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Hydration of slag-blended cements

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ABSTRACT

In this paper, the hydration of slag in blended cements is investigated through the measurement of hydration reaction indicators such as portlandite content, non-evaporable and free water, and hydration heat. Three substitution rates of cement by slag were used (30%, 50% and 70%). The tests were performed at two constant temperatures (20 °C and 40 °C) in order to assess the activation energy of the different components. A multiphasic hydratation model is proposed to take account of the difference of kinetics of each main phase (clinker and slag) and the hydration kinetic law proposed considers interactions between the two phases. It includes the activation of the dissolution of slag by alkalis released by the clinker phases in the pore solution, the portlandite consumption by slag and the effect of temperature and moisture content on the reaction kinetics. The model is able to simulate the evolution of hydration products and adjust the hydration product stoechimetry to the rates of slag and the current temperature automatically and instantaneously. Its reliability is shown through its ability to fit the whole experimental plan results with a single parameter set. Among these parameters are the hydration heat of slag and its water consumption. The model and its parameters should be useful to simulate other types of slag-blended cement.

1. Introduction

Ground granulated blast furnace slag is produced when iron ore is reduced by coke at about 1350–1550 °C in a blast furnace. Molten iron, the main product of the blast furnace, is extracted from the ore, while the other components form a liquid slag. Granulated slag is produced by quenching the liquid slag with a large amount of water to produce sand-like granulates [1]. The granulates normally contain more than 95% of glass. Generally, they are ground to fine powder, called ground granulated blast furnace slag (GGBS). This is used as a mineral addition in replacement of clinker in blended cements and shows both cementitious behavior (latent hydraulic activity) and some pozzolanic characteristics (reaction with portlandite).

Mixing à binder composed of pure slag with water leads to hydration at so low rate that it is usually mixed with an activator to accelerate the slag hydration reactions. Many activators are reported in the literature to stimulate the reaction of slag. From Chen [1], the most commonly used activators for GGBS are sulfates, Portland cement, sodium silicate, calcium hydroxide and, in rare cases, caustic soda (NaOH). Many of these activators contain alkali metal (e.g. Li, Na, K), and thus they are called alkali activators. Puertas et al. [2] and Ben Haha et al. [3] activated slag hydration with sodium hydroxide and hydrous sodium metasilicate (commonly named water glass). Zivica [4] studied the influence of sodium hydroxide, sodium carbonate, and sodium silicate as activators of slag reaction. These experiments showed that the hydration kinetics and the hydration product C–S–H formed depended on the type of activator used to accelerate slag hydration. Concerning the composition of the calcium silicate hydrate formed by alkali activated slag (AAS) [5], studies show that aluminum is incorporated into the silicate chains of C–S–H formed and its Ca/Si ratio appears to be limited to about 1.1, which is low compared to that of Portland cement C–S–H. This finding has been confirmed by Puertas et al. [2] through microstructural analysis. In construction, slag is generally blended with Portland cement and consequently the main activator of slag used in practice is clinker.

Compared with alkali-activated slag, the slag-blended cement hydration process is more complex, due to the coexistence of clinker hydration and slag reaction. One of the principal reasons for the use of slag in blended cements is the reduction of the heat released during the hydration process. The experimental investigations of Sakai et al. [6] and Binici et al. [7] show that the heat of hydration decreases as slag content increases. But the heat released increases with the fineness of the slag or cement in the blended cements. The chemical and thermal activation of the hydration of slag when blended with Portland cement has been studied by Roy and Idorn [8] through experimental measurements and a literature review. This study indicates that the hydration of slag is activated by the

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alkali released by clinker hydration in the blended cements and temperature rise during the early hydration process provides energy to activate alkali-hydroxide attack on the slag particles. The activation by alkali and thermal activation may be synergistic. The hydration rate of slag in blended cements then depends on the curing conditions. Escalante et al. [9] studied the reactivity of slag-blended cement pastes, with 30% and 50% of slag hydrated at 10 °C, 30 °C and 50 °C for up to 6 months. The degree of hydration of slag measured by the selective dissolution method showed that higher curing temperatures increased the reactivity of the slag and, as the percentage of slag replacement was increased, its reactivity was reduced. These results are in agreement with the mechanism explained by Roy and Idorn [8] and previously described. A good indicator of the progress of the hydration of slag in blended cements is the level of its pozzolanic reaction indicated by the calcium hydroxide content. Experimental studies by several authors, e.g. Escalante et al. [9], Saeki and Monteiro [10], and Pane and Hansen [11] show that slag hydration reactions consume the portlandite produced by clinker in blended cements. Reactivity can vary to a great extent from one slag to another. Bougara et al. [12] experimental investigation showed that the reactivity of slag cements depended on the origin of the slag used. Other factors are known to contribute to the reactivity of slag: chemical composition, slag processing (glass content, structure, cooling rate, ...), pore solution, etc. Prediction of the hydration development of slag-blended cements needs to account for the principal factors that influence the reactivity of slag and the main interactions between clinker and slag hydration reactions in blended-cements. This modeling is essential for better understanding of the performance of slag in concrete and for evaluating the feasibility of using a certain type of slag in engineering practice.

Several models have been proposed in the literature to evaluate the development of properties of slag-blended concrete. Chen and Brouwers [13] propose reaction models for slag-blended cements. The models developed are based on stoechimetry calculations in order to correlate the chemical compositions of the unhydrated main phases (slag and cement) with the quantities of hydration products and the composition of the C–S–H formed at final hydration. These calculations are coupled with Van Eijk [14] hydration model to predict the microstructure development of slag-blended cements. This approach is based on microstructure modeling, such as CEMHYD3D (Bentz [15]) and HYMOSTRUC (Breugel [16]) which compute microstructure development during hydration well but require long computing time when dealing with massive structures. At the same scale of modeling, Wang et al. [17] developed a multi-phase kinetic model to simulate the hydration of slag-blended cements. The proposed model deals with the hydration kinetics of each component of clinker minerals (C_3S, C_2S, C_3A and C_4AF) and slag. The heat release by hydration is calculated according to the degree of hydration of each of the previous components of slag cement and the water consumption by hydration reactions are explicitly calculated. Schindler and Folliard [18] have developed a general kinetic hydration model that can predict the heat evolution of cementitious materials. The proposed modeling includes the prediction of total heat of hydration, degree of hydration, ultimate degree of hydration, temperature sensitivity, and the temperature associated with the hydration of concrete. This hydration model is suitable to predict the heat and temperature evolutions in semi-adiabatic conditions. De Schutter [20,21] proposed hydration model of slag-blended cements that treated the heat production of clinker and slag separately. This model has been validated in adiabatic tests. However, on the construction site, there is heat exchange between the structure and the environment and the effect of water content on hydration is not explicitly taken into account. Therefore the aim of this paper is to propose hydration model that deals with the exchange between the structure and the environment by explicitly taking account of the combined effects of temperature and water content on the hydration kinetics. The proposed model should be applicable to real massive structures and account for the mechanisms involved. For this, a multiphasic hydration model is proposed in which the main components considered are the solid phases, clinker and slag.

