

2020-08-27

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Recommended Citation

Holmes, N., Kelliher, D. & Tyrer, M. (2020). Thermodynamic cement hydration modelling using HYDCEM. *CERI: Civil Engineering Research in Ireland (CERI) 2020, 27th. August, online.*

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Thermodynamic cement hydration modelling using HYDCEM

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ABSTRACT: Thermodynamics have been successfully applied to the field of cement hydration science to predict the formation of phase assemblages and pore solution chemistry. For any cement hydration model to be accepted, it must provide accurate forecasts of which solids may form and how the cement will dissolve over time. This is particularly important for the ongoing development of new sustainable cements and understanding their hydration behaviour in service.

HYDCEM is a cement hydration model that simulates volumetric changes of cement and gypsum dissolution and product growth that, up to now, assumed which solids would form. In order to improve its usefulness, the PHREEQC geochemical software has been coupled with HYDCEM to provide more sophisticated and flexible predictions of which phases may form under equilibrium conditions and generate their change in volume over time for curing temperatures between 5–45°C, variable w/c ratio and cement oxide compositions. To incorporate the coupling of PHREEQC into the model, HYDCEM was re-written in the C# programming language (previously coded in MATLAB) which also improved overall performance and functionality.

This paper presents analysis of a cement system with a w/c ratio of 0.5 at a curing temperature of 20°C and provides predictions of the phase assemblage, phase and product changes in volume and heat evolution over a 1,000-day period in one hour time-steps.

KEY WORDS: Thermodynamics; cement hydration; C#.

1 INTRODUCTION

Thermodynamic modelling of hydration is a very powerful technique to understand the formation of phase assemblages and the influence of temperature and chemical compositions. As the production of cements move towards more sustainable methods and materials, accurate predictions of phase assemblages will continue to be of importance. Much research has been undertaken to predict such phase assemblages using thermodynamic models derived from oxide proportions, w/c ratio and curing temperatures. The most common thermodynamic model used for cement hydration assemblage generation is GEMS [1], which employs a Gibbs free energy minimization approach using the CEMDATA thermodynamic database for cementitious materials [2,3].

The prediction of precipitated phases during cement hydration using the HYDCEM model [4-7] are based on published phase assemblages. While these descriptions are based on thermodynamic analysis (using GEMS), it does not allow HYDCEM the flexibility to determine by itself, which phases will form. It assumes, albeit based on extensive literature, for plain cements, the precipitation of C-S-H, portlandite, monosulphate, hemihydrate, hydrotalcite & ettringite for any oxide proportions. In short, its predicted assemblage was originally prescriptive, only allowing predicted phase assemblages quantities to vary.

This paper presents how HYDCEM has been coupled with the PHREEQC geochemical model [8] to thermodynamically predict which phases will precipitate. These predictions will be used to undertake volume calculations using stoichiometries determined by the model. This will allow it to predict phase assemblages of the cement under investigation from its oxide proportions. As PHREEQC is C based, HYDCEM has been

re-written in C# (previous versions were written in MATLAB) so the user can still perform a full analysis with minimum effort after the input file has been completed but calls MATLAB to present the results graphically.

1.1 Thermodynamic cement databases

A thermodynamic cement database will include those properties of solids that are present in cement. Over the years, many cement-based thermodynamic databases have been developed as described in [2, 3]. However, the most common database now used for cement thermodynamic modelling is CEMDATA [2] that can determine the type, composition, amount and volume of hydrates that may form. The database has been developed based on particular thermodynamic data in the literature coupled with experimental analysis for temperatures between 0–100°C. CEMDATA Version 18.1 is the most recent version of the database and has been successfully used to various cements including ordinary Portland cement, calcium aluminate, calcium sulfoaluminate, blended and alkali activated materials [2]. Importantly here, CEMDATA has also been developed in the correct syntax (.dat format) to be used by the PHREEQC allowing expansion through addition of new data with relative ease.

