

Lecture 4 Hydrated Portland cement



Process calculations: Part 2

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Tutorial – process: hydration of Portland cement

Hydration of Portland cement

1) Hydration of PC - single system

Lecture 3

2) Influence of limestone on hydration of PC

– process file

a) Mass based output

b) Volume based output

c) Composition of aqueous phase

Lecture 4

3) Influence of fly ash on hydration of PC

– process file

Process file - hydration of PC + limestone

Description of analytical problem

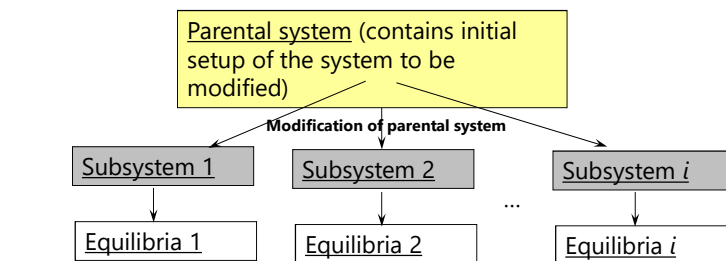
- Addition of increasing amounts of limestone to OPC
- We want to assess the chemical and mineralogical consequences of the addition of increasing amounts of limestone, as calcite, in a systematic way.
- Related phase changes
 - a) mass changes
 - b) volume changes
 - c) changes in the aqueous phase composition

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Process file - hydration of PC + limestone

Process simulations - Short introduction

- simulation of stepwise processes, e.g. dissolution, incremental addition, mixing, titration
- especially useful if a regular change of the bulk composition occurs in the process
- simulation of incremental temperature changes



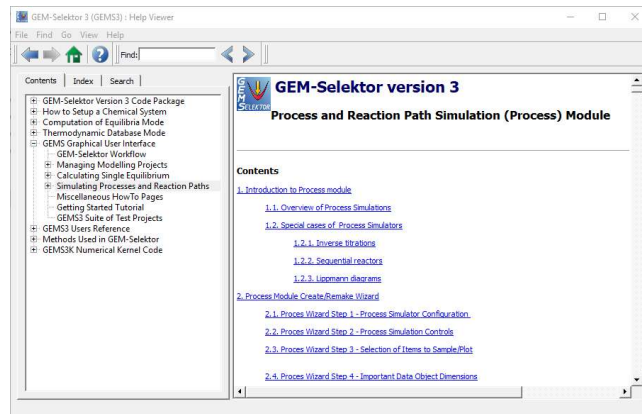
Structure of process simulator

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Process file - hydration of PC + limestone

Process simulations - Short introduction

- GEMS uses a built in math script interpreter to execute process simulations and other functions (similar to the macros in Excel)
- a description of the math script interpreter and used expressions can be found in the related GEMS help file



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Process file - hydration of PC + limestone

Experimental problem:

Blending of the **hydrated cement** from the previous example ...

Normative phase composition [g/100 g]

Alite ^c	66.5
Belite ^c	10.3
Aluminate ^c	7.5
Ferrite ^c	8.5
MgO(periclase) ^c	0.9
CaO (free) ^d	0.93
CaCO ₃ ^d	0.6
CaSO ₄ · 2H ₂ O ^d	3.1
K ₂ SO ₄ ^b	1.3
Na ₂ SO ₄ ^b	0.21

Present as solid solution in the clinker phases

K ₂ O ^d	0.054
Na ₂ O ^d	0.33
MgO ^d	0.94
SO ₃ ^d	0.11

Available in CEMDATA18 as predefined composition «PC»

Parental system

... with various amounts of **limestone**

B. Lothenbach et al. / Cement and Concrete Research 38 (2008) 848–860

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Process file - hydration of PC + limestone

Experimental problem:

Addition of increasing amounts of limestone to PC
up to 10% in steps of 0.2%)

Assumptions:

- initial amount of cement constant = 100 g
"cement" = PC + limestone (= 100% CaCO_3)
- w/b ratio = 0.50 (50 g water), constant
- addition of 0.1 g O_2 , constant
- 100% hydration

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Process file - hydration of PC + limestone

We use the single file created previously now as parent file for
the process simulation.

Single calculations →

Process calculations →

Phase/species	L	Ty	On/
aq_gen	75	a	+
gas_gen	6	g	+
C3(AF)S0.84H	2	s	+
CSHQ	6	s	+
ettringite-AlFe	2	s	-
ettringite-FeAl	2	s	-
monosulph-AlFe	2	s	-
monosulph-FeAl	2	s	-
straetlingite	2	s	+
ettringite	2	s	+
SO4_OH_AFm	2	s	+
OH_SO4_AFm	2	s	+
SO4_CO3_Aft	2	s	+
CO3_SO4_Aft	2	s	+
hydrotalc-pyro	2	s	+
MSH	2	s	+
Al(OH)3am	1	s	+
Al(OH)3mic	1	s	-
Gibbsite	1	s	-

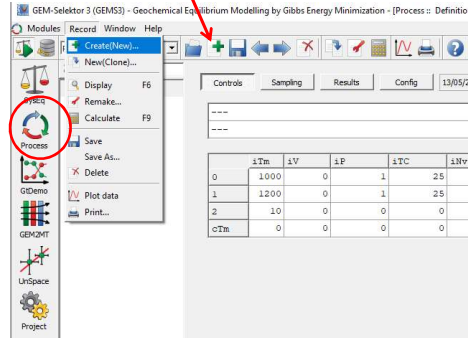
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Process file - hydration of PC + limestone

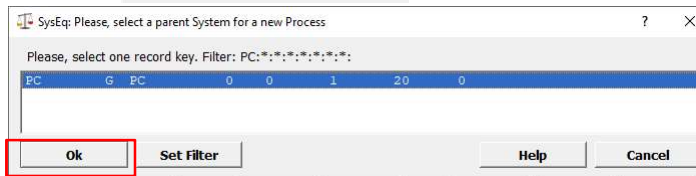
Create new
process file

1.

or click here

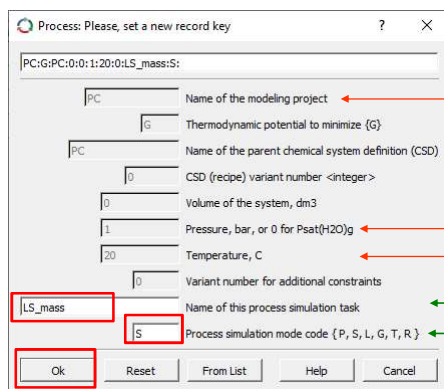


Select parent file



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Process file - hydration of PC + limestone



project name

pressure

temperature

file name of process simulation

simulation type

user input

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Process file - hydration of PC + limestone

Choice of simulation type:

In the case of incremental limestone addition we directly change the bulk composition

→ Sequential change of bulk composition

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass: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 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

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Process file - hydration of PC + limestone

Wizard available for process files

1. Adapt temperature and step size for stored individual calculations
2. Select PC and CaCO_3 (as we want to vary their relative amounts)
3. Select Aqua and O_2

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass: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	20	0	0	0	0	0	0
Until	1200	0	1	20	0	0	0	0	0	0
Step	1	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	CaSO4	H2	MgCO3	SO2
DComp	CaSO4.05H2O	H2S	MgO	SiO2
IComp	CaSiO3	H2SO4	MgSO4	
Phases	Fe2O3	K2CO3	Na2CO3	
DC-lower	FeCO3	K2O	Na2O	
DC-upper	FeO	K2SO4	Na2SO4	
Molality	FeOOH	KOH	NaOH	
Sorbed	FeS	Mg(OH)2	O2	
	Gypsum	MgSi2O5(OH)4	PC	

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modC[1] =: cNu;
xa_([PC]) =: cNu * 1;
xa_([CaCO3]) =: cNu * 1;
xa_([Aqua]) =: cNu * 1;
xa_([O2]) =: cNu * 1;

