This paper presents a theoretical analysis of the hydration and hydrated layers of blast furnace slag grains in high-volume blast furnace slag cement. Hydrated high-volume blast furnace slag cement paste contains a large number of unreacted slag grains, and hydrated layers are observed surrounding the unreacted slag grains. To analyze the hydration reaction of the blast furnace slag components, an extended effective coefficient is adopted instead of the conventionally used Tomosawa’s equation. This makes it possible to explain the rate of heat liberation of blast furnace slag in comparison to that of ordinary Portland cement. The simulation results for the thickness of the hydrated layer around the slag particles in terms of its conversion radius dependence are in good agreement with the measured values.

Key-words: Blast furnace slag, Blast furnace slag cement, Hydration, Hydrated layer, Tomosawa’s equation, Heat liberation, Ordinary Portland cement, Simulation, Inner hydrated layer, Outer hydrated layer, Diffusion coefficient, Size distribution, Conversion radius

1. Introduction

Reducing the volume of CO₂ discharged in the cement industry is an essential step toward a low-carbon society.¹,² The use of cement additives such as blast furnace slag (BFS) and fly ash has therefore been evaluated. In conjunction with green procurement, BFS cement containing 40% BFS has recently come to be used in practical applications. A study on the practical use of cement focusing on 60–70% BFS has also been conducted. Our research focused on BFS in high-volume blast furnace slag (HVBFS) cement, aiming at its practical use.³ HVBFS cement is highly useful for reducing CO₂ in the cement industry⁴.

We have reported the hydration and hydration products of HVBFS cement at 20°C.⁵ The formation of ettringite (Aft) was found to be key to the performance of HVBFS cement, since it impacts factors such as low dry shrinkage or autogenous shrinkage and the development of strength. We observed that a large number of unreacted slag grains remained in the hydrated HVBFS cement paste with hydrated layers surrounding in. More specifically, both inner and outer hydrated layers were observed in the hydrated layers.⁷

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Microscopic analysis of the strength of BFS cement has been conducted previously,⁶ but no investigation of the details of the reaction layer of the slag particles has yet been conducted. To analyze the hydration reaction of BFS, we formulated a hydration equation for this study that included an expanded effective diffusion coefficient, thus enabling analysis of the BFS component reaction in isolation. The hydration reaction data for BFS alone were extracted from the hydration reaction data for HVBFS cement. We calculated the thickness of the hydration reaction layer around the slag particle surfaces, moreover, and compared it with the experimental results.

2. Theoretical consideration

Tomosawa’s equation, which is used to analyze hydration reactions of cement, is as follows:⁸

\[
\frac{-d\alpha}{dt} = \frac{3C_{\text{w}}}{\rho C_0} + \frac{1}{r_0\alpha^{2/3} \left( \frac{1}{k_d} + \frac{1}{k_e} \right)} + \frac{\alpha^{-1/3} - [n - (n - 1)\alpha]^{-1/3}}{D_e}
\]  

(1)

where \(-d\alpha/dt\) is the rate of the reaction, \(\alpha\) is the degree of non-reaction (1 \(-\alpha\) is the reaction ratio), \(r_0\) is the particle radius, \(C_{\text{w}}\) is the water concentration surrounding the particles, \(n\) is the volume ratio of hydration product to...
We used the following parameters in this calculation:

\[ k_d = \frac{B_d}{(1 - \alpha)^{n_1}} + C_d(1 - \alpha)^{n_2} \]  

(2)

where \( B_d \) is the coefficient for the formation of a protective layer with no diffusion and \( C_d \) is the coefficient for the destruction of the protective layer. It has previously been determined phenomenologically that the parameters \((n_1, n_2)\) in Eq. (2) are \((1, 2)\) and \((1.5, 3)\) for alite and belite, respectively. The effective diffusion coefficient \( D_e \) is written as diffusion coefficient \( D_E \) multiplied by a function of \( \alpha \) as follows:

\[ D_e = D_E \left( \ln \frac{1}{1 - \alpha} \right)^{n_3} \]  

(3)