2 HYDCEM CEMENT HYDRATION MODEL

HYDCEM is a cement hydration model, previously written in MATLAB, that forecasts volumetric changes in phases and hydrates over time [7]. It provides predictions of phase assemblage, degree of hydration, heat release, compressive strength and chemical shrinkage over time for any w/c ratio and curing temperature between 5 to 45°C. The original aim of HYDCEM was to complement more sophisticated

thermodynamic models and provide users with a reasonable prediction of hydration behaviour over time that was easy to set up, analyse and post-process its results. The user input included, amongst others, clinker chemistry (oxide fraction), solid phase densities, species molar mass and heat of hydration, as enthalpies of reaction. The previous version followed a well-structured set of routines that reasonably predicted the cement phase and gypsum proportions, volume stoichiometries and growth of hydration products including C-S-H, calcium hydroxide, hydrogarnet (if applicable), hydrotalcite, ettringite and monosulphate over time.

As PHREEQC is a C-based computer language, it was decided to re-write HYDCHEM in C# so coupling and follow on computations could be more computationally effective. C# is a multi-purpose object-orientated programming (OOP) language developed by Microsoft as part of the .NET Framework [10]. C# is a high-level language that is widely used for desktop and web applications and is popular for game development. By defining variables and pre-allocation, C# is computationally efficient with automatic garbage collection. Using OOP simplifies programming as it optimises the code allowing users to continually develop it. C# uses methods or functions which are part of a class and can be used in any instance of the object of that class and can be re-used multiple times.

2.1 PHREEQC geochemical model

PHREEQC is a Geochemical model [8] for thermodynamic calculations to predict which solids may precipitate in cement-based systems using an appropriate database. PHREEQC undertakes thermodynamic equilibrium calculations by solving the law of mass action (LMA). This approach is also used by EQ3/6 [11] and CHESS [12] whereas GEMS [13,14] undertakes its predictions by minimising the Gibbs free energy of the system under analysis. Both approaches are acceptable with very few differences in their prediction using the same database.

The iphreeqc set of modules allows PHREEQC to be coupled with programming languages without the need to read from or write to files [15] through a library. The iphreeqc COM module can be used by any software that supports the COM interface whereas the C++ class, libraries and Dynamic Link Library (DLL) can be compiled into C-based programmes. Input information and results transfer occurs via the internal computer memory. The iphreeqc module allows PHREEQC to be run within models like HYDCHEM simultaneously without the user having to move between separate models and securing data transfer including results. Coupling PHREEQC with other programmes such as DuCOM [16], a speciation solver [17], COMSOL [18] and EXCEL [19] to model cement hydration has been reported in the literature and is a rapidly developing field.

2.2 Equilibrium reaction equations

Equilibrium reactions are represented by mass-action equations [20]. The pure phase equilibrium is given by Equation 1, where K_p is the thermodynamic equilibrium constant for phase p (Equation 2), γ_i is the activity coefficient of ion i , c_i is the concentration of ion i (mol/L) and $n_{i,p}$ is the stoichiometric coefficient for ion i in phase p , T is the temperature (K), R is the universal gas constant (8.31451 J/(mol K)) and the term $\Delta_r G_T^0$ is the standard Gibbs energy of

reaction (Equation 3). The basic principles of thermodynamic calculations and how it deals with chemical reactions can be found in the literature [20, 21].

$$K_p = \prod_i (\gamma_i c_i)^{n_{i,p}} \quad (1)$$

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

$$\Delta_r G_T^0 = \sum \Delta_r G_{T,products}^0 - \sum \Delta_r G_{T,reactants}^0 \quad (3)$$

3 THERMODYNAMIC ANALYSIS

Table 1 shows the oxide proportions of a plain PC from a leading Irish cement manufacturer with a w/c ratio of 0.5, curing temperature of 20°C and the elemental compositions required by the thermodynamic model. The PHREEQC desktop user interface is shown in Figure 1. The oxide proportions are converted to the appropriate units (here g/L) using their molar masses. The pH in the analysis was initially given as 7 and charge balanced. The initial set of results present information on the solution, not the solids, which in the first calculation are oversaturated in the predicted solution. PHREEQC calculates how saturated the solution is with respect to each solid phase. When the Saturation Index (SI, log scale) is positive, a phase may precipitate from the solution. When the SI is negative, the solution has the capacity to dissolve a phase, if it is predicted. Where the saturation index is zero the solution phase is at equilibrium with the solid phase and will neither dissolve nor precipitate.

