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Analysis of Hydration-Mechanical-Durability Properties of Metakaolin Blended Concrete

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Abstract: Metakaolin (MK) is a highly active pozzolanic material and MK is increasingly used in producing high performance concrete. This study presents an integrated hydration-mechanical-durability model for evaluating various properties of metakaolin blended concrete. First, a blended hydration model is proposed for simulating the hydration of composite binders containing MK that considers the dilution effect and pozzolanic reaction due to metakaolin addition. The interactions between the metakaolin reaction and cement hydration were taken into account by means of the contents of calcium hydroxide and capillary water in hydrating the composite binder. The reaction degrees of cement and metakaolin were calculated using the hydration model. Second, the gel-space ratio of the MK blended concrete was determined based on the reaction degrees of the composite binders and proportions of concrete mix. Moreover, concrete compressive strength was calculated using the gel-space ratio. Third, the volumetric phase fractions were calculated based on the reaction degrees of the binders. Chloride penetrability of metakaolin blended concrete was analyzed through the capillary porosity of concrete. The proposed integrated hydration-mechanical-durability model is valuable for the material design of metakaolin blended concrete.

Keywords: metakaolin; hydration; strength; chloride penetrability; model

1. Introduction

High reactive metakaolin is made through the calcination of a highly pure kaolinite and grinding the products to a fine particle size. Metakaolin presents various advantages in concrete, such as increased strength, increased resistance to chemical attack, enhanced concrete finishes, reduced shrinkage, and reduced permeability [1]. Due to these advantages, metakaolin is widely used in producing high performance and high strength concrete.

Considerable experimental studies have been performed regarding material characteristics, hydration, and the mechanical and durability properties of metakaolin (MK) blended concrete [2–10]. Bai et al. [2] reported that MK blended concrete had a lower slump than control concrete because MK has a higher specific surface than cement. Poon et al. [3] performed experimental studies on the degree of reaction of MK for MK blended cement paste and showed that at early curing ages, the rate of reaction of MK in cement-MK blends was higher than silica fume in cement-silica fume blends. Güneyisi et al. [4] and Wong [5] pointed out that the compressive strength was improved in MK blended concrete due to the pozzolanic reaction of MK. Ferreira et al. [6] and Poon et al. [7] stated that chloride diffusivity decreased as MK replacement levels increased. Ramezanianpour [8] and Duan et al. [9] indicated that durability aspects, such as the resistances about sorptivity, water penetration, salt ponding, and carbonation, were improved due to MK additions. Brooks and Johari [10] reported that MK could reduce concrete creep as MK blended concrete had a denser microstructure, a stronger binder matrix, and a modified interfacial transition zone.

When compared with abundant experimental studies [2–10], the theoretical hydration-mechanical-durability models for MK blended concrete are relatively limited. Cabrera et al. [11] suggested that the pozzolanic reaction of MK was controlled by diffusion. The MK reaction can be described using the Jander diffusion equation. Razak and Wong [12] evaluated the efficiencies of MK for concrete containing various MK contents and water to binder ratios at various curing periods. Dvorkin et al. [13] proposed three-parameter polynomial models to calculate the content of the superplasticizer, concrete strength, and efficiency factor of MK. Badogiannis et al. [14] proposed a diffusion-binding model for chloride ingress into MK blended concrete that considered the efficiency of MK. Kunther et al. [15] developed thermodynamic modeling of the hydration of cement-MK-limestone ternary blended concrete. These theoretical models [11–15] are useful for evaluating the properties of MK blended concrete; however, the current theoretical models [11–15] are not perfect as some of the points are not covered. The model provided by Cabrera et al. [11] did not take into account the hydration of cement and was not valid for cement-MK binary blends. Kunther et al. [15]'s hydration model mainly focused on the chemical aspects of MK blended concrete. Furthermore, the effects of the MK reaction on concrete strength and durability were not fully considered [15]. Additionally, the studies undertaken by Razak and Wong [12], Dvorkin et al. [13], and Badogiannis et al. [14] mainly concentrated on the efficiency of MK. The efficiency factor of mineral admixtures is convenient for evaluating the properties of blended concrete; however, the efficiency factor shows some limitations as the efficiency factor changes with concrete mixing proportions and curing times [1]. For mechanical or durability aspects such as compressive strength or chloride ingress, the efficiency factors are also different. Moreover, using the efficiency factor is difficult when evaluating the compositions of reaction products, such as the calcium hydroxide content in cement-MK blends. Summarily, the efficiency factor is a macro indicator on the effect of mineral admixtures. The efficiency factor does not much consider the micro characteristics of MK, such as the kinetic reaction processes of MK, reaction degree for MK, and the reaction products of concrete containing MK [12–14].

To overcome the limitations of the current studies and systematically analyze the properties of concrete containing MK, this study presents an integrated hydration-mechanical-durability model for MK blended concrete. Furthermore, a kinetic hydration model was proposed to calculate the reaction degree of binders. Moreover, based on the reaction degree of the binders and proportions of concrete mix, the mechanical and durability aspects of MK blended concrete were evaluated.

2. Modeling of Hydration for Metakaolin Blended Concrete

2.1. Model for Cement Hydration

Our previous studies [16,17] presented a Portland cement hydration model. This hydration model considered the kinetic stages involved in the hydration of cement, such as the initial dormant stage, the chemical-reaction related stage, and the diffusion related stage. The model of cement hydration considers water withdrawal due to the lack of capillary water regarding high strength concrete. The equation of cement hydration is simplified as follows [16,17]:

$$\frac{d\alpha}{dt} = f(B(T), C(T), D_e(T), k_r(T), r_0) * C_{w-free} * (S_w/S_0) \quad (1)$$

where $\frac{d\alpha}{dt}$ is the rate of hydration; T is the curing temperature; B and C are the rate of coefficients in initial dormant process (B describes the generation of initial impermeable layer, and C describes the elimination of initial impermeable layer); k_r is the rate of coefficient in the reaction controlled process; D_e is the rate of coefficient in diffusion controlled process; r_0 is the unreacted cement particle radius; S_w is the effective contact area between the surrounding capillary water and cement particles [16,17], S_0 is the total area if cement hydration products develop unconstrained; C_{w-free} is the capillary water content ($C_{w-free} = \left(\frac{W_{cap}}{W_0}\right)^r$ where W_{cap} is the capillary water content in hardening concrete; W_0 is the content of water in the proportions of concrete mix; and r is an empirical factor considering the approachability of capillary water from the outer hard shell to the inner anhydrous part of the cement particles ($r = 2.6 - 4\frac{W_0}{B}$, where B is the binder content in the mix proportions).

