

## Research Article

# Analysis of Hydration and Optimal Strength Combinations of Cement-Limestone-Metakaolin Ternary Composite

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Metakaolin (MK) is an aluminosilicate pozzolan material and can contribute to property development of concrete due to the pozzolanic reaction. Limestone (LS) powder presents the dilution effect, nucleation effect, and chemical effect on hydration of cement. When metakaolin and limestone are used together, due to the additional chemical reaction between the aluminum phase in MK and limestone, the synergetic benefit can be achieved. This study presents a hydration model for cement-limestone-metakaolin ternary blends. Individual reactions of cement, metakaolin, and limestone are simulated separately, and the interactions among cement hydration, limestone reaction, and metakaolin reaction are considered through the contents of calcium hydroxide and capillary water. The hydration model considers the pozzolanic reaction of metakaolin, chemical and physics effects of limestone, and synergetic effect between metakaolin and limestone. Furthermore, the gel-space ratio of hydrating concrete is calculated using reaction degrees of binders and concrete mixtures. The strength development of ternary blends is evaluated using the gel-space ratio. Based on parameter analysis, the synergetic effect on strength development is shown and the optimal combinations of cement-limestone-metakaolin ternary blends are determined.

## 1. Introduction

Metakaolin is increasingly used in modern concrete industry. The addition of metakaolin can make many advantages on the performance of concrete. Metakaolin can enhance workability and finishing ability, increase compressive and flexural strength, and reduce chloride permeability. However, metakaolin-blended binary concrete has some drawbacks. As the replacement level of cement by metakaolin increases, an increased amount of superplasticizer is necessary to reach the required consistency. The material cost of the metakaolin is higher than that of cement. To avoid these drawbacks, the substitution level of cement by metakaolin is generally lower than 25%. Summarily, the benefits of metakaolin, such as mechanical performance and extended service life, may overcome its negative effect. Metakaolin is a very promising supplementary cementitious material for the concrete industry [1, 2].

Limestone powder can improve the workability, reduce the bleeding, and reduce the amount of CO<sub>2</sub> emission of the concrete industry. The price of limestone is much lower than

that of metakaolin. The addition of limestone lowers the late-age strength of concrete. When limestone and metakaolin are used together, the pozzolanic reaction of metakaolin can contribute to concrete late-age strength. In addition, metakaolin has a high aluminum content which can react with limestone, form carboaluminate phases, and increase solid volume and strength of concrete. This is the synergetic effect of ternary concrete. While metakaolin or limestone is added individually, the synergetic effect cannot be achieved. In summary, when using metakaolin- and limestone ternary-blended concrete, the economic benefit and strength benefit can be achieved [1, 2].

Many experimental studies have been done about workability, mechanical, and durability aspects of cement-limestone-metakaolin ternary blends. Vance et al. [3] reported that, for cement-limestone-metakaolin ternary blends, the yield stress reduces as the limestone content increases. This is because of the particle packing, water demand, and interparticle spacing and contacts. Vance et al. [4] found that the synergetic effect of limestone and MK incorporation can improve early-age properties and

maintain late-age properties of concrete. Alvarez et al. [5] presented that combined mixtures of limestone and MK enhance compressive strength compared with 100% Portland cement concrete. Ramezaniapour and Hooton [6] presented that carboaluminate hydrates are formed for cement-limestone-MK ternary blends, and there is an optimum level of limestone in terms of the maximum strength and minimum porosity. Perlot et al. [7] reported that ternary-blended mix presents a real benefit for carbonation durability performances due to the refinement of the pore structure. Sotiriadis et al. [8] reported that the use of MK in the limestone cement concrete retards and inhibits deterioration due to the sulfate attack and improves its durability.

Compared with abundant experimental studies, the theoretical models about cement-limestone-metakaolin ternary blends are very limited. Antoni et al. [9] made the thermodynamic model for cement-limestone-metakaolin ternary blends and present phase assemblage for different combinations of binders. Shi et al. [10, 11] presented the thermodynamic model for carbonation and chloride ingress of cement-limestone-metakaolin ternary blends. Changes in phase assemblages and total porosities due to carbonation and chloride exposure are evaluated [10, 11]. The thermodynamic models [9–11] mainly focus on the chemical aspect of ternary blends, such as the phase assemblages of hydrated concrete and reaction products between concrete and ingress ions. However, limited works was done about mechanical aspects, such as the evaluation of strength development and optimal combinations of binders of ternary blends [9–11].

Optimal combinations of binders of ternary blends are an interesting topic for concrete manufacture and construction company. This study presents a blended hydration model for ternary blends considering the synergetic effect between limestone and MK. The strength development of ternary blends is evaluated using reaction degrees of binders and gel-space ratios. Based on parameter analysis, the optimal combinations of cement-limestone-metakaolin ternary blends are determined.