To determine which phases may form, all possibilities are equilibrated by setting their SI to zero and if a phase becomes oversaturated, it will precipitate. This addition to the initial solution input is entered under the EQUILIBRIUM PHASES data block. HYDCHEM undertakes these steps and following a number of runs, the predicted solid phases are determined. At this stage a degree of scientific judgement must be exercised by the user, to prevent prediction of unrealistic phases in the equilibrium assemblage. Many databases contain entries for high temperature or high pressure phases, which will not spontaneously form during hydration. In the example reported here, only cement hydrate phases have been selected, yet the model maintains the flexibility to consider much more complex systems. HYDCHEM sweeps through the output and using coded decision making tools, outputs the solids that should be included in the follow-on analysis that are described below.

3.1 Hydrogarnet

The output suggests that all of the hydrogarnet (C_3AH_6) would dissolve and re-precipitate as siliceous hydrogarnet ($C_3AS_{0.4}H_{5.18}$). This would be expected behaviour in blended cements but not necessarily in a pure Portland cement. Previous researchers [9] found that C_3AH_6 hydrogarnet was the only crystalline phase detected at temperatures ranging from 25-105°C. To overcome this anomaly, a second analysis is undertaken to allow the siliceous hydrogarnets to remain oversaturated.

3.2 AFm phases

Monosulphate is a commonly occurring hydrate during cement hydration that forms when gypsum has been consumed and

Table 1 Cement chemical analysis and PHREEQC input

Cement oxide (g/100g)		PHREEQC Input	
SiO ₂	19.04	Temp	20
Al ₂ O ₃	5.01	pH	7 charge
Fe ₂ O ₃	2.83	pe	4
CaO	63.4	Redox	pe
MgO	2.31	Units	g/L
Na ₂ O	0.28	Density	1
K ₂ O	0.54	Al	0.53
CaO free	1.71	C	0.12
CO ₂	2.2	Ca	9.062
SO ₃	2.65	Fe	0.396
Soluble Na ₂ O	0.14	K	0.09
Soluble K ₂ O	0.43	Mg	0.279
Phase proportions		Na	0.042
C ₃ S	57.35	S	0.212
C ₂ S	11.32	Si	1.78
C ₃ A	8.49	water	1 kg
C ₄ AF	8.61		

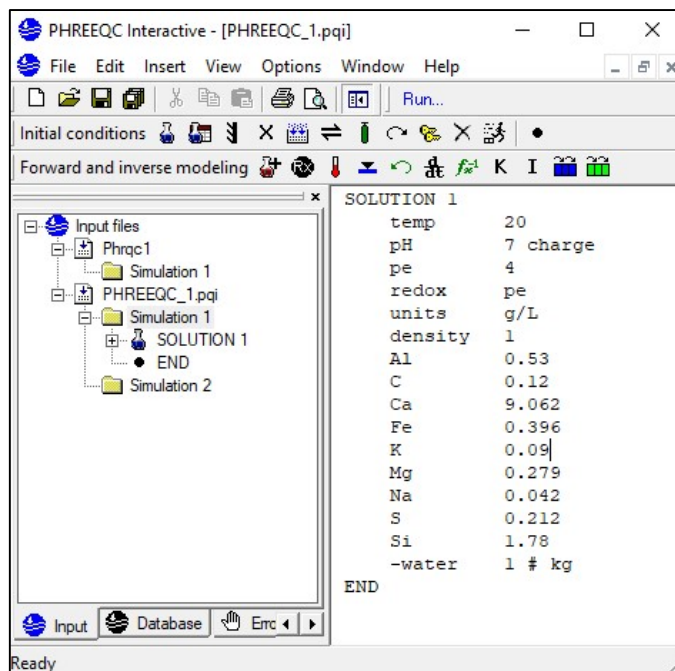


Figure 1 PHREEQC interactive input screen

ettringite reacts with remaining C₃A's [22].

Monosulphate can be converted to ettringite in the presence of sulphates, which contributes to the cracking found during sulphate attack. The output from the PHREEQC analysis suggests that monosulphate will dissolve and not precipitate. Previous research suggests that monosulphate would be expected to precipitate from the cement described in Table 1 [23]. Therefore, monosulphate is included in the list of solids expected to equilibrate with the liquid despite its apparent metastability with respect to hydrogarnet.

