HYDRATION KINETICS MODEL OF SUPERSULFATED CEMENT

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Abstract

Supersulfated cement, with higher waste utilization and less cement clinker is the inevitable trend of the development of green material in the rapid developed industrial era. For the wide use of supersulfated cement in our country, the hydration heat is analyzed in this paper. The hydration kinetic parameters are obtained from the hydration heat and hydration heat rate curves measured by the isothermal calorimeter and the simulation based on the Krstulovic-Dabic model. The results show that the hydration heat process after induction period was divided into three periods, nucleation and crystal growth (NG), phase boundary reaction (I), diffusion (D) and the simulation curve shows good trend of hydration and the connecting point of the three hydration processes. The NG process is not consistent with the ideal model, and the hydration rate is relatively slower than simulation rate because of its low content of clinker. The hydration heat of supersulfated cement is extremely low; in addition the second exothermic peak comes much later, which has important significance for large volume concrete pouring.

1. INTRODUCTION

Supersulfated cement is less clinker cement or no clinker cement, which is mainly composed of ground granulated blast furnace slag and takes gypsum as sulfate activator, a little amount of clinker or lime as alkali activator. The component ratio is usually as follows: 75%-85% of slag; some sulfates (such as dihydrate gypsum and anhydrous gypsum), about 10%-20%; and 1%-5% of alkaline composition (such as clinker or lime). Supersulfated cement is made directly by the mixtures of the three raw materials, often mixed with 1% mass ratio of coagulant, and in ball mill to be grinded to suitable particle size. Granulated blast furnace slag is a kind of by-product of steel plant and iron-making industry, and which usually results in waste accumulation, taking up a lot of land, and polluting the environment. With the
development of the concrete industry, these wastes are being making full use of. Because of containing more calcium oxide, alumina, this kind of slag becomes potentially activity after grinding to certain fineness, and can be activated by the excitation by sulfates to replace some cement as mineral admixture. But slag as the dosage of mineral admixture is generally not more than 50%, and the utilization rate is not high, while the slag content of supersulfated cement can reach almost 80%, thus making full use of the potential activity of slag. Studies show that granulated blast furnace slag which has high content of calcium oxide and magnesium oxide, especially when it also contains enough of the alumina (at least 14% - 15%) is suitable for producing supersulphated cement, and will have a reasonable strength development process. This cement is energy-saving cement because of its low cost, simple production process and better use of industrial slags [1]. It is also an environment-friendly cementitious material due to its high durability, low hydration heat, and waste-utilization.

When the powders of supersulfated cement mixed with water, physical and chemical reaction happens simultaneously [2], eventually generates non-homogeneous paste. Although there are some ettringite and gypsum crystals in hydration products, the most important hydration product of it is hydrated silicate gel (C-S-H gel), nearly 70% in cement paste. As a result, the formation of the C-S-H gel plays a key role to the setting and hardening of the cement, and the hydration mechanism of the cementitious material will directly influence the hydration heat and heat release rate.

In order to make the supersulfated cement better used in our country, as well as study the characteristics of local waste slag, and then apply it to the production of cement, and additionally make the prediction of the development of the cement performance more stable, this paper investigated the mechanism of hydration reaction and set up the hydration kinetics model according to the test results of isotherm hydration heat on the supersulfated cement based on the Krstulovic-Dabic model.

2. RAW MATERIALS AND EXPERIMENTAL

The chemical compositions of SSC used in this experiment and the slag chemical compositions are shown in Table 1. SSC contains high content of SO₃ because of high content of gypsum. Al₂O₃ content of slag is 14.500%, which is suitable for producing supersulphated cement. The water to cement ratio is 0.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td>0.235</td>
<td>5.379</td>
<td>11.630</td>
<td>25.810</td>
<td>0.335</td>
<td>12.240</td>
<td>0.572</td>
<td>41.250</td>
<td>1.178</td>
</tr>
<tr>
<td>slag</td>
<td>0.297</td>
<td>6.705</td>
<td>14.500</td>
<td>32.320</td>
<td>0.032</td>
<td>2.810</td>
<td>0.661</td>
<td>40.230</td>
<td>0.985</td>
</tr>
</tbody>
</table>

The test of hydration heat was measured by isothermal calorimeter instrument at the
temperature of 20 °C. Isothermal calorimeter instrument is TAM Air, with an eight channel trace heat meter, and the test temperature range from 5 to 90 °C, the temperature fluctuation is less than ±0.02 °C, the precision can reach ± 20μW.

