Hydration Kinetics Model of Slag-blended Cement System

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Abstract. Slag is a fine-grained glassy material formed from molten slag of blast furnace when it is quenched, and it is kind of active admixture. Therefore, the slag as admixtures mixed into cement based materials, whose activity can play an important role in the hydration reaction and improve the mechanical properties of cement based materials. In this paper, the influence of the kinetics of hydration of slag and cement was analyzed, and the dynamics equation of the hydration of slag Portland cement system was established. The influence of slag on slag Portland cement system hydration process was analyzed mainly from the water binder ratio, temperature and the ratio of the influence of slag on slag Portland cement system hydration process. The results show that, the increasing of water binder ratio, temperature increasing and the cement particle specific surface area increasing can accelerate the hydration process of slag Portland cement system in different degree.

1. Introduction

Cementitious material is a very important component in cementitious materials. Slag is a glassy substance formed mostly by the blast furnace melting slag when it is suddenly cooled, and it is also called Blast-Surnace Slag. Its main components are composed of CaO, MgO, SiO₂ and Al₂O₃, which have unstable structural characteristics and high potential activity. Under the action of activator, the reaction energy with water can be cemented with coarse and fine aggregate to form a good performance concrete. Therefore, as mineral admixture into cement based materials, the dense cement formed by hydration of cement can effectively prevent the erosion of the external medium, and has a good corrosion resistance [1-4], which is now widely used in practical engineering.

With the continuous and extensive development and utilization of slag in the world, many researchers have carried out a large number of experiments to explore the hydrodynamic factors affecting the slag cement composite cementitious system. However, the systematic research on the cementitious system is still in the initial stage of [4]. The study of Hashim [5] showed that higher temperature could stimulate the slag activity in the cementitious system, and the degree of reaction would increase with the increase of temperature. Lumley [6] and other studies show that the content of Ca (OH)₂ in composite cementitious system decreases with the increase of slag reaction. Liu Rengguang’s [7] research shows that high temperature curing can improve the early reaction degree of slag cement cementitious system, but it will hinder the hydration degree of the later stage of the system.
Thus, there are also differences in the microscopic process of the hydration of slag cement cementitious system due to the difference between the experimental materials, the means of observation and the focus of research and so on. Therefore, it is necessary to establish and discuss the hydrodynamic model of the slag cement.

2. Kinetics process of cement paste
In general, [8], the chemical equation of hydration of Portland cement can be expressed by (1) ~ (8).

\[
\begin{align*}
C_3S + 5.3H & \rightarrow CSH + 1.3CH \\
C_2S + 4.3H & \rightarrow CSH + 0.3CH \\
C_3A + 3C\bar{S}H_2 + 26H & \rightarrow C_6A\bar{S}_3H_{32} \\
C_4AF + 3C\bar{S}H_2 + 30H & \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \\
2C_3A + C_6A\bar{S}_3H_{32} + 4H & \rightarrow 3C_4A\bar{S}H_{12}
\end{align*}
\]

The main components of cement clinker include $C_3S$, $C_2S$, $C_3A$ and $C_4AF$, thus, their hydration degree can be expressed in the following way:

\[
\alpha(t) = \alpha_{C_3S}m_{C_3S} + \alpha_{C_2S}m_{C_2S} + \alpha_{C_3A}m_{C_3A} + \alpha_{C_4AF}m_{C_4AF}
\]

According to [9], the hydration kinetic equation of each mineral component of cement can be expressed as equation (10).

\[
\frac{d\alpha}{dt} = \frac{A(\alpha)}{\tau_x(T)}
\]

In the formula, $A(\alpha)$ is the chemical binding force, $\tau_x(T)$ is the characteristic time.

\[
A(\alpha) = \frac{1 - (\alpha - \alpha_0)}{-\ln[1 - (\alpha - \alpha_0)]^{1/\lambda}}
\]

\[
\tau_x(T) = \tau_x(T_0)\exp \left[ \frac{E_{ax}}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]
\]

In the formula, $\tau_x(T_0)$ is the characteristic time of the hydration reaction at 20°C, $\tau_x(T_0)$ is the initial hydration degree of the mineral components of each phase, the R is Fugadero constant, and the T is the absolute temperature, $E_{ax}$ is the surface activation energy of the mineral components of each phase.

According to [10], the kinetic parameters used for this process are given in Table 1. All values are determined for a fineness $\phi = 3602 cm^2 / g$ and an average, particle size $R = 5 \times 10^{-4} cm$.

| Clinker $(w/c)$ | $\tau_x(T_0)$ | $m$ | $D(cm^2/h)$ | $\alpha_0$ | $\tau_x$ | $E_{ax}/R$ (KJ/mol) |
|----------------|----------------|-----|-------------|------------|----------|---------------------|
| $C_3S$ 0.3     | 13.5           | 1.86| $4.2 \times 10^{-9}$ | 0.02       | 0.60     | 37.39               |
| $C_3S$ 0.4     | 12.7           | 1.78| $1.05 \times 10^{-10}$ | 0.4        | 0.60     | 20.78               |
| $C_3S$ 0.5     | 11.9           | 1.72| $2.64 \times 10^{-10}$ | 0.00       | 0.60     | 35.71               |
| $C_3S$ 0.3     | 71.2           | 1.10| $6.64 \times 10^{-13}$ | 0.04       | 0.60     | 20.78               |
| $C_3S$ 0.4     | 65.3           | 1.04| $2.64 \times 10^{-10}$ | 0.00       | 0.60     | 35.71               |
| $C_3S$ 0.5     | 60.9           | 0.96| $2.64 \times 10^{-10}$ | 0.00       | 0.60     | 35.71               |
| $C_3A$ 0.3     | 57.7           | 1.14| $2.64 \times 10^{-10}$ | 0.04       | 0.60     | 35.71               |
| $C_3A$ 0.4     | 53.4           | 1.06| $2.64 \times 10^{-10}$ | 0.04       | 0.60     | 35.71               |
3. Kinetics model of Slag-Cement Cementitious System