CEMDATA contains three types of hemicarbonate phase, namely hemicarbonate10.5, hemicarbonate and hemicarbonate9. Despite not being a very well characterised AFm phase, the literature ([9], [24, 25]) suggests hemicarbonate will be present in PC with very low carbonate

contents from 5-40°C and absent/unstable at higher temperatures (>50°C). As shown in the literature [3], hemicarbonate is predicted to precipitate from Portland cements. However, while thermodynamically it is not predicted to form, it will be included in the list.

3.3 Aft Phases

Four ettringite types are included in the CEMDATA database. Only one type is needed so the stoichiometric ettringite is used here as the AFt phase. In AFt, the functional/exchangeable anion (sulphate in ettringite) can be exchanged for chloride, carbonate, borate, hydroxyl and others to make a family of compounds. Similarly, the structural units (aluminates) can be exchanged with ferrate and others, to produce more complex salts. This is because most of ettringite is open space with channels running the length of the lattice, leaving plenty of space for substitutions, without changing the essential character of the structure. Lastly, it's reasonable to assume all magnesium partitions into hydrogarnet.

3.4 C-S-H

C-S-H is a gel-like solid and the main phase in hydrating cement with a typical calcium/silica (Ca:Si) ratio of ~1.8. Blast furnace slags, PFA and silica fume blends have typical Ca:Si ratios of 1.4, 1.0 and < 1 respectively. Using the cement described in Table 1, the C-S-H predicted to form (SI = 0) is CSH3T-T2C which is one of five alternatives in CEMDATA and is described, along with supporting literature, in [2] and [26]. CSH3T-T2C is more consistent with the tobermorite-like structure of C-S-H [27] and has a Ca:Si ratio of 1.5 (C₃S₂H₅) [2]. The range of C-S-H models in CEMDATA is to account for the variations in the Ca:Si ratio > 1 which affects its solubility. Space precludes a full description of C-S-H solubility models here.

3.5 Summary

One cannot assume that because a phase is oversaturated, it will automatically precipitate so an understanding of the underlying chemistry is important. A model helps the user to understand a system but it does not always predict what would be expected. Therefore, the hydrate assemblage should be kept as simple as possible, employing reasonable assumptions if a phase expected form is not thermodynamically predicted. While not oversaturated in the initial analysis, monosulphate and hemicarbonate are included in the final assemblage for Portland cements. If they are predicted to form, they will be allowed to do so. If not, they will still be included but not present in the predicted hydrate assemblage. These assumptions are summarised below:

- C₃AH₆ should be used as the hydrogarnet phase in Portland cement systems;
- The stoichiometric ettringite is the only AFt phase;
- Monosulphate and hemicarbonate should be included in the phase assemblage of PC cements to accommodate carbonate when present;

The following rules are also included in the model to mimic the expected kinetics of a hydrating cement:

- Ettringite is precipitated when gypsum is present;
- Monosulphate is precipitated if gypsum is depleted but ettringite is still present:

- Hydrogarnet is precipitated if gypsum and ettringite are both depleted.

The following section describes the re-written HYDCEM model into the C# programming language.

4 HYDCEM IN C#

The input for the model is provided via a Windows form, as shown in Figure 2(a). The analysis begins when all data required is input. When complete, the analysis time is given and the results are plotted on separate tabs.

4.1 C# programming language

C# (pronounced C-sharp) is a high-level, multi-paradigm (e.g. object-oriented programming, structured programming, etc.) language developed by Microsoft [28] and executed by the Common Language Runtime (CLR) within its .NET platform. It combines the power of C++ with the programming simplicity of Visual Basic. Its extensive class library provides the user with functionality, compilers, debuggers and other development tools. The key advantage of C# is that the code is “managed” meaning all memory requirements are fully managed by the CLR, removing the need of the developer to consider memory management issues. This is paralleled in the development of PHREEQC which, once implemented in C, made full use of dynamic array addressing. The consequence is that even for complex chemistries, economic use of memory is assured, which in turn allows shorter run times, even on relatively modest architecture

HYDCEM was prototyped in MATLAB®, but began to experience very long runtimes as the program grew in complexity. A decision was made to move HYDCEM development over to the C# platform, as the runtimes would reduce substantially and the opportunity to utilize OOP. The easy addition of more classes and methods/functions make future editing and development tasks easy to undertake. C# is a modern, powerful, yet easy to learn programming language with extensive online learning resources and in-built class libraries that is free to install on most PC's. As both C# and PHREEQC are both C-based languages, coupling them is relatively straightforward. Post processing of the results is carried out in MATLAB®. HYDCEM automatically generates an “m” file, used within MATLAB® to produce all output.

