A Benchmarking of Slag Blended Cement Hydration Models

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Abstract.

Several slag-blended cement hydration models widely used in the cement research field are benchmarked in this work, with a focus on their hypothesis, assets and drawbacks. The effect of slag on the hydrating mixture and the hydration products composition and quantities is considered. Different cement hydration models are presented in this study: analytical models such as Chen & Brouwers' and Kolani's models and generic numerical hydration models as CEMGEMS and VCCTL. Powers' and Tennis & Jennings' models are also used for comparison for compositions without slag-substitution. Computed results obtained with these models such as the degree of hydration and the hydration products composition and quantities are compared with experimental results found in the literature.

Keywords: Hydration, Cement, Slag, Degree of hydration, Multi-physics modeling

1 Introduction

Concrete represents 90% of the construction market [1]. It is considered as the most consumed material in the world [2]-[3], succeeding water. In the context of sustainable development, the optimization and reduction of the use of cementitious materials is therefore becoming a core issue for the reduction of pollution in the construction sector.

One of the solutions that can insure this reduction is the partial substitution of clinker by mineral additions. These additions affect the hydration reactions and are generally industrial by-products such as fly ash, blast furnace slag and silica fume.

While the hydration processes of ordinary Portland cements is widely studied in literature, the slag-blended cement was given less attention. The influence of slag can be identified according to several aspects, especially the hydration reactions and the degree of hydration of the material.

In a study involving slag-blended cement hydration modeling, one must select a model with the best suited characteristics. The model characteristics may be of a chemo-physical nature (such as the chemical composition of the output phases) or a technical nature (the model execution time for example). The model choosing process should naturally be a first step before finally selecting a desired hydration model and basing further modeling hypothesis and exploration. Doing a benchmarking of existing

models contributes to making a well-informed choice of a hydration model considering its purpose (research or engineer application) while being well informed on its limits.

Several multi-component hydration models based on microstructure modeling have been proposed previously (CEMHYD3D [4], CEMGEMS [5], [6]…). These models describe best the microstructure evolution during hardening but require a long computing time, which is not favorable in applications that are time sensitive. Here lies the importance of analytical models, that provides reliable results in short periods of time such as Chen and Brouwers' [7]–[10] and Kolani's [11] models. Additionally, models [12], [13] that do not take slag substitution into consideration are also included for comparison purposes on ordinary Portland cement

The different models investigated hereafter are:

- Powers' model [12],
- Tennis and Jennings's model [13] ,
- CEMGEMS' model [5],
- VCCTL's model [14],
- Chen & Brouwers' models [8]–[10],
- Kolani's model [11].

Note that several other slag blended cement hydration models have been proposed by Stephant [15] , Merzouki [16], Königsberger [17], Kinomura [18], Elakneswaran [19], Thomas [20], Phreeqc [21]. These more recent models are promising but have not been treated in this benchmark due to time considerations.

The paper is organized as follows: the models are presented in section 2 and compared to experimental data in section 3. A conclusion is drawn in section 4.

2 Models

The benchmarked models are detailed below, in order to assess their reliability along with other criteria such as computation time and physical input parameters (consideration of temperature, curing conditions, oxides composition for the reagents). Ultimately, phases quantities will be compared, especially the portlandite formation that can be found experimentally with a good reliability.

Powers' model [12] is applied for the pure clinker hydration only. It is used as reference and a foundation for further models. Tennis & Jennings' model [13] improves on Powers model, by taking into consideration time and further phases details. But it is also non-applicable to slag blended cement.

Chen & Brouwers' model [8]–[10] represents an approximation of physical behavior based on comprehensive chemical formulas. This analytical model is relatively fast. It does not offer a proper kinetic modeling; therefore, it can be coupled with a kinetic model such as offered in Meinhard [21] or Mounanga [22].

Kolani's model [11] is an iterative analytical model, with relatively fast results, giving more details such as kinetics and heat flux.

CEMGEMS [5] is a fast-numerical model, but does not provide time depending results, and has technical limitations such as the imposition of reactive oxides which may not be present in the original mixture.

VCCTL [14] is a numerical model based on the CEMHYD3D system widely used in literature but has a long computation time.

2.1 Brief Overview of cement composition

Cement is a hydraulic binder that, when mixed with water, forms a paste that hardens and provides mechanical resistance and stability to the structure. The characteristics of the slag and cement composition used by Kolani [11] are shown in table 1.

