



Hydration of slag-blended cements

B. Kolani^{a,b}, L. Buffo-Lacarrière^a, A. Sellier^{a,*}, G. Escadeillas^a, L. Boutillon^b, L. Linger^b

^a Université de Toulouse, UPS, INSA, LMDC (Laboratoire Matériaux et Durabilité des Constructions), 135 Avenue de Rangueil, F-31077 Toulouse Cedex 04, France

^b VINCI Construction Grands Projets, 5 cours Ferdinand de Lesseps, F-92851 Rueil-Malmaison Cedex, France

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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 multiphase hydration 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 stoichiometry 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.

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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

* Corresponding author. Tel.: +33 5 61 55 60 06.

E-mail address: alain.sellier@insa-toulouse.fr (A. Sellier).

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 stoichiometry 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 ₂ O ₃	4.4	11.2
Fe ₂ O 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 ₂ O	0.74	0.5
Na ₂ O	0.13	0.3
P ₂ O ₅	0.33	–
S [–]	0.03	1
Cl [–]	0.04	0.01

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