Three-dimensional computer modeling of slag cement hydration

Wei Chen · H. J. H. Brouwers · Z. H. Shui

Abstract A newly developed version of a three-dimensional computer model for simulating the hydration and microstructure development of slag cement pastes is presented in this study. It is based on a 3-D computer model for Portland cement hydration (CEMHYD3D) which was originally developed at NIST, taken over in the authors' group and further developed. Features like the digitized 3-D microstructure, the cellular automata (CA) algorithm for simulating the random walking, phase transformation for simulating the chemical reactions, are retained. But, the 3-D microstructure was reconstructed allowing for slag particles as binder in the system. Algorithms and rules are developed to account for the interaction between Portland cement hydration and slag reaction in the paste, of which the mechanisms were revealed in the studies by Chen and Brouwers [(2007) J Mater Sci 42(2):428; (2007) J Mater Sci 42(2):444] Methods for considering the various factors on the reactivity of slag in hydrating slag cement pastes are proposed, mainly for the oxide composition of slag and the alkalinity in the pore solution composition. A comparison between the model predictions and the experimental results in literature shows that the presented computer model can successfully predict the hydration process and the microstructure development of hydrating slag cement paste.

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Introduction

The use of slag cement in construction practice has attracted much attention because slag as a by-product is often cheaper than Portland cement. Furthermore, concrete made from slag cement has also certain engineering advantages, such as low heat release, low permeability and good durability in aggressive environments [1]. Since the slag is an industrial by-product, use of slag has many environmental advantages, such as low energy cost, use of secondary raw material and low pollutant gas emission. These advantages make it preferable to the conventional binders in practice.

Many researches have been carried out on the hydration and performance of slag cement since its first application. As an outcome, long-established knowledge is obtained, according to which various national standards are established for guiding practice purpose. However, until now most of the knowledge is empirically established. In many national standards, the criteria for the acceptance and processing of slag are performance related (EN 197-1, ASTM C989-05, GB/T203-1994). In other words, a series of time consuming and costly tests need to be conducted before one type of slag cement is accepted for application in engineering practice.

Benefiting from the rapid development in cement chemistry knowledge and computer science, computer modeling of the cement hydration process is possible. Several computer models have been developed in various groups, which can simulate the chemical reactions going on during the hardening process of cement paste, and the microstructure development [2–4]. Most of these models deal with Portland cement hydration, with or without some mineral additives like fly ash and silica fume. Typical model outputs of the computer models are the hydration

degrees of constituents, heat evolvement, microstructural characteristics, etc.

However, to the authors' knowledge, 3-D computer models for the slag cement hydration are still to be developed although several computer models for the Portland cement hydration are available now. Bentz [5] did an attempt to simulate the reaction of slag with CEM-HYD3D (NIST version). The model treats the hydration products of slag as a homogenous mix, namely "slag gel", whose properties are postulated from the slag composition and are independent on other factors. However, the individual hydration products identified in experiments [6–9] are not distinguished. As the hydration products in hydrating slag cement paste are principally similar to those existing in the Portland cement system and their compositions vary with the recipes of the paste and compositions of the initial materials [10, 11] it would be expected that this "slag gel" does not actually exist in the paste, and the assembly of the products can have various physical and chemical properties. Therefore, treating the products individually and representing the changing microstructure with precise descriptions of their properties is expected to give accurate predictions of the real hydrating paste.

The new development of the theories about the reaction of slag in cement in the works of Chen and Brouwers [10, 11] enables modeling this process of individual reactions with a 3-D computer-based model. The types of reaction products, their quantities and properties can be predicted with the new theories, with considerations to the interactions between the reactions of slag and clinker in cement.
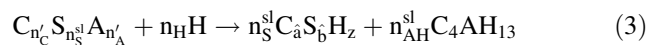
Recent developments of the 3-D computer model CEMHYD3D can be found in Chen [12] and Chen and Brouwers [13]. In this study, this model CEMHYD3D is extended for modeling the slag cement hydration. For developing this computer model, three important aspects are considered: an appropriate theory about the chemical reaction of slag in cement, consideration to the different slag reactivities, and establishment of the computer model. Therefore, the research in this study is presented following these aspects.

Hydration reaction of slag cement

First, the theories proposed by Chen and Brouwers [10, 11] for modeling the slag cement reaction are briefly introduced. 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
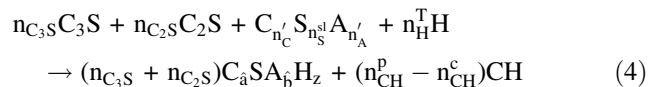
(calcium to silicon molar ratio; notation in cement chemistry is used, i.e., $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$ etc.) and the high contents of A substituting for S in the bridging tetrahedral of a dreierkette structure. The substitution degree is depending on the C/S ratio of C–S–H and the amount of A available for the substitution [10, 11].

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

$$M_{n_M^{sl}} A_{n_A^{HT}} + n_H^{HT} H \rightarrow n_{HT} M_5 A H_{13} \tag{1}$$

$$C_{n_C^{AFt}} A_{n_A^{AFt}} \bar{S}_{n_{\bar{S}}^{sl}} + n_H^{AFt} H \rightarrow n_{AFT} C_6 A \bar{S}_3 H_{32} \tag{2}$$

$$C_{n_C'} S_{n_S^{sl}} A_{n_A'} + n_H H \rightarrow n_S^{sl} C_{\hat{a}} S_{\hat{b}} H_z + n_{AH}^{sl} C_4 A H_{13} \tag{3}$$

in which n_M^{sl} and $n_{\bar{S}}^{sl}$ 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 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} depends on n_C', n_S^{sl} and n_A', which is computed as: $n_C' = n_C^{sl} - 2n_S^{sl}$ and $n_A' = n_A^{sl} - n_S^{sl}/3 - n_M^{sl}/5$. It is not formed in some slag cement pastes due to the low alumina content of the slag. â and b̂ are the C/S and A/S ratios (in moles) in C–S–H. It is note-worthy that the water contents in all the hydration products depend on the hydration state that the products are subject to. The detailed computation methods for the parameters in Eqs. 1–3 are presented in the work of Chen and Brouwers [10].

If slag is mixed with clinker, 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:

$$n_{C_3S} C_3 S + n_{C_2S} C_2 S + C_{n_C'} S_{n_S^{sl}} A_{n_A'} + n_H^T H$$
$$\rightarrow (n_{C_3S} + n_{C_2S}) C_{\hat{a}} S A_{\hat{b}} H_z + (n_{CH}^p - n_{CH}^c) CH \tag{4}$$

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; â is the C/S ratio in the equilibrated product C–S–H and b̂ 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 number of moles of CH produced by clinker hydration and n_{CH}^c is the number of moles of CH consumed by the slag reaction. The detailed methods for computing the parameters in Eq. 4 are presented in the previous work [11]. Only the method for computing the amount of CH consumed by the slag reaction is included as:

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

with

$$p = \frac{1.8n_S^{sl} - n_C'}{n_{CH}^p + 1.8n_S^{sl} - n_C'} \tag{6}$$

Reactivity of slag in cement

In this Section, the reactivity of slag is discussed considering various factors. Methods for predicting the reactivity of slag with different compositions and in various alkaline environments are proposed based on experimental observations. The hydration rate of slag is an indispensable parameter when simulating the reaction of slag in cement. It depends among others on the intrinsic reactivity of slag. The latent hydraulic property of slag is well known, i.e., the slag reacts at a remarkable rate when the environment is suitable, an alkaline environment in case of concrete. The reactivity of slag is the objective of numerous researches, and is still not adequately understood yet. Several factors are known to influence the reactivity of slag, for example, the presence of crystalline minerals, chemical composition, geometrical characteristics, temperature, glass structure, and the alkaline environment.

Methods to characterize the reactivity

The reactivity of slag can be characterized in several different ways, including the strength development, hydration degree of slag, corrosion rate, the amount of retained water in hydrating slag cement paste, etc. Each of these methods has its advantages and disadvantages, which are briefly reviewed below.

