MODELLING OF CEMENT HYDRATION USING PHREEQC CODE

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Abstract

Modelling the hydration process of cement-based materials is a very useful method to predict, understand and describe the behaviour of this very complex process which is crucial for undertaking the long-term performance and service life predictions of cement-based materials. Based on PHREEQC geochemical software capacity to perform thermodynamic equilibrium calculations by solving the law of mass action (LMA) and using an appropriate thermodynamic database, hydration products formation and precipitation were thermodynamically predicted for a commercial cement type using its oxide composition in powder form. To build the model which simulates the hydration kinetic and assemblage phases over time, the method developed by Parrott and Killoh was used and integrated in PHREEQC code. This method is a mathematical representation of the three main processes involved in clinker dissolution and hydration products formation: nucleation and growth, diffusion and formation of a hydration shell. Furthermore, for a comparative study, PHREEQC and GEMS softwares were used and the results were found in good agreement. The results shown that PHREEQC can predict with reasonable accuracy the mass of fully hydrated products, clinker kinetic hydration and accumulation phases, proving that PHREEQC has potential to be a very powerful tool that, with a proper programming, may be used to predict the behaviour and durability of cement based materials in various environments, a very important aspect for demonstrating the safety function associated with cementitious engineered barriers in a radioactive waste repository.

Keywords: *PHREEQC, Modelling, Hydration, Kinetics*

Introduction

Cement based materials are one of the most important materials used both in immobilisations of low- and intermediate-level radioactive waste and in the construction of radioactive waste disposal facilities due to their good performance in various environments and the ability to act as a physical barrier to prevent human intrusion and as a chemical barrier to prevent or retard the release of radionuclides from the disposal zone.

During the last few years, several thermodynamic cement models have been developed and applied to cementitious systems in order to predict the long-term behaviour under conditions relevant to disposal facilities for low and intermediate level radioactive waste.

Most important cementitious materials properties such as workability, setting behaviour, strength development, but also durability, are related to the cement hydration process. Thus, the specific material design must be based on a deep understanding of the process, especially of the early hydration [1], understanding that can be facilitated by thermodynamic modelling.

Thermodynamic modelling of the interactions between solid and liquid phases in cements, using geochemical speciation codes, allows following the observed macroscopic evolution of the solid and liquid phase during cement hydration at molecular scale, and therefore can be the basis for understanding many of the observed experimental results. Thermodynamic modelling, particularly used in the interpretation of experimental results, requires an understanding of what are the solids that can be expected to dissolve or precipitate as reactions proceed to reach thermodynamic equilibrium [1, 2].

This study presents how PHREEQC geochemical code models the hydration kinetics of cement and thermodynamically predicts which phases will precipitate. These predictions are used to undertake mass and volume calculation using stoichiometries determined by the model. Further, we could predict phase assemblages of the cement under investigation from its oxide proportions and molar masses.

PHREEQC geochemical code and appropriate databases

PHREEQC is a free of charge computer software, developed by USGS [3] in C++ programming language, and designed to perform a wide variety of aqueous geochemical calculations and predictions between solids, liquids and gases at equilibrium. Using appropriate databases, PHREEQC can perform speciation and saturation - index calculations, simulate kinetically controlled reactions and transport calculations, along with many other reaction types, according to Parkhust and Appelo [4].

The quality of thermodynamic modelling results directly depends on the accuracy and completeness of the thermodynamic database used. An appropriate database will include relevant thermodynamic data for solid cementitious substances [5]. The most common database used for cement thermodynamic modelling is CEMDATA, developed by Lothenbach [6] (last version 18.1), having the advantage that can be used both in PHREEQC and GEMS [7] codes. The database has been developed based on particular thermodynamic data in the literature coupled with experimental analysis for temperatures between 0 - 1000 ^{0}C. It has been successfully used to various cements including, ordinary Portland cement, calcium aluminate, calcium sulfoaluminate, blended and alkali activated materials [2].

Thermodynamic modelling of cement

Thermodynamic modelling is based on thermodynamic equilibrium calculations which can predict the composition in a system composed of aqueous, solid and gaseous phases at the temperature and pressure of interest. According to Lothenbach [5], the two basic approaches are used to solve the geochemical equilibrium problem in geochemical modelling, namely:

- solving the law of mass action (LMA) equations,
- minimizing the Gibbs free energy of the system.

