

W. Chen; H.J.H. Brouwers

The reaction of slag in cement: theory and computer modelling

For a better understanding of the performance of slag in concrete, evaluating the feasibility of using one certain type of slag and possible improvement of its use in practice, fundamental knowledge about its reaction and interaction with other constituents is important. While the researches on hydrating Portland cement paste is quite abundant, researches on theory of slag cement reaction are rather scarce. At least three difficulties impede the advancement: (a) The lack of knowledge about the chemistry of slag reaction; (b) The complexity involved with respect to the interaction between the two constituents in slag cement (slag and Portland cement); (c) The reactivity of slag in cement. Efforts on clarifying these three factors will be proven valuable when evaluating the reactivity of a slag, predicting the microstructure development and investigating the durability aspects of the concrete made with slag.

Microstructural modelling of cement hydration is expected to provide a reliable representation of the real hydration process. It can on the one hand deepen the understanding of the material, and on the other hand extrapolate properties outside the available data. The ultimate goal of microstructural modelling is to predict the performance of cement-based materials throughout its service life. Benefiting from the rapid development in computer science, and the fundamental knowledge about the chemistry of cement hydration, several computer models have been developed in various groups to simulate the microstructure development of hydrating cement paste (/9/,/7/,/15/,/16/) Most of the models available now are focused on the Portland cement hydration, while very few models are able to deal with slag cement hydration, yet.

In this study, theoretical models available for the reaction of both pure slag (alkali-activated) and slag-blended cement are reviewed. They were developed by using stoichiometric computations. For the slag-blended cement, models accounting for the interaction between the slag and clinker reactions were proposed, involving the CH (notation in cement chemistry is used, e.g. C = CaO, S = SiO₂, A = Al₂O₃, H = H₂O etc.) consumption and the composition equilibrium of the C-S-H. These theoretical models are further incorporated into a 3-D computer model, CEMHYD3D, originally developed for simulating the Portland cement hydration /7/, with special considerations to the reactivity of slag in cement.

The reaction of slag in cement

The reaction of slag in cement with and without interaction with the clinker hydration is extensively discussed in previous works of the current authors (/4/,/5/) and is briefly reviewed here.

The hydration products of slag are principally the same as those identified in hydrating Portland cement paste, with the additional presence of a hydrotalcite-like phase. The composition of the main hydration product, C-S-H, however, is obviously influenced by the presence of slag, and is thus different from that in hydrating Portland

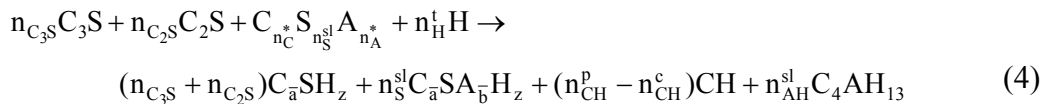
cement paste. It is marked by a relatively lower C/S ratio and the high contents of A substituting for S in the bridging tetrahedral of a dreierkette structure /12/. The substitution degree is dependent on the C/S ratio of C-S-H and also the amount of A available for substitution /12/.

The reaction of pure slag (alkali-activated) is written as:



in which n_M^{sl} and n_S^{sl} are the moles of M and \bar{S} in slag, respectively; n_A^{HT} and n_A^{AFt} are the moles of A combined in the hydrotalcite-like phase and ettringite, respectively; n_H^{HT} and n_H^{AFt} are the moles of water combined in the hydrotalcite phase and ettringite; n_{HT} , n_{AFt} and n_{AH}^{sl} are the moles of hydration products the hydrotalcite phase, ettringite and tetracalcium aluminate hydrate, respectively; z is the water content in C-S-H; n_S^{sl} is the moles of S from slag; n_C^* and n_A^* are the moles of C and A from slag remaining available for the products C-S-H and C_4AH_{13} . The formation of C_4AH_{13} virtually depends on n_C^* , n_S^{sl} and n_A^* , which is determined by the slag compositions. \hat{a} and \hat{b} are the C/S and A/S ratios (in moles) in C-S-H. It is worth noting that the water contents in all the hydration products depend on the hydration state that the products are subject to. Detailed computation methods for the parameters in eqs. (1)–(3) may be found in previous work /12/.

