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A Numerical Hydration Model to Predict the Macro and Micro Properties of Cement–Eggshell Powder Binary Blends

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Abstract: This study aims to propose a hydration kinetic model for the cement–eggshell powder binary system and predict the performance development of composite concrete through this model. The specific content and results of the model are as follows. First, based on the cumulative hydration heat of the cement and eggshell powder binary system in the first seven days, the parameters of the cement hydration model and the eggshell powder nucleation parameter are calibrated. These parameters remain constant regardless of the mix ratio. Secondly, the hydration heat of the cement–eggshell powder binary system over 28 days is calculated using the hydration model. The results show that at 28 days, for specimens with 0%, 7.5%, and 15% eggshell powder substitution, the cement hydration degrees are 0.832, 0.882, and 0.923, respectively. The hydration heat per gram of cement is 402.69, 426.88, and 446.73 J/g cement, respectively, while the hydration heat per gram of binder is 402.69, 394.86, and 379.72 J/g binder, respectively. Additionally, the hydration model is used to calculate the chemically bound water and calcium hydroxide content of the cement–eggshell powder binary system. At 28 days, for samples with 0%, 7.5%, and 15% eggshell powder, the chemically bound water content is 0.191, 0.188, and 0.180 g/g binder, respectively, and the calcium hydroxide content is 0.183, 0.179, and 0.173 g/g binder, respectively. Finally, a power function is used to regress the calculated hydration heat with experimentally measured compressive strength and surface electrical resistivity. The correlation coefficients for compressive strength and surface electrical resistivity are 0.8474 and 0.9714, respectively. This is because the strength weak point effect of eggshell powder has minimal impact on hydration heat and surface electrical resistivity experiments but significantly affects the strength experiment.

Keywords: eggshell powder; hydration model; compressive strength; hydration heat; hydration products

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1. Introduction

Concrete is one of the most widely used building materials. At present, experimental research on concrete is very extensive, such as strength development, chemical composition, durability, and hydration heat. In addition to extensive experimental research, some researchers have proposed theoretical models to predict the development of various properties of concrete materials.

A hydration model is a type of concrete material model. At present, many hydration models of concrete have been established. According to the types of cementitious materials, hydration models can be roughly divided into the following categories:

The review of hydration models of Portland cement concrete is as follows. The hydration model of Bregugel [1,2] considered the influence of cement mineral composition, cement particle distribution, curing temperature, and water–cement ratio on concrete performance. Through the regression of experimental results, the relationship between the input parameters of the model and the mineral composition of cement is obtained. Based on the hydration model, the hydration degree, pore structure, and compressive strength of concrete are predicted. The hydration model proposed by Park et al. [3] calculated the hydration degree, pore structure formation, relative humidity change, and hydration heat release of high-strength concrete. The relationship between the hydration model parameters and the composition of concrete materials is obtained by using the neural network method. B. Lothenbach and F. Winnefeld [4] proposed a multi-component hydration model to calculate the hydration degree of cement. Their method considered the thermodynamic equilibrium between solid hydration products and pore solution, and calculated the composition of hydration products and the concentration of ions in pore solution. The hydration model proposed by Bentz [5] considered the influence of the water–cement ratio and spatial distribution of hydration products on hydration rate, which is suitable for both general strength concrete and high strength concrete. The hydration model proposed by Scrivener et al. [6] considered the growth of calcium silicate hydrate (C-S-H), the formation of hydration exothermic peak, the reduction in reaction rate in the late reaction, and the influence of pore structure on hydration reaction rate.

With the development of concrete technology, more and more mineral admixtures are used in concrete production. There are many types of mineral admixtures, and common mineral admixtures mainly include silica fume, fly ash, slag, and limestone powder.

First, the literature on silica fume is summarized as follows. Papadakis [7] proposed chemical reaction equations for silica fume based on the microscopic analysis of the cement–silica fume binary system and calculated the final composition and porosity of the reaction products of the cement–silica fume binary mixture. The model proposed by Bentz et al. [8] considered the reaction heat of cement and the reaction heat of silica fume, calculated the specific heat of silica fume concrete during hardening, and predicted the adiabatic temperature rise and the composition of hydration products of concrete mixed with silica fume. The model proposed by Yajun and Cahyadi [9] determined the calcium hydroxide produced by cement hydration and the calcium hydroxide consumed by silica fume, and calculated the reactivity of silica fume and the property development of concrete through the change in calcium hydroxide content. The model proposed by Maekawa et al. [10] considered the nucleation effect and chemical reaction effect of silica fume, obtained the hydration heat released by unit mass of silica fume and the amount of calcium hydroxide consumed by unit mass of silica fume, and predicted the development process of compressive strength under different mix proportions and different curing temperatures.

Secondly, the literature review on fly ash is summarized as follows. Based on microstructure experiments, Papadakis [11] proposed chemical reaction equations to predict the final composition and porosity of the reaction products of low calcium fly ash, and confirmed the correctness of the model through experiments with a curing time of 1 year. Baert et al. [12] used the power function method to simulate the reactivity of cement mineral components and the reactivity of fly ash, clarified the kinetic process of cement hydration and fly ash reaction, and studied the influencing factors of fly ash reaction. The model proposed by Kinomura and Ishida [13] considered the influence of calcium hydroxide on the reactivity of fly ash, and calculated the reactivity and hydration heat of fly ash under different mix proportions and curing conditions. The hydration model proposed by Krishnya et al. [14] calculated the reactivity of cement and the reactivity of fly ash, and obtained the composition and compressive strength development of various reaction products through thermodynamic calculations.

Again, the literature review on slag is as follows. De Schutter [15] simulated the hydration process of cement with high slag content, distinguished the reactions of cement and slag through the experimental results of isothermal hydration heat, and calculated the heat release of hardening concrete. The development of various properties of concrete was predicted based on the heat release. Chen and Brouwers [16] proposed a model that considered the effect of slag on the Ca–Si and Al–Si ratios of hydration products, clarified the calculation model of hydration products of slag concrete, and quantitatively calculated the composition of C-S-H and other hydration products, chemical shrinkage, and capillary water content. Luan et al. [17] proposed a model that, collecting the measurement results of slag reactivity by various researchers, highlighted the controlling factors of slag reaction, and found the hydration heat released when the unit mass of slag reacts. Königsberger and Carette [18] proposed a hydration model that calculated the reactivity of cement mineral composition, slag reactivity, and the composition of hydration products of slag concrete, and verified the correctness of the proposed model through 54 different mix ratios in seven different laboratories.

Finally, the review of the research model on limestone powder is as follows. Bentz [19] proposed a model that considered the physical effects and chemical reactions of limestone, calculated the strength of concrete through the gel–space ratio, and found that when limestone was used in low water–binder ratio concrete, the increasing reactivity of cement can reduce the loss of strength. Poppe and Schutter [20] discovered the effect of limestone on the hydration exothermic peak based on isothermal hydration heat analysis, and calculated the hydration heat release and temperature change of concrete containing a large amount of filler materials. The model proposed by Barbara [21] calculated the hydration degree of cement mineral composition, considered the chemical reaction between limestone and the aluminum phase in the cementitious material, and clarified the effect of this chemical reaction on the hydration solid products and pore solution. Mohamed et al. [22] proposed a hydration model that considered the reactivity of cement, the acceleration effect of limestone on cement hydration, and the chemical reaction products of limestone.