The rate coefficients B, C, k_r, and D_e can be determined based on the compound compositions of cement [16,17]. The influence of curing temperature on the rate of cement hydration is described through Arrhenius's law [16,17]. Regarding high strength concrete—which has a low water to cement ratio—the hydration degree is lowered because of the withdrawal of capillary water. The water withdrawal mechanism is considered through (S_w/S_0) and C_{w-free} in Equation (1). (S_w/S_0) describes the reduction of the contact area between the hydrating cement particle and ambient capillary water, and C_{w-free} considers the decreasing capillary water concentration.

Summarily, the reaction degree of cement is calculated using the model of cement hydration. Moreover, the thermal properties, mechanical properties, and durability aspects of concrete can be analyzed using the cement hydration degree [16,17]. The cement hydration model is further validated through experimental results for concrete with multiple mixing proportions and cement types. However, as the cement hydration model does not take into account the effect of MK, the hydration model (Equation (1)) cannot be used to analyze the hydration of MK blended concrete.

2.2. MK Reaction Model

Metakaolin is a highly reactive pozzolanic material which reacts with calcium hydroxide (CH). The reaction products of metakaolin include calcium silicate hydrate (CSH), C_4AH_{13}, C_3AH_6, and C_2ASH_8 [18]. Dunster et al. [18] designed trimethylsilylation studies of the hydration of metakaolin-calcium hydroxide paste. Based on the relationship between the amount of consumed CH and reacted metakaolin, they found that when 1 g of metakaolin reacted, 1.6 g of calcium hydroxide was consumed, and 0.4 g of chemically combined water was produced. Therefore, the content of CH in composite concrete containing MK can be determined as below:

$$CH(t) = RCH_{CE} * C_0 * \alpha - v_{MK} * \alpha_{MK} * P \quad (2)$$

where $CH(t)$ is the calcium hydroxide content; RCH_{CE} is the produced CH when 1 unit mass cement hydrates; v_{MK} is the consumed CH when 1 unit mass of MK reacts (v_{MK} = 1.6 [18]); α_{MK} is the reaction degree of MK, and P is the mass of MK in mix proportions. $RCH_{CE} * C_0 * \alpha$ represents the amount of produced CH from cement hydration, and $v_{MK} * \alpha_{MK} * P$ is the amount of consumed CH from the MK reaction.

The amount of chemically combined water W_{cbm} in the MK blended concrete is determined as follows:

$$W_{cbm} = v * C_0 * \alpha + 0.4 * P * \alpha_{MK} \quad (3)$$

where v denotes the content of chemically combined water when 1 unit mass cement hydrates (v = 0.25 [16,17]). $v * C_0 * \alpha$ and $0.4 * P * \alpha_{MK}$ are the contents of the chemically combined water produced from the hydration reaction of cement and pozzolanic reaction of MK, respectively [18].

The amount of capillary water W_{cap} in the MK blended concrete is calculated as follows:

$$W_{cap} = W_0 - 0.4 * C_0{}^{*}\alpha - 0.55 * \alpha_{MK} * P \quad (4)$$

where $0.4 * C_0 * \alpha$ and $0.55 * \alpha_{MK} * P$ are the mass of capillary water consumed from the hydration reaction of cement and the pozzolanic reaction of MK, respectively [19]. $0.4 * C_0 * \alpha$ is the summation of chemically and physically combined water from cement hydration; and $0.55 * \alpha_{MK} * P$ is the summation of chemically and physically combined water from the MK reaction [19].

Snelson et al. [20] experimentally studied the isothermal heat release of MK blended concrete. They reported that like cement hydration, the reaction of cement-MK blends included an initial dormant process, a chemical reaction related process, and a diffusion related process. In addition, as metakaolin is a pozzolanic material, the reaction of MK was dependent on the CH content in cement-MK blends [21]. When considering these points, similar to the cement hydration equation [16,17], the reaction of MK can be described as follows:

$$\frac{d\alpha_{MK}}{dt} = \frac{m_{CH}(t)}{P} \frac{3\rho_w}{v_{MK} r_{MK0} \rho_{MK}} \frac{1}{\left(\frac{1}{k_{dMK}} - \frac{r_{MK0}}{D_{eMK}}\right) + \frac{r_{MK0}}{D_{eMK}}(1-\alpha_{MK})^{\frac{-1}{3}} + \frac{1}{k_{rMK}}(1-\alpha_{MK})^{\frac{-2}{3}}} \quad (5)$$

$$k_{dMK} = \frac{B_{MK}}{(\alpha_{MK})^{1.5}} + C_{MK} * (\alpha_{MK})^3 \quad (6)$$

$$D_{eMK} = D_{eMK0} * \ln\left(\frac{1}{\alpha_{MK}}\right) \quad (7)$$

where ρ_w is the density of water; r_{MK0} denotes the MK particle radius, ρ_{MK} denotes the MK density; k_{dMK} is the reaction rate parameter in the initial dormant stage (B_{MK} and C_{MK} are reaction parameters [16,17]); D_{eMK0} denotes the incipient diffusion parameter; and k_{rMK} denotes the reaction rate parameter in the chemical reaction related stage. In Equation (5), the term $\frac{m_{CH}(t)}{P}$ considers the pozzolanic reaction activity of MK.

Aside from the chemical effect, the addition of MK has a dilution effect on cement hydration [12]. When MK is used to partially replace cement, the water to cement ratio increases. Regarding high strength concrete—which has a low water to powder ratio—the dilution effect due to the MK addition is crucial [16,17]. This dilution effect is taken into account by the C_{w-free} term in Equation (1).

