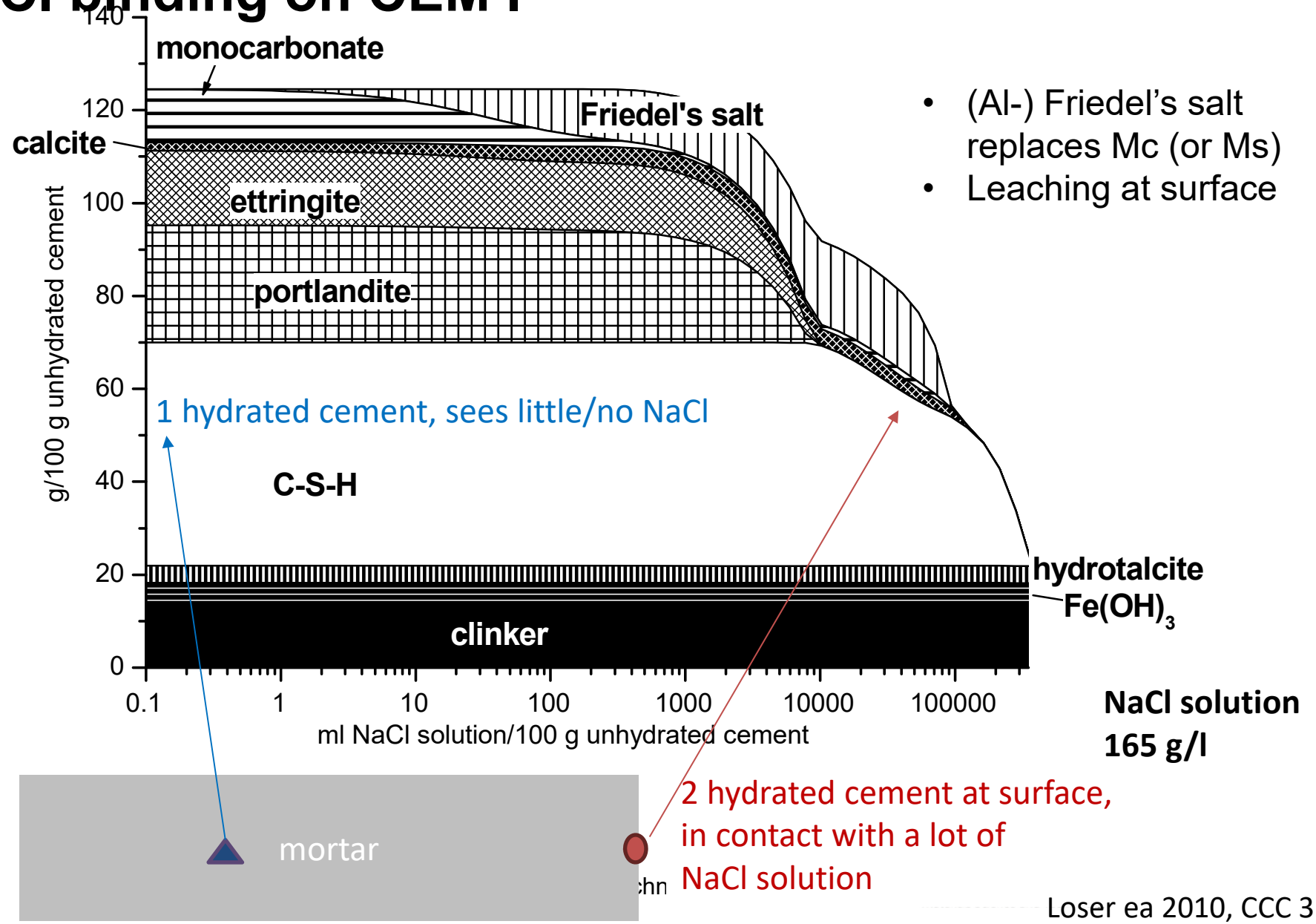
Simple modelling approach: Cl binding on CEM I



- (Al-) Friedel's salt replaces Mc (or Ms)
- Leaching at surface

Loser ea 2010, CCC 32

GOAL:
Predict phase changes when adding an increasing amount of ..

NaCl solution → seawater

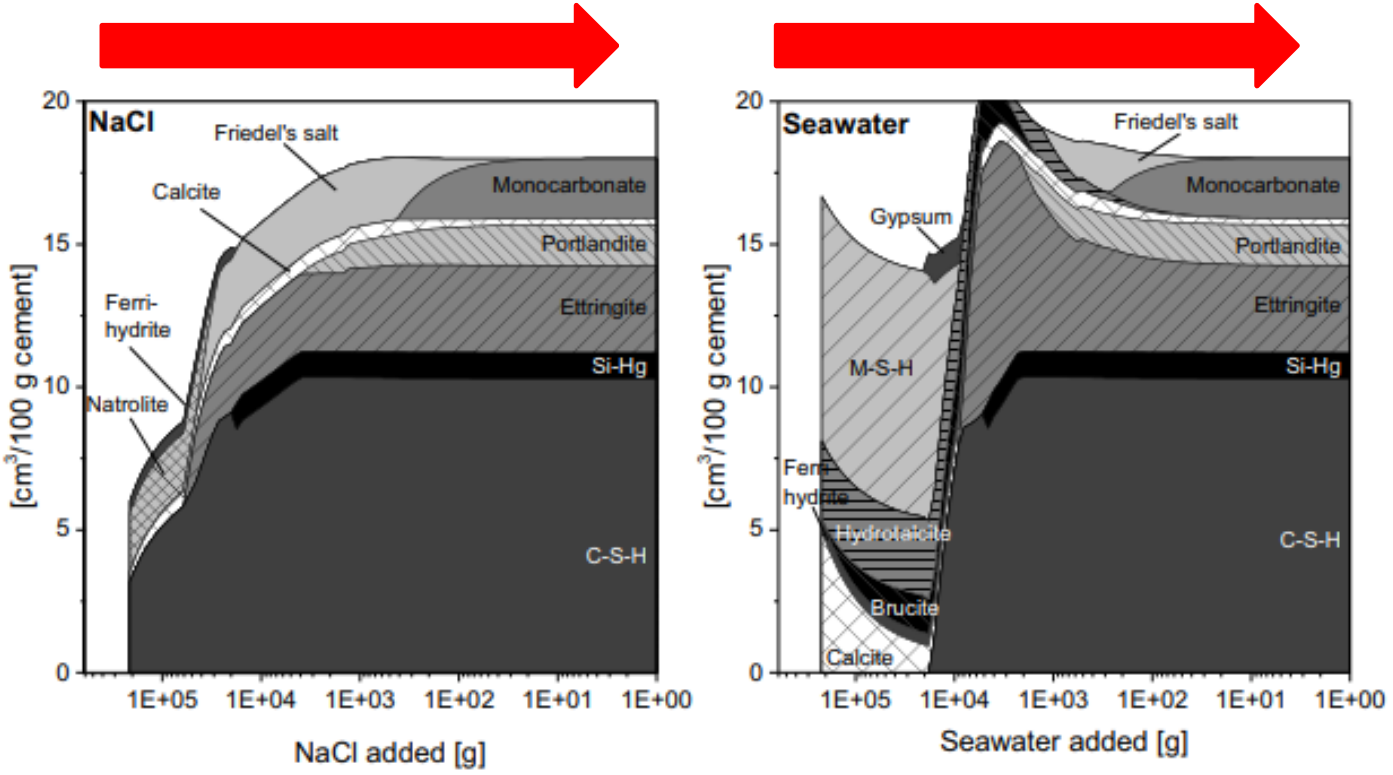


Fig. 10. Predicted volume of the phases in the PC paste upon exposure to increasing amounts of NaCl solution (left) or seawater (right) in [cm^3/100 g cement].

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

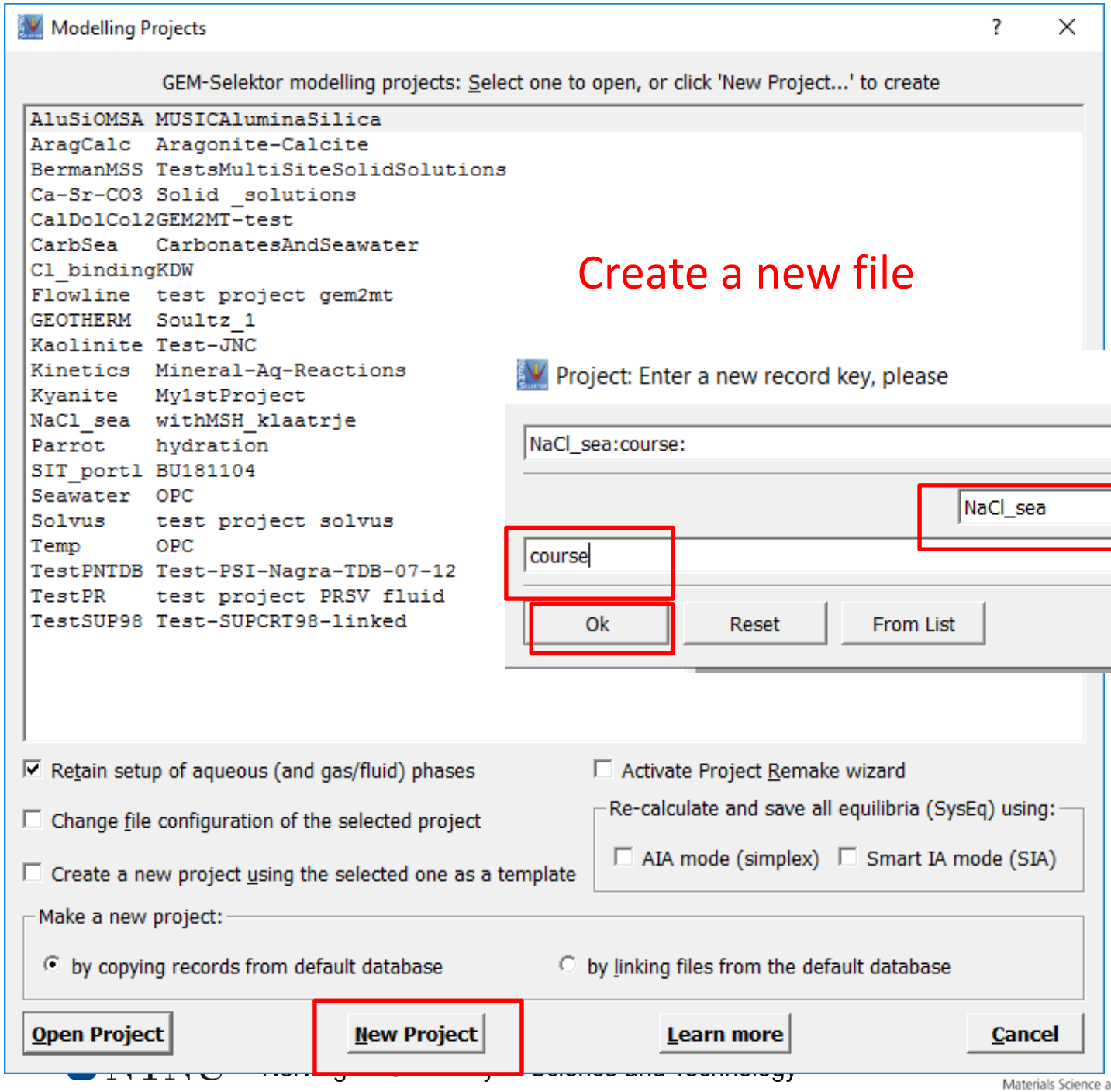
Task: calculate the phase changes in PC paste exposed to sea water

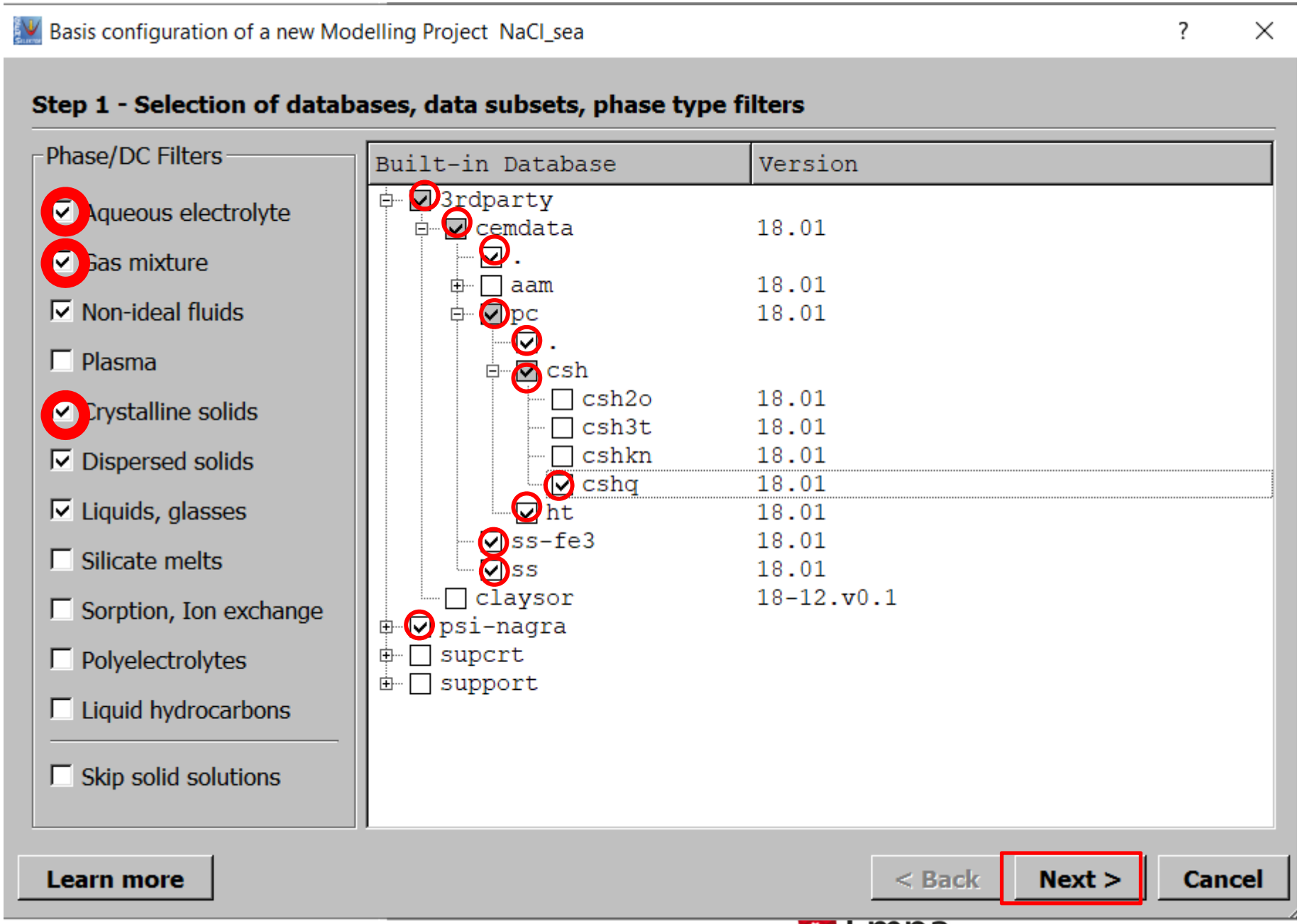
Content

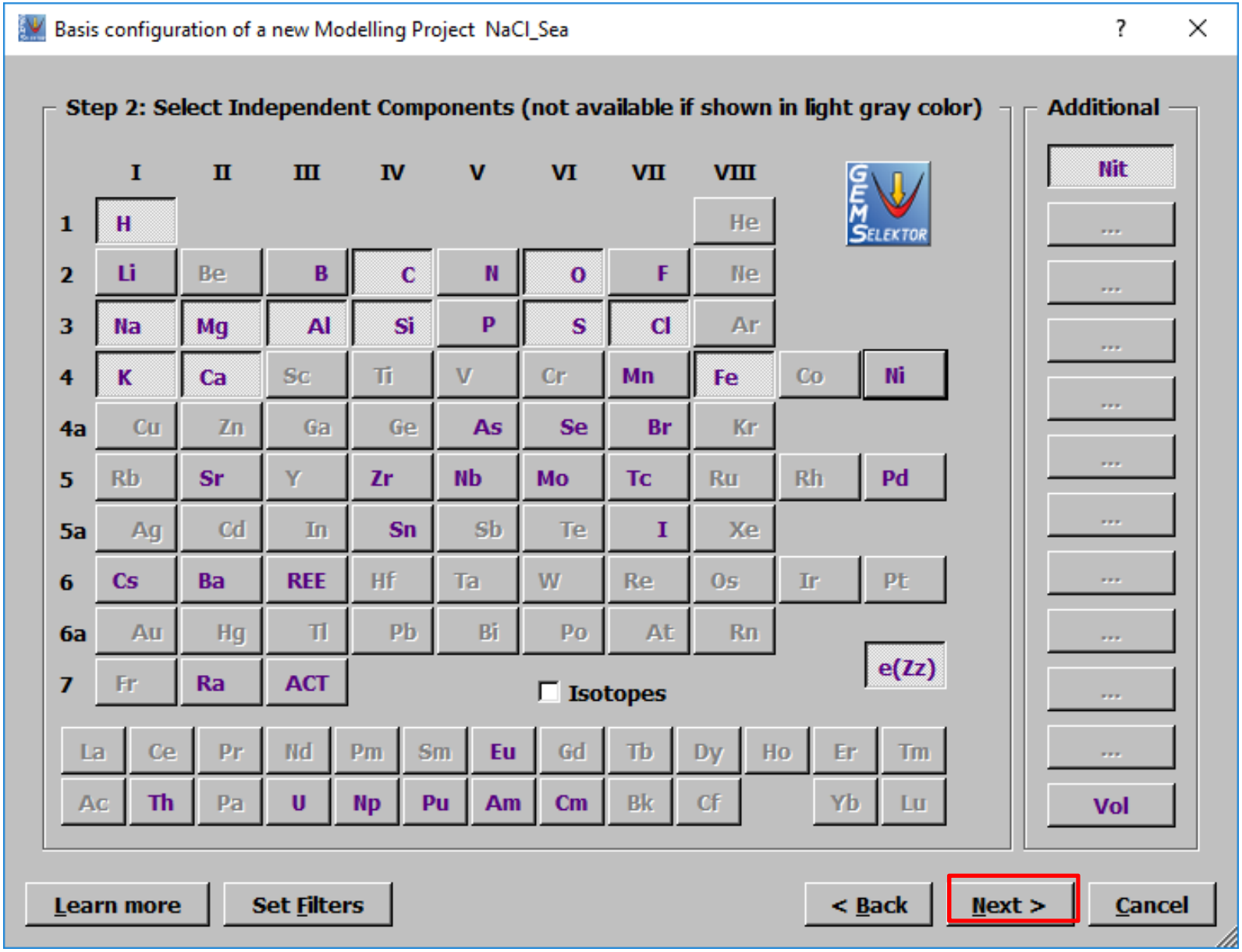
Example: calculate the phase changes in PC paste exposed to NaCl solution

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

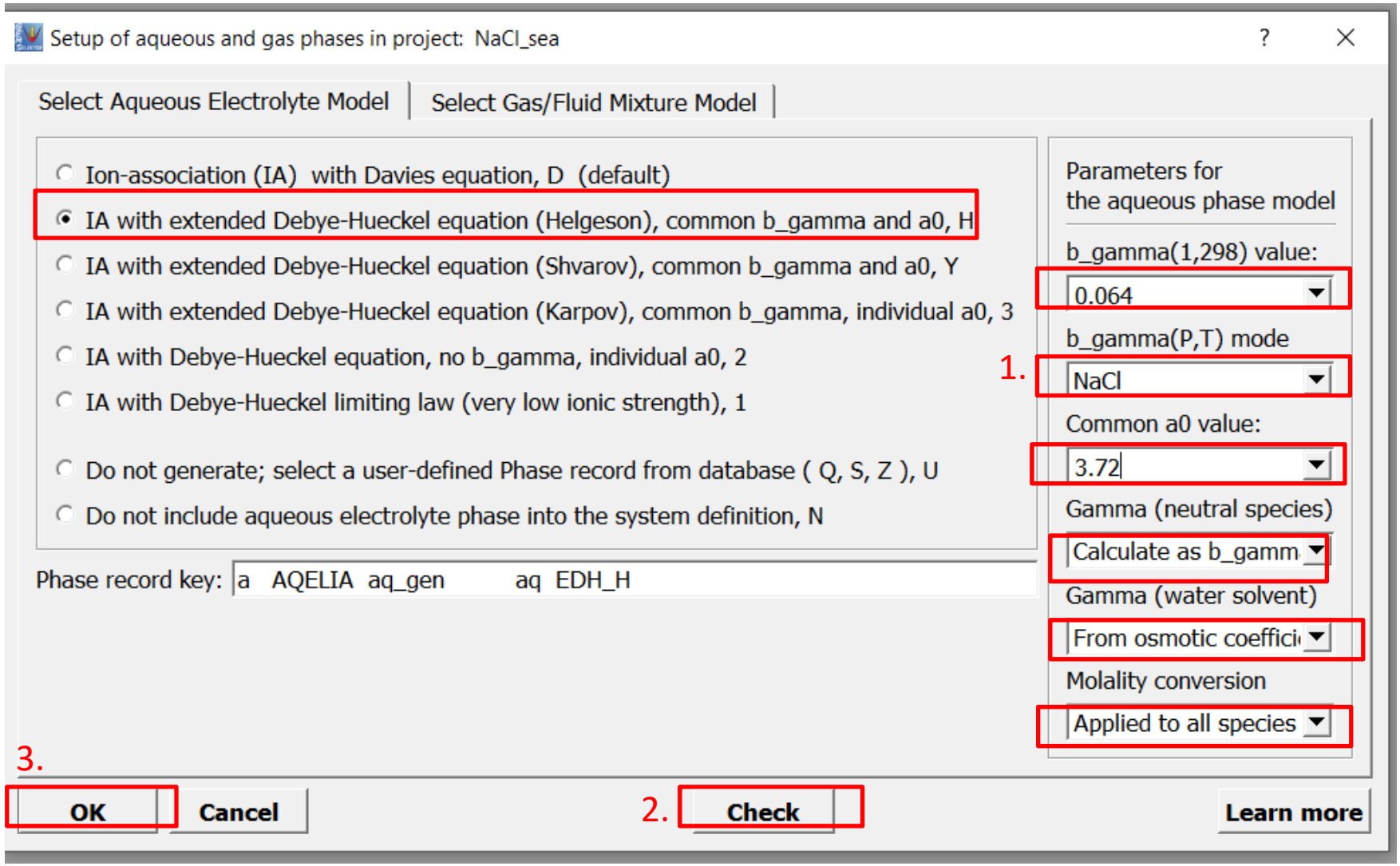
Task: calculate the phase changes in PC paste exposed to sea water