We need to edit this later

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Process file - hydration of PC + limestone

Wizard available for
process files

GEM-Selektor Process Setup: PC;G;PC;0:0:1:20:0;LS_Mass;S:

1. Select solids:
choose
2. **phM** => **mass (in g);**
=> we can adapt
skript later

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	aq_gen	yp[0] = 1;
ue	gas_gen	yp[1][0] = phM[CSHQ];
b	C3(AF)S0.84H	yp[1][1] = phM[Portlandite];
Cb	CSHQ	yp[1][2] = phM[C3(AF)S0.84H];
m_t	ettringite	yp[1][3] = phM[ettringite];
lgm_t	ettringite	yp[1][4] = phM[ettringite];
icM	SO4_OH_AfM	yp[1][5] = phM[SO4_CO3_Af];
Xa	OH_SO4_AfM	yp[1][6] = phM[C4ASH16];
Xwa	SO4_CO3_AfM	yp[1][7] = phM[SO4_OH_AfM];
phM	CO3_SO4_AfM	yp[1][8] = phM[OH_SO4_AfM];
	hydrotalc-pyro	yp[1][9] = phM[C4Ac0.5H12];
	MISH	yp[1][10] = phM[C4AcH11];
	Al(OH)3am	yp[1][11] = phM[Calcite];
	Al(OH)3mic	yp[1][12] = phM[OH-hydrotalcite];
	Kaolinite	yp[1][13] = phM[aq_gen];
	Graphite	
	Mayenite	
	Belite	
	Aluminate	
	Alite	
	Ferrite	
	CA	
	CA2	
	C2AH75	
	C3AH6	
	C4AH13	
	C3FS0.84H	
	C3FS1.34H	
	C4ASH12	
	C4ASH14	
	C4ASH16	
	Dolomite-c	
	C4ASH9	
	Chabazite	
	ZeoliteP	
	C2ASH55	
	Anhydrite	
	C4ACH9	
	C4Ac0.5H105	
	C4Ac0.5H12	
	C4Ac0.5H9	
	C4AcH11	
	C6ASH13	
	hemihydra	
	Iron	
	Fe-carboni	
	Siderite	
	Magnetite	

Masses of phases (in grams) in equilibrium

Learn more

< Back Next> Cancel

We need to edit this later

Process file - hydration of PC + limestone

Numerical settings of process simulation

GEM-Selektor Process Setup: PC;G;PC;0:0:1:20:0;LS_Mass;S:

Step 4 - Important data object dimensions

Spin boxes below define the dynamic memory configuration of the process simulator.

Number of steps

Dimensions of sampled and experimental data

54 nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' vector.

2 Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be nPS.

14 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.

0 Number of rows in the xEp, yEp arrays for experimental data (optional)

0 Number of columns in the xEp, yEp arrays for experimental data (optional)

Optional entries of experimental data possible to compare with calculations

Allocation of optional data vectors

☐ CSD variant # ('VTm') ☐ Volume V, l ('VV') ☐ Pressure P, bar ('VP')

☐ Temperature T ('VT') ☐ Constraints # ('VNV') ☐ Process extent Nu ('Vtu')

☐ Process extent pXi ('vpXi') ☐ Kinetic parameters ('vKin') ☐ Time Tau ('vTau')

Learn more

< Back Next> Cancel

Convenient to
«overestimate»
because maybe more
phases occur than
expected

Process file - hydration of PC + limestone

Additional settings

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass: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](#)

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Save the equilibria of each step independently
⇒ Good to check each calculations
⇒ But can make files big
⇒ Can also be turned off

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
Process file - hydration of PC + limestone

Additional settings

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass: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 'PName' and 'PNote' lines. Check the process iterators for correct ranges and increments.
- (2) Modify the simulation control script 'P_expr', if necessary. Some example scripts 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

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Process file - hydration of PC + limes

cNu: running number
can be used for various calculation
here: fraction of CaCO_3

Project: PC:G:PC:0:0:1:20:0:1:5-mass:S: 27/03/2020, 12:37

addition of limestone to PC **project description** => Total 54 calculation

pressure temp

	iTm	iV	iP	ITC	iNv	iTau	ipXi	inu	ipH	ipw
0	1000	0	1	20	0	0	0	0	0	0
1	1200	0	1	20	0	0	0	0	0	0
2	1	0	0	0	0	0	0	0	0	0
cTm	1053	0	1	20	0	0	0	0	0	0

Start value
End value
Step size
of indices for the stored
individual single files

Modify text to
(\$ = comment)

When finished
Click somewhere
(outside active box)
=> else GEMS might
ignore changes

\$ amount of limestone, PC contains already 0.6 g CaCO_3 ,
\$ will be written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_{{CaCO3}} =: modC[J][0];

\$ amount of PC
xa_{{PC}} =: 100-modC[J][0];

\$ PC written in 2nd column;
modC[J][1] =: 100-modC[J][0];

\$ water and oxygen
xa_{{Aqua}} =: 50;
xa_{{O2}} =: 0.1;

* We start at -0.6 as our cement
contains already 0.6% CaCO_3 , and we
want to model also the hydrates
without any limestone

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Process file - hydration of PC + limestone



describes output of calculated
data as table and graph

Controls **Sampling** Results Config 13/05/2019, 13:41

NeIt 9999 0 Next 1 I 0 J 0 Jp 0

pSTkey

cTau 0 cpXi 0 cXi

cpH 0 cpe 0 cEh

\$ x-axis: fraction of calcite in cement
\$ PC contains already 0.6% CaCO_3
xp[J] =: xa_{{CaCO3}}+0.6;

\$ y-axis in g per 100g unhydrated cement
yp[J][0] =: pHM[{{CSHQ}}];
yp[J][1] =: pHM[{{Portlandite}}];
yp[J][2] =: pHM[{{C3(AF)S0.84H}}];
yp[J][3] =: pHM[{{ettringite}}]+pHM[{{SO4_CO3_Aft}}]+pHM[{{CO3_SO4_Aft}}];
yp[J][4] =: 0;
yp[J][5] =: 0;
yp[J][6] =: pHM[{{C4AsH16}}]+pHM[{{SO4_OH_Afm}}]+pHM[{{OH_SO4_Afm}}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: pHM[{{C4Ac0.5H12}}];
yp[J][10] =: pHM[{{C4AcH11}}];
yp[J][11] =: pHM[{{Calcite}}];
yp[J][12] =: pHM[{{OH-hydratecalcite}}];
yp[J][13] =: pHM[{{aq_gen}}];

Definition of x-axis: 2 equivalent options
xp[J] =: xa_{{CaCO3}}+0.6;
xp[J] =: modC[J][1]+0.6;

Definition of output on a mass
basis, e.g. C-S-H
yp[J][0] =: pHM[{{CSHQ}}];

Ettringite (summarized):
yp[J][3] =: pHM[{{ettringite}}]
+pHM[{{CO3_SO4_Aft}}]+
pHM[{{SO4_CO3_Aft}}];

Mass pore solution:
yp[J][13] =: pHM[{{aq_gen}}];

Columns yp[J][0], yp[J][1], ...
if you change order, change also the headings below

pX_Nam limestone

pNam CSHQ Portlandite C3(AF)S0.84H ettringite --

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EDSIPM: IPM Main Descent:

IPM convergence criterion tolerance (Pa_DK) could not be reached (more than Pa_JIM iterations done);