Therefore, a kinetic reaction equation (Equation (5)) for the MK reaction is proposed. This equation considers the kinetic processes involved in the MK reaction and the dependence of the MK reaction on the calcium hydroxide content. For cement-MK blends, the proposed hydration model simulates the individual reactions of the cement and MK, and takes into account the mutual interactions between the reaction of MK and the cement hydration through the CH content (Equation (2)) and capillary water content (Equation (4)). As the proposed model considers the interactions between the reaction of MK and cement hydration, the coefficients of the composite binder hydration model do not change with the proportions of concrete mix. When the concrete mix (binder content, water to binder ratios, MK replacement levels) changes from one to another, these coefficients are constants.

The calculation flowchart is shown in Figure 1. For each time step, the reaction degrees of MK and cement were calculated using the blended hydration reaction model. The amount of CH, chemically combined water, capillary water, volumetric phase fractions, and compressive strength were determined based on the reaction degrees of the binders and the proportions of the concrete mix. The durability aspect such as chloride penetrability was considered through the micro structure of concrete.

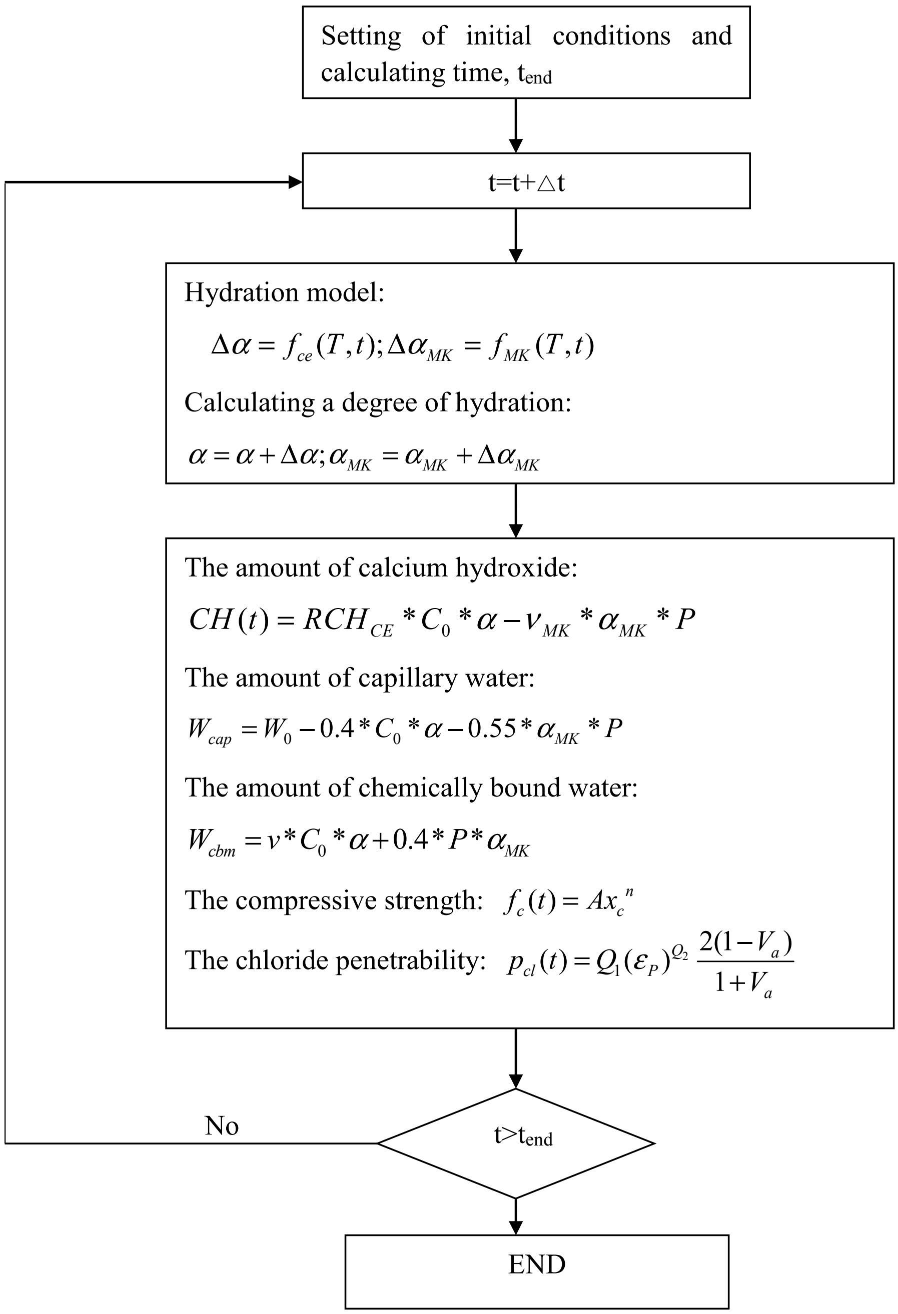

Figure 1. Flowchart of calculation.

3. Property Evaluations of MK Blended Concrete

3.1. Materials and Methods

The proposed MK blended hydration model was validated through the experimental results from Poon et al. [3,7]. Poon et al. [3,7] experimentally measured the reaction degree of MK, the calcium hydroxide content, compressive strength, and chloride penetrability in cement-MK blends.

The preparations of samples are summarized as follows [3,7]: Table 1 shows the compound compositions of the binders (cement and MK). The specimens for measuring the reaction degree of MK, the calcium hydroxide content, and compressive strength were paste specimens (water to powder ratio 0.3); and specimens for chloride penetrability were concrete (water to powder ratio 0.3 and 0.5). The MK content ranged from 0–20%. The specimens were taken from mounds after 1 day, and were wet-cured at 27 °C. At the Days 3, 7, 28, and 90, the reaction degrees of MK were measured based on the selective dissolution method, the CH content was measured using a differential scanning calorimeter, and the chloride penetrability was measured using ASTM C1202 (the total charge passed during a six-hour test, with the unit of charge passed in coulombs).

Table 1. The chemical and physical properties of cement and metakaolin.