Modelling Projects
GEM-Selektor modelling projects: Select one to open, or click 'New Project...' to create
AluSiOMSA MUSICAluminaSilica
AragCalc Aragonite-Calcite
BermanMSS TestsMultiSiteSolidSolutions
Ca-Sr-CO3 Solid _solutions
CalDolCol2GEM2MT-test
CarbSea CarbonatesAndSeawater
Cl_bindingKDW
Flowline test project gem2mt
GEOTHERM Soultz_1
Kaolinite Test-JNC
Kinetics Mineral-Aq-Reactions
Kyanite My1stProject
NaCl_sea withMSH_klaatrje
Parrot hydration
SIT_portl BU181104
Seawater OPC
Solvus test project solvus
Temp OPC
TestPNTDB Test-PSI-Nagra-TDB-07-12
TestPR test project PRSV fluid
TestSUP98 Test-SUPCRT98-linked
Create a new file
Project: Enter a new record key, please
NaCl_sea:course:
NaCl_sea
Name of the modeling project
course
Comment to the project definition
Ok
Reset
From List
Help
Cancel
Retain setup of aqueous (and gas/fluid) phases
Activate Project Remake wizard
Change file configuration of the selected project
Re-calculate and save all equilibria (SysEq) using:
AIA mode (simplex)
Smart IA mode (SIA)
Create a new project using the selected one as a template
Make a new project:
by copying records from default database
by linking files from the default database
Open Project
New Project
Learn more
Cancel


Basis configuration of a new Modelling Project NaCl_sea
Step 1 - Selection of databases, data subsets, phase type filters
Phase/DC Filters
Aqueous electrolyte
Gas mixture
Non-ideal fluids
Plasma
Crystalline solids
Dispersed solids
Liquids, glasses
Silicate melts
Sorption, Ion exchange
Polyelectrolytes
Liquid hydrocarbons
Skip solid solutions
Built-in Database
Version
3rdparty
cemdata 18.01
.
aam 18.01
pc 18.01
.
csh
csh2o 18.01
csh3t 18.01
cshkn 18.01
cshq 18.01
ht 18.01
ss-fe3 18.01
ss 18.01
claysor 18-12.v0.1
psi-nagra
supcrt
support
Learn more
< Back
Next >
Cancel

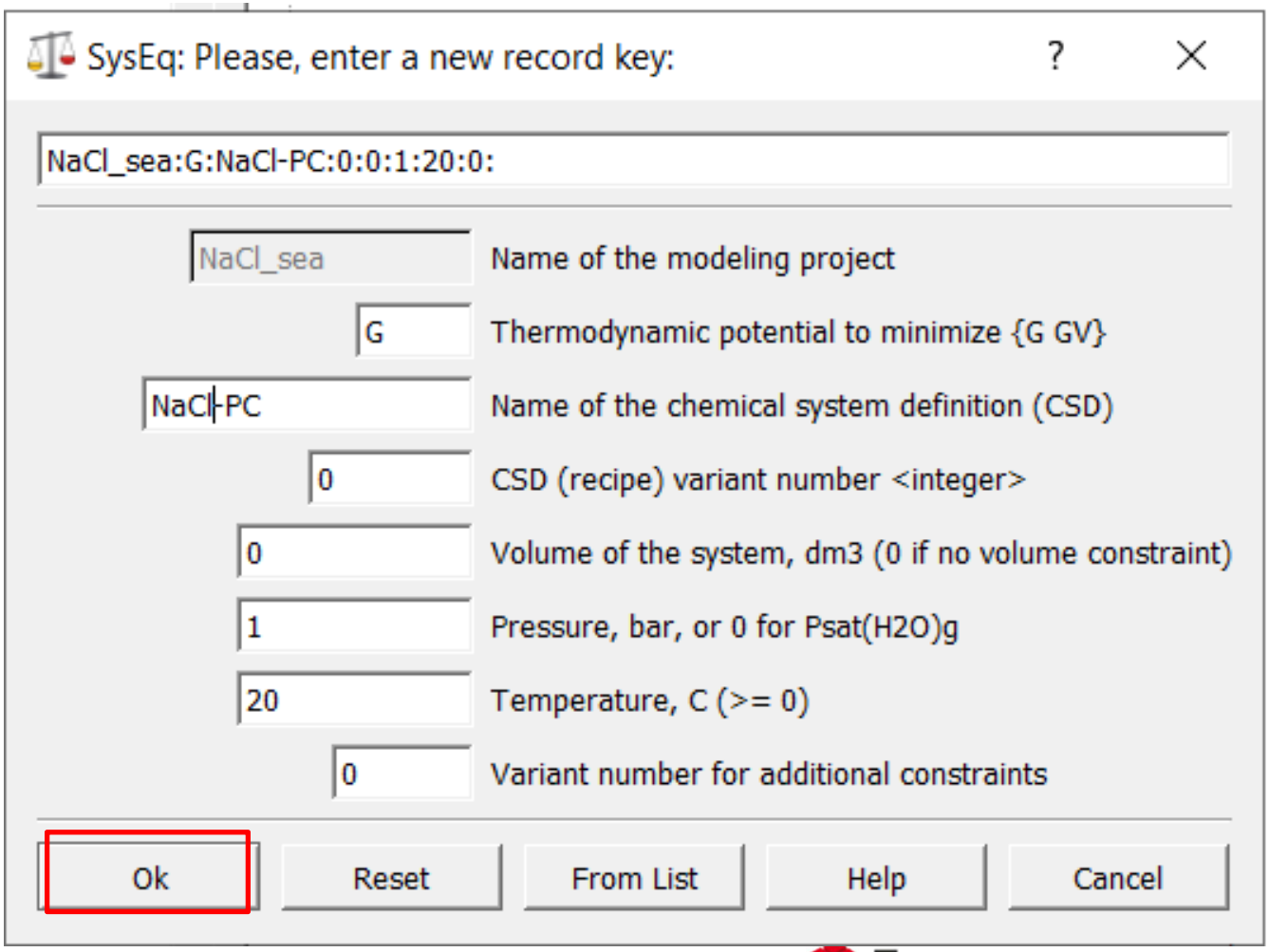


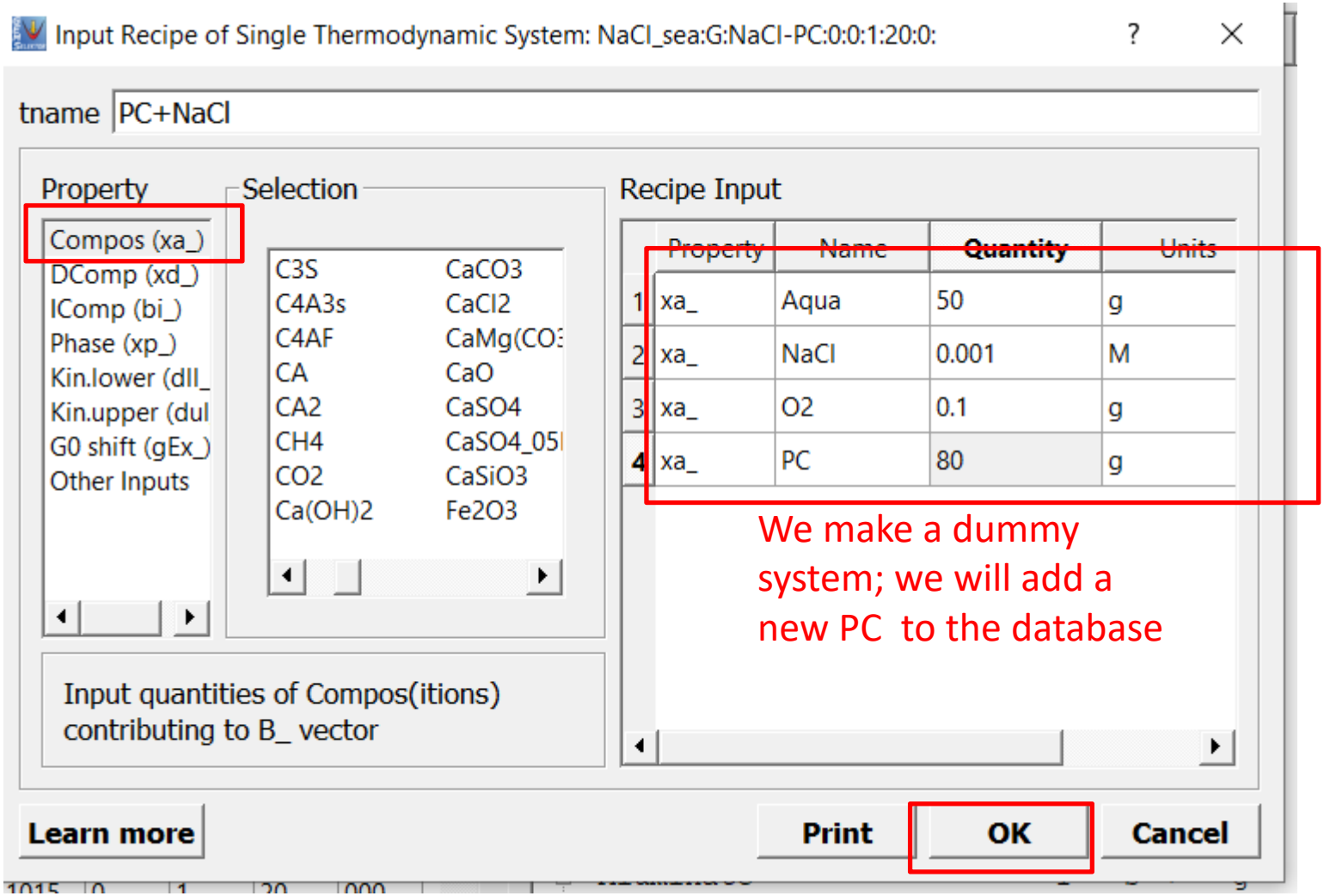
Choose the elements you will have in your system

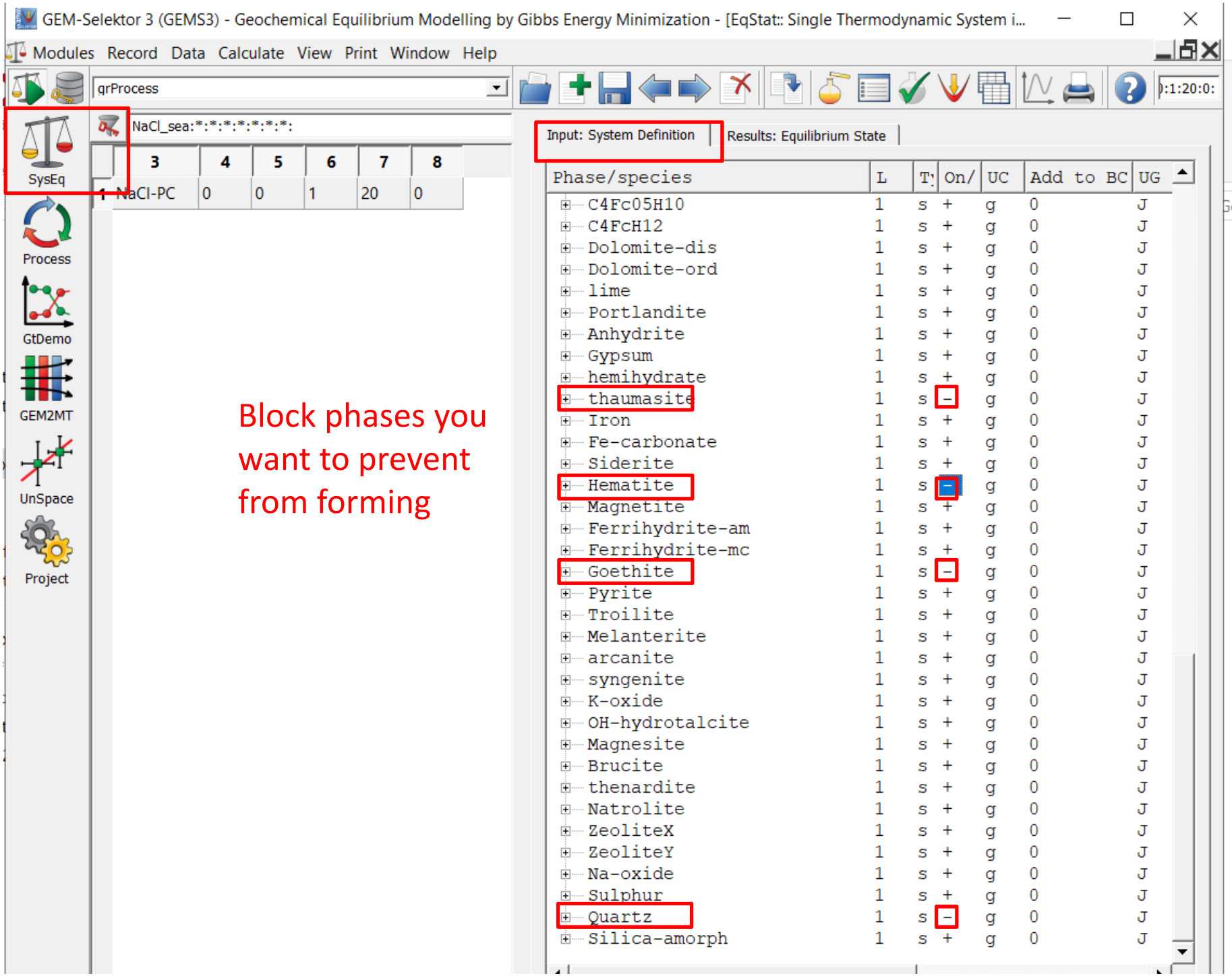

Setup of aqueous and gas phases in project: NaCl_sea
Select Aqueous Electrolyte Model
Select Gas/Fluid Mixture Model
Ion-association (IA) with Davies equation, D (default)
IA with extended Debye-Hueckel equation (Helgeson), common b_gamma and a0, H
IA with extended Debye-Hueckel equation (Shvarov), common b_gamma and a0, Y
IA with extended Debye-Hueckel equation (Karpov), common b_gamma, individual a0, 3
IA with Debye-Hueckel equation, no b_gamma, individual a0, 2
IA with Debye-Hueckel limiting law (very low ionic strength), 1
Do not generate; select a user-defined Phase record from database (Q, S, Z), U
Do not include aqueous electrolyte phase into the system definition, N
Phase record key: a AQELIA aq_gen aq EDH_H
Parameters for the aqueous phase model
b_gamma(1,298) value:
0.064
b_gamma(P,T) mode
1.
NaCl
Common a0 value:
3.72
Gamma (neutral species)
Calculate as b_gamm
Gamma (water solvent)
From osmotic coeffici
Molality conversion
Applied to all species
3.
OK
Cancel
2.
Check
Learn more

Name your single file

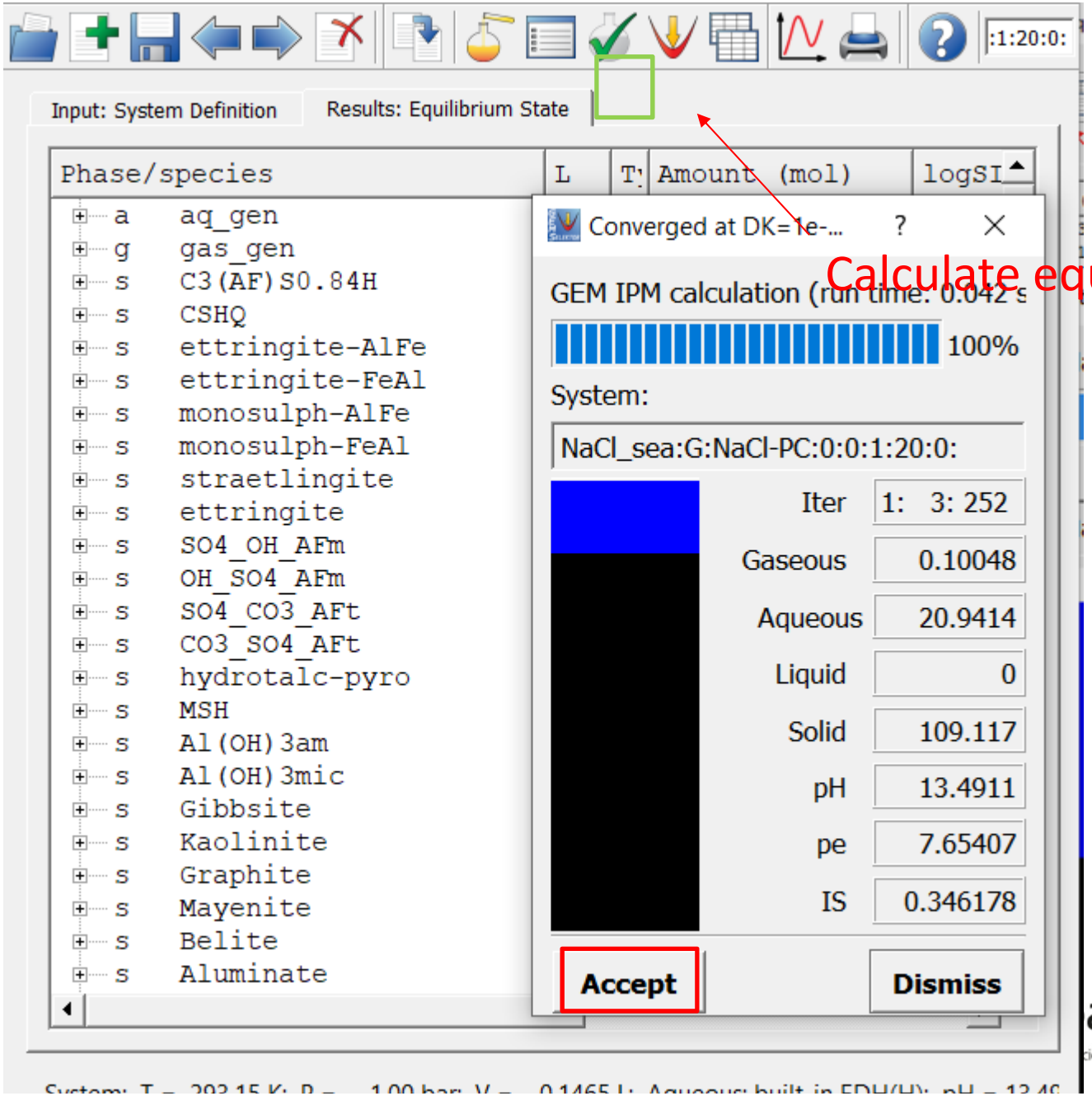
Temperature




Input Recipe of Single Thermodynamic System: NaCl_sea:G:NaCl-PC:0:0:1:20:0:
tname PC+NaCl
Property
Compos (xa_)
DComp (xd_)
IComp (bi_)
Phase (xp_)
Kin.lower (dll_
Kin.upper (dul
G0 shift (gEx_)
Other Inputs
Selection
C3S
C4A3s
C4AF
CA
CA2
CH4
CO2
Ca(OH)2
CaCO3
CaCl2
CaMg(CO3
CaO
CaSO4
CaSO4_05
CaSiO3
Fe2O3
Recipe Input
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
Input quantities of Compos(itions) contributing to B_ vector
Learn more
Print
OK
Cancel


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat:: Single Thermodynamic System i...
Modules Record Data Calculate View Print Window Help
qrProcess
SysEq
Process
GtDemo
GEM2MT
UnSpace
Project
NaCl_sea:*:*:*:*:*:*:*:
3 4 5 6 7 8
1 NaCl-PC 0 0 1 20 0
Input: System Definition
Results: Equilibrium State
Phase/species L T On/ UC Add to BC UG
C4Fc05H10 1 s + g 0 J
C4FcH12 1 s + g 0 J
Dolomite-dis 1 s + g 0 J
Dolomite-ord 1 s + g 0 J
lime 1 s + g 0 J
Portlandite 1 s + g 0 J
Anhydrite 1 s + g 0 J
Gypsum 1 s + g 0 J
hemihydrate 1 s + g 0 J
thaumasite 1 s – g 0 J
Iron 1 s + g 0 J
Fe-carbonate 1 s + g 0 J
Siderite 1 s + g 0 J
Hematite 1 s – g 0 J
Magnetite 1 s + g 0 J
Ferrihydrite-am 1 s + g 0 J
Ferrihydrite-mc 1 s + g 0 J
Goethite 1 s – g 0 J
Pyrite 1 s + g 0 J
Troilite 1 s + g 0 J
Melanterite 1 s + g 0 J
arcanite 1 s + g 0 J
syngenite 1 s + g 0 J
K-oxide 1 s + g 0 J
OH-hydrotalcite 1 s + g 0 J
Magnesite 1 s + g 0 J
Brucite 1 s + g 0 J
thenardite 1 s + g 0 J
Natrolite 1 s + g 0 J
ZeoliteX 1 s + g 0 J
ZeoliteY 1 s + g 0 J
Na-oxide 1 s + g 0 J
Sulphur 1 s + g 0 J
Quartz 1 s – g 0 J
Silica-amorph 1 s + g 0 J
Block phases you want to prevent from forming

1 Check the system

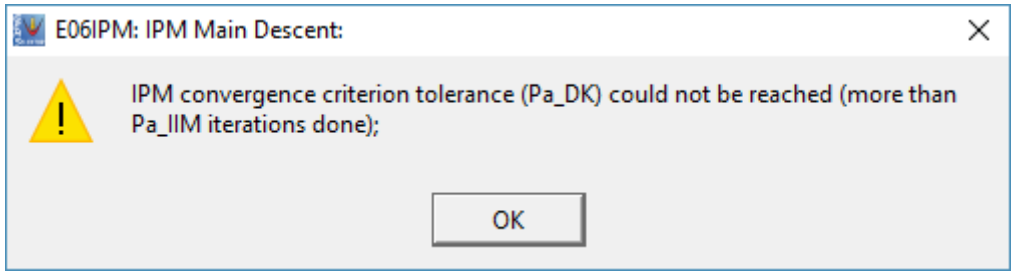


Calculate equilibrium

Accept to see the results

GEMS – Convergence problem

This error message might occur :