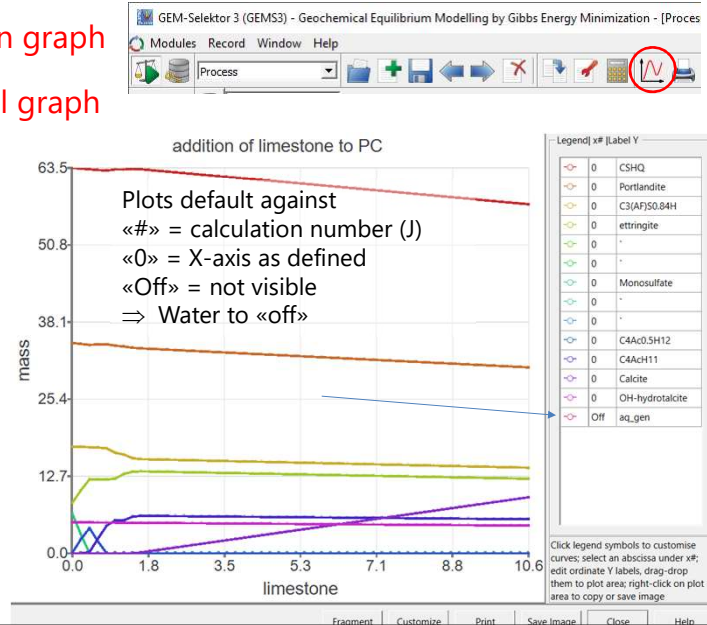
OK

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Process file - hydration of PC + limestone

1. open graph

2. label graph



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Process file - hydration of PC + limestone

Modify the graph as you prefer: example

Customize Graph: addition of limestone to PC

Graph

0 - Lines/Symbols

addition of limestone to PC

Axis Setup

Abscissa grid 5 limestone Add unit of x-axis

Ordinate grid 8 mass Add unit of y-axis

Graph x: 0 10

y: 0 64

Fragment x: 0 0

y: 0 0

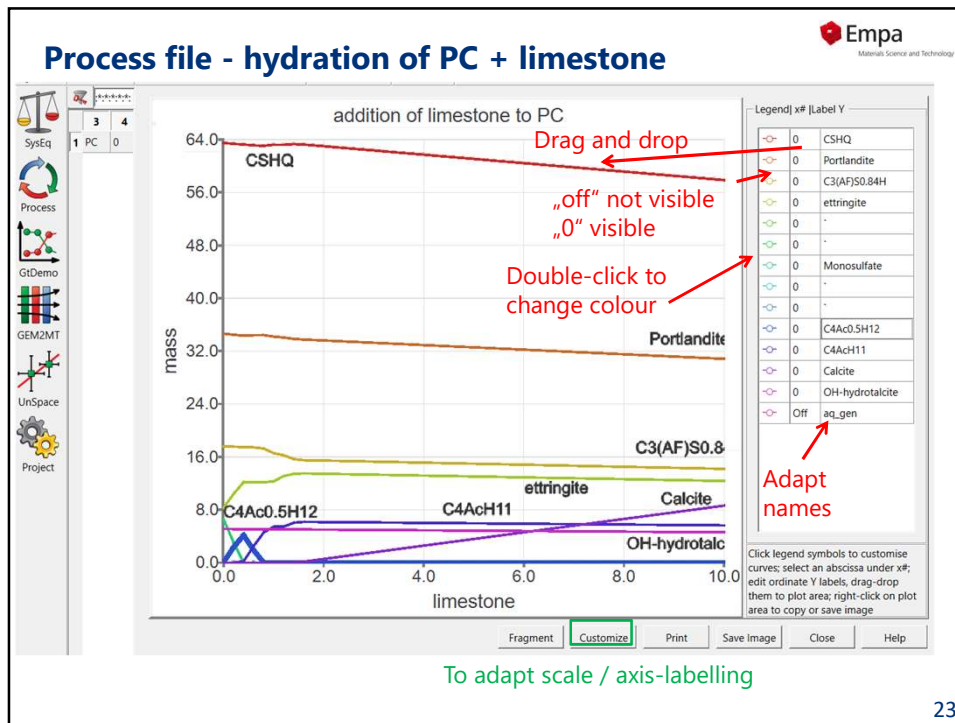
Label font: Change Font... Sans Serif, 14, -1, 5, 400, 0, 0, 0, 0, 0, 0, 0, 0, 1

Background: Change Color...

OK Cancel Apply Help

Min - max
0 - 0: autoscale

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Process file - hydration of PC + limestone

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Modify the graph as you prefer: example

Customize Graph: addition of limestone to PC

Graph

1 - Cumulative

addition of limestone to PC

Axis Setup

Abscissa grid 5 limestone Add unit of x-axis

Ordinate grid 7 mass Add unit of y-axis

Graph x: 0 10

y: 0 140

Fragment x: 0 0

y: 0 0

Label font: Change Font... Sans Serif,14,-1,5,400,0,0,0,0,0,0,0,0,1

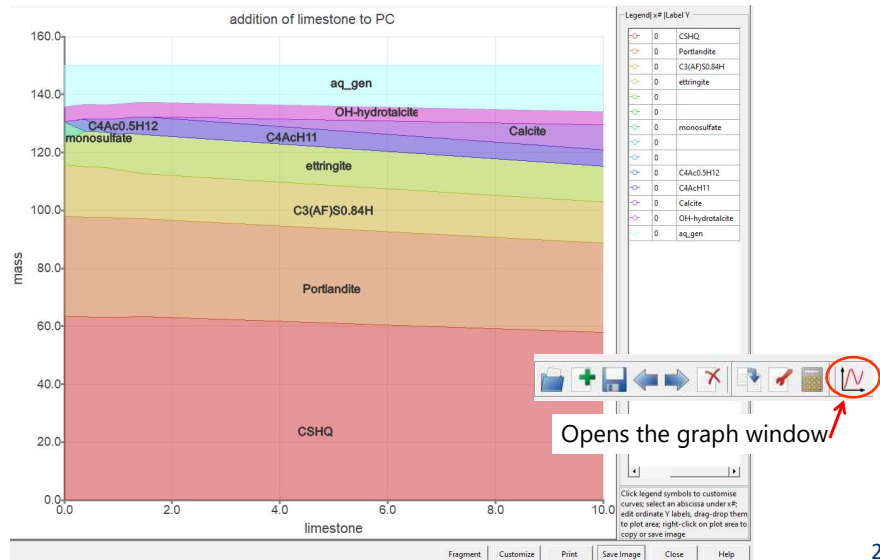
Background: Change Color...

OK Cancel Apply Help

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Process file - hydration of PC + limestone

Cumulative graph – good to check if a phase is missing in the output (as everything incl. water) needs to sum up to 150 g in this example)



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Process file - hydration of PC + limestone

Numerical output

Possibility of simple copy and paste of the data into other programs e.g. Excel or Origin

addition of limestone to PC						pY_Nam		mass
pX_Nam	limestone	CSHQ	Portlandite	C3 (AF) S0.84H	ettringite			
0	0	63.47953	34.63977	17.57782	8.325552	0	0	0
1	0.2	63.35415	34.47733	17.54384	10.38858	0	0	0
2	0.4	63.24718	34.32545	17.46471	12.19496	0	0	0
3	0.6	63.12069	34.40284	17.42985	12.17059	0	0	0
4	0.8	63.04952	34.42419	17.26622	12.1448	0	0	0
5	1	63.21118	34.18831	16.56108	12.31385	0	0	0
6	1.2	63.20575	34.05228	16.24585	13.08273	0	0	0
7	1.4	63.31221	33.84896	15.66943	13.42436	0	0	0
8	1.6	63.24648	33.74393	15.49346	13.503	0	0	0
9	1.8	63.11851	33.67438	15.4622	13.47583	0	0	0
10	2	62.99054	33.60484	15.43094	13.44865	0	0	0
11	2.2	62.86257	33.53529	15.39968	13.42148	0	0	0
12	2.4	62.7346	33.46576	15.36842	13.39431	0	0	0
13	2.6	62.60662	33.39622	15.33716	13.36714	0	0	0
14	2.8	62.47866	33.32669	15.3059	13.33996	0	0	0
15	3	62.35069	33.25716	15.27464	13.31279	0	0	0
16	3.2	62.22272	33.18764	15.24338	13.28562	0	0	0
17	3.4	62.09475	33.11812	15.21212	13.25845	0	0	0
18	3.6	61.96679	33.0486	15.18086	13.23127	0	0	0
19	3.8	61.83882	32.97909	15.1496	13.2041	0	0	0
20	4	61.71085	32.90958	15.11834	13.17693	0	0	0
21	4.2	61.58289	32.84008	15.08708	13.14976	0	0	0
22	4.4	61.45493	32.77058	15.05582	13.12258	0	0	0
23	4.6	61.32696	32.70108	15.02456	13.09541	0	0	0
24	4.8	61.199	32.63158	14.9933	13.06824	0	0	0