Through the above literature review, we can see that for concrete with mineral admixtures, most of the previous hydration models focused on traditional mineral admixtures, such as silica fume, fly ash, slag, and limestone powder. Eggshell powder is a powdered product after grinding discarded eggshells. It is currently mainly used in the livestock and poultry industry, and its application in the field of concrete is still limited. The main chemical component of eggshell powder is calcium carbonate, which is similar to limestone powder, but unlike limestone powder, eggshell powder is much softer. This difference in physical properties will affect the development of various properties of concrete. In order to fill the gap in theoretical research on eggshell powder concrete, this paper proposes a numerical hydration model of the cement–eggshell powder binary system. Through this hydration model, the developments of hydration heat, compressive strength, hydration products, and surface electrical resistivity of concrete are predicted. The authors believe that our model fills the gap in theoretical research and can promote the recycling of eggshell powder and the sustainable development of the overall social industry.

2. Hydration Model of Cement–Eggshell Powder Binary Blends

2.1. Hydration Model of Cement

In the binary system of cement–eggshell powder, the hydration reaction of cement plays a leading role. The presence of eggshell powder plays a physical role and a chemical role. The physical role mainly includes a dilution effect and a nucleation effect. The chemical role means that the eggshell powder can react with the aluminum phase in cement to form carbo-aluminate. Generally speaking, the main component of eggshell powder is calcium carbonate, which has a weak chemical reaction ability. Some studies have reported that the reactivity of calcium carbonate is 5% at 180 days [19] and 1–2% at 28 days [23]. This study is mainly concerned with the development of material properties of the cement–eggshell powder binary system from the beginning of mixing to 28 days. The reactivity of eggshell powder is very low within this time range, so in this study, the chemical reaction of eggshell powder is ignored.

The hydration reaction of cement is a process that develops dynamically over time. The hydration rate of cement can be calculated using the following Equation (1):

$$\frac{d\alpha}{dt} = \frac{3\rho_w}{(v+w_g)r_0\rho_c}\left[\frac{W_0-0.38C_0\alpha}{W_0}\right]\left[\frac{S_w}{S_0}\right]\frac{1}{\left(\frac{1}{B/\alpha^{1.5}+C\alpha^3}-\frac{r_0}{D_{e0}\ln\left(\frac{1}{\alpha}\right)}\right)+\frac{r_0}{D_{e0}\ln\left(\frac{1}{\alpha}\right)}(1-\alpha)^{\frac{-1}{3}}+\frac{1}{kr}(1-\alpha)^{\frac{-2}{3}}} \tag{1}$$

In this Equation (1), α and t represent the degree of hydration and time, respectively. B, C, kr, and De_0 are parameters describing the cement hydration process. Parameter B is related to the rapid heat release process at the beginning of hydration. Parameter C is related to the gradual increase in hydration heat at the end of the latent period. Parameter kr is related to the phase boundary reaction period of the hydration reaction. Parameter De_0 is related to the diffusion period of the hydration reaction. $De_0\ln(1/\alpha)$ means that when the hydration reaction is about to end (α = 1), the hydration heat release rate is approximately equal to 0. These reaction process parameters B, C, kr, and De_0 can be calculated from the mineral composition of cement or calibrated from the experimental results of hydration heat.

First, Equation (1) considers some physical parameters of cement and water. r_0 represents the average particle size of cement particles, ρ_c represents the density of cement, and ρ_W represents the density of water. Secondly, Equation (1) considers some chemical reaction constants of the hydration reaction process, ν represents the chemically bound water in the reaction of 1 g of cement and water (ν = 0.23), w_g represents the physically bound water in the reaction of 1 g of cement and water (w_g = 0.15), (v + w_g) represents the total mass of water consumed when 1 g of cement and water reacts, 0.38 g = (0.23 g + 0.15 g), and finally, Equation (1) considers the effects of capillary water and pore structure formation on the hydration rate. W_0 represents the initial mass of mix water, C_0 represents the initial mass of cement in the mix, ($W_0 - 0.38\,C_0\alpha$) represents the mass of capillary water remaining during hydration, and ($W_0 - 0.38\,C_0\alpha$)/W_0 represents the ratio of the mass of capillary water to the mass of initial water during hydration. At the beginning of hydration (α = 0), this ratio is 1. As hydration proceeds, the value becomes less than 1. On the other hand, S_0 represents the contact area between cement particles and water at the beginning of hydration, and S_W represents the contact area between cement particles and water during hydration. At the beginning of the hydration reaction, the ratio of S_W/S_0 is also 1. As the hydration proceeds, S_W/S_0 becomes less than 1. In general, S_W/S_0 is a function of the degree of hydration, which describes the effect of reducing the hydration rate caused by the formation of pore structure.

2.2. Physical Effect Model of Eggshell Powder

2.2.1. Dilution Effect

When eggshell powder is used to replace partial cement, the mass ratio of cement to water increases, which accelerates the reaction of cement. This is the dilution effect of eggshell powder. The dilution effect of eggshell powder is considered using the item ($W_0 - 0.38\,C_0\alpha$)/W_0.

2.2.2. Nucleation Effect

During the hydration process of cement, eggshell powder is similar to an inert filler. A part of the hydration product can be formed on the surface of the eggshell powder, thereby reducing the thickness of the hydration product on the cement surface, reducing the resistance of capillary water to the anhydrous cement, and accelerating the diffusion process of the hydration reaction. We use the following Equation (2) to consider the nucleation effect of eggshell powder:

$$De_0{}' = De_0\left(1 + \mathrm{nu} \times \frac{\mathrm{EG}_0}{\mathrm{EG}_0 + \mathrm{C}_0}\right) \tag{2}$$

De_0' represents the diffusion parameter considering the nucleation effect of eggshell powder, EG_0 represents the mass of eggshell powder in the mix, and nu is the nucleation effect parameter of eggshell powder. $EG_0/(EG_0 + C_0)$ represents the substitution rate of eggshell powder. When the substitution amount of eggshell powder is 0, De_0' is the same as De_0.

2.3. Summary of Eggshell Powder Hybrid Hydration Model

The hydration model proposed in this paper considers the hydration reaction of cement, the dilution effect of eggshell powder, and the nucleation effect of eggshell powder. The input parameters of the model include the parameters B, C, kr, and De_0 (shown in Equation (1)) of the cement hydration model and the nucleation parameter nu (shown in Equation (2)) of eggshell powder. These parameters can be obtained through calibration of experimental results. Furthermore, based on the hydration degree calculated by the eggshell powder hybrid hydration model, the property development of hybrid concrete can be predicted.

3. Performance Predictions of Cement–Eggshell Powder Binary System

3.1. Experimental Summary

In our previous study [24], we conducted macroscopic and microscopic experimental studies on the cement–eggshell powder binary system. The experimental details are shown in the Supplementary Materials section. In this study, the experimental results of previous studies are used to verify the hybrid hydration model proposed in Section 2. The summary of previous experimental studies is as follows:

Experimental materials: Portland cement was used for cement, the main component of the eggshell powder used was calcium carbonate, and the sand used was standard sand.

Sample mix proportion and curing: The replacement ratio of eggshell powder to binder was 7.5% and 15%. The mass ratio of sand to binder was two, and the mass ratio of water to binder was 0.5. All samples were sealed and cured at a curing temperature of 20 °C.

Test methods: The experimental tests included microscopic tests (cement slurry specimens) and macroscopic tests (mortar specimens). The microscopic tests included the test of isothermal hydration heat from the beginning of mixing to 7 days, and the thermogravimetric analysis (TGA) at the ages of 1 day and 28 days. According to the experimental results of TGA, the mass of chemically bound water and the mass of calcium hydroxide were calculated. The macro tests include compressive strength test and surface electrical resistivity test. The test ages include 3 days, 7 days and 28 days.

