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Research on the early age mechanical properties of concrete based on hydration kinetics

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Abstract. In the era of advanced construction techniques, the enhancement and regulation of the functionality of concrete, a widely utilized construction material, has gained significant prominence. The study delves into the exploration of the properties and heat reaction behavior during hydration of various composite cementitious materials with the incorporation of three distinct mineral additives: microspheres, cellulose, and early strength shrinkage reducing agent for early strength enhancement. Analyzing the impact of cement hydration reactions on the early-age performance of concrete, the Krstulovic-Dabic hydration kinetics model was utilized to simulate and study the hydration process of the composite cementitious system in concrete. The findings reveal that the introduction of microspheres and cellulose hinders the advancement of early-age strength in concrete, whereas the utilization of an early strength shrinkage reducing agent proves to be beneficial in enhancing early-age strength. Enhancing the hydration reaction rate is observed with the addition of early strength shrinkage reducing agent, whereas the presence of microspheres and cellulose slows down this process. The rate of hydration reaction accelerates, resulting in a greater early-age strength of the concrete.

Keywords: Mechanical properties, Cement hydration, Hydration kinetics.

1. Introduction

With the increasing demands for concrete performance in practical applications, especially in tunnel, water conservancy and hydropower, mining, and other projects, the significance of concrete in construction cannot be underestimated. The exploration of concrete's mechanical properties in the early stages, through the lens of hydration dynamics, has garnered significant attention in the realm of architecture. The cornerstone for the strength development in concrete lies in the hydration process of cement, which directly impacts its performance during the early stages. Hence, an exploration into the dynamics of hydration enables a deeper comprehension of the progression in mechanical properties of concrete during the initial stages.

Currently, extensive studies have been conducted regarding the hydration process of materials based on cement and the impact of various additives on the initial properties of concrete. For example, Krstulovic and colleagues Introduced was a model regarding the kinetics of cement hydration, proposing that the process consists of three fundamental stages: Crystallization nucleation and crystal growth(*NG*), Phase boundary reaction(*I*), Diffuse(*D*) [1]; Yan Peiyu et al. [2] characterizing the three fundamental processes in the cement-based materials' hydration reaction, the Krstulovic hydration kinetics model was utilized, along with the experimental data on hydration heat release, to analyze integral and

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differential equations provided by the model. Parameters of kinetic action, such as the reaction rate constant, order of action, activation energy perceived, and the correlation between rate and reactivity in each reaction phase, were procured; Zhang Luchen et al. [3] by conducting orthogonal experiments, the impact of aluminate liquid accelerator, silica fume, and fly ash on shotcrete performance was analyzed, resulting in the determination that an optimal combination of these components can minimize cement usage, enhance shotcrete strength, decrease cracking, and mitigate rebound and dust issues; Dong Zhenping et al. [4] analyzed the law of influence of fly ash content, mineral powder content and coal gangue content on concrete strength through early compressive strength tests of admixture concrete with different types and amounts of admixture, and studied the interaction of double and triple admixture on concrete strength; He Wenchao et al. [5] studied the effects of fly ash microspheres on the compressive strength, elastic modulus, and creep of concrete, finding that while early compressive strength and elastic modulus decrease, long-term strength and modulus significantly improve.

Building on these researches, this study systematically analyzed the thermal hydration characteristics of composite cement materials by utilizing three different types of mineral additives: microspheres, cellulose, and early strength shrinkage reducing agent. Through the utilization of the Krstulovic-Dabic hydration kinetic model, an investigation into the hydration process of a composite cementitious system in concrete was simulated and explored. This study provides valuable insights for improving the early strength and mechanical characteristics of concrete during its initial stages.

2. Mix ratio design and test scheme

2.1. Raw materials

Pure Portland cement is the type of cement utilized in this study. The mineral admixtures include microspheres, cellulose, and an early strength shrinkage reducing agent. The accelerator accounts for 8% of the cementing material. Tables 1-3 provide the physical properties and other relevant indicators of the materials.

Table 1. Physical Property Indicators of Cement.

Cement	Density (g/cm^3)	Specific surface area (m^2/kg)	Initial setting time (min)	Final setting time (min)
Ordinary Portland cement	3.15	349	151	210

Table 2. Chemical composition of microsphere.

Ingredient	Content/%	Ingredient	Content/%
SiO_2	56.6	Fe_2O_3	5.3
CaO	4.8	Na_2O	1.4
MgO	1.3	K_2O	3.3
Al_2O_3	26.5	SO_3	0.8

Table 3. Physical Property Indicators of Early Strength Shrinkage Reducing Agent.

