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Enhanced Model and Simulation of Hydration Process of Blast Furnace Slag in Blended Cement

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Abstract

A hydration model for cementitious materials was applied to slag blended cement. The original model was found to overestimate the hydration degree of slag, and the influence of the slag ratio on the hydration degree not to be well simulated either. The hydration mechanism of slag was investigated, considering the role of calcium hydroxide as activator and the Ca/Si ratio of C-S-H. It is assumed that for low Ca/Si ratio, the C-S-H inner product has a stronger resistance against ion diffusion and thus influences the hydration process significantly. Accordingly an enhanced model for slag hydration is proposed. Finally, the enhanced model is verified by both hydration degree and heat generation tests.

1. Introduction

In Japan blast furnace slag (BFS) is widely used in the cement and concrete industry. As a by-product during steel manufacture, it is broadly agreed that concrete made with slag blended cement has many advantages, including better chloride resistance, lower permeability and higher strength at later age. From the viewpoint of circular economy and sustainable development, blast furnace slag is a promising mineral admixture in the concrete industry. However, some disadvantages are also reported, such as larger drying and autogenous shrinkage, which tend to induce early age cracks and decrease the durability of structures. Beside, BFS concrete is more sensitive to the curing conditions. Insufficient water supply during curing may retard the hydration process and cause a significant decrease in the long-time properties. Therefore, for the purpose of promoting the efficient application of blast furnace slag, it is of great necessity to investigate the properties of BFS blended cement.

Hydration is a process that represents the reaction and mass conversion of cement, and therefore the percentage of hydrated cementitious materials is closely tied to microstructure development and affects other properties. Slag blended in Portland cement has a more complicated hydration mechanism, since slag is a latent hydraulic material and the reactivity is significantly influenced by calcium hydroxide (CH), which acts as activator. Meas-

urement of heat generation, such as the adiabatic temperature rise test, is usually used to assess the hydration status. However, because it is difficult to separate the heat released by slag accurately, this method is not capable of evaluating the reaction of the slag separately. On the other hand, several test methods have been developed for quantitatively analyzing the hydration degree of slag separately, such as selective dissolution (Kondo and Ohsawa 1969; Luke and Glasser 1987; Lumley *et al.* 1996; Demoulian *et al.* 1980; Battagin 1992; Escalante *et al.* 2001), XRD (Kondo *et al.* 1975; Hoshino *et al.* 2006), Differential Scanning Calorimetry (DSC) (Totani *et al.* 1980; Imoto *et al.* 2006) and image analysis (Feng *et al.* 2004; Kurumisawa *et al.* 2007). Thanks to advances in techniques, test methods are becoming more accurate and reveal the hydration process and reactivity of slag. For instance, Luke and Glasser (1987) modified the EDTA dissolution and studied pastes with 30% slag ratio until 12 months. They reported that within 1 month around 40% of the slag reacted while the hydration degree was up to 60% after 12 months. Lumley *et al.* (1996) studied the effects of the water-to-cementitious material (herein refer to both cement and slag, and is simplified as w/b, i.e. water-to-binder) ratio and slag ratio, and they indicated that 30-55% of the slag hydrated in 28 days and 45-75% in 1-2 years. They also found that as the w/b ratio decreased or the slag ratio increased, the hydration degree decreased, and the slag type also influenced the reactivity. Escalante *et al.* (2001) also reported that the reactivity of slag decreased with the w/b ratio or with increases of the slag ratio. They pointed out also that the hydration degree increases with the temperature, and the values after 6 months were 20-50% in the range of 10-30°C. In Japan, Iyoda and Dan (2007) and Sakai *et al.* (2004) also confirmed that the hydration degree depends on the slag ratio, and that for a long time most of the values remain much lower than 100%. Based on the above reviews, the following characteristics of slag hydration can be identified: for long time curing, the hydration is still far from completed even if sufficient water

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supplied. Most of the data show that the hydration degree is less than 60% and a large proportion of slag remains unhydrated. Moreover, the slag ratio influences hydration significantly and a higher ratio induces lower hydration.

Several models have been proposed to simulate the hydration of slag cement. In this paper, a multi-component hydration heat model developed by Kishi (1994, 1995, 1996, 1997) and Maekawa *et al.* (2008) is investigated. In this model, hydration and heat generation of components in cement including clinkers such as C_3S , C_2S , C_3A , C_4AF , and mineral admixtures such as fly ash and blast furnace slag are treated respectively by the Arrhenius law of chemical reaction and then integrated together. This model has been verified by adiabatic temperature rise tests for both Portland cement and slag blended cement concrete. On the other hand, verification of the hydration degree of slag has not been carried out, because of the scarcity of reliable data when the model was established. Based on the above reviews of the hydration degree, recent test methods have become more accurate and some common characteristics are found. Therefore, in order to further expand the application of the multi-component hydration heat model, it is necessary to investigate its applicability on prediction of hydration degree. Before describing this investigation, the simulation of slag hydration in the multi-component hydration heat model is introduced briefly first.