3.2. Calibration of Hydration Parameters

According to the content mentioned in the previous Section 2, the parameters B, C, kr, and De_0 of the hydration model can be calibrated through the experimental results of hydration degree. Hydration heat is one of the indicators of hydration degree.

The relationship between hydration heat and hydration degree is shown in Equation (3) as follows:

$$\alpha = Q(t)/Q_{max} \tag{3}$$

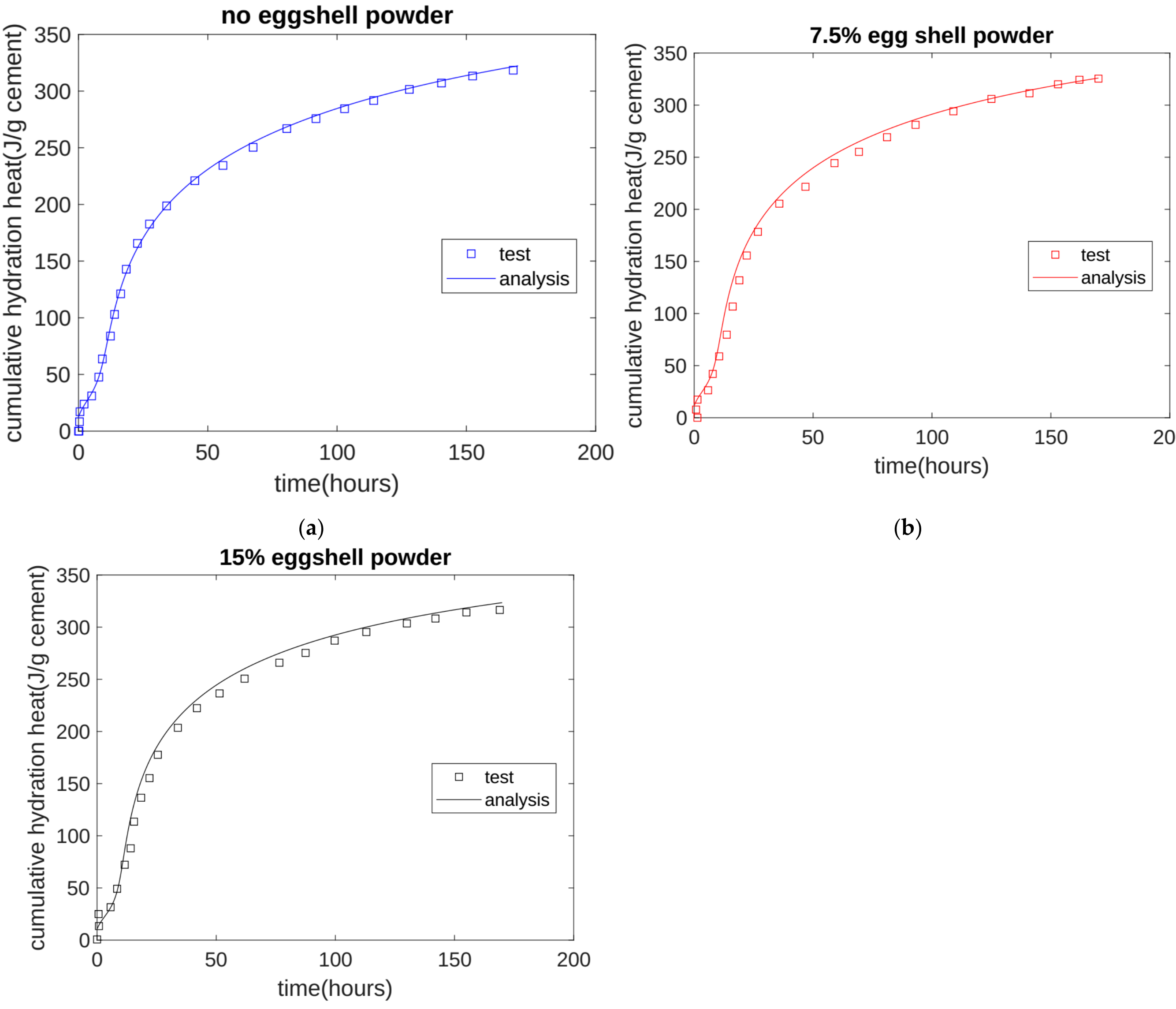
where Q(t) is the result of the cumulative hydration heat measured experimentally, and Q_{max} is the hydration heat released when the 1 g cement is fully hydrated. According to the mineral composition of cement, the maximum hydration heat of 1 g cement is calculated to be $Q_{max} = 484$ J/g cement [8].

The calibration of hydration model parameters is divided into two steps. First, based on the cumulative hydration heat measurement results of cement paste without eggshell powder, the numerical regression method is used to calibrate the parameters B, C, kr, and De_0 of the cement hydration model. Secondly, keeping the parameters B, C, kr, and De_0 unchanged, the nucleation effect parameter nu of eggshell powder was calibrated according to the measurement results of the cumulative hydration heat of 15% eggshell powder. The parameters of these hydration models are presented in Table 1.

Table 1. The values of input parameters of hybrid hydration model.

B (cm/h)	C (cm/h)	kr (cm/h)	De_0 (cm^2/h)	Nu
7.04×10^{-9}	0.0023	3.24×10^{-5}	8.97×10^{-11}	8

The calculation results of the early hydration heat are shown in Figure 1. Figure 1a shows that in the early stage of the hydration reaction, the cumulative hydration heat increases rapidly. This is because in the early stage of the hydration reaction, the rapid reactions of C_3A and C_3S releases a large amount of hydration heat. After about 50 h, the growth rate of hydration heat slows down. This is mainly because diffusion becomes the controlling process of the hydration reaction, which reduces the rate of heat release. From Figure 1a to Figure 1b,c, the cumulative hydration heat of cement based on unit mass increases slightly. This is mainly because the physical effect of eggshell powder accelerates the hydration of cement and releases more heat.



(**a**) (**b**)

(**c**)

Figure 1. Analysis results of hydration heat. (**a**) Analysis results of hydration heat of no eggshell powder specimen. (**b**) Analysis results of hydration heat of 7.5% eggshell powder specimen. (**c**) Analysis results of hydration heat of 15% eggshell powder specimen.

3.3. Evaluation of Long-Term Hydration Heat and Long-Term Hydration Degree

After obtaining the values of parameters of the hydration model (shown in Table 1), we can calculate the long-term hydration heat and long-term hydration degree. The calculation results of the long-term hydration heat are shown in Figure 2a. At 28 days age, for the specimens with 0%, 7.5%, and 15% eggshell powder replacement, the hydration heat based on each gram of cement is 402.69, 426.88, and 446.73 J/g cement, respectively. As the eggshell powder replacement increases, we can see that the heat release based on unit mass of cement increases. This is because the physical effects of eggshell powder, namely the dilution effect and nucleation effect, accelerate the hydration reaction of cement [5]. Figure 2b shows the calculation results of the long-term hydration degree. At 28 days age, for the specimens with 0%, 7.5%, and 15% eggshell powder replacement, the cement hydration degree is 0.832, 0.882, and 0.923, respectively. The development trend of the hydration degree is similar to that of the hydration heat. In the early stage, before about 200 h, the hydration degree increased rapidly. After 200 h, the hydration degree entered a plateau period and the growth rate became slow. At the later stage of the reaction, 28 days, the hydration degree almost stopped with the increase in age. This shows that the compressive strength test age to measure Portland cement concrete based on 28 days of age is roughly reasonable. Figure 2c shows the calculation results of long-term hydration heat based on 1 g binder. At 28 days of age, for specimens with 0%, 7.5%, and 15% eggshell powder substitution, the hydration heat based on each gram of binder is 402.69, 394.86, and 379.72 J/g binder, respectively. When the hydration heat is expressed as per gram of binder, the cumulative hydration heat of 28 days decreases with the increase in eggshell powder substitution. This is because in the later stage of hydration, the dilution effect of eggshell powder plays a dominant role, reducing the cumulative hydration heat [5]. While nucleation increases the cumulative heat of hydration per gram of cement (Figure 2a), dilution decreases the heat of hydration per gram of binder (Figure 2c).