Strength development

Strength development of mortar or concrete samples made from slag cement is probably the most commonly used method in the past. Mortar or concrete samples are made with binders containing slag mixed with a certain proportion of activators or clinker. The samples are cured and their strength is tested at planned ages. The differences of the strength are used to evaluate the reactivity of slag. The strength development is used as the grading requirement on the slag reactivity index in ASTM C989-05.

The advantages of this method include:

(1) It tests the most relevant property of cement and concrete to engineering practice, the strength. Hence, the results can be connected to construction demand directly.

(2) The facilities and knowledge involved in this test are widely available, and the procedure is well documented.

However, the disadvantage of this method is also obvious: the strength development of the samples is not necessarily proportional to the slag reaction degree in the paste, mortar or concrete. It is influenced by the slag composition as well. Some slags produce more C–S–H—the principle binder in cement paste—than the others [11]. In other words, the more reactive slag does not always lead to higher strength of the samples.

Reaction degree

The reaction degree of slag at given age is the most direct result accounting for the different slag reactivities. It is defined as the proportion of slag that reacts at a certain age to the total amount present at the beginning. The more reactive slags have higher hydration degrees if the other test conditions are kept the same. The reaction degree of slag in cement can be determined by measuring the quantity of unreacted slag in the paste via selective dissolution [14], thermal decomposition [15], or point counting [16].

The advantage of using this factor to evaluate the reactivity of slag is that it gives directly the quantity of slag that has reacted. Therefore, the results can closely represent the different slag reactivities. However, the disadvantages cannot be ignored either. First, measuring the reaction degree of slag demands complex experimental setups, and specific knowledge about the chemical reactions going on during the treatment. Careless operation and inadequate experience can lead to significant errors in the results. Second, uncertainties in the methods in the measurements add to the disadvantages. For example, in the selective dissolution method, some hydration products of slag are not soluble in the liquid, leading to a higher amount of anhydrous slag and hence to an underestimation of the reaction degree of the slag. Third, the measured hydration degrees of slag by using different techniques do not always agree with each other [15]. Hence, the validity of the techniques is frequently questioned.

Corrosion rate

The corrosion rate of slag in an alkaline solution can also be used to evaluate the reactivity of slag in an alkaline environment [17]. It is originally proposed to determine the resistance of glass to external corrosion (German standard DIN 12111). The slag is boiled in alkaline water for some time, and the weight loss, or the amount of alkali released from the glass, is measured. While this method is relatively easy to realize, and gives direct results about the slag reaction rate, it is an accelerated method, which can hardly represent the real reaction process of slag in practice.

Water retention

The amount of water retained in hydrating slag cement pastes is also used to evaluate the slag reactivity in blended cement, besides its common use for Portland cement paste [18]. It uses the amount of water retained in the paste after being subjected to standard drying procedures, for example, D-Dried, P-Dried, or heated at 105 °C. Like the strength development, this index is also indirectly related to the slag hydration degree and contributions from other reactants should be taken into account, which is normally difficult.

Besides the methods mentioned above, there are also some other ones used, such as the quantification of the –74 ppm signal in ^{29}Si MAS-NMR spectra and heat evolvement [15, 19]. Results from these measurements give indications about the reactivity of slag as well.

Factors on the reactivity

The reactivity of slag is influenced by several factors, some being the inherent properties of the slag itself, and the other being environmental factors. A schematic illustration of factors on the reactivity of slag is included in Fig. 1. Some of these factors are discussed in the following sections.
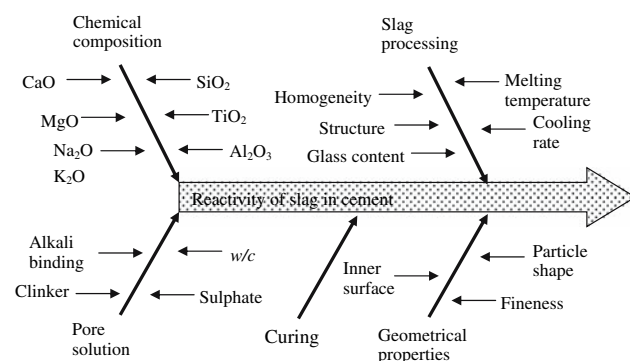

Fig. 1 Factors on the reactivity of slag, modified from Wolter et al. [20]

Structure of slag

The structure of slag is an inherent property of slag itself. It involves how the structure of slag is built up. Among the various structural theories of glasses, the random network theory proposed by Zachariasen [21] for the structure of oxide glasses may be the most suitable one to describe the structure of vitreous slag. This structure is based on a distorted 3-D network formed by the oxides.

The network forming elements are characterized by small ionic radii and by high possible ionic valences. They are surrounded by four oxygen atoms (co-ordination number 4) in the form of a tetrahedron. The network is formed in such a way that distinct oxygen atoms belong to two tetrahedra at the same time, called bridging oxygens (BO) (Fig. 2). One typical network former is silica. With the vitreous blastfurnace slag it forms SiO_4^{4-}-tetrahedra, $Si_2O_6^{7-}$ groups, chains and other polymerization products. The negative valences of these anionic groups are neutralized by the positive valences of cations, called network modifiers. The inclusion of network modifiers break the bonded oxygens and form non-bridging oxygen (NBO), O^-, and free oxygen O^{2-}. The most typical network modifier within the vitreous blastfurnace slag is the Ca^{2+} ion. The polymerization grade of the network forming SiO_4^{4-}-tetrahedra is reduced with increasing content of network modifiers, indicating that the glass has a smaller stability and a higher chemical reactivity.

To determine the structure of slag involves complex techniques and equipments which are not widely available. Furthermore, the states of bond and coordination numbers of constituents do not always lead to the same conclusions on the reactivities of the blastfurnace slag. The most significant conclusion for this research so far is that the more strongly the structure is distorted, the more reactive the slag is [23].

An important property with respect to how severe the network is distorted is 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 co-ordinated atoms (e.g., Si), usually denoted as NBO/T ratio (Fig. 2). The NBO/T ratio is suitable for this purpose because [24]:

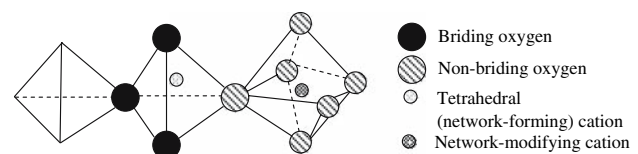(1) The number of NBO is proportional to the number of moles of oxide addition;

Fig. 2 Definition of non-bridging oxygen per tetrahedrally coordinated cations (NBO/T), after Mysen [22]

(2) Addition of alkali or alkaline-metal oxides to silica increases the overall O/Si ratio of the silicate;

(3) Increasing the number of NBO results in the progressive breakdown of the silicate structure into smaller units.

It is known in the silicate chemistry that both the physical properties of slag melt and chemical resistance of glasses in it depend on the NBO/T ratio [25, 26]. The NBO/T ratio of glass in normal granulated blastfurnace slag can be directly calculated from its oxide compositions.

Clark and Zoitos [27] correlated the calculated free energy of glass hydration for over 150 glasses with the number of non-bridging oxygen (calculated in a similar way as the NBO/T ratio with the T replaced by the total moles of oxides Si). The results are shown in Fig. 3a. It appeared that there is a linear relationship between the calculated free energy and the NBO of glasses. Since generally lower free energy of hydration corresponds to also lower stability of glass in the alkaline environment, glasses with higher NBO values are more reactive than those with lower NBO values.

Wolter et al. [20] measured the hydrolytic reactivity of ground slag grains by boiling 0.03 g of slag with various compositions for 1 h in 50 mL distilled water and titrating the leached alkalis with 0.01 mol/L HCl. The amount of HCl needed is taken as a measure for the hydrolytic reactivity. The authors also investigated the glass structure of the slags. A good correlation between the hydrolytic reactivity and the NBO/T ratio of the glass in slag is observed (Fig. 3b), confirming that the structure of slag has an important influence on the reactivity of slag. A clear linear relationship between the reactivity of slag in the distilled water and its NBO/T value is observed.