2. Simulation of slag hydration (Kishi and Maekawa 1996, 1997)

A reference heat rate that represents the heat generation process under isothermal condition (293 K) is first assumed for slag. Taking into account various factors such as temperature, available free water, CH content and slag fineness, the hydration heat rate under real condition is computed following the equation:

$$H_{sg} = \min(\beta_{sg}, \lambda_{sg}) \cdot H_{sg, T_0}(Q_{sg}) \exp \left\{ -\frac{E_{sg}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\} \quad (1)$$

where H_{sg} is the hydration heat rate under real condition, H_{sg, T_0} is the reference heat rate at 293 K, Q_{sg} is the accumulated heat during hydration, E_{sg} is the activation energy of slag, R is the gas constant, T_0 is the reference temperature (293 K), and T is the real temperature. β_{sg} is the coefficient considering the effect of available free water, and λ_{sg} is the coefficient expressing hydration stagnation due to CH insufficiency.

The hydration degree is computed by the following equation:

$$\alpha_{sg} = \frac{Q_{sg}}{Q_{sg, \infty}} \quad (2)$$

where α_{sg} is the hydration degree of slag and $Q_{sg, \infty}$ is the

ultimate heat in the case of complete hydration of the slag. For per unit weight of slag, the value of $Q_{sg, \infty}$, i.e. the specific heat, is assumed as 525.0 kJ/kg.

In Eq. 1, except for temperature effect, β_{sg} and λ_{sg} are the other two factors that noticeably affect the hydration process. The coefficient considering the effect of available free water, β_{sg} , is obtained by the following equation:

$$\beta_{sg} = 1 - \exp \left\{ -r \left\{ \left(\frac{\omega_{free}}{100 \cdot \eta_{sg}} \right) / s_{sg}^2 \right\}^s \right\} \quad (3)$$

where η_{sg} represents the normalized cluster thickness of inner product, ω_{free} is the free water percentage. Physical water existing in micro-pores sustains continued hydration and serves as space which hydrates precipitate. This portion of water is regarded as free water. Lack of free water would induce the stagnation of later hydration, e.g. low water-cement ratio concrete. s_{sg} is the normalized Blaine value of blast furnace, and r and s are material constants. The following equation is given for η_{sg} :

$$\eta_{sg} = 1 - \left(\frac{Q_{sg}}{Q_{sg, \infty}} \right)^{\frac{1}{3}} \quad (4)$$

For ω_{free} , under sealed conditions, this equation can be simplified as follows:

$$\omega_{free} = \frac{W_{total} - \sum W_i}{C} \quad (5)$$

where W_{total} is the initial water weight, W_i is the water consumed by various components in the cementitious binder, and C is the unit cement weight in the paste.

The coefficient expressing hydration stagnation due to CH insufficiency, λ_{sg} , is calculated by:

$$\lambda_{sg} = 1 - \exp \left\{ -2.0 \left(\frac{F_{CH}}{R_{SGCH}} \right)^{1.5} \right\} \quad (6)$$

where F_{CH} is the CH content in the paste, and R_{SGCH} is the amount of CH required for fully hydration of slag at the next time interval.

3. Investigation on applicability of the model to slag

3.1 Simulation of hydration degree of slag and CH content

Data of several tests from other researchers were collected and corresponding simulations based on Eq. 2 were conducted. All the tests were carried out with only slag blended in Portland cement. Cement pastes were cured under normal temperature with sufficient water supply. The experiment details are shown in Table 1. Comparison between experiment and analysis are illustrated in Fig. 1, which shows that differences exist. For

Table 1 Details of hydration degree tests.

No.	Researcher	Slag ratio	w/b	Blaine value	Curing temperature	Test method
a	Iyoda and Dan (2007)	20%, 42%, 67%	0.5	4760	20°C	Selective dissolution
b	Sakai <i>et al.</i> (2004)	20%, 50%	0.5	4200	20°C	Selective dissolution
c	Takamatsu and Maruyama (2009)	30%, 45%	0.4	4050	20°C	Selective dissolution
d	Sagawa and Nawa (2006a)	50%	0.5, 0.4, 0.3	4000	20°C	XRD-Rietveld
e	Sagawa <i>et al.</i> (2010)	45%	0.5	4000 6000	20°C	XRD-Rietveld
f	Lumley <i>et al.</i> (1996)	30%, 50%, 60%	0.4	4510	20°C	Selective dissolution
g	Lumley <i>et al.</i> (1996)	30%	0.4, 0.6	4510	20°C	Selective dissolution
h	Lumley <i>et al.</i> (1996)	60%	0.4, 0.6	4510	20°C	Selective dissolution

most cases, the analysis value appears higher than the test data, which implies that the hydration degree may be overestimated to a certain extent. Moreover, the relationship of the hydration and slag ratio seems hardly obvious in analysis. When the slag ratio is less than 50%, there appears to be no difference between analytical curves. Only when the slag ratio is as high as 67% in **Fig. 1-(a)** do the hydration curves reduce after around 20 days.