## 2. Hydration Model and Strength Model for Ternary Blends

**2.1. Hydration Model.** For MK- and limestone-blended concrete, the hydration of cement, the reaction of MK, and reaction of limestone coexist. In this study, we simulate the hydration of cement, MK, and limestone, respectively. Meanwhile, the interactions among cement hydration, metakaolin reaction, and limestone reaction are considered through the contents of capillary water and calcium hydroxide in hydrating blends.

**2.1.1. Cement Hydration Model.** The hydration of cement can be described using a kinetic model shown in our former studies [12]. The degree of hydration  $\alpha$  can be calculated as  $\alpha = \int_0^t (d\alpha/dt)dt$ , where  $t$  is the time and  $d\alpha/dt$  is the rate of hydration, which can be determined as follows:

$$\frac{d\alpha}{dt} = f(B, C, De, kr) * \lambda_1 * \lambda_2, \quad (1)$$

where  $B$  and  $C$  are the rate-determining coefficients in the initial dormant period,  $De$  is the reaction parameter in the diffusion-controlled period,  $kr$  is the reaction parameter in the phase boundary-controlled period,  $\lambda_1$  considers the reduction of the hydration rate due to development of microstructure, and  $\lambda_2$  considers the reduction of hydration rate due to the consumption of capillary water ( $\lambda_2 = W_{cap}/W_0$ , where  $W_{cap}$  is the amount of capillary water and  $W_0$  is the amount of water in concrete mixtures).

The kinetic processes involved in cement hydration, such as the initial dormant process, phase boundary reaction process, and diffusion process, are considered in the cement hydration model. The input variables of the cement hydration model are cement compound compositions, Blaine surface of cement, concrete mixing proportions, and curing conditions. The values of hydration parameters  $B$ ,  $C$ ,  $De$ , and  $kr$  can be determined using cement compound compositions. Furthermore, the reaction degree of cement can be calculated automatically using hydration parameters  $B$ ,  $C$ ,  $De$ , and  $kr$ . The effect of curing temperature on cement hydration is considered using Arrhenius law [12]. For high-strength concrete, the water-to-cement ratio is low, and the hydration rate is significantly lowered due to the reduction of capillary water [13, 14]. This effect is considered using capillary water concentration  $\lambda_2$ . Summarily, the proposed cement hydration model is valid for concrete with different strength levels, different types of Portland cement, and different curing conditions [12].

**2.1.2. MK Reaction Model.** The reaction process of MK also consists of the initial dormant process, phase boundary reaction process, and diffusion process, which is similar with the processes involved in hydration of cement [15]. On the contrary, MK is a pozzolanic material. The reaction rate of the pozzolanic reaction is dependent on the amount of calcium hydroxide in blends [16, 17]. Considering the kinetic reaction processes and the essence of MK as the pozzolanic material, Wang [15] proposed that the reaction equation of MK can be written as follows:

$$\frac{d\alpha_{MK}}{dt} = f(B_{MK}, C_{MK}, De_{MK}, kr_{MK}) * \frac{CH(t)}{P}, \quad (2)$$

where  $\alpha_{MK}$  is the reaction degree of MK,  $d\alpha_{MK}/dt$  is the reaction rate of MK,  $B_{MK}$  and  $C_{MK}$  are reaction parameters of MK in the dormant period,  $De_{MK}$  is the reaction parameter of MK in the diffusion-controlled period,  $kr_{MK}$  is the reaction parameter of MK in the phase boundary-controlled period,  $CH(t)$  is the content of calcium hydroxide in blends, and  $P$  is the content of MK in concrete mixtures. The verifications of the MK reaction model are available in our former study [15]. An integrated hydration-strength-durability model for MK-blended concrete is proposed for evaluating the reaction degrees of binders, strength development, and chloride penetrability [15].

**2.1.3. Limestone Reaction Model.** The addition of limestone powder presents the dilution effect, nucleation effect, and chemical effect on hydration of cement. In this study, dilution effect is considered through the amount of capillary water, nucleation effect is considered through a nucleation effect indicator, and chemical effect is considered through a logarithm function with multiple modification factors [18, 19].

The hydration products of cement can form on the surface of limestone powder. This is called as the nucleation effect. The nucleation effect indicator of limestone powder can be written as follows [2]:

$$L_r = \frac{LS_0 * S_{LS}}{C_0 * S_C}, \quad (3)$$

where  $L_r$  is the limestone nucleation effect indicator;  $LS_0$  and  $C_0$  are the mass of limestone and cement in mixing proportions, respectively; and  $S_{LS}$  and  $S_C$  are the Blaine surface area of limestone powder and cement, respectively.