Specific surface area(m^2/kg)	8h Compressive strength(MPa)	28d Compressive strength ratio(%)	Shrinkage ratio (%)	Radioactivity	
				Internal illumination index I_{Ra}	External illumination index I_r
⩾500	⩾4.0%	⩾105	90	⩽1.0	⩽1.0

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2.2. Test method

2.2.1. Determination of early age strength of concrete

Based on the guidelines provided in the 'Standard Test Methods for Physical Mechanical Properties of Concrete' (GB/T 5008-1-2019), the compressive strength and split tensile strength of four distinct types of hydraulic binders, namely CC (concrete group without admixtures), CE (microsphere), CELL (cellulose), and AC (early strength shrinkage reducing agent), were determined following a 24-hour standard curing period. Table 4 provides the detailed breakdown of the composition and specifications of each cementitious material.

Table 4. Composition of each group of cementitious materials.

Group number	Material code	Cement /g	Water /g	Stone /g	Sand /g	Microsphere /g	Cellulose /g	Early strength shrinkage reducing agent /g
1	CC	432	192	651	977	0	0	0
2	CE	388.8	192	651	977	43.2	0	0
3	CELL	432	192	651	977	0	4.32	0
4	AC	432	192	651	977	0	0	21.6

2.2.2. Determination of hydration heat of cement

As per the guidelines provided in the document titled 'Method for Determining Cement Hydration Heat (GB_T12959-2008)', the hydration heat of four distinct cementitious materials, namely CC, CE, CELL, and AC, was evaluated using a C80 microcalorimeter (direct method) [6-7]. By utilizing the calorimeter in a constant temperature setting, this technique allows for direct measurement of the temperature alteration of cement mortar (due to hydration) within the calorimeter, by computing the total of heat gained and lost in the calorimeter to attain the hydration heat of cement hydration within 1d.

3. Hydration kinetics model of cement-based materials

The impact of the hydration process on the development of concrete mechanical properties is significant. Dynamic simulation and description of hydration kinetics can effectively unveil the internal mechanism and characteristics of gelled materials. The Krstulovic-Dabic model, an acclaimed and typical representation, posits that three primary stages constitute the hydration reaction in materials based on cement: Crystallization nucleation and crystal growth (*NG*), Phase boundary reaction (*I*), Diffuse (*D*). Simultaneous occurrence of the three processes is feasible, and the progression of the hydration process relies on the slowest among them [8-10].

Crystallization nucleation and crystal growth(*NG*):

$$[-ln(1-\alpha)]^{1/n} = K_1(t-t_0) = K_1^{'}(t-t_0) = K_{NG}(t-t_0)$$

Phase boundary reaction(*I*):

$$[1-(1-\alpha)^{1/3}]^1 = K_2 r^{-1}(t-t_0) = K_2^{'}(t-t_0) = K_I(t-t_0)$$

Diffuse(*D*):

$$[1-(1-\alpha)^{1/3}]^2 = K_3 r^{-2}(t-t_0) = K_3^{'}(t-t_0) = K_D(t-t_0)$$

By differentiating the above three equations, we can obtain the dynamic equations, which represent the hydration rates of the *NG*, *I* and *D* processes.

Differential expression of *NG* process:

$$\mathrm{d}\alpha/\mathrm{d}t = F_1(\alpha) = K_1^{'} n(1-\alpha)[-ln(1-\alpha)]^{n-1/n}$$

Differential expression of *I* process:

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

Differential expression of D process:

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

Where α is hydration degree; $K_1(K_1')$, $K_2(K_2')$, $K_3(K_3')$ are hydration reaction rate constants of the three hydration reaction processes. t_0 is the time when the induction period ends; n is the order of reaction; r is the diameter of the particles involved in the reaction.

4. Results and discussion

4.1. Development law of early age strength of concrete

Table 5 displays the recorded compressive and splitting strength values for each experimental group. Based on the data presented in Table 5, the compressive strength of the cement block replaced by microspheres (CE) is slightly lower, while the splitting strength is significantly lower compared to the CC group. The specimens containing cellulose (CELL) exhibited a notable decline in both compressive and splitting strength. Enhancing the compressive and splitting strength of the specimens is achieved through the application of the early strength shrinkage reducing agent (AC). The introduction of microspheres and cellulose into concrete has been found to have adverse effects on the initial strength, however, the effectiveness of boosting this strength with the presence of an early strength shrinkage reducing agent has been shown.

Table 5. The strength values of sprayed concrete with various admixtures in terms of compressive and splitting.

Group	Compressive strength /MPa	Splitting strength /MPa
CC	6.50	0.40
CE	6.32	0.26
CELL	4.11	0.17
AC	6.90	0.44

4.2. Hydration and heat release characteristics of composite cementitious materials

Figure 1 and Figure 2 respectively show the relationship between hydration heat release and hydration rate of CC, CE, CELL and AC different cementing materials with time. The observation from Figure 2 reveals that despite the fact that microspheres and cellulose have an effect on increasing the initial heat release peak value and delaying its occurrence, they also play a role in diminishing the time taken for the second heat release peak value and accelerating its arrival. Overall, the presence of microspheres and cellulose can hinder the maximum rate of hydration heat reaction, reduce the peak rate of volcanic ash reaction, and expedite the arrival of the peak value.

