

Supplementary material

CemGEMS – an easy-to-use web application for thermodynamic modelling of cementitious materials

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A. About GEM and GEMS

The GEM (Gibbs energy minimization) approach for computing the chemical equilibrium phase assemblages and speciation in complex chemical systems normally uses a single mass balance for the entire system, set up by the total amounts of chemical elements and zero charge. Stoichiometries (formulae) of all chemical substances in the system are thus built from elements and charge. Thermodynamic phases are defined each including one or more substances (chemical species, components) and may have additional physical properties, such as the specific surface area. Multi-component phases are called *solutions*, with a mixing behaviour described by a chosen activity model (ideal or non-ideal mixing). Each substance is provided at input with its formula, and values of the standard Gibbs energy per mole g° , molar volume V° , enthalpy h° , absolute entropy S° and heat capacity Cp° at reference temperature T_0 (25 °C) and pressure p_0 (1 bar = 10^5 Pa), all taken from the chemical thermodynamic database after the (automatic) correction to pressure p and temperature T of interest, if needed.

In the GEM method, the activities and concentrations of chemical species are treated separately within each phase, taking into account the appropriate standard/reference states and activity coefficients. The equilibrium phase assemblage conformant to the Gibbs phase rule is selected automatically from a large list of stoichiometrically feasible phases. The equilibrium partitioning in a heterogeneous multiphase system, including aqueous solution, gas mixture, one or several solid solutions, many pure solid phases, and, optionally, sorption phases, is computed simultaneously for

all phases. The “Interior Points Method” (IPM-3) algorithm, implemented in the GEMS3K code [1], performs such computations efficiently because, in addition to the *primal solution* (i.e. speciation vector \mathbf{x} of mole amounts of substances), it calculates the complementary *dual solution* vector \mathbf{u} (equilibrium chemical potentials of elements and charge at the state of interest). The power of GEM IPM-3 lies in comparing the chemical potentials obtained from primal \mathbf{x} and dual \mathbf{u} vectors for each substance and phase. For instance, such comparisons let the algorithm to decide whether a phase is stable or unstable; to detect when the equilibrium state problem is solved; and to provide the stability criteria for all phases and their components in the output.

The GEMS (<http://gems.web.psi.ch/>) includes code packages and default thermodynamic databases:

- GEM-Selektor v.3 (GEMS3): the interactive code package for geochemical modelling by Gibbs energy minimization;
- GEMS3K: the standalone code for solving for complex (geo)chemical equilibria;
- GEMSFITS: the generic parameter optimization code coupled with GEMS3K;
- GEMS TDB: default chemical thermodynamic databases for GEM-Selektor package.

GEM-Selektor v.3 (<https://gems.web.psi.ch/GEMS3>) is a code package for interactive thermodynamic modelling of heterogeneous aqueous and non-aqueous chemical systems, especially those involving metastability and dispersity of mineral phases, solid solution - aqueous solution equilibria, and adsorption/ion exchange. It includes a built-in enhanced

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PSI-Nagra Chemical Thermodynamic Database 12/07 in both thermochemical and reaction formats, and an advanced multi-widget GUI (graphical user interface) with a context-sensitive help system. Extended with the Cemdata thermodynamic database (see below), GEM-Selektor has been widely used in the cement chemistry community since 2007.

The GEMS3K [1] is a standalone C++ code implementing the efficient numerical engine of GEMS. The code includes the TSolMod library [2] of built-in models of non-ideal mixing in phases-solutions, relevant to a wide range of applications (in particular, for cement chemical engineering). The GEMS3K code can be downloaded and coupled to other codes such as reactive mass transport simulators, parameter optimizers, or the CemGEMS back-end, where it is called via a C++ / Python interface xGEMS (<https://bitbucket.org/gems4/xgems>). The input files (in key-value or JSON format) for initializing GEMS3K can be exported per mouse-click from the GEM-Selektor v.3 GUI; the runtime data exchange within coupled code in computer memory can be done using TNode API (application programming interface).