In our former study [2], based on the experimental results of hydration degree of cement in cement-limestone binary blends, Wang and Luan [2] proposed that the nucleation effect of limestone powder can be described as follows:

$$k_{rLS} = k_r (1 + 1.2L_r), \quad (4)$$

$$D_{eLS} = D_e (1 + 1.2L_r), \quad (5)$$

where  $k_{rLS}$  is the updated phase boundary reaction coefficient in cement-limestone blends, 1.2 is enhancing coefficients of  $k_r$  [2],  $D_{eLS}$  is the updated diffusion coefficient in cement-limestone blends, and 1.2 is enhancing coefficients of  $D_e$  [2].

Until now, the experimental results about the reaction degree of limestone are very limit. Tentatively, Wang and Luan [2] proposed an empirical model with multi-modification factors for analyzing the reaction degree of limestone. The empirical model considers the effects of various factors on the chemical reaction of limestone, such as limestone replacement ratios, mineral admixtures additions, limestone fineness, cement fineness, water-to-binder ratio, and curing temperature. The empirical model for the limestone reaction is shown as follows:

$$\alpha_{LS1} = 0.0087 \ln(t) - 0.0265, \quad t > 21 \text{ hours}, \quad (6)$$

$$\alpha_{LS} = \alpha_{LS1} * m_1 * m_2 * m_3 * m_4 * m_5 * m_6, \quad (7)$$

where  $\alpha_{LS1}$  is the reaction degree of limestone in a reference mixture. This reference mixture is Portland cement, and limestone binary blends with a water-to-binder ratio 0.5 and 20% limestone addition cured at 20°C.  $m_1$  considers the effect of limestone replacement ratios on the reaction degree of limestone,  $m_2$  considers the effect of limestone fineness,  $m_3$  considers the effect of cement fineness,  $m_4$  considers the effect of MK addition,  $m_5$  considers the effect of the water-to-binder ratio, and  $m_6$  considers the effect of the curing temperature. Table 1 shows the summary of influencing factors of the limestone reaction. As limestone replacement ratio increases,

reaction degree of LS decreases. While fineness of limestone, fineness of cement, MK addition, and water to binder ratio increase, the reaction degree of LS increases. Especially, for modification factor  $m_4 = 1 + (Al_{MK}\alpha_{MK}P/Al_C\alpha_C)$ , where  $Al_{MK}$  is the aluminum content in MK,  $Al_C$  is the aluminum content in cement,  $Al_{MK}\alpha_{MK}P$  in the numerator is reacted aluminum content from the MK reaction, and  $Al_C\alpha_C$  in denominator is the reacted aluminum content from the cement reaction. Because the aluminum content in MK is much higher than that in cement, the addition of MK can significantly improve the reactivity of limestone. The factor  $m_4$  considers the synergetic effect of limestone and MK. A higher aluminum content and a higher reactivity of MK are effective to enhance the reactivity of limestone.

Summarily, this study considers the dilution effect, nucleation effect, and chemical effect of limestone additions. The enhancement of limestone reactivity due to the addition of metakaolin is considered through a modification factor. The influences of other factors, such as limestone replacement ratio, fineness of binders, and water-to-binder ratios, are also considered in the limestone reaction model.

**2.1.4. Interaction Model among Cement, Metakaolin, and Limestone.** In this study, the interactions among cement hydration, metakaolin reaction, and limestone reaction are considered through the contents of capillary water and calcium hydroxide. Maekawa et al. [13] proposed that, as 1 g cement hydrates, 0.4 g capillary water will be consumed. Dunster et al. [20] proposed that, as 1 g metakaolin reacts, 0.55 g capillary water will be consumed. Bentz [21] proposed that, as 1 g limestone reacts, 1.62 g capillary water will be consumed. For hydrating cement-metakaolin-limestone ternary blends, the content of capillary water can be determined as follows:

$$W_{cap} = W_0 - 0.4 * C_0 * \alpha - 0.55 * \alpha_{MK} * P - 1.62 * LS_0 * \alpha_{LS}, \quad (8)$$

where  $0.4 * C_0 * \alpha$ ,  $0.55 * \alpha_{MK} * P$ , and  $1.62 * LS_0 * \alpha_{LS}$  are the contents of consumed water from cement hydration, metakaolin reaction, and limestone reaction, respectively [13, 20, 21]. The consumption of capillary water from the 1 g limestone reaction is much higher than those of cement and metakaolin. This is because the reaction products of limestone powder are monocarboaluminate and ettringite which contains abundant water.

For hydrating cement-metakaolin-limestone ternary blends, the content of calcium hydroxide can be determined as follows:

$$CH(t) = RCH_{CE} * C_0 * \alpha - v_{MK} * \alpha_{MK} * P, \quad (9)$$

where  $RCH_{CE}$  means the mass of CH produced from the hydration of 1 unit mass of cement and  $v_{MK}$  means the mass of CH consumed from the reaction of 1 unit mass of metakaolin [15].  $RCH_{CE} * C_0 * \alpha$  is the mass of CH produced from cement hydration.  $v_{MK} * \alpha_{MK} * P$  is the mass of CH consumed from the metakaolin reaction.