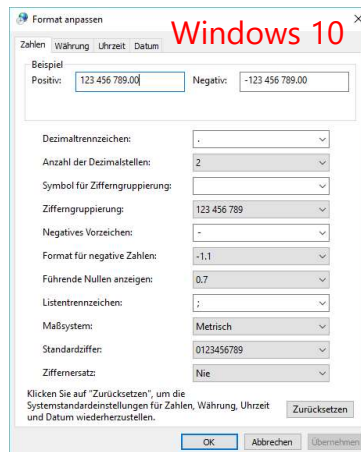
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Process file - hydration of PC + limestone

Copying data to or from Excel files

We need **decimal points,**
not commas !

*Change your excel to use „ . “
as a decimal point
in the control panel of Windows*



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Process file - hydration of PC + limestone

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

Modules Record Data Calculate View Print Window Help

SingleSystem

PC: System

Input: System Definition | Results: Equilibrium State |

	3	4	5	6	7	8
1	PC	0	0	1	20	0
2	PC	1000	0	1	20	000
3	PC	1001	0	1	20	000
4	PC	1002	0	1	20	000
5	PC	1003	0	1	20	000
6	PC	1004	0	1	20	000
7	PC	1005	0	1	20	000
8	PC	1006	0	1	20	000
9	PC	1007	0	1	20	000
10	PC	1008	0	1	20	000
11	PC	1009	0	1	20	000
12	PC	1010	0	1	20	000
13	PC	1011	0	1	20	000
14	PC	1012	0	1	20	000
15	PC	1013	0	1	20	000
16	PC	1014	0	1	20	000
17	PC	1015	0	1	20	000
18	PC	1016	0	1	20	000
19	PC	1017	0	1	20	000
20	PC	1018	0	1	20	000

Phase/species

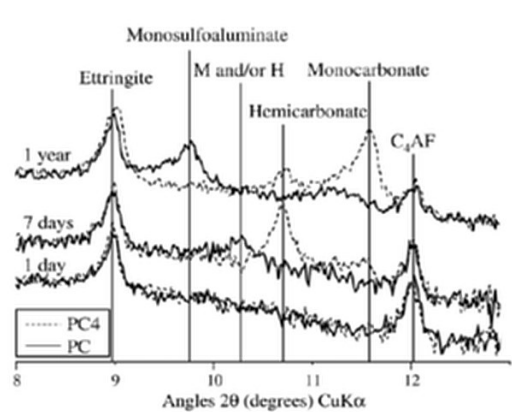
	L	T	On/	UC	Add to	BC	UG	G0
aq_gen	75	a	+	g	0	J	0	0
gas_gen	6	g	+	g	0	J	0	0
C3(A,F)S0.84H	2	s	+	g	0	J	0	0
CSHQ	6	s	+	g	0	J	0	0
ettringite-AlFe	2	s	-	g	0	J	0	0
ettringite-FeAl	2	s	-	g	0	J	0	0
monosulph-AlFe	2	s	-	g	0	J	0	0
monosulph-FeAl	2	s	-	g	0	J	0	0
ettringite	2	s	+	g	0	J	0	0
SO4	2	s	+	g	0	J	0	0
SO4 AFT	2	s	+	g	0	J	0	0
CO3 SO4 AFT	2	s	+	g	0	J	0	0
MSH	2	s	+	g	0	J	0	0
Al(OH)3mic	1	s	+	g	0	J	0	0
Gibbsite	1	s	+	g	0	J	0	0
Kaolinite	1	s	+	g	0	J	0	0
Graphite	1	s	+	g	0	J	0	0
Mayenite	1	s	+	g	0	J	0	0
Belite	1	s	+	g	0	J	0	0
Aluminate	1	s	+	g	0	J	0	0

a record of the equilibrium phase assemblage at each step is automatically saved

it can be assessed individually (e.g. to search for "missing phases" in the output)

Background: Limestone addition to PC

Formation of monosulfoaluminate in carbonate free paste, whereas monocarboaluminate+AFt are predominant in calcite blended paste



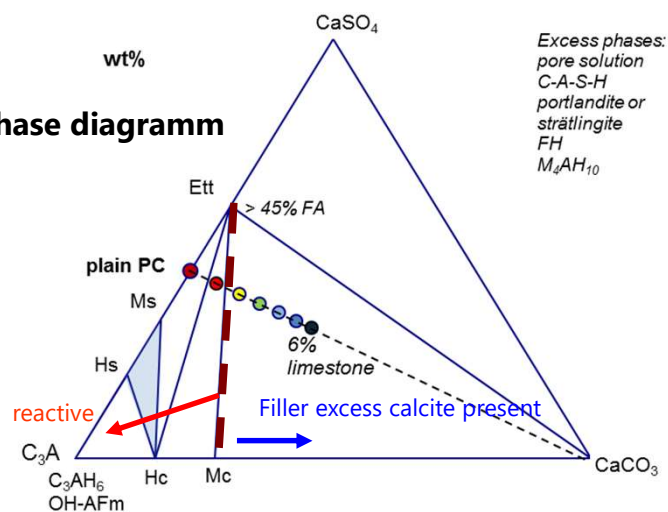
Lothenbach et al 2008, CCR 38

Good agreement between experiments and calculations

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Background: Limestone addition to PC

Phase diagram



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Process file - hydration of PC + limestone

The past example has shown that adding limestone causes significant mineralogical changes during cement hydration.

While these changes affect the qualitative composition of the phase assemblages they also affect the quantities of phases present.

Thus an influence on the specific volumes of the hydrated phases in dependence of the limestone content is likely.



Modification of the existing process to plot

- *specific volumes of the individual phases present in the chosen example*
- *composition of the liquid phase*

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Process file - hydration of PC + limestone

Example calculation of volume changes:

Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

Calculation of volumes is based on individual molar volumes of each phase included in the database

Ettringite with 32 H2O			
((H2O) 2) Ca6Al2 (SO4) 3 (OH) 12 (H2O) 24			
M0	1255.1108	3z	0 ab
V0d	70.703003		0
G0d	-15205936		---
H0d	-17535007		---
S0d	1900		---
Cp0d	2174.3604		0
PrTr	1		25
LamST	---		---
BetaIp	---		---
0	Lothenbach_ea:2008:pap:	logK	-44.9: S
1	Ederova_ea:1979:pap:	Cp	
2	Taylor:1997:book:	V0	(dens 1775 kg/m3)

For example ettringite:

Theor. density: 1.775 g/cm³ (derived from fitted unit cell size)

Molar volume

$$= 1255.11 \text{ g/mol} / 1.775 \text{ g/cm}^3 = 707 \text{ cm}^3/\text{mol}$$

$$1 \text{ cm}^3/\text{mol} = 10^{-1} \text{ J/bar} \rightarrow \underline{70.7 \text{ J/bar}}$$

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Process file - hydration of PC + limestone

Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

Hints:

- Clone "old" process (ensure that you are in process mode) and save it under a different name (suggested name: LS_Vol).
- Select same parent system.
- Only change the output part of the process file to calculate volume instead of mass.
example:

mass:

`yp[J][0] =: pHM[{CSHQ}];`

volume:

`yp[J][0] =: pHVol[{CSHQ}];`

- Efficient: copy to word and use "replace" `yp[J][0] =: Xa[{CSHQ}]; => Moles`
- Change y-axis labelling to "volume" and make a cumulative plot.