Name	cement notation	chemical formula	Clinker composition	Slag composition
Calcium oxide, or lime	C	CaO	63.13	42.30
Silicon dioxide, or silica	S	SiO2	20.68	35.90
Aluminum oxide, or alumina	A	Al2O3	4.40	11.20
Iron oxide, or rust	F	Fe2O3	2.34	0.30
Magnesium oxide, or periclase	M	MgO	2.10	8.00
Sulfur trioxide	$\bar{S}$	SO3	3.27	0.20

Table 1. Clinker and slag oxide composition for the Cement paste used in Kolani [11]

The hydration of cement starts instantly when mixed with water. The reaction progresses upon contact of the binder with water and occurs with heat release. Hydration reactions are affected by many factors such as: the phase composition of the cement and the presence of different ions in the crystalline phase, the particle size distribution, the water to binder ratio, the curing temperature, the presence of chemical admixtures [22]… Main hydration products and their chemical formulas are presented in table 2.

Abbreviation	Chemical formula	Name
CH	$Ca(OH)_2$ or $CaO \cdot H_2O$	Calcium hydroxide
C-S-H	x $CaO{\cdot}SiO_2{\cdot}$y H_2O	Calcium silicate hydrate
C-S-A-H	x $CaO{\cdot}SiO_2{\cdot}$y $Al_2O_3{\cdot}$z H_2O	Calcium aluminate hydrate
AFt	$C_6(A,Fe)S_3H_{32}$	Calcium trisulfoaluminate hydrate/ettringite
AFm	$C_4(A,Fe)SH_{12}$	Calcium monosulfoaluminate
Cc	$CaCO_3$	Calcium carbonate
HT	M_5AH_{13}	Hydrotalcite
HG	$C_6AFS_2H_8$	Hydrogarnet
AH	C_4AH_{13}	Tetracalcium
Mc	$Ca_4Al_2(CO_3)(OH)_{12}.5H_2O$	Calcium Monocarboaluminate

Table 2. Different hydration products and their chemical formulas

2.2 Ordinary Portland cement analytical models

Powers' Model. Powers' model [12] is a simple model involving three different phases solely, with no further detailing: the hydration products, the anhydrous clinker and capillary pores. Different models found in the literature are based on Powers' model but considering different cement additives (such as slag [15], fly ash [23] …) . Because of the simplicity of its original model, it cannot be taken into consideration when developing a slag blended cement model, it is only studied here to be taken as a reference when talking about hydration of pure clinker, with no slag added.

The clinker, water and hydration products quantity evolve during the hydration process depending on the initial water to cement ratio (w/c) as well as the curing conditions. The hydration advancement degree is described using the mass ratio of hydrated clinker to initial anhydrous clinker (α).

The volume fractions of the anhydrous clinker, hydration products and capillary pores are calculated using the following formulas:

$$f_a = \frac{1-\alpha}{1+\rho_a w/c}; \qquad f_h = \frac{k_h \alpha}{1+\rho_a w/c}; \qquad f_{cp} = \frac{\rho_a w/c + (1-k_h)\alpha}{1+\rho_a w/c}$$

where:

f_a: volume fraction of anhydrous clinker [m^3/m^3],
f_h: volume fraction of hydration products [m^3/m^3],
f_{cp}: volume fraction of capillary pores [m^3/m^3],
ρ_a: density of anhydrous clinker (to be taken equal to 3.13) [$kg.m^{-3}$],
k_h: volume of produced hydrates (to be taken equal to 2.13) [m^3].

Tennis and Jennings' model. Tennis and Jennings's model [13] is a hydration model based on chemical reactions more detailed than Power's model. It distinguishes the anhydrous clinker phases (Alite, Belite, Aluminate and Ferrite), gypsum and the various hydration products phases (calcium hydroxide, hydrogarnet, CH, AFm, Aft…). It also studies the kinetics of the reaction based on the Avrami's equations for each phase. These equations describe the kinetics of the hydration of the different cement phases. The model is based on the stoichiometric reactions for the hydration of the principal phases of clinker: C3S, C3A, C2S and C4AF.

The deficiency in this model lies in the hypothesis that all the ettringite will react to form monosulfate, even though experimentally, it is proven that some ettringite is found at the end of the hydration process [24]. Another problematic point is the Bogue [25] calculation, converting the oxides present in the clinker to the clinker phases, which is only an approximation and doesn't provide exact values [26], [27]. Further, according to the authors themselves, Avrami equations are too simplistic to describe finely the hydration kinetics of cement paste.