Activators

The blastfurnace slag is known to be a latent hydraulic material, i.e., certain kinds of activators need to be present to trigger the reaction. However, this effect is dependent on the nature of the activator itself, besides its dosage in the mix. Gypsum, lime and alkali hydroxides are the most typical activators, closely related to the slag-blended cement and super-sulfated slag cement. Water-glass (i.e., sodium silicate solution) is sometimes used as well.

When the slag is activated with Portland cement, there is actually a combined effect by the solutions of alkali hydroxide (NaOH, KOH), gypsum (early ages) and CH. If they are considered separately, the alkali hydroxide shows the most efficient activation effect compared to the others. CH shows a good effect during the early ages, but the effect is surpassed by the gypsum after about two weeks. However, if the alkali hydroxides are used as activators, the reaction at later ages is obviously impeded, of which the mechanism is unknown, yet.

Compared to the activation effect of alkali hydroxide, water-glass shows better performance [19]. Even if the pH value of the water-glass solution is lower than the NaOH solution, the reaction rate of slag is higher when the former is used as activators. Na_2CO_3 has an inferior activation effect compared to both NaOH and water-glass solution. When water-glass (Na_2SiO_4 solution) is used as activators, there seems to be an optimum dosage, corresponding to 4 m/m% (as Na_2O) [19].

According to Chen and Brouwers [10, 11], the CH and gypsum cannot be taken as simple activators only. They also enter the slag reaction and are bound in the hydration products. Hence, they might change the reaction behavior as well. The role of NaOH and KOH is simply that of activators.

Presence of crystalline minerals

It is known that a certain fraction of crystalline minerals could form during the cooling process of slag. On the one hand, the effect of crystalline mineral is obvious if a big part of the ground slag is present in the form of totally

Fig. 3 Correlation between NBO (or NBO/T) value and reactivity of glasses and slag. (a) Free energy of glass hydration, from Clark and Zoitos [27]; (b) Hydrolytic reactivity of GGBFS, from Wolter et al. [20]
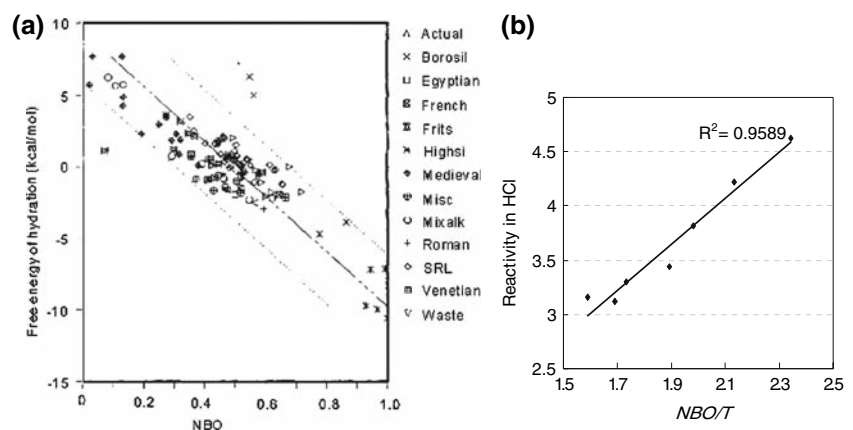
crystallized grains; the strength will accordingly be much lower than that without any crystalline minerals. If, on the other hand, crystals of smaller size are tightly intergrown with the vitreous slag, they will most likely be of unessential influence on the strength. A higher strength could be expected if the crystals are homogeneously distributed in the vitreous slag as submicroscopic crystal nuclei. Furthermore, it has to be considered that tiny crystalline grains improved the grindability of slag. It is observed that crystalline content up to about 5 m/m% could be beneficial for the strength development [28, 29].

Oxide composition of slag

The oxide composition of slag characterizes the inherent nature of the slag. Therefore, a lot of efforts are made to relate the reactivity of blastfurnace slags to its chemical composition analysis. Some conclusions are drawn based on a large set of experiments involving 24 slags and 192 slag cements [23]:

(1) An increase of the Al_2O_3 content above 13 m/m% increases the early strength only. The 91-day strengths are even lower at higher aluminum contents.
(2) Partly the effect of the minor components is so strong that after 7 days already some blastfurnace slags with 11 m/m% Al_2O_3 show higher strengths than those with 15 m/m% Al_2O_3.
(3) MgO in the range up to 11-m/m% has quantitatively the same effectiveness as CaO has.
(4) In every case MnO has a negative effect.
(5) The influences of P_2O_5 and alkalis depend on the kind of clinker used and on the testing age. After 28 days P_2O_5 always proves positive.
(6) The statistical examination of TiO_2 (up to 1 m/m%), Fe_2O_3 (up to 2 m/m%), and sulfur (up to 2 m/m%) does not prove any significant influence.
(7) Besides the clinker content and the fineness, the strength developments of the blastfurnace slag cements also considerably depend on the kind of clinker.

As mentioned before, on the one hand, the reactivity of slag is strongly influenced by the structure of the slag, which is difficult to determine in practice. On the other hand, the oxide composition is relatively easy to measure. The NBO/T ratio builds the bridge between the structure of glass in normal granulated blastfurnace slag and its oxide compositions. It can be calculated from the oxide composition of glass in slag and be used to evaluate the reactivity of slag. In this research, the NBO/T ratio is used to evaluate the effect of oxide composition of glass in slag on its reactivity.

Particle shape and particle size also play an important role on the reactivity of the slag. Sato et al. [30] did a series of experiments on the hydration of blastfurnace slag particles. The hydration of ground commercial slag, with various particle sizes and various activators is investigated. Samples with five different particles sizes (3.27, 4.05, 5.86, 8.66 and 13.36 μm by volume mean diameter) were prepared. The samples hydrated with a solution/slag ratio of 10 in NaOH solutions, saturated CH solutions or previously stirred Portland cement suspension as alkaline activators. The amount of hydrated slag is measured by determining the soluble part of the hydration products using salicylic-acid-acetonemethanol solution. The thickness of hydrated layer with time was calculated using the slag hydration rate and the PSD of slag, assuming the slag particles to be spherical. The authors concluded that the thickness of hydrated layer of particle does not depend on the particle size. The rate of hydration is actually proportional to the outer surface area. Therefore, it is expected that fine slag particles hydrate much faster than the coarser ones.

pH value of pore solution

The reaction rate of glass is known to be highly dependent on the chemical environment it is subject to [31]. It is regarded as a concern to the "durability" of glass if the structural glasses are the interests of investigation. A typical example is the archaeological glass. The pore solution is thus important concerning the reactivity of glass in slag cement. Considering the stability of two major network-forming elements in glass, the silica and alumina, the solutions can be characterized roughly into three regions: the acid (pH value below 5), the natural (pH value between 5 and 9) and the basic (pH values above 9) [32]. Normal glass is quite stable in the natural environment, as proven by its wide use in the construction industry. The most relevant region in cementitious material system is the basic environment. When the pH value of the solution increases above 9, the breakdown of the silicate lattice is enhanced.