This is introduced to modify the reaction ratio \( 1 - \alpha \), that decreases more rapidly than in the ordinary diffusion process, at the stage where the reaction rate decreases after the most active reaction is completed, and the degree of hydration reaches \( 1/e \) and \( D_e \) becomes \( D_E \). In the case of ordinary Portland cement (OPC), it takes the common values \( n = 2, \nu = 0.25, \rho_C = 3.15 \text{ [g/cm}^3\text{]}, n_3 = 2, \) and \( C_{\infty} = 1 \). Equation (1) deals with one-particle radius only; it must therefore be expanded in a general-sized distribution system, as follows:(10)

\[ \frac{-d\alpha}{dt} = -\sum f(r_i)(d\alpha(r_i, t))/dt \]  

(4)

where \( f(r_i) \) is the normalized particle size distribution of OPC and \( r_i \) is the radius of the \( i \) particle.

We formulated an analysis procedure specially for the hydration reaction of BFS because it is different from OPC. The characteristic feature of the rate of hydration of BFS is a relatively sharp peak appearing after the peak of normal alite. We believe that this sharp peak arises from \( \text{AFt} \) that is generated rapidly when BFS reacts with anhydrite. We believe that the reaction specific to BFS is the process of generating \( \text{AFt} \) from its reaction with gypsum. Parameter \( \gamma \) gives the ratio of the reaction of the slag to the reaction specific to alite. For example, the rate of the reaction of radius \( r_0 = 1 \mu m \) calculated by Eq. (1) is shown in Fig. 1. We used the following parameters in this calculation: \( k_i = 1 \times 10^{-6} \text{ [cm/h]}, B_d = 1 \times 10^{-8} \text{ [cm/h]}, C_d = 6 \times 10^{-5} \text{ [cm/h]}, D_E = 2 \times 10^{-11} \text{ [cm}^2\text{/h]}, C = 0.4, \) and \( (n_1, n_2, n_3, n_4) = (1, 2, 2, 2) \). In this example, the contributions from the reactions of alite \((\gamma = 0)\), the slag \((\gamma = 1)\), and both alite and the slag \((\gamma = 0.5)\) are presented in Figs. 1(a)–1(c), respectively. In fact, the reaction velocity of the slag has the form of the plot in Fig. 1(c).

3. Experiments

3.1 Preparation of specimens

We used OPC manufactured by the Japan Cement Association in our experiments. Depending on the composition of the HVBFS cement, OPC consisted of mainly BFS (blast furnace slag) with an anhydrite ratio of 30:65:5 wt%. The chemical compositions of OPC, BFS, and

![Graphical representation](image-url)

**Fig. 1.** Rate of reaction calculated by Tomosawa’s equation [Eq. (1)]. Here, effective diffusion \( D_e \) is used as given in Eq. (5) and not Eq. (3): (a) \( \gamma = 0 \) (alite only), (b) \( \gamma = 1 \) (BFS only), (c) \( \gamma = 0.5 \) (alite + BFS).
anhydrite are presented in Table 1. The experimental results for the rate of heat liberation and overall heat liberation of the HVBFS cement are shown in Figs. 2(a) and 2(b), respectively. The OPC powder and additions were kneaded by hand for 10 min while pouring water to obtain a predetermined water-powder ratio of 0.4 to form a paste. The specimens were then cured indoors at 20°C in curing tanks for accurate temperature control. After predetermined aging times of 7 and 28 days, the hydration was stopped by the addition of acetone, and each specimen was dried in an aspirator for 24 h.

3.2 Measurement of the reaction ratio of BFS

The reaction ratio of the BFS was measured using the salicylic acid acetone methanol method. We identified the hydration products by X-ray diffraction. For observation of the hydration structure, a reflection electron image was taken using field emission-scanning electron microscopy (FE-SEM). Hardened material samples that were aged for 28 days following the end of hydration treatment were investigated. After a sample was dried under reduced pressure for more than 24 h, it was crushed into small pieces of about $7\times7\times3$ mm$^3$ and impregnated with epoxy resin. After vacuum defoaming of the sample for more than 24 h, one side of the sample was polished to obtain a mirror surface. The surface of the sample was coated using a carbon coater to improve its electrical conductivity. The observation conditions were as follows: Atmospheric pressure $1.0\times10^{-4}$ Pa in the chamber, acceleration voltage of 15 kV, spot diameter 8 nm, working distance 8 mm, and observation magnification of 1000–20,000 times.