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Process file - hydration of PC + limestone

PC:G:PC:0:0:1:20:0:LS_Vol:S:

Controls Sampling Results Config 13/05/2019, 15:59

NeIt 9999 54 Next 0 I 0 J 53 Jp 53

pSTkey PC:G:PC:0:0:1:20:0: cTm 1053 cNV 0

cTau 0 cpXi 0 cXi 1 cNu 10

cpH 0 cpe 0 cEh 0 cT 293.15

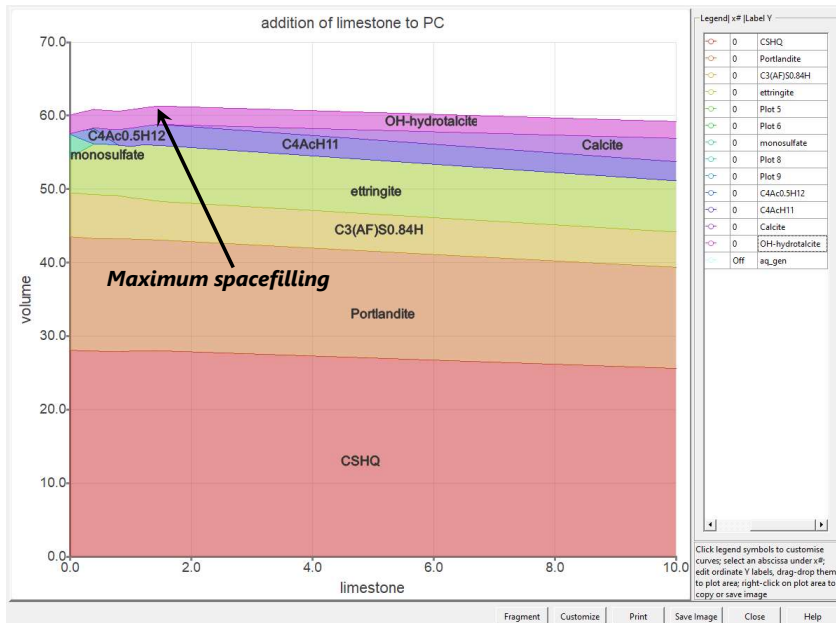
```
$ x-axis: fraction of calcite in cement
$ PC contains already 0.6% CaCO3
xp[J] =: xa_{[CaCO3]}+0.6;
$
$ y-axis in g per 100g unhydrated cement
yp[J][0] =: pHVol[{CSHQ}];
yp[J][1] =: pHVol[{Portlandite}];
yp[J][2] =: pHVol[{C3(AF)S0.84H}];
yp[J][3] =: pHVol[{ettringite}]+pHVol[{SO4_CO3_Aft}];
yp[J][4] =: 0;
yp[J][5] =: 0;
yp[J][6] =: pHVol[{C4AsH16}]+pHVol[{SO4_OH_AFM}]+pHVol[{OH_SO4_AFM}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: pHVol[{C4Ac0.5H12}];
yp[J][10] =: pHVol[{C4AcH11}];
yp[J][11] =: pHVol[{Calcite}];
yp[J][12] =: pHVol[{OH-hydratolite}];
yp[J][13] =: pHVol[{aq_gen}];
```

`yp[J][0] =: pHVol[{CSHQ}];`

Efficient:
copy to word and
use "replace"
Copy back

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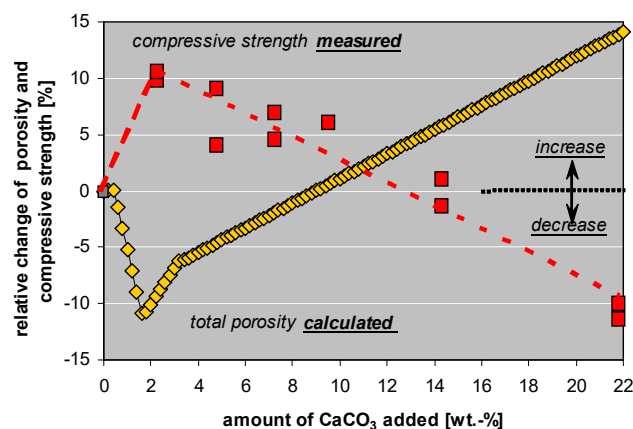
Process file - hydration of PC + limestone



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Process file - hydration of PC + limestone

Possible Links: Thermodynamics vs. engineering properties



one example of a good correlation between predicted changes of relative porosity and measured compressive strength

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Process file - hydration of PC + limestone

Example calculation of pore solution composition:

- Clone "old" process (ensure that you are in process mode) and save it under a different name (suggested name: LS_sol).
- Select same parent system.
- Only change the output part of the process file to calculate ionic concentrations. Use the recipe wizard.
- Plot aqueous composition as total molality [mmol/kg] and pH

Aqueous composition:

yp[J][0] =: m_t[Ca]; *total concentration (as measured e.g. by ICP-OES or IC)*

yp[J][0] =: lgm_t[Ca]; *log total concentration (as measured e.g. by ICP-OES or IC)*

yp[J][0] =: my[Ca+2]; *species concentrations*

yp[J][0] =: 10^lga[Ca+2]; *species activity (as measured by ion selective electrode)*

yp[J][0] =: pH; *gives pH ! Very sensitive to temperature*

yp[J][0] =: IS; *ionic strength*

yp[J][0] =: my[OH-]; *hydroxide concentration (molal)*

this example

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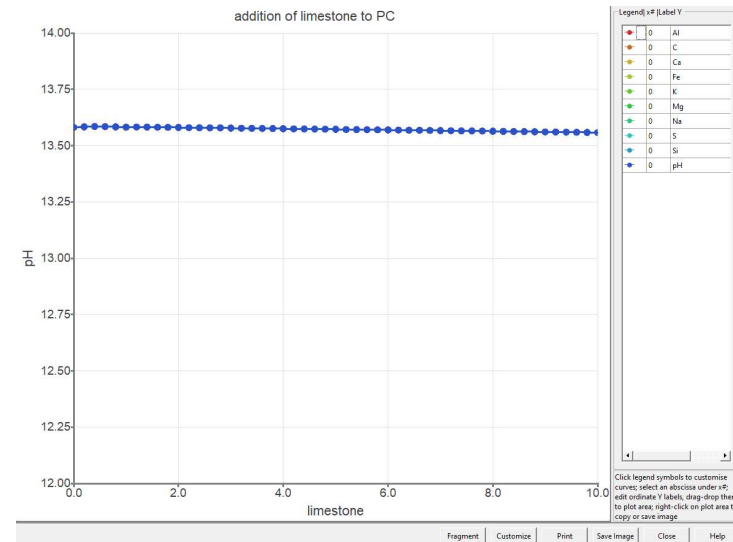
Process file - hydration of PC + limestone

Controls	Sampling	Results	Config	27/03/2020, 13:55
NeIt	9999	0	Next	1
I	0	J	0	Jp
pSTkey	PC:G:PC:0:0:1:20:0:			cTm
cTau	0	cpXi	0	cXi
cNu	1	cpH	0	cpe
cEh	0	cT		
<pre> \$\$x axis: total fraction of CaCO3 in cement \$PC contains already 0.6 wt% xp[J] =: xa_{{CaCO3}}+0.6; yp[J][0] =: lgm_t[Al]; yp[J][1] =: lgm_t[C]; yp[J][2] =: lgm_t[Ca]; yp[J][3] =: lgm_t[Fe]; yp[J][4] =: lgm_t[K]; yp[J][5] =: lgm_t[Mg]; yp[J][6] =: lgm_t[Na]; yp[J][7] =: lgm_t[S]; yp[J][8] =: lgm_t[Si]; yp[J][9] =: pH; </pre>				
<p>yp[J][0] =: lgm_t[Al]; log total concentration (as measured e.g. by ICP-OES or IC)</p>				