3.4. Prediction of the Amount of Hydration Products

Based on the hydration degree of cement, we can predict the amount of chemically bound water and calcium hydroxide produced. Assuming that the chemically bound water is proportional to the hydration degree of cement, the calculation equation of chemically bound water W(t) is as follows [1–3]:

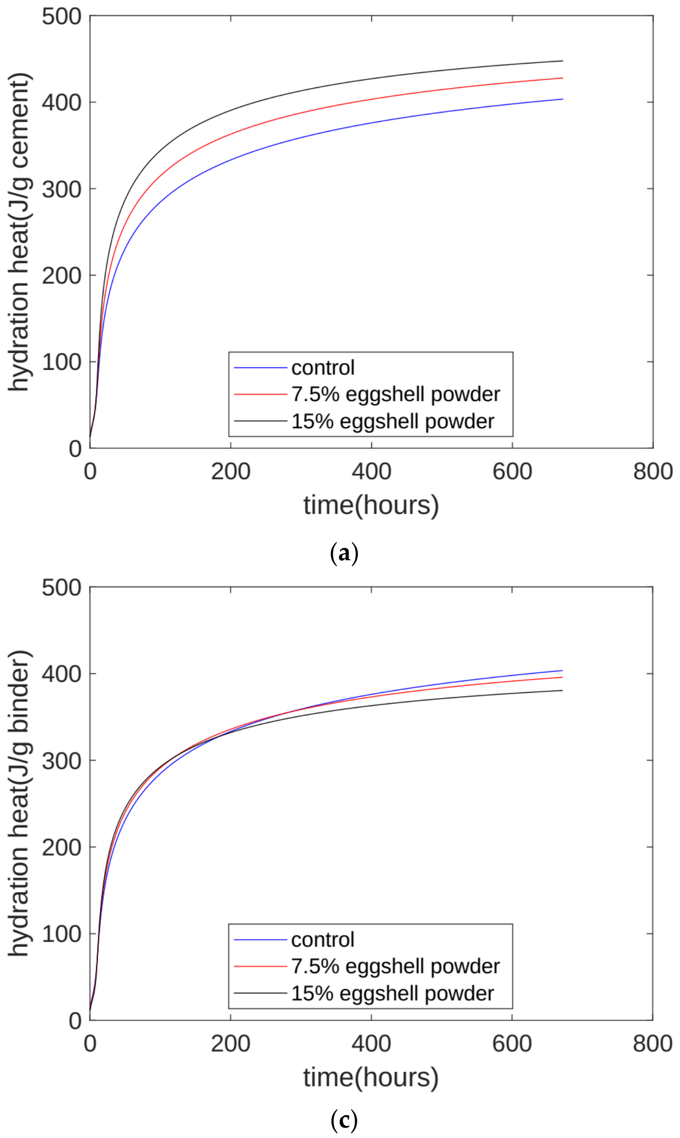
$$W(t) = C_0 \times \alpha \times 0.23 \tag{4}$$

The coefficient 0.23 in Equation (4) means that when 1 g of cement reacts completely, the mass of chemically bound water produced is 0.23 g. We need to note that the chemically bound water calculated by Equation (4) is based on the unit mass of cement, and the chemically bound water measured experimentally is based on the unit mass of binder. It needs to be transformed to compare with the experimental results.

Assuming that the content of calcium hydroxide and cement is proportional, the mass of calcium hydroxide CH(t) is calculated as follows [1,2]:

$$CH(t) = C_0 \times \alpha \times 0.22 \tag{5}$$

The coefficient 0.22 in Equation (5) means that when 1 g of cement reacts completely, the mass of calcium hydroxide produced is 0.22 g [24]. This 0.22 is specific to the cement we used [24]. For other types of cement, the mass of calcium hydroxide produced per unit mass of cement will be different [25].



(**a**) (**b**) (**c**)

Figure 2. Long term hydration heat and hydration degree. (**a**) Long term hydration heat for 1 g cement. (**b**) Long term hydration degree. (**c**) Long term hydration heat for 1 g binder.

Figure 3a shows the calculated results of chemically bound water. Similar to the heat of hydration, chemically bound water is also one of the indicators for measuring the degree of cement hydration. In the early stage, the chemically bound water increases rapidly, and in the later stage, the increase rate of chemically bound water is not obvious. Overall, the calculated results are in good agreement with the experimental results. At the early age of 1 day, the calculated chemically bound water is slightly lower than the experimentally measured chemically bound water. This is because in our simulation, it is assumed that the hydration rates of all cement mineral components C_3S, C_2S, C_3A, and C_4AF are the same. In fact, compared with other components, the hydration rate of C_2S is slower. Correspondingly, the chemically bound water generated by C_2S appears later than the chemically bound water of other components. Therefore, the measured value of chemically bound water is slightly higher than the predicted value of chemically bound water in one day. Figure 3b shows the calculated results of calcium hydroxide. Calcium hydroxide is also a hydration product of cement. Both C_3S and C_2S will produce calcium hydroxide when they are hydrated. In one day, the calculated results of calcium hydroxide are also slightly lower than the experimental results. This is also because the calcium hydroxide generated by C_2S appears later than the calcium hydroxide generated by C_3S, resulting in the measured value of calcium hydroxide being slightly higher than the predicted value of calcium hydroxide in one day.