4.2 HYDCEM program structure

HYDCEM is implemented as a DLL library that may be then be utilised within a choice of front ends, e.g. a simple Console application or a full Windows application as in this paper. HYDCEM consists of a number of classes that produce all the functionality required for the simulation. These classes and their main properties and methods are described below.

Simulation: This abstract class contains all the methods required to carry out a full HYDCEM simulation and are described below.

Dictionaries: In the **PhaseClass**, cement phases are instantiated from the original cement mix data. Its main properties are the degree of hydration, weight and volume histories of the phase computed during the simulation.

PhasePKClass, derived from **PhaseClass**, has extra information required for the Parrot & Killoh [20] algorithm. Its

main method is **NextAlpha**, which generates the degrees of hydration when invoked from the **Simulation** class.

ProductClass is instantiated from the PHREEQC analysis and contains the predicted hydration product.

Objects: **SimulationDataClass** contains primary data and information required and generated by the **Simulation** class. **SimTimeClass** generates the time steps for the simulation and contains derived data such as arrays of times in hours and days. The **OxideContentClass** stores the oxide input.

Public methods: The **ParrotKillohClass** is required by the **Simulation** class to instantiate a **ParrotKillohClass** object containing the information required by the Parrot & Killoh algorithm. **PhreeqcClass** imports the Phreeqc DLL and provides C# methods invoking selected Phreeqc functions. Its main method is **RunPhreeqc**, which carries out a Phreeqc analysis and outputs a list of predicted hydration products.

Abstract Classes: **MolarMass**, **Stoichiometries** and **Denisties** are abstract class containing the molar masses, stoichiometric information and densities.

5 ANALYSIS AND RESULTS

The phase assemblage of the cement described in Table 1 is shown in Figure 3 with a processing time of 9 ms.

The dissolution of the cement phases is shown using the degree of hydration for each using the Parrot and Killoh method [29]. The change in volumes are calculated using stoichiometries for the silicates, aluminates, ferrites and magnesium [7]. The C₃S phase is shown to be more reactive over time than the other phases as expected. The phase assemblage shows the growth of C-S-H, calcium hydroxide, monosulphate (AFm) and ettringite (AFt) and dissolution of gypsum. As gypsum is depleting, the volume of ettringite is increasing up to approximately 10hrs after which it remains constant until monosulphate growth begins. At 72hrs (in accordance with the literature), monosulphate is precipitated. The precipitates are predicted by the thermodynamic model that are read into HYDCEM to calculate their volume change over time employing the rules described in Section 3.5. As may be seen, as well as the expected solids (C-S-H, calcium hydroxide, AFM), hydrotalcite, hemihydrate and small quantities of iron hydroxide (FH) are also predicted to precipitate.

6 CONCLUSIONS

Cement hydration is a highly complex process that involves competing chemical reactions and physical changes over many time scales. Therefore, any model that attempts to predict it has to incorporate a reasonable level of sophistication using accurate input data. The HYDCEM model described here attempts to do just this employing thermodynamic predictions to show long-term phase and product changes over time, as well as other useful outputs within a very user-friendly platform within a modern and powerful programming language.

Work is underway to incorporate limestone and supplementary cementitious materials into the model so cement scientists can develop new, more environmentally friendly products.

HYDCEM v3.0

HYDCEM

Simulation

Data OK

Run

Timings

-

-

Input Data Stoichiometry Data

Binder oxide composition (%)

SiO2	19.04	CO2	2.20
Al2O3	5.01	SO3	2.65
Fe2O3	2.83	Soluble Na2O	0.14
CaO	63.4	Soluble K2O	0.43
MgO	2.31	K2SO4	0
Na2O	0.28	Na2SO4	0
K2O	0.54	MgO periclase	0
CaO free	1.71		