In the first part of this paper, the results of an experimental program performed on slag-blended cement are presented. These results show the portlandite and water consumption and the heat release during the hydration process. This experimental contribution to the understanding of the hydration process of slag-blended cement is followed by the multiphasic hydration model which is fitted onto the experimental measurements. The model presented is based on stoichiometric calculations and takes portlandite consumption by the hydration of slag into account.

2. Materials and test methods

The experimental program was performed with binders composed of CEM I 52.5 N cement and blast furnace slag from Fos sur Mer in France. This slag complies with European standard NF EN 15167-1 and is obtained by drying and grinding of granulated slag from blast furnaces. In this paper the term "clinker" is used to mean Portland cement CEM I 52.5 N. The chemical compositions of the clinker and the slag used are given in Table 1. All the experiments were carried out on mortar, the composition of which is given in Table 2.

The main indicators of the development of the hydration process measured during our experimental program are shown in Table 3. The measurements were made on mortar specimens composed of blended cement containing 30%, 50% and 70% of slag and pure clinker. The heats of hydration were measured on mortar which had an initial temperature of 20 °C. The other tests were performed, at each age, on specimens conserved at two constant temperatures (20 °C and 40 °C) in order to assess the effects of thermal activation on hydration reactions of slag-blended Portland cements.

The heat of hydration was measured by a Langavant semi-adiabatic calorimeter test according to European standard NF EN 196-9. The test consists of inserting a cylindrical box containing freshly prepared mortar in a calorimeter to measure the heat evolution. These measurements were performed with the four binders mentioned above.

For the other tests shown in Table 3, the mortars were stirred uniformly, immediately cast in plastic cylindrical tubes and then cured at 20 °C and 40 °C until tested. At each testing age, the hydration was stopped by soaking the samples in nitrogen at −196 °C so

Table 1
Chemical oxide composition of Clinker and Slag.

Oxide composition	% By weight	
	Clinker	Slag
SiO_2	20.68	35.9
Al_2O_3	4.4	11.2
Fe_2O_3	2.34	0.3
TiO_2	0.29	0.7
MnO	0.04	0.4
CaO	63.13	42.3
MgO	2.10	8
SO_3	3.27	0.2
K_2O	0.74	0.5
Na_2O	0.13	0.3
P_2O_5	0.33	–
S^-	0.03	1
Cl^-	0.04	0.01

Table 2
The mortar mix proportions.

Binder (clinker + slag)	350 g
Standard sand	1050 g
Water	175 g

Table 3
Quantities measured during hydration development.

Quantity measured	Time (hours and days)	Technique
Heat of hydration	0–120 h	Langavant
Free water	3 h, 6 h, 9 h, 1 d, 2 d, 7 d, 28 d, 90 d	Lyophilization
Combined water	3 h, 6 h, 9 h, 1 d, 2 d,7 d, 28 d, 90 d	TG–DTG
Portlandite content	3 h, 6 h, 9 h, 1 d, 2 d, 7 d, 28 d, 90 d	TG–DTG

that the free water became solid, thus stopping all hydration reactions.

The free water was measured by lyophilization. This operation removed the free water, which was in the solid phase, from the sample by vacuum evaporation of the ice without melting. The principle was that the solid water was heated at very low pressure and thus sublimed, passing directly from the solid to the gaseous state. The difference in mass before and after lyophilization gave the free water.

The combined water and portlandite content were obtained by thermogravimetric analysis which was carried out using an ADAMEL Lhomargy T2HT oven connected to a data acquisition system. The results of these experiments are shown in the next section.

3. Experimental results

In this section, the discontinuous lines in the figures are derived from modeling explained in the next section; the points correspond to experimental results.

The variations of the heat of hydration, deduced from the Langavant tests, are shown in Figs. 1 and 2 for the different mortars.

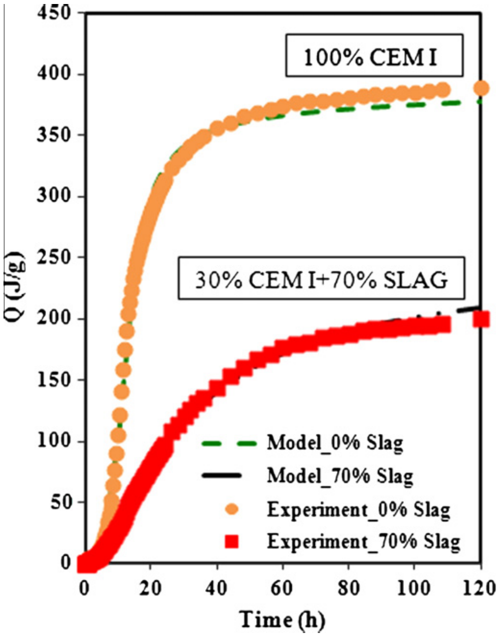

Fig. 1. Calibration of heat of hydration of pure Portland cement and blended cement with 70% of slag.

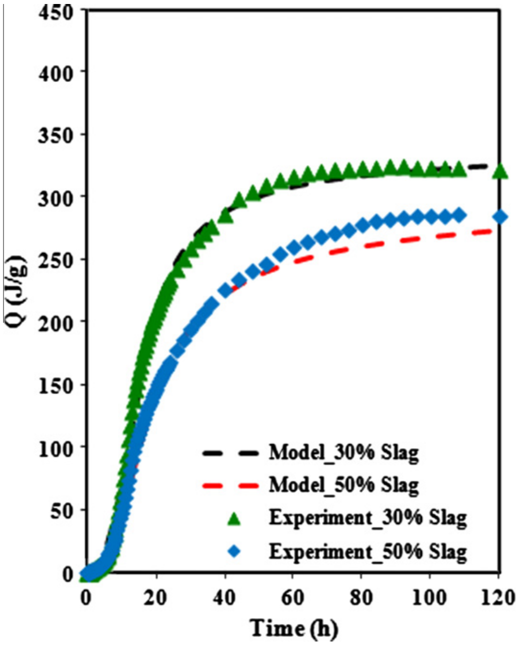

Fig. 2. Prediction of heat of hydration of blended cements with 30% and 50% of slag.