Figure 2 represents the CH content measured by the TG-DTA method in test-(a) in **Table 1** and the analysis. For both the analysis and experiment, the amount of CH declines as the slag ratio increases. However, it seems that when the slag ratio is 67%, the analytical result is underestimated. CH is completely consumed and the value stays zero after 15 days, while the experiment indicates that some CH always remains. Kwak *et al.* (2004) also reported that even for a high slag ratio of 70%, CH in the paste is detectable at a later age. Therefore, it can be deduced that analysis may overrate consumption of CH for a high slag ratio, causing remaining CH to be underestimated. Combined with the analysis in **Fig. 1**, some correlation seems to exist. If the hydration degree is suitably reduced, CH consumption is reduced and a better result in terms of CH content can be expected.

Hence, the authors presume that current model has some limitations. As described in Section 1, the model was verified by the adiabatic temperature rise test, and the heat generation was found to be well simulated and the temperature history of concrete to be traced properly. On the other hand, it is probable that for slag, the model has some limitations with regard to the hydration degree. As these limitations may hinder further simulation such as pore structure development, the authors assume that appropriate modifications of the model are called for. This must be preceded by an investigation of the major

factors that may affect hydration in the current model. Only after a clear understanding of the working mechanism of these factors and the causes of the discrepancies is gained can modifications be conducted.

3.2 Key parameter tracing in the model

As presented in Section 2, in the current model, two factors may noticeably affect the hydration process, i.e. β_{sg} and λ_{sg} . Case (a) in **Table 1** is selected, and the values of β_{sg} , λ_{sg} and $\min(\beta_{sg}, \lambda_{sg})$ are output and illustrated in **Fig. 3** according to Eq. 3 and Eq. 6. Their effects on the hydration rate can be clearly grasped. For low ratios such as 20% and 42%, β_{sg} dominates the hydration process, while for 67% the alleviative effect at later age is attributed to λ_{sg} . The development of $\min(\beta_{sg}, \lambda_{sg})$ is consistent with the analytical results in **Fig. 1-(a)**.

Next, the discussion focuses on the influence of CH. λ_{sg} affects hydration only when the slag ratio is 67%, because the analytical result of CH amount in **Fig. 2** is almost zero. However, the test result indicates that some amount of CH always exists, while the hydration process is still reduced. In other words, the fact is that even though sufficient CH remains, the hydration rate may still be influenced significantly. Thus it appears that the current approach does not adequately describe this phenomenon.

3.3 Discussion of hydration mechanism of slag blended in cement

It is well agreed that the principle hydrates of slag are C-S-H gels. Compared with Portland cement, researchers found that as the slag ratio increases, C-S-H gels produced by slag show a lower Ca/Si ratio (Harrison *et al.* 1987; Shi *et al.* 1992; Richardson and Groves 1992; Gollop and Taylor 1992, 1996), as illustrated in **Fig. 4**. The physical properties of C-S-H may vary due to the reduced Ca/Si ratio. Richardson *et al.* (1994, 2004) re

Fig. 1 Comparison of hydration degree based on original model.

ported that in the case of a high Ca/Si ratio, C-S-H has a fibrillar-like morphology, while in the case of a low Ca/Si ratio, the morphology tends to be of the crumpled foil type. This implies a transition of hydrates from essentially one-dimensional growth to two-dimensional growth, resulting in higher tortuosity and specific surface area in micro-pores. Moreover, the electrical charges on the surface of hydrates are influenced by the Ca/Si ratio. The surface of hydrates from Portland cement is usually positively charged (Elakneswaran *et al.* 2009; Glasser 1992; Nakarai *et al.* 2006). According to the research from Glasser (1992), as the Ca/Si ratio declines, the electric charges become less positive, and when the Ca/Si ratio is lower than 1.2-1.3, the surface charge of C-S-H reverses to negative, and C-S-H tend to bind alkali cations. Studies on the pore solution (Bhatty and Greening 1978; Chatterji 1979; Hong and Glasser 1999; Shehata and Thomas 2006) indicated that the available alkali concentration decreases as the slag ratio increases or the Ca/Si ratio decreases, which also supports the reversal of surface charge and ion binding capacity of C-S-H.