Binders	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	SO_3 (%)	Specific Gravity	Specific Surface (cm^2/g)
cement	21.0	5.9	3.4	64.7	0.9	-	-	2.6	3.15	3520
MK	53.2	43.9	0.38	0.02	0.05	0.17	0.10	-	2.62	12,680

3.2. Results and Discussion

3.2.1. Reaction of Neat Cement Paste

Based on the compound compositions of cement, the reaction parameters of the cement hydration model (Equation (1)) can be determined. Furthermore, the development of the cement hydration degree can be calculated as the curing time progresses. The CH content can be determined based on the cement hydration degree and the proportions of the concrete mix. As shown in Figure 2, as the water to cement ratio of the neat paste increased from 0.3 to 0.5, the CH content normalized by the cement mass also increased because when the water to cement ratio increases, the capillary water concentration C_{w-free} increases, as does the reaction degree of cement.

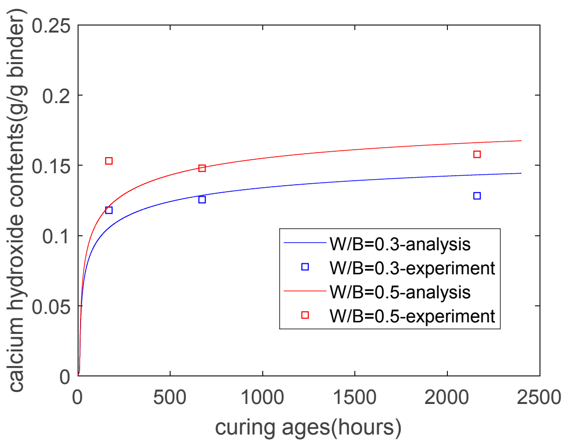

Figure 2. Hydration of neat Portland cement.

3.2.2. Reaction of Cement-MK Blends

Based on the reaction degree of MK at different times, the coefficients of the MK reaction model were determined and are presented in Table 2. These reaction rate coefficients did not change with the MK replacement levels. As shown in Figure 3a, when the MK replacement level increased from 10 to 20%, the activation effect of CH became weaker, and the reaction degree of MK decreased [16,17]. As shown in Figure 3b, for cement-MK blends, both the cement hydration and the MK reaction affected the CH contents. At early stages, the generation of CH from the cement hydration was dominant, and the CH content increased as the curing time progressed. At later stages, the consumption of CH from the MK reaction was dominant, and CH content decreased as curing times developed. At the same curing times, as the MK replacement levels increased, the CH contents decreased.

Table 2. Coefficients of the metakaolin (MK) reaction model.

B_{MK} (cm/h)	C_{MK} (cm/h)	k_{rMK} (cm/h)	D_{eMK0} (cm^2/h)
2.6×10^{-8}	0.52	7.21×10^{-7}	3.5×10^{-11}

Figure 4 shows the parameter studies on the degree of binder reaction in the MK blended concrete. The effects of water to binder ratios, MK replacement levels, and specific surface on the reaction degree of MK were all considered in the parameter studies. When the MK partially replaced cement, the reaction degree of the cement was enhanced due to the dilution effect, whereas capillary water consumed from the MK reaction (Equation (4)) lowered the reaction degree of the cement. The holistic results on the reaction degree of cement in the MK blended concrete were dependent on the combined actions of the increasing and decreasing factors. Regarding the concrete with a lower water to powder ratio (0.3), as shown in Figure 4a, when the MK replacement level was 10%, the increase in reaction degree of cement was marginal. Similarly, when 10% or 20% MK was used in concrete with a higher water to binder ratio (0.5), the increase in the reaction degree of cement was also marginal. However, for concrete with a water to binder ratio of 0.3% and 20% MK, the increase in the reaction degree of cement was obvious. This was because for concrete with a low water to binder ratio and a high MK content, the dilution effect from the MK addition was dominant.

As shown in Figure 4b, when the water to binder ratio rose from 0.3 to 0.5, the usable space for depositing the reaction products increased, as did the reaction degree of the MK [16,17]. When the MK replacement levels increased from 10% to 20%, the reaction degree of MK decreased significantly. This was because of the increase in available depositing space for the high water to binder ratios mix. Similarly, Lam et al. [22] and Chen et al. [23] also found that for fly ash or slag composite binders, the reaction degree of mineral admixture increased when the water to binder ratio increased or the mineral admixture placement level decreased.

As shown in Figure 4c (with a water to binder ratio of 0.3 and MK replacement level of 10%), when the specific surface of MK increased, the reaction degree of MK also increased. Similarly, Chen et al. [23] also found that at the same curing age, the finer slag had a higher reaction degree than the coarser slag.

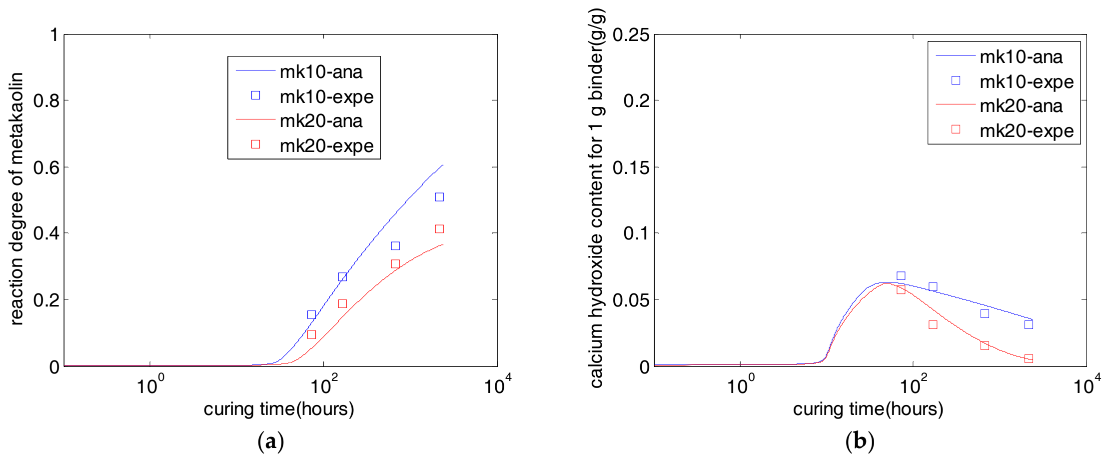

Figure 3. Hydration of cement-MK blends. (**a**) reaction degree of MK; and (**b**) calcium hydroxide content in cement-MK blends (W/B = 0.3).