Reaction of silicate glass with aqueous solution. The corrosion of silicate glasses by aqueous solutions can be described in terms of three chemical reactions [31]:

(1) The penetration of a proton from water into the glassy network, replacing an alkali ion:

$$\equiv Si-OR + H_2O \leftrightarrow \equiv Si-OH + R^+ + OH^- \qquad (7)$$
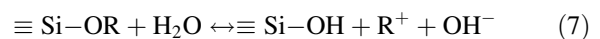
in which R is the alkali ion.
(2) The hydroxyl ion in solution disrupts siloxane bond in glass:

$$\equiv Si-O-Si \equiv\ +\ OH^- \leftrightarrow \equiv Si-OH^+ \equiv Si-O^-$$

$$(8)$$
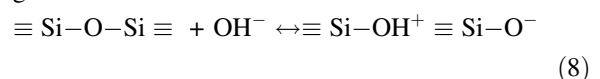
(3) The non-bridging oxygen formed in Eq. 8 interacts further with a molecule of water producing a hydroxyl ion, which is free to repeat reaction 2 over again:

$$\equiv Si-O^- + H_2O \leftrightarrow \equiv Si-OH + OH^- \qquad (9)$$
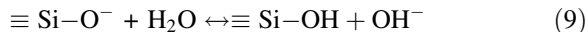
Penetration of a bare proton, as suggested in reaction (7), is energetically improbable for the hydration energy of H^+ to H_3O^+ is very high and negative (about –367 kcal per mol). Therefore, reactions (8) and (9) dominate the dissolution of silicate glass. The hydroxyl ion serves as the source of hydroxyl for further breaking of siloxane bond on the glass surface in reaction (8). Therefore, an increase in the activity of hydroxyl ion in the solution will favor increased removal of silica.

Dependence on the pH value. After mixing the water with cement, the liquid phase contains substantial amount of ions, giving it the name "pore solution". The pore solution is normally basic, due to the instantaneous dissolution of alkalis in clinker [33]. The pH of the pore solution depends on many factors, like the w/c ratio, alkali level and type of cement and cement compositions.

The high pH value of the pore solution obvious promotes the dissolution process of glass in slag [34]. The study of El-Shamy et al. [35] showed that all the silicate glasses become particularly susceptible to decomposition for pH beyond 9 to 10 (Fig. 4).

Paul [31] calculated the solubility of SiO_2 using a thermodynamic approach and considering the effect of pH of the solution. The results are shown in Fig. 5. Again, it is found that the solubility of SiO_2 is greatly enhanced when the pH goes above 9.

Zhou et al. [36] measured the hydration degree of slag in AAS pastes at different ages. The fineness of the slag is 600 m^2/kg. Paste sample are prepared with a w/c ratio of 0.45. Activators are prepared by adding NaOH to the water glass to achieve different alkalinities. Their pH values range from 12.5 to 14.7 (estimated from the composition of the activator, see Zhou et al. [36]). The degree of slag reaction is measured by a solvent extraction method. The measured hydration degrees at given age are plotted in
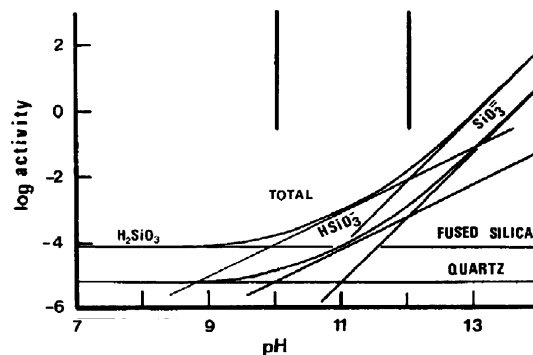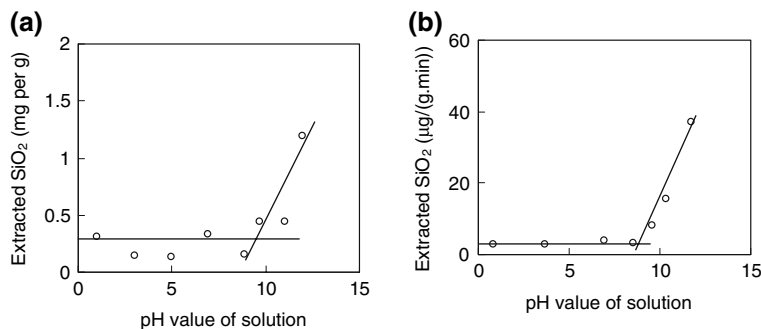
Fig. 5 Stability of SiO_2 in aqueous solutions at different pH (25 °C, after [31])
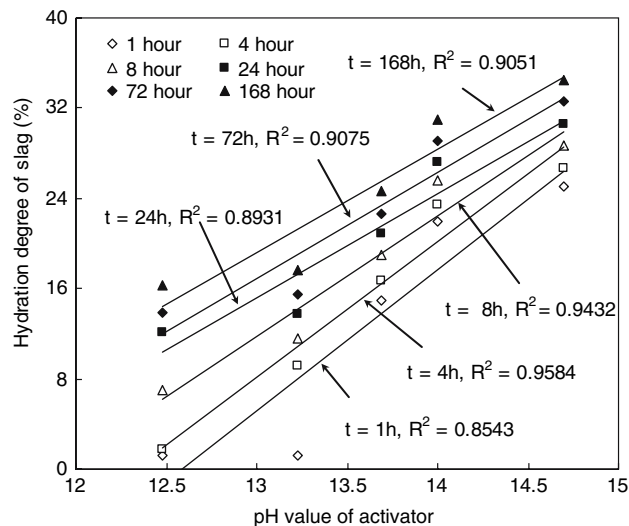
Fig. 6 Hydration degree of AAS at various ages as a function of the pH value of activators (after Zhou et al. [36], pH values above 13.69 are calculated from the composition of the activators)

Fig. 6 versus the pH value of the activators. It can be seen that an approximately linear relation exists between the hydration degree and the pH values of the activators at the ages investigated. Based on the above discussed literature, it is postulated that

$$\beta_1 = a_1 \cdot pH + b_1 \qquad (10)$$

Fig. 4 Effect of pH value of solution on the rate of extraction of SiO_2 from (**a**) a fused silica powder at 90 °C; (**b**) 25 Na_2O, 75 SiO_2 glass grains at 35 °C, after El-Shamy et al. [35]

in which a_1 is the slope coefficient of the line and b_1 is the intercept. The mean value of a_1 fitted using the experimental data of Zhou et al. [36] is 0.105. The value of b_1 depends on the time elapsed.

Effect of temperature

The influence of temperature on the slag reaction rate is very obvious. 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 activation energy, E_a for hydration [37–39]. The Arrhenius equation can be written in the form:

$$k_T = A \times \exp\left(\frac{-E_a}{RT}\right) \tag{11}$$

in which k_T is a rate constant, R is the gas constant (8.314×10^{-3} kJ/(mol·K)) and A is a constant. Typical values for the activation energy of slag are between 50 and 59 kJ/mol [37]. This value is apparently higher than the values measured for Portland cement hydration, about 38.44–40.20 kJ/mol [40].

Concluding remarks

The conclusions on the effect of different factors on the hydraulic reactivity can diverse due to the characterization methods. Several methods are available, including direct and indirect ones. While their significance to different applications can vary, the conclusions might be merely drawn from the tests designed for the specific objectives. The hydration rates and degrees measured with different methods could differ from each other greatly [15].

As said, the strength test is probably the most widely used and easiest method employed generally. The principle strength-bearing agent in hydrating slag paste is calcium silicate hydrate (C–S–H), similar to that of the Portland cement system. Therefore, reaction of glasses containing only calcium and silicon is expected to yield the highest strength. However, the reaction can only proceed very slowly. The presence of other constituents is thus important for distorting the network structure. Therefore, the glass is on a higher energy level, therefore less stable and possessing a higher reactivity.

Computer modeling 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. By Chen [12] and Chen and Brouwers [13] the so-called New Model of the CEMHYD3D model for Portland cement is discussed in detail. This New Model is chosen as the basis and extensions are made for modeling the slag cement hydration.

The computer modeling process for the slag cement hydration is essentially similar to that for the hydration of Portland cement. 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 series 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.