TABLE 1: Summary of influencing factors of the limestone reaction.

Factor	Equation	Influencing trend
Limestone replacement ratios	$m_1 = 0.2 / (LS_0 / (C_0 + LS_0))$	As the limestone replacement ratio increases, $\alpha_{LS}$ decreases
Fineness of limestone	$m_2 = 1.0131 - 0.0144 * d_{LS}$ , where $d_{LS}$ is an average diameter of limestone	As fineness of limestone increases, $\alpha_{LS}$ increases
Fineness of cement	$m_3 = 0.55 (S_C / S_{C1}) + 0.45$ , where $S_{C1}$ is the Blaine surface of cement used in the reference study	As fineness of cement increases, $\alpha_{LS}$ increases
Metakaolin additions	$m_4 = 1 + (Al_{MK} \alpha_{MK} P / Al_C \alpha C_0)$	As the MK addition increases, $\alpha_{LS}$ increases
Water-to-binder ratios	$m_5 = \alpha / \alpha_{0.5}$ , where $\alpha_{0.5}$ is the reaction degree of cement in the reference study	As water-to-binder ratio increases, $\alpha_{LS}$ increases
Curing temperature	$m_6 = 1$	Curing temperature does not present significant influence on $\alpha_{LS}$

Summarily, the effect of cement hydration, metakaolin reaction, and limestone reaction on the contents of capillary water and calcium hydroxide is considered. The capillary water content can be used for the cement hydration model (equation (1)), and the calcium hydroxide content can be used for the metakaolin reaction model (equation (2)). In addition, because the blended hydration model has considered the interactions among cement, metakaolin, and limestone reactions, the coefficients of the hydration model do not vary with different mixtures. When the mixtures change from one to another, the coefficients of the hydration model are constant.

**2.2. Strength Development Model.** The gel-space ratio denotes the ratio of the volume of binder hydration products to the sum of volume of hydrated binders and capillary pore. For cement-metakaolin-limestone blends, 1 ml hydrated cement, 1 ml reacted metakaolin, and 1 ml reacted limestone occupy 2.06 ml of space [16, 22], 2.52 ml space [16, 22], and 4.1 ml space, respectively. Reacted products of 1 ml limestone can occupy much higher space than those of cement (4.1 vs. 2.06). This is due to the development of ettringite and monocarboaluminate from the limestone reaction. Considering the reactions of cement, metakaolin, and limestone, the gel-space ratio of cement-metakaolin-limestone ternary-blended cement can be determined as follows:

$$x_c = \frac{2.06(1/\rho_C)\alpha C_0 + 2.52(1/\rho_{MK})\alpha_{MK}P + 4.1(1/\rho_{LS})\alpha_{LS}LS_0}{(1/\rho_C)\alpha C_0 + (1/\rho_{MK})\alpha_{MK}P + (1/\rho_{LS})\alpha_{LS}LS_0 + W_0}, \quad (10)$$

where  $\rho_C$ ,  $\rho_{MK}$ , and  $\rho_{LS}$  are densities of cement, metakaolin, and limestone powder, respectively.

According to Powers' strength theory, the compressive strength of hydrating concrete can be evaluated using the gel-space ratio as follows:

$$f_c(t) = Ax_c^n, \quad (11)$$

where  $f_c(t)$  is the concrete compressive strength,  $A$  is the intrinsic strength of concrete, and  $n$  is the strength exponent.

For cement-metakaolin-limestone blends, cement, metakaolin, and limestone will affect the intrinsic strength of concrete and strength exponent. We assume that the intrinsic strength of concrete  $A$  and strength exponent  $n$  is

proportional to the weight fractions of cement, metakaolin, and limestone in the mixing proportion as follows:

$$A = a1 * \frac{C_0}{C_0 + P + LS_0} + a2 * \frac{P}{C_0 + P + LS_0} + a3 * \frac{LS_0}{C_0 + P + LS_0}, \quad (12)$$

$$n = b1 * \frac{C_0}{C_0 + P + LS_0} + b2 * \frac{P}{C_0 + P + LS_0} + b3 * \frac{LS_0}{C_0 + P + LS_0}, \quad (13)$$

where coefficients  $a1$ ,  $a2$ , and  $a3$  in equation (12) represent the contributions of cement, metakaolin, and limestone to the intrinsic strength of concrete, respectively, and the units of  $a1$ ,  $a2$ , and  $a3$  are MPa; the coefficients  $b1$ ,  $b2$ , and  $b3$  in equation (13) represent the contributions of cement, metakaolin, and limestone to the strength exponent, respectively. For neat Portland cement concrete without limestone or metakaolin, the strength of concrete only pertains to  $a1$  and  $b1$ . For metakaolin-blended binary concrete without limestone, the strength of concrete pertains to coefficients  $a1$ ,  $a2$ ,  $b1$ , and  $b2$ . For ternary-blended concrete, the strength of concrete pertains to coefficients  $a1$ ,  $a2$ ,  $a3$ ,  $b1$ ,  $b2$ , and  $b3$ . These coefficients  $a1$ ,  $a2$ ,  $a3$ ,  $b1$ ,  $b2$ , and  $b3$  do not change for various mixing proportions of concrete.