Simulation Time Steps

Duration of Simulation: 1000 days

Constant: 24001 time steps

Time Step: 60 min

Variable: 149 time steps

Initial Time Step: 0.1 min

Growth Factor (>1): 1.1

Parrot-Kiloh

Blaine Surface Area (m2/kg): 429

Cement Properties

w/c ratio: 0.5

Limestone Percentage (%): 0

Curing Temperature (deg C): 20

Mortar Compressive Strength

Intrinsic strength of cement (MPa): 35

n (2.6-3.0): 2.6

Figure 2 HYDCEM front end for data input

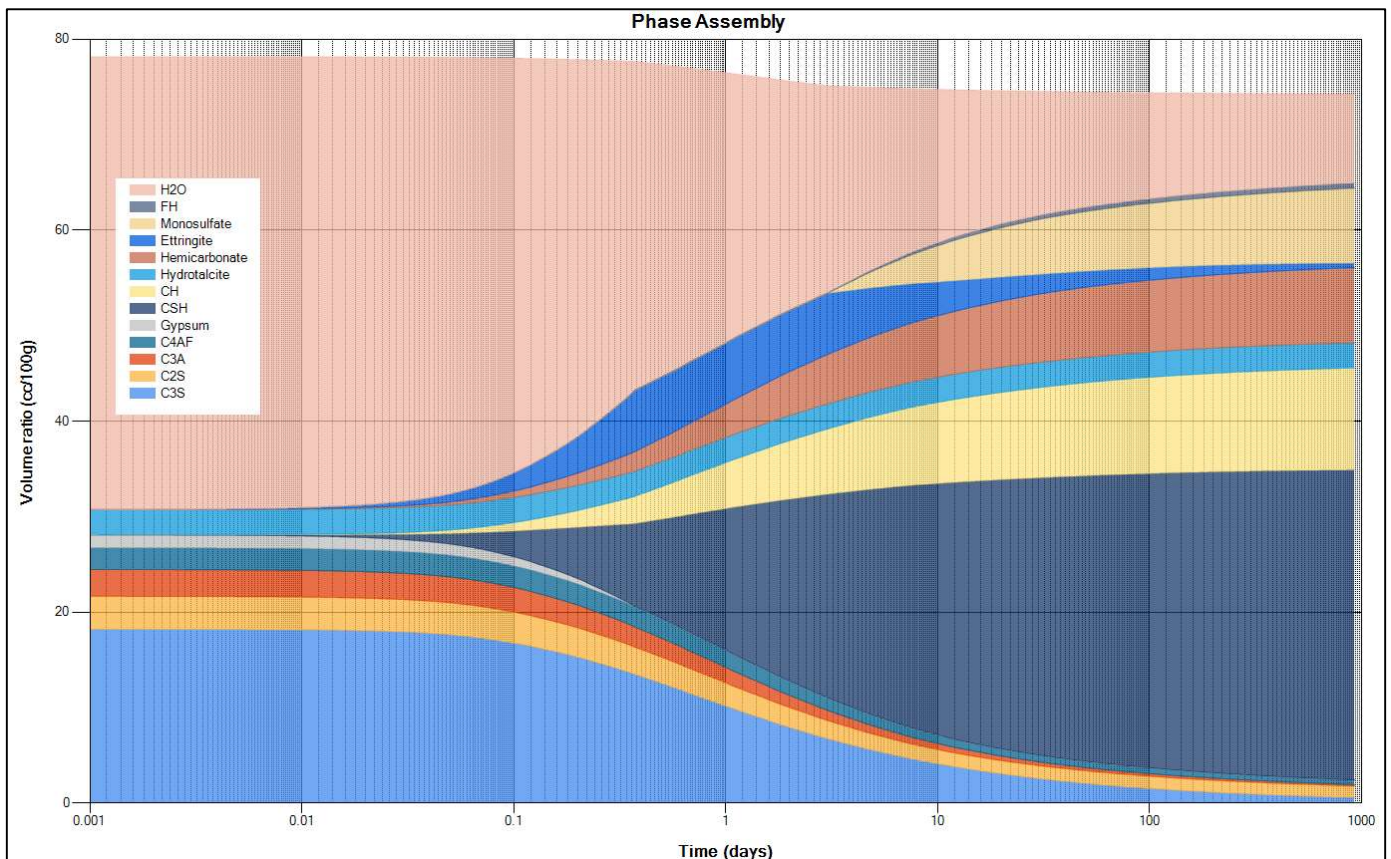


Figure 3 Phase assemblage

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