The curves show that the heat of hydration decreases when the substitution rate of slagfig increases. The comparison of the heat of hydration of the different binders containing slag (30%, 50% and 70%) with that of the binder composed of pure clinker, at 120 h, indicates that the heats of hydration of the slag-blended cements are greater than that corresponding to the proportion of clinker contained in the blended cements and this reveals the exothermic activity of slag.

Incorporating slag in the binder lowers the heat of hydration because the hydration kinetics of slag is lower than that of clinker and requires the presence of alkali, which comes from the clinker dissolution in the pore solution (Roy and Idorn [8]).

The combined water evolution in the mortars tested is shown in Fig. 3.

There is an increase of combined water versus time because of water consumption by hydration reactions. Whatever the curing temperature, at each age, there is a decrease in the combined water when the substitution rate of slag increases. For the same mix proportions, this can be explained by the fact that slag hydration has the slowest kinetics. Consequently, the more slag the binder contains, the less water it consumes for hydration.

The free water measured during our experiments is shown in Fig. 4. The decrease of free water with time is due to the water consumption by hydration reactions. The free water is the water remaining after the combined water has been subtracted. So the increase of free water with slag substitution rate is explained in the same way as the decrease of combined water with increasing slag substitution rate.

The variations of portlandite content in specimens during hydration development were measured and are plotted in Fig. 5. For mortars containing pure clinker, the portlandite content increases with age. This confirms the production of portlandite by clinker hydration reactions. For samples containing slag, the portlandite content increases up to 48 h and decreases continuously after that. As the hydration kinetics of slag is lower than that of clinker, up to 48 h, the clinker hydration process advances more rapidly than that of slag. Beyond 48 h, the hydration kinetics of clinker is slowed by the formation of hydration products around the grains of clinker. During this time, the slag hydration reactions

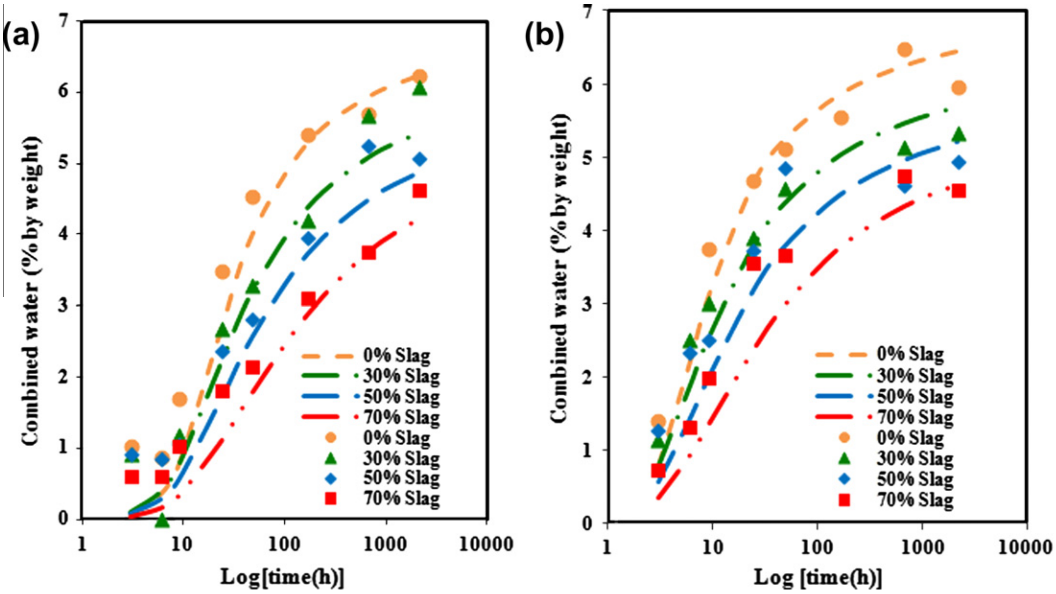

Fig. 3. Comparison between the combined water predicted by modeling and the experimental results (discontinuous lines represent modeling and points correspond to experimental results). (a) Specimens cured at 20 °C and (b) specimens cured at 40 °C.

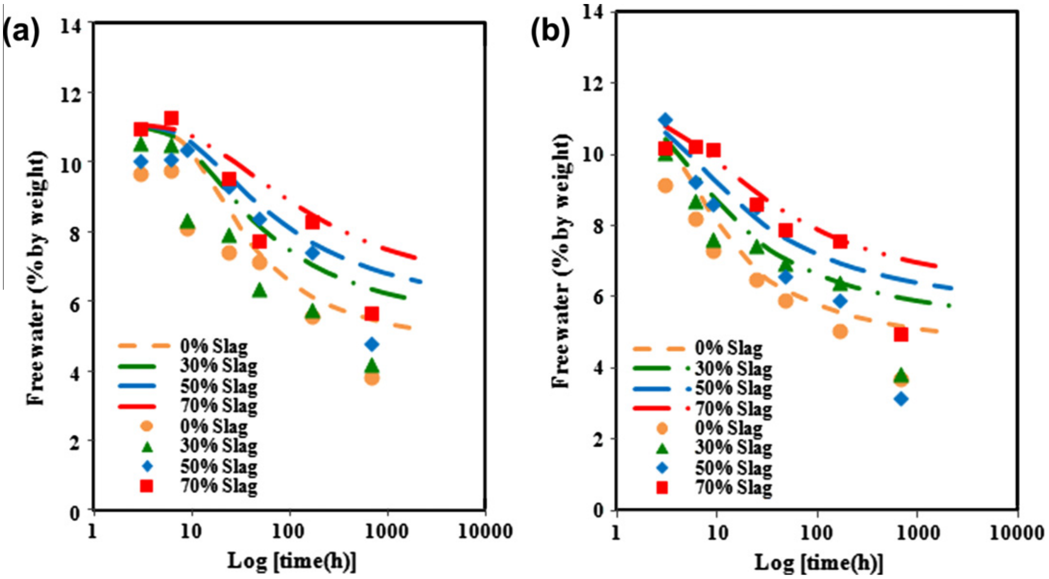

Fig. 4. Comparison between the free water predicted by modeling and the experimental results (discontinuous lines represent modeling and points correspond to experimental results). (a) Specimens cured at 20 °C and (b) specimens cured at 40 °C.

progress and consume the portlandite produced by the clinker more and more.

4. Modeling

4.1. Stoichiometric calculations

The hydration model proposed is based on stoichiometric calculations to correlate the chemical composition of clinker and slag with the quantities of their hydration products. From Adenot [23], the main hydration products of clinker include C–S–H, portlandite (CH) and aluminate phases such as calcium hydrated monosulfoaluminate ($C_4A\bar{S}H_{12}$), ettringite ($C_6A\bar{S}_3H_{32}$) and hexahydrate (C_3AH_6) [26].