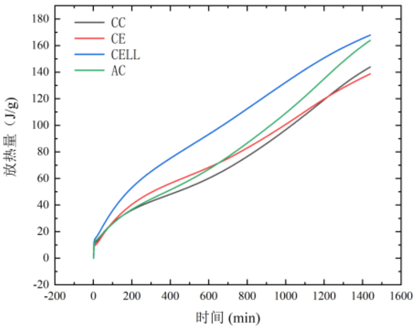

Figure 1. Relationship between hydration heat release and time of composite cementitious materials.

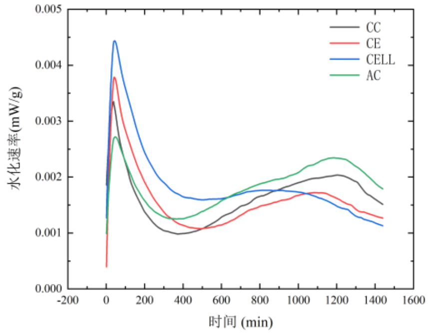

Figure 2. Relationship between hydration heat release rate and time of composite cementitious materials.

The use of an early strength shrinkage reducing agent can result in a decrease in the initial peak of hydration heat release, but it may lead to a significant increase in the rate of the subsequent exothermic reaction, aligning with the earlier enhancement in compressive and splitting strength of the AC group mentioned previously. Despite the rise in the first reaction peak value of hydration heat release observed post the introduction of microspheres and cellulose, there was a noticeable decrease in both the reaction rate and overall amount of hydration heat release in the second part of hydration, corresponding to the early compressive and splitting strength of CE and CELL groups as mentioned above.

4.3. Hydration kinetics analysis of composite cementitious materials

The relationship between $d\alpha/dt$ and α in the hydration process of CC, CE, CELL and AC is plotted to obtain Figure 3-Figure 6. The intersection point between *NG* and *I* and the intersection point between *I* and *D* in the figure are represented by α_1 and α_2 respectively. That is the change point of the $NG \rightarrow I$ process and the change point of the $I \rightarrow D$ process. It can be seen from the figure that Krstulovic-Dabic hydration kinetics model can well reflect the hydration reaction process of the composite gelling system, especially the $NG \rightarrow I$ process. Concurrently, it further signifies the intricate and ongoing nature of the hydration process within the composite gelling system, rather than a singular reaction.

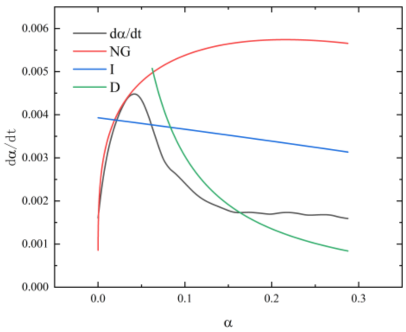

Figure 3. The relationship between $d\alpha/dt$ and α in the hydration process of CC group.

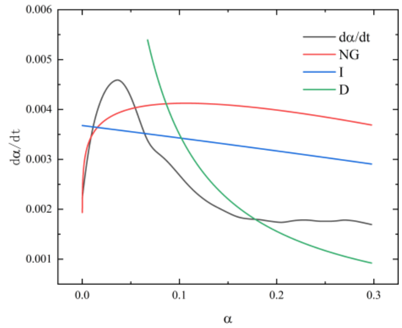

Figure 4. The relationship between $d\alpha/dt$ and α in the hydration process of CE group.

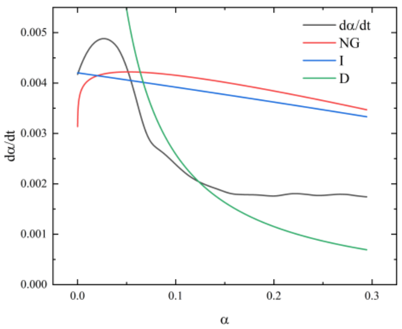

Figure 5. The relationship between $\mathrm{d}\alpha/\mathrm{d}t$ and α in the hydration process of CELL group.

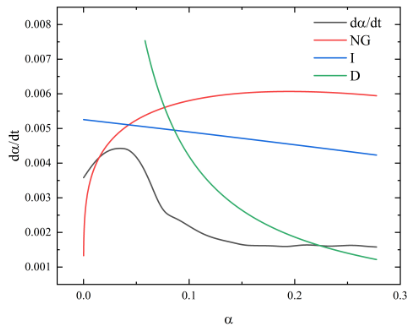

Figure 6. The relationship between $\mathrm{d}\alpha/\mathrm{d}t$ and α in the hydration process of AC group.