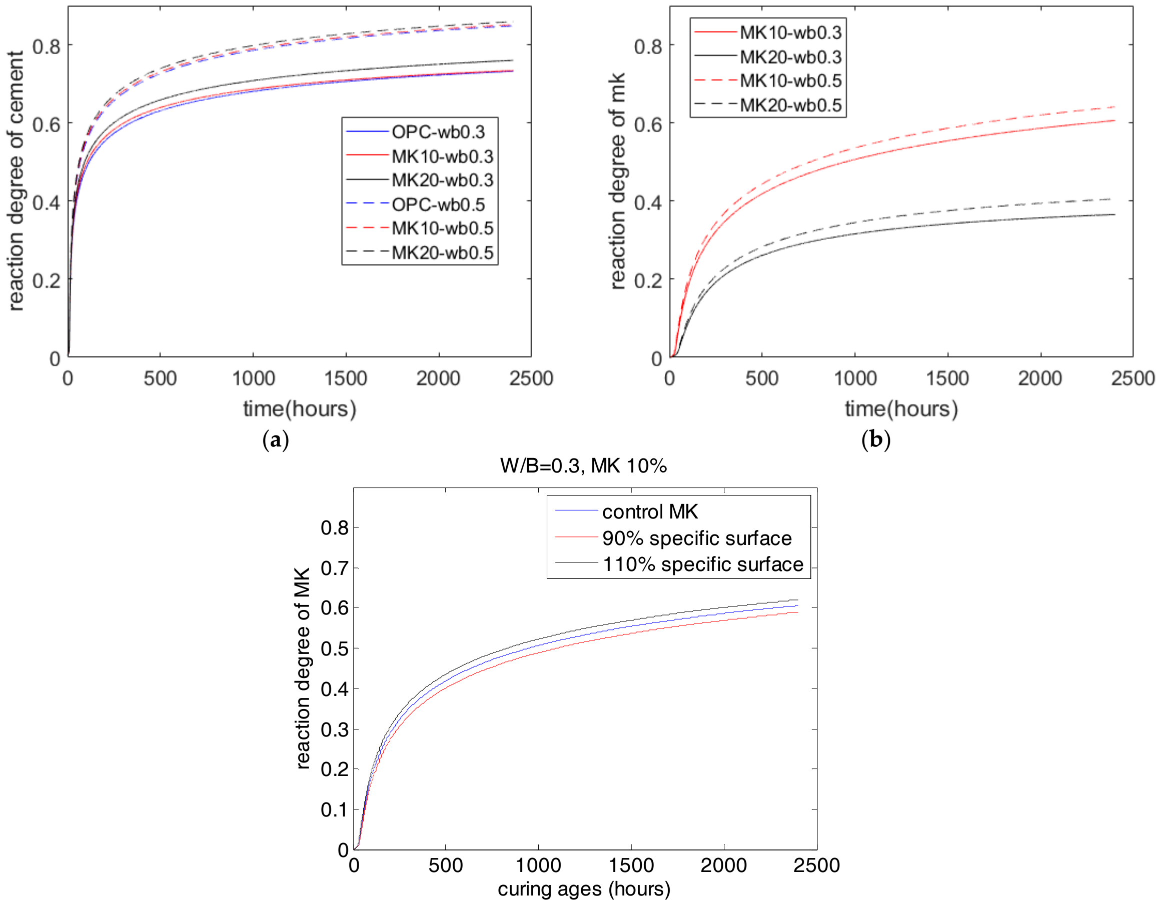

Figure 4. Parameter studies of the reaction degree of binders. (**a**) reaction degree of cement; (**b**) reaction degree of MK; and (**c**) effect of specific surface on reaction degree of MK.

3.2.3. Strength Development of Cement-MK Blends

The reaction products of binders fill the pore spaces of concrete. Mechanical properties such as compressive strength, develop with the progress of binder reactions. According to Powers' strength theory, concrete compressive strength can be calculated as follows:

$$f_c(t) = A{x_c}^n \tag{8}$$

where $f_c(t)$ is concrete compressive strength; A is the intrinsic strength of concrete; x_c is the gel-space ratio of concrete; and n is the strength exponent. The gel-space ratio denotes the volumetric ratio of the binder reaction products to the summation of the hydrated binders and capillary pore. For cement-MK blends, 1 mL of hydrated cement takes up 2.06 mL of space [22], and 1 mL of reacted MK occupies 2.52 mL of space [22]. When considering the cement hydration and MK reaction, the gel-space ratio of MK blended concrete can be calculated as:

$$x_c = \frac{2.06(1/\rho_C)\alpha C_0 + 2.52(1/\rho_{MK})\alpha_{MK}P}{(1/\rho_C)\alpha C_0 + (1/\rho_{MK})\alpha_{MK}P + W_0} \tag{9}$$

where ρ_C is the density of cement.

For cement-MK blends, Poon et al. [3] found that as the replacement level of MK increased, so did the compressive strength. However, once the replacement level of MK exceeded 10%, the concrete compressive strength decreased. Similarly, Ramezanianpour and Jovein [8] found that when the water to binder ratios were 0.4 and 0.35, the concrete containing 12.5% MK had a higher strength than the concrete with 10% and 15%. Wong and Razak [5] also reported that when the water to binder ratios were 0.27, 0.3, and 0.33, the concrete containing 10% MK showed a higher strength than the concrete with 5% and 15% MK. Wild and Khatib [24] found that when the water to binder ratio was 0.55, the mortar containing 10% MK showed a higher strength than the mortar with 5% and 15% MK. These findings described in References [3,5,8,24] may relate to the compositions of the reaction products and the intrinsic strength of concrete. Hence, we assumed that the intrinsic strength of concrete was a parabolic function of MK replacement levels as follows:

$$A = a1 + a2 * \frac{P}{C_0 + P} + a3 * \left(\frac{P}{C_0 + P}\right)^2 \tag{10}$$