To evaluate the quantity of each hydration product, two opposing hypotheses are made about the formation of aluminate phases and, as explained below, only one will be kept. The first is to consider that ettringite is formed but hexahydrate is not and the second hypothesis is to consider the reverse situation where hexahydrate is formed but ettringite is not. The molar balance of oxides in clinker hydration products is shown in Table 4 and, for each case above, we can assess the quantity of hydration products at complete hydration by means of stoichiometric coefficients. In Table 4, as proposed by Richardson [32], the value of 1.75 is used for the C/S molar ratio of C–S–H formed by clinker [33].

According to Chen and Brouwers [13], the main hydration products of slag, when blended with clinker, include C–S–H in which some alumina replaces silica to form C–S–A–H, hydrotalcite (M_5AH_{13}), ettringite ($C_6A\bar{S}_3H_{32}$) and AFm phase (C_4AH_{13}). The molar balance of oxides in hydration products of slag according to Chen and Brouwers [13] is shown in Table 5.

In slag-blended cements, the molar ratio C/S of C–S–A–H formed is still higher than the C/S ratio of pure slag, indicating

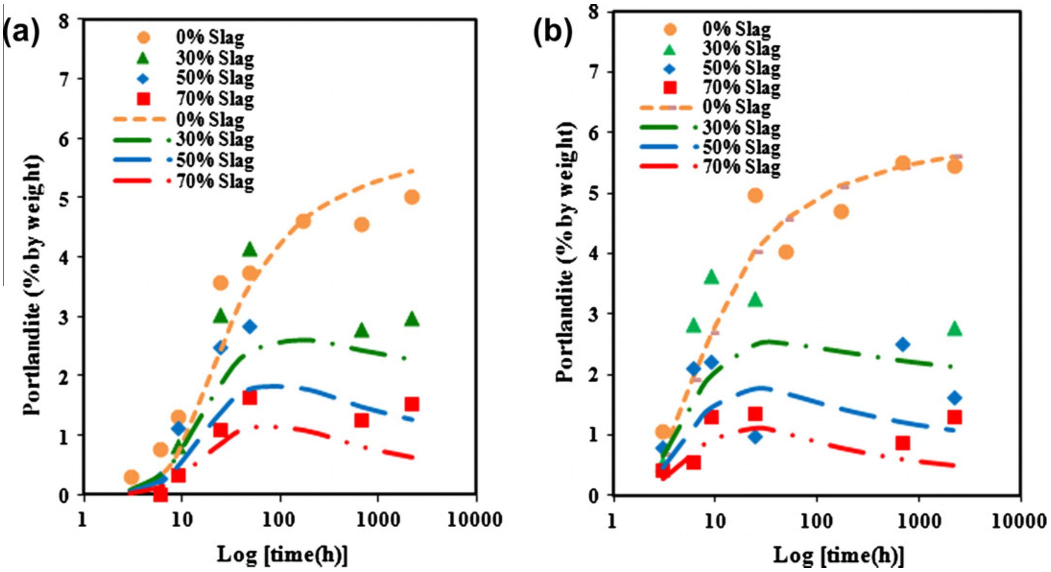

Fig. 5. Comparison between the portlandite content predicted by modeling and the experimental results (discontinuous lines represent modeling and points correspond to experimental results). (a) Specimens cured at 20 °C and (b) specimens cured at 40 °C.

Table 4
Molar balance of oxides in hydration products of clinker.

Hydration product	Molar balance				
	CaO	Sio_2	Al_2O_3	SO_3	H_2O
C–S–H	1.75	1			2.35
CH	1				1
$C_4A\bar{S}H_{12}$	4		1	1	12
$C_6A\bar{S}_3H_{32}$	6		1	3	32

enrichment in calcium of the C–S–A–H formed by consuming the CH produced by clinker reactions.

4.1.1. CH consumption

The calcium demand by the C–S–A–H of slag-blended cements is supplied by the CaO of anhydrous slag particles completed by a part of the CH formed by clinker hydration and consumed during slag hydration. In fact, to form their C–S–A–H, slag in blended cements can get calcium from the dissolution of CH or from the remaining calcium in the unhydrated slag. The amount of CH available depends on the progress of the reactions of clinker. Similarly, the calcium available from the anhydrous slag is variable because it is consumed during the hydration process of the slag. Clearly, the quantity of calcium available in each source varies during the development of hydration reactions. This raises the question of the distribution of the calcium demand for hydration of the slag between the two sources identified. It is proposed to supply the calcium demand of the slag reactions proportionally to the quantities of calcium available in each source. To do this, two distribution coefficients were introduced and representing the proportion of calcium coming respectively from the CH available ($k_c(t)$) and the remaining CaO of the anhydrous slag ($k_{sl}(t)$). Thus, consumption of the CH produced by clinker and the CaO of the unhydrated slag are managed by the following relations:

$$\underbrace{\frac{\partial CH}{\partial \alpha^l}}_{Portlandite\ \ consumption} = k_C \underbrace{\left(\left(\frac{C}{S}\right)^{csl}(t)\times\frac{\partial CSAH_l}{\partial \alpha^l}+6\times\frac{\partial AFt_l}{\partial \alpha^l}+4\times\frac{\partial AH_l}{\partial \alpha^l}\right)}_{Calcium\ \ demand\ \ of\ \ slag\ \ reactions} \quad (1)$$

$$\underbrace{\frac{\partial C^l}{\partial \alpha^l}}_{Slag\ \ CaO\ \ consumption} = k_{sl} \underbrace{\left(\left(\frac{C}{S}\right)^{csl}(t)\times\frac{CSAH_l}{\partial \alpha^l}+6\times\frac{AFt_l}{\partial \alpha^l}+4\times\frac{AH_l}{\partial \alpha^l}\right)}_{Calcium\ \ demand\ \ of\ \ slag\ \ reactions} \quad (2)$$

where $\frac{\partial X}{\partial \alpha^l}$ is the variation of the molar quantity of the hydration product X with the degree of hydration of slag α^l. The theoretical quantities of slag hydration products at complete hydration are obtained through the stoichiometric coefficients balance (Table 5) and shown in Table 6. $\left(\left(\frac{C}{S}\right)^{csl}\right)$ represents the molar ratio CaO/SiO_2 of C–S–A–H formed by slag when blended with clinker and obtained at each time step as shown in the next section. The distribution coefficients of the calcium available in the different sources are determined as followed:

$$k_c(t) = \frac{CH(t)}{CH(t)+C^l(t)} \quad \text{and} \quad k_{sl}(t) = \frac{C^l(t)}{CH(t)+C^l(t)} \quad (3)$$

where $CH(t)$ is the available CH and $C^l(t)$ is the quantity of CaO remaining in unhydrated slag at each time step during the hydration process.