Herein the hydration scheme of slag is discussed according to the basic information of activation (Tanaka *et al.* 1983; Taylor 1990). At the starting stage, due to the activation by Ca^{2+} , the protective film on the surface of the slag particle is destroyed. The internal structure, which is an anionic network composed of O, Si and other elements, starts to decompose, and silicate ions such as $\text{Si}(\text{OH})_4$ are released into the solution. When silicate ions contact Ca^{2+} , a reaction occurs and hydrates start to precipitate. Like in the case of Portland cement, hydrates from slag can be divided into two categories, i.e. the inner product and the outer product. The inner product consists of hydrates generated inside the radius of the original particle and closely bond around an unhydrated core, while the outer product precipitates outside the range of the original particle and fills in capillary pores. In order to sustain hydration, it is necessary for silicate ions released from slag to diffuse outside the inner product, or alkali cations to diffuse inside. The inner product may show resistance against ion diffusion, i.e. as hydration goes on and the thickness of the inner product increases, the diffusivity of ions through the inner product becomes lower. Accordingly, the reaction becomes slower or even stagnates. Therefore, the thickness of the inner product is a crucial factor that dominates the hydration rate of slag.

As discussed above, the Ca/Si ratio of hydrates is reduced with increases in the slag ratio, and the physical properties of C-S-H may vary accordingly. Hence, when we discuss the resistance effect of the inner product, not only its thickness but also the various other physical properties have to be taken into account. In this study, the authors assume that the physical properties of C-S-H influence the hydration process from two aspects. First, since C-S-H with a lower Ca/Si ratio has a morphology that is foil-like rather than fibrillar, the tortuosity of gel

Fig. 2 Comparison of CH content based on original model.

Fig. 3 Parameter tracing.

Fig. 4 Ca/Si ratio of C-S-H with various slag ratios.

pores becomes higher. This implies more twists and forks in pores, resulting in a much longer path for ions to diffuse through the inner product. The other factor may be the alternated electric charge on the surface of C-S-H. As indicated by Elakneswaran *et al.* (2009), pores with a diameter of less than 10 nm show the electrical double layer (EDL) effect. The inner product contains mainly gel pores and a large proportion of gel pores have a diameter smaller than 10 nm, and thus the EDL effect of the inner product is obvious. In the case of C-S-H with a high Ca/Si ratio, the surface is positively charged. The repelling effect of the positive charge layer restrains the movement of Ca^{2+} towards the inner product. The principal ion movement is that of silicate ions that are released through the inner product. When the electric charges become less positive or even negative due to the lower Ca/Si ratio, the principal ion movement may change. Due to the absorbing effect, more Ca^{2+} ions

move toward the inner product and react with silicate ions near it. The reverse ion movement implies that denser inner product having stronger resistance against ion diffusion is formed. Further ion diffusion may be blocked and the hydration rate afterwards is reduced significantly. The above discussion about the relationship between the hydration of the slag and inner product is illustrated in Fig. 5. Accordingly, the authors conclude that for a lower Ca/Si ratio due to both higher tortuosity and reversed electric charge, the inner product layer shows higher resistance to ion movement. This may be the main reason that the hydration degree decreases as the slag ratio increases.

4. Enhanced hydration model for blast furnace slag

4.1 Modification on hydration rate

From the discussion in Section 3.3, it can be seen that the hydration process is closely associated with the inner product because of its resistance to ion movement. This resistance depends on both the thickness and intrinsic properties of C-S-H. In the original model, although the thickness of the inner product is included in Eq. 3, it provides constant evaluation for various slag ratios. In other words, the various intrinsic properties of C-S-H due to the Ca/Si ratio are not taken into account. On the other hand, coefficient λ_{sg} , which represents the inefficiency of CH, seems unnecessary because it has been proved that a sufficient amount of CH exists in the paste even for high slag ratios as described in Section 3.2.

Hence in the modification λ_{sg} is not utilized and all factors are integrated into coefficient β_{sg} . Since the hydration degree is related to the w/b ratio and slag fineness,

Fig. 5 Influence of inner product on ion movement and hydration of slag.

those factors in Eq. 3, i.e. ω_{free} and s_{sg} , need to be reserved. Moreover, the most important issue is how to simulate the effect of the inner product. When the thickness of inner product is zero, i.e. the starting of hydration, no resistance from the inner product exists. As the thickness of the inner product increases, the hydration rate should decrease. Furthermore, as explained in Section 3.3, for a lower Ca/Si ratio, the inner product shows stronger resistance towards ion movement, so the effect needs to be more significant. Therefore, an available approach is to establish an influential coefficient which includes the thickness of inner product as the principal variable and meanwhile reflects the effect of Ca/Si ratio. According to Fig. 4, the Ca/Si ratio of C-S-H shows a clear correlation with the slag ratio, and thus the slag ratio seems a proper index of the influence of the Ca/Si ratio. For the inner product, as it becomes thicker, the ion diffusion is strongly resisted so the hydration rate decreases sharply rather than gradually. The exponential formula seems appropriate to describe the significant relationship between inner product thickness and the resistance effect. Therefore, the effect of the inner product is proposed by a new coefficient χ , defined as follows:

$$\chi = \exp(-a \cdot \eta_{sg}^b) \quad (7)$$

where η_{sg} is the thickness of the inner product, which has the same definition in Eq. 4. a and b are intrinsic parameters that are the functions of the slag ratio, given by:

$$\begin{aligned} a &= 19.0 - 20.0 \cdot p_{sg} \\ b &= 2.2 - 3.0 \cdot p_{sg} \end{aligned} \quad (8)$$