This model predicts the volume fractions of various compounds. It also quantifies the porosity, partitioning it into capillary porosity and C-S-H porosity. It further distinguishes different C-S-H types (high-density C-S-H (HD C-S-H) and low-density C-S-H (LD C-S-H)). It also calculates the chemical shrinkage and can be used to compute physical properties of the cement.

Unfortunately, this model is only appropriate to the slag cement hydration computation. This model will serve as a reference for further models' validation in the limiting case of no substitution by slag.

2.3 Analytical models for slag blended cement

Chen & Brouwers' model. Chen & Brouwers [8]–[10] proposed three different models for each of the hydration of the pure clinker, alkali-activated slag and slag blended cement. These models are based purely on the chemical reactions and stochiometric calculations, based on different hypothesis for each model.

Starting with the initial oxide compositions and their proportions in the mixture, the hydration of the two main constituents (clinker and slag) is investigated separately, and then established considering the interaction of the hydration products. A mixture of the products of both Portland cement's hydration and slag's hydration is to form. The amount of CH formed by the Portland cement hydration is partially consumed by the slag hydration (Pietersen and Bijen, 1994 [28] ; Regourd, 1980 [29] ; Richardson and Groves, 1992 [30]).

The most questionable product is the C-A-S-H whose composition varies depending on its calcium to silicon C/S ratio and aluminum to silicon ratio A/S. Chen [7] proposed three different models for slag-blended cement based on stoichiometry calculations, mainly to determine the C/S and the A/S ratios in the C-A-S-H, which impact the stoichiometry of the hydration reactions and the molar volume and weights of the C-A-S-H.

It is well established that the C/S ratio is lower in slag blended cement pastes than that in ordinary Portland cement pastes, indicating that the slag reaction is consuming additional calcium. This additional demand is provided by the CH formed by the hydration of the Portland cement. The curing time has been found to have minor effect on the stoichiometry of C-A-S-H, contrarily to the slag proportions that modify strongly that stoichiometry. In fact, when increasing the slag over cement ratio, the C/S ratio in C-A-S-H decreases while the A/S ratio increases [7].

Three models are examined, depending on the different degrees of aluminum substitutions for silicone in C-S-H. These models are used to quantify the hydration products and to determine the composition of C-S-H based on stochiometric calculations.

The three models have the following hypotheses:

1) **Model 1:** No CH enters the C-S-H formed by the slag hydration.
2) **Model 2:** CH enters C-S-H from the slag hydration to sustain a C/S ratio 1.8, a common value for ordinary Portland cement paste.
3) **Model 3:** Part of the CH enters C-S-H from the slag hydration.

Once the three models have been developed, a comparison to a series of experimental results has been carried out, Only the third model is retained in the present work.

The results given by this model do not explicitly depend on time, but on the degrees of hydration of clinker and slag.

Kolani's Model. Kolani [11] proposed an incremental model based on the identification of the degrees of hydration, heat exchange, and the hydric state. A set of partial differential equations is established to govern the evolution of the corresponding variables with time. This multiphasic model takes into consideration the difference in the kinetics of hydration of the slag and cement constituents, combined to a stochiometric chemical model.

The interactions between the phases integrates a statistical approach to predict the stoichiometry of the C-S-H formed. The kinetics model proposed by Buffo-Lacarriere [30] is adapted to take into consideration the slag blended cement hydration' specifications.

The main equations governing this model can be resumed in these equations:

– The rate of hydration of the anhydrous phases i in {clinker, slag} is:

$$\dot{\alpha}_i = A_i \cdot g_i \cdot \pi_i \cdot h_i \cdot s_i$$

where $\dot{\alpha}_i, A_i, g_i, \pi_i, h_i, s_i$ are respectively: the time derivative of the hydration degree of phase i, a global fitting parameter, the dissolution activation, the water availability, the thermic activation and the chemical activation detailed further in [12] .

– The water and heat conservation equations:

$$\dot{W} = -div\left(-D_{w0}\exp(pW)\,\overrightarrow{grad}W\right) + \sum Q_{th,i}^{W} \cdot f_i \cdot \dot{\alpha}_i$$

$$\rho c \cdot \dot{T} = -div\left(-\lambda\overrightarrow{grad}T\right) + \sum Q_{th,i}^{W} \cdot f_i \cdot \dot{\alpha}_i$$

where $W, T, D_{w0}, p, f_i, Q_{th\,i}^{W}, Q_{th\,i}^{T}, \lambda$ are respectively: the water content of the cement, the cement temperature, fitting parameter of the Mensi law (1998) [31], another fitting parameter of the Mensi law, anhydrous compound i dosage, water consumed by compound i, total hydration heat for compound i and the cement thermic conductivity.