If the slag is mixed with Portland cement, its reaction interacts with the hydrations of clinker phases, thus changing its reaction equation as well. The coupled reactions equations for slag and the calcium silicates in clinker are written as:



in which the equations for the hydrotalcite phase and ettringite from slag are the same as eqs. (1) and (2) and are thus excluded. The reaction equations for the aluminate and ferrite phases in clinker (with gypsum if present) are omitted as well because it is assumed that the slag reaction interacts mainly with the calcium silicates; n_{C_3S} and n_{C_2S} are the moles of alite and belite in clinker; n_H^t is the total amount of water combined in the products C-S-H and CH; \bar{a} is the C/S ratio in the equilibrated product C-S-H and \bar{b} is the A/S ratio in C-S-H formed by the slag hydration. The same degree of A substitution for S takes place in C-S-H from clinker hydration as well, but it is omitted for simplification purpose. n_{CH}^p is the mole of CH produced by clinker hydration and n_{CH}^c is the mole of CH consumed by the slag reaction.

Methods for computing the parameters in eq. (4) were presented in the previous work /4/. The method for computing the fraction of CH consumed (p) by the slag reaction is included here as:

$$n_{CH}^e = p \cdot n_{CH}^p = p \cdot (1.2n_{C_3S} + 0.2n_{C_2S}) \quad (5)$$

with

$$p = \frac{1.8n_S^{sl} - n_C^*}{n_{CH}^p + 1.8n_S^{sl} - n_C^*} \quad (6)$$

The reactivity of slag in cement

The hydration rate of slag is an indispensable parameter when modelling the reaction of slag in cement and simulating the microstructure development. It is often defined as the slag reactivity by the rate of slag reaction with water. The latent hydraulic property of slag is well known, which means the slag reacts at a remarkable rate when the environment is suitable, an alkaline environment in case of the construction practice. The reactivity of slag is the objective of numerous researches, and is still not adequately understood, yet. Several factors are known to contribute to the reactivity of slag, for example, the components composition, chemical composition, geometrical properties, temperature, glass structure, and the alkali environment (Figure 1). A few of these factors are addressed in this section, including the chemical composition of slag, the pore solution composition and temperature.

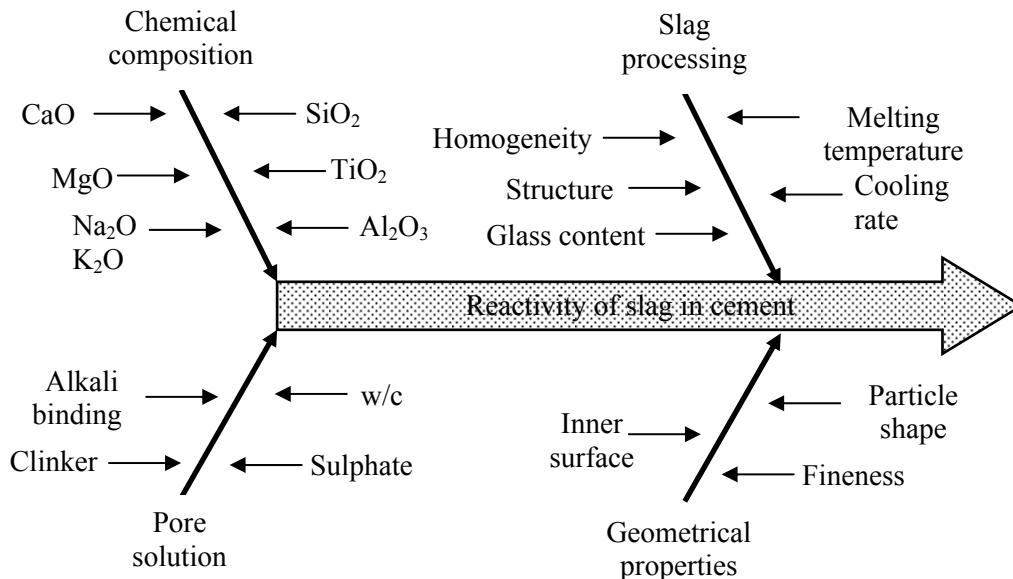


Figure 1. Factors on the reactivity of slag in cement (modified from Olbrich et al. /18/).

The chemical composition is an important indication to how severe the network is distorted and to the degree of depolymerisation of a silicate melt. This can be expressed by the ratio of non-bridging oxygen atoms to the number of tetrahedrally coordinated atoms (e.g. Si), usually denoted as NBO/T ratio. The NBO/T ratio is suitable for this purpose because: (1) The number of NBOs is proportional to the number of moles of oxide addition; (2) Addition of alkali or alkaline-metal oxides to silica must increase the overall O/Si ratio of the silicate; and (3) Increasing the number of NBOs results in the progressive breakdown of the silicate structure into smaller units. It is known in silicate chemistry that the physical properties of slag melt depend on the NBO/T ratio /10/. The NBO/T ratio for the glass in normal granulated blastfurnace slag can be calculated from its oxide composition with a few approximations /10/.