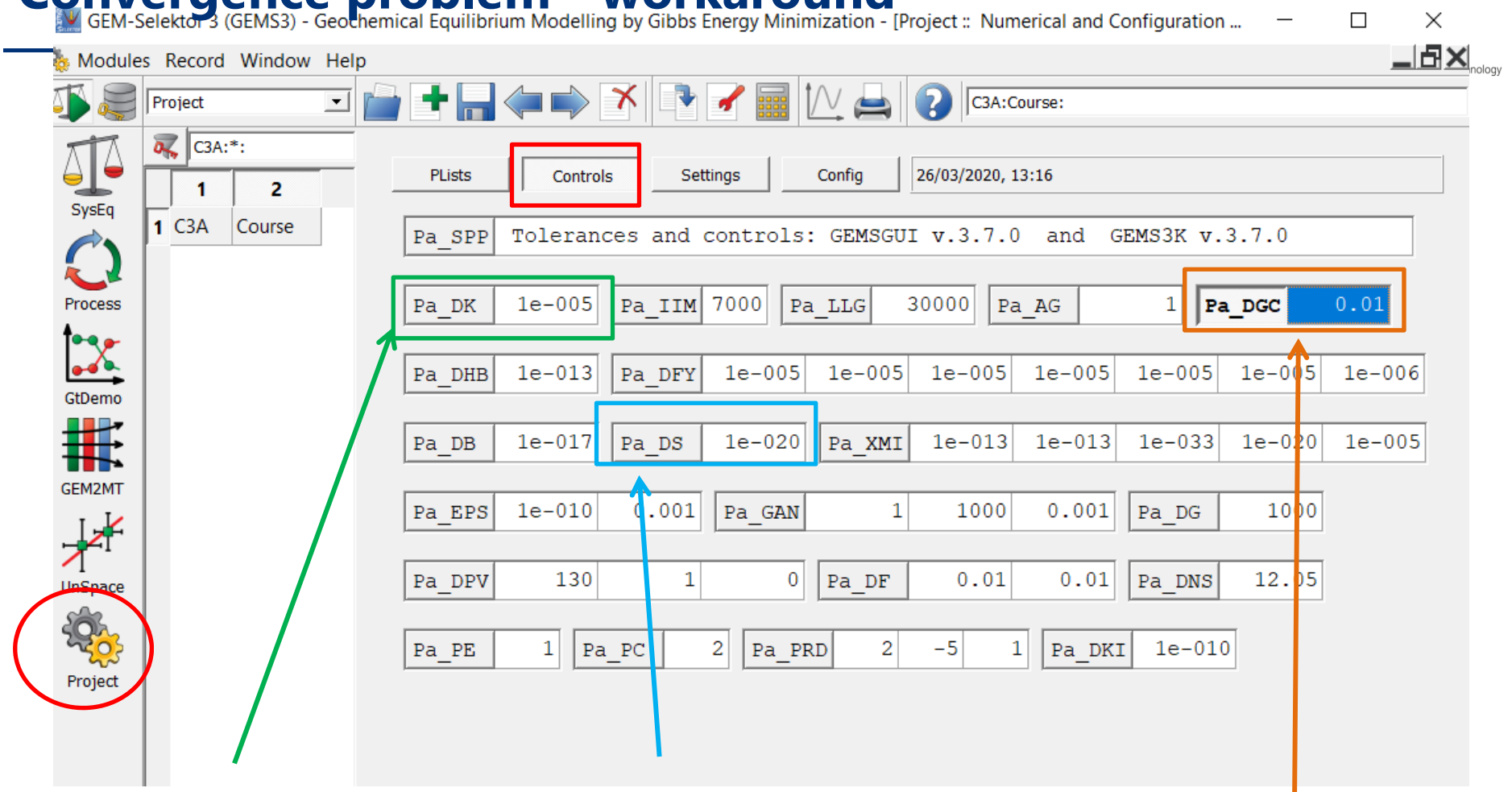


The reason is the current solid solution model, e.g. for Al-Fe-AFt.

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. Covergence 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.(

E => **0.01 works**

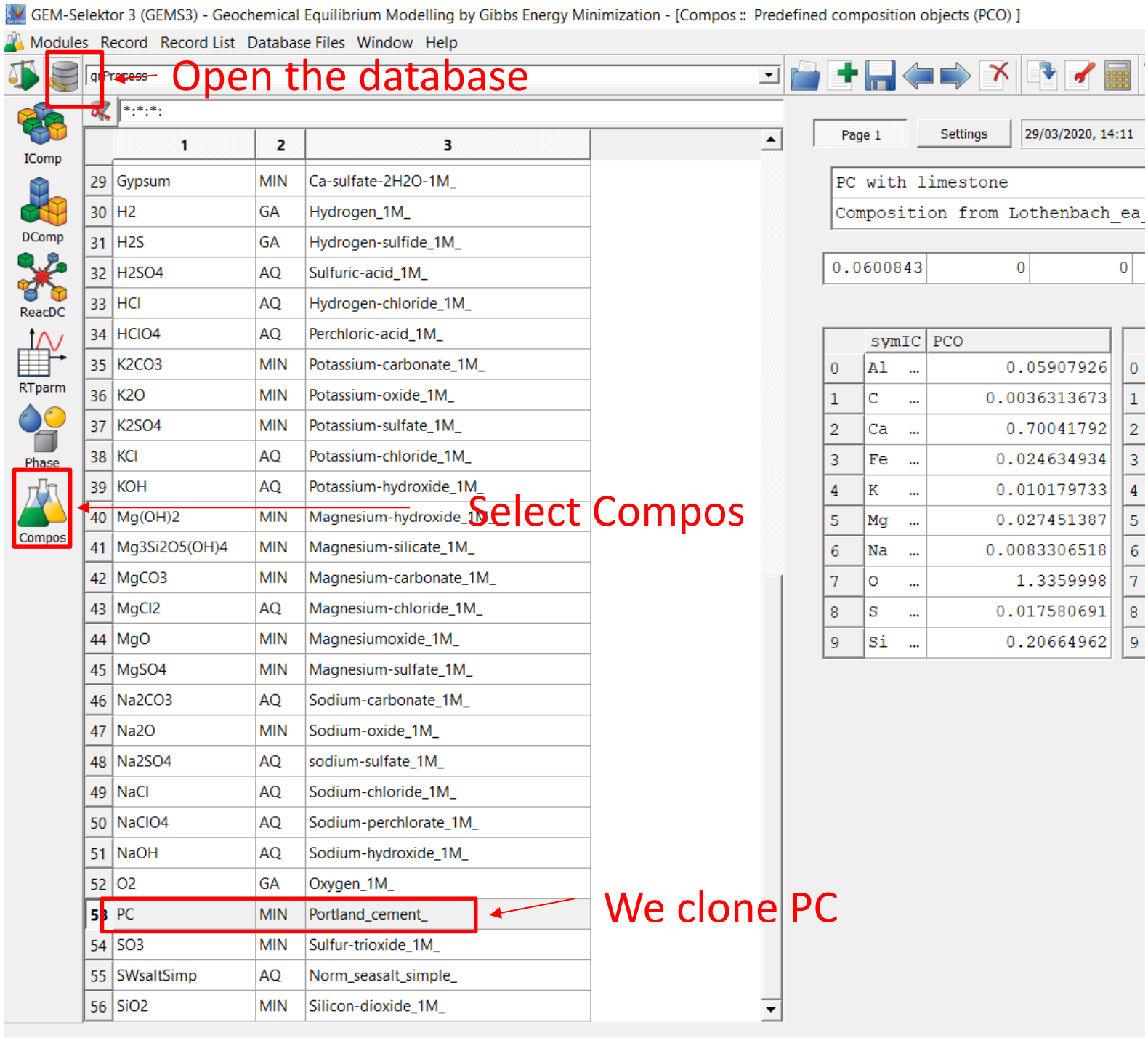
Do not touch the other values !!!

Content

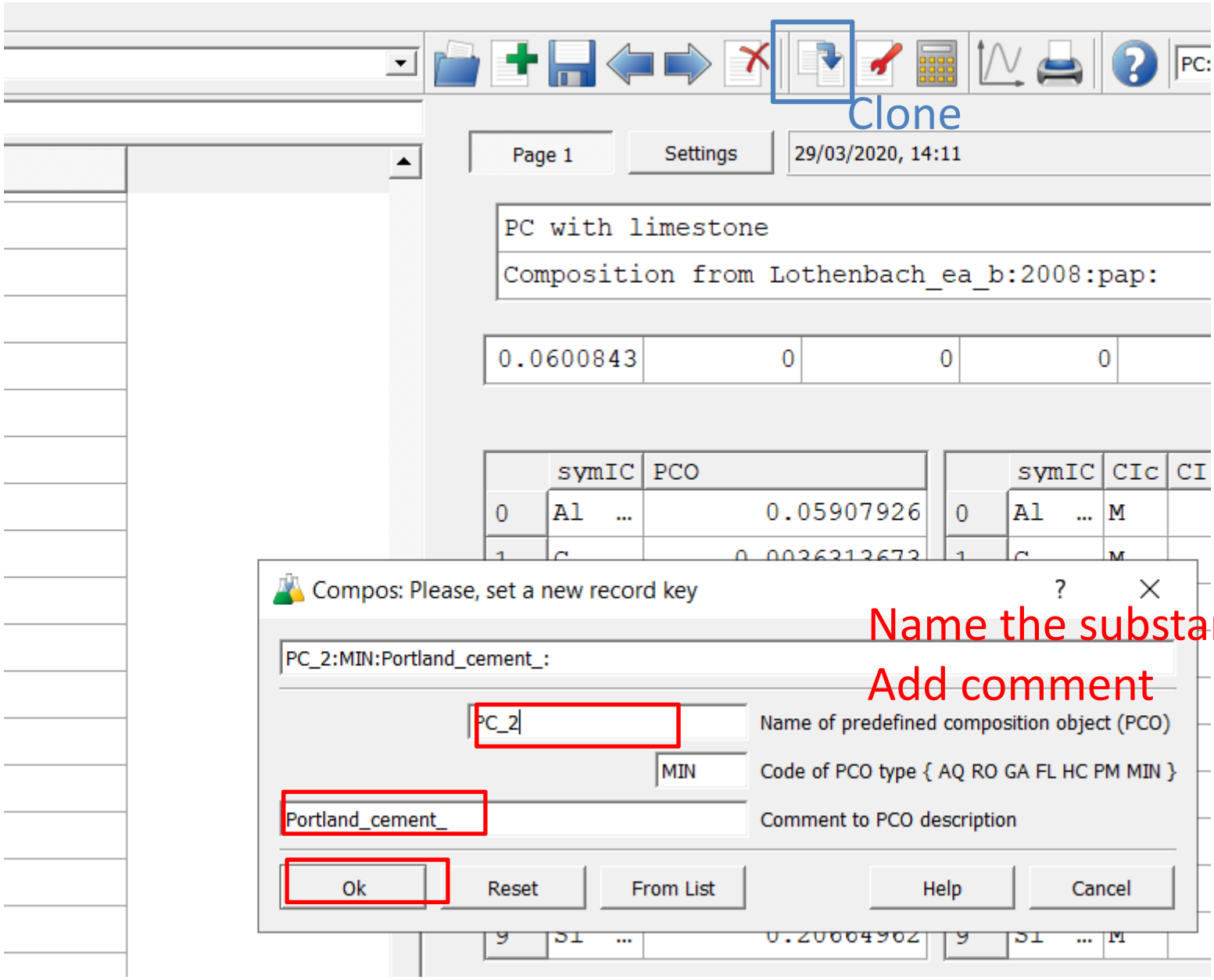
Example: calculate the phase changes in PC paste exposed to NaCl solution

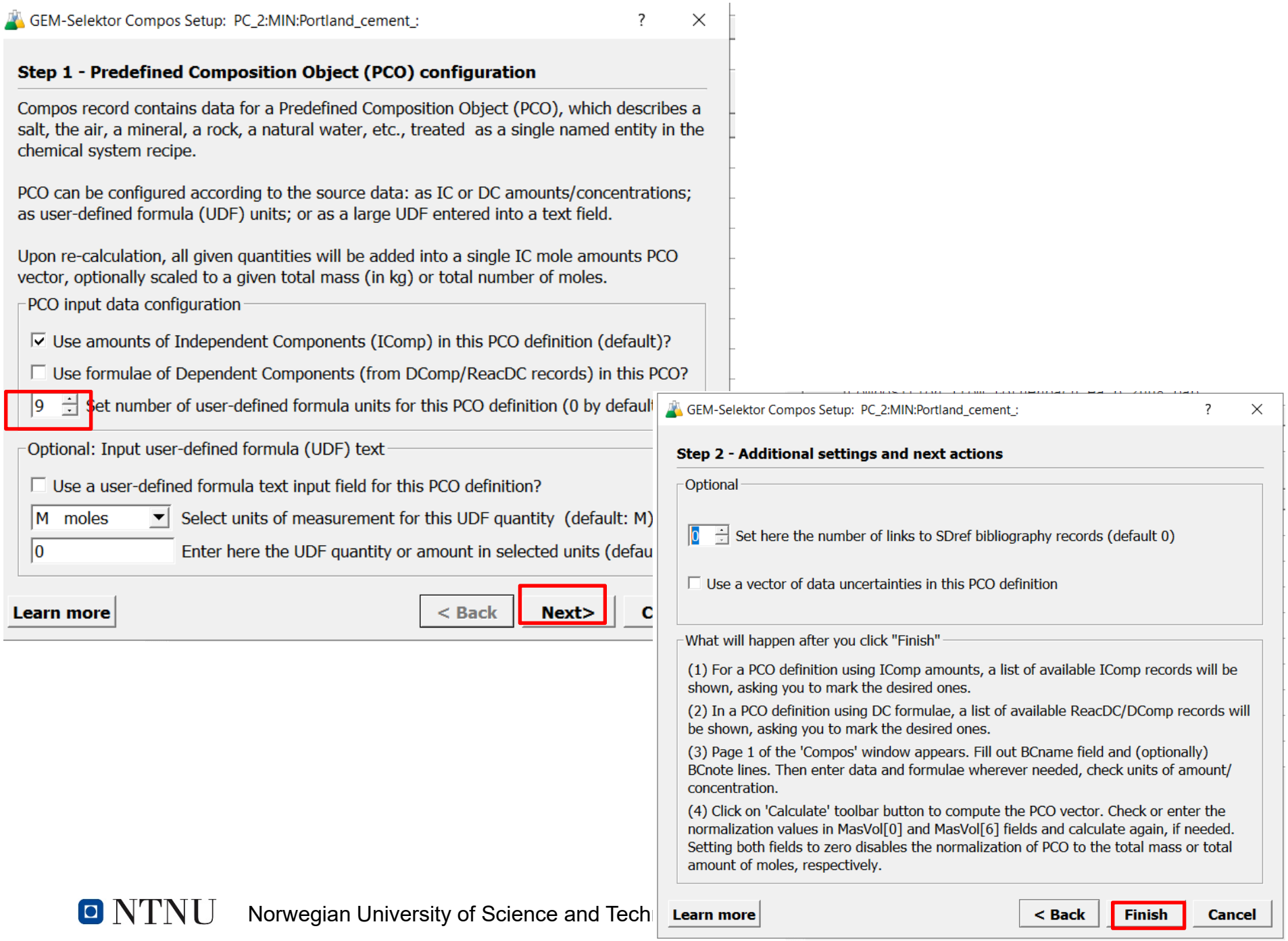
1. Create Single System – SysEq ☺
2. Make predefined composition of PC
3. Make Process

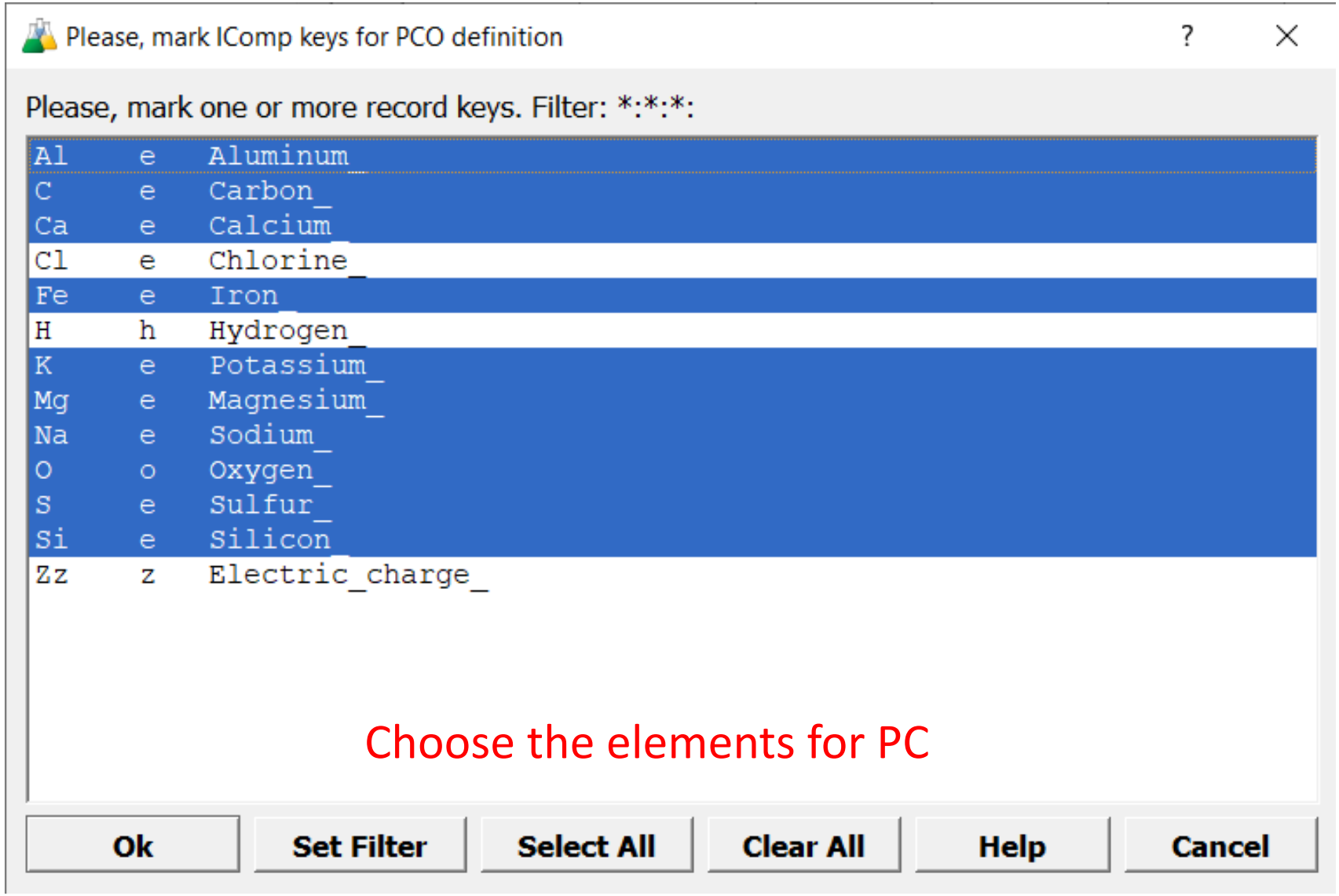
Task: calculate the phase changes in PC paste exposed to sea water



	1	2	3
29	Gypsum	MIN	Ca-sulfate-2H2O-1M_
30	H2	GA	Hydrogen_1M_
31	H2S	GA	Hydrogen-sulfide_1M_
32	H2SO4	AQ	Sulfuric-acid_1M_
33	HCl	AQ	Hydrogen-chloride_1M_
34	HClO4	AQ	Perchloric-acid_1M_
35	K2CO3	MIN	Potassium-carbonate_1M_
36	K2O	MIN	Potassium-oxide_1M_
37	K2SO4	MIN	Potassium-sulfate_1M_
38	KCl	AQ	Potassium-chloride_1M_
39	KOH	AQ	Potassium-hydroxide_1M_
40	Mg(OH)2	MIN	Magnesium-hydroxide_1M_
41	Mg3Si2O5(OH)4	MIN	Magnesium-silicate_1M_
42	MgCO3	MIN	Magnesium-carbonate_1M_
43	MgCl2	AQ	Magnesium-chloride_1M_
44	MgO	MIN	Magnesiumoxide_1M_
45	MgSO4	MIN	Magnesium-sulfate_1M_
46	Na2CO3	AQ	Sodium-carbonate_1M_
47	Na2O	MIN	Sodium-oxide_1M_
48	Na2SO4	AQ	sodium-sulfate_1M_
49	NaCl	AQ	Sodium-chloride_1M_
50	NaClO4	AQ	Sodium-perchlorate_1M_
51	NaOH	AQ	Sodium-hydroxide_1M_
52	O2	GA	Oxygen_1M_
53	PC	MIN	Portland_cement_
54	SO3	MIN	Sulfur-trioxide_1M_
55	SWsaltSimp	AQ	Norm_seasalt_simple_
56	SiO2	MIN	Silicon-dioxide_1M_