Regenerating the initial microstructure

The initial microstructure of slag cement paste is reconstructed using the water/binder ratio and the PSD of clinker, slag and gypsum (if present in the system). The way of distributing clinker phase follows from those used by Bentz [2] and Van Eijk [4], using totally random distribution or phase correlation file. The glass and crystalline minerals 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. The density of the crystalline mineral is assumed to be 3.15 g/cm^3 (density of merwinite) if the crystalline mineral is not identified. The user can also opt to assign all the slag particles as glass phase since in some slags the crystalline mineral exists in such a small extent that it is not detected. In the New Model modified for slag cement hydration, the 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 are ground together, they have identical PSD. The same options for gypsum are also provided.

Dissolution of slag pixel

In each hydration cycle, the pixels marked as glass are enabled to dissolve. The occurrence of dissolution is determined by the "dissolution probability" of a slag pixel and its position in the hydrating particle.

Consideration to the OH$^-$ concentration

Since the dissolution rate of glass is dependent on the ion concentration of pore solution in the real paste [31, 34–36],

the dissolution probability is related to the pH value of the activation solution. For solutions other than the Portland cement suspension, the pH value can be determined from the ion concentrations. If Portland cement is used as activator, the methods proposed by Chen and Brouwers [41] for modeling the pore solution composition of hydrating slag cement pastes are used. Then, the pH value is calculated from the concentration of OH^-. The calculated value of pH in each cycle is used for the dissolution of the glass pixel in the next cycle.

In the methods for predicting the alkali concentrations in the pore solution of hydrating cement paste proposed by Chen and Brouwers [41], two different binding capacities for C–S–H in hydrating cement paste are found, either for the neat Portland cement or for the blended cement. They are significant different from each other. However, it is less likely that the replacement of Portland cement clinker with a small proportion of slag can change the binding capacity of C–S–H dramatically. All the data calculated for blended cement are obtained with slag proportions higher than 20-m/m% slag. For very low slag proportions (for example, 5 m/m%), the alkali binding behavior of C–S–H may be close to that of C–S–H in neat Portland cement paste. The hydrotalcite content in the paste is also very low. In this case, most of the alkalis are still bound in the C–S–H, which is not accounted for in the methods proposed by Chen and Brouwers [41]. In the computer model, distinction is therefore made between C–S–H formed by the Portland cement hydration and that by the slag reaction. In each hydration cycle, the numbers of C–S–H pixels formed by the Portland cement hydration and by the slag reaction are counted. The C–S–H pixels originated from the Portland cement hydration is taken to possess the alkali-binding capacity of C–S–H in neat Portland cement paste (C/S = 1.8); and the C–S–H from slag reaction another alkali-binding capacity, which is determined with the methods proposed by Chen and Brouwers [41]. Again, the partition theory proposed by Chen and Brouwers [41] is applied. Three types hydration products in the blended cement paste can actually bind alkalis: the C–S–H from the Portland cement hydration, that from the slag reaction and the hydrotalcite (from the slag reaction as well). The alkali-binding capacity of C–S–H follows from the theories of Chen and Brouwers [33, 41]. Again, a non-linear equation is established with the alkali concentration as the only unknown. Solving the equations gives the alkali concentrations in the pore solution.

According to Fig. 6, the reactivity of slag is linearly proportional to the pH value of the activation solution. Hence, a coefficient accounting for the pH of the activator is proposed as:

$$\beta_1 = \begin{cases} 0 & (\text{pH} < 9) \\ a_1 \times (\text{pH} - 9) & (\text{pH} > 9) \end{cases} \quad (12)$$

in which pH is the pH value of the pore solution; a_1 is a slope coefficient of the linear correlation, equal to 0.105 in the experiments of Zhou et al. [36]. The value 9 is set according to the findings summarized in 'pH value of pore solution'.

Note that in Eq. 12, if the pH value of the pore solution is lower than 9, $\beta_1 = 0$, indicating that the glass in slag does not react. This case corresponds to the very slow reaction rate of slag if there is no activator in the system, known as the latent hydraulic property. For the pore solution of hydrating cement paste and concrete, normally pH > 9 [41].

Consideration to the chemical composition

The effect of the chemical composition of glass in slag on its reactivity is accounted for with its NBO/T value. It is shown in Fig. 3b that there is a linear relationship between the reactivity of glass in slag and its NBO/T value. Therefore, a coefficient regarding the oxide composition of slag is proposed as:

$$\beta_2 = a_2 \cdot (\text{NBO/T}) \quad (13)$$

in which a_2 is the slope correlation of the linear relation between the NBO/T ratio of glass in slag and the reactivity, equal to 2.116 if calculated from the data of Wolter et al. [20] (see Fig. 3b). Note that the data by Wolter et al. [20] cannot be applied right away because of the employed accelerated methods.

Dissolution probability of glass pixel

Considering the effects of oxide composition and alkalinity of pore solution on the slag reactivity, the dissolution probability of a glass pixel in the New Model is thus calculated as:

$$\begin{aligned} P_{\text{glass}} &= P_{\text{glass}}^0 \cdot \beta_1 \cdot \beta_2 \\ &= \begin{cases} 0 & (\text{pH} \leq 9) \\ P_{\text{glass}}^0 \, \beta' \cdot (\text{NBO/T}) \cdot (\text{pH} - 9) & (\text{pH} > 9) \end{cases} \end{aligned} \quad (14)$$

in which P_{glass}^0 is the dissolution probability of glass pixel, empirically set beforehand. In this study, the value of P_{glass}^0 is set to be 0.0013, which should not be varied by the user of the computer model. $\beta' = a_1 \cdot a_2$ and is a parameter depending on some other factors that influence the slag reactivity, for example, structural defects, micro-crystalline

grains etc. The value of β' is set empirically by the user and can be calibrated from experimental results.

Reaction of slag pixel

Immediately after the glass pixel dissolves, it converts into several phases, including diffusing ettringite, hydrotalcite, diffusing C–S–H and C_4AH_{13} (if formed) preserving the right volume stoichiometry (Fig. 7). The volume stoichiometry is calculated from the reaction theory proposed by Chen and Brouwers [11] 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.

When simulating the hydration of slag cement, models proposed by Chen and Brouwers [11] are slightly modified taking use of the model output. In their work, the C/S and A/S ratios of C–S–H are determined by the compositions of slag and clinker and the slag proportions in the cement. The degree of slag hydration is based on the conditions in which the pastes are cured and the curing age. The complete hydration of the clinker is assumed. In the real pastes of slag-blended cement, the clinker phases and slag are reacting simultaneously. These simultaneous reactions are represented in the computer model by the congruent dissolution of slag and clinker pixels. At each hydration cycle, the number of reacted clinker phases and slag can be counted. Therefore, to chemically represent the reactions going on in the paste, they are calculated in each cycle using the number of dissolved calcium silicates and glass pixels in the modified model. 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 is also observed in the experiments of Richardson and Groves [7].

The hydrotalcite forms in the exact situation of glass pixels for that the magnesia content of slag is the least mobile and it is used to demarcate the original location of slag grains in practice [1]. In this way, the microstructure of the slag cement paste can be represented accurately. The diffusing C–S–H is located again in the neighbor site of the reactant in a $17 \times 17 \times 17$ box to simulate the growth of C–S–H around the grains. Diffusing ettringite and solid C_4AH_{13} pixels are located randomly inside the microstructure.

The reaction stoichiometry of clinker hydration is also changed because the composition of C–S–H in the modified model is influenced by the presence of slag. In each hydration cycle, a scan over all the reactants is performed; hence, a batch of pixels is dissolved. Due to the dissolution of C_3S, C_2S and glass pixels, additional diffusing C–S–H, diffusing ettringite, diffusing CH, solid C_4AH_{13} and hydrotalcite pixels are to be added after the dissolution. Hence, after the scan, the amount of dissolved C_3S, C_2S and glass pixels are counted. The composition of C–S–H at the respective cycles is calculated accordingly. Then, the properties of C–S–H are also calculated. With the properties of C–S–H, the number of pixels to be added is determined according to the reaction stoichiometry.