PHREEQC software undertakes thermodynamic equilibrium calculations using the first approach, whereas the second one is used by GEMS code [5, 8].

To determine if a phase is in equilibrium, dissolved or precipitated, the PHREEQC model uses Eq.(1), where K_p is the thermodynamic equilibrium constant for the phase, γ_i is the ion activity coefficient, c_i is the ion concentration (mol/L) and $n_{i,p}$ is the stoichiometric coefficient of the ion in the phase.

The thermodynamic equilibrium constant for the phase, K_p at a given temperature T (in Kelvin) is determined using Eq. (2), where $\Delta_r G_T^0$ is the standard Gibbs energy of reaction at temperature T (see Eq. (3)), R is the universal gas constant (8.31451 J/mol K) and $\Delta_f G_T^0$ is the Gibbs free energy of formation for a species (product or reactant) at a given temperature [2, 9, 10].

$$K_p = \prod_1 \left(\gamma_i c_i\right)^{n_{i,p}} \tag{1}$$

$$K_p = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right) \tag{2}$$

$$\Delta_r G_T^0 = \sum \Delta_f G_{T\,products}^0 - \sum \Delta_f G_{T\,reactants}^0 \tag{3}$$

The cement used in this study for the thermodynamic modelling was a commercial cement CEM II/A-L type [11], which oxide proportions and normative phase composition are shown in Table 1. The first step was to convert the OPC oxide proportions and normative phase from grams into moles, as PHREEQC operates such that each simulation is calculated in terms of molal quantities – that is, moles of substance per kilogram of solution [2]. The hydration model takes into account a w/c ratio of 0.5, so 50 g of water is added to the system. The starting pH is set to 7, but charge balanced (the sum of positive charges equals the sum of negative charges in solution) at equilibrium to reflect the solution composition.

For qualitative and quantitative prediction of the hydrates phases that will form during the hydration process, the saturation index (SI) of user specified hydrates was set to zero under the **EQUILIBRIUM_PHASES** keyword. In PHREEQC **Output** sheet, a phase that has a negative SI is assumed to be under-saturated and will dissolve into the solution. If the SI is positive, the solution is over-saturated and the solid may form. If a phase has SI = 0, this will neither dissolve nor precipitate. Along with setting the SI for the solid phases to zero, the amount of moles of each phase that can dissolve is input data [2].

Table 1. Composition of the cements used in PHREEQC modelling, [11]

Chemical composition	**[g/100 g OPC]**	**Normative phase composition**	**[g/100 g OPC]**
CaO	61.5	Alite (C_3S)	44
SiO_2	17.4	Belite (C_2S)	17
Al_2O_3	4.3	Aluminate (C_3A)	7.4
Fe_2O_3	2,3	Ferrite (C_4AF)	7.1
CaO(free)	0.70	CaO(free)	0.7
MgO	1.7	$CaCO_3$	15
K_2O	0.87	$CaSO_4$	2.7
Na_2O	0.09	K_2SO_4	1.4
CO_2	6.6	Na_2SO_4	0.1
SO_3	2.7	K_2O	0.09
		Na_2O	0.05
		MgO	1.7
		SO_3	0.12

Table 2 shows the fully hydrated mass of C-S-H (calcium silicate hydrate), Portlandite, ettringite, monosulfate, monocarbonate, hydrotalcite and calcite, the predicted hydrates to be formed by cement hydration. For comparative studies, GEMS is also used to calculate the mass of hydrates.

It can be seen that both approaches are acceptable with very few differences, due to the fact they rely on the same fundamental properties and their predictions are based on the same database (CEMDATA). One of the differences consists in different values for the C-S-H amount, and may be due to the fact that PHREEQC predicts a form just CSH3T-T2C, which is one of the five alternatives in CEMDATA, being more consistent with the tobermorite-like structure of C-S-H [8]. As regarding the precipitation of monocarbonate instead of monosulfate, this is due to the presence of calcite according to [2, 12].