4. Simulation

4.1 Simulation of blast furnace slag hydration

To simulate hydration of the BFS element only, it is necessary to isolate it from the HVBFS cement. For simplicity, it is assumed that the hydration reaction of HVBFS cement is a linear combination of the hydration reactions of each component (OPC, BFS), and can be given as follows:

$$-\frac{dc_{\text{HVBFS}}}{dr} = -\frac{1}{\sum m_j \rho_j} \sum m_j \frac{dc_j}{dr} \quad (j = \text{OPC, BFS})$$

(6)

where $m_j$ and $\rho_j$ are the mass and density of component $j$, respectively.

Let $f_j(r_i)$ be the normalized particle size distribution of component $j$, where $r_i$ is the radius of the $i$th particle of component $j$. Thus, the hydration reaction of each component $j$ is written as follows:

$$-\frac{dc_j}{dr} = -\sum_i f_i(r_i) \frac{dc_j(r_i, t)}{dr}$$

(7)

Equation (6) provides an adequate approximation when the interactions between the components during the hydration reaction can be eliminated, and the hydration of the HVBFS cement can thus be simulated by varying the ratio of the components at the start of the reaction. By using the hydration reaction data for the OPC and HVBFS cement, the heat liberation of BFS can be calculated as the difference between the heat liberations of the HVBFS cement and OPC using the following expression derived from Eq. (6):

$$-\frac{dc_{\text{BFS}}}{dr} = -\left(\frac{m_{\text{OPC}}}{\rho_{\text{OPC}}} + \frac{m_{\text{BFS}}}{\rho_{\text{BFS}}}\right) \frac{dc_{\text{HVBFS}}}{dr} + \frac{m_{\text{OPC}}}{\rho_{\text{OPC}}} \frac{dc_{\text{OPC}}}{dr}$$

(8)

The experimental results for the rate of heat liberation and heat liberation of OPC are shown in Figs. 3(a) and 3(b), respectively. The calculated results for the rate of heat liberation and the heat liberation of the BFS are shown in Figs. 4(a) and 4(b), respectively. The dotted lines in the figures correspond to the simulated values calculated by
Fig. 3. (a) Comparison of experimental data and results for the rate of heat liberation of OPC. (b) Comparison of experimental data and simulation results for heat liberation of OPC.

Fig. 4. Particle size distribution of BFS powder.

Fig. 5. (a) Comparison of experimental data using Eq. (8) and simulation results using Eq. (8) for the rate of heat liberation of BFS. (b) Comparison of experimental data using Eq. (8) and simulation results using Eq. (8) for heat liberation of BFS.

Table 2. Fitting parameters determined by Eqs. (1) and (5) calculated using particle size distribution

| Parameter | BFS |
|-----------|-----|
| $k_t$ [cm/h] | $2.0 \times 10^{-6}$ |
| $B_d$ [cm/h] | $3.0 \times 10^{-10}$ |
| $C_d$ [cm/h] | $8.0 \times 10^{-5}$ |
| $D_e$ [cm$^2$/h] | $3.1 \times 10^{-11}$ |
| $C$ | 0.4 |
| $n_1$ | 1 |
| $n_2$ | 2 |
| $n_3$ | 2 |
| $n_4$ | 2 |
| $y$ | 0.7 |

where the effective diffusion coefficient $D_e$ is expressed as Eq. (5), and $f_{BFS}(r_t)$ is the particle size distribution of BFS as shown in Fig. 5. When $n = 2.3$ is used, the results show good agreement between the theoretical and experimental values, as shown in Fig. 4. The fitting parameters for the same are listed in the right column under the heading “BFS” in Table 2.