2.4 Numerical models for slag blended cement

CEMGEMS. CEMGEMS [5] [6] is a web platform that provides an easy user-interface thermodynamic models for cementitious material hydration in the cement chemistry and engineering domain. This web app is developed and maintained in Switzerland at CONGINEER Ltd, thanks to funding from the international Nanocem consortium. The CEMGEMS web app uses the developed UpToDate GEMS3K code to compute chemical speciation by Gibbs energy minimization (GEM) according to the standard thermodynamic data from the Cemdata18 (Empa) and PSI/Nagra chemical thermodynamic databases.

CEMGEMS is used to compute the hydration process, the interstitial pore solution, the heat exchange and much more using a simple, intuitive user interface with changeable input parameters offering the results under plot views and data tables formats.

VCCTL. The Virtual cement and concrete testing laboratory (VCCTL) [4] is a virtual laboratory software where cement paste and concrete materials are computed in a virtual environment. It has been researched and developed for over 30 years [32]–[35]. The goal of this computational modeling of cement and concrete hydration is to provide an accurate and time-saving virtual fast prototyping tool that enables for the investigation of the characteristics of various hypothetical combination designs combining regularly used concrete components [36]. A solution like this might drastically minimize the amount of time and effort required to generate and qualify concrete mixes for industrial purposes.

It operates on any random mixture of cement powders, fillers, aggregates or any other cementitious material under a wide range of curing conditions. Transport properties, alongside with thermal and mechanical properties are determined over the course of the hydration. It has a graphical user interface allowing the creation, hydration and estimation of the 3D cement material microstructure.

It is based on the CEMHYD3D system, widely used in literature and for many cement types: slag blended cement [8], limestone blended cement [37], and has many applications such as porosity depercolation repercolation [38], microstructural studies [39].

3 Comparison

3.1 Summary of models' characteristics

A comparison between the models, regarding the input and output parameters are summarized in table 3 below. As shown, each model presents different assets and limitations regarding the input and output parameters as well as the computational time.

	Model	Powers	Tennis & Jennings	Chen & Brouwers	Kolani	CEMGEMS	VCCTL
Input	Appropriate for slags	×	×	✓	✓	✓	✓
	Slag composition	×	×	✓	✓	✓	×
	Temperature	×	×	×	✓	✓	✓
	Curing conditions	✓	✓	✓	×	×	✓
Output	Time dependency	×	✓	×	✓	×	✓
	C/S of the C-S-H	×	×	✓	✓	×	×
	Heat flux	×	×	×	✓	✓	✓
	Pore solution	×	×	×	×	✓	✓
Computation time		Instantly	Instantly	Instantly	< 1 min	Few minutes	6 hours avr.

Table 3. A summary of the assets and limitations of some slag-blended cement hydration models

3.2 Comparison on the quantity of consumed and produced phases

To compare the model predictions of the quantity of consumed and produced phases, a simulation by Chen & Brouwers [8]–[10], Kolani [12], CEMGEMS [5] and VCCTL [9] models was done for slag-blended cements with clinker and slag oxide composition presented in table 1. Four types of cement presented by [12] are treated with slag over cement ratio equal to 0%, 30%, 50% and 70%. These cements were treated in isothermal conditions and constant temperature equal to 20°C. A slag substitution rate of 50% was taken, with a water over binder ratio equal to 0.5, a clinker hydration degree of 0.98 and a slag hydration rate of 0.34. These values of hydration degrees correspond to the maximum hydration degrees simulated using VCCTL at 365 days. The results of these calculations are presented in figure 1 below. The volume fractions' comparison of the phases regarding the porosity, the C-S-H, the C-A-S-H shows relatively close results, at the exception of hydrates formation of which VCCTL shows a large underestimation.