Based on the previous propositions, the quantity of CH available is determined by deducing the quantity of portlandite consumed

Table 5
Molar balance of oxides in hydration products of slag.

Hydration product	Molar balance					
	CaO	Sio_2	Al_2O_3	SO_3	MgO	H_2O
C–S–A–H	C/S	1	A/S			H/S
M_5AH_{13}			1		5	13
$C_6A\bar{S}_3H_{32}$	6		1	3		32
C_4AH_{13}	4		1			13

Table 6
Total quantity of hydration products of slag.

Hydration product	Total quantity (10^{-5} mol/g of slag)
C–S–A–H	597.34
M_5AH_{13}	39.70
$C_6A\bar{S}_3H_{32}$	0.83
C_4AH_{13}	5.90

by slag hydration reactions (relation (1)) in the quantity of portlandite produced by clinker reactions as followed:

$$\underbrace{d\mathrm{CH}}_{\textit{Portlandite available}} = \underbrace{\frac{\partial \mathrm{CH}}{\partial \alpha^c}}_{\textit{Portlandite produced}} d\alpha^c - \underbrace{\frac{\partial \mathrm{CH}}{\partial \alpha^l}}_{\textit{Portlandite consumed}} d\alpha^l \tag{4}$$

where $\frac{\partial \mathrm{CH}}{\partial \alpha^c}$ is the variation of the molar quantity of CH produced with the evolution of the degree of hydration of clinker α^c. With the clinker used in this study (Table 1), the theoretical molar quantity of CH at complete hydration of clinker equals to 353×10^{-5} mol/g of clinker. $\frac{\partial \mathrm{CH}}{\partial \alpha^l}$ is the variation of the molar quantity of CH needed to supply the calcium demand for the formation of the hydration products of slag and shown in relation (1).

Similarly, the remaining CaO of unreacted slag is computed as followed:

$$dC^l = -\frac{\partial \mathrm{CH}}{\partial \alpha^l} d\alpha^l \tag{5}$$

4.1.2. Evolutive stoichiometry of C–S–A–H formed by slag-blended cement

The molar ratio C/S of the C–S–A–H formed by slag when blended with cement is between those of C–S–H from pure clinker and C–S–A–H from pure slag and depends on the quantity of CH available and the remaining calcium of the slag itself. The originality of the proposed model lies in relation (6), which gives the evolutive molar ratio C/S of C–S–A–H instantaneously formed by slag when it is blended with clinker.

$$\left(\frac{C}{S}\right)^{csl}(t) = \left(\frac{C}{S}\right)^{pc} \cdot k_c(t) + \left(\frac{C}{S}\right)^{psl} \cdot k_{sl}(t) \tag{6}$$

where $\left(\left(\frac{C}{S}\right)^{pc}\right)$ is the molar ratio C/S of C–S–H formed by pure clinker and is equal to 1.75 according to Richardson [32]. $\left(\left(\frac{C}{S}\right)^{psl}\right)$ is the molar ratio C/S of C–S–A–H formed by pure slag and is equal to 1.16 for our slag (according to stoichiometric calculations derived from Table 5). $k_c(t)$ and $k_{sl}(t)$ are distribution coefficients which describe the calcium consumption from available CH and from slag itself in proportion to the amounts available in each source (see relation (3)).

With this formulation the more CH there is, the more the slag hydration product tends towards that of a pure C–S–H leading to a C/S that evolves not only with the slag content but also, for a given slag substitution rate in the binder, according to the relative kinetics of portlandite production and slag consumption. The A/S ratio used in this modeling is equal to that of pure slag (0.1) obtained through the molar balance of oxides in hydration products of slag (Table 5).

4.1.3. Water retention

In Table 5, the water retained by C–S–A–H formed by slag is not shown (H/S). In the literature, Taylor [30] proposes several values for the molar ratio H/S of calcium silicate hydrate gel according to its structure: 0.83 for dry tobermorite, 1.5 for jennite, 2.0 for plombierite, etc. Depending on the saturation state, Jennings and Tennis [31] proposed a molar ratio H/S of 1.5 for the C–S–H in dry conditions and 4.0 for C–S–H in saturated conditions. For pure clinker, Adenot [23] proposed to evaluate the water demand of the C–S–H formed according to its stoichiometry by the relation: 0.8 + C/S. For the C–S–A–H formed by the hydration of pure slag, Chen and Brouwers [13] proposed to use the value of 1.2.

In this model, it is proposed to vary the molar ratio H/S of C–S–A–H formed by slag according to its molar ratio C/S by a linear interpolation between the water demand of C–S–H formed by pure clinker and the water demand of C–S–A–H formed by pure slag. Varying the C/S ratio means that the C–S–A–H formed at each calculation time has a different composition and consequently the water demand has to vary. The water retention $\left(\left(\frac{H}{S}\right)^{csl}\right)$ of C–S–A–H formed by slag when blended with clinker is computed as follows:

$$\left(\frac{H}{S}\right)^{csl}(t) = \left(\frac{C}{S}\right)^{csl}(t) + 1.45 \times \left(\left(\frac{C}{S}\right)^{csl}(t) - 1.2\right)^{+} \tag{7}$$

where $(X)^{+}$ is the positive part of X, which is equal to 0 if X is negative or X if X is positive.

If the quantities of all hydration products from clinker and slag are known at each calculation time, the total water retained by hydration products can be calculated as follows:

$$\begin{aligned} dH_{combined} = {} & \underbrace{\left(2.35\frac{\partial \mathrm{CSH}}{\partial \alpha^c} + 12\frac{\partial \mathrm{AF}m}{\partial \alpha^c} + 6\frac{\partial \mathrm{HEXA}}{\partial \alpha^c}\right) d\alpha^c}_{\textit{Water demand of clinker products except CH}} \\ & + \underbrace{\left(\left(\frac{H}{S}\right)^{csl}\frac{\partial \mathrm{CSAH}}{\partial \alpha^l} + 13\frac{\partial \mathrm{HT}}{\partial \alpha^l} + 32\frac{\partial \mathrm{AF}t}{\partial \alpha^l} + 13\frac{\partial \mathrm{AH}}{\partial \alpha^l}\right) d\alpha^l}_{\textit{Water demand of slag products}} + d\mathrm{CH} \end{aligned} \tag{8}$$

where $\frac{\partial X}{\partial \alpha^c}$ is the variation of the molar quantity of the hydration product X with the degree of hydration of clinker α^c. The theoretical quantities of clinker hydration products at complete hydration are obtained through the stoichiometric coefficients balance (Table 4) and shown in Table 7. $\frac{\partial X}{\partial \alpha^l}$ is the variation of the molar quantity of the hydration product X with the degree of hydration of slag α^l. The theoretical quantities of slag hydration products at complete hydration are obtained through the stoichiometric coefficients balance (Table 5) and shown in Table 6. $\frac{\partial X}{\partial \alpha^l}$ is the water demand of the C–S–A–H formed by slag when blended with clinker. This water demand varies at each time step with the molar ration C/S of the C–S–A–H formed as shown in relation (7). dCH is the molar quantity of CH available which depends at each time step on the interactions between clinker and slag and notably of the quantity of CH consumed by slag reactions (relation (1)). Note that the formation of one mole of CH requires one mole of water.