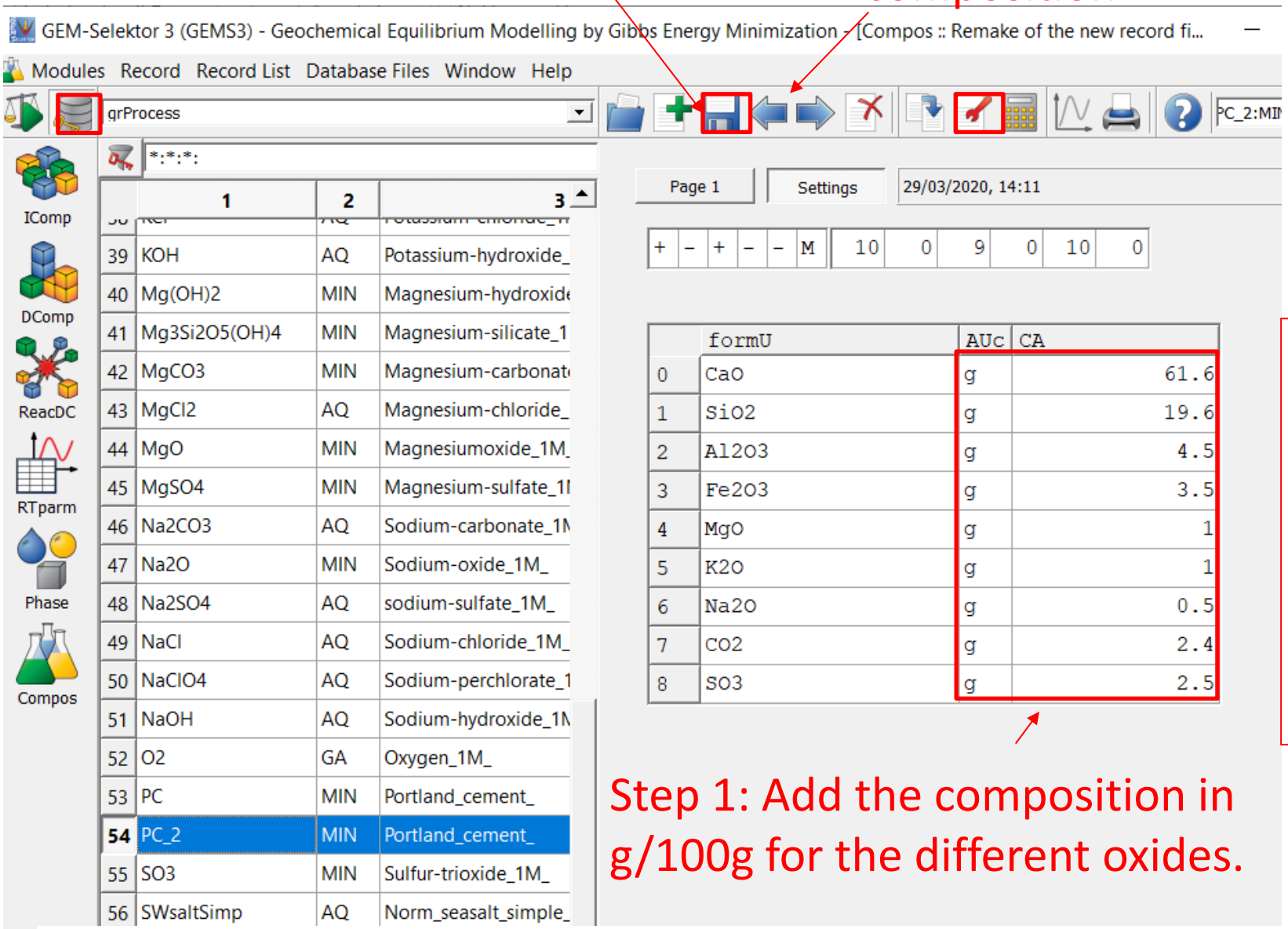

Clone
Page 1
Settings
29/03/2020, 14:11
PC with limestone
Composition from Lothenbach_ea_b:2008:pap:
0.0600843
0
0
0
symIC
PCO
0
Al ...
0.05907926
Compos: Please, set a new record key
PC_2:MIN:Portland_cement_:
PC_2
Name of predefined composition object (PCO)
MIN
Code of PCO type { AQ RO GA FL HC PM MIN }
Portland_cement_
Comment to PCO description
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 defaul
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 (defau
Learn more
< Back
Next>
C
GEM-Selektor Compos Setup: PC_2:MIN:Portland_cement_:
Step 2 - Additional settings and next actions
Optional
0
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) BCnote 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


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_
O o Oxygen_
S e Sulfur_
Si e Silicon_
Zz z Electric_charge_
Choose the elements for PC
Ok
Set Filter
Select All
Clear All
Help
Cancel

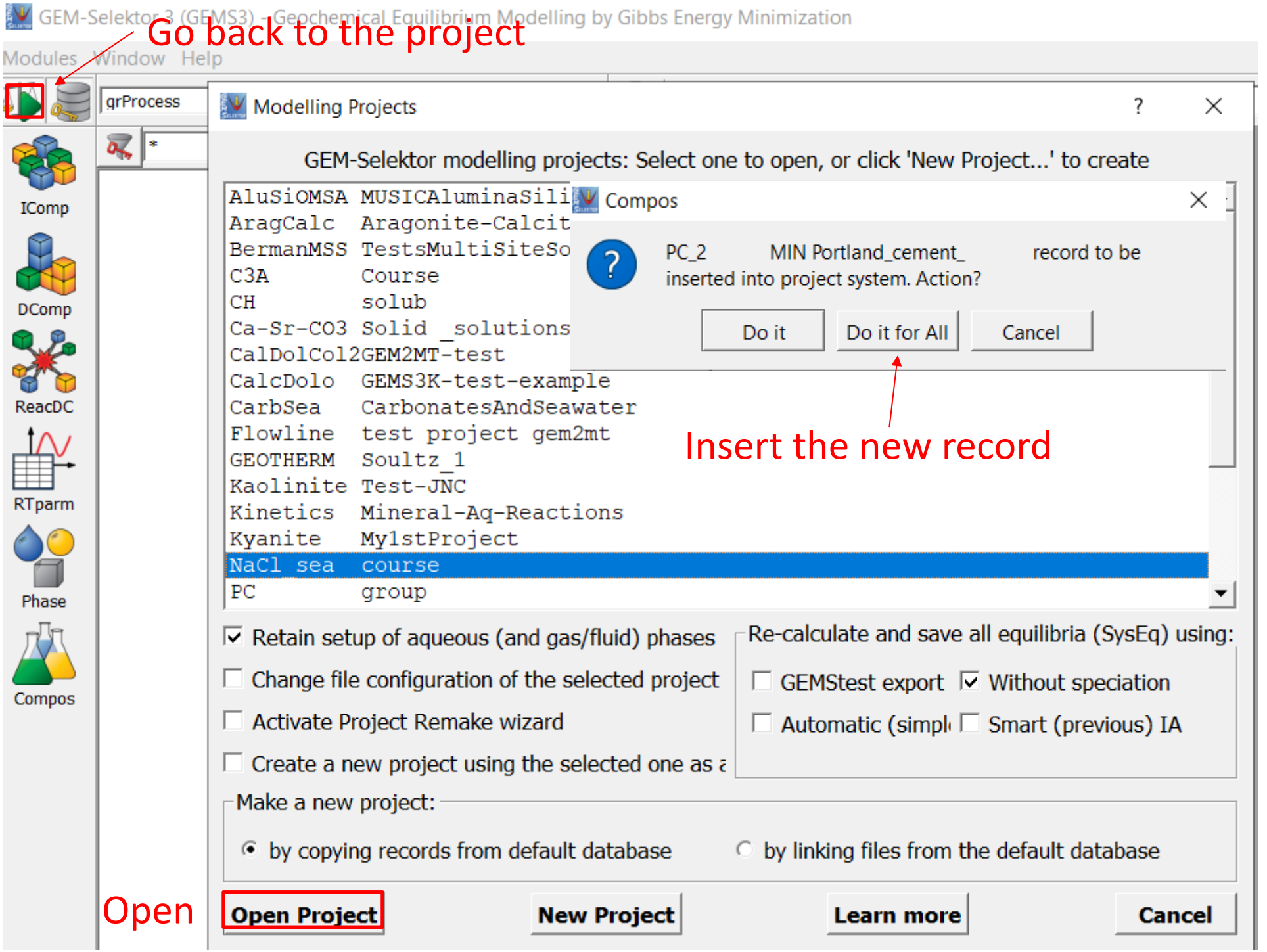
Step 3: Save

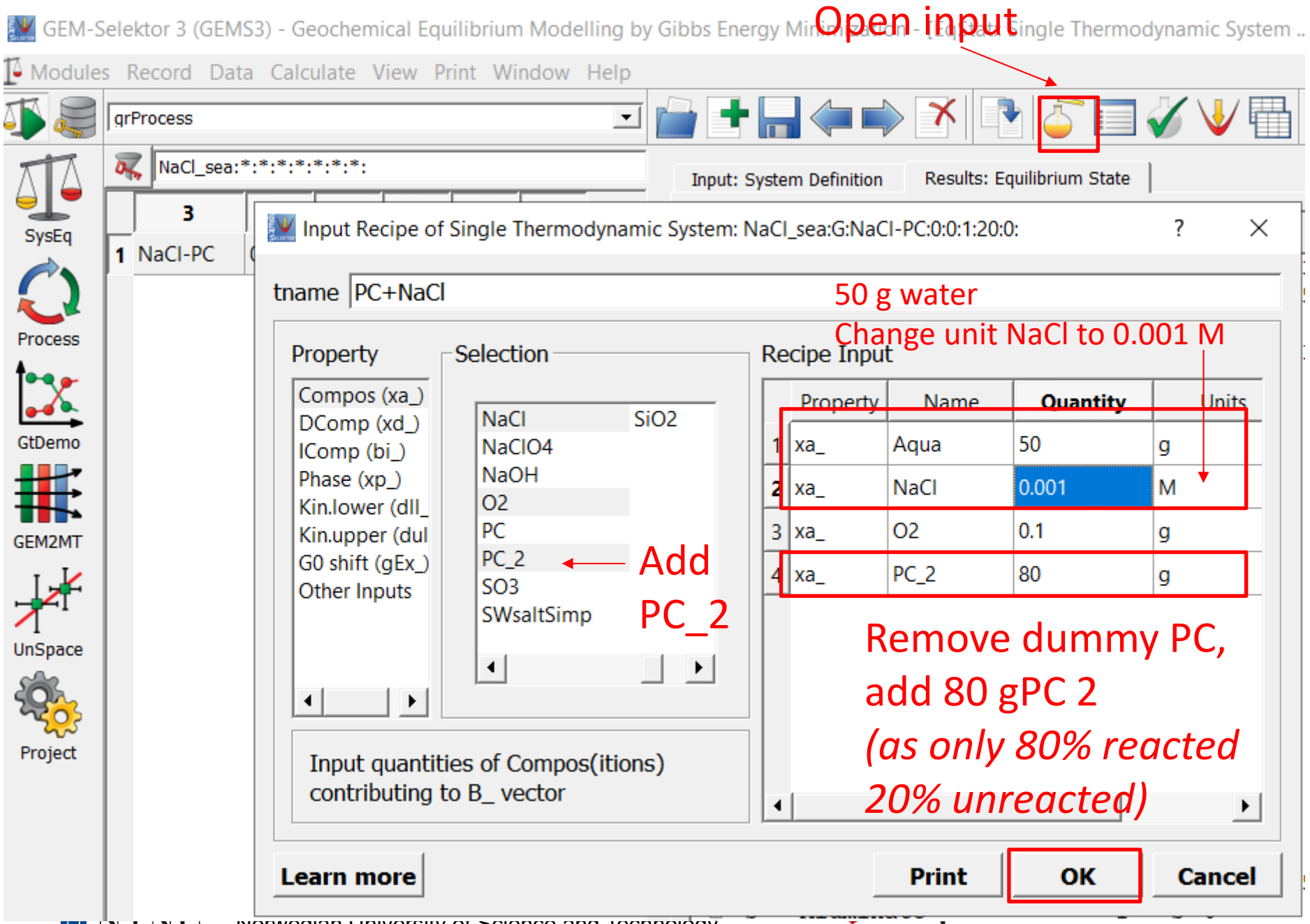
Step 2: Calculate the composition

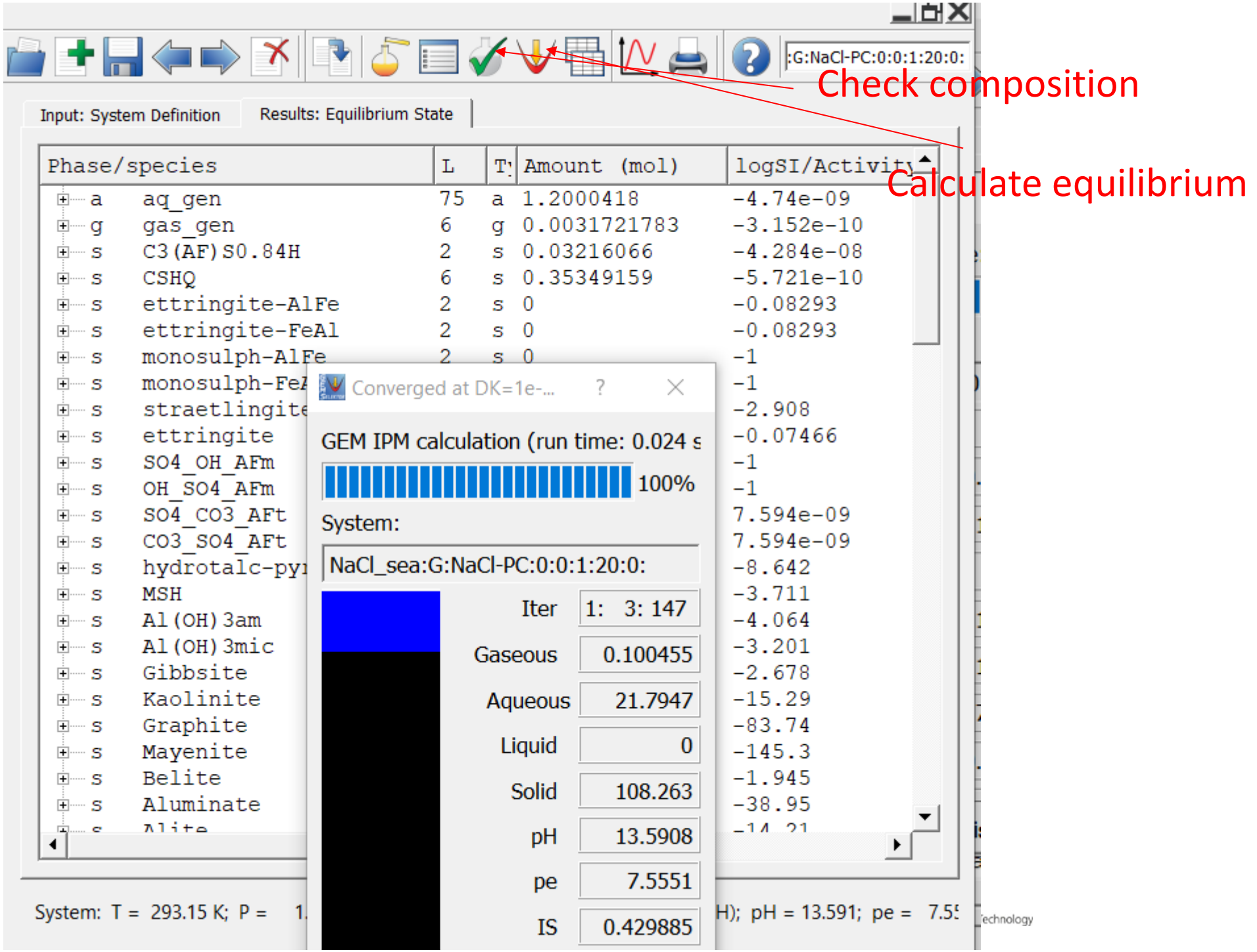


Step 1: Add the composition in g/100g for the different oxides.

61.6
19.6
4.5
3.5
1
1
0.5
2.4
2.5


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization
Modules Window Help
Go back to the project
grProcess
Modelling Projects
GEM-Selektor modelling projects: Select one to open, or click 'New Project...' to create
AluSiOMSA MUSICAluminaSili
AragCalc Aragonite-Calcit
BermanMSS TestsMultiSiteSo
C3A Course
CH solub
Ca-Sr-CO3 Solid _solutions
CalDolCol2GEM2MT-test
CalcDolo GEMS3K-test-example
CarbSea CarbonatesAndSeawater
Flowline test project gem2mt
GEOTHERM Soultz_1
Kaolinite Test-JNC
Kinetics Mineral-Aq-Reactions
Kyanite My1stProject
NaCl sea course
PC group
Compos
PC_2 MIN Portland_cement_ record to be inserted into project system. Action?
Do it
Do it for All
Cancel
Insert the new record
IComp
DComp
ReacDC
RTparm
Phase
Compos
Retain setup of aqueous (and gas/fluid) phases
Change file configuration of the selected project
Activate Project Remake wizard
Create a new project using the selected one as a
Re-calculate and save all equilibria (SysEq) using:
GEMStest export
Without speciation
Automatic (simpl
Smart (previous) IA
Make a new project:
by copying records from default database
by linking files from the default database
Open
Open Project
New Project
Learn more
Cancel


Open input
GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Input Single Thermodynamic System ..
Modules Record Data Calculate View Print Window Help
qrProcess
NaCl_sea:*:*:*:*:*:*:*:*:
Input: System Definition
Results: Equilibrium State
SysEq
Process
GtDemo
GEM2MT
UnSpace
Project
3
1 NaCl-PC
Input Recipe of Single Thermodynamic System: NaCl_sea:G:NaCl-PC:0:0:1:20:0:
tname PC+NaCl
50 g water
Change unit NaCl to 0.001 M
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
PC_2
SO3
SWsaltSimp
SiO2
Add PC_2
Recipe Input
Property Name Quantity Units
1 xa_ Aqua 50 g
2 xa_ NaCl 0.001 M
3 xa_ O2 0.1 g
4 xa_ PC_2 80 g
Remove dummy PC, add 80 gPC 2
(as only 80% reacted 20% unreacted)
Input quantities of Compos(itions) contributing to B_ vector
Learn more
Print
OK
Cancel


:G:NaCl-PC:0:0:1:20:0:
Check composition
Calculate equilibrium
Input: System Definition
Results: Equilibrium State
Phase/species
L
T
Amount (mol)
logSI/Activity
a aq_gen 75 a 1.2000418 -4.74e-09
g gas_gen 6 g 0.0031721783 -3.152e-10
s C3(AF)S0.84H 2 s 0.03216066 -4.284e-08
s CSHQ 6 s 0.35349159 -5.721e-10
s ettringite-AlFe 2 s 0 -0.08293
s ettringite-FeAl 2 s 0 -0.08293
s monosulph-AlFe 2 s 0 -1
s monosulph-FeA -1
s straetlingite -2.908
s ettringite -0.07466
s SO4_OH_AFm -1
s OH_SO4_AFm -1
s SO4_CO3_AFt 7.594e-09
s CO3_SO4_AFt 7.594e-09
s hydrotalc-py -8.642
s MSH -3.711
s Al(OH)3am -4.064
s Al(OH)3mic -3.201
s Gibbsite -2.678
s Kaolinite -15.29
s Graphite -83.74
s Mayenite -145.3
s Belite -1.945
s Aluminate -38.95
Converged at DK=1e-...
GEM IPM calculation (run time: 0.024 s
100%
System:
NaCl_sea:G:NaCl-PC:0:0:1:20:0:
Iter 1: 3: 147
Gaseous 0.100455
Aqueous 21.7947
Liquid 0
Solid 108.263
pH 13.5908
pe 7.5551
IS 0.429885
System: T = 293.15 K; P =
H); pH = 13.591; pe =

1.

EqIC | EqPh | EqDC | EqSurf | EqGen | 01/09/2020, 16:31

2.

PC+NaCl

Volume of phases formed in cm3

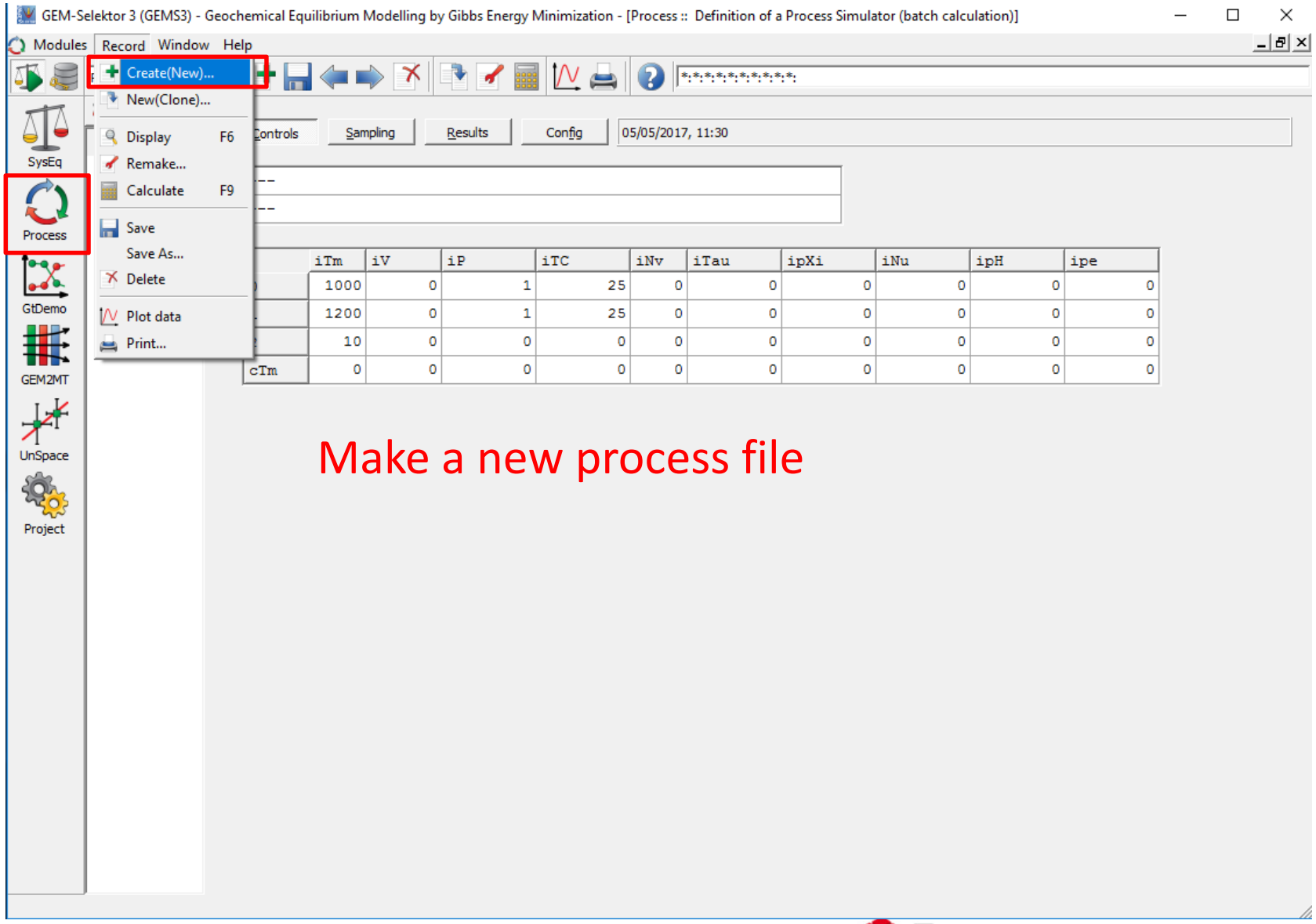
	PHnam		L1	Xa	Fa	phVol	phM
0	a	aq_gen	75	1.2000418	-4.7403874e-009	21.348212	21.794679
1	g	gas_gen	6	0.0031721783	-3.151912e-010	77.318629	0.10045529
2	s	C3(AF)S0.84H	2	0.03216066	-4.2839481e-008	4.6921773	13.863534
3	s	CSHQ	6	0.35349159	-5.7209551e-010	21.890504	49.557111
4	s	ettringite-AlFe	2	0	-0.082931306	0	0
5	s	ettringite-FeAl	2	0	-0.082931306	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	-2.9077778	0	0
9	s	ettringite	2	0	-0.074661509	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	0.028999967	7.594368e-009	6.7742513	12.017409
13	s	CO3_SO4_AFt	2	3.686145e-007	7.5943679e-009	8.6106554e-0…	0.0001527516
14	s	hydrotalc-pyro	2	0	-8.6422713	0	0
15	s	MSH	2	0	-3.7112017	0	0
16	s	Al(OH)3am	1	0	-4.0644775	0	0