Good correlations between the hydrolytic reactivity and the NBO/T ratio of the slag are observed /11/, indicating the structure of slag has an important influence on the reactivity of slag. The reactivity of slag in distilled water is approximately linearly dependent on the NBO/T ratio of the slag.

Pore solution composition has a strong influence on the reactivity of slag as well. When the pH value of the solution increases above 9, the breakdown of the silicate lattice of glass is enhanced. Researches on the corrosion of glass in a basic environment are relatively scarce till now. Zhou et al. /19/ measured the hydration degree of slag in alkali-activated slag cement pastes at different ages. The pH values of the activators range from 12.48 to 14.7. The degree of slag reaction was measured by a solvent extraction method. It was found that the measure hydration degrees at given age is linearly related to the pH values of the solution.

Temperature influences the slag reaction rate very obviously. The slag reaction rate is even more sensitive than that of Portland cement systems. Several investigators have determined the temperature dependence of the heat evolution by calorimetry and applied the Arrhenius equation, or some variant of it, to the data thus obtained in order to calculate the activation energy, E_a for hydration. The Arrhenius equation can be written in the form:

$$k_T = K \cdot \exp \frac{-E_a}{RT} \quad (7)$$

Typical values for the activation energy E_a of slag are between 50–59 kJ·mol⁻¹ /6/.

Computer modelling of slag cement hydration

With the knowledge about the chemistry and reactivity of slag reaction in cement, computer modeling the hydration of slag cement paste and its microstructure development is possible. The three-dimensional computer-based cement hydration model CEMHYD3D is chosen as the basis and extensions are made for modeling the slag cement hydration.

The computer modelling process for the slag cement hydration is essentially similar to that for the hydration of Portland cement hydration /1/,/16/. An initial microstructure is firstly generated, representing the starting system. Then, a number of hydration cycles are executed to simulate the continuous disappearance of cement and

formation of products. A serial of reaction rules are obeyed in each hydration cycle, established with the chemical knowledge on slag cement reaction. One specialty of the slag reaction is its reactivity, which is influenced by some factors and is addressed in the previous section.

The initial microstructure of slag cement paste is reconstructed using the water/binder ratio and the particle size distributions (PSD) of clinker, slag and gypsum (if present in the system). The way of distributing clinker phase follows from those used by Bentz /1/ and van Eijk /16/, using totally random distribution or phase correlation file. The glass and crystalline phases in the slag are distributed using random partition based on their volume fractions in the slag, which is calculated beforehand from their mass fractions in the slag.

PSD of slag is accounted for in two ways. The user can calculate the numbers of particles for each particle size using the PSD of slag; or, if the PSD of slag is unknown, the user can opt to use the cement PSD for slag. If the slag and cement is ground together, they share the same PSD. The same options for gypsum are also provided.

Dissolution takes place when two conditions are met, concerning the “dissolution probability” of slag voxel and its position in the hydrating particle.

While the reaction rate of glass is dependent on the ion concentration of pore solution in the real paste /19/, the dissolution probability is related to the pH value of the activation solution. For solutions other than the OPC suspension, for example NaOH solutions, the pH value can be determined from the ion concentrations. If OPC is used as activator, the method proposed by Brouwers and van Eijk /2/ for determining the alkali concentration of the pore solution is used, which reads:

$$C_i = \frac{n_i^f}{V_w + R_{d,i} \cdot m_{C-S-H}} \quad (8)$$

in which C_i is the concentration of alkali i in the pore solution; n_i^f is the moles of alkali i released by the cement hydration, V_w is the volume of pore solution, $R_{d,i}$ is the alkali binding factor, and m_{C-S-H} is the mass of C-S-H in the paste. The parameter n_i^f , V_w , and m_{C-S-H} can be computed with the 3-D computer model CEMHYD3D. The value of $R_{d,i}$ depends on the composition of C-S-H and the alkali concentration itself. Methods for determining the values of $R_{d,i}$ can be found in /3/. Then, the pH value can readily be computed from the OH^- concentration in the pore solution.