The approach proposed above to determine the water demand during the hydration of slag-blended cement is original because contrary to usual methods, the water demand per gram of slag at complete hydration is not known in advance. The water demand of the blended cement is evaluated at each time step and depends on the evolutive stoichiometry of the C–S–A–H formed by slag during the hydration process.

The free water is calculated by deducting the combined water previously calculated (relation (8)) from the initial water content.

4.2. Hydration kinetic law

The hydration kinetic law below, proposed by Buffo-Lacarrière et al. [28], is modified to simulate the hydration of slag-blended cements:

$$\dot{\alpha}_i = A_i \cdot g_i \cdot \pi_i \cdot h_i \cdot S_i \tag{9}$$

In which A_i is a calibration constant, which depends on the anhydrous grinding, g_i is the chemical activation term, π_i accounts for the water accessibility to anhydrous phases, h_i is the thermal activation and S_i

Table 7
Total quantity of hydration products of clinker.

Hydration product	Total quantity (10^{-5} mol/g of clinker)
C–S–H	344.09
$C_4A\bar{S}H_{12}$	40.82
C_3AH_6	2.31

describes the interaction between portlandite and mineral additions. The terms g_i, π_i and S_i are modified.

As observed experimentally by Alexandre and Sebileau [22], the dissolution of slag when blended with clinker is activated by the alkalis released by clinker dissolution in the interstitial solution. In our model, the amount of clinker dissolved during hydration reactions is used as the main indicator of the alkalis available for the activation of slag dissolution. In the case of clinker, its dissolution is activated by supersaturation of the interstitial solution followed by the precipitation of new hydrates. The clinker dissolution is also driven by its quantity already present in interstitial solution. Thus, we proposed to describe the activation of the dissolution by the following expression, whatever the mineral addition considered:

$$g_i = \begin{cases} \frac{\alpha_c C_{p0_{clinker}}}{Wp} & if\ i = mineral\ addition \\ \frac{\alpha_c C_{p0_{clinker}}}{MIN(W_{p_s}, W_p)} & if\ i = clinker \end{cases} \tag{10}$$

where α_c is the degree of hydration of clinker, $C_{p0clinker}$ is the initial volumetric concentration of clinker in the paste and Wp is the volumetric concentration of water in the paste.

For the clinker phase, the supersaturation of the interstitial solution is a local phenomenon so the pore solution concerned is that around or near the grain. We define a water content threshold W_{ps} that represents the maximum supersaturation volume around the clinker grain. This water content threshold corresponds to the volumetric concentration of water in the paste for a water to cement ratio of 0.4. This value is derived from calibration of the proposed model on different types of clinker. When the water content exceeds this value, the water content threshold proposed is used to calculate the supersaturation. The clinker dissolution activation term is expressed as shown in relation (10). In the expression proposed $MIN(W_{ps}, W_p)$ is the minimum of the two values W_{ps} and W_p.

During the hydration process, layers of hydration products form around each anhydrous phase. These hydrate layers progressively separate the anhydrous grains from water. This slows the hydration kinetics and can even stop reactions. The difficulty of access of free water to anhydrous grains increases as hydration reactions develop. Consequently the hydration kinetics must depend on the difficulty water has in accessing anhydrous grains. The expression below is proposed to model this phenomenon for each phase "i":

$$\pi_i = exp\left[\frac{-1}{n}\left(\frac{\bar{r}_{m_i}}{r_k}\right)^n\right] \tag{11}$$

where n is a calibration parameter which controls the shape of the hydration kinetic law, r_k is a calibration parameter that represents the characteristic thickness of hydrate layers beyond which hydration kinetics decrease, and $\bar{r}_{m_i}$ is the current thickness of hydrate layers around anhydrous grains "i".

The following expression proposed by Buffo-Lacarrière et al. [28] is used to evaluate the hydrate layers:

$$\bar{r}_{m_i} = \frac{C_{phyd_i}}{W_p \cdot Ø_p \cdot C_{panh_i}} \tag{12}$$

where C_{phyd_i} is the volumetric concentration of hydration products of phase "i", C_{panh_i} is the volumetric concentration of anhydrous phase "i", $Øp$ is the porosity of the paste and W_p is the free water volumetric concentration in the paste. Note that these quantities are derived from the calculation of the evolution of hydration products given in the previous section.

The hydration of mineral additions is chemically activated by the CH produced by clinker in blended cements. In the case of pozzolanic additions, the kinetics of secondary reactions are linked to the quantity of CH available. In addition to the amount of CH available in blended cements, the hydration reactions of slag are also activated by the calcium content in the anhydrous slag. Thus, the hydration kinetics of slag must be linked to the quantity of CH available and to the quantity of the calcium remaining in the anhydrous slag. To take this chemical activation of mineral additions into account, which also describes the main interaction with clinker, the following expression is used:

$$S_i = \begin{cases} 1 & if\ i = clinker \\ C_{P_{CH}} & if\ i = pozzolan \\ C_{P_{CH}} + C_{P_{CaO}} & if\ i = slag \end{cases} \tag{13}$$

where $C_{P_{CH}}$ and $C_{P_{CaO}}$ are respectively the volumetric concentration of available CH and the remaining volumetric concentration of CaO from anhydrous slag. These quantities are evaluated according to the stoichiometric calculations presented in the previous section.

The effect of temperature on the hydration reaction kinetics is modeled by the following Arrhenius [27] based relation:

$$h_i = \exp\left(\frac{-E_{a_i}}{R}\left[\frac{1}{T} - \frac{1}{293}\right]\right) \tag{14}$$

where E_{ai} is the activation energy of phase "i", R is the gas constant (8.314 J/mol°K) and T is the temperature (K).