Furthermore, the hydration process parameters for the gelling materials in the four groups were also obtained, as shown in Table 6.

Table 6. Four sets of parameters during the hydration process of cementitious materials.

Group	n	K_1'	K_2'	K_3'	Hydration mechanism	α_1	α_2	α_2-α_1
CC	1.321	0.007816	0.001310	0.0000750	*NG→I→D*	0.0272	0.0834	0.0562
CE	1.127	0.005239	0.001226	0.0000864	*NG→I→D*	0.0156	0.1020	0.0864
CELL	1.056	0.004925	0.001401	0.0000639	*NG→I→D*	0.0203	0.0669	0.0466
AC	1.276	0.008222	0.001752	0.0001035	*NG→I→D*	0.0429	0.0860	0.0431

According to the data in the table, K_3' in the four groups of experiments is significantly smaller than K_1' and K_2', indicating that among the three basic processes of hydration reaction, the rate of diffusion (*D*) is significantly lower than that of crystallization nucleation and crystal growth (*NG*) and phase boundary reaction (*I*). It controls the rate of the whole hydration reaction. The values of n and α_2-α_1 in the cellulose group are lower than those in the CC control group, this suggests that the inclusion of cellulose led to a noticeable enhancement in the pace of cement hydration reactions, resulting in the hydration heat release rate reaching a higher level at the beginning but almost no second heat release peak. The values of n and α_2-α_1 in the early strength shrinkage reducing agent group decreased significantly compared with the control group, and the values of K_3' increased significantly. This suggests that by incorporating an early strength shrinkage reducing agent, there is an observable enhancement in the pace and intensity of the second volcanic ash reaction.

5. Conclusion

The presence of microspheres and cellulose in concrete mineral admixtures can hamper the early age strength of concrete, but this can be counteracted by incorporating appropriate early strength shrinkage reducing agents. Enhancing the early-age strength and mechanical properties of concrete can be achieved by appropriately reducing the content of microspheres and cellulose in concrete mineral admixtures and incorporating suitable early strength shrinkage reducing agents.

The enhancement of the secondary reaction of volcanic ash due to the introduction of an early strength shrinkage reducing agent leads to an acceleration and intensification of the overall hydration process. Conversely, the incorporation of microspheres and cellulose results in a decrease in the overall rate of hydration reaction.

With the acceleration of the hydration reaction rate, concrete exhibits an increased early age strength. Thus, practical steps can be implemented to heighten the pace of concrete's hydration reaction, effectively boosting its initial strength.

References

[1] Krstulovic R and Dabic P. A conceptual model of the cement hydration process [J]. Cem Concretes, 2000, 30(5): 693−698.

[2] Yan Peiyu and Zheng Feng. Kinetics model for the hydration mechanism of cementitious materials [J]. Journal of the Chinese ceramic society, 2006(05): 555-559.

[3] Zhang Luchen, Li Shuchen and Li Shucai, et al. Effect on the performance of shotcrete mixed with silica fume and fly ash [J]. Journal of Shandong university (Engineering science), 2016, 46(05): 102-109.

[4] Dong Zhenping, Zhang Chengzhong and Sun Guangshuai, et al. Experimental research on early strength of mineral admixture concrete [J]. Concrete, 2017(10): 83-86+92.

[5] He Wenchao, Xue Jing and Wang Wei. Research on strength and creep characteristics of concrete containing fly ash microbead [J]. Inorganic chemicals industry, 2023, 55(01): 124-128+158. DOI:10. 19964/j.issn.1006-4990.2022-0084.

[6] Zhang Xiaoping, Liu Yan and Ji Xian-Kun, et al. Analysis of hydration heat test method of cement [J]. Sichuan Cement, 2020(10): 7-8+25.

[7] Luo Gang and Deng Youning. Development of a device for measuring heat of hydration of cement (Direct method) [J]. Jilin Building Materials, 1998(03): 13-15.

[8] Zeng Kelin, Wen Dongchang and Yang Rong, et al. Effect of Temperature Rising Inhibitor on Early Hydration Kinetics of Composite Cementitious Material [J]. Bulletin of the Chinese ceramic society, 2023,42(08): 2712-2721. DOI:10. 16552/j.cnki.issn1001-1625. 2023.08.001.

[9] Fernandez-Jimenez A, Puertas F and Arteaga A. Determination of kinetic equations of alkaline activation of blast furnace slag by means of calorimetric data [J]. J Therm Anal Calori, 1998, 52(2): 945−955.

[10] de Schutter G. Hydration and temperature development of concrete made with blast-furnace slag cement [J]. Cem Concr Res, 1999, 29(1): 143−149.