GEMSFITS [3] consists of the code and GUI (graphical user interface) for inverse modelling and GEM input parameter optimization against various kinds of the experimental data. GEMSFITS uses the NLOpt code package (maintained at MIT), and is coupled with the GEMS3K code for calculation of equilibrium states. GEMSFITS provides various tools for statistical analysis, up to Monte-Carlo evaluation of confidence intervals of fitted parameters. Results of fitting and statistics can be visualized and exported in tabular and graphic formats.

TDB (thermodynamic data bases) are included into GEMS to broaden its applicability in research and practice. Default TDB includes the PSI-Nagra chemical thermodynamic database converted into GEMS formats, as well as the SUPCRT92 (Slop98.dat) dataset imported into GEMS format. Several third-party TDB plugins for specific applications can be downloaded separately and plugged into the GEM-Selektor installation folder at any time.

The Cemdata18 TDB [4] is the most relevant extension of PSI-Nagra TDB for cement chemistry, including CemGEMS applications. In the GEM-Selektor code, thermodynamic data is automatically corrected for temperature and pressure of interest. Thermodynamic data for wide T,P ranges can be exported into GEMS3K I/O files as look-up tables, also used in the CemGEMS back-end.

B. The modified Parrot and Killoh (mP&K) cement hydration model

The kinetic cement hydration model of Parrot and Killoh [5] describes the dissolution of clinker constituents (phases) C_3S , C_2S , C_3A , C_4AF , with a set of empirical equations for the different rate-controlling mechanisms, including nucleation and growth of hydrated phases, and diffusion of solutes. The dissolution rates at any time by each of these mechanisms depend on the instantaneous degree of hydration α , w/c ratio, and six empirical parameters for each clinker phase (Table SB). The empirical equations of the mP&K model as modified and used in [6] and implemented in CemGEMS are shown in Fig. SB1.

The overall rate (1/day, time t in days) used in the last equation in Fig. SB1 is the minimum of three rates defined by three uppermost equations, the first of which is the rate of nucleation and growth (of hydrated products) with the rate constant K_1 ; The second one is the rate of diffusion (of dissolved components) with the rate constant K_2 ; and the third one is the rate of secondary products shell formation, with the rate constant K_3 . T is the actual temperature (K) and T_0 is the reference temperature (298.15 K). Parameters such as rh (relative humidity), w/c (water/binder mass ratio), and specific surface area in m^2/kg are obtained from the parent recipe for the process.

The values of empirical parameters K_1 , N_1 , K_2 , K_3 , N_3 , H , and E_a (activation energy in J/mol) in this order are provided as parameters values in spans of the Hydration-MPK process templates of CemGEMS (Table SB1).

It is important to know that the rates and reaction extents (degrees) in the mP&K model, computed at time t , depend on the rates computed at the previous time step (at time $t-1$) and on the time step duration dt . This is in contrast with the applications 4PL/5PL model, where the reaction extent only depends on the current time step (and value of time) t , but not on any previous history of the simulation.

This mP&K model is not very accurate at early hydration times (less than a day as it has been developed based on long-term XRD data only), where other kinetic or empirical hydration models should be used instead.

Table SB1. Parameters of the mP&K model used in "Hydration-MPK" process templates.

Constituent/ Parameter	Alite	C_3S	Belite	C_2S	Aluminate C_3A	Ferrite C_4AF	MgO^1	M
K_1	1.5		0.5		1.0	0.37	0.5	
N_1	0.7		1.0		0.85	0.7	1.0	
K_2	0.05		0.02		0.04	0.02	0.02	
K_3	1.1		0.7		1.0	0.4	0.7	
N_3	3.3		5.0		3.2	3.7	5.0	
H	2.0		1.55		1.8	1.65	1.55	
E_a , J/mol	41570		20785		54040	34087	20785	

¹ Assumed the same as for C_2S . Data from [6] with minor modifications. Note for the hydration of PC and PC blended with fly ash example of De Weerd et al. [7] some of the parameters were adapted: alite: $K_2 = K_3 = 10$; belite and MgO : $N_3 = 10$; aluminate: $K_3 = 10$, $N_3 = 5$, and ferrite: $K_2 = 0.015$ and $K_3 = 0.2$.