where $a1$, $a2$, and $a3$ are strength coefficients (MPa). Based on the compressive strength of MK blended paste at different curing stages (3, 7, 28, and 90 days), the strength coefficients $a1$, $a2$, and $a3$ of the strength model were determined as 164, 292, and −782, respectively. The strength exponent was determined as 2.2. As shown in Figure 5, due to the high reactivity of metakaolin, the strength of MK blended paste had a higher strength than the control paste ever since the early stages. For the plain paste, the increment of strength after 28 days was marginal, which was due to the cement hydration essentially stopping after 28 days. For the MK blended paste, after 28 days, the strength continuously increased due to the contribution of the MK reaction. At both the early and late stages, the paste containing MK showed higher strength than plain paste. For the cement-MK blended pastes, the paste containing 10% MK had a higher strength than the other MK contents (5% and 20% MK). Figure 5e shows that the analysis results generally conformed to the experimental data. The correlation coefficient between the analysis results and experimental data was 0.97. Therefore, the proposed hydration-strength integrated model is useful to calculate the compressive strength development of various cement-MK blends at both early and late stages.

Using the blended hydration model for cement-MK blends, the volumetric phase fractions of the hydrating cement-MK paste can be calculated as follows:

$$V_1 = \frac{C_0}{\rho_c}(1 - \alpha) \tag{11}$$

$$V_2 = \frac{P}{\rho_{MK}}(1 - \alpha_{MK}) \tag{12}$$

$$V_3 = \frac{2.06C_0}{\rho_c}\alpha \tag{13}$$

$$V_4 = \frac{2.52P}{\rho_{MK}}\alpha_{MK} \tag{14}$$

$$V_5 = 1 - V_1 - V_2 - V_3 - V_4 \tag{15}$$

where V_1, V_2, V_3, V_4, and V_5 are the volumes of unreacted cement, unreacted MK, cement hydration products, MK reaction products, and capillary porosity, respectively. Figure 6 shows the evolution of volumetric phase fractions of the MK composite paste (water to binder ratio 0.3% and 10% MK). As binder hydration developed, the volume of unreacted cement or MK decreased. Due to the depositing of binder reaction products, the capillary porosity was reduced. At the early stages, the capillary porosity decreased rapidly. At later stages, due to the reduction of capillary water contents and the shift of the dominant kinetic stage from the chemical reaction-related stage to the diffusion-related stage, the reaction rate of the binder decreased. Hence, at late stages, the capillary porosity decreased at a slow rate.

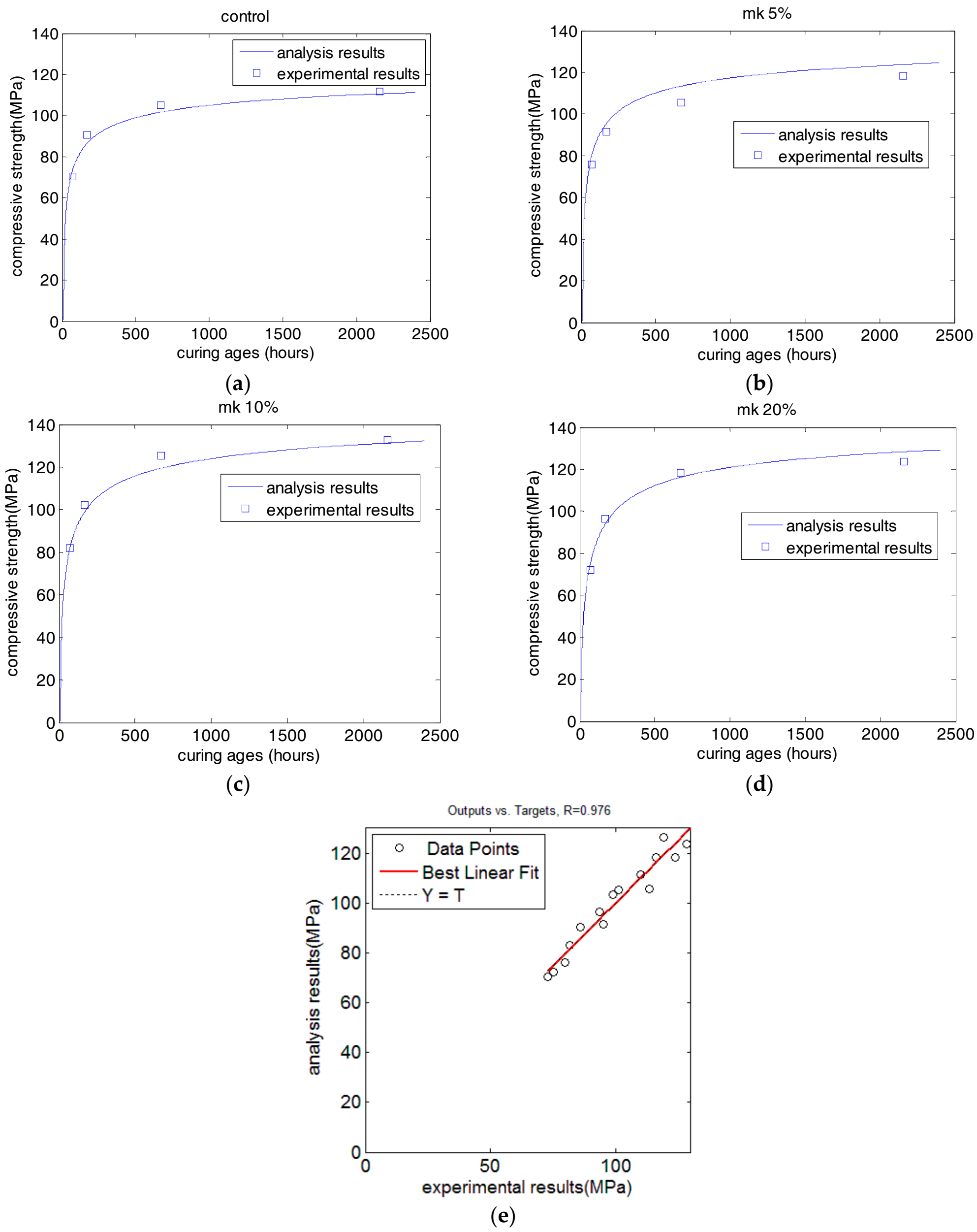

Figure 5. Strength development of cement-MK paste. (**a**) control; (**b**) MK 5%; (**c**) MK 10%; (**d**) MK 20%; and (**e**) comparison between the analysis and experimental results (W/B = 0.3).