The hydration process of the slag cement cementitious system is more complex, including the hydration process of cement and slag, and the CH (calcium hydroxide) in the hydration products of cement will also affect the hydration of the slag. Richardson’s [12] studies show that slag and CH react as follows:

\[
C_{7.88}S_{7.39}AM_{3} + n_{CH} CH + n_{H} H \rightarrow n_{C:SH} C_{(c:S)}SH_{4}\Lambda (A/S) + n_{AH} C_{4.6}AH_{d}
\]  

(10)

The reaction of slag can be considered separately from the hydration reaction of cement, thus, the hydration process of the slag can be considered by the Knudsen model, and the dynamic process can be expressed in the next formula.

\[
\alpha_{SL}(t) = \alpha_{SL}^{u} \frac{k(t-t_{0})^{n}}{1+k(t-t_{0})^{n}}
\]  

(11)

Where \( \alpha_{SL}/\alpha_{SL}^{u} \) is the reaction degree, K is the reaction rate constant, t is time, \( t_{0} \) is the characteristic time, and N is the reaction index. The reaction constant K follows the Arrhenius equation [13], that is,

\[
k = k_{0}e^{-E/RT}
\]  

(12)

In the formula: \( K_{0} \) is the factor of index term, E is surface activation energy, R is gas constant and \( T \) is adiabatic temperature. If there is no obvious induction period, it is \( n=1 \) and \( t_{0}=0 \). Therefore, the overall hydration kinetics equation of slag cement cementing system can be expressed as:

\[
\alpha(t) = (1-p) \cdot \alpha_{cem}(t) + p \cdot \alpha_{SL}(t)
\]  

(13)

Where p is the content of slag.

4. A hydrodynamic calculation example of Slag-Cement Cementitious System

In order to verify the hydrodynamic model of the slag cement cementitious system, the data in literature [14] are used, and the content of the mineral components and the model parameters of each phase are shown as follows:

| Oxide (%) | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃  | TiO₂ | MnO  | P₂O₅ | Na₂O | K₂O  | Blaine (cm²/g) | Density (g/cm³) |
|-----------|------|-------|-------|------|------|------|------|------|------|------|------|----------------|----------------|
| OPC       | 20.68| 4.4   | 2.34  | 63.13| 2.1  | 2.63 | 0.29 | 0.04 | 0.33 | 0.13 | 0.74 | 3400           | 3.20            |
| Slag      | 35.9 | 11.2  | 0.3   | 42.3 | 8    | 0.12 | 1.90 | 0.4  | 0    | 0.3  | 0.5  | 3460           | 2.89            |

4.1 Hydration kinetics curves of Slag-Cement Cementitious System under different water binder ratios

It is assumed that the temperature is 20°C, and the water gel ratio (w/b) is 0.3, 0.4, 0.5, and the data in Table 2 can be replaced by (9), the hydration kinetics expression of the cement can be obtained. According to [11] - [13], the hydrodynamic expression of slag can be obtained, and the amount of slag is 25% and 50%, and the different water can be obtained according to [13]. The hydration kinetics curves of Slag-cement Cementitious System are compared with the experimental results in document [14], as shown in Figures 1 (a) and 1 (b).
In Fig. 1 (a) and (b), the changing law which contains 25% slag and 50% slag in Slag-Cement Cementitious System were showed with different water bind ratios respectively. Under the same age, the nominal hydration degree of the system will increase with the increase of water binder ratio. In the case of high slag content (50%), the effect of water to cement ratio on the hydration process of Slag-Cement Cementitious System is smaller than that of low slag content (25%). When the ratio of water to binder ratio is greater than 0.4, the effect of increasing water glue ratio on the hydration process of the system can almost be ignored. This is because when the slag content is up to 50%, and the water binder ratio is greater than 0.4, the moisture is enough to make the system used to participate in hydration reaction.

4.2 Hydration kinetics curves of Slag-Cement Cementing System under the condition of different specific surface area

It is assumed that the ratio of water to glue is 0.32, the ambient temperature is 30°C, and the different specific area of cement is 3000 cm²/g, 3500 cm²/g, 4000 cm²/g respectively. The hydrodynamic curves of the slag cement cementitious system under the different specific surface area are obtained, such as Figure 2 (a) and 2 (b).

It can be seen from the above diagram that the hydration rate of slag cement cementitious system increases with the increase of specific surface area of cement under different specific area. This is because the greater the specific surface area of the cement, the greater the contact area of the cement particles and water, thus speeding up the hydration rate at the early age of the slag cement.
cementitious system. However, with the increase of specific surface area, it has little effect on the hydration rate of the system, and has little effect on the final hydration degree of the system.

5. Conclusion
In this paper, the mineral composition of the slag and cement is considered, and the hydration kinetics equation of the slag cement cementitious system is established according to the three stages of its hydration process. The hydration process of the slag cement cementitious system is analyzed from three aspects of water gel ratio, temperature and cement fineness, and the results are compared with the experimental results. The following conclusions are as follows:

1. The increase of water binder ratio can significantly accelerate the early hydration rate of the slag cement cementitious system, but it has little effect on the later stage of hydration, and the effect on the hydration rate is almost negligible when the slag content is high.

2. The increase of temperature can accelerate the early hydration process of slag cement cementitious system, and when slag content is higher, this effect will be more significant.

3. The increasing specific surface area of cement can accelerate the early hydration process of the slag cement cementitious system, but it has little effect on the later stage of hydration, and has little effect on the final hydration degree of the system.

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