The consumption of CH by the slag hydration is simulated by reducing the number of diffusing CH pixels to be added. The number of pixels to reduce is calculated from Eq. 5 using the numbers of diffusing CH pixels generated by the clinker hydration and dissolved glass pixels. The remaining diffusing CH pixels are added randomly, as described previously and are then treated as in neat OPC hydration [13].

Fig. 7 State transition diagram for the new computer model with slag hydration, modified from Bentz [42]
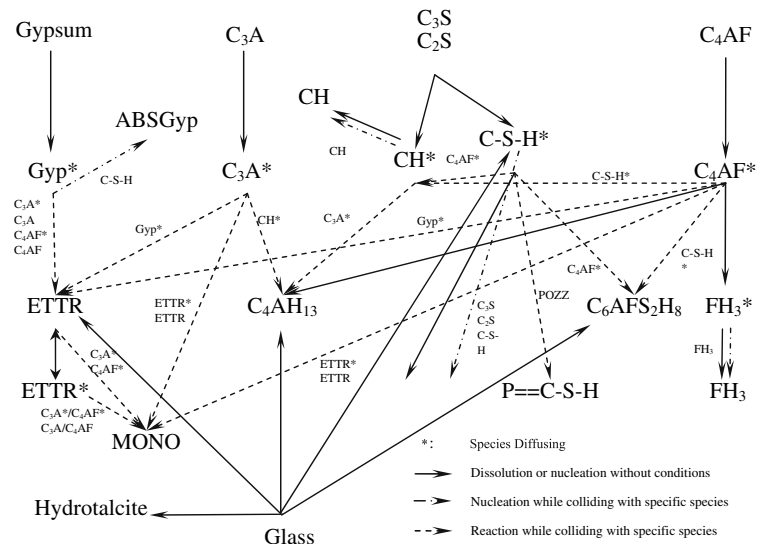
Relating the cycles to real time

Bentz [2] proposed a method to relate the number of cycles executed in the simulation to the real time as:

$$t = B \cdot (\text{cycles})^2 \tag{15}$$

Since the empirical relation is proven successful for modelling Portland cement hydration [2], here it is postulated and it is verified whether it is valid for slag cement hydration as well.

Simulation results

For simulating the hydration of slag cement, the following information is needed: (a) the composition and PSD of clinker 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 on a cycle basis and then converted into time.

After 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. In the following discussion, model outputs are compared to the experimental results. They are further used to investigate several factors on the hydration of slag cement.

The microstructure development of slag cement pastes is first simulated using the slag cement from the research of Richardson and Groves [7]. The compositions of slag and Portland cement (Slag I and PC I) are listed in Table 1. The same w/c ratio of 0.4 as in the experiment is used in the simulation, as well as curing in a sealed condition at 20 °C. The slag proportion in the mix is 50 m/m%. The value of β' used in the simulation is set to be 0.25 (dimensionless), and the time conversion factor is taken to 3.5×10^{-3} h/cycle^2, which is based on the New Model for OPC hydration [13].

The phase development of hydration products and the disappearance of slag and clinker are plotted in Fig. 8 in volume fractions. Minor products are excluded from the plot because of the scale.

One can see from the results that the clinker phases react much faster than the slag. After one year, almost all the clinker phases have reacted, while about 50% of the slag is still anhydrous. C–S–H is the most abundant products in the paste. One remarkable characteristic of the phase composition is the low content of CH. Instead of increasing

Table 1 Composition of Portland cement and slag used in experiments (m/m %)

Oxide	PC I[a]	PC II[c]	Slag I[a]	Slag II[b]	Slag III[c]
C	65.9	64.09	41.7	41.8	43.39
S	20	19.46	37.2	35.4	35.46
A	6.19	4.87	11	12.9	12.16
M	1.33	0.48	7.74	6.3	6.32
$\bar{S}$	2.65	3.52	3.68	0	0
F	3.03	0.281	0.38	0.3	0.63
T	0.3	0	0.68	1.65	0
P	0	0	0	0	0
N	0.19	0.02	0.64	0.26	0.15
K	0.86	0.6	0.55	0.38	0.5
NBO/T	–	–	2.026	1.864	1.98
Bogue composition					
C$_3$S	65.52	75.54			
C$_2$S	10.61	3.77			
C$_3$A	11.98	13.46			
C$_4$AF	9.16	0.92			
C$\bar{S}$H$_2$	4.68	6.46			

[a] From Richardson and Groves [7]

[b] AAS, from Sato et al. [30]
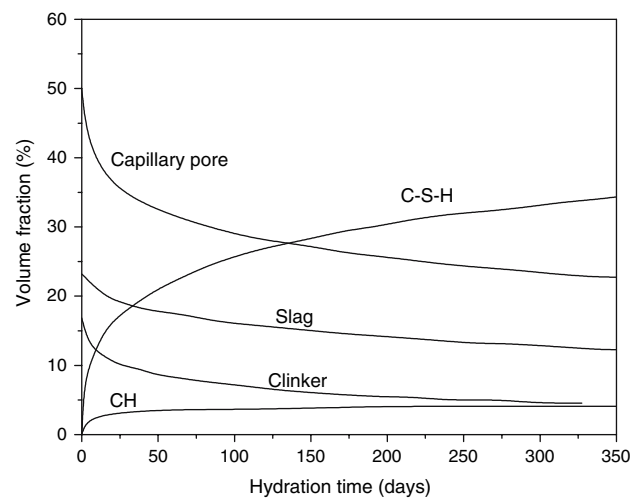
[c] From Battagin [43]

Fig. 8 Simulated volume fraction of hydration products and reactants in hydrating slag cement paste, with the slag cement from Richardson and Groves [7], slag proportion 50 (m/m)%, w/c = 0.4, T = 20 °C, $B = 3.5 \times 10^{-3}$ h/cycle^2, $\beta' = 0.25$

continuously as the case in hydrating Portland cement paste, the level of CH is almost constant after 4 weeks of hydration. The distribution of phases can partly explain the low permeability of the resultant microstructure. As C–S–H is a highly amorphous product, the pores in it are normally so small that it can be actually regarded impermeable for gas

and liquid. Therefore, with increasing volume fraction of C–S–H, the paste becomes less permeable as well.

Discussion

Influence of particle size on the slag hydration

The effect of particle size on the slag hydration is investigated using the New Model and compared to the measurements by Sato et al. [30]. They measured the hydration degrees of alkali-activated slag particles with narrow-ranged sizes. The microstructure is generated in such a way that all the particles have the same size as the mean diameter (on volume basis) used in the experiments. Particles with the closest size to the mean diameter are used because particles used in the simulation are not exactly spherical and the particle size distribution is discrete. For example, for the sample with mean diameter 3.27 μm, the digital particles with size 3 μm are used. The microstructure has the same water/binder ratio as that used in the experiments. The slag has also the same composition as in the experiment, which is listed in Table 1 (Slag II).

A simulation is carried out with the same condition as also used in the experiments. The water/slag ratio is 10. The activator used is NaOH solution with the concentration 0.1 mol/L. The slurry is cured at 20 °C. The parameter β' is again set to be 0.25 and the time conversion factor is now fitted to be 4.2×10^{-3} h/cycle². The average size of remaining slag particles is calculated using the amount of anhydrous slag pixel, the number of particles and the PSD of slag given in the literature preserving the total volume. The hydrated thickness is calculated according to the difference between the initial size and the size of the hydrated slag particle. The simulation results are shown in Fig. 9a. One can see from the results that the thickness of the hydrated layer is not significantly influenced by the particles size of slags. The layer thickness increases with time due to the continuous dissolution of glass from slags. But, it does not change significantly with different particle sizes. The predictions also show a good agreement with the measurement in the experiment, in which the activator NaOH solution is used. The presence of activators in AAS paste is simulated by introducing the corresponding ions (for example, Na⁺ and OH⁻ ions for NaOH solution) with the planned concentrations in the starting pore solution. Parts of these ions are incorporated into the solid products. The change of the pore solution composition is predicted with the methods presented in Chen and Brouwers [41].