$$R_{i,T} = \frac{K_1}{N_1} (1 - \alpha_i) (-\ln(1 - \alpha_i))^{(1-N_1)} \left(\frac{rh - 0.55}{0.45} \right)^4 \frac{\text{surface area}}{385} e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{i,T} = \frac{K_2 \times (1 - \alpha_i)^{2/3}}{1 - (1 - \alpha_i)^{1/3}} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{i,T} = K_3 \times (1 - \alpha_i)^{N_3} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

degree of hydration of each clinker phase

- *initial* $\alpha_i = \alpha_{i-1} + \Delta t \cdot R_{i-1}$
- *later, for $\alpha_{i-1}(\text{total}) > H \cdot w/c$;*
 $H \cdot w/c = \text{critical degree of hydration}$
 $\alpha_i = \alpha_{i-1} + \Delta t \cdot R_{i-1} \cdot (1 + 3.333 \cdot (H \cdot w/c - \alpha_i))^4$

Hydration is reduced with time at low w/c

Figure SB1. Equations of the mP&K hydration kinetics model for Portland cements as used in CemGEMS web app (from [6] with minor modifications). Cement specific input: surface area [m²/kg], initial w/c (water-cement) mass ratio, clinker composition.

C. Calcium sulfoaluminate cement

Table SC1. Analyses of CSA clinker, anhydrite and limestone, adapted after [8]. In the thermodynamic modelling, perovskite, spinel, dolomite and quartz were assumed to be inert. A reaction degree of 0.3 was assigned to belite, gehlenite and periclase. All other phases were allowed to fully react.

	X-ray fluorescence analysis (mass-%)			Quantitative X-ray diffraction (mass-%)		
	CSA clinker	anhydrite	limestone	CSA clinker	anhydrite	limestone
CaO	35.87	41.68	56.59	C ₄ A ₃ S̄	68.1	
SiO ₂	5.41	0.18	0.39	CA	3.2	
Al ₂ O ₃	42.61	<0.02	0.16	CA ₂	0.7	
Fe ₂ O ₃	1.55	0.03	0.09	C ₁₂ A ₇	1.4	
MgO	1.01	0.51	0.41	C ₂ AS	19.1	
K ₂ O	0.53	<0.02	0.02	β-C ₂ S	1.7	
Na ₂ O	<0.03	<0.03	<0.03	CT	3.9	
TiO ₂	2.100	0.010	0.020	M	0.6	
P ₂ O ₅	0.113	<0.003	0.022	MA	1.1	
Cr ₂ O ₃	0.032	0.005	0.004	C ₅ S̄		95.2
MnO	0.023	0.006	0.019	C ₅ S̄H ₂		2.5
SO ₃	8.52	56.21	0.05	C ₃ C̄		99.1
L.O.I. ^b	1.98	1.22	42.12	CM ₂ C̄		2.3
Total	99.75	99.85	99.93	S		0.8
				Wet chemistry (mass-%)		
				Na ₂ SO ₄ ^b	0.02	
				K ₂ SO ₄ ^b	0.31	
				Free lime ^c	0.06	

^a loss on ignition determined at 1050°C

^b analyzed by ion chromatography in a 1:10 dissolution at a sample ager of 10 min

^c according to [9]