Finally, three parameters (A, r_k and n) have to be fitted for each type of anhydrous material (one for clinker and another for slag in our case). These parameters characterize the ability of an anhydrous phase to react more or less rapidly, and they have to be characterized for each binder type as follows.

4.3. Calibration of hydration kinetic law

Three parameters are calibrated for the hydration kinetic law of each phase (clinker and slag) in Langavant semi-adiabatic calorimeter tests. For blended cements, the fitting parameters of clinker are first calibrated using results from a Langavant test performed on binder composed of pure clinker (Fig. 1). The clinker parameters are used to fit the slag hydration kinetic law parameters on the binder composed of 70% slag and 30% clinker (Fig. 1). The heat of hydration at final hydration of clinker and slag, the activation energy of each phase and the calibrated kinetic parameters are shown in Table 8.

The activation energy of clinker is calculated by means of the formula proposed by Schindler [19] based on the Blaine specific surface area of clinker and the C_3A and C_4AF components of clinker minerals. The activation energy of slag comes from Fernández-Jiménez and Puertas [24] experimental investigations. The heat of hydration of clinker at final hydration is determined by means of its mineral component as proposed by Schindler [19]. The value of 461 J/g used as the total heat of hydration of slag is recommended by Kishi and Maekawa [25].

4.4. Validations

As explained in the previous section, the hydration kinetic law parameters of clinker and slag are calibrated on Langavant semi-adiabatic calorimeter tests of mortars with binders containing 0% and 70% of slag. For these specimens, the combined water, the free water and the portlandite content predicted must be validated.

Table 8
Hydration model parameters.

	A_i	r_k	n_i	Ea_i/R (K)	Q_∞^T (J/g)
Clinker	3.48	2.25	0.29	5372	476
Slag	5.00E−06	3.8	0.55	7000	461

With the calibrated parameters of clinker and slag, the hydration reactions of specimens containing 30% and 50% of slag are simulated. The prediction of heat release, combined water, free water and portlandite content by the proposed model will be compared to experimental measurements.

4.4.1. Heat release during hydration process

The prediction of heat release during the hydration of specimens containing 30% and 50% of slag are plotted in Fig. 2. In our model, the heat released by the hydration process of blended cements is obtained from the sum of the heat released by each phase (clinker and slag). Only limited data are available in the literature to characterize the total heat of hydration of slag. The value of 461 J/g recommended by Kishi and Maekawa [25] is used in our modeling. The results shown in Fig. 2 are in good agreement with experimental measurements. The differences between experiments and simulations could possibly be attributed to an overestimation of heat loss compensation in Langavant semi-adiabatic calorimeter tests. To validate the total hydration heat proposed by Kishi and Maekawa [25], it is necessary to control other variables that depend on the hydration and are available experimentally. These are the evolution of combined water, free water and portlandite amount during hydration. If all these variables are compatible with experimental results for each hydration degree, the degree of hydration of slag is realistic and, consequently, as the Langavant test is well modeled, the hydration heat proposed for slag is also realistic.

4.4.2. Combined water during hydration process

The combined water predicted by modeling is compared to TG–DTG measurements in Fig. 3. The measured combined water of specimens containing 30%, 50% and 70% of slag compared to measurements of pure clinker specimens shows greater values than would be expected if we substituted the clinker by an inert material. This means that, for slag-blended cements, hydration reactions of both clinker and slag contribute to the combined water and consumed water. The model proposed in this paper deals with this phenomenon by counting the water retained by the different hydration products of slag in the predicted combined water (see relation (8)). Whatever the conservation temperature of the specimens, the computed values of combined water correspond well with experimental results.

4.4.3. Free water

The free water evolution predicted is compared to the measurements in Fig. 4. In our simulations, the free water content is obtained by subtracting the combined water from the initial water content. The quantities predicted are in good general agreement with the experimental results. The scattering between experiments and modeling could come from the sample preparation procedure (freezing specimens until the test age, cutting of slices of samples with a saw, etc.).

4.4.4. Portlandite amounts during hydration process

The comparisons of the portlandite content predicted by modeling and measured by TG–DTG are shown in Fig. 5. In the hydration of pure clinker, the portlandite content only increases with the hydration development because portlandite is one of the hydration products of clinker. In slag-blended cements the portlandite is produced by clinker and consumed by slag hydration. In the proposed model, the portlandite consumption by slag is proportional to the quantity available from clinker hydration. More precisely, the calcium required for the hydration of slag is evaluated at each calculation time and this demand is supplied by the available portlandite and the remaining calcium of unhydrated slag (see relations (1) and (2)). Despite the experimental scatter induced by the process, results obtained by the proposed approach are in accordance with the experimental results. Note the compatibility between the four types of results (Langavant test, combined water, free water, portlandite content) for the different temperatures and slag rates in binder, with a single parameter set. This is a validation, since an error in hydration heat or in the stoichiometry of hydration products would inevitably lead to an error on at least one of the curves above.

4.4.5. Validation on experimental results from the literature

4.4.5.1. Long-term slag hydration degree. To confirm the ability of the model to assess the degree of hydration, we use the measurements of degrees of reaction of slag in blended cements made by Lumley et al. [29]. In his experimental measurements, Lumley et al. [29] investigated the degree of reaction of different types of slag (seven) in blended cements. The degree of reaction of slag was measured using the Ethylene Diamine Tetraacetic Acid (EDTA) extraction method. The potential sources of error in the method are discussed and corrected. More details on this method can be found in Lumley et al. [29]. Two of the panels of slag tested by Lumley et al. [29] were used to validate our model. The chemical composition of the slag used is shown in Table 9. The water to binder ratio of the slag-blended cement paste was 0.4 and the paste was cured at 20 °C until the time of the test. The pastes contained 60% of each of the slags shown in Table 9 and 40% of the same clinker. The degree of reaction of slag in the blended cement paste was measured from 28 days to 2 years. To model the hydration of the pastes, the hydration kinetic parameters of clinker and slag have to be known. As Lumley et al. [29] did not perform Langavant tests, the following assumptions are proposed. For the clinker kinetic law, the parameters are calibrated on our Langavant calorimeter test on pure clinker (Fig. 1). The kinetic parameters of the two slags are calibrated on our Langavant calorimeter test of the binder containing 70% of slag (Fig. 1). Even if these assumptions are not optimal for the material used by Lumley et al. [29], they allow realistic differential kinetics between clinker and slag to be adopted. The hydration development of the different pastes is then simulated up to 2 years and the degrees of reaction of slag obtained are compared to the experimental measurements in Fig. 6. These results show that, despite the approximation formulated for short-term hydration kinetic parameter laws, the model accurately predicts the long-term degree of hydration of slag (up to 2 years), when blended with clinker.