For the particles with different sizes, although they have the same hydrated layer thickness, the amount of hydrated slag is different due to the different size. The hydration degree of slag particles as a function of curing time is shown in Fig. 9b. One can see that slag particles with different sizes have significantly different hydration degree at the same curing age. The hydration degree for finer particles (from fine to coarse ones, A, B, C, D, E) is larger. The finest particle (A) has a hydration degree approximately three times higher than the coarsest particle (E). A simple calculation using the same hydrated layer thickness yields the same value. The difference in the hydration degree illustrates how the finer particles achieve higher hydration degrees.

Hydration degree of slag in cement

Since the computer can predict the layer thickness and the hydration degree of single particle quite well, it can be used to predict the overall hydration degree of slag in the
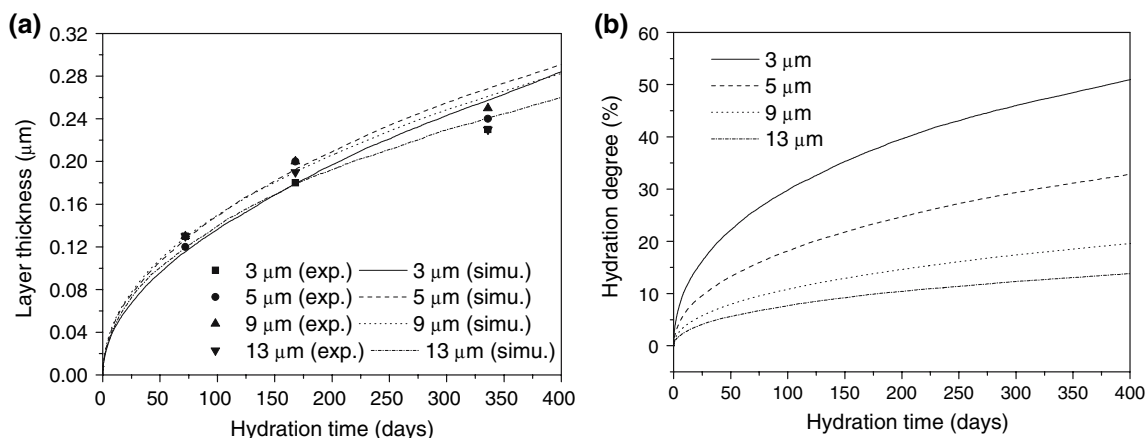

Fig. 9 Hydrated layer thickness and hydration degree of slag particles, (**a**) predicted hydrated layer thickness and measurements by Sato et al. [30], (**b**) predicted hydration degree. $T = 20$ °C, $B = 4.2 \times 10^{-3}$ h/cycle², $\beta' = 0.25$

hydrating cement. The influences of slag proportion in the cement and w/c ratio on the slag hydration degree are investigated in this section.

The slag cements used by Battagin [43] are used for the simulation. Battagin [43] used a selective dissolution method with EDTA solution to determine the hydration degree of slag in the laboratory-made cements. Slag cements with 35, 50 and 70 m/m% slag proportions are selected for comparison. The compressive strength of mortar samples and degree of slag hydration are measured. The compositions of used cement (namely PC II) and slag (namely Slag III) are listed in Table 1, respectively. The PSD of the slag and Portland cement is not given in the literature, and is taken to be the same as those of the slag and Portland cement tested in the research project of Chen [12]. The simulations are carried out with a w/c ratio of 0.48 at 23 °C, as also used in the experiment. The value of β' is set again to be 0.25. The fitted value of B is 4.5×10^{-3} h/cycle^2. The degrees of slag hydration are shown together with the degrees measured in the experiments in Fig. 10a.

It can be seen that the hydration degrees of slag in the hydrating slag cement are well predicted. For the slag proportions tested in the experiment, their influence on the hydration degree is shown to be minor, which is again in good accordance with the experimental observations. The minor influence of slag proportions in cement on its hydration degree is also observed in other studies [44, 45].

Simulations on the hydration of slag cement pastes with different w/c ratios are carried out as well. The slag cement in the study of Battagin [43] with 50 m/m% slag is used. The simulation results are shown in Fig. 10b. One can see that the hydration degrees with relatively larger w/c ratio (0.48 and 0.60) are obviously higher than the degree with a smaller w/c ratio (0.30). Therefore, larger w/c ratios are favorable for achieving higher slag hydration degrees. This is reasonable because for pastes with larger w/c ratios, there is more water and space available for the reaction and growth of products. At a paste level, there is also more water available for the hydration of cement. In the sealed state, as the hydration is largely dependent on the amount of water available, the larger w/c ratios enhance the glass hydration. With regard to the model, there is a larger chance for the dissolution of glass pixels because more of them are in contact with pores.

However, this "expedition effect" diminishes with increasing w/c ratios, according well with the experimental observations by Battagin [43]. The difference between the hydration degrees with a w/c ratio of 0.48 and 0.60 is already quite small.

The attenuation of the expedition effect is explained as following: If the w/c ratio is low, the pastes will gradually be densified; hence, all the capillary pores is filled with products. Then, the hydration is impeded due to the limit of space for the growth of products. As pointed out by Chen and Brouwers [10], for the AAS paste, if the water/slag ratio is lower than approximately 0.40, achieving a complete hydration of slag is difficult because of the limit of space. This limiting effect also applies to the slag cement. However, if the w/c ratio keeps increasing, the hydration of slag particles becomes more dissolution-controlled, which means the possibility of dissolution governs the hydration degree. As the possibility of dissolution depends on the reactivity of slag, the chemical composition of pore solution and the chances of being attacked (in contact with water), the limit of space for product growth no longer determines the slag hydration degree. Therefore, for pastes with large w/c ratios, the hydration degree of slag does not vary significantly.
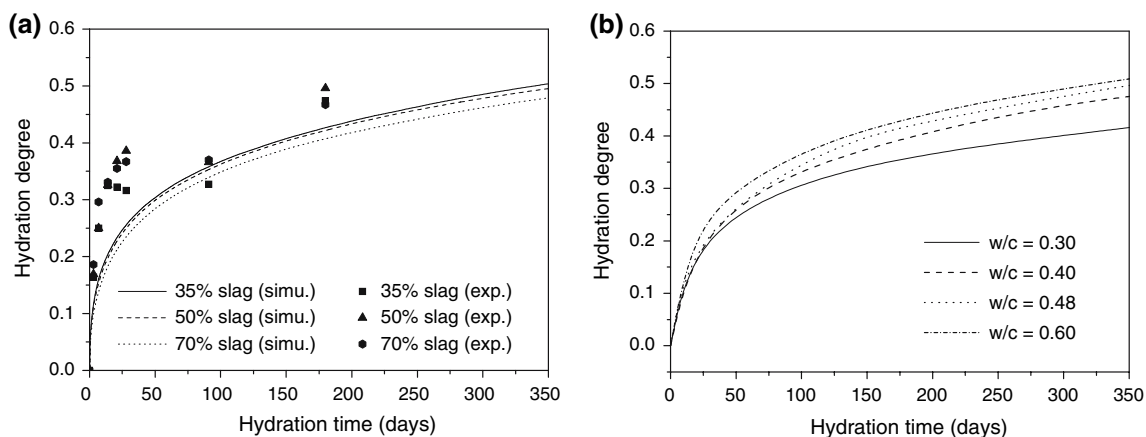

Fig. 10 Hydration degree of slag in slag cement: Effect of (**a**) slag proportion and (**b**) w/c ratio. $T = 23$ °C, $B = 4.5 \times 10^{-3}$ h/cycle^2, $\beta' = 0.25$. Measurements in (**a**) are taken from Battagin [43]

CH content in the paste

DTA combined with TGA can be used to quantify the various phases in cement paste. It is shown to be an accurate and reliable technique to determine the amount of CH in slag cement paste [46]. The interaction between the CH produced by the clinker hydration and the slag hydration is of primary interest for investigating slag cement hydration, and is also predicted with the computer model. Again the slag-blended cement from the study of Battagin [43] is used (PC II and Slag III in Table 1). The simulation is carried out with the same conditions as used for Fig. 10. Different slag proportions as 0, 35, 50, 65 and 90 m/m% are used. The amount of CH in the paste is plotted in Fig. 11b versus the curing time in g per 100 g original cement.