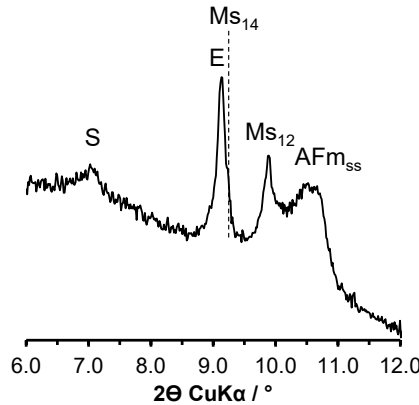
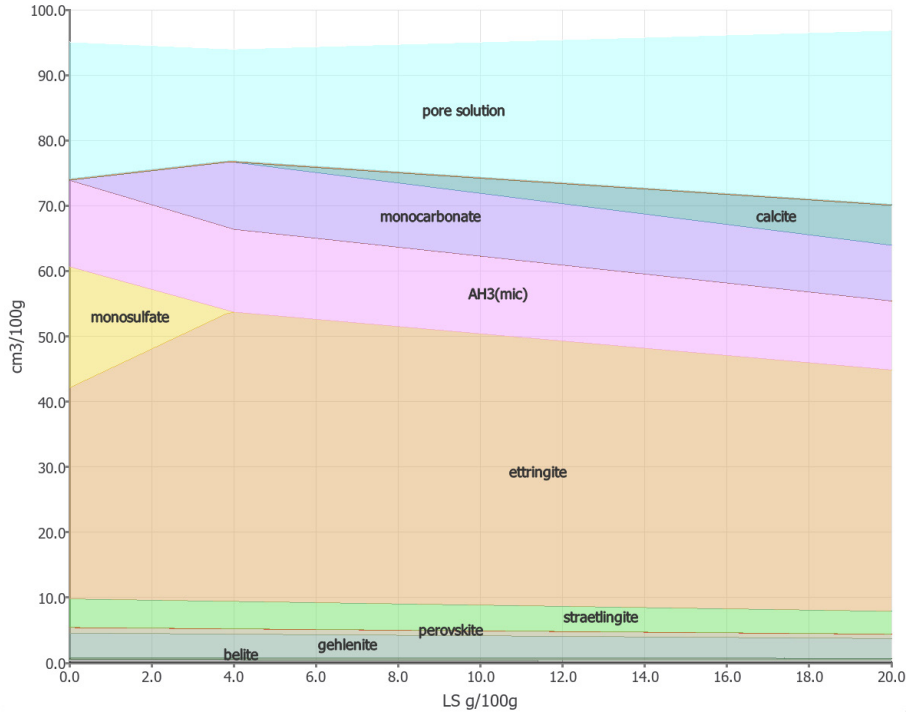


Figure SC1. XRD pattern of the plain CSA clinker between 6 and 12° 2θ. AFm_{ss} = AFm solid solution, E = ettringite, Ms₁₂ = monosulfate with 12 molecules of hydrate water, Ms₁₄ = monosulfate with 14 molecules of hydrate water, S = strätlingite

D. Effect of limestone addition calculated with GEM-Selektor (for comparison)

A) Limestone addition, M = 1.1 (GEM-Selektor)



B) Limestone addition, M = 2.1 (GEMS)