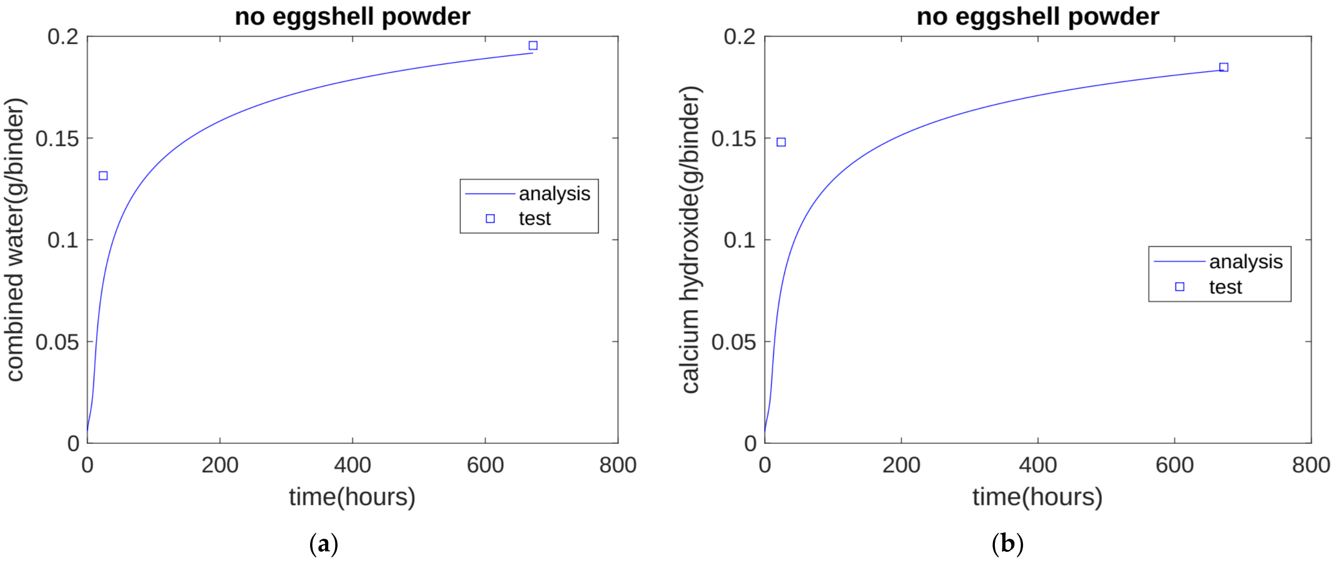
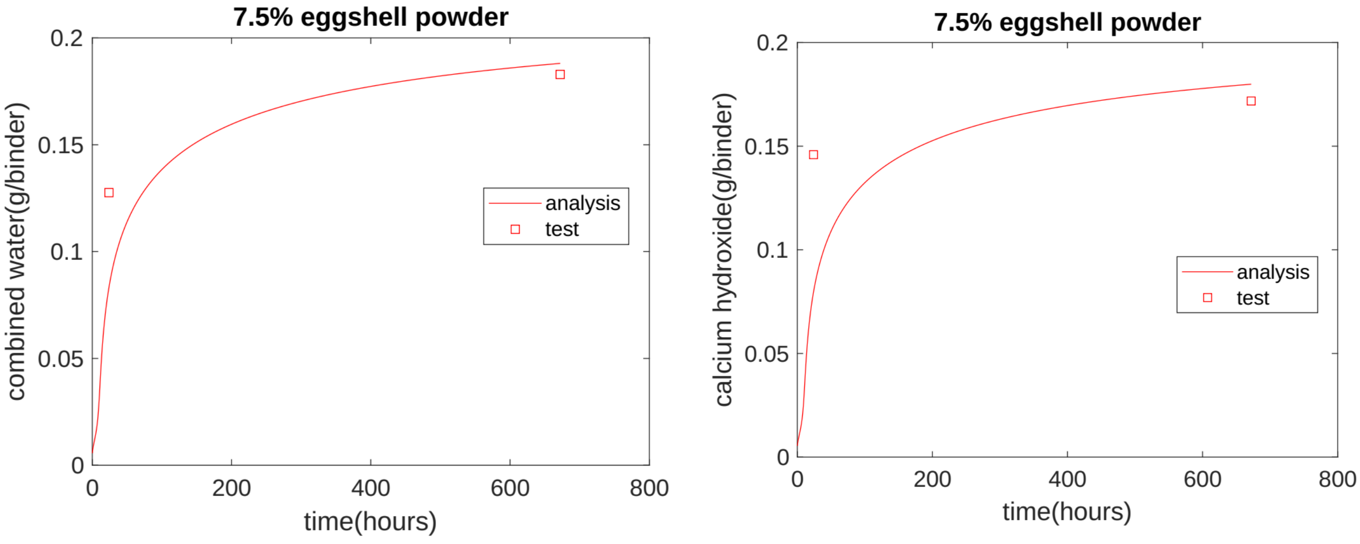


Figure 3. Combined water and calcium hydroxide contents—no eggshell powder. (**a**) Combine water content—no eggshell powder. (**b**) Calcium hydroxide content—no eggshell powder.

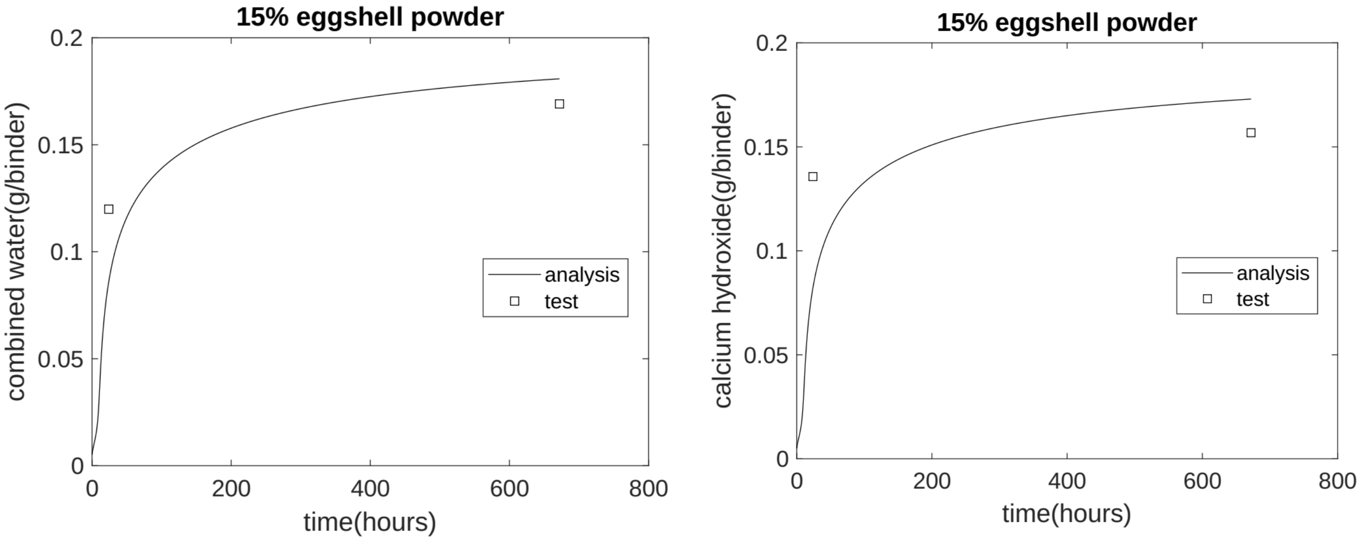
Figure 4a,b show the predicted results of chemically bound water and calcium hydroxide for the 7.5% eggshell powder specimen, and Figure 5a,b show the predicted results of chemically bound water and calcium hydroxide for the 15% eggshell powder specimen. From Figure 3a, Figure 4a, and Figure 5a, we can see that at 28 days, for the samples with eggshell powder content of 0%, 7.5%, and 15%, the chemically bound water at 28 days is 0.191, 0.188, and 0.180 g/g binder, respectively. As the eggshell powder content increases from 0 to 15%, the mass of chemically bound water per gram of binder decreases. This is because in the later stage of curing, as the eggshell powder content increases, the dilution effect of the eggshell powder plays a dominant role, reducing the amount of chemically bound water generated. From Figure 3b, Figure 4b, and Figure 5b, at 28 days, for samples with 0%, 7.5%, and 15% eggshell powder, the calcium hydroxide at 28 days is 0.183, 0.179, and 0.173 g/g binder, respectively. The development trend of calcium hydroxide is similar to that of chemically bound water. In addition, we can see that at 28 days, as shown in Figure 5a (15% eggshell powder), the calculated chemically bound water is slightly higher than the experimental chemically bound water. This may be because in the calculation, we ignored the pore refinement effect of the chemical reaction of eggshell powder. In our calculation, it is assumed that all capillary water ($W_0 - 0.38\ C0\alpha$) can be used by cement hydration. However, the chemical reaction of eggshell powder will refine the pores, resulting in an increase in the fine pore content [26,27]. In fact, the capillary water available for cement hydration reaction is lower than ($W_0 - 0.38\ C0\alpha$). Since this pore refinement effect is not considered in our calculation, the calculated values of hydration degree and chemically bound water are slightly higher. At 28 days, for the specimens containing 15% eggshell powder, the calculated results of chemically bound water and calcium hydroxide are slightly higher than the experimental results.