The flowchart of calculation is proven in Figure 1. Each time step, the response levels of cement, metakaolin, and limestone powder are calculated by utilizing ternary-blended hydration model. The quantity of CH and capillary water are based on using reaction levels of binders and concrete mixtures. In addition, the gel-space ratio of hydrating concrete is decided, thinking about the contributions from reactions of cement, metakaolin, and limestone reactions. By utilizing Powers' strength theory, the compressive strength of hardening concrete is calculated.

### 3. Verifications of Proposed Models

**3.1. Verification of Hydration Model.** Experimental results from Antoni et al. [9] are used to verify the proposed blended hydration model and strength development model.

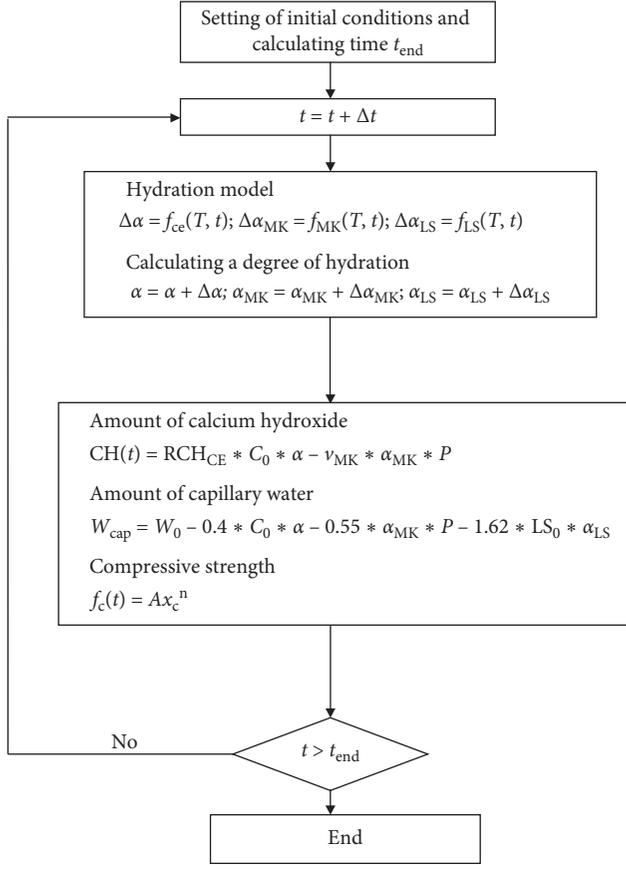


FIGURE 1: Flowchart of simulation.

Antoni et al. [9] measured the reaction degrees of binder and compressive strength of cement-MK-LS ternary-blended concrete. The chemical compositions of cement, metakaolin, and limestone are shown in Table 2. The mixing proportions are shown in Table 3. Paste specimens with a water-to-binder ratio of 0.4 were used for measuring reaction degree of binders. Mortar specimens with a water-to-binder ratio of 0.5 were used for measuring compressive strength. For cement-limestone binary blends, the replacement ratio of limestone was 15%, while for cement-metakaolin binary blends, the replacement ratio of metakaolin was 30%. For ternary-blended specimens, the sum of limestone and metakaolin ranged from 15% to 60%, and the mass ratio of metakaolin to limestone was fixed as 2. The reaction degrees and strength were measured at the ages of 1, 7, 28, and 90 days.

The input parameters of the ternary-blended cement hydration model are concrete mixtures, curing temperature, and compound compositions and Blaine surface areas of binders. By using the blended cement hydration model, the reaction degree of MK and LS is calculated and shown in Figure 2.

As shown in Figure 2(a), the sequences of the reaction degree of MK from higher to lower are B15 > B30 > MK30 > B45 > B60. This can be explained using the MK reaction model (equation (2)). As shown in equation (2), the reaction degree of MK mainly depends on the mass ratio of cement to

TABLE 2: Chemical compositions of binders.

	Cement (%)	Limestone (%)	Metakaolin (%)
SiO <sub>2</sub>	21.01	0.04	50.62
Al <sub>2</sub> O <sub>3</sub>	4.63	0.06	46.91
Fe <sub>2</sub> O <sub>3</sub>	2.60	0.05	0.38
CaO	64.18	56.53	0.02
MgO	1.82	0.10	0.09
SO <sub>3</sub>	2.78	-	0.08
Na <sub>2</sub> O	0.20	0.04	0.28
K <sub>2</sub> O	0.94	0.04	0.18
TiO <sub>2</sub>	0.14	0.03	1.29
Others	0.44	0.02	0.16
Loss on ignition (LOI)	1.26	43.09	0.00
Total	100.0	100.0	100.0

TABLE 3: Mixing proportions of specimens [9].