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Process file - hydration of PC + limestone

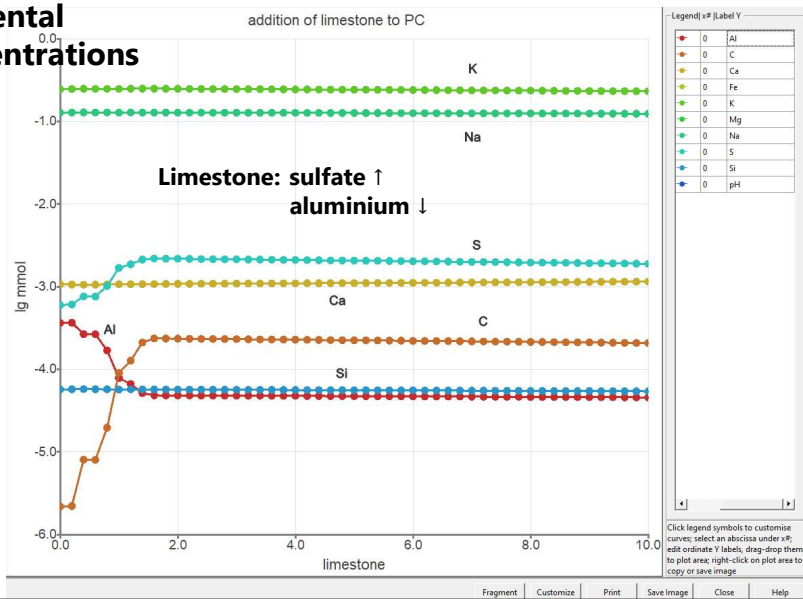
pH - value



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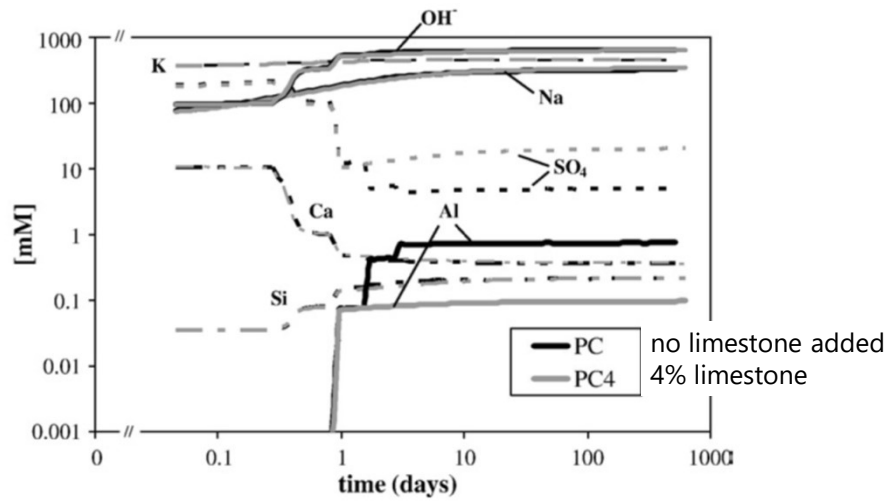
Process file - hydration of PC + limestone

Elemental concentrations



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Process file - hydration of PC + limestone



Lothenbach et al 2008, CCR 38

Limestone: sulfate ↑
aluminium ↓

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Process file - hydration of PC + limestone

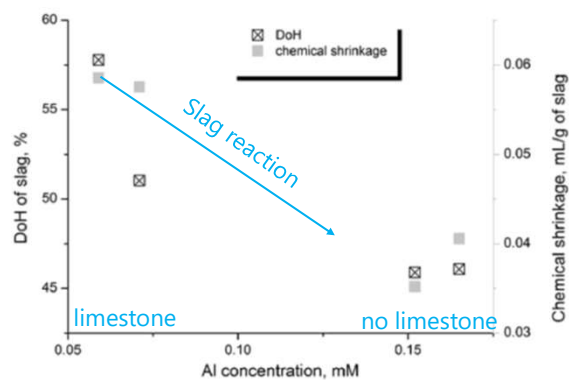


Fig. 21. The relationship between Al concentration in the pore solution and degree of hydration of slag at 28 days. Note, there is $\pm 2\%$ error associated with the method for measuring the DoH of slag.

Adu-Amankwah et al 2017, CCR 100

Limestone: sulfate ↑
aluminium ↓

⇒ High Al suppresses slag and alite reaction
⇒ Limestone accelerates

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Process file - hydration of PC + fly ash

The past example has shown that adding limestone causes significant mineralogical changes during cement hydration.

We now take a look what will happen when we use fly ash instead of limestone.

In a second step we replace 5% of PC by limestone in those blends



Modification of the existing process to plot

- PC blended with fly ash (0-20 mass-% replacement in steps of 0.4 mass-%)
 - PC blended with fly ash (0-20 mass-% replacement in steps of 0.4 mass-%), subtraction of 5 mass-% of PC by limestone
- Mass-based output only.*

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Process file - hydration of PC + fly ash

Example:

- Modification of the existing process to plot a) masses and b) specific volumes of the individual phases present in the chosen example
- Use an "artificial fly ash" with 100% glass content and simplified composition
- Assume 100% hydration of the fly ash and congruent dissolution
- Vary fly ash content between 0 and 20% in steps of 0.4%
- Create a predefined composition for fly ash (FA)

Hints:

- Clone the project with limestone addition (mass-based), name it e.g. FA_mass
- Modify the input part:
 - Vary fly ash content: `modC[J][0] =: cNu*0.4;`
 - Fly ash quantity as `xa_[{FA}] =: ...`
 - Remember that there is no limestone in the fly ash
 - Activate C_3AH_6 in the parent file
- Check for missing phases (look at the calculated single files). Add them to the output part. Label the graph correctly.
- When the mass-based file runs smoothly, clone the file, name it e.g. FA_Vol and modify the output part to display specific volumes (optional individual work)

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Process file - hydrated of PC + fly ash

Composition of fly ash

average glass composition

XRF-analysis ^a [wt%]		Mineralogical phase composition ^b [wt%]		Glass composition [wt%]	
F1		F1		F1	
SiO ₂	50.9	Mullite	8.2	SiO ₂	54.4
Al ₂ O ₃	24.7	Quartz	7.0	Al ₂ O ₃	24.8
Fe ₂ O ₃	7.3	Hematite	0.7	Fe ₂ O ₃	5.7
CaO	3.7	Magnetite	0.8	CaO	4.6
MgO	1.8	Anhydrite		MgO	2.1
K ₂ O	3.9	Periclase		K ₂ O	4.9
Na ₂ O	0.9	Lime		Na ₂ O	1.1
TiO ₂	1.1	Amorphous	83.3	TiO ₂	1.4
Mn ₂ O ₃	0.1			Mn ₂ O ₃	0.1
P ₂ O ₅	0.8			P ₂ O ₅	0.9
SO ₃	0.4 ^c			SO ₃	0.0
SrO					
LOI	3.5				
C	2.7 ^d				
Sum	99.1		100.0		100.0

We only consider the «big four» to make it simpler.

Deschner et al., Cem Concr. Res. 42 (2012), 1389-1400.