In addition, because the experimental results of Figures 3–5 are from reference [24], in which the authors only give the test results of two time points (1 day and 28 days), we cannot add more test time points in this paper. In future research, more samples/experiments should be used to verify the correctness of the proposed model.



(**a**) (**b**)

Figure 4. Combined water and calcium hydroxide contents—7.5% eggshell powder. (**a**) Combine water content—7.5% eggshell powder. (**b**) Calcium hydroxide content—7.5% eggshell powder.



(**a**) (**b**)

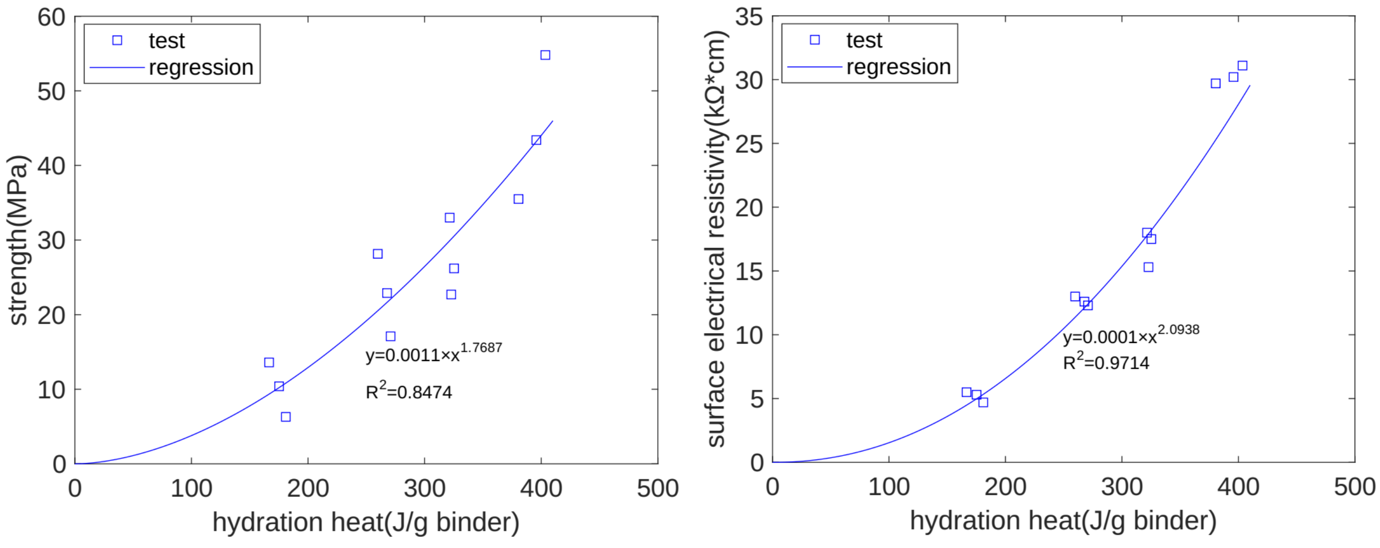
Figure 5. Combined water and calcium hydroxide contents—15% eggshell powder. (**a**) Combine water content—15% eggshell powder. (**b**) Calcium hydroxide content—15% eggshell powder.

3.5. Prediction of Compressive Strength and Surface Electrical Resistivity

We used the hydration model to calculate the cumulative hydration heat results for 3, 7, and 28 days. In our previous study, the compressive strength results for 3, 7, and 28 days were experimentally measured [24]. Using the power exponential function, the compressive strength Fc(t) and hydration heat Q(t) for 3 days, 7 days, and 28 days were regressed, and we found that the relationship between the two is:

$$\mathrm{Fc(t)} = 0.0011 \times \mathrm{Q(t)}^{1.7687} \tag{6}$$

For compressive strength, as shown in Figure 6a, the correlation coefficient between the experimental results and the predicted results is 0.8474.



(**a**) (**b**)

Figure 6. Evaluation of strength and surface electrical resistivity using hydration heat. (**a**) Relation between hydration heat and strength. (**b**) Relation between hydration heat and surface electrical resistivity.

Similarly, in our previous study, the surface electrical resistivity results for 3, 7, and 28 days were experimentally measured [24]. Using the power exponential function to regress the hydration heat Q(t) and surface electrical resistivity R(t) at 3 days, 7 days, and 28 days, we found that the relationship between the two is:

$$R(t) = 0.0001 \times Q(t)^{2.0938} \tag{7}$$

For surface electrical resistivity, as shown in Figure 6b, the correlation coefficient between the experimental results and the predicted results is 0.9714.

By comparing the compressive strength and surface electrical resistivity, we can find that the correlation coefficient of the compressive strength prediction (0.8474) is lower than that of the electrical resistivity prediction (0.9714). We think this is not a mathematical coincidence. First, this is because the compressive strength is closely related to the solid composition of the products. Compared with other solid components, eggshell powder is relatively soft, which is equivalent to the weak point of the strength experiment. This weak point effect has little effect in the hydration heat experiment, but has a great effect in the strength experiment. Secondly, electrical resistivity mainly depends on the capillary water content of the material. For the hydration heat experiment and the surface electrical resistivity experiment, both are closely related to the physical effects of eggshell powder, so the correlation coefficient of electrical resistivity prediction is higher than that of compressive strength prediction.

4. Discussion

The main advantages and disadvantages of the proposed model in this paper are as follows:

First, one of the advantages of the proposed model is that this paper uses the experimental results of the cumulative hydration heat of the first 7 days to calibrate the cement hydration model parameters B, C, kr, and De_0 and the eggshell powder nucleation effect parameter nu. These parameters do not change with the change in the experimental mix ratio. When researchers use other mix ratios to conduct experiments, the model proposed by us can automatically calculate the experimental results corresponding to the new mix ratio, such as hydration heat, microscopic hydration products, compressive strength, and surface electrical resistivity. Therefore, the proposed model can greatly reduce the cost of the experiment and save the time of the experiment.

Second, the second advantage of this paper is that the hydration model proposed in this paper covers multiple levels of prediction. The macro level includes the development of compressive strength and the development of surface electrical resistivity. The strength prediction results are helpful for construction management and structural design, and the surface electrical resistivity results are helpful for the evaluation of steel corrosion rate. The micro level includes hydration heat and the formation of hydration products. The prediction of hydration heat helps to evaluate the early temperature cracking of hardening concrete, and the formation of hydration products helps to estimate the mechanics and durability of concrete from the micro level. The authors believe that these multi-level evaluation models are helpful for the material design of eggshell powder hybrid concrete and promote the recycling of eggshell powder.