Content

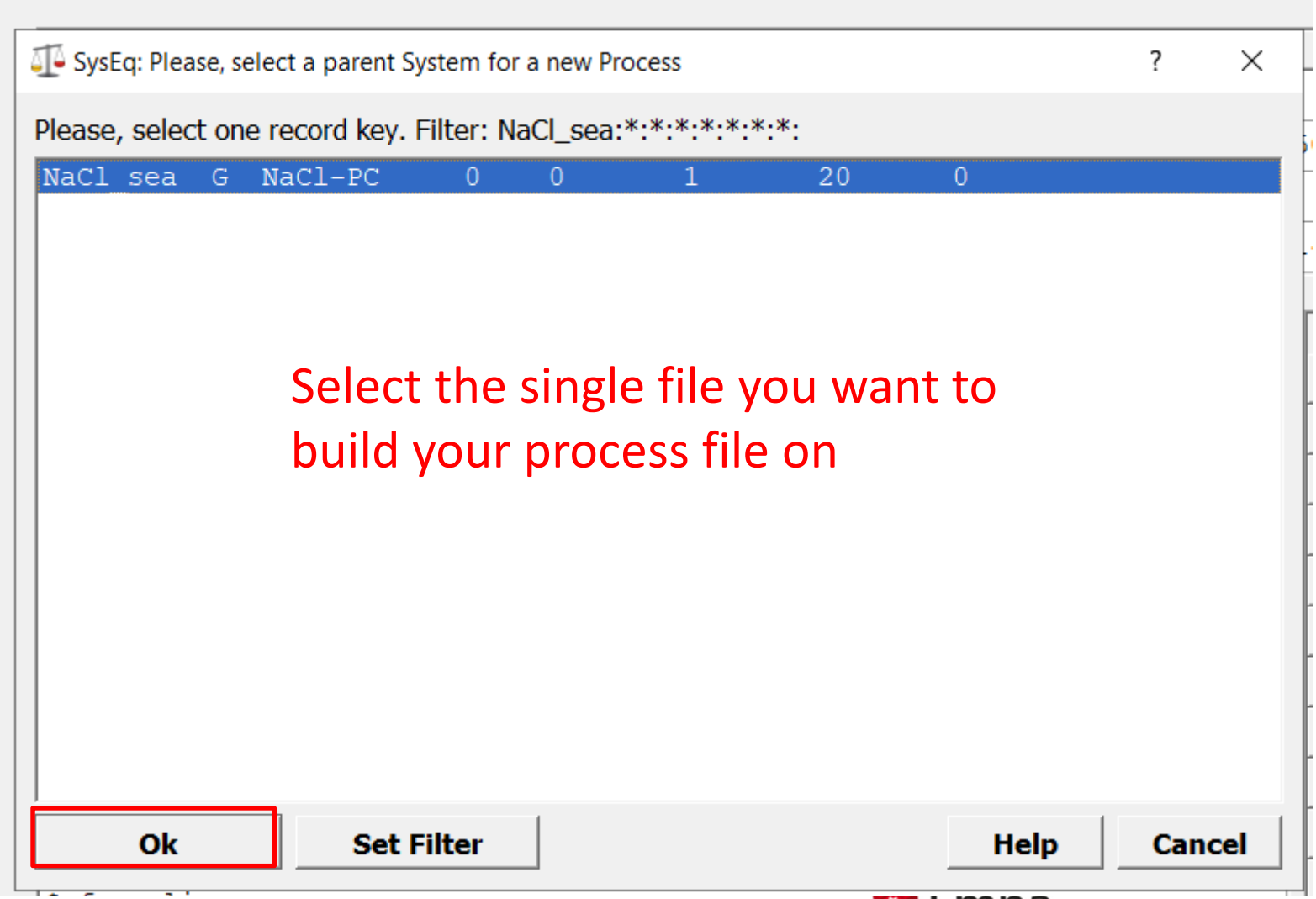
Example: calculate the phase changes in PC paste exposed to NaCl solution

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

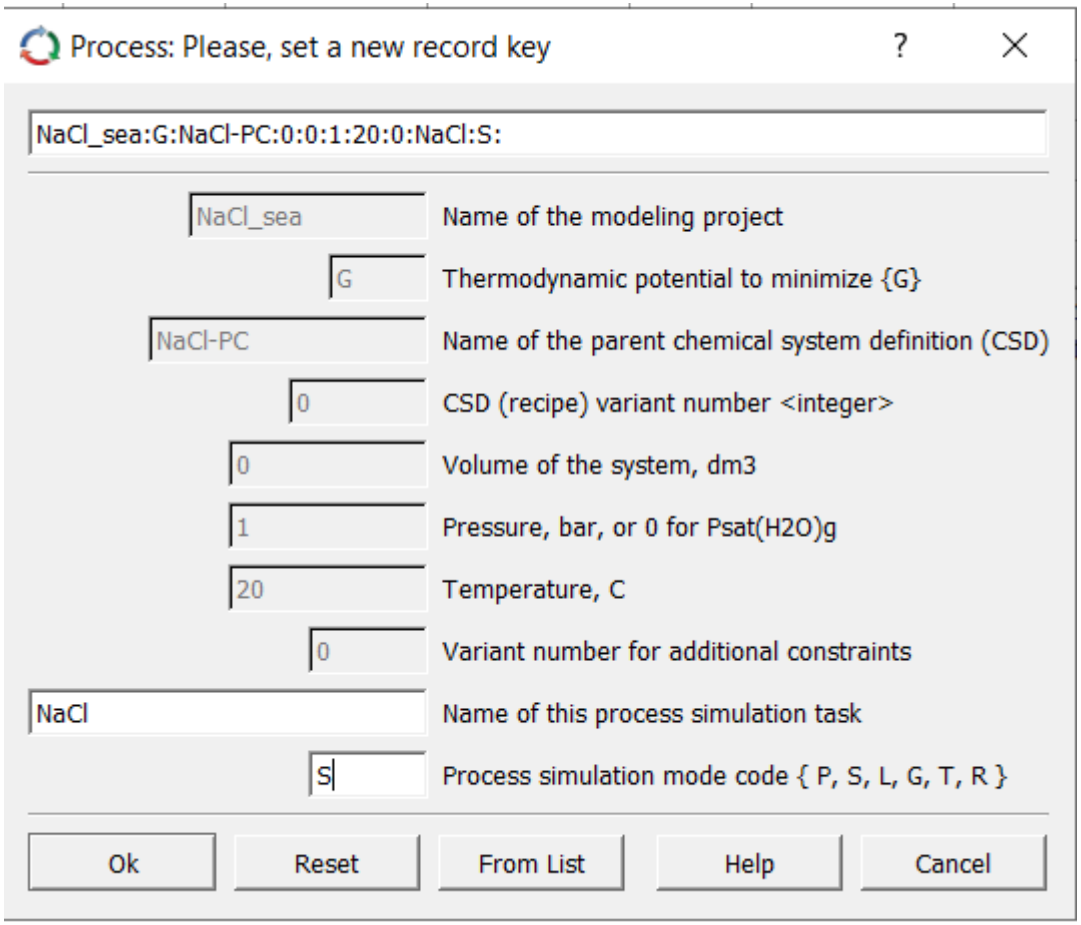
Task: calculate the phase changes in PC paste exposed to sea water


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]
Modules
Record
Window
Help
Create(New)...
New(Clone)...
Display F6
Remake...
Calculate F9
Save
Save As...
Delete
Plot data
Print...
SysEq
Process
GtDemo
GEM2MT
UnSpace
Project
Controls
Sampling
Results
Config
05/05/2017, 11:30
iTm iV iP iTC iNv iTau ipXi iNu ipH ipe
1000 0 1 25 0 0 0 0 0 0
1200 0 1 25 0 0 0 0 0 0
10 0 0 0 0 0 0 0 0 0
cTm 0 0 0 0 0 0 0 0 0 0
Make a new process file