The effect of the chemical composition of slag on its reactivity is accounted for with its NBO/T value. Slags with the ideal composition CS (pure calcium silicate glass with molar ratio of C/S = 1) are expected to have the most stable network (the least distorted SiO_4^{4-} -tetrahedral) and are the least reactive /14/. Hence, its NBO/T value (1.936) is taken as the basis for evaluating the reactivity of slags with other compositions

Then, the dissolution probability for glass voxel in CEMHYD3D is calculated as:

$$\begin{aligned} P'_{glass} &= P_{glass}^0 \cdot \beta_1 \cdot \beta_2 = P_{glass}^0 \cdot [a_1 \cdot \frac{(NBO/T)}{1.936}] \cdot [a_2 \cdot (pH - 9)] \\ &= P_{glass}^0 \cdot \beta' \cdot \frac{(NBO/T)}{1.936} \cdot (pH - 9) \end{aligned} \quad (9)$$

in which P_{glass}^0 is the dissolution probability of glass voxel, empirically set beforehand and is valid for all slags; $\beta' = a_1 a_2$ and is a parameter depending on some other factors that influence the slag reactivity, for example, structural defects and micro-crystalline grains. The value of β' is set empirically. Detailed meaning and values of the parameters used in the simulation can be found in /3/.

Reaction of slag is simulated by converting the dissolved glass voxels into several phases, including diffusing ettringite, hydrotalcite, diffusing C-S-H and C_4AH_{13} (if formed) preserving the right volume stoichiometry. The volume stoichiometry was calculated from eq. (4) with the properties of the products. Note that in the volume stoichiometry, the volume of C-S-H furthermore depends on its composition, namely C/S and A/S ratios. The composition of C-S-H is calculated in each cycle using the number of dissolved calcium silicates and glass voxels. While the number of dissolved species can differ in each cycle, local variation in the compositions of C-S-H exists in the resultant microstructure. This local variation of compositions of C-S-H was observed in the experiment by Richardson and Groves /12/ as well.

The consumption of CH by the slag hydration is simulated by reducing the number of diffusing CH voxels to be added. The number of voxels to reduce is calculated from eq. (5) using the numbers of diffusing CH voxels generated by the clinker hydration and dissolved glass voxels. The remaining diffusing CH voxels are added randomly, as described previously.

In each hydration cycle, properties evolving during the hydration process such as chemical shrinkage, heat release, non-evaporable water and porosity, are calculated using the inherent properties of the reaction and physical or chemical properties of the products. They can be used for calibrating and validating the model, and for further use, for example, predicting properties of the paste.

For simulating the hydration of slag cement, following information is needed: (a) the composition and PSD of Portland cement and gypsum (if present); (b) the composition of slag, including the oxide composition and fractions of glass and crystalline part; (c) PSD of slag; (d) fraction of slag in the paste; (e) water/binder ratio and (f) curing condition, including the temperature and sealed/saturated state. The hydration is carried out in a cycle basis and then converted into time scale.

Simulation results

Simulation was carried out for the microstructure development of slag cement pastes from the research of Richardson and Groves /12/. The compositions of slag and OPC are listed in Table 1. The w/c ratio is 0.4, used in the simulation as well. Curing in a sealed condition at 20 °C was used. The slag proportion in the cement is taken to be 50%.

The phase development of hydration products and the disappearance of slag and clinker are plotted in Figure 2 in volume fractions. Minor products are excluded from the plot because of the scale. It can be seen from the results that the clinker phases reacts much faster than the slag. After one year, most of the clinker phases have reacted, while about 50% of the slag is still unreacted. C-S-H is the most abundant products in the paste. One remarkable characteristic of the phase fraction is the low level of CH.

Instead of keeping rising as in OPC paste, the level of CH is almost constant after 4 weeks of hydration /17/. The distribution of phases can partly explain the low permeability of the resultant microstructure. As C-S-H is a highly amorphous product, the pore sizes in it are normally small so that the C-S-H is less permeable for gas and liquid than the other products.

Table 1. Oxide composition of OPC and Slag used in experiments (mass%) /12/

Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	NBO/T
OPC	0.19	1.33	6.19	20	2.65	0.86	65.9	3.03	-
GGBFS	0.64	7.74	11	37.2	3.68	0.55	41.7	0.38	2.038

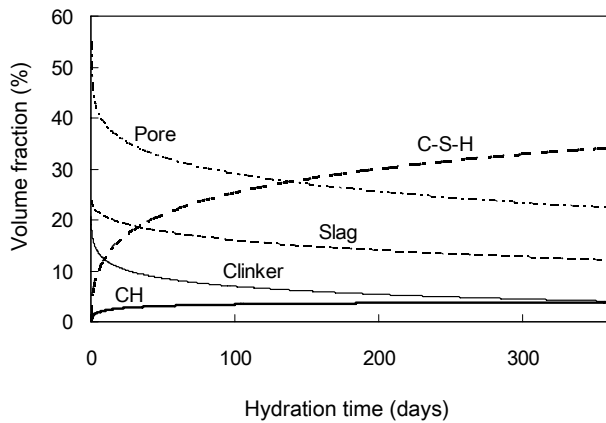


Figure 2. Predicted volume fractions of phases in the hydrating slag cement paste.