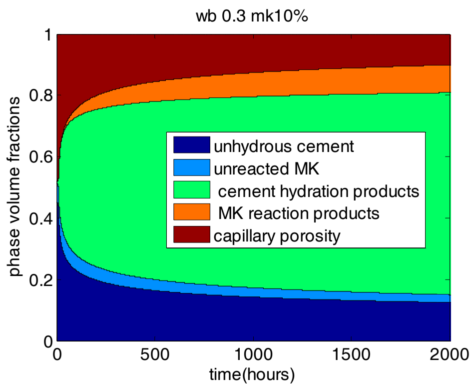

Figure 6. Phase volume fraction of cement-MK paste.

3.2.4. Chloride Penetrability

Poon et al. [7] measured the chloride penetrability of MK blended concrete using ASTM C1202. The chloride penetration resistance of concrete is determined through an electrical indicator: the total charge passed during a six-hour test. Chloride penetrability mainly depends on concrete conductivity, which relates to many factors such as capillary porosity in paste, aggregate content, binder composition (cement and mineral admixture contents), pore solution conductivity, and temperature effect [25]. For structural concrete, the variance of aggregate content is marginal and the average aggregate volume is about 65–75% of concrete volume [26,27]. Capillary porosity in paste and binder compositions are the most influencing factors of chloride penetrability in concrete [7].

Using the MK blended hydration model, the capillary porosity in paste can be calculated. Figure 7 shows the relationship between the total charge passed and the capillary porosity of the paste. The water to powder ratios of concrete varied between 0.3–0.5, the MK contents ranged between 0% and 20%, and testing stages ranged from early to late stages (3, 7, 28, and 90 days). This figure shows that at the same capillary porosity, the MK blended concrete had a lower chloride penetrability than the control concrete. Therefore, as the MK content increased, chloride penetrability became much lower. This is because the MK addition lowers the average capillary pore diameter and increased the percentage of fine capillary pores in concrete [7]. In addition, the calcium silicate hydrate (CSH) gel produced from the pozzolanic reaction had a finer gel pore than that produced by cement hydration. This difference in CSH compound also contributed to the lower chloride penetrability [27].

Fan and Wang [28] proposed that the chloride penetrability of concrete could be calculated using a power function of capillary porosity of paste as follows:

$$p_{cl}(t) = Q_1 (V_5)^{Q_2} \frac{2(1 - V_a)}{2 + V_a} \quad (16)$$

where p_{cl} is chloride penetrability; Q_1 is intrinsic chloride penetrability; Q_2 is the exponent of chloride penetrability; and V_a is the volume of aggregate. V_5 is the volume of capillary porosity in paste which can be calculated from Equation (15). The item $Q_1 (V_5)^{Q_2}$ considers the effect of binder hydration on chloride penetrability. The item $\frac{2(1-V_a)}{2+V_a}$ considers the dilution effect of the aggregate on chloride penetrability.

The coefficients Q_1 and Q_2 are dependent on the MK replacement levels. We approximately assumed that the values of Q_1 and Q_2 were linearly dependent on weight fractions of cement and MK as follows:

$$Q_1 = Q_{1c} \frac{C_0}{C_0 + P} + Q_{1mk} \frac{P}{C_0 + P} \quad (17)$$

$$Q_2 = Q_{2c} \frac{C_0}{C_0 + P} + Q_{2mk} \frac{P}{C_0 + P} \quad (18)$$

where Q_{1c} and Q_{1mk} are the intrinsic chloride penetrability of cement and MK, respectively; and Q_{2c}, and Q_{2mk} are the penetrability exponent of cement and MK, respectively. The units for Q_{1c} and Q_{1mk} are coulombs. For plain concrete without MK, the chloride penetrability only depends on Q_{1c} and Q_{2c}. For the MK blended concrete, chloride penetrability is dependent on Q_{1c}, Q_{2c}, Q_{1mk}, and Q_{2mk}. For concrete with different mixing proportions at different stages, the values of Q_{1c}, Q_{2c}, Q_{1mk}, and Q_{2mk} are constants.

Based on the experimental results shown in Figure 7, the values of Q_{1c}, Q_{1mk}, Q_{2c}, and Q_{2mk} were determined as 20,399, −44,460, 1.57, and 7.13, respectively. The intrinsic chloride penetrability of the control concrete, 10% MK concrete, and 20% MK concrete were 20,399, 15,953, and 11,507, respectively. The values of intrinsic chloride penetrability of concrete had a wide range (from 20,399 to 11,507) and decreased due to the MK addition, which was similar to the intrinsic chloride diffusivity of silica fume blended concrete, as shown in Oh and Jang [27]. The deceasing intrinsic chloride penetrability is because the pozzolanic reaction of MK can refine the gel pores of hydration products [29]. On the other hand, the value of penetrability exponent Q_{2mk} was much higher than that of Q_{2c}. This was due to the capillary pore size refinement from the MK additions. Given a certain capillary porosity, an increase in the penetrability exponent reduces chloride penetrability. Figure 8a,b show that the analysis results could reflect the general trends of chloride penetrability. As binder hydration developed, the capillary porosity decreased, as did the chloride penetrability. As the water to binder ratio of concrete increased, capillary porosity and chloride penetrability also increased. When MK partially replaced cement, because of the decreasing intrinsic chloride penetrability and the increase in the penetrability exponent, the chloride penetrability decreased. Figure 8c shows that the analysis results generally conformed to the experimental data. The correlation coefficient between the analysis results and experiment data was 0.96.