	Cement (%)	Limestone (%)	Metakaolin (%)
PC	100	0	0
LS15	85	15	0
MK30	70	0	30
B15	85	5	10
B30	70	10	20
B45	55	15	30
B60	40	20	40

MK. As the ratio of cement to MK increases, the activation effect from cement hydration is enhanced, and reaction degree of MK increases. The mass ratios of cement to MK were 8.5, 3.5, 2.33, 1.83, and 1 in the mixtures of B15, B30, MK30, B45, and B60, respectively. The orders of reaction degree of MK are consistent with the mass ratios of cement to MK.

As shown in Figure 2(b), the sequences of reaction degree of limestone from higher to lower are B15 > B30 > B45 > B60. The proposed ternary-blended hydration model can reflect this trend of reaction degree of LS. In this study, the mass ratio of MK to LS in ternary blends is constant, and the difference of the reaction degree of LS is mainly due to the variations of the cement-to-limestone ratio. The mass ratios of cement to LS were 17, 7, 3.66, and 2 in the mixtures of B15, B30, B45, and B60, respectively. As the mass ratio of cement to LS decreases, the reaction degree of LS also decreases (parameter  $m_1$  of equation (7)). The trend of the reaction degree of LS is consistent with the mass ratio of cement to LS. In addition, the reaction degree of LS at 1 day is almost zero. This also agrees with our analysis. As shown in equation (6), we assumed that the reaction of LS starts after 21 hours. Furthermore, the reactivity of LS is very low. At the age of 90 days, the reaction degree of LS for B15 is 12% which is much lower than cement.

Figure 3 shows the parameter analysis of the hydration model. Figure 3(a) shows the reaction degree of LS in cement-LS binary blends. As limestone replacement ratio increases, the reaction degree of limestone decreases. Similar to the contents shown in Figure 3(a), Aqel and Panesar [23]

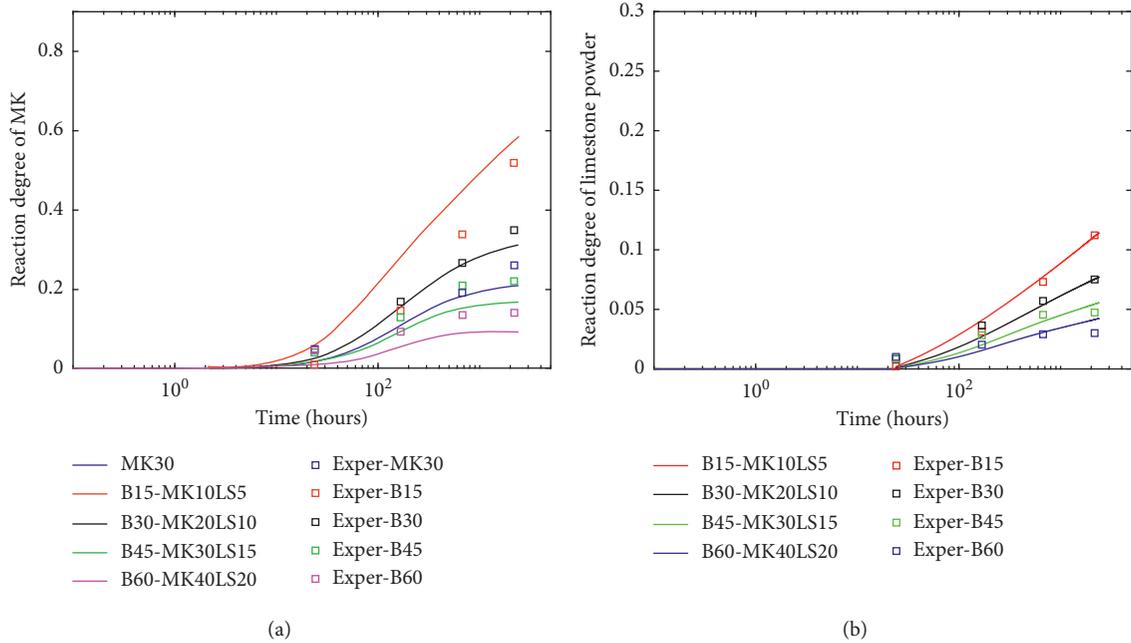


FIGURE 2: Verification of the hydration model: (a) reaction degree of MK; (b) reaction degree of LS.

also found the reactivity of limestone will be lower with the increasing of limestone content.