The composition of C-S-H is important in the studies on cementitious material because C-S-H is the principle binder providing most of the desirable properties. The composition of C-S-H governs its various properties, including both physical and chemical properties. It is the subject of numerous researches, and one general conclusion is that blending slag with OPC clearly decreases the C/S ratio in C-S-H /8/,/12/. Increasing the slag proportions in the slag cement decreases the C/S ratio.

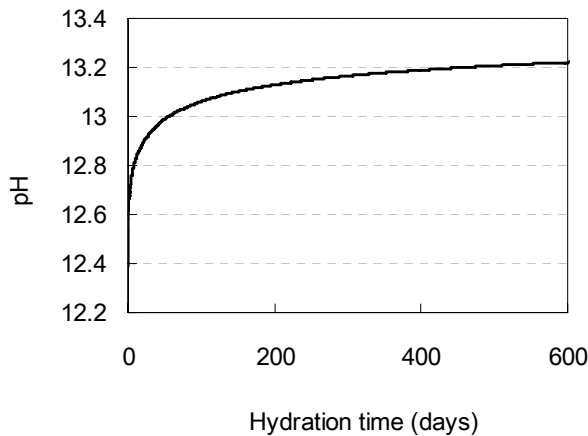


Figure 3. Predicted pH value development in the pore solution of the hydrating slag cement paste

The predicted pH value development of the pore solution is plotted in Figure 3. It can be seen that the pH value increases steadily during the early ages and reaches approximately a constant value after about 400 days. These trends of changes of pH value and alkali concentrations in the pore solution are observed in the experiments of Schäfer /13/ as well.

The composition of C-S-H is predicted with the computer model and is compared with the experimental results by Richardson and Groves /12/ (Figure 4). Both the C/S and A/S ratios were measured in the experiments at different ages. It can be seen that both parameters for the composition of C-S-H are well predicted with the model. At early hydration stages, the C/S ratios are slightly lower than the late ages because more clinker phases dissolve at this moment. As the consequence, more CH is available for the hydration of slag. Furthermore, very little slag has reacted during the early ages. As a whole, the composition of C-S-H changes only slightly with curing time.

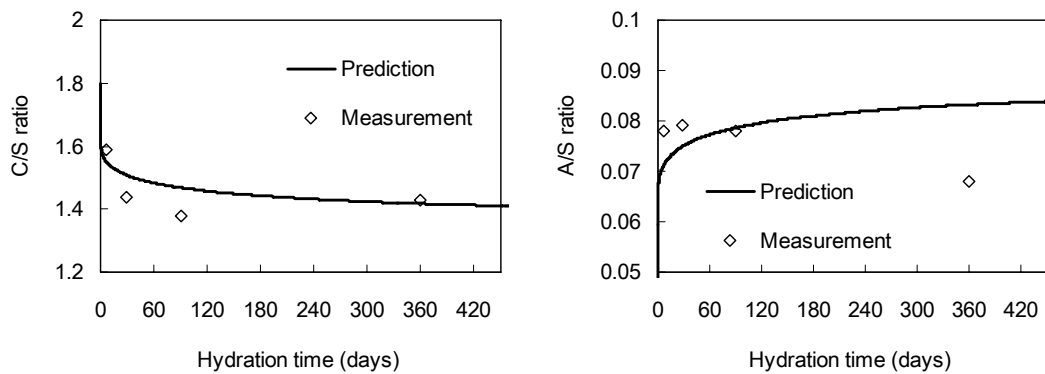


Figure 4. Predicted and measured composition of C-S-H (experimental data from /12/)

Conclusions

The reaction of slag in cement is much less well understood compared to that of Portland cement. Newly introduced theories are proven to be valuable when predicting the performance of slag in cement and the long-term behavior of concrete made from slag. Based on these theories, computer models are developed, which can represent the microstructure development three-dimensionally. The reactivity of slag deserves special attention because it is influenced by many factors. At least three of them are accounted for during the modelling process, including the chemical composition of slag, the pore water composition and the temperature. The 3-D computer model is successful in predicting the composition of the products and is able to predict the microstructure development.

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Authors:

W. Chen M.Sc.
Department of Construction Management
and Engineering (CME)
Faculty of Engineering Technology
University of Twente
P.O. Box 217

NL – 7500 AE Enschede

Dr. ir. H.J.H. Brouwers
Department of Construction Management
and Engineering (CME)
Faculty of Engineering Technology
University of Twente
P.O. Box 217

NL – 7500 AE Enschede