In Eq. 8, p_{sg} is the slag ratio. Therefore, the value development of χ depends on the slag ratio. Herein Eq. 8 is not directly derived from experiment. Instead, it is empirically proposed to alter the hydration heat. On the other hand, the basis of Eq. 8 is the intrinsic properties of C-S-H which depends on the Ca/Si ratio and its influence on ion movement. In other words for Eq. 8 the physical meaning relating to microscopic mechanism of hydration exists. Figure 6 plots the curves of χ versus η_{sg} when the slag ratio changes from 20% to 70%. All the functions decrease as the thickness of the inner product increases, which implicitly represents the resistance by the inner product to ion diffusion. Besides, for a higher slag ratio, the function decreases more sharply from the beginning. This has clear physical meaning that the C-S-H inner product has a stronger retardation effect on ion movement the lower the Ca/Si ratio. When χ is integrated into β_{sg} , it is applicable to the simulation of the development of the hydration degree for various slag ratios.

Accordingly, in the enhanced model, the new expression for β_{sg} is given by:

$$\beta_{sg} = \left\{ 1 - \exp \left\{ -r \cdot \left\{ \left(\frac{\omega_{free}}{20.0} \right) / s_{sg}^2 \right\}^s \right\} \right\} \cdot \chi \quad (9)$$

Fig. 6 function χ versus η_{sg} .

where ω_{free} , s_{sg} are defined as in Eq. 3, and r and s are also the same material constants.

In Eq. 9, χ is integrated into β_{sg} . The effects of the available free water and slag fineness are reserved by ω_{free} and s_{sg} . Unlike the original model, the thickness of the inner product, η_{sg} , is extracted and included in χ . This means that the inner product has an independent effect on the hydration rate from the available free water or slag fineness. For instance, even if sufficient water is provided such as a high w/b ratio, later hydration may still tend to stagnate. Therefore, this separate treatment substantially corresponds to the mechanism of hydration.

4.2 Verification by hydration degree of slag and CH content

The enhanced model is verified by experiments in Table 1, and the results are illustrated in Fig. 7. For most cases, the analytical results are much improved, showing the dependence of the hydration process on the slag ratio. For different w/b ratios, the enhanced model can also give better results, except the slag ratio 20% in case (a) in Table 1, for which neither the analyses before and after modification provide good agreement with the experiment, since the test data is even higher than 90%. For other cases, because hydration degrees are largely decreased in the enhanced model, the values become much closer to the test data especially at early age. For long period such as after 91d, the analysis is slightly deviating from the test data. This is because that the hydration rate in the analysis is not completely zero. On the other hand, some tests such as case (a) show that hydration completely stagnates around 91d, while in case (g) the hydration can gradually proceed until quite long period. More accurate measurement and simulation until quite long time need to be conducted in the future research. In any case, comprehensively speaking the simulation of slag hydration is greatly improved. Moreover, besides the factors that are taken into account in the model, the hydration degree of slag is also influenced by other factors, such as the chemical composition or glass content of the slag. For those factors which are not included in the model, their influences on the hydration degree should be

Fig. 7 Comparison of hydration degree based on enhanced model.

studied in the future to allow more precise prediction. Besides the hydration degree, the analysis for CH content for case (a) in **Table 1** is shown in **Fig. 8**. The enhanced model provides much better simulation. Even for a high slag ratio of up to almost 70%, CH is still not completely consumed, which is simulated well by the enhanced model.

The tests adopted in **Table 1** are all under the reference temperature (293 K). If the curing temperature increases, a higher hydration degree of slag will be obtained (Escalante *et al.* 2001). In the original model, this effect is included in Eq. 1 and it still remains after modification of the model. Therefore in order to expand the applicability of the modified model, the hydration degrees of slag under various curing temperatures are also analyzed. The results are compared with test data from Sagawa and Nawa (2006b). In the research, 40% of the Portland cement is replaced by slag and the cement pastes are cured in water with temperatures of 5°C, 20°C and 40°C. The w/b ratio is 0.5. The hydration degrees of slag are measured by the XRD-Rietveld method. The analysis based on original and enhanced model, and their comparison with analysis are given in **Fig. 9**. Similar with cases under normal temperature shown in **Fig. 1** and **Fig.**

7, the original model highly overestimates the hydration degree of slag, while the analysis based on enhanced model is consistent with the test data. This means that the modified model is applicable to various temperature ranges.