3. BASIC DYNAMIC PRINCIPLE OF CHEMICAL REACTION[3-5]

The kinetic equation of homogeneous phase reaction under isothermal condition is as follows:

\[
dc/dt = k(T)f(c)
\]  

(1)

in which \(c\) is the liquid concentration, \(T\) represents the thermodynamic temperature, \(k(T)\) is the reaction rate constant and \(f(c)\) is the reaction mechanism function.

In the heterogeneous phase system, such as cement based material, the liquid concentration \(c\) is no longer applicable. The conversion degree \(\alpha\) is then taking from reactant to product as a substitute (the cement based material by hydration degree). Arrhenius theorem \(k(T) = A e^{E_a/RT}\) is adopted to define the reaction rate constant, thus obtains the isothermal kinetics equation of heterogeneous phase system as follows:

\[
da/dt = k(T)f(\alpha) = A e^{E_a/RT}f(\alpha)
\]  

(2)

In which \(A\) is pre-exponential factor, \(E_a\) is apparent activation energy, \(R\) is Avogadro constant, \(T\) represents the thermodynamic temperature, \(f(\alpha)\) is the reaction mechanism function and \(t\) is the reaction time.

The study of the chemical kinetic reaction is to characterize and simulate the reaction process and to explore the reaction mechanism though solving those equations above and getting the kinetic parameters. This paper was to simulate the reaction process based on the isothermal kinetics equation under the condition of heterogeneous phase system.

4. HYDRATION KINETIC MODEL BASED ON SUPERSULFATED CEMENT

4.1 The exothermic process division of cement based material

At present, the kinetic parameters of the hydration reaction of the cementitious materials were achieved by testing the hydration heat release rate using the isothermal calorimetry method. Then through the following equations,

\[
1/P = 1/P_\infty + (t_0)/[P_\infty(t - t_0)]
\]  

(3)

\[
\alpha(t) = P(t)/P_\infty
\]  

(4)

Draw the curve of hydration degree with time based on the isothermal calorimetry testing data, which will be needed to set up the hydration kinetic model. Then calculate the constant \(n\) and hydration rate constant \(K\) of the compound gel system according to the Krstulovic-Dabic model [6-8], thus reflects the hydration mechanism and rules of the supersulphated cement in different hydration stages. The isothermal calorimetry method is very sensitive for some low hydration degree of cement based material in early hydration,
especially for the early hydration acceleration period and reduction period. Additionally, it is more convenient to analyze how different factors affect the hydration rate during and before the acceleration period of the cementitious material. In this paper, the hydration heat release rate and heat quantity at different time were tested using this method.

Based on the characteristics of hydration heat, the hydration process of cement based material generally can be divided into five stages. Taking the supersulfated cement as an example is in this paper. As is shown in Figure 1, five stages[9-10] are divided into: rapid response (0-A-B), which has just started contact with water to produce cement, corresponds to the first exothermic peak heat release rate curve; induction period (B-C), which is relative dormant state, the hydration rate is very low, and the hydration reaction is relatively inert; acceleration period(C-D), the hydration heat release rate of rapidly rising stage; deceleration phase (D-E), the hydration rate rapidly falling stage, the acceleration period and reduction period constitutes the heat release curve of second exothermic peak; recession(E-F), namely the end stage, the heat release rate close to zero.

![Figure 1: Hydration heat liberation rate and quantity of SSC](image)

Due to the fact that the heat quantity released before the end of the induction period (i.e., the area of the first exothermic peak in the heat release rate curve, 0-A-B) generally accounts for only about 5% of the total hydration heat quantity, which can be ignored relative to the hydration process[3,11]. In practical engineering, the mixing heat release under the influence of water tend to be included in the initial casting temperature, and the supersulfated cement (especially in the absence of added coagulant) gets the relatively slow for early development and the hydration heat quantity is very low. Therefore, the first exothermic peak is always ignored in the process of the hydration heat; at the same time, due to the very low hydration rate of induction period, the continuous heat quality of induction period is also ignored. So the discussion of hydration heat starts from the end of the induction period (the point C in Figure 1), hydration heat release rate from the point C starts rising rapidly.
4.2 The introduce of Krstulovic-Dabic model

Hydration reaction of cement-based materials is divided into three basic processes according to Krstulovic-Dabic model, namely nucleation and crystal growth (NG), phase boundary reaction (I) and diffusion (D). These three control processes may occur simultaneously, and also can occur alone or in pairs, but the hydration rate of the overall development process depends on the one which reacts slowest, that is, the control process of the slowest reaction controls the reaction rate and mechanism of corresponding stage. Krstulovic gives the integral and differential expression of the three processes to express the kinetic equation [6-8, 12] of the relationship between the hydration process and reaction time, that is:

Nucleation and crystal growth (NG):

$$[-\ln(1-\alpha)]^{1/n} = K_1(t - t_0) = K'_1(t - t_0)$$  \hspace{1cm} (5)

Phase boundary reaction (I):

$$[1 - (1-\alpha)^{1/3}]^1 = K_2 r^{-1}(t - t_0) = K'_2(t - t_0)$$  \hspace{1cm} (6)

Diffusion (D):

$$[1 - (1-\alpha)^{1/3}]^2 = K_3 r^{-2}(t - t_0) = K'_3(t - t_0)$$  \hspace{1cm} (7)

In which $\alpha$ is the hydration degree, i.e., the hydration degree of spherical particles of cement; $K$ is the reaction rate constant of hydration reaction; $n$ is reaction order; $R$ is the diameter of reacted particle; $t_0$ is the end time of the induction period.

At the same time, kinetic equation can be got from the differential of above three types to express the hydration rate of the three processes, that is:

Nucleation and crystal growth (NG):

$$\frac{d\alpha}{dt} = F_1(\alpha) = K_1 n(1-\alpha)[-\ln(1-\alpha)]^{1/n}$$  \hspace{1cm} (8)

Phase boundary reaction (I):

$$\frac{d\alpha}{dt} = F_2(\alpha) = 3K_2' (1-\alpha)^{2/3}$$  \hspace{1cm} (9)

Diffusion (D):

$$\frac{d\alpha}{dt} = F_3(\alpha) = \frac{3[K_3'(1-\alpha)^{2/3}]}{1-(1-\alpha)^{2/3}}$$  \hspace{1cm} (10)

This model is a considerable representative hydration dynamic model of the current academic, through which the hydration heat of cement based on materials, can be controlled, and it will be easier to understand the affecting factors of every stage. While there are some problems about this model, such as the boundaries between the various processes is not clear at the station that the model divides hydration reaction process into three basic processes, and the correlation between the experimental data and models at the boundaries is poor.
4.3 The hydration process simulation of supersulfated cement

The hydration mechanism of supersulfated cement is different from that of ordinary Portland cement, and the hydration of ordinary Portland cement is based mainly on alkali-activated, and the main hydration products are calcium hydroxide and calcium silicate hydrate (C-S-H gel). But in the hydration process of supersulfated cement, taking gypsum as sulfate activator and clinker as alkaline activator, the hydration of slag is acts by the excitation of these two substances, and the main hydration products are ettringite and low-alkaline calcium silicate hydrate gel. So the main hydration products of ordinary Portland cement are calcium hydroxide and calcium silicate hydrate in the early stage, while the main hydration products of supersulfated cement is calcium silicate hydrate, ettringite and a small amount of gypsum. Even so, the main hydration products of supersulfated cement is calcium silicate hydrate gel.

Taking Knudsen extrapolation equation (formula (3)) to fit linearly the hydration heat release curve of supersulfated cement (the hydration heat curve in Figure 1) which is measured by isothermal calorimeter, as Figure 2 shows, the maximum heat release $P_{\text{max}}=125\text{J/g}$ can be calculated. $P_{\text{max}}$ is the heat released by some hydrated cementitious materials in the experiment process, but not the theoretical heat release. The cementitious materials can’t be fully hydrated in actual project, so it is reasonable to take part hydration here. The degree of hydration $\alpha(t)$ can be calculated by $P_{\text{max}}$ according formula (4), putting $\alpha(t)$ into formula (5), and making the $\ln[-\ln(1-\alpha)]-\ln(t-t_0)$ double logarithmic curve, then through linear fitting to get kinetics parameters ($n$ and $K_1'$) of nucleating and crystal growth process, as Figure 3 shows.

Similarly, putting the hydration degree $\alpha(t)$ into equation (6) and (7), to get the curves of $[1-(1-\alpha)^{1/3}] — (t-t_0)$ and $[1-(1-\alpha)^{1/3}]^2 — (t-t_0)$, so that it can obtain the kinetic parameters $K_2'$ of phase boundary reaction (I) parameter and $K_3'$ of diffusion process (D) parameter by linear fitting, as shown in Figure 4 and 5. The hydration kinetic parameters of SSC are shown in Table 2.