One can see from Fig. 11a that the CH content in the slag cement paste is clearly lower than the level in Portland cement paste. It decreases with increasing slag proportions in the cement and increases rapidly at early ages due to the fast hydration of clinker phases, following by approximately constant values at later age. The trend of the increase and the values are in good agreement with the measurements by Kondo and Ohsawa [47] and Hinrichs and Odler [44]. They found that the level of CH is obviously lower in slag cement paste than in Portland cement paste, and is lowered with increasing slag proportions. While the contents in Portland cement pastes keep increasing during the curing ages, the contents in the slag cement pastes remains almost constant after 7 days of curing. For some slag cement pastes, it decreases slightly with increasing time. It is clear that replacing Portland cement with slag reduces the CH level in the paste, and with increasing proportions the level is reduced.

Composition of the hydration product C–S–H

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 replacing Portland cement with slag clearly decreases the C/S ratio in C–S–H [7, 48–50]. Increasing the slag proportions in the slag cement decreases the C/S ratio in C–S–H.

The composition of C–S–H is predicted with the computer model and is compared with the experimental results by Richardson and Groves [7]. Both the C/S and A/S ratios are measured in the experiments at different ages. The predicted and measured average C/S ratios are plotted in Fig. 12a, and the average A/S ratios in Fig. 12b.

During the simulation, the C/S and A/S ratios in each hydration cycle are calculated according to the numbers of dissolved clinker and glass pixels. Since at each cycle the numbers are different from numbers in the other cycles, the C/S and A/S ratios actually fluctuate in a certain range. This gives some local variations in the composition of C–S–H, which is also observed in the experiments. The model outputs are the average compositions of C–S–H calculated at each cycle and in time.

One can see that both the trend and values of the compositions are well predicted with the model considering the scatter in the measurement. At early hydration stages, the C/S ratios are slightly lower than the later ages because more clinker phases dissolve at this moment. As the consequence, more CH is available for the hydration of slag. As a whole, the composition of C–S–H changes only slightly with curing time.
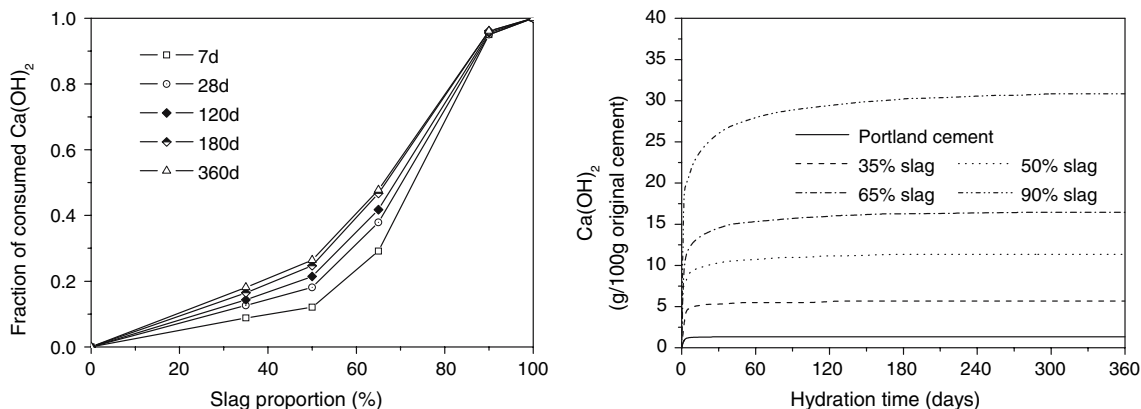

Fig. 11 Simulated CH consumption by the slag reaction, predicted with the recipe from Battagin [43] (PC II and Slag III in Table 1). $T = 20\ °C$, $B = 4.5 \times 10^{-3}$ h/cycle^2, $\beta' = 0.25$
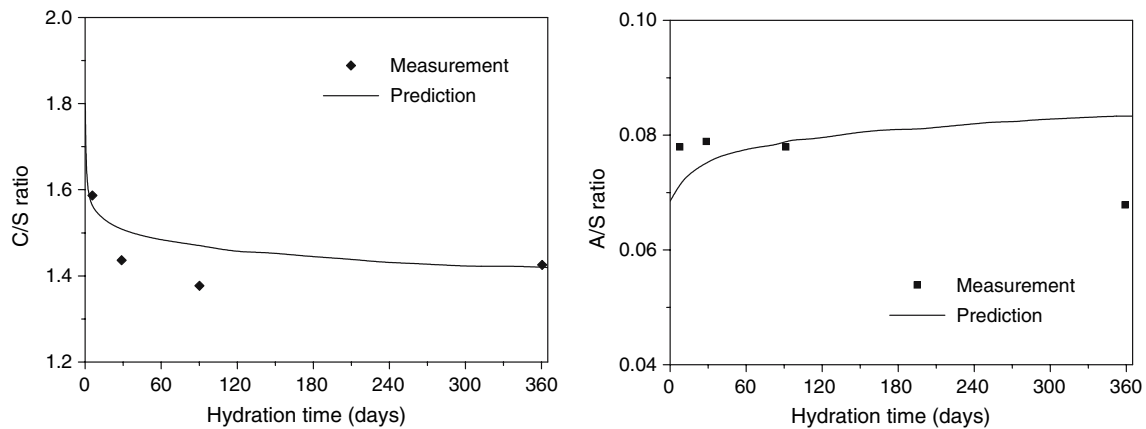
Fig. 12 Predicted and measured composition of C–S–H as a function of hydration time, experimental data taken from Richardson and Groves [7]. $T = 20\ °C$, $B = 3.5 \times 10^{-3}$ h/cycle^2, $\beta' = 0.25$

Conclusions

In this study, a newly developed version of a 3-D computer model CEMHYD3D, which was originally developed for modeling the Portland cement hydration, is addressed. The model is extended for simulating the hydration and microstructure development of slag cement paste. The theoretical models proposed by Chen and Brouwers [10, 11] used and incorporated into the computer model, with special considerations on the reactivity of slag. A few most relevant factors on the slag reactivity are discussed, such as the oxide composition, geometrical characteristics, pH value of pore solution and temperature. Methods are proposed to account for these factors in the simulation process. The model predictions are validated with measurements in experiments, and the model is further used to investigate a few properties of hydrating slag cement paste, for example, the CH content in the paste, effect of particle size on the slag hydration, hydration degree of slag, and composition of the C–S–H. It is found that the reactivity of slag highly depends on the alkalinity of the pore solution it is in contact with. There seems to be a linear relationship between the pH value of the solution and the reaction rate of slag particles (pH > 9). The NBO/T value of the glass in slag is a good indicator for the reactivity of slag in regard to its oxide composition.

The simulation results show that the extended model is able to simulate the hydration process of slag cement paste in an accurate way and can be used to predict various properties of the hydrating paste. It appears that for all simulated slag cements, the time constant B is about 4×10^{-3} h/cycle^2, also found for Portland cement [13], and that $\beta' = 0.25$ seems to be valid for all slags. This indicates that the model among others accounts correctly for w/c, fineness, slag composition, pore water composition, slag reactivity etc. Another remarkable characteristic of the phase composition of hydrating slag cement paste is the low content of CH. The volume fraction of CH in the paste is almost constant after 4 weeks of hydration. The thickness of the hydrated layer of the slag particle is not significantly influenced by its particle size. The hydration degree of slag is not obviously affected by the slag proportions up to approximately 70 m/m%. But, with a higher w/c ratio, the hydration of slag particle is obviously enhanced. The composition of the major hydration product, C–S–H, is also well predicted with the present model.

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