Third, the main disadvantage of the proposed model is that compared with other models, this paper does not consider the chemical reaction of eggshell powder [28]. The chemical reaction of eggshell powder can refine the pores and improve the durability [29,30]. When the aluminum content of the binder is relatively high, the reaction between the calcium carbonate in the eggshell powder and the aluminum phase in the binder can generate more carbo-aluminate. In future research, more experimental studies on the chemical reaction of eggshell powder should be carried out. After obtaining a large number of experimental results, the chemical reaction effect and pore refinement effect of eggshell powder should be considered in the hydration model.

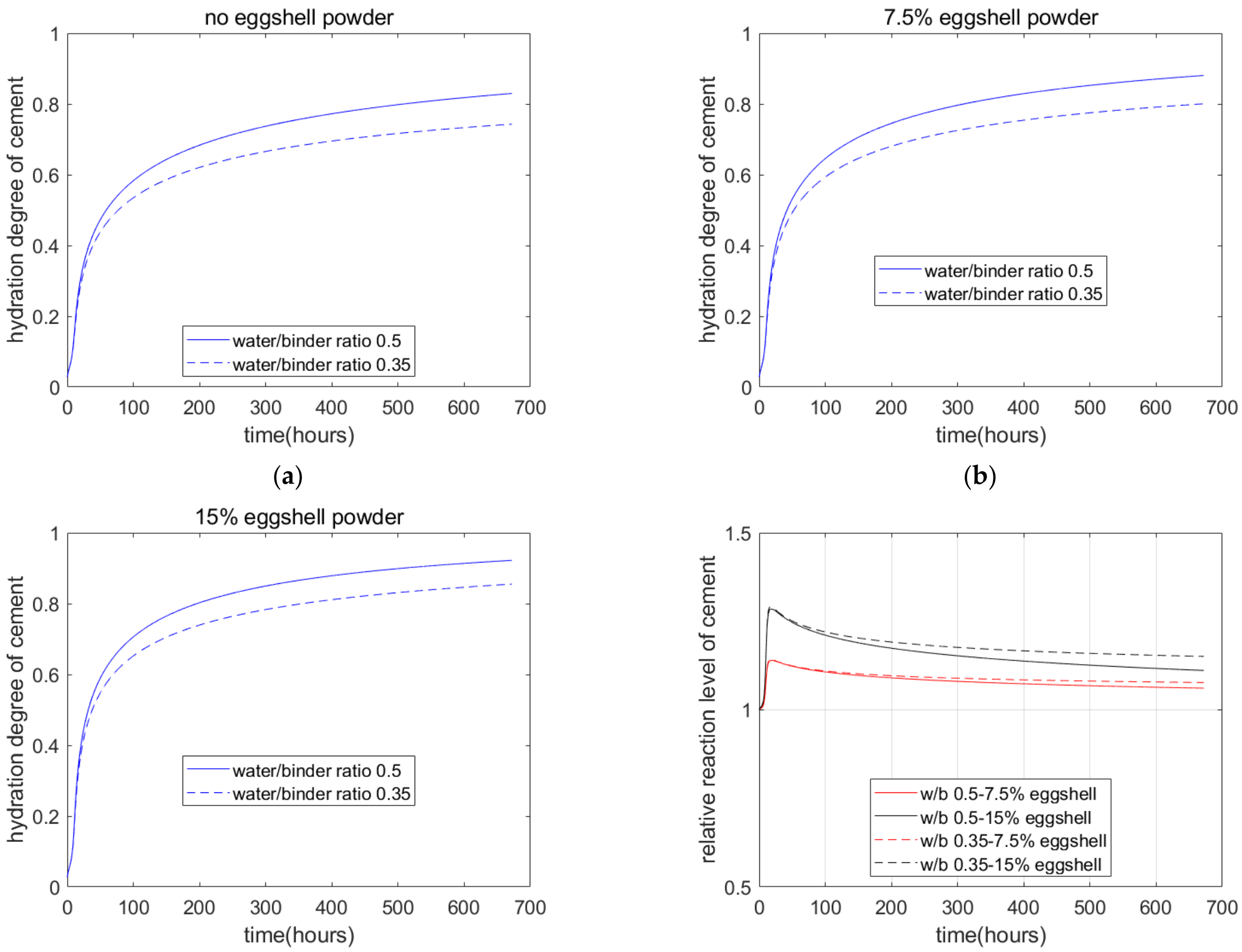
Fourth, another major disadvantage of the proposed model is that the input parameters of the model are obtained by calibration of the experimental results of cumulative hydration heat. Some researchers may not have the experimental conditions for cumulative hydration heat measurement. In this case, the researchers can collect the hydration degree of various types of cements through literature surveys, and the hydration model parameters B, C, kr, and De_0 corresponding to each type of cement can be obtained. Then, the relationship between the mineral composition of cement and the hydration model parameters is obtained through neural networks or other regression methods.

5. Comparison of Proposed Model with the Three-Parameter Hydration Model [24,31,32]

The hydration model in our recent papers [24,31,32] belongs to the three-parameter hydration model. The advantage of the three-parameter hydration model is that the model form is simple and there are only three parameters. These three parameters can be easily regressed from the experimental results.

Although the three-parameter model has the advantage of simple form, we need to note that the three-parameter model also has disadvantages that cannot be ignored. The most important disadvantage is that when the mix ratio of concrete changes, the values of the input parameters of the three-parameter model need to be regressed. In contrast, the model proposed in this article takes into account the influence of water–binder ratio and eggshell powder substitution. When the mix ratio of concrete changes, there is no need to regress the input parameters. Using Equations (1) and (2) of the hydration model and the relevant input parameters (Table 1), we can automatically calculate the relevant hydration degree.

Figure 7 shows the parameter analysis of the hydration model proposed in this paper. In the parameter analysis, two water–binder ratios of 0.50 and 0.35 and two eggshell powder replacement amounts of 7.5% and 15% were considered. As shown in Figure 7a–c, the reaction level of cement decreases with the decrease in water–binder ratio. As the replacement amount of eggshell powder increases, the reaction level of cement increases.



(**a**) (**b**)

(**c**) (**d**)

Figure 7. Parameters study of proposed hydration model. (**a**) No eggshell powder, water–binder ratios 0.50 and 0.35. (**b**) A proportion of 7.5% eggshell powder, water–binder ratios 0.50 and 0.35. (**c**) A proportion of 15% eggshell powder, water–binder ratios 0.50 and 0.35. (**d**) Effects of eggshell powder contents and water–binder ratio on relative reaction level of cement.

Figure 7d shows the effect of the replacement amount of eggshell powder (7.5% and 15%) and water–binder ratios (0.35 and 0.50) on the relative reaction level of cement. Relative reaction level is defined as follows:

Relative reaction level = reaction level of cement in the mix containing eggshell powder/reaction level of cement in the mix without eggshell powder

where the water–binder ratio of the numerator and denominator corresponding to the mix is the same.

As shown in Figure 7d, the relative reaction level of cement increases with the decrease in the water–binder ratio of concrete. This is because of the dilution effect of eggshell powder. The results in Figure 7d show that compared with a higher water–binder ratio 0.50, in concrete with a lower water–binder ratio 0.35, using eggshell powder as a filler can obviously promote cement hydration, improve cement reaction level, avoid cement waste, and achieve energy-saving effects. The trend of analysis results shown in Figure 7d is consistent with Bentz's experimental results [5].

It is important to recall again that the results in Figure 7a–d cannot be obtained using the three-parameter model [24,31,32] and can only be obtained using the hydration kinetics model proposed in this paper.