Figure 3(b) shows the reaction degree of MK in cement-MK binary blends. As MK replacement ratio increases, the activation effect from cement hydration becomes weaker, and the reaction degree of MK decreases. Similar to the contents shown in Figure 3(b), Poon et al. [24] also found similar results that the reaction degree of MK will be lower as the content of MK increases.

Figure 3(c) shows the effect of MK additions on the reaction degree of LS. The addition of MK presents the twofold effect on reaction of LS. First, when MK is added to replace partial cement in the mixtures, the mass ratio of cement to LS decreases which will lower the reaction degree of LS (this is considered through parameter  $m_1$  of equation (7)). However, the aluminum content in MK (46%) is about ten times of the aluminum content in cement (4.6%). The addition of MK will enhance the reaction of LS (this is considered through parameter  $m_4$  of equation (7)). Because the enhancing effect is much more significant than the lowering effect, the addition of MK can increase the reaction degree of limestone (shown in Figure 3(c)). Similar to the contents shown in Figure 3(c), many researchers [4, 9] also experimentally found that reactivity of limestone can be improved due to MK addition.

Figure 3(d) shows the effect of metakaolin and limestone contents on the reaction degree of cement. When metakaolin and limestone are used to replace partial cement, the reaction degree of cement is improved due to the dilution effect and nucleation effect (the dilution effect is considered through parameter  $\lambda_2$  in equation (1), and the nucleation effect is considered through equations (4) and (5)). Similar to the contents shown in Figure 3(d), Lam et al. [25] also found that the addition of mineral admixtures can improve the reaction degree of cement.

**3.2. Verification of Strength Development Model.** By using the cement-MK-LS ternary-blended hydration model, the gel-space ratio of hydrating concrete can be calculated (equation (10)). Furthermore, based on the strength of concrete at different ages, the values of strength coefficients of  $a_1$ ,  $a_2$ , and  $a_3$  and  $b_1$ ,  $b_2$ , and  $b_3$  can be calibrated ( $a_1 = 140$  MPa,  $a_2 = 258$  MPa,  $a_3 = 120$  MPa,  $b_1 = 3.85$ ,  $b_2 = 1.13$ , and  $b_3 = 1.34$ ). These coefficients do not vary with concrete mixtures. The values of  $a_1$  and  $b_1$  relate to cement hydration, the values of  $a_2$  and  $b_2$  relate to the metakaolin reaction, and the values of  $a_3$  and  $b_3$  relate to the limestone reaction. For cement-metakaolin binary blends, the development of strength relates to  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$ . For cement-limestone binary blends, the development of strength relates to  $a_1$ ,  $a_3$ ,  $b_1$ , and  $b_3$ . For cement-metakaolin-limestone ternary blends, the development of strength relates to  $a_1$ ,  $a_2$ ,  $a_3$ ,  $b_1$ ,  $b_2$ , and  $b_3$ . The analyzed results of compressive strength are shown in Figure 4. The analysis results generally agree with experimental results. At the ages of 28 days, the B15 concrete (cement 85% + metakaolin 10% + limestone 5%) has a highest strength than other mixtures. This may be because of the synergetic effect of metakaolin and limestone.

Because the strength coefficients of strength evaluation equation are constants for different concrete mixtures, we can make parameter analysis for different concrete mixtures. Figure 5(a) shows the strength development of cement-limestone binary blends. At the early age, due to the nucleation effect, the strength of limestone blends concrete shows higher strength than control concrete. While at late ages, due to the dilution effect, the strength of limestone blends concrete is lower than control concrete. As the contents of limestone increases from 10% to 20%, the late-age strength decreases. The trend shown in Figure 5(a) agrees with Bonavetti et al.'s [19] studies about strength development of limestone-blended concrete.