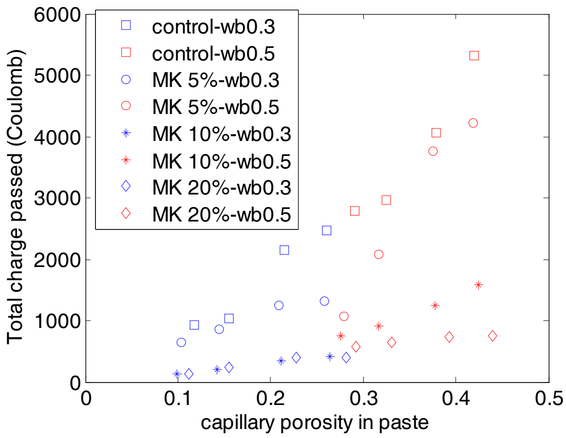

Figure 7. Chloride penetrability vs. capillary porosity.

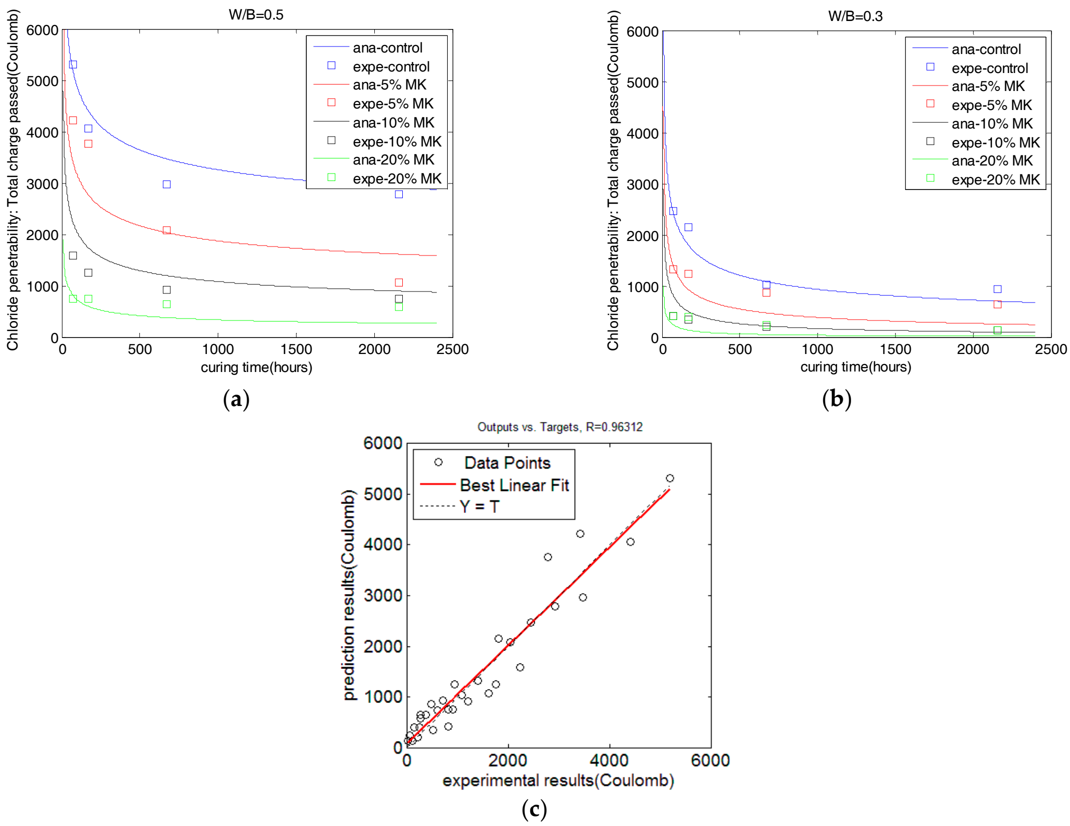

Figure 8. Evaluation of chloride penetrability. (**a**) water to binder ratio 0.5; (**b**) water to binder ratio 0.3; and (**c**) a comparison between the prediction results and the analysis results.

3.2.5. Discussion about Reaction Degree and Efficiency Factor

The efficiency factor is a widely used indicator for evaluating the properties of concrete containing supplementary cementitious materials (SCMs). Although the efficiency factor is convenient, it has some limitations. For concrete with various proportions of mix, at various curing ages, the efficiency factors are different. The efficiency factors for mechanical properties and durability are also different. Therefore, it is difficult to evaluate the chemical aspects, such as the calcium hydroxide content, by using the efficiency factor in the SCMs blended concrete. Comparatively, in this study, we did not use an efficiency factor. Instead, we used the reaction degree of the SCMs to estimate the properties evolution of MK blended concrete. The coefficients for the hydration model (Section 3.2), strength model (Section 3.3), and chloride penetrability model (Section 3.4) were constants. When the SCM replacement levels, water to binder ratios, and curing ages were changed, these coefficients did not vary. The compositions of reaction products, such as calcium hydroxide content, could be evaluated using the reaction degrees of binders (Section 3.2). Summarily, regarding a multiple properties evaluation of blended concrete, such as the chemical-mechanical-durability properties, the reaction degree was much more effective than the efficiency factor given that the reaction degree can serve as a link between the macro properties and micro compositions of concrete.

4. Conclusions

This study presented an integrated hydration-mechanical-durability model for evaluating various properties of metakaolin blended concrete.

First, a kinetic reaction model for the MK reaction was proposed. Like cement hydration, the MK reaction consists of three kinetic stages: an initial dormant stage, a chemical reaction controlled stage, and a diffusion controlled stage. The dilution effect and pozzolanic reaction due to the addition of metakaolin were analyzed. CH content and capillary water content were used as indicators to consider the interactions between the metakaolin reaction and cement hydration.

Second, the reaction degrees of cement and metakaolin were calculated using the hydration model. As the MK replacement level decreased, or the water to binder ratio increased, the degree of MK reaction increased. The gel-space ratio of the concrete containing MK was determined considering the reaction degrees of the binders and proportions of concrete mix. Concrete compressive strength was calculated using the gel-space ratio.

Third, the volumetric phase fractions were calculated based on the reaction degrees of the binders. Chloride penetrability can be described as a power function of the capillary porosity of paste. The coefficients for the hydration model, strength model, and chloride penetrability model did not vary for different concrete mixing proportions and curing ages. Regarding the multiple properties evaluations of blended concrete, such as the chemical-mechanical-durability properties, the reaction degree was much more effective than the efficiency factor given that the reaction degree can serve as a link between the macro properties and micro compositions of concrete.

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