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Process file - hydrated PC + fly ash

Fly ash as predefined composition

Two options for input:

recalculation in mol-%

Glass composition [wt%]	
F1	
SiO ₂	54.4
Al ₂ O ₃	24.8
Fe ₂ O ₃	5.7
CaO	4.6
MgO	2.1
K ₂ O	4.9
Na ₂ O	1.1
TiO ₂	1.4
Mn ₂ O ₃	0.1
P ₂ O ₅	0.9
SO ₃	0.0

	in glass g/100g	normalised g/100g	molar mass g/mol	normalised mol/100g
SiO ₂	54.4	60.6	60.08	1.00943076
Al ₂ O ₃	24.8	27.6	101.96	0.27116236
Fe ₂ O ₃	5.7	6.4	159.69	0.03979282
CaO	4.8	5.4	56.08	0.0954203
total	89.7	100		

recalculation in atom-%

	normalised mol/100g
Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Different options for input in predefined composition

Option 1: Input in g oxide

Option 2: Input in mol elements

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Process file - hydrated PC + fly ash

Make a predefined composition for fly ash

Input: System Definition Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity
aq_gen	69	a	0.74137657	-6.317e-10
gas_gen	6	g	0.0031839841	-1.115e-9
C3 (AF) S0.84H	2	s	0.040769951	-1.148e-9
CSHQ	6	s	0.44660885	-5.789e-10
ettringite-AlFe	2	s	0	-1
ettringite-FeAl	2	s	0	-1
monosulph-AlFe	2	s	0	-1
monosulph-FeAl	2	s	0	-1
straetlingite	2	s	0	-1.43
ettringite	2	s	0.0097500224	8.224e-9
SO4 OH AFm	2	s	0	-1
OH SO4 AFm	2	s	0	-1
SO4 CO3 AFm	2	s	0	-1
CO3 SO4 AFm	2	s	0	-1
hydrotalc-pyro	2	s	0	-9.748
MSH	2	s	0	-4.257
Al (OH) 3am	1	s	0	-3.33
Al (OH) 3mic	1	s	0	-2.466
Gibbsite	1	s	0	-1.943
Kaolinite	1	s	0	-13.82
Graphite	1	s	0	-85.21
Mavenite	1	s	0	-135.1

Click here to assess the copy of the database associated with this project

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Make a predefined composition for fly ash

Page 1 Settings 01/02/2018, 09:11

PC with limestone
Composition from Lothenbach_ea_b:2008:pap:

svmIC	PCO	svmIC	CIc	CI	
0	Al ...	0.05907926	0	Al ... M	0
1	C ...	0.0036313673	1	C ... M	0
2	Ca ...	0.70041792	2	Ca ... M	0
3	Fe ...	0.024634934	3	Fe ... M	0
4	K ...	0.010179733	4	K ... M	0
5	Mg ...	0.027451387	5	Mg ... M	0
6	Na ...	0.0083306518	6	Na ... M	0
7	O ...	1.3359998	7	O ... M	0
8	S ...	0.017580691	8	S ... M	0
9	Si ...	0.20664962	9	Si ... M	0

Click here to assess the list of predefined compositions and to create a new one

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Use «Record – New(Clone)» from the pull-down menu or click here («Record – Remake» allows you to change an existing record)

To create a new entry, it is best to clone an existing one - we chose to clone the entry PC

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Make a predefined composition for fly ash: option 1, add g oxides

Can be used to add g oxides 4 as CaO, Al₂O₃, SiO₂, Fe₂O₃

Will have to written manually

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Make a predefined composition for fly ash: option 1 and 2

Please, mark IComp keys for PCO definition

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

Al	e	Aluminum
C	e	Carbon
Ca	e	Calcium
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

Select the elements you need + O
(same procedure for input option 1 and 2)

Ok Set Filter Select All Clear All Help Cancel

51

Make a predefined composition for fly ash: option 1, add g oxides

FA:MIN-fly-ash:

Compos : Calculation finished OK (elapsed time: 0.0 s).

Page 1 Settings 07/03/2022, 13:05

FA

Composition from Deschner_ea_b:2012:pap:

0.1	0	0	0	0	0	0	4.7721953
-----	---	---	---	---	---	---	-----------

	symIC	PCO		symIC	CIcl	CI
0	Al e	0.54138197	0	Al e	M	0
1	Ca e	0.096295479	1	Ca e	M	0
2	Fe e	0.080156203	2	Fe e	M	0
3	O o	3.0457686	3	O o	M	0
4	Si e	1.0085829	4	Si e	M	0

3) Once everything is entered, recalculate ...

1) ... and save new record.

⇒ Enter 0.1
Normalises everything to 100 g (0.1 kg)

2) Enter values
Composition normalised to 100g

Write CaO, Al₂O₃,
SiO₂, Fe₂O₃

Case sensitive!

Page 1 Settings 07/03/2022, 13:05

+ - + - M 5 0 4 1 5 0

Deschner_ea:2012:pap: FA composition

	formU	AUcl	CA
0	CaO	g	5.4
1	SiO ₂	g	60.6
2	Al ₂ O ₃	g	27.6
3	Fe ₂ O ₃	g	6.4

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Make a predefined composition for fly ash: option 2, mol elements

Compos: Please, set a new record key

FA:MIN:Fly-ash:

FA MIN Fly-ash

Code of PCO type { AQ RO GA FL HC PM MIN }

Comment to PCO description

Ok Reset From List Help Cancel

Instead of g oxides we use mol of elements

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?

☐ 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

1 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 BName field and (optionally) BNote 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

53

Make a predefined composition for fly ash: option 2, mol elements

Page 1 Settings 05/02/2016, 10:50

FA, simplified, normalised to 100 g

Composition from Deschner_ea:2012:pap:

0.1 0 0 0 0 0 0 0 0

svmIC	PCO	svmIC	CIC	PCO
0	Al ...	0	Al ...	0.54232
1	Ca ...	1	Ca ...	0.09542
2	Fe ...	2	Fe ...	0.07959
3	O ...	3	O ...	3.04715
4	Si ...	4	Si ...	1.00943

normalised
mol/100g

Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Enter values

When everthing is entered, recalculate ... and save new record.

equivalent options, minor difference due rounding off (number of digits ...

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Single calculation - hydration of PC + fly ash

Modelling Projects

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

AlusioMSA MUSICAluminaSilica
AragCalc Aragonite-Calcite
BermanMSS TestsMultiSiteSolidSolutions
C3A Course
CFASH neaTDB_SIT
CSA CSA system
Ca-Sr-CO3 Solid_solutions
CaldoCol2GEM2MT-test
CaldoColo GEM3K-test-example
Flowline test project gem2mt
GEOTHERM Soultz_1
Kaolinite Test-JMC
Kinetics Mineral-Aq-Reactions
Kyanite Mv1stProject
PC course

☒ Retain setup of aqueous (and gas/fluid) phases
☐ Change file configuration of the selected project
☐ Activate Project Remake wizard
Make a new project:
☒ by copying records from default database ☐ by linking file

Open Project New Project

Compos

FA MIN Fly_ash_1M_ record to be inserted into project system.
Action? **Do it** Do it for All Cancel

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

tname PC

Property Selection

Compos (xa_)	Al(OH)3	CaCO3	H2SO4	PC
DComp (xd_)	Al2O3	CaMg(CO3)2	K2CO3	SO3
IComp (bi_)	Al2Si2O5(OH)4	CaO	K2O	SiO2
Phase (xp_)	Aqua	CaSO4	K2SO4	
Kin.lower (dll_)	C12A7	CaSO4_05H2O	KOH	
Kin.upper (dul_)	C2S	CaSiO3	Mg(OH)2	
G0 shift (gEx_)	C3A	FA	Mg3Si2O5(OH)4	
Other inputs	C3S	Fe2O3	MgCO3	
	C4A3s	FeCO3	MgO	
	C4AF	FeO	MgSO4	
	CA	FeOOH	Na2CO3	
	CA2	FeS	Na2O	
	CH4	Gypsum	Na2SO4	
	CO2	H2	NaOH	
	Ca(OH)2	H2S	O2	

Then go back to your project

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Process file - hydration of PC + fly ash