4.3 Modification of reference heat rate of slag

Based on the modification in Section 4.1, it is probable that not only the hydration degree but also heat generation are influenced. This is easy to understand, as in the modified model, hydration degrees are greatly reduced, but the specific heat of slag $Q_{sg,\infty}$ in Eq. 2 still remains 525.0 kJ/kg, which implies that total heat generation is reduced. Therefore in order to ensure the predictability of heat generation, the authors considered modifying the value of specific heat. Few test data on the specific heat of slag are available in the literature. Goto *et al.* (2006, 2009) synthesized slag-simulated glasses in the system of CaO-Al₂O₃-SiO₂ and measured heat generation during hydration. They proposed that the specific heat of slag is 571.2 kJ/kg. Referring to this data, the authors assume that in the enhanced model, the value of $Q_{sg,\infty}$ is 630.0 kJ/kg, which is 1.2 times the value in the original model. This value is not far from Goto's test considering the difference between real and synthesized slags. Meanwhile with the increased value, effective compensation for the heat generation can be obtained. The new function of the reference heat rate is also increased by multiplying both the original reference heat rate with the constant value of 1.2, as illustrated in **Fig. 10**. Direct verification by test curve from slag is unavailable, since it is difficult to accurately separate the heat of the slag from that of the total blended cement. Herein, the authors decide to compare total heat generation of Portland cement blended with slag under isothermal condition. Gruyaert *et al.* (2010) measured the total heat generation of BFS cement by isothermal calorimetry with various slag ratios. The w/b ratio is 0.50 and the isothermal conditions are 10°C, 20°C and 35°C. In this study, corresponding analysis by the modified model were carried out and compared with their measurement as shown in **Fig. 11**. For slag ratio 0%, i.e. OPC, the

Fig. 8 Comparison of CH content based on enhanced model.

(a) Original model

(b) Enhanced model

Fig. 9 Hydration degree under various temperatures based on the original and enhanced models.

Table 2 Mix proportion of BFS concretes used for verification (Maekawa *et al.* 2008, p.82).

Types	w/b (%)	Unit weight (kg/m ³)				
		Water	Cement	Slag	Sand	Gravel
SG400	39.3	157	240	160	645	1,129
SG300	49.3	148	180	120	757	1,129
SG200	78.5	157	120	80	854	1,089

analysis follows Kishi's original model. Its agreement with the test data suggests that the disturbance from the Portland cement part in blended cement can be neglected. Furthermore, when we turn to the BFS cases, for all the isotherm condition and slag ratios, both the process and final heat can be well traced. Therefore, it can be concluded that the modification of the specific heat and referent heat rate of slag is reasonable. Herein it has to be pointed out that although the enhanced model is supported by the heat generation test, the specific heat value 630.0 kJ/kg adopted in the model is not directly verified due to the scarcity of test data available. Measurement of the specific heat of slag should be carried out in future research.

Finally, as mentioned in Section 1, the original model was verified by the adiabatic temperature rise test of BFS concrete. In order to remain consistent with the original model, the adiabatic temperature rise adopted in the original verification is analyzed again with the modified model. The mix proportions of BFS concrete are shown in **Table 2**, and comparison of results is shown in **Fig. 12**. Obviously, with increased specific heat and decreased hydration degree, the modified model provides similar evaluation of adiabatic temperature rise as the original model. Therefore, the modified model can be used not only under isothermal condition but also adiabatic condition.

5. Summary and conclusions

In this study, the hydration process of slag blended in cement is investigated based on the intrinsic properties of the inner product. As the original model appears not to provide proper prediction of the hydration degree, the hydration mechanism of slag is investigated again, considering the influence of CH as activator and the chemo-physical properties of C-S-H in slag hydration. Since the Ca/Si ratio of C-S-H decreases as the slag ratio increases, resulting in both higher tortuosity and changed positive electric charge accumulation in C-S-H, it is assumed that the C-S-H inner product has a strong resistance to ions movement, and therefore the subsequent hydration tends to be retarded. Based on the above assumption, an enhanced model is proposed, taking into

Fig. 10 Reference heat rate of slag before and after modification.

Fig. 11 Comparison of isothermal heat generation based on modified model.

Fig. 12 Adiabatic temperature rises based on original and modified model.

account the resistance effect. Finally, the enhanced model is applied to simulation of slag hydration, and the results indicate good agreement with the experiment data. Moreover, the amount of CH in the paste and heat generation of slag cement can also be simulated accurately.