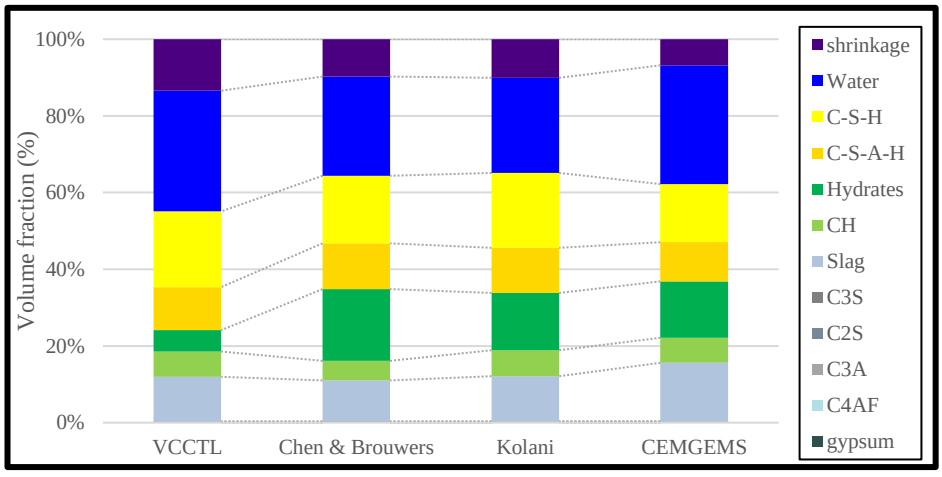

Figure 1. Phases comparison using VCCTL [14], Chen & Brouwers [8]–[10], Kolani [11] and CEMGEMS [5] models for a slag substitution rate of 50%, a water over binder ratio equal to 0.5, a clinker hydration degree of 0.98 and a slag hydration rate of 0.34. The key "hydrates" denotes all hydration products not already listed in the other keys.

Another type of validation is the comparison of the volume fractions provided by experimental campaigns carried out by Kolani [11]. For these types of comparison, experimental initial composition and conditions are taken into consideration, and the hydration rate of slag and clinker is pre-specified.

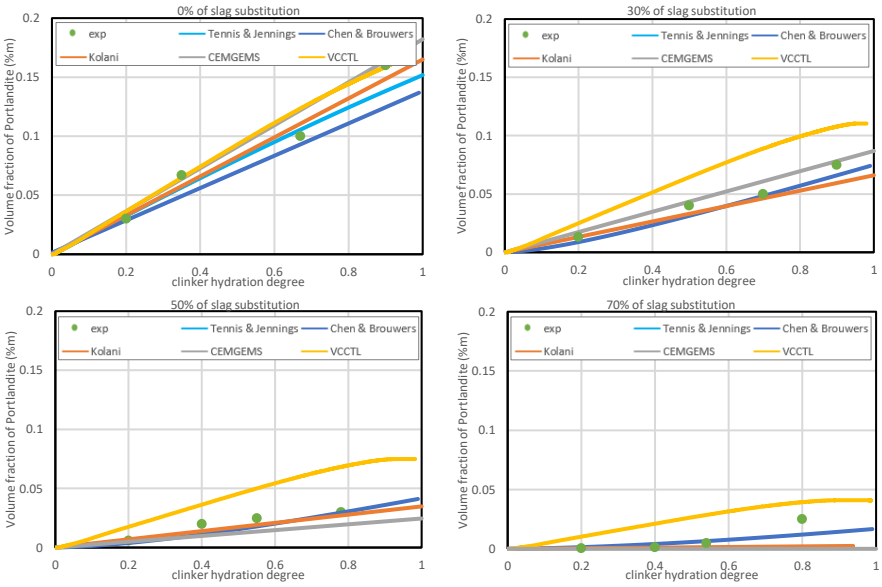

Figure 2. Variation of the portlandite volume fraction depending on the clinker hydration degree as proposed by different models, validated by experimental results from Kolani [9] Mixtures containing 0%, 30%, 50% and 70% slag substitution ratio respectively.

Results are favorable, according to experimental data provided by Kolani [11], at the exception of VCCTL which overestimates the portlandite content.

The validation of others hydration products presents several issues. First, the different models do not consider exactly the same hydration products. For example, calcium monosulfoaluminate is considered as a product of slag-blended cement hydration by Kolani [11] but not by Chen & Brouwers [8]–[10]). Second, experimental techniques such as XRD or TGA can be interpreted differently by various authors leading to different estimation of the nature and quantities of hydration products [37].

4 Conclusion

A description was made of different types of models: analytical models such as Chen & Brouwers' model or Kolani's model, and numerical models such as CEMGEMS or VCCTL.

- While each type of model has its own assets and drawbacks, analytical ones seem to provide reliable results (relatively close values of porosity, portlandite, C-S-H, C-A-S-H and other hydration products) in short computational time.
- Numerical models require more computational time with outputs comparable to analytical model ones.
- All these outputs models fit well to experimental data for the portlandite content, with a slight over estimation by VCCTL.

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