PC:G:PC:0:0:1:20:0:PC_FA:S:

Controls Sampling Results Config 27/03/2020, 13:29

Clone LS_mass
(use number of steps = 51)

addition of FA to PC

GEMS tutorial

Change to 2000 to not overwrite PC-LS

change to 0% FA as start up to 20% FA
change to 0.4 step size

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	2000	0	1	20	0	0	0	0	0
1	2100	0	1	20	0	0	0	0	0
2	1	0	0	0	0	0	0	0.4	0
cTm	1000	0	1	20	0	0	0	0	0

\$ amount of FA,
\$will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_{{FA}} =: modC[J][0];

\$ amount of PC
xa_{{PC}} =: 100-modC[J][0];

\$PC written in 2nd column;
modC[J][1] =: 100-modC[J][0];

We have calcite only in the PC

We now add fly ash instead of limestone
xa_{{FA}} =: modC[J][0];

modC[0]

0
1
2
3
4
5
6

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Process file - hydration of PC + fly ash

Controls	Sampling	Results	Config	31/05/2023, 17:42	
NeIt	9999	51	Next	0	
I	0	J	50	Jp	50
pStkey	PC:G:PC:0:0:1:20:0:			cTm	2050
cTau	0	cpXi	0	cXi	1
cpH	0	cpe	0	cEh	0
				cNu	
				cT	

```

$ x-axis: fraction of FA in cement
xp[J] =: xa_{{FA}};
$
$ y-axis in g per 100 g unhydrated cement
yp[J][0] =: phM[{{CSHQ}}];
yp[J][1] =: phM[{{Portlandite}}];
yp[J][2] =: phM[{{C3(AF)S0.84H}}];
yp[J][3] =: phM[{{ettringite}}]+phM[{{SO4_CO3_AfT}}]+phM[{{CO3_SO4_AfT}}];
yp[J][4] =: phM[{{straetlingite}}];
yp[J][5] =: phM[{{C3AH6}}];
yp[J][6] =: phM[{{C4AsH16}}]+phM[{{SO4_OH_AfM}}]+phM[{{OH_SO4_AfM}}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: phM[{{C4Ac0.5H12}}];
yp[J][10] =: phM[{{C4AcH11}}];
yp[J][11] =: phM[{{Calcite}}];
yp[J][12] =: phM[{{OH-hydrotalcite}}];
yp[J][13] =: phM[{{aq_gen}}];
    
```

Change comment, change x-axis

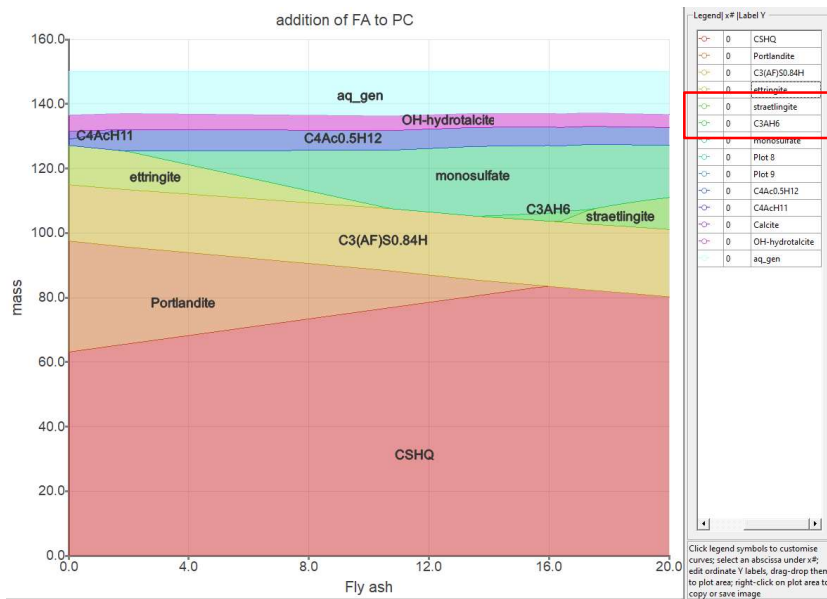
New phase: $(\text{CaO})_2\text{Al}_2\text{O}_3\text{SiO}_2(\text{H}_2\text{O})_{7-8}$

New phase: Katoite

=> Label also columns

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Process file - hydration of PC + fly ash



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Process file - hydration of PC + fly ash

What happens, when we replace 5% of PC by limestone?

Controls
Sampling
Results
Config
27/03/2020, 15:27

addition of FA to PC+Cc
GEMS tutorial

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	2000	0	1	20	0	0	0	0	0
1	2100	0	1	20	0	0	0	20	
2	1	0	0	0	0	0	0	0.4	
cTm	2000	0	1	20	0	0	0	0	0

```

$ amount of FA,
$will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_[{FA}] =: modC[J][0];

$ amount of PC
xa_[{PC}] =: 100-modC[J][0]-5;
xa_[{CaCO3}] =: 5;

$PC written in 2nd column;
modC[J][1] =: 100-modC[J][0]-5;

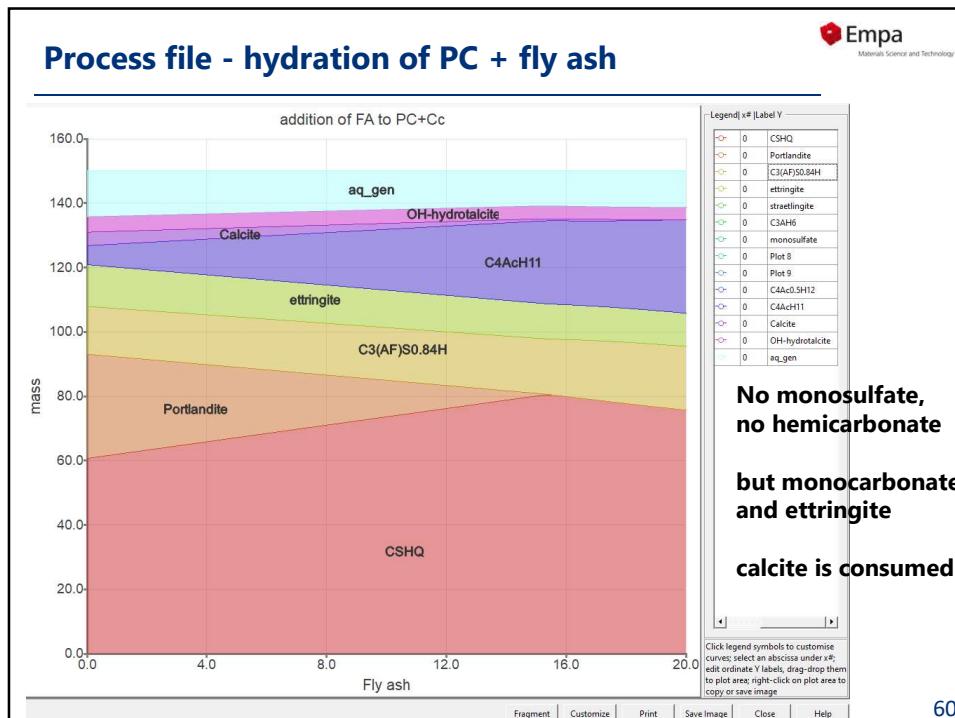
```

mo
0
1
2
3
4
5
6

We subtract the 5% LS from the PC ...
... and add 5% CaCO₃.

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Process file - hydration of PC + fly ash



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Process file - hydration of PC + fly ash

Addition of fly ash to PC:

- Less portlandite, more C-S-H (Ca/Si of C-S-H decreases, not shown)
- Ettringite destabilized, formation of monosulfate
=> ternary blends with fly ash and limestone favourable to stabilize ettringite (see e.g. de Weerd et al., Cem. Concr. Res. 41 (2011), 279-291)
- Strätlingite appears after consumption of portlandite