Table 2. Predicted mass of fully hydrated products for 100 g OPC

Hydration products	PHREEQC Outputs	GEMS Outputs Mass [g]
C-S-H	42.775	54.400
Portlandite	25.265	24.074
Ettringite	14.935	15.329
Monosulfate	0	0
Monocarbonate	12.221	13.699
Hydrotalcite	4.699	2.458
Calcite	12.811	11.696
Water	13.939	15.258

Cement hydration modelling

The hydration of cements can be assumed to take place via dissolution and precipitation processes [11]. In this study, the model proposed by Parrot and Killoh [11] for cement hydration was coded in RATES PHREEQC's keyword to estimate the dissolution and hydration degree of each cement clinker phases (C3S- tricalcium silicate, C2S- bicalcium silicate, C3A- tricalcium aluminate, C4AF- ferrite phase) as function of time. The Model proposed by Parrot and Killoh is mathematically described by the Eqs. (4) - (6), which represent nucleation and growth [2], diffusion, and formation of a hydration shell, respectively.

$$R_{t1} = \frac{K_1}{N_1}(1-a_t)(-\ln(1-a_t))^{(1-N_1)} \quad (4)$$

$$R_{t2} = \frac{K_2(1-a_t)^{2/3}}{1-(1-a_t)^{1/3}} \quad (5)$$

$$R_{t3} = K_3(1-a_t)^{N_3} \quad (6)$$

The controlling rate (R_t) from the above equations is considered the lowest value of hydration rate for any time step. The values of the associated empirical parameters K, N and H used for the three phases of hydration are those proposed by Lothenbach [11] and are presented in Table 3.

The hydration degree of clinker mineral a_t, at the time t, is calculated from the hydration degree of the mineral a_t the previous time step (a_{t-1}), the time interval (Δ_t), and the hydration rate of the clinker mineral at the previous time step ($R_{t1,2,3-1}$) as given in [2, 9]:

$$a_t = a_{t-1} + \Delta_t \cdot \min(R_{t1,2,3-1}) f_{w/c} \beta_H \frac{A^{\left(\frac{E_a}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right)}}{A_0} \quad (7)$$

where

$$f_{w/c} = \left(1 + 3.333 \cdot \left(H^m \frac{w}{c} - a_t\right)\right) \cdot 4 \ , \ a_t > H \cdot w/c \quad (8)$$

$$f_{w/c} = 1, \ a_t \le H \cdot w/c \quad (9)$$

$$\beta_H = \left(\frac{RH - 0.55}{0.45}\right) \quad (10)$$

Here, we have: w/c - water to cement ratio, A - the Blaine surface area of cement [m^2/kg], A_0 - the reference surface area of cement [= 385 m^2/kg], E_a - the apparent activation energy of clinker mineral [J/mol], T_0 - the reference temperature (= 293.15 K), and RH - the relative humidity, which is 1 in fully hydrated sistems, and H^m - the critical degree of the clinker mineral [2, 9, 11].

Table 3. Parameters used in the Parrot and Killoh degree of hydration analysis [2, 11]

Parameters	C_3S	C_2S	C_3A	C_4AF
K_1	1.5	0.5	1	0.37
N_1	0.7	1	0.85	0.7
K_2	0.05	0.006	0.04	0.015
K_3	1.1	0.2	1	0.4
N_3	3.3	5	3.2	3.7
H^m	1.8	1.35	1.6	1.45
E_a	41.57	20.785	54.04	34.087

The predicted degree of hydration (using Eqs. (3 - 5)) and phase weight changes over time (1000 days), using the Portland cement with properties presented in Table 1, are shown in Figs 1 and 2, respectively.

As it can be observed from these figures, the hydration process is more intense in the first hours after onset, starting with rapidly hydration of C3A. C3A is known for its reactivity, and in absence of gypsum, this phase formation can lead to an undesirable instantaneous setting. C3S, the most important phase for the mortar strength development during the first 28 days of hydration, dissolves congruently and quite rapidly after coming in contact with water. C2S and C4AF react much slower, and contribute to the long-term strength of the cement based materials mortar.

The dissolution of C3S and C2S add silicate ions to the solution, which lead to growth of calcium silicate hydrate gel (C–S–H) [13] and calcium hydroxide. Dissolution of C3A and C4AF add aluminate ions to the solution, needed for the growth of minerals such as ettringite or calcium monosulfoaluminate [13].