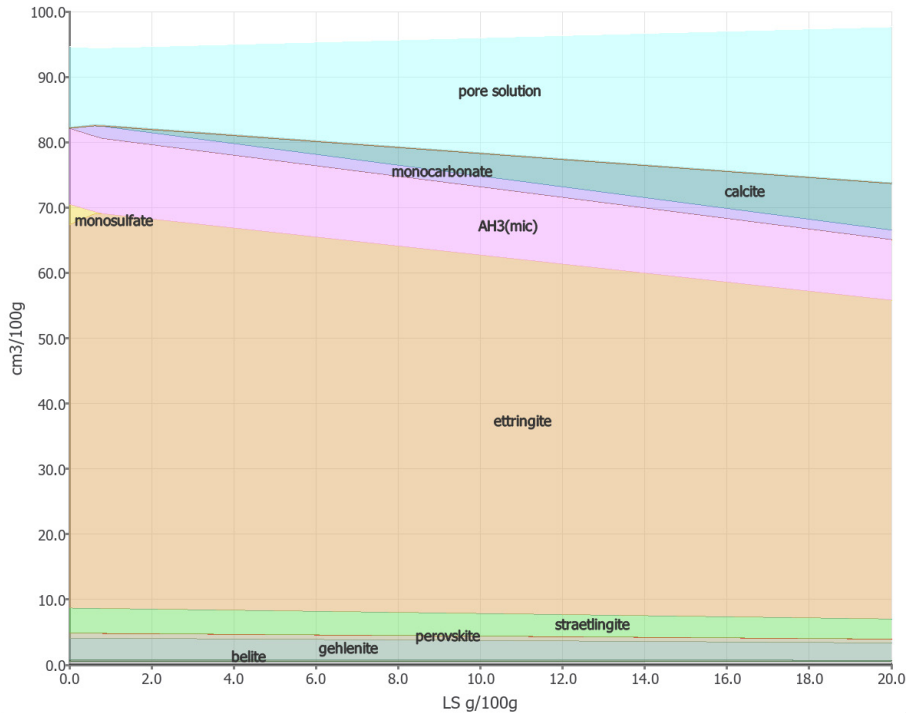
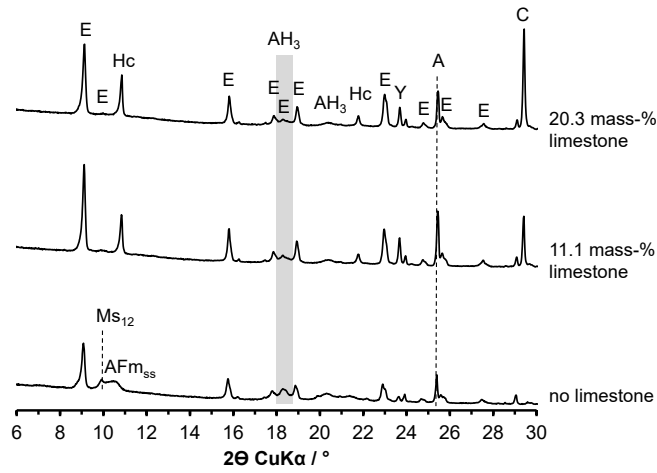


Figure SD1. Thermodynamic modelling of phase volumes depending on the replacement of CSA clinker + anhydrite by limestone using GEM-Selektor. A water/solid ratio of 0.74 and a temperature of 20°C were assumed. A) M = 1.1 (86.2 mass-% CSA clinker and 13.8 mass-% anhydrite), and B) M = 2.1 (75.8 mass-% CSA clinker and 24.2% anhydrite). Some minor phases such as siliceous iron-containing hydrogarnet and hydrotalcite are not indicated in the graphs as they are hardly visible.

A) Limestone addition, M = 1.1 (XRD)



B) Limestone addition, M = 2.1 (XRD)

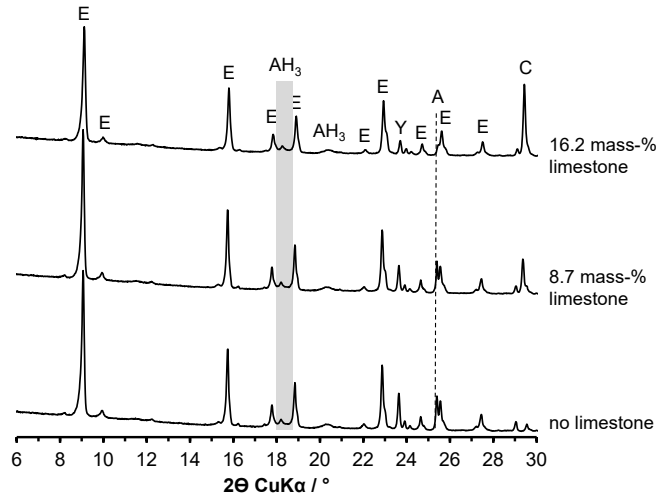


Figure SD2. XRD patterns of CSA clinker blended with different amounts of anhydrite and limestone, hydrated at 20°C for 90 d using a water/binder ratio of 0.74, adapted after [8]. A) M = 1.1 (86.2 mass-% CSA clinker and 13.8 mass-% anhydrite), and B) M = 2.1 (75.8 mass-% CSA clinker and 24.2% anhydrite). A = anhydrite, AFm_{ss} = AFm solid solution, AH₃ = microcrystalline aluminum hydroxide, C = calcite, E = ettringite, Hc = hemicarbonate, Ms₁₂ = monosulfate with 12 molecules of hydrate water, Ms₁₄ = monosulfate with 14 molecules of hydrate water, S = strätlingite, Y = ye'elimite.