Make a new process

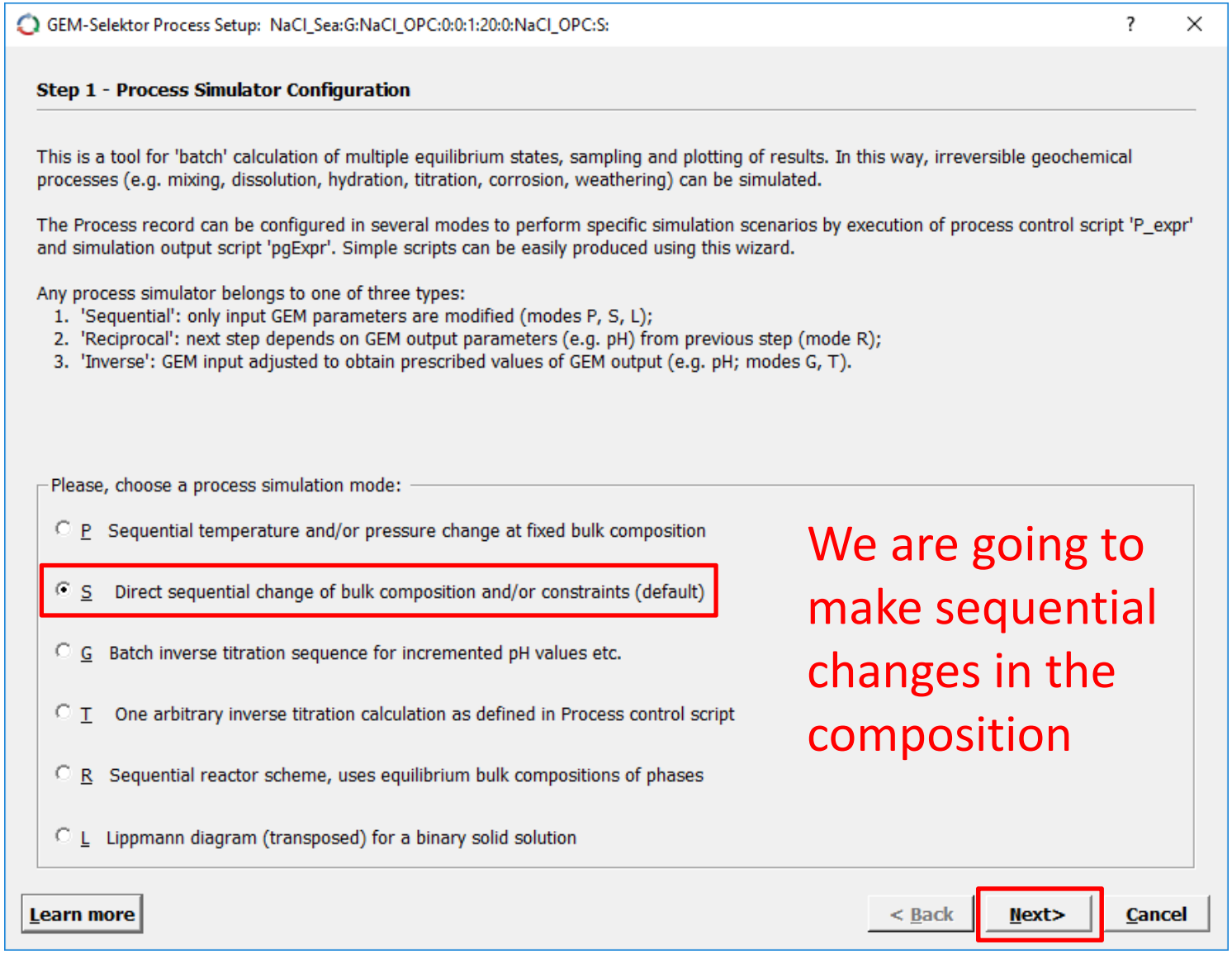


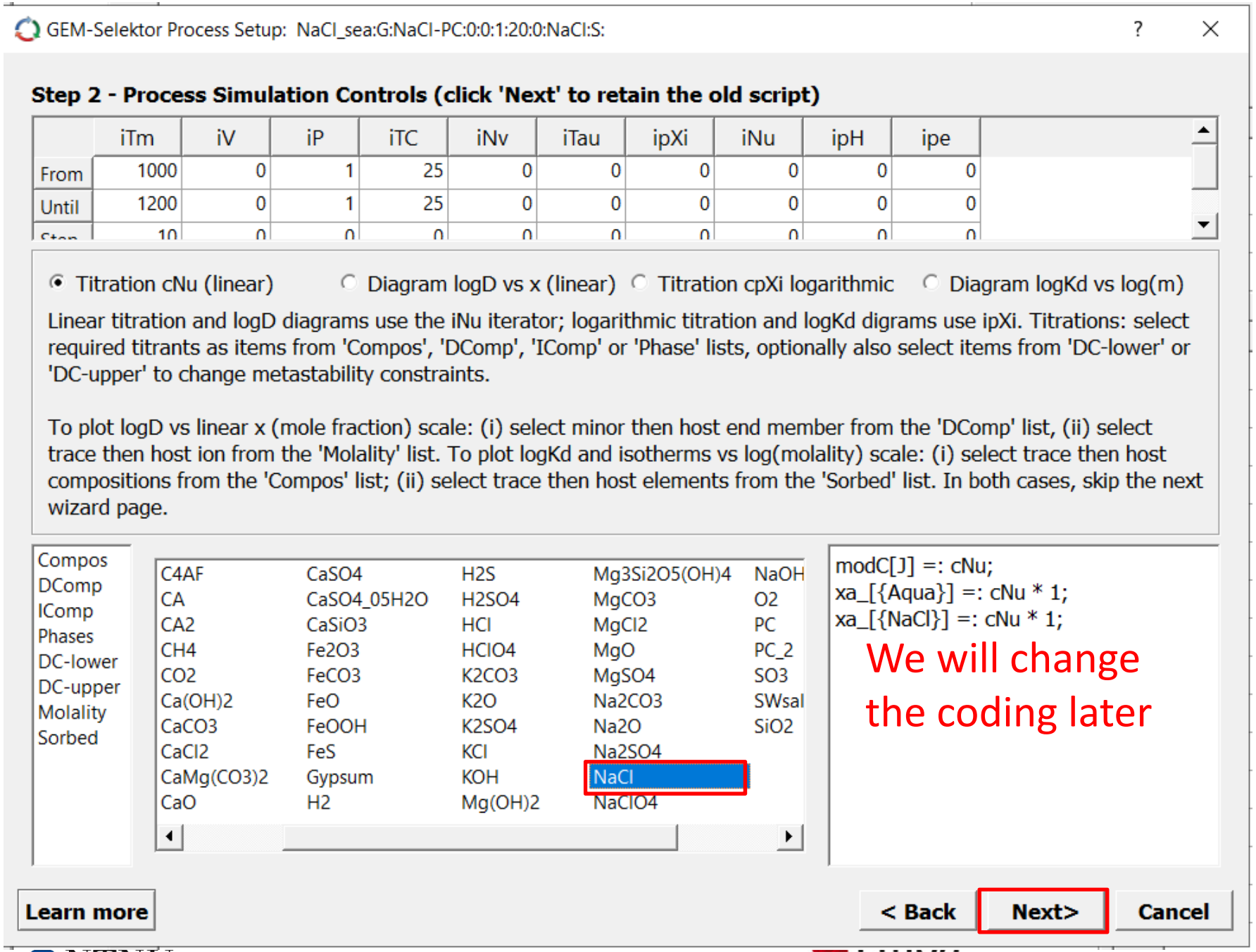
Make a new process

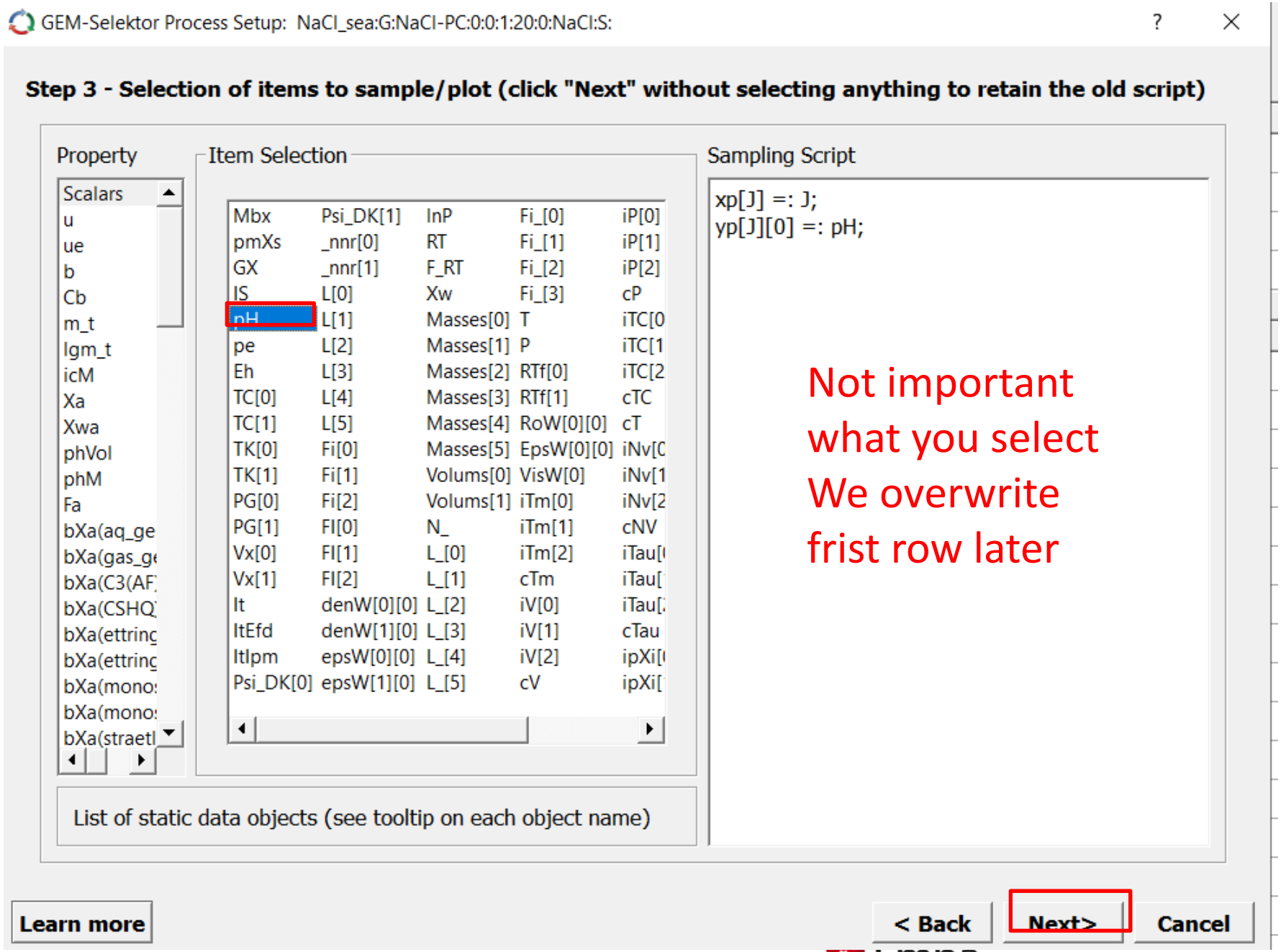


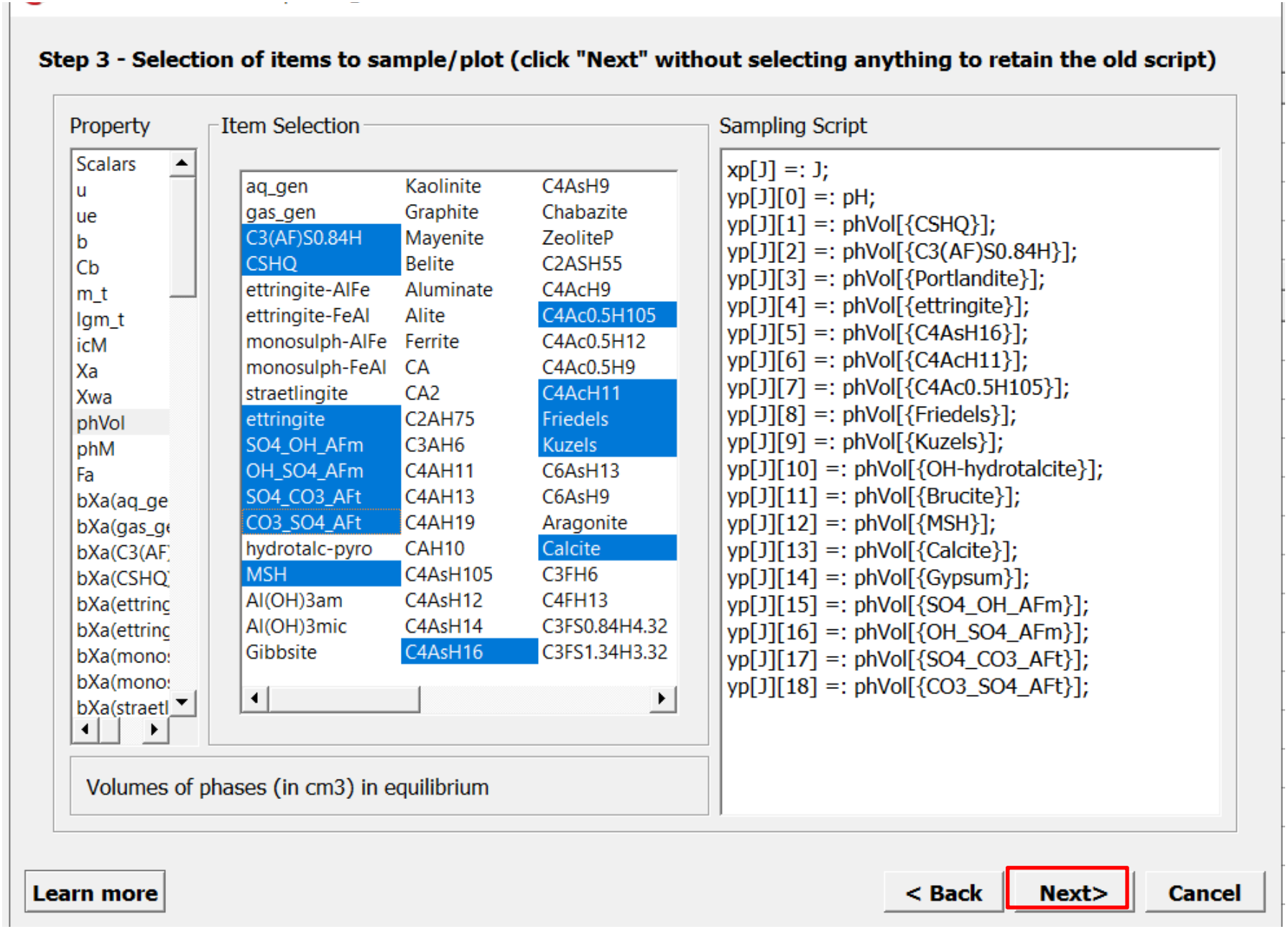
Name your process file

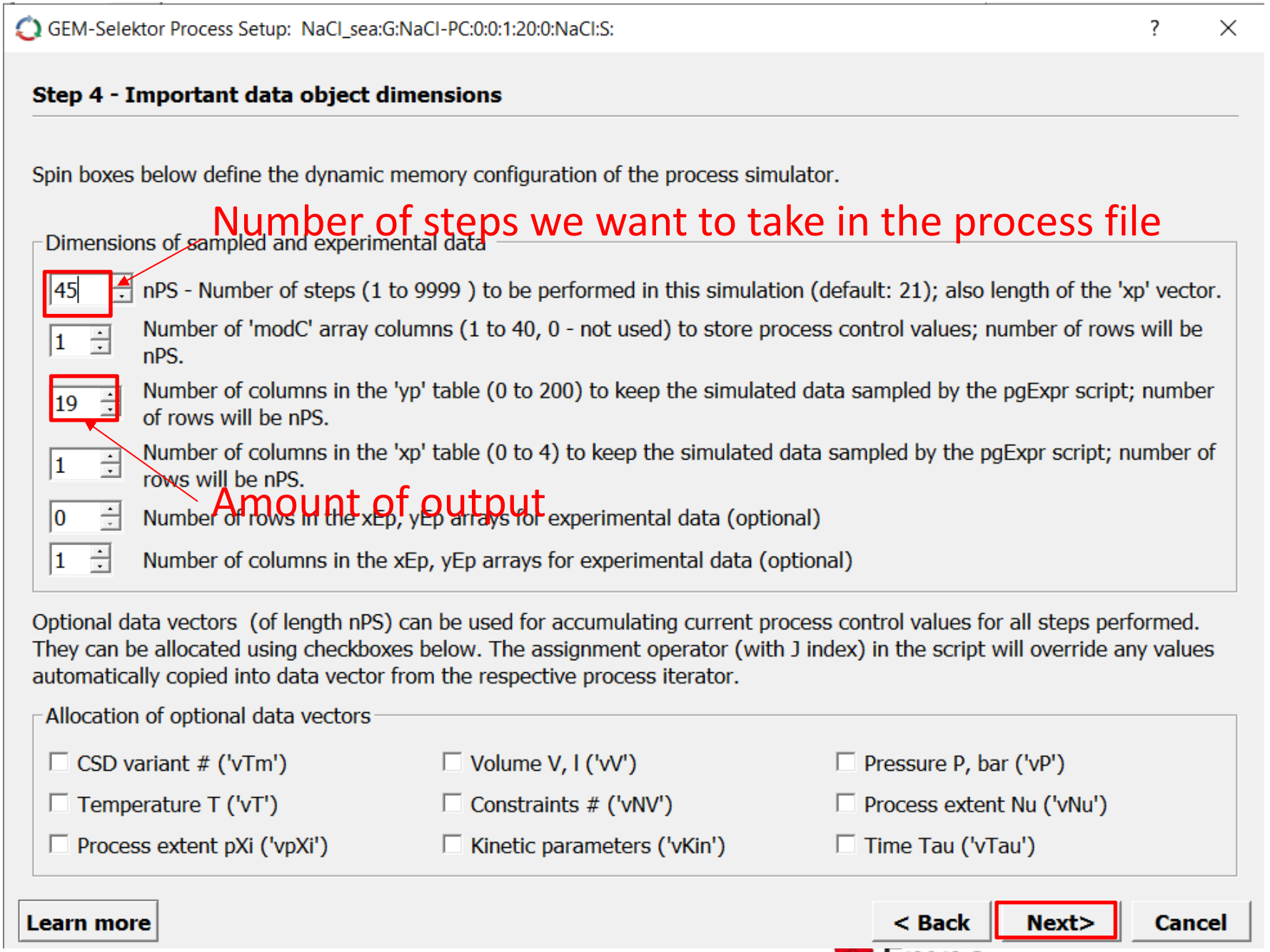
S → sequential changes

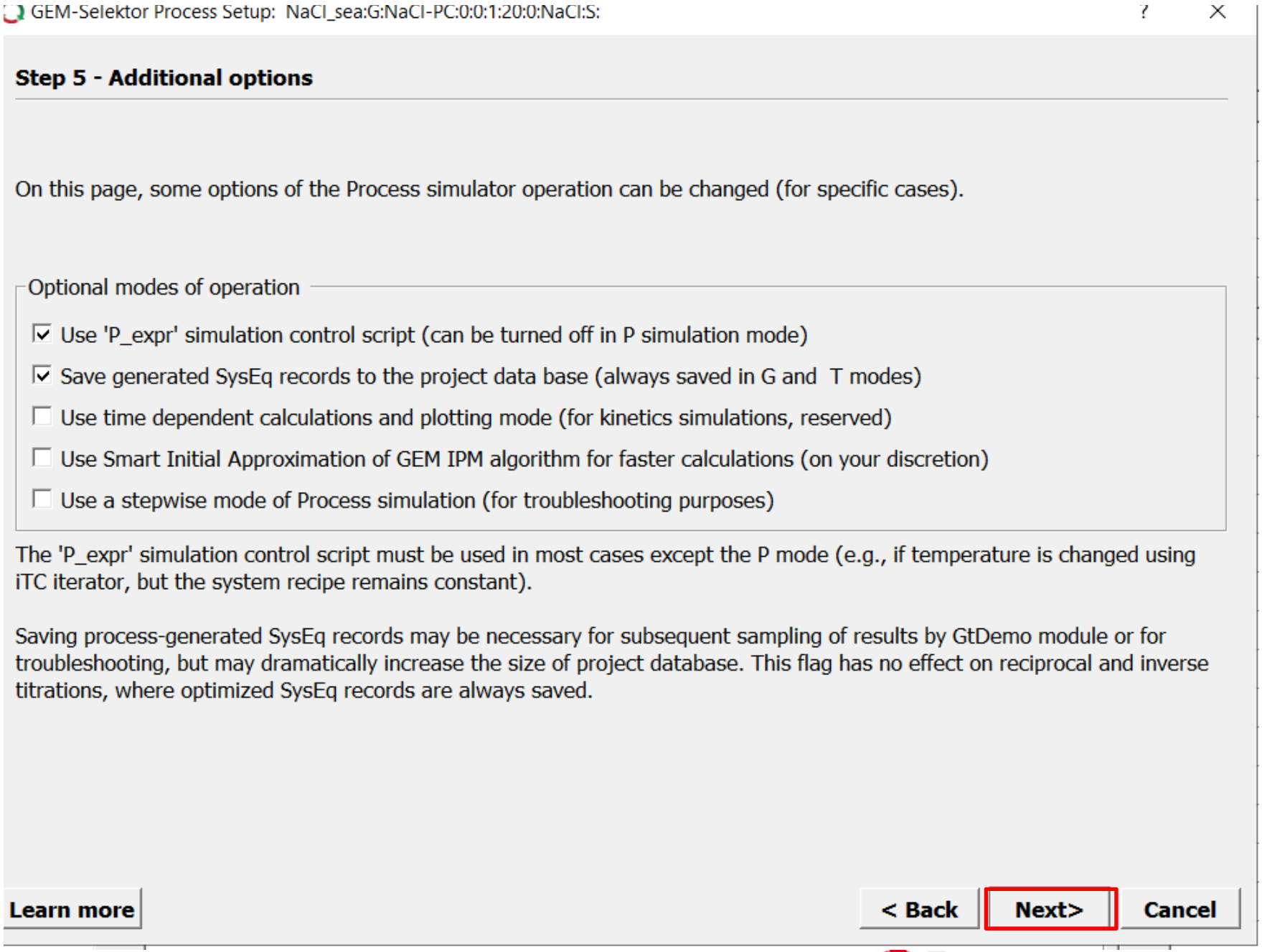

GEM-Selektor Process Setup: NaCl_Sea:G:NaCl_OPC:0:0:1:20:0:NaCl_OPC:S:
Step 1 - Process Simulator Configuration
This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, irreversible geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) can be simulated.
The Process record can be configured in several modes to perform specific simulation scenarios by execution of process control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be easily produced using this wizard.
Any process simulator belongs to one of three types:
1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from previous step (mode R);
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; modes G, T).
Please, choose a process simulation mode:
P Sequential temperature and/or pressure change at fixed bulk composition
S Direct sequential change of bulk composition and/or constraints (default)
G Batch inverse titration sequence for incremented pH values etc.
T One arbitrary inverse titration calculation as defined in Process control script
R Sequential reactor scheme, uses equilibrium bulk compositions of phases
L Lippmann diagram (transposed) for a binary solid solution
We are going to make sequential changes in the composition
Learn more
< Back
Next>
Cancel

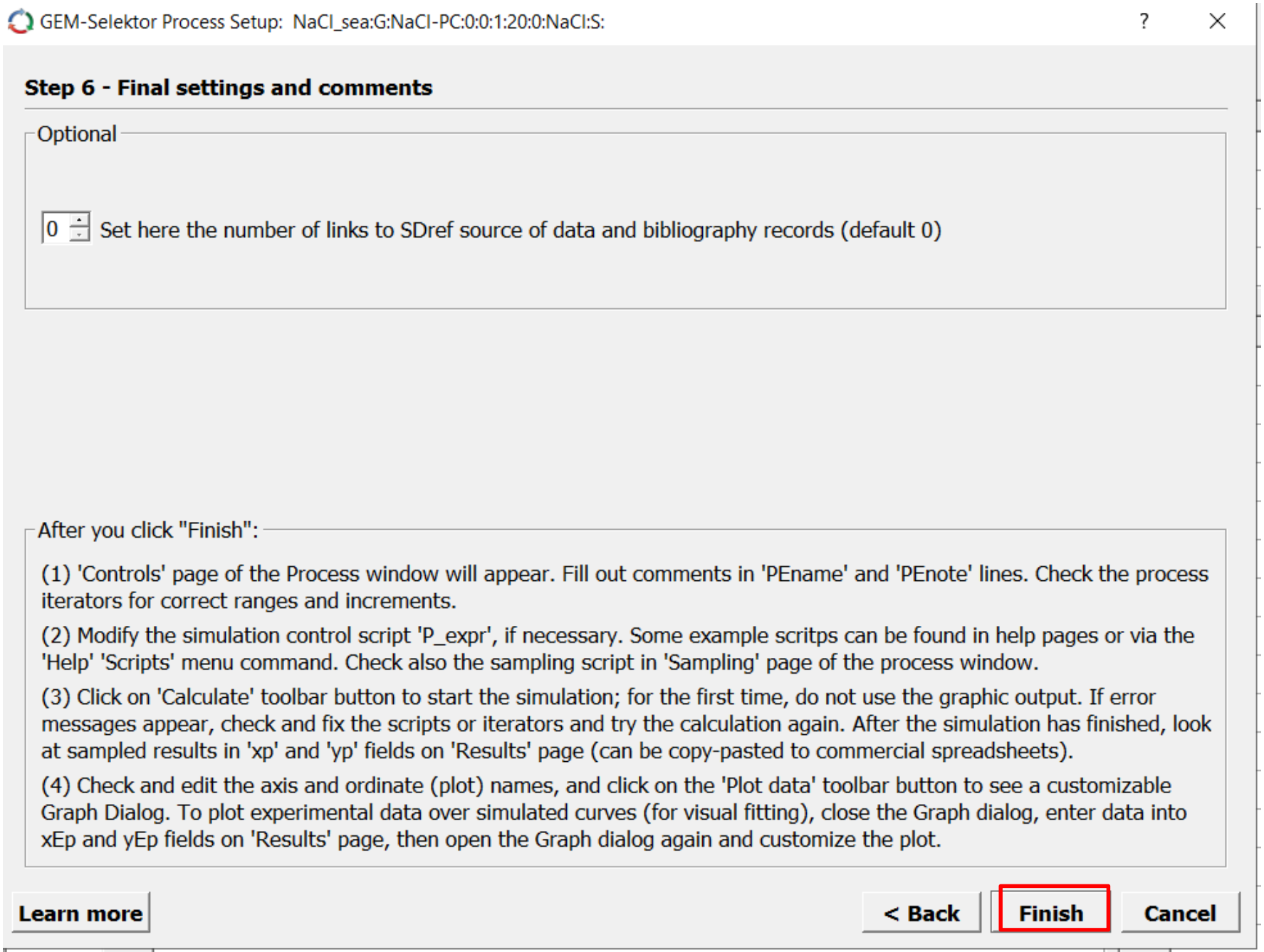

GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Step 2 - Process Simulation Controls (click 'Next' to retain the old script)
iTm iV iP iTC iNv iTau ipXi iNu ipH ipe
From 1000 0 1 25 0 0 0 0 0 0
Until 1200 0 1 25 0 0 0 0 0 0
Titration cNu (linear)
Diagram logD vs x (linear)
Titration cpXi logarithmic
Diagram logKd vs log(m)
Linear titration and logD diagrams use the iNu iterator; logarithmic titration and logKd digrams 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
C4AF CaSO4 H2S Mg3Si2O5(OH)4 NaOH
CA CaSO4_05H2O H2SO4 MgCO3 O2
CA2 CaSiO3 HCl MgCl2 PC
CH4 Fe2O3 HClO4 MgO PC_2
CO2 FeCO3 K2CO3 MgSO4 SO3
Ca(OH)2 FeO K2O Na2CO3 SWsal
CaCO3 FeOOH K2SO4 Na2O SiO2
CaCl2 FeS KCl Na2SO4
CaMg(CO3)2 Gypsum KOH NaCl
CaO H2 Mg(OH)2 NaClO4
modC[J] =: cNu;
xa_[{Aqua}] =: cNu * 1;
xa_[{NaCl}] =: cNu * 1;
We will change the coding later
Learn more
< Back
Next>
Cancel

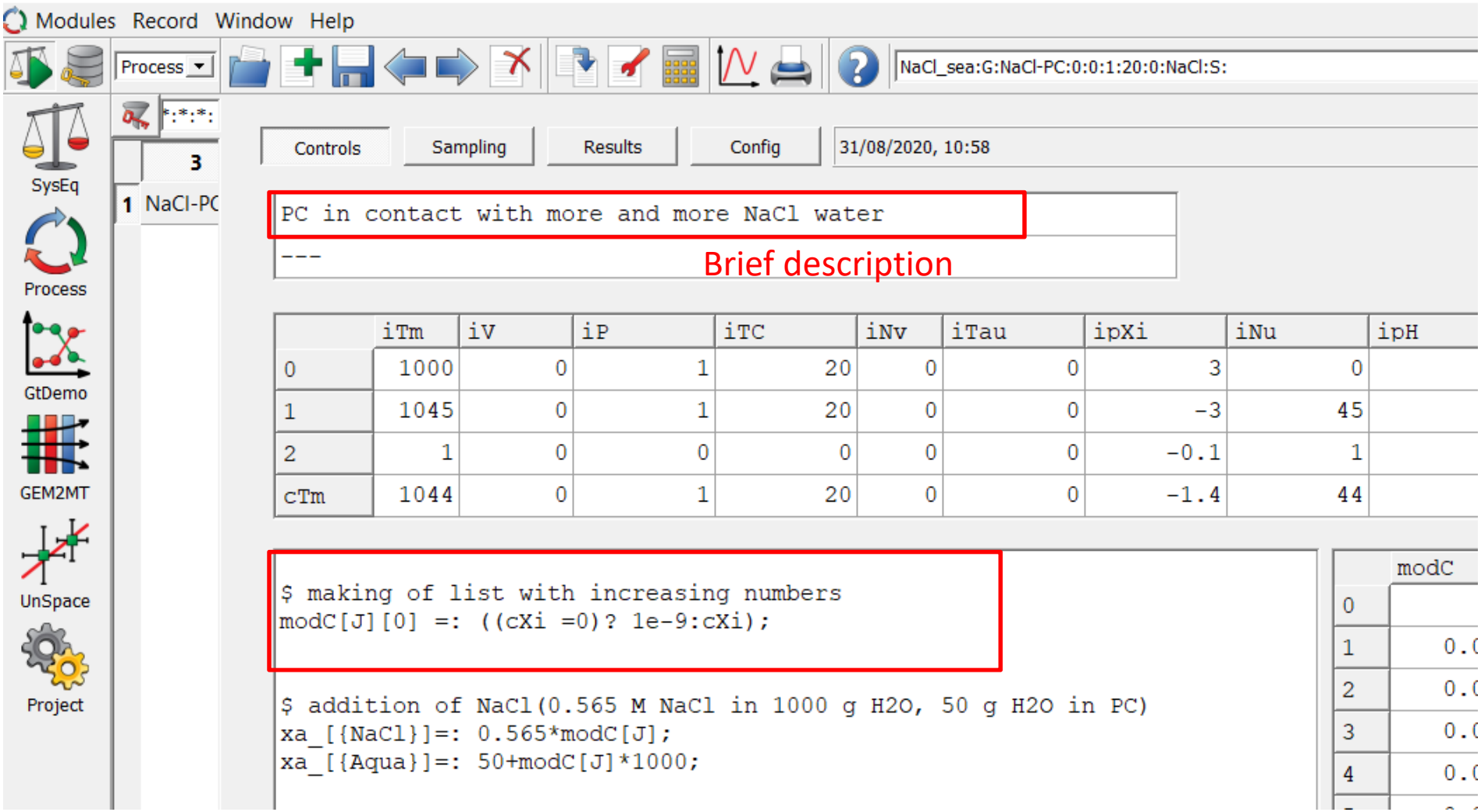

GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Step 3 - Selection of items to sample/plot (click "Next" without selecting anything to retain the old script)
Property
Item Selection
Sampling Script
Scalars
u
ue
b
Cb
m_t
lgm_t
icM
Xa
Xwa
phVol
phM
Fa
bXa(aq_ge
bXa(gas_ge
bXa(C3(AF
bXa(CSHQ
bXa(ettring
bXa(ettring
bXa(monos
bXa(monos
bXa(straetl
Mbx Psi_DK[1] InP Fi_[0] iP[0]
pmXs _nnr[0] RT Fi_[1] iP[1]
GX _nnr[1] F_RT Fi_[2] iP[2]
IS L[0] Xw Fi_[3] cP
pH L[1] Masses[0] T iTC[0
pe L[2] Masses[1] P iTC[1
Eh L[3] Masses[2] RTf[0] iTC[2
TC[0] L[4] Masses[3] RTf[1] cTC
TC[1] L[5] Masses[4] RoW[0][0] cT
TK[0] Fi[0] Masses[5] EpsW[0][0] iNv[0
TK[1] Fi[1] Volums[0] VisW[0] iNv[1
PG[0] Fi[2] Volums[1] iTm[0] iNv[2
PG[1] FI[0] N_ iTm[1] cNV
Vx[0] FI[1] L_[0] iTm[2] iTau[
Vx[1] FI[2] L_[1] cTm iTau[
It denW[0][0] L_[2] iV[0] iTau[
ItEfd denW[1][0] L_[3] iV[1] cTau
Itlpm epsW[0][0] L_[4] iV[2] ipXi[
Psi_DK[0] epsW[1][0] L_[5] cV ipXi[
xp[J] =: J;
yp[J][0] =: pH;
Not important
what you select
We overwrite
frist row later
List of static data objects (see tooltip on each object name)
Learn more
< Back
Next>
Cancel


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_ge
bXa(gas_ge
bXa(C3(AF
bXa(CSHQ
bXa(ettring
bXa(ettring
bXa(mono
bXa(mono
bXa(straetl
Item Selection
aq_gen
gas_gen
C3(AF)S0.84H
CSHQ
ettringite-AlFe
ettringite-FeAl
monosulph-AlFe
monosulph-FeAl
straetlingite
ettringite
SO4_OH_AFm
OH_SO4_AFm
SO4_CO3_AFt
CO3_SO4_AFt
hydrotalc-pyro
MSH
Al(OH)3am
Al(OH)3mic
Gibbsite
Kaolinite
Graphite
Mayenite
Belite
Aluminate
Alite
Ferrite
CA
CA2
C2AH75
C3AH6
C4AH11
C4AH13
C4AH19
CAH10
C4AsH105
C4AsH12
C4AsH14
C4AsH16
C4AsH9
Chabazite
ZeoliteP
C2ASH55
C4AcH9
C4Ac0.5H105
C4Ac0.5H12
C4Ac0.5H9
C4AcH11
Friedels
Kuzels
C6AsH13
C6AsH9
Aragonite
Calcite
C3FH6
C4FH13
C3FS0.84H4.32
C3FS1.34H3.32
Sampling Script
xp[J] =: J;
yp[J][0] =: pH;
yp[J][1] =: phVol[{CSHQ}];
yp[J][2] =: phVol[{C3(AF)S0.84H}];
yp[J][3] =: phVol[{Portlandite}];
yp[J][4] =: phVol[{ettringite}];
yp[J][5] =: phVol[{C4AsH16}];
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-hydrotalcite}];
yp[J][11] =: phVol[{Brucite}];
yp[J][12] =: phVol[{MSH}];
yp[J][13] =: phVol[{Calcite}];
yp[J][14] =: phVol[{Gypsum}];
yp[J][15] =: phVol[{SO4_OH_AFm}];
yp[J][16] =: phVol[{OH_SO4_AFm}];
yp[J][17] =: phVol[{SO4_CO3_AFt}];
yp[J][18] =: phVol[{CO3_SO4_AFt}];
Volumes of phases (in cm3) in equilibrium
Learn more
< Back
Next>
Cancel


GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Step 4 - Important data object dimensions
Spin boxes below define the dynamic memory configuration of the process simulator.
Number of steps we want to take in the process file
Dimensions of sampled and experimental data
45
nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' vector.
1
Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be nPS.
19
Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
1
Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
Amount of output
0
Number of rows in the xEp, yEp arrays for experimental data (optional)
1
Number of columns in the xEp, yEp arrays for experimental data (optional)
Optional data vectors (of length nPS) can be used for accumulating current process control values for all steps performed. They can be allocated using checkboxes below. The assignment operator (with J index) in the script will override any values automatically copied into data vector from the respective process iterator.
Allocation of optional data vectors
CSD variant # ('vTm')
Volume V, l ('vV')
Pressure P, bar ('vP')
Temperature T ('vT')
Constraints # ('vNV')
Process extent Nu ('vNu')
Process extent pXi ('vpXi')
Kinetic parameters ('vKin')
Time Tau ('vTau')
Learn more
< Back
Next>
Cancel


GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Step 5 - Additional options
On this page, some options of the Process simulator operation can be changed (for specific cases).
Optional modes of operation
Use 'P_expr' simulation control script (can be turned off in P simulation mode)
Save generated SysEq records to the project data base (always saved in G and T modes)
Use time dependent calculations and plotting mode (for kinetics simulations, reserved)
Use Smart Initial Approximation of GEM IPM algorithm for faster calculations (on your discretion)
Use a stepwise mode of Process simulation (for troubleshooting purposes)
The 'P_expr' simulation control script must be used in most cases except the P mode (e.g., if temperature is changed using iTC iterator, but the system recipe remains constant).
Saving process-generated SysEq records may be necessary for subsequent sampling of results by GtDemo module or for troubleshooting, but may dramatically increase the size of project database. This flag has no effect on reciprocal and inverse titrations, where optimized SysEq records are always saved.
Learn more
< Back
Next>
Cancel


GEM-Selektor Process Setup: NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Step 6 - Final settings and comments
Optional
0
Set here the number of links to SDref source of data and bibliography records (default 0)
After you click "Finish":
(1) 'Controls' page of the Process window will appear. Fill out comments in 'PEname' and 'PEnote' lines. Check the process iterators for correct ranges and increments.
(2) Modify the simulation control script 'P_expr', if necessary. Some example scritps can be found in help pages or via the 'Help' 'Scripts' menu command. Check also the sampling script in 'Sampling' page of the process window.
(3) Click on 'Calculate' toolbar button to start the simulation; for the first time, do not use the graphic output. If error messages appear, check and fix the scripts or iterators and try the calculation again. After the simulation has finished, look at sampled results in 'xp' and 'yp' fields on 'Results' page (can be copy-pasted to commercial spreadsheets).
(4) Check and edit the axis and ordinate (plot) names, and click on the 'Plot data' toolbar button to see a customizable Graph Dialog. To plot experimental data over simulated curves (for visual fitting), close the Graph dialog, enter data into xEp and yEp fields on 'Results' page, then open the Graph dialog again and customize the plot.
Learn more
< Back
Finish
Cancel



$ 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;

NTNU

Modules Record Window Help

Process

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

SysEq

Process

GtDemo

GEM2MT

UnSpace

Project

::*:

3

1 NaCl-PC

Controls | Sampling | Results | Config | 31/08/2020, 10:58

PC in contact with more and more NaCl water

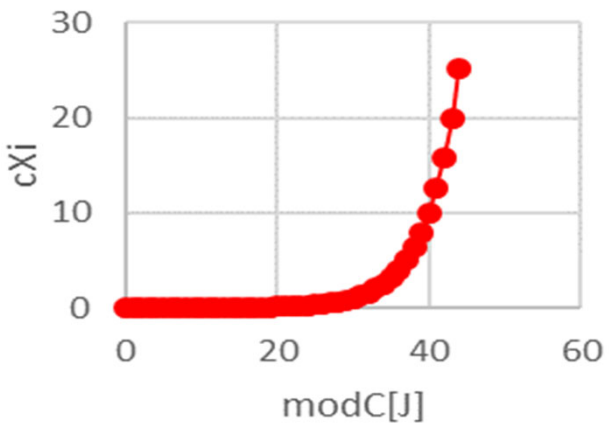
Will fill in automatically

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	1000	0	1	20	0	0	3	0	
1	1045	0	1	20	0	0	-3	45	
2	1	0	0	0	0	0	-0.1	1	
cTm	1044	0	1	20	0	0	-1.4	44	

```
$ 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;
```

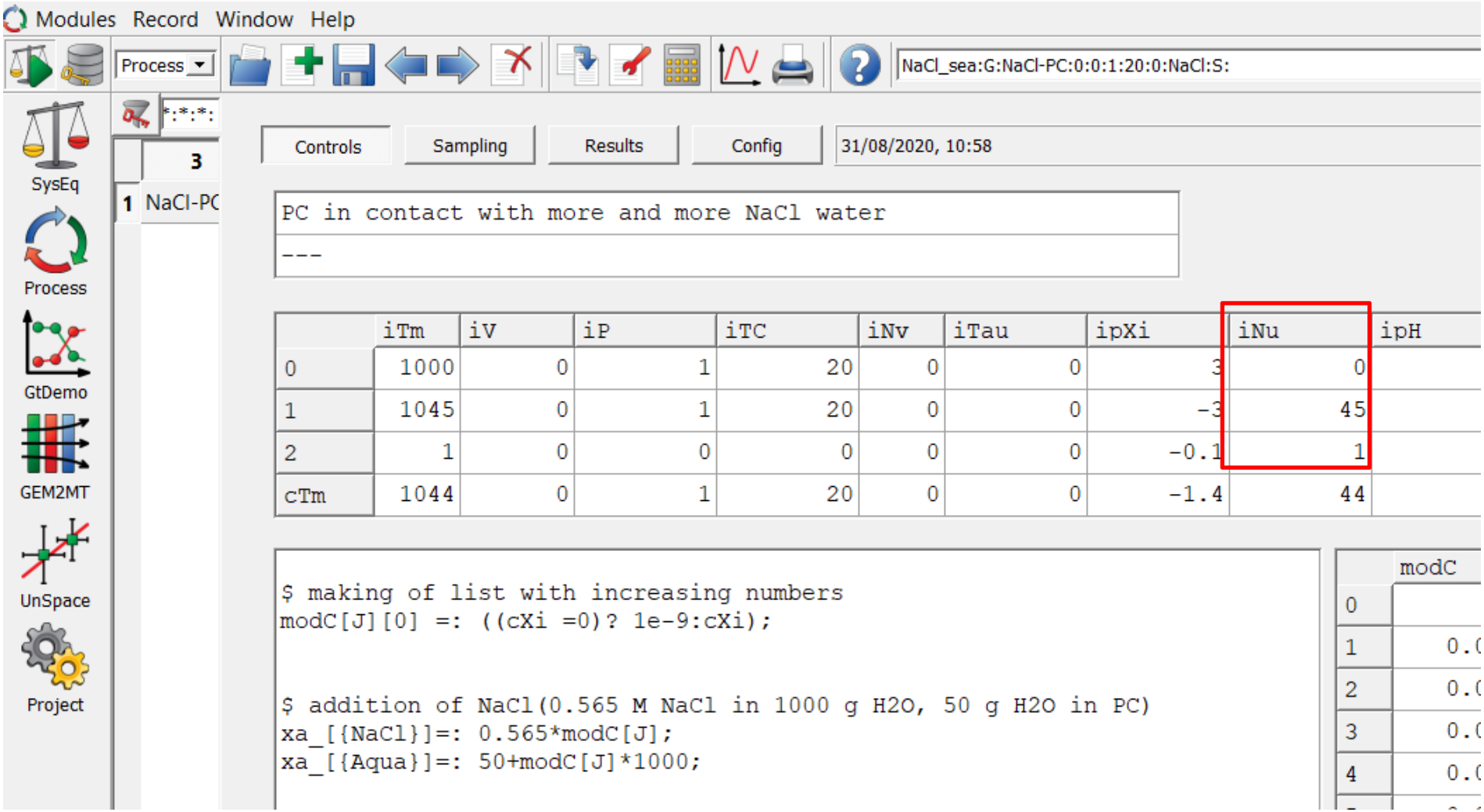
	modC
0	
1	0.0
2	0.0
3	0.0
	0.0



We use pXi (= -logXi) to make a logaritmic list of numbers

pXi=-log(Xi) or Xi=10^(-pXi)

- Start X0=10^-3=0.001
- Step X2=10^0.1=1.259
- Stop X1=10^3=1000

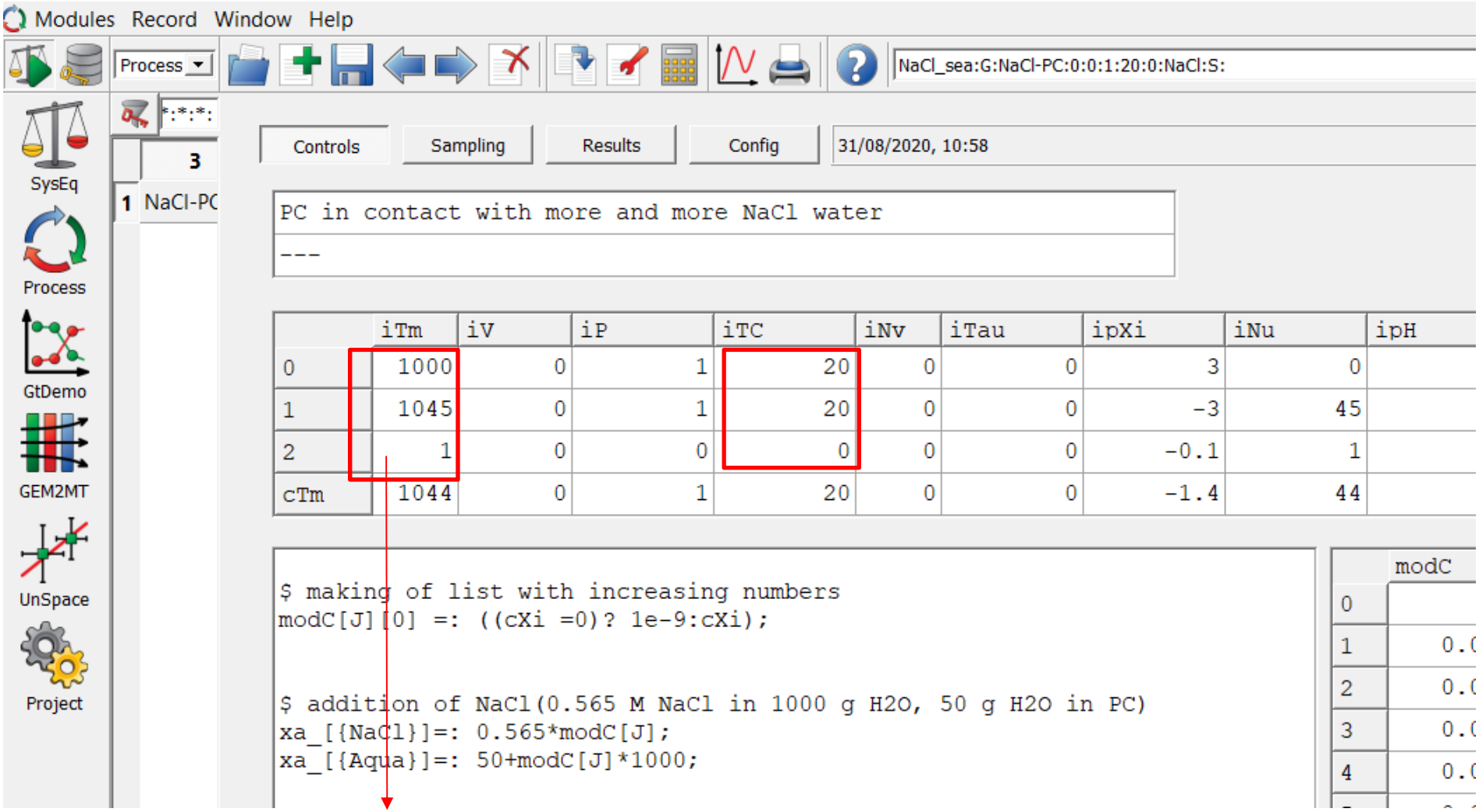


	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	1000	0	1	20	0	0	3	0	
1	1045	0	1	20	0	0	-3	45	
2	1	0	0	0	0	0	-0.1	1	
cTm	1044	0	1	20	0	0	-1.4	44	

	modC
0	
1	0.0
2	0.0
3	0.0
4	0.0

iNu gives a linear list

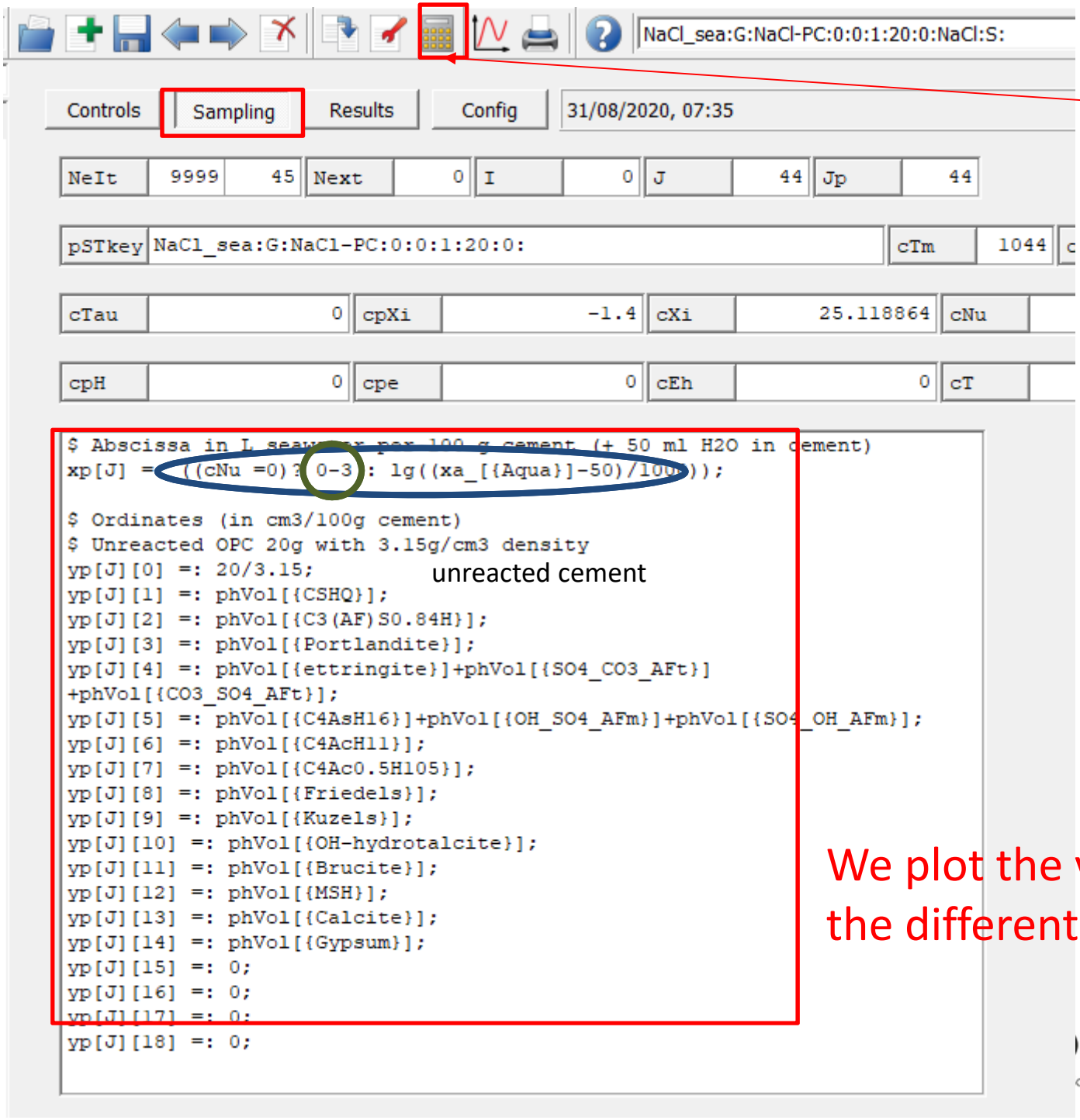
- Start iNu0=0
- Step iNu2=1
- Max iNu1=45