4.4.5.2. The stoichiometry of slag hydration products. The microstructure and composition of slag-blended cements containing different proportions of slag were analyzed by Richardson and Groves [34] using Transmission Electron Microscopy (TEM) with microanalysis combined with Electron Microprobe Analysis (EMPA). The speci-

Table 9
Chemical oxide composition of slag L and slag T from Lumley [29].

Oxide composition	% By weight	
	Slag T	Slag L
SiO_2	33.0	35
Al_2O_3	11.8	12.3
Fe_2O_3	1.6	0.6
TiO_2	0.59	0.52
Mn_2O_3	0.64	0.43
CaO	41.3	40.9
MgO	9.0	7.8
SO_3	0.13	0.30
K_2O	0.51	0.83
Na_2O	0.32	0.64
P_2O_5	0.01	0.01
S^-	0.86	1.1

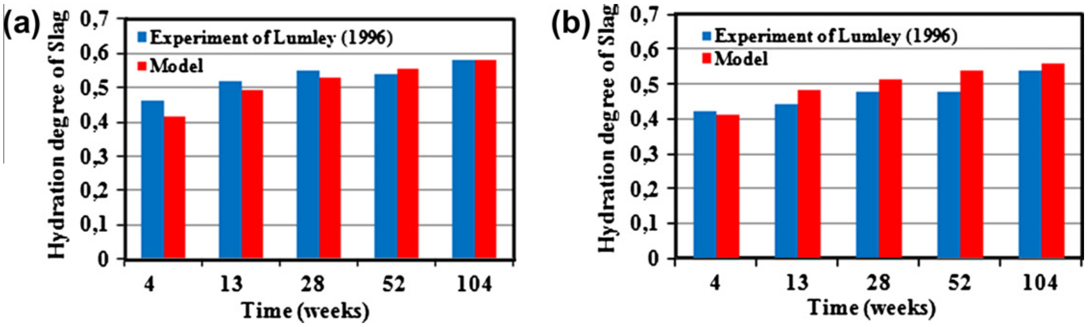

Fig. 6. Comparison between the degree of hydration of slag predicted by modeling and the experimental results. (a) Slag L and (b) slag T.

Table 10
Chemical oxide composition of clinker and Slag from Richardson [34].

Oxide composition	% By weight	
	Clinker	Slag
SiO_2	20.0	37.2
Al_2O_3	6.19	11.0
Fe_2O_3	3.03	0.38
TiO_2	0.30	0.68
Mn_2O_3	0.06	0.73
CaO	65.9	41.7
MgO	1.33	7.74
SO_3	2.65	3.68
K_2O	0.86	0.55
Na_2O	0.19	0.64
P_2O_5	–	–
S^-	–	–

mens analyzed included nine slag substitution rates varying from 0% to 100%. The chemical composition of the clinker and slag used by Richardson and Groves [34] is shown in Table 10. The water to binder ratio of the slag-blended cement paste was 0.4. The paste specimens were sealed in plastic tubes and cured at 20 °C. The C/S ratios of the C–S–H formed were measured at 14 months. This experiment was modeled in order to validate the predictions of our model. The hydration kinetics of the clinker and slag used in these experiments were calibrated on the heat of hydration measured with a Langavant semi-adiabatic calorimeter on pure clinker and on binder containing 70% of slag respectively during our experiments (Fig. 1). These parameters were used to simulate the hydration the nine slag-blended cement pastes. The molar ratio C/S of the C–S–H obtained by modeling at 14 months of hydration is compared to experimental measurements in Fig. 7. The predicted molar ratios C/S of C–S–H are in good agreement with experiments. These ratios reflect the CH consumption by slag hydration, which assumes a good capacity of the model to predict both the CH consumption by slag hydration whatever the substitution rate of slag, and the method adopted to predict the C/S according to the available calcium sources (see relation (6)). The comparison of the evolution of the C/S ratio with hydration development predicted by modeling with experimental measurements is planned in our future work and will allow validating directly the C/S ratio at all maturities.

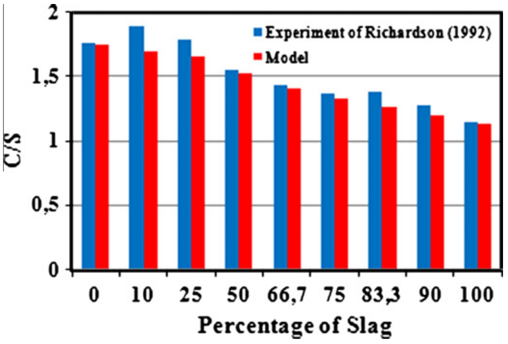

Fig. 7. Comparison between the molar ratio C/S of C–S–H formed predicted by modeling and the experimental results.

5. Conclusions

The hydration of slag-blended cements was investigated in this study. A large experimental program was performed to measure the main hydration reaction indicators such as heat release, free and combined water, and portlandite content. A multiphasic hydration model is proposed to take the difference of hydration kinetics between clinker and slag into account. With a single set of parameters, the proposed model is able to fit the whole experimental plan carried out for this study and also other results from the literature. The confrontation of model and experiment explains and confirms that:

- The stoichiometry of hydration products during slag-blended cement hydration depends on the instantaneous calcium amount supplied by portlandite from clinker and anhydrous residual slag.
- As the activation energy and kinetic parameters of clinker and slag are very different, the stoichiometric obtained at a given hydration degree depends not only on the slag substitution rate but also on the temperature during the hydration.
- The parameter set implemented in this model uses the hydration heat of 461 J/g proposed by Kishi and Maekawa [25]. This value, combined with an original method to adapt the hydration product Stoichiometry automatically, allows a large experimental data set to be fitted, including several slag types.
- Adopting the hydration heat of 461 J/g and an activation energy of 58 kJ mol^{-1} for slag, together with the proposed method to determine hydration product Stoichiometry, reduces the number of parameters to be fitted for a given blended cement to the kinetic parameters (A, r_k, n) for clinker, and (A, r_k, n) for slag. The first can be fitted on a Langavant test performed with pure clinker, the second with a Langavant test in which a substitution rate of 70% can be adopted.
- The parameters obtained allow any other slag substitution rate to be simulated without performing new Langavant tests.
- The results obtained are then usable to simulate real structures in which the temperature can be very different from those of the Langavant tests. In fact, the model is able not only to

increase kinetics through the Arrhenius activation laws, as is usually the case for other conventional hydration models, but also to automatically adapt the slag product stoichiometry to the field conditions.

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