![Figure 2](image1.png)  
![Figure 3](image2.png)
Figure 4: Determination of kinetic factors (n and \( K'_2 \)) of phase boundary reaction (I) process from linear regression

Figure 5: Determination of kinetic factors (n and \( K'_3 \)) of diffusion process (D) process from linear regression

Table 2: Hydration kinetic parameters of SSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydration temperature</th>
<th>n</th>
<th>( K'_1 )</th>
<th>( K'_2 )</th>
<th>( K'_3 )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td>20</td>
<td>2.161</td>
<td>0.0698</td>
<td>0.023</td>
<td>0.0052</td>
<td>0.19</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The kinetic parameters obtained above are substituted into the formula (8) to (10), then it can obtain the kinetic curves of reaction rates \( F_1(\alpha) \), \( F_2(\alpha) \) and \( F_3(\alpha) \) of nucleation and crystal growth (NG), phase boundary reaction (I) and diffusion process (D) with the hydration degree of \( \alpha \). Making a graph of \( F_1(\alpha) \), \( F_2(\alpha) \) and \( F_3(\alpha) \) with \( \alpha \). Such as the solid lines in Figure 6, and the dotted line indicates the degree of hydration with time of the calculated hydration curve.

Figure 6: Hydration rate curves for SSC

From the above Figure 6, three processes after induction period of ordinary portland
cement are nucleation and crystal growth (NG) (before the hydration degree of $\alpha_1$), phase boundary reaction (I) (between the hydration degree of $\alpha_1$ and $\alpha_2$) and diffusion process (D) (after the hydration degree of $\alpha_2$). They are basically consistent with the SSC, and phase boundary reaction and diffusion processes fit a higher degree. Also the turning point at the intersection is also consistent with the rate curve. Only the first stage of nucleation and crystal growth has some access with the rate curve, however, the underlying trend is consistent.

Three curves of $F_1(\alpha)$, $F_2(\alpha)$ and $F_3(\alpha)$ can basically segmented analog the actually hydration rate curve $d\alpha/dt$ that is obtained by heat-measurement experiments of SSC. This shows that SSC hydration reaction process is not a single, but also has complex process with multiple reaction mechanisms. There are different control factors at different reaction stages. In the early hydration, having more adequate water and fewer hydration products, the nucleation and crystal growth plays a leading role; with prolonged hydration, the hydration products are more and more, and ion mobility becomes difficult. The hydration turns to phase boundary reaction (I) and then turns to diffusion process (D).

The SSC clinker content is only 1% to 5%. In the early hydration, clinker minerals are dissolved in water, and tricalcium aluminate first hydration to generate hydrated calcium aluminate. While the gypsum is dissolved in water to produce sulfuric acid ion, reacting with the hydrated calcium aluminate and generating ettringite (AFt). Then tricalcium silicate hydration, indicating the end of the induction period and produces more calcium hydroxide and C-S-H gel. At the same time, active alumina in slag will react with calcium hydroxide and sulfuric acid ion, generating ettringite (AFt). This will promote the formation of hydroxyl radicals, making the reaction form a virtuous cycle, and then produce more CSH gel and hydration products ettringite. Also the ettringite can enhance early strength of SSC.

So for SSC hydration, the Krstulovic-Dabic model can simulate the hydration of cement in a certain extent. Although the effect is not particularly good, it is able to react with the trend of hydration and control the process of various stages. The total heat of cementitious materials is reduced with increasing slag. In this paper, SSC measured maximum heat release is $P_{\text{max}} = 125\text{J/g}$, and indeed it is lower than the ordinary Portland cement. This also shows that the SSC is low heat cement, and conducive to mass concrete pouring. The second exothermic peak of cementitious material hydration is reduced with the slag increasing. The second exothermic peak of general cement is at 10h approximately, while the second exothermic peak of SSC is after 25h in this experiment. This shows that SSC postpones the second exothermic peak.

5. CONCLUSION

The hydration kinetic parameters can be obtained from the hydration heat and hydration heat rate curves measured by the isothermal calorimeter and then simulated based on the Krstulovic-Dabic model. The results show that the hydration heat process after induction period was also divided into three periods, nucleation and crystal growth (NG), phase boundary reaction (I), diffusion (D) and the simulation curve shows good trend of hydration.
and the connecting point of the three hydration processes. The NG process is not consistent with the ideal model, and the hydration rate is relatively slower than simulation rate because of its low content of clinker. The hydration heat of supersulfated cement is extremely low, and the second exothermic peak comes much later, which has important significance for large volume concrete pouring.

REFERENCES