References

- Battagin, A. F., (1992). "Influence of degree of hydration of slag on slag cement." In: *Proceedings of the 9th International Congress on the Chemistry of Cement*, New Delhi, India, Vol.3, 166-172.
- Bhatty, M. S. Y. and Greening, N., (1978). "Interaction of alkalis with hydrating and hydrated calcium silicates." In: *Proceedings of 4th International Conference on Effects of Alkalis in Cement and Concrete*, Purdue August 1978, 87-112.
- Chatterji, S., (1979). "The role of $\text{Ca}(\text{OH})_2$ in the breakdown of portland cement concrete due to alkali-silica reaction." *Cement and Concrete Research*, 9(2), 185-188.
- Demoulian, E., Gourdin, P., Hawthorn, F. and Vernet, C., (1980). "Influence of slags chemical composition and texture on their hydraulicity." In: *Proceedings of 7th International Congress on the Chemistry of Cement*, Paris. Vol.2, 89-104.
- Elakneswaran, Y., Nawa, T. and Kurumisawa, K., (2009). "Electrokinetic potential of hydrated cement in relation to adsorption of chlorides." *Cement and Concrete Research*, 39(4), 340-344.
- Escalante, J. I., Gomez, L. Y., Johal, K. K., Mendoza, G., Mancha, H. and Mendez, J., (2001). "Reactivity of blast-furnace slag in portland cement blends hydrated under different conditions." *Cement and Concrete Research*, 31(10), 1403-1409.
- Feng, X., Garboczi, E. J., Bentz, D. P., Stutzman, P. E. and Mason, T. O., (2004). "Estimation of the degree of hydration of blended cement pastes by scanning electron microscope point-counting procedure." *Cement and Concrete Research*, 34(10), 1787-1793.
- Glasser, F. P., (1992). "Chemistry of alkali-aggregate reaction." In: R. Swamy, Ed. *The Alkali-Silica Reaction in Concrete*, Van Nostrand Reinhold, New York. 30-53.
- Gollop, R. S. and Taylor, H. F. W., (1992). "Microstructural and microanalytical studies of sulfate attack: I. ordinary Portland cement paste." *Cement and Concrete Research*, 22(6), 1027-1038.
- Gollop, R. S. and Taylor, H. F. W., (1996). "Microstructural and microanalytical studies of sulfate attack: IV. reactions of a slag cement paste with sodium and magnesium sulfate solutions." *Cement and Concrete Research*, 26(7), 1013-1028.
- Goto, S., (2009). "Hydration of hydraulic materials – a discussion on heat liberation and strength development." *Advances in Cement Research*, 21, 113-117.
- Goto, S., Fujimori, H., Hidaka, A. and Ioku, K., (2006). "Effect of components on the rate of heat liberation of hydration in the system of glass/gypsum/lime." *Journal of the European Ceramic Society*, 26, 771-776.
- Gruyaert, E., Robeyst, N. and De Belie, N., (2010). "Study of hydration of Portland cement blended with blast-furnace slag by calorimetry and thermogravimetry." *Journal of Thermal Analysis and Calorimetry*, 102, 941-951.
- Harrison, A. M., Winter, N. B. and Taylor, H. F. W., (1987). "Microstructure and microchemistry of slag cement pastes." In: L. Struble and P. Brown, Eds. *Materials Research Society Symposium Proceedings*,