E. Carbonation of Portland cement, aqueous phase

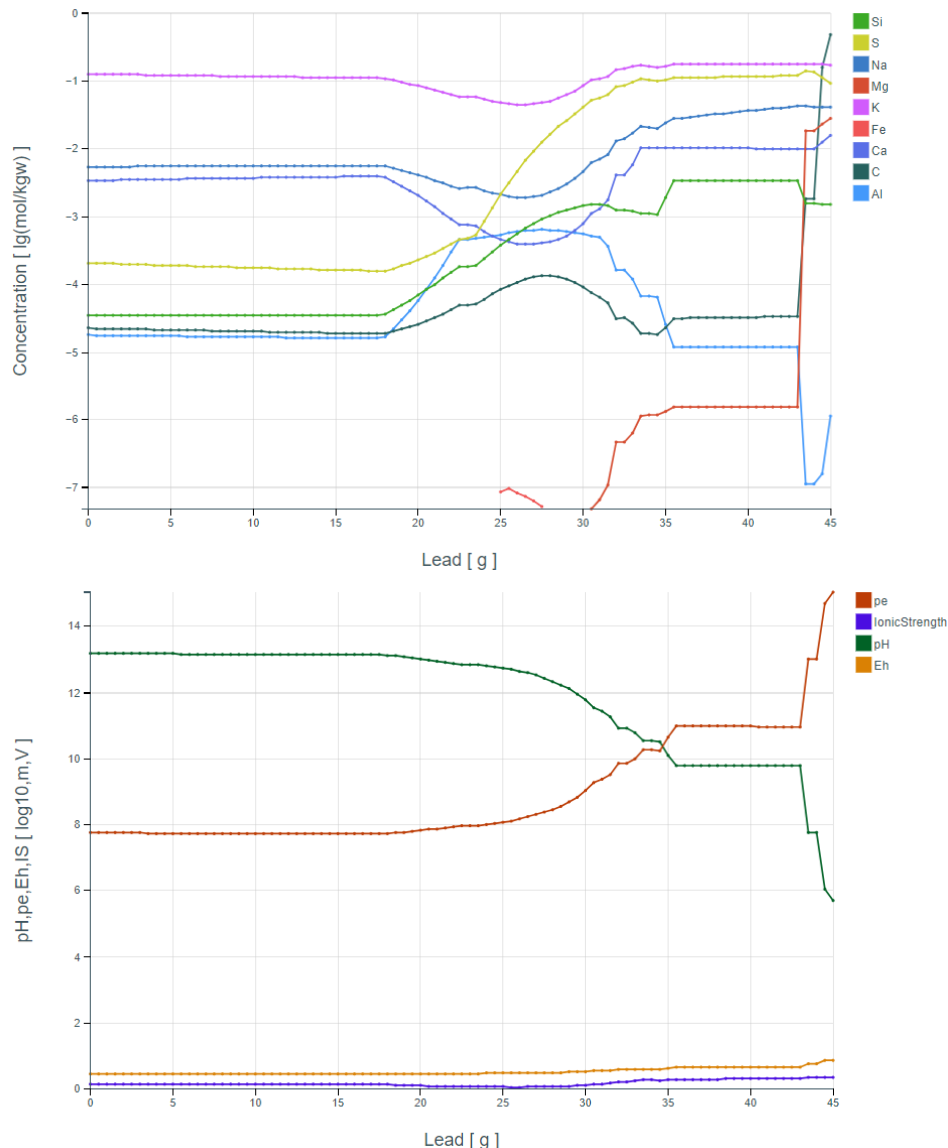


Figure SE1. Thermodynamic modelling of the composition of the aqueous phase during carbonation of a white PC at W/B = 0.5, 20°C and degree of hydration 90%, screen image from CemGEMS. The undegraded cement paste is shown on the left-hand side, while moving to the right, more and more CO₂ (mass in grams) reacts with the hydrates.

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