Numbering of the single files

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

Calculation stops as soon as any max is reached

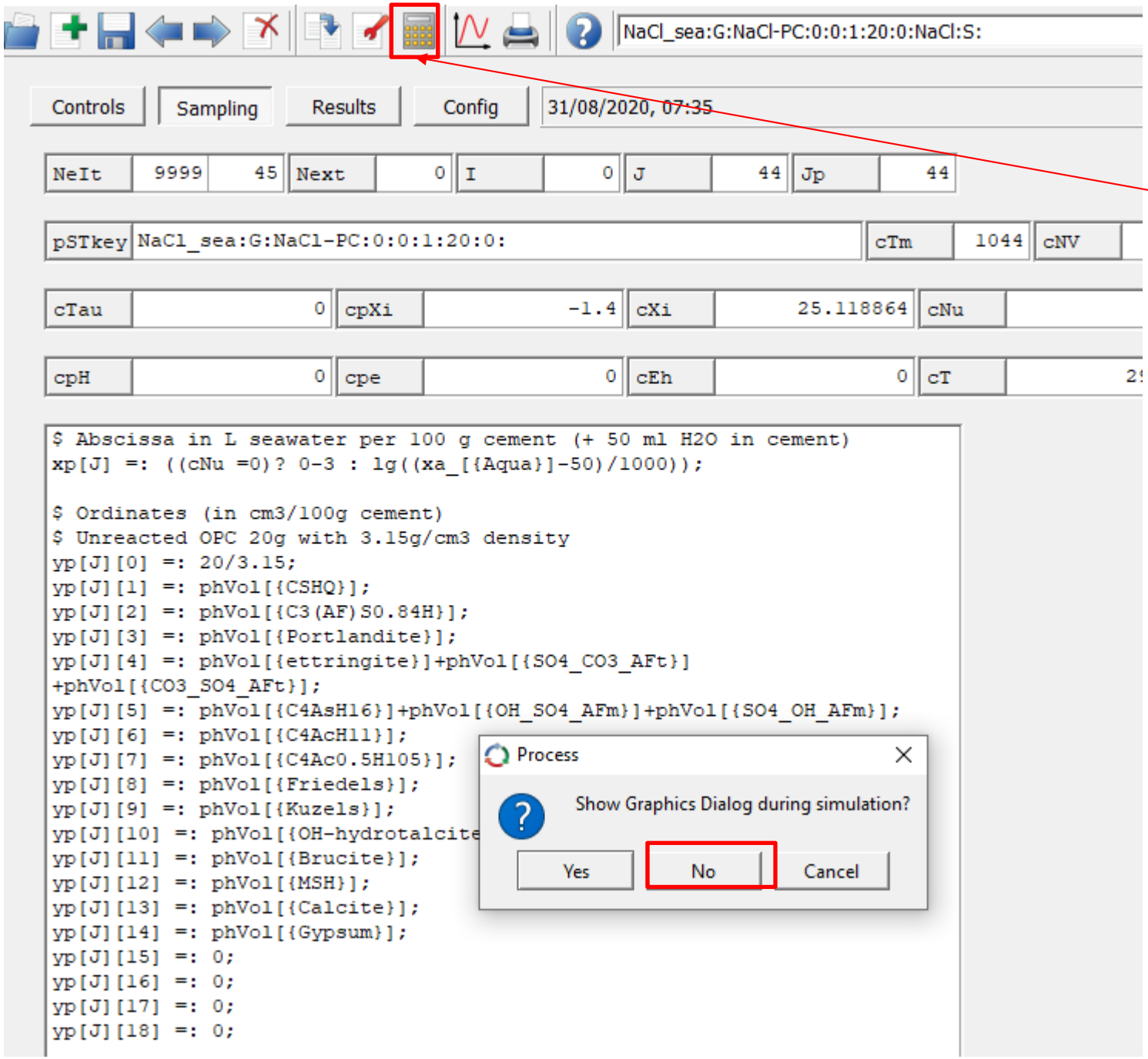


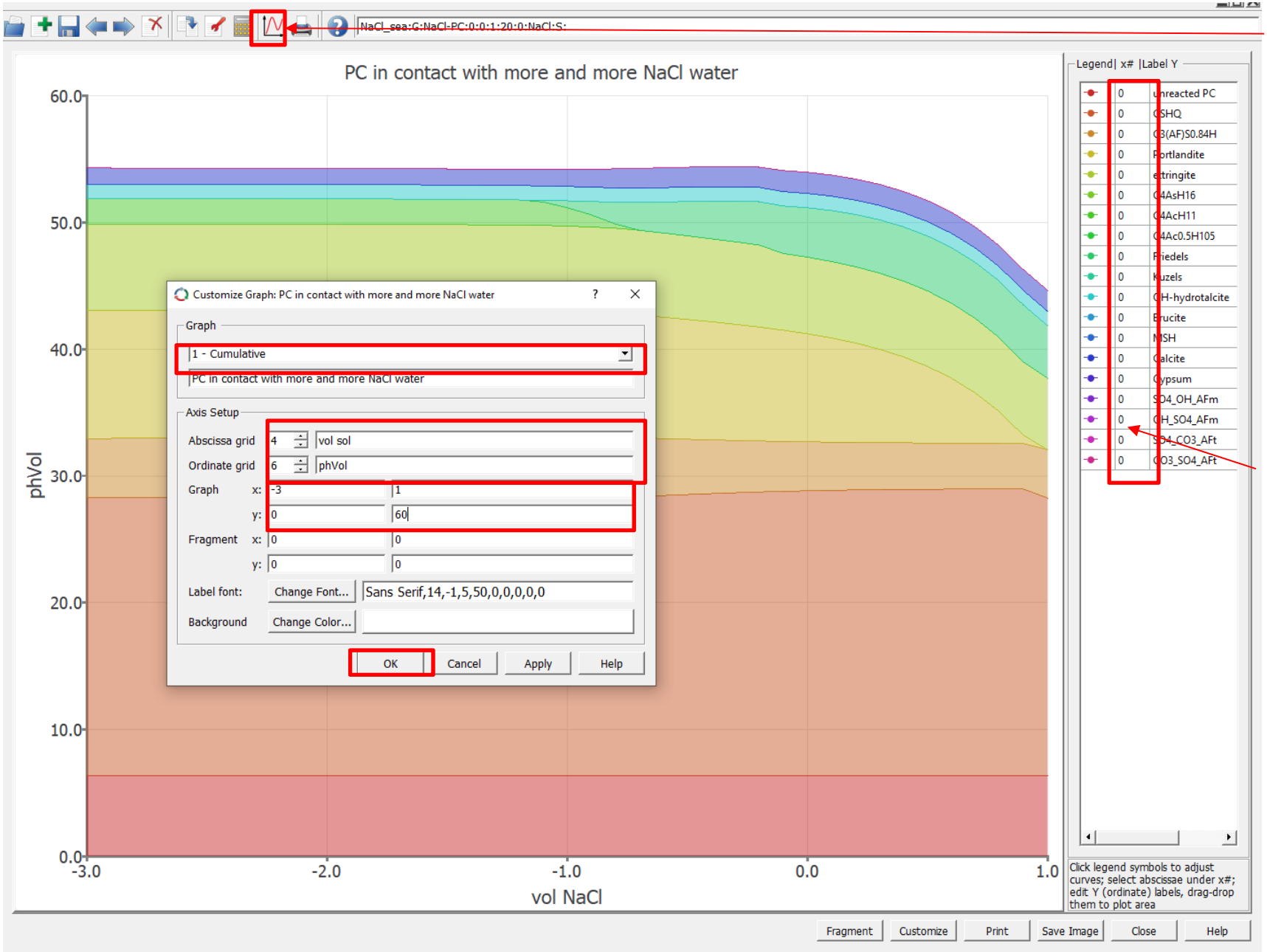
2. calculate

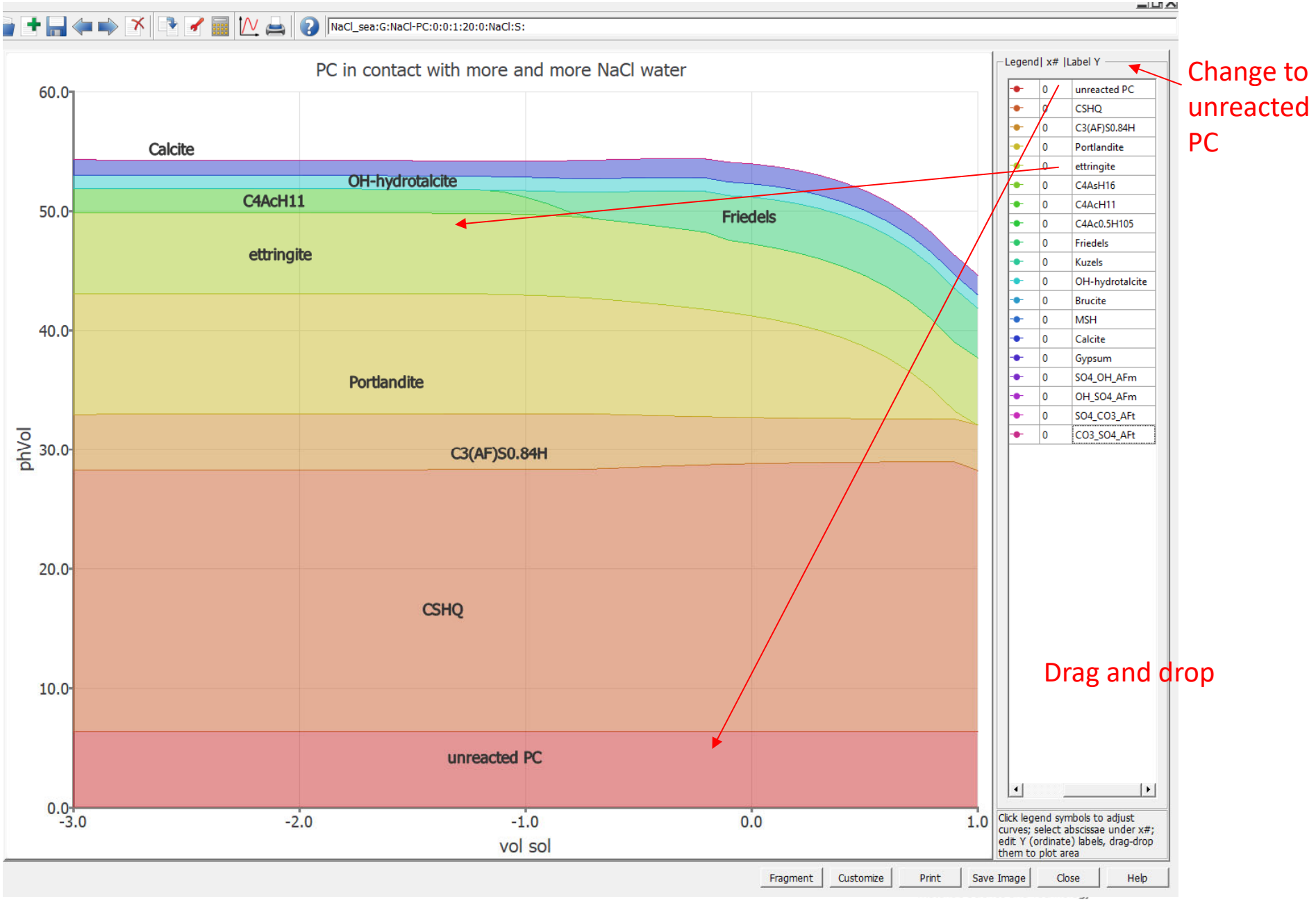
(If ? Then : else)

0-3: Gems needs an operator first

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


NaCl_sea:G:NaCl-PC:0:0:1:20:0:NaCl:S:
Controls
Sampling
Results
Config
31/08/2020, 07:35
NeIt 9999 45
Next 0
I 0
J 44
Jp 44
pSTkey NaCl_sea:G:NaCl-PC:0:0:1:20:0:
cTm 1044
cNV
cTau 0
cpXi -1.4
cXi 25.118864
cNu
cpH 0
cpe 0
cEh 0
cT
$ Abscissa in L seawater per 100 g cement (+ 50 ml H2O in cement)
xp[J] =: ((cNu =0)? 0-3 : lg((xa_[{Aqua}]-50)/1000));
$ Ordinates (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-hydrotalcite
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;
Process
Show Graphics Dialog during simulation?
Yes
No
Cancel
calculate

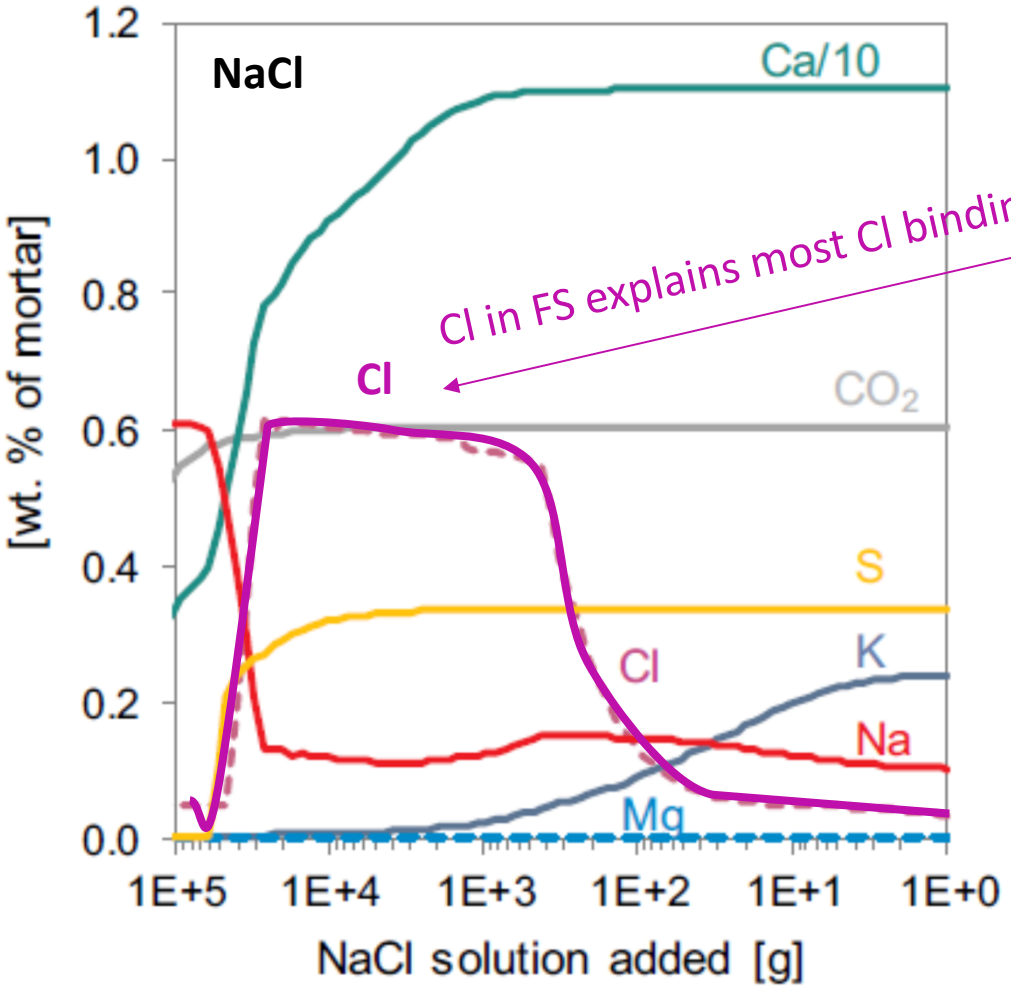

plot
PC in contact with more and more NaCl water
Customize Graph: PC in contact with more and more NaCl water
Graph
1 - Cumulative
PC in contact with more and more NaCl water
Axis Setup
Abscissa grid
Ordinate grid
Graph x:
y:
Fragment x:
y:
Label font:
Change Font...
Sans Serif,14,-1,5,50,0,0,0,0,0
Background
Change Color...
OK
Cancel
Apply
Help
Legend| x# |Label Y
Unreacted PC
CSHQ
C3(AF)S0.84H
Portlandite
ettringite
C4AsH16
C4AcH11
C4Ac0.5H105
Friedels
Kuzels
OH-hydrotalcite
Brucite
MSH
Calcite
Gypsum
SO4_OH_AFm
OH_SO4_AFm
SO4_CO3_AFt
CO3_SO4_AFt
Change to 0
Click legend symbols to adjust curves; select abscissae under x#; edit Y (ordinate) labels, drag-drop them to plot area
Fragment
Customize
Print
Save Image
Close
Help
phVol
vol NaCl



Change to unreacted PC

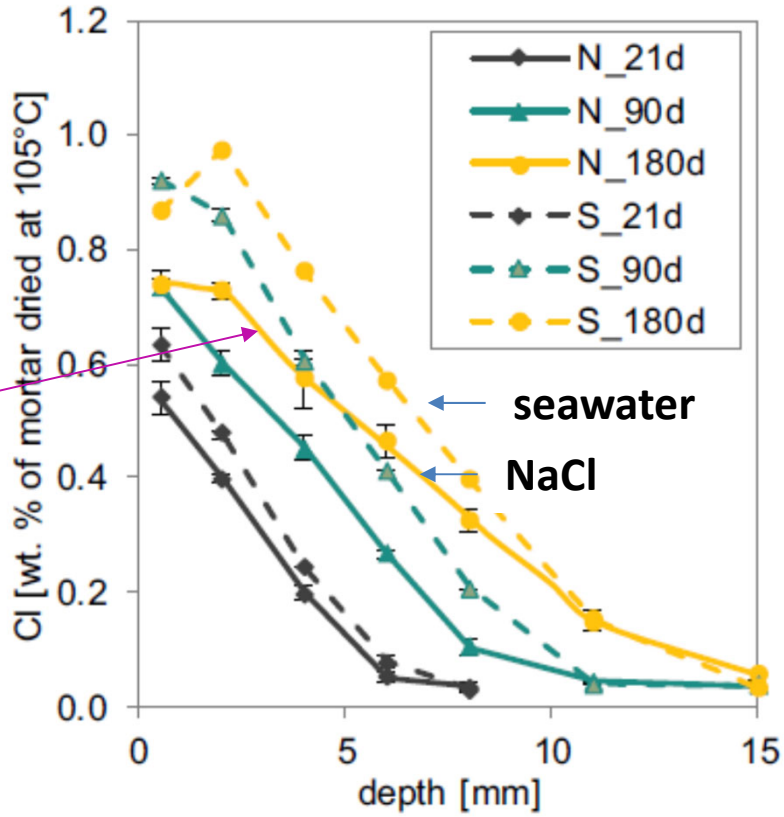
Drag and drop

Case study 2: NaCl



Cl in FS explains most Cl binding

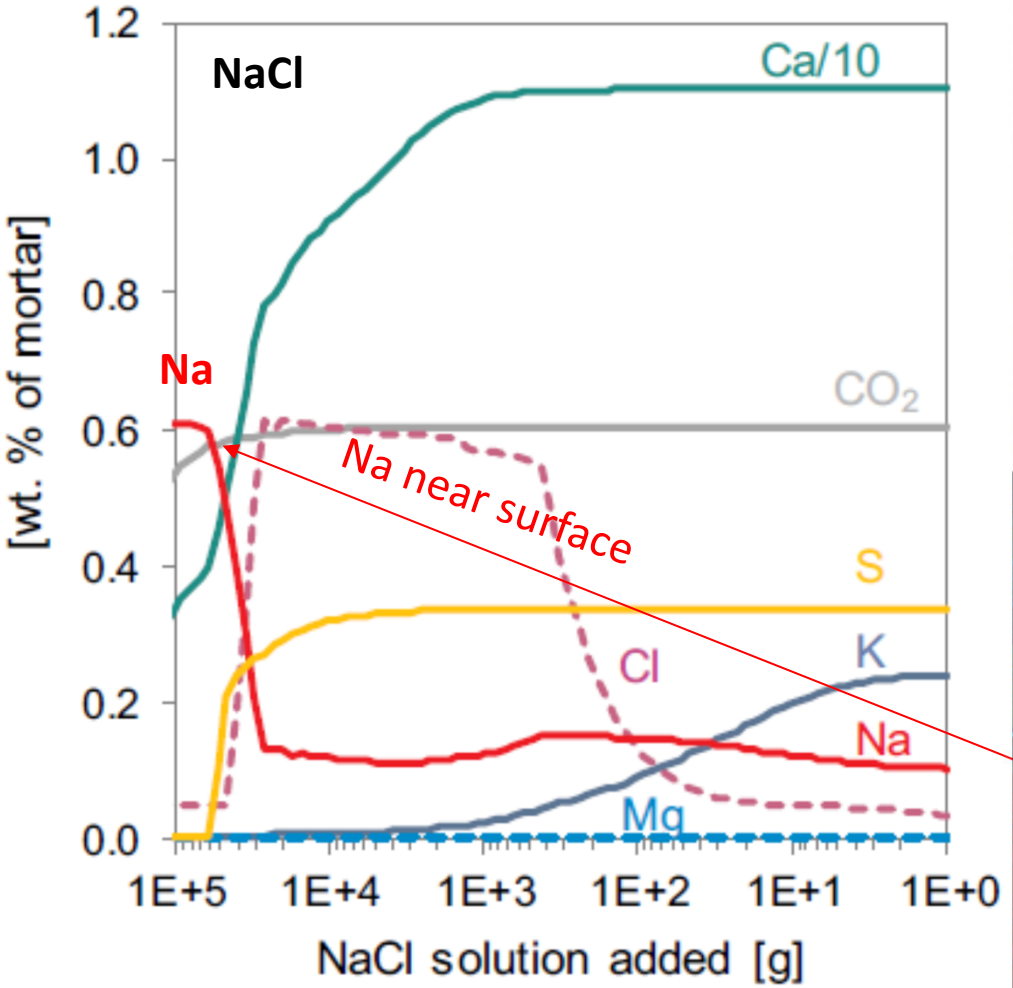
Total Cl: FS +CSH

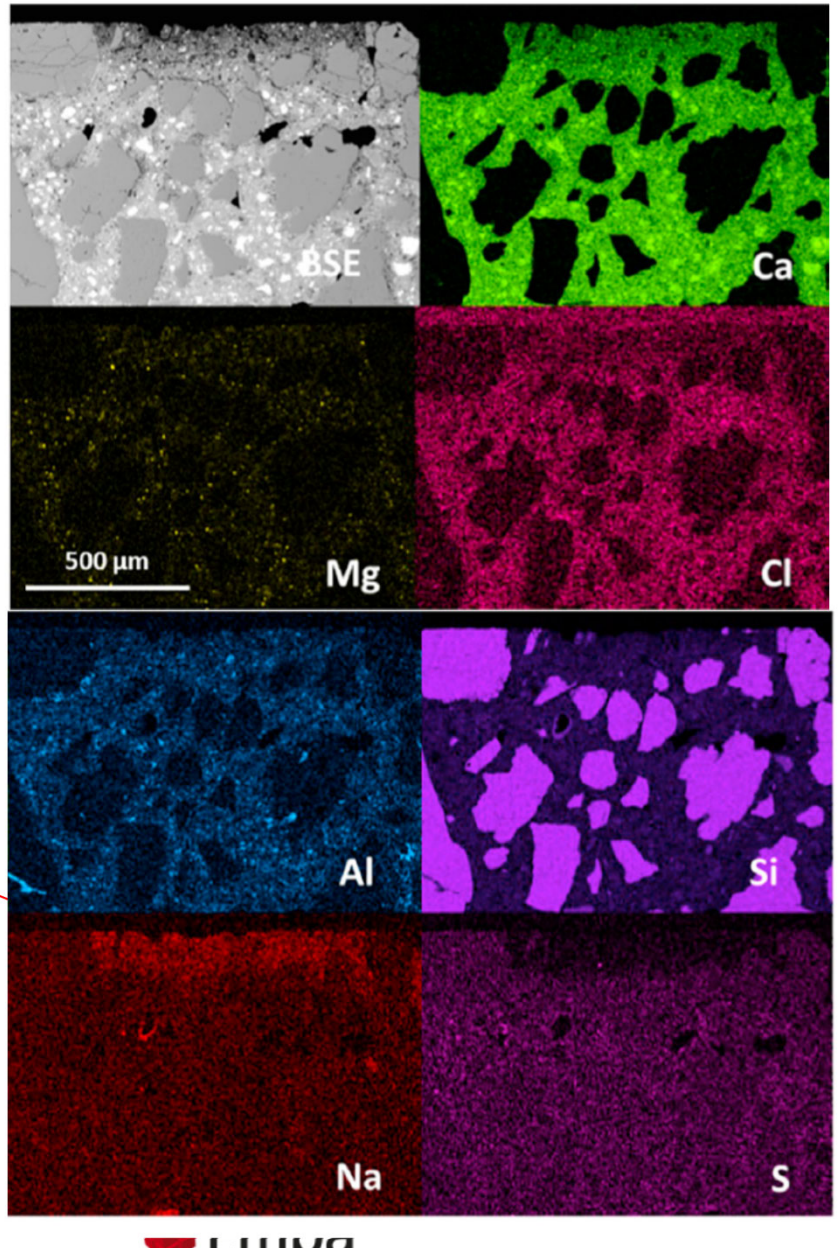


De Weerdt ea 2019, CCR 115

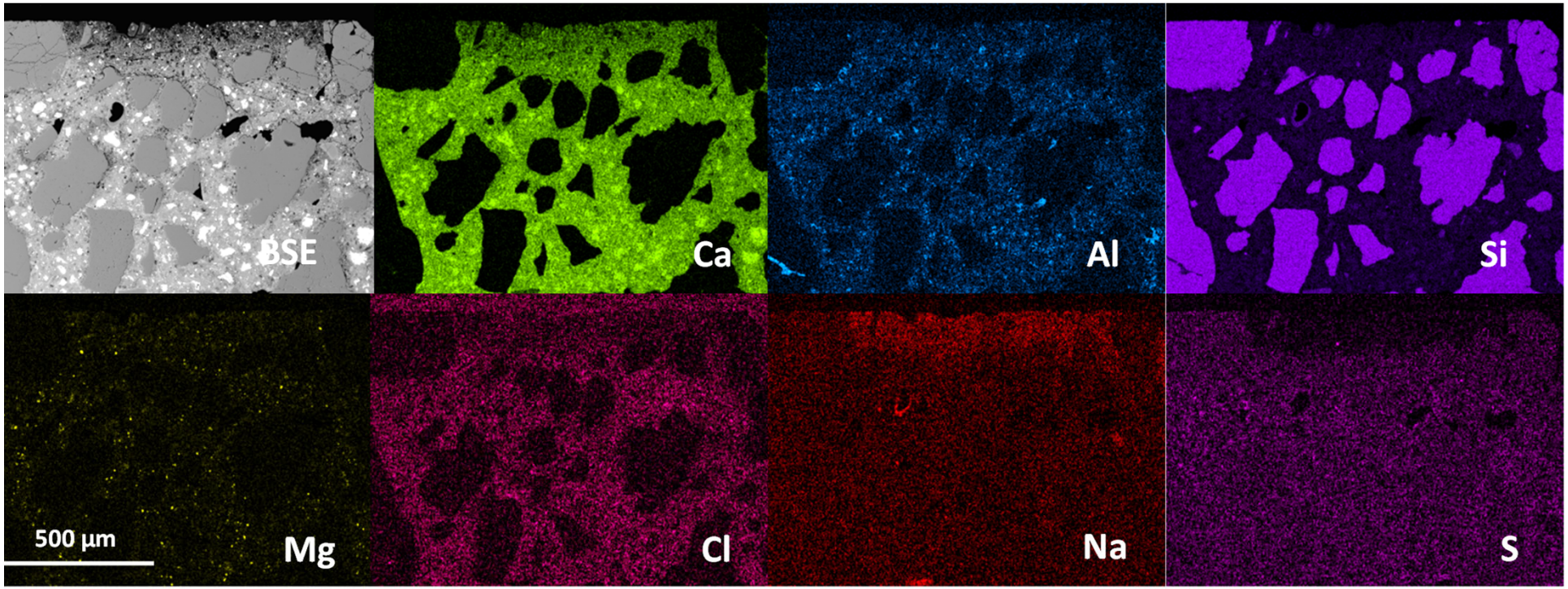
De Weerdt ea 2019, CCR 115

Case study 2: NaCl





De Weerdt ea 2019, CCR 115


BSE
Ca
Al
Si
500 µm
Mg
Cl
Na
S