4.2 Thicknesses of hydrated products formed on slag particle surfaces

Hydration reactions start when a particle (radius $r_0$) comes to contact with the surrounding water. The hydrated product formed on the particle surface has two parts, an inner product ($r_1 \leq r \leq r_0$) and an outer product ($r_0 \leq r \leq R_t$), as shown in Fig. 6. The radius of a non-reactive cement particle $r_t$ and the radii of reaction products formed on cement particle $R_t$ with an initial radius of $r_0$ are obtained using residual fraction $\alpha$, as follows:

$$
-D_e \int f_{BFS}(r_t) \frac{d\alpha_{BFS}}{dr} = \frac{3C_w\alpha}{vP_{BFS}} \sum_i f_{BFS}(r_i) \frac{1}{r_i^2} \\
\times \left( \frac{1}{r_t\alpha^{2/3}} \left( \frac{1}{k_d} + \frac{1}{k_f} \right) + \frac{\alpha^{-1/3} - [n - (n - 1)\alpha]^{-1/3}}{D_e} \right) $$

(9)
where the volume of the hydration product is \( n \) times the volume of the reacted portion \( (n = 2.3) \). The thicknesses of the inner product \( r_0 - r_t \), outer product \( R_t - r_0 \), and total hydration product \( R_t - r_t \) are calculated as follows:

\[
\begin{align*}
    r_t &= \alpha^{1/3} r_0 \\
    R_t &= [n - (n - 1)\alpha]^{1/3} r_0
\end{align*}
\]

A large number of slag grains remained unreacted in the hydrated high-volume slag cement paste. Hydrated layers were observed surrounding the unreacted slag grains, as shown in Fig. 7. Both inner and outer hydrated layers are seen. The interface between the inner and outer products corresponds to the original surface of the BFS before the hydration reaction.

We therefore measured the inner and outer hydrated layers surrounding approximately 30 particles of varying in sizes and arranged them around the conversion radii of the particles. The measured thicknesses of the inner and outer hydrated layers are shown in Fig. 8. The average thicknesses of the inner and outer layers were about 0.26 and 0.29 \( \mu m \), respectively. In the figure, the black (thickness of inner product) and red (thickness of outer product) curves are the numerical results calculated using Eqs. (12) and (13), respectively. Based on the surface of the original slag particle, we define the coordinates of the surface of the outer layer to be positive and those of the inner layer to be negative. According to this simulation, the thickness of the hydrated layer depends on the particle size, and the outer layer tends to be thicker than the inner layer.

The measured thickness of the total hydration product is presented in Fig. 9. The thicknesses of the layers seem to be almost constant, regardless of the grain size, at approximately 0.5 \( \mu m \). The simulation curve is calculated theoretically using Eq. (14). Several experimental values deviate from the simulation curve, but it can be seen that the experimental values generally lie approximately along the theoretical curve.

5. Conclusion

It is proposed that estimation of blast furnace slag hydration in HVBFS cement be conducted using the measured heat liberations of HVBFS cement and OPC. The hydration of the slag was simulated by Tomosawa’s equation using the effective diffusion coefficient, which replaced the conventional form in the expanded expression. The thicknesses of the hydrated layers observed surrounding slag grains remained unreacted in the hydrated high-volume slag cement paste. Hydrated layers were observed surrounding the unreacted slag grains, as shown in Fig. 7. Both inner and outer hydrated layers are seen. The interface between the inner and outer products corresponds to the original surface of the BFS before the hydration reaction.

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![Fig. 6. Diagram of the hydration reaction of a particle with radius \( r_0 \). Radii \( r_t \) and \( R_t \) are radii of non-reactive cement particles and hydrate products formed on respective particle surfaces.](image)

![Fig. 7. Backscattered electron image of a hydrated layer by EF-SEM. The unreacted BFS core is surrounded by the inner product with a clear interface between them.](image)

![Fig. 8. Comparison of the experimental and theoretical values of the conversion radius dependence of the thicknesses of the inner and outer hydrated layers.](image)
the unreacted slag grains were explained by the corresponding theoretical values in terms of conversion radius dependence.

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Fig. 9. Comparison of the experimental and theoretical values of the conversion radius dependence of the hydration layer thickness.

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