6. Summary of Proposed Model and Eggshell Powder Utilization in Concrete

6.1. Physical and Chemical Mechanisms for the Cement–Eggshell Powder Binary System

The effects of eggshell powder mainly include physical effects and chemical effects.

The physical effects of eggshell powder mainly include dilution effect and nucleation effect. The dilution effect means that when eggshell powder replaces part of cement, the mass ratio of water to cement increases, the concentration of capillary water increases, and the hydration reaction rate can be increased. This study considered the dilution effect of eggshell powder through Equation (1). The nucleation effect means that part of the cement hydration products can be formed on the surface of eggshell powder, which can reduce the thickness of the hydration products on the cement surface, reduce the resistance of capillary water to anhydrous cement, and increase the hydration reaction rate. This study considered the nucleation effect of eggshell powder through Equation (2).

The main component of eggshell powder is calcium carbonate, which can react with the aluminum phase in the cementitious material to form calcium aluminate. However, for the cement–calcium carbonate binary system, the reactivity of calcium carbonate is very weak. Zhao et al. reported that the reaction level of calcium carbonate was about 1–2% at 28 days [23]. Therefore, the chemical effect of eggshell powder was ignored in this study, and only the physical effect of eggshell powder was considered.

6.2. Verifying the Correctness of the Hydration Model

In order to verify the correctness of the hydration model proposed in this paper, this paper adopts multiple experimental results, for example, experiments on cumulative hydration heat, hydration products, compressive strength, and surface resistivity. These multiple quantitative experiments ensure the correctness of the model proposed in this paper.

In addition, this paper adds parameter analysis of the hydration model. Parameter analysis belongs to qualitative verification, and the trend of the results of parameter analysis in this paper is consistent with the trend observed by previous researchers in experiments [5].

In short, the quantitative verification of multiple experiments and the qualitative parameter analysis ensure the correctness of the model proposed in this paper.

6.3. The Validity of the Experimental Data on Which the Model Is Based

The quantitative experimental results used in this paper come from our own experiments. The relevant experiments are performed in accordance with the operating specifications, and the papers on the experimental results have been reviewed and published [24]. The qualitative results cited in this paper come from papers by well-known scholars in this field, published in top journals in this field [5]. These can prove the correctness of the experimental results used in this paper.

6.4. The Relationship between Cumulative Hydration Heat and Concrete Properties

Equations (6) and (7) are obtained from regression analysis. We calculated the cumulative hydration heat at 3 days, 7 days, and 28 days through the hydration model. In reference [24], the authors tested the strength at the same ages and the surface electrical resistivity at the same ages. This paper obtained the relationship between cumulative hydration heat and strength (Equation (6)) and the relationship between cumulative hydration heat and surface electrical resistivity (Equation (7)) through power function regressions.

The use of a power function to determine the relationship between cumulative hydration heat and concrete properties is not our original idea, but mainly comes from reference [33].

In addition to a power function, some researchers also use linear function to regress the relationship between cumulative hydration heat and concrete properties. In recent work [32], we found that the regression effects of the power function and linear function are similar, with no obvious difference.

6.5. Effect of 5% Organic Matter in Eggshell Powder on Concrete Properties

For different long-term properties of concrete, 5% organic matter has different effects. The results of this study found that for compressive strength, 5% organic matter will significantly reduce the 28-day compressive strength. This is because organic matter has low hardness and is equivalent to the weak points of the strength test. However, for surface electrical resistivity, organic matter has little effect. This is because surface electrical resistivity is mainly affected by capillary water content and pore size distribution of concrete, and has little to do with the solid composition of hydration products.

6.6. Using Eggshell Powder in Concrete Mixtures

Experimental studies have indeed found that when eggshell powder is used in general-purpose concrete, it will reduce the strength of concrete, which limits the application of eggshell powder in general-purpose concrete [24].

However, some researchers [34] have found that when the carbonation curing method is used to make concrete, the addition of eggshell powder can increase the amount of carbonation products, significantly improve the strength of concrete, and consume carbon dioxide during the production process, achieving good environmental and construction effects.

In summary, eggshell powder is not suitable for general-purpose concrete construction, but is suitable for carbonation curing concrete.

7. Conclusions

This paper proposes a hydration kinetic model of the cement–eggshell powder binary system, which considers the dilution and nucleation effects of eggshell powder. Through this hydration model, the development of the thermal/mechanical/chemical/durability properties of the cement–eggshell powder binary system concrete is predicted. The specific contents of the proposed model are as follows:

First, based on the cumulative hydration heat of the binary system from the beginning of mixing to the age of 7 days, the parameters of the cement hydration model and the nucleation parameter of eggshell powder are calibrated. These parameters do not change with the change in water–binder ratios or eggshell powder contents.

Second, the cumulative hydration heat of the binary system at the age of 28 days is calculated using the hydration model. It was found that at 28 days, for the specimens with 0%, 7.5%, and 15% eggshell powder replacement, the cement hydration degrees were 0.832, 0.882, and 0.923, respectively, and the cumulative hydration heat based on each gram of cement was 402.69, 426.88, and 446.73 J/g cement, respectively. With the increase in eggshell powder replacement, the heat release based on unit mass of cement increased due to the physical effect of eggshell powder.

Third, it was found that at 28 days, for the specimens with 0%, 7.5%, and 15% eggshell powder replacement, the cumulative hydration heat based on each gram of binder was 402.69, 394.86, and 379.72 J/g binder, respectively. When the hydration heat is expressed as the result per gram of binder, with the increase in eggshell powder replacement, the cumulative hydration heat at 28 days decreased. This is because in the later stage of hydration, the dilution effect of eggshell powder played a dominant role, reducing the cumulative hydration heat.

Fourth, the hydration model was used to calculate the chemically bound water and calcium hydroxide contents of the binary system at 28 days. At 28 days, for samples with 0%, 7.5%, and 15% eggshell powder, the chemically bound water was 0.191, 0.188, and 0.180 g/g binder, respectively. The calcium hydroxide at 28 days was 0.183, 0.179, and 0.173 g/g binder, respectively. In the later stage of hydration, the dilution effect makes reducing the chemically bound water and calcium hydroxide contents.

Fifth, the calculated hydration heat and a power function were used to regress the relationship between the cumulative hydration heat and compressive strength, and the cumulative hydration heat and surface electrical resistivity. For compressive strength, the correlation coefficient is 0.8474. For surface electrical resistivity, the correlation coefficient is 0.9714. This is because eggshell powder is relatively soft compared to other solid components, which is equivalent to the weak point in the strength experiment. The weak point effect of eggshell powder has little effect in the experiments of hydration heat and surface electrical resistivity, but has a significant effect in the strength experiment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app14135775/s1, Figure S1. Particle size distributions of cement and eggshell powder [24]. Figure S2. XRD patterns of cement and eggshell powder [24]. Figure S3. Test results of compressive strength [24]. (a) Compressive strength results of ES0, ES7.5, and ES15 at different ages. (b) Compressive strength based on ES0 normalization. Figure S4. Resistivity test results of ES0, ES7.5, and ES15 [24]. Figure S5. Curves of ES0, ES7.5, and ES15 for 1 day. (a) TGA; (b) DTG [24]. Figure S6. Curves of ES0, ES7.5, and ES15 for 28 days. (a) TGA; (b) DTG [24]. Table S1. Chemical compositions of cement and eggshell powder [24]. Table S2. Mixtures of samples [24]. Table S3. Combined water and portlandite of ES0, ES7.5, and ES15 for 1 day and 28 days [24].

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