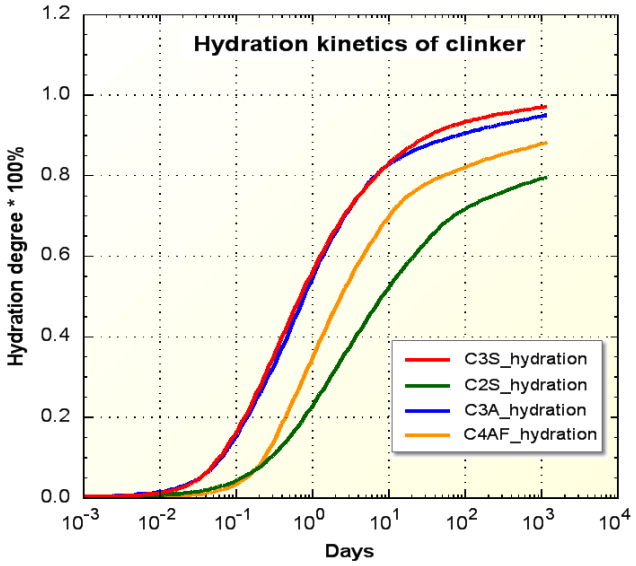


Fig. 1. Hydration kinetics of cliker phases

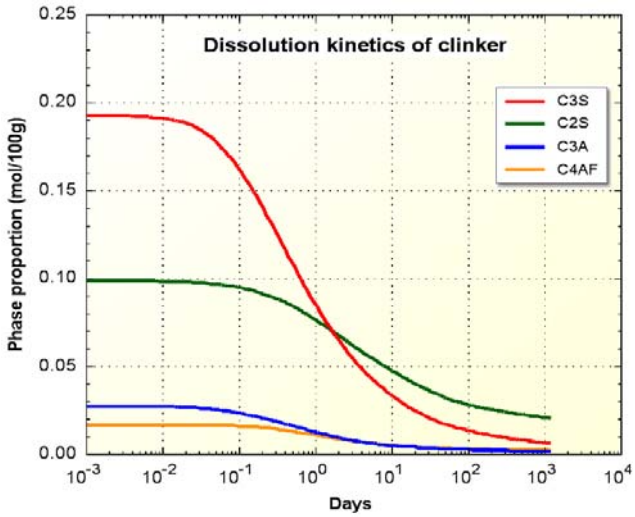


Fig. 2. Dissolution kinetics of cliker phases

Using the modelling hydration coupled with the GEMS software, developed by Paul Scherrer Institut [7], a comparative study was also performed. The results are presented in Fig. 3, and a good agreement between PHREEQC and GEMS models can be noticed.

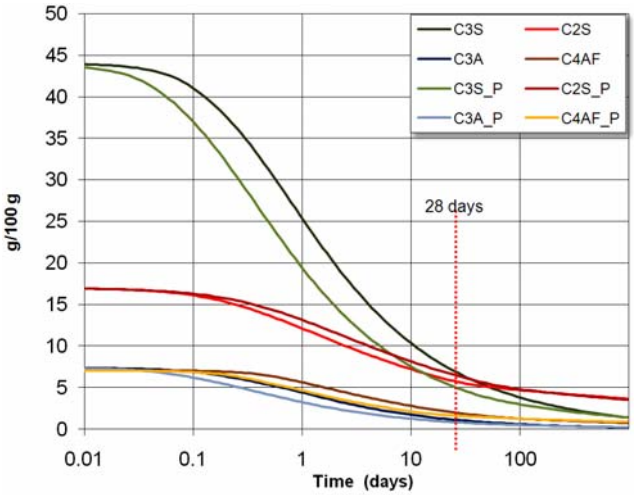


Fig. 3. Comparative graphical representation of dissolution kinetics between PHREEQC (*P extension*) outputs and GEMS outputs (*without extension*)

Conclusions

It is clear that the modelling of cement hyhdration is quite challenging and requires a lot of knowledge and practice.

The work performed so far demonstrates that PHREEQC can reasonably predict the formation of solid hydrates in a cement system, model the hydration of cement clinker phase and provides a phase assemblage.

The predicted weight percentages and the hydration kinetics are comparable with those obtained by other authors ([2, 8, 11]).

The authors' future works aim to develop models that can predict mortar compressive strength and simulate chemical degradation of concrete. These are important information to be used in predicting the behaviour and durability of cement based materials in various environments, a very important aspect for demonstrating the safety function associated with cementitious engineered barriers in a radioactive waste repository.

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