- Materials Research Society, Pittsburgh. 85, 213-222.
- Hong, S. Y. and Glasser, F. P., (1999). "Alkali binding in cement pastes: Part I. the C-S-H phase." *Cement and Concrete Research*, 29(12), 1893-1903.
- Hoshino, S., Yamada, K. and Hirao, H., (2006). "XRD/Rietveld analysis of the hydration and strength development of slag and limestone blended cement." *Journal of Advanced Concrete Technology*, 4(3), 357-367.
- Imoto, H., Sakai, E., Hukui, R. And Daimon, M., (2006). "Measurement of blast furnace slag content ratio in cement by DSC." In: *Proceedings of the Japan Concrete Institute*. 28(1), 29-34. (In Japanese)
- Iyoda, T. and Dan, Y., (2007). "The Effect of temperature on hydration rate of slag in blended cement." In: *Proceedings of JSCE 333 Committee Symposium*. II59-62. (In Japanese)
- Kishi, T. and Maekawa, K., (1994). "Thermal and mechanical modeling of young concrete based on hydration process of multi-component cement minerals." In: R. Springeschmid, Ed. *Proceedings of the International RILEM Symposium on Thermal Cracking in Concrete at Early Ages*, Munich. 11-18.
- Kishi, T. and Maekawa, K., (1995). "Multi-component model for hydration heat of portland cement." *Journal of Materials, Concrete Structure and Pavements* (JSCE), 29, 97-109. (In Japanese)
- Kishi, T. and Maekawa, K., (1996). "Multi-component model for hydration heat of blended cement with blast slag and fly ash, *Journal of Materials, Concrete Structures and Pavements* (JSCE), 33, 131-143. (In Japanese)
- Kishi, T. and Maekawa, K., (1997). "Multi-component model for hydration heating of blended cement with blast furnace slag and fly ash." *Concrete library of JSCE*, 30, 125-139.
- Kondo, R., Abo-el-enein, S. A. and Daimon, M., (1975). "Kinetics and mechanisms of hydrothermal reaction of granulated blast furnace slag." *Bulletin of the Chemical Society of Japan*, 48(1), 222-226.
- Kondo, R. and Ohsawa, S., (1969). "Studies on a method to determine the amount of granulated blast furnace slag in cement." In: *Proceedings of the 5th International Symposium on the Chemistry of Cement*, Tokyo. IV, 255-262.
- Kurumisawa, K., Nawa, T. and Elakneswaran, Y., (2007). "Study on chloride permeability and microstructure of blast furnace slag blended paste." In: *Proceedings of JSCE 333 Committee Symposium*, II37-40. (In Japanese)
- Kwak, D., Kokubu, K., Lee, C. and Lee, K., (2004). "Influence of replacement ratio on pore structure of concrete with ground granulated blast furnace." In: *Proceedings of JCI*, 26(1), 783-788. (In Japanese)
- Luke, K. and Glasser, F. P., (1987). "Selective dissolution of hydrated blast furnace slag cements." *Cement and Concrete Research* 17(2), 273-282.
- Lumley, J. S., Gollop, R. S., Moir, G. K. and Taylor, H. F. W., (1996). "Degrees of reaction of the slag in some blends with portland cements." *Cement and Concrete Research*, 26(1), 139-151.
- Maekawa, K., Ishida, T. and Kishi, T., (2008). "Multi-scale modeling of structural concrete." London and New York: Taylor & Francis.
- Nakarai, K., Ishida, T. and Maekawa, K., (2006). "Modeling of calcium leaching from cement hydrates coupled with micro-pore formation." *Journal of Advanced Concrete Technology*, 4(3), 395-407.
- Richardson, I. G., (2004). "Tobermorite/jennite and tobermorite/calcium hydroxide-based models for the structure of C-S-H: applicability of hardened pastes of tricalcium silicate, β -dicalcium silicate, portland cement, and blends of portland cement with blast-furnace slag, metakaolin, or silica fume." *Cement and Concrete Research*, 34(9), 1733-1777.
- Richardson, I. G., Brough, A. R., Groves, G. W. and Dobson, C. M., (1994). "The characterization of hardened alkali-activated blast-furnace slag pastes and the nature of the calcium silicate hydrate (C-S-H) phase." *Cement and Concrete Research*, 24(5), 813-829.
- Richardson, I. G. and Groves, G. W., (1992). "Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag." *Journal of Materials Science*, 27, 6204-6212.
- Sagawa, T., Ishida, T., Luan, Y. and Nawa, T., (2010). "Hydrate composition analysis and micro structure characteristics of portland cement-blast furnace slag system." *Journal of JSCE E*, 66(3), 311-324. (In Japanese)
- Sagawa, T. and Nawa, T., (2006a). "Hydration of blast furnace slag cement and effect of water to cement ratio on hydration of blast furnace slag cement." *Cement Science and Concrete Technology*, 60, 82-87. (In Japanese)
- Sagawa, T. and Nawa, T., (2006b). "Quantitative hydration analysis of blast furnace slag cement by Rietveld method." *Cement Research and Technology*, 17, 1-11. (In Japanese)
- Sakai, E., Imoto, H. and Daimon, M., (2004). "Hydration and strength development of blastfurnace slag cement." In: *Proceedings of JCI*, 26(1), 135-140. (In Japanese)
- Shehata, M. H. and Thomas, M. D. A., (2006). "Alkali release characteristics of blended cements." *Cement and Concrete Research*, 36(6), 1166-1175.
- Shi, C., Day, R. L., Wu, X. and Tang, M., (1992). "Microstructure and performances of alkali-slag cement pastes." In: *Proceedings of 9th International Congress on the Chemistry of Cements*, New Delhi, India. 3, 298-304.
- Takamatsu, N. and Maruyama, I., (2009). "Study on volume deformation and hydration degree of blast furnace slag replaced matrix." In: *Proceedings of JCI*, 31, 187-192. (In Japanese)

- Taylor, H. F. W., (1997). "Cement Chemistry." 2nd ed. Thomas Telford Ltd.
- Tanaka, H., Totani, Y. and Saito, Y., (1983). "Structure of hydrated glassy blast furnace slag contents." *ACI Special Publication*, 79, 963-977.
- Totani, Y., Saito, Y., Kageyama, M. and Tanaka, H., (1980). "The hydration of blast furnace slag cement." *In: Proceedings of the 7th International Congress on the Chemistry of Cement*, Paris, 1980. 2 III, 95-98.