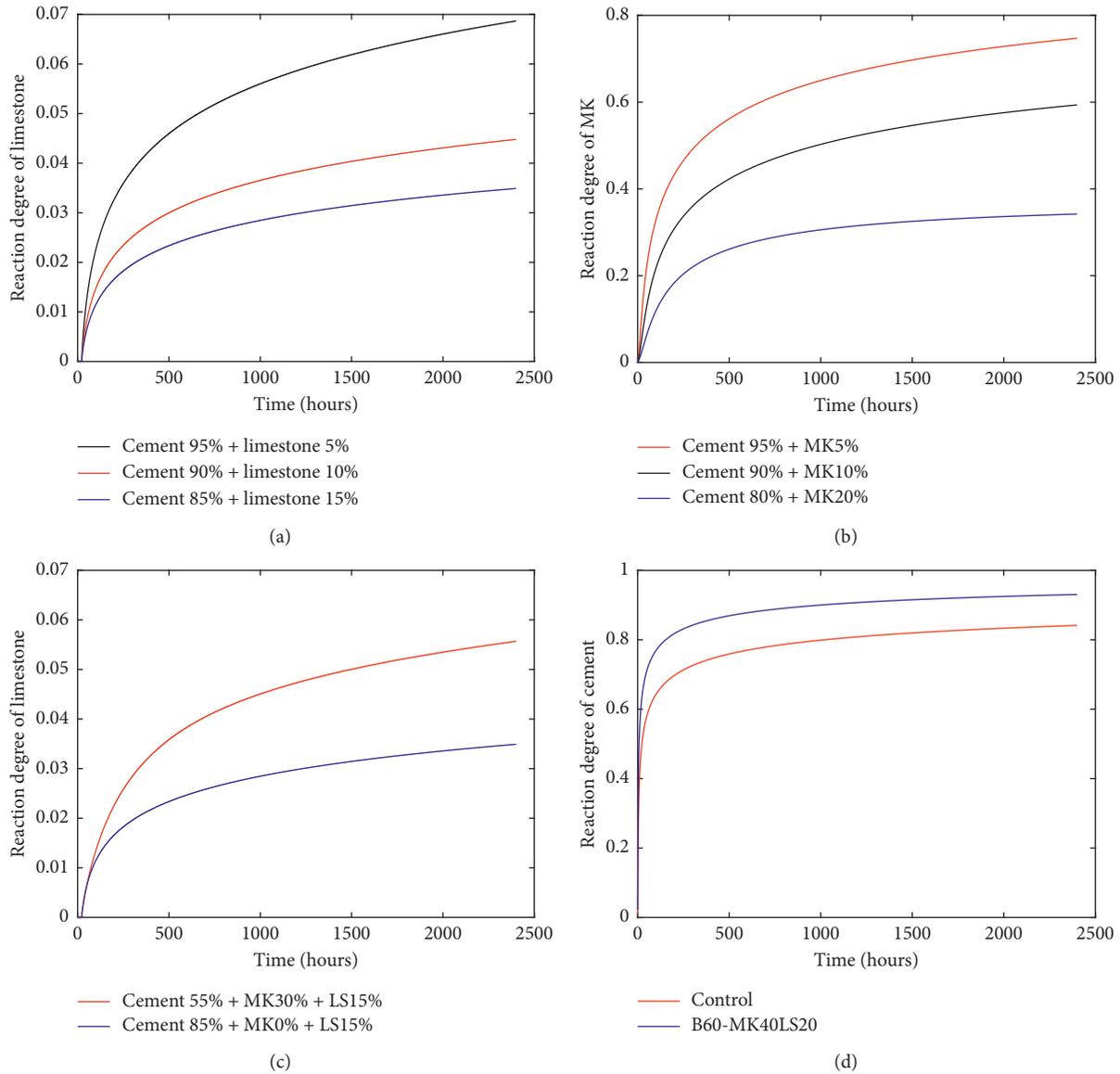


FIGURE 3: Parameter analysis of reaction degree of binders: (a) effect of limestone contents on the reaction degree of limestone; (b) effect of metakaolin contents on the reaction degree of metakaolin; (c) effect of metakaolin contents on the reaction degree of limestone; (d) effect of metakaolin and limestone contents on the reaction degree of cement.

Figure 5(b) shows the strength development of cement-metakaolin binary blends. Metakaolin-blended concrete has a higher strength than control concrete. As the contents of metakaolin increases from 5% to 10%, the strength also increases. The trend shown in Figure 5(b) agrees with Poon et al.'s [24] studies about strength development of metakaolin-blended concrete.

Damidot et al. [26] studies the strength development of 70% cement + 30% clay-limestone ternary blends. The sum of clay and limestone was fixed as 30%, and the weight fraction of clay/(clay + limestone) ranges from 0 to 100% [26]. Damidot et al. [26] found that, at the age of 28 days, the mix with 70% metakaolin has the highest strength than other mixes. This is because of the synergetic effect of limestone and metakaolin [26]. Based on the proposed strength development in this study, we make parameter analysis of

strength development for 70% cement + 30% clay-limestone ternary blends. In our analysis, the sum of clay and limestone is also fixed as 30%, the weight fractions of clay/(clay + limestone) are given as 0, 25%, 50%, 75%, and 100%, and the ages of parameter analysis are 1.5 days, 3 days, 28 days, and 90 days, respectively. The results of parameter analysis are shown in Figures 6(a)–6(d). As shown in Figure 6(a), at the age of 1.5 days, the strength of blended concrete is higher than base Portland cement. This is because of the nucleation effect of limestone. While as shown in Figures 6(b)–6(d), at the age of 3 days, 28 days, and 90 days, when the  $mk/(mk + limestone)$  equals to zero (the content of metakaolin is zero, and binder consists of 30% limestone and 70% cement), the strength of limestone-blended concrete is lower than base Portland cement. This is because of the dilution effect of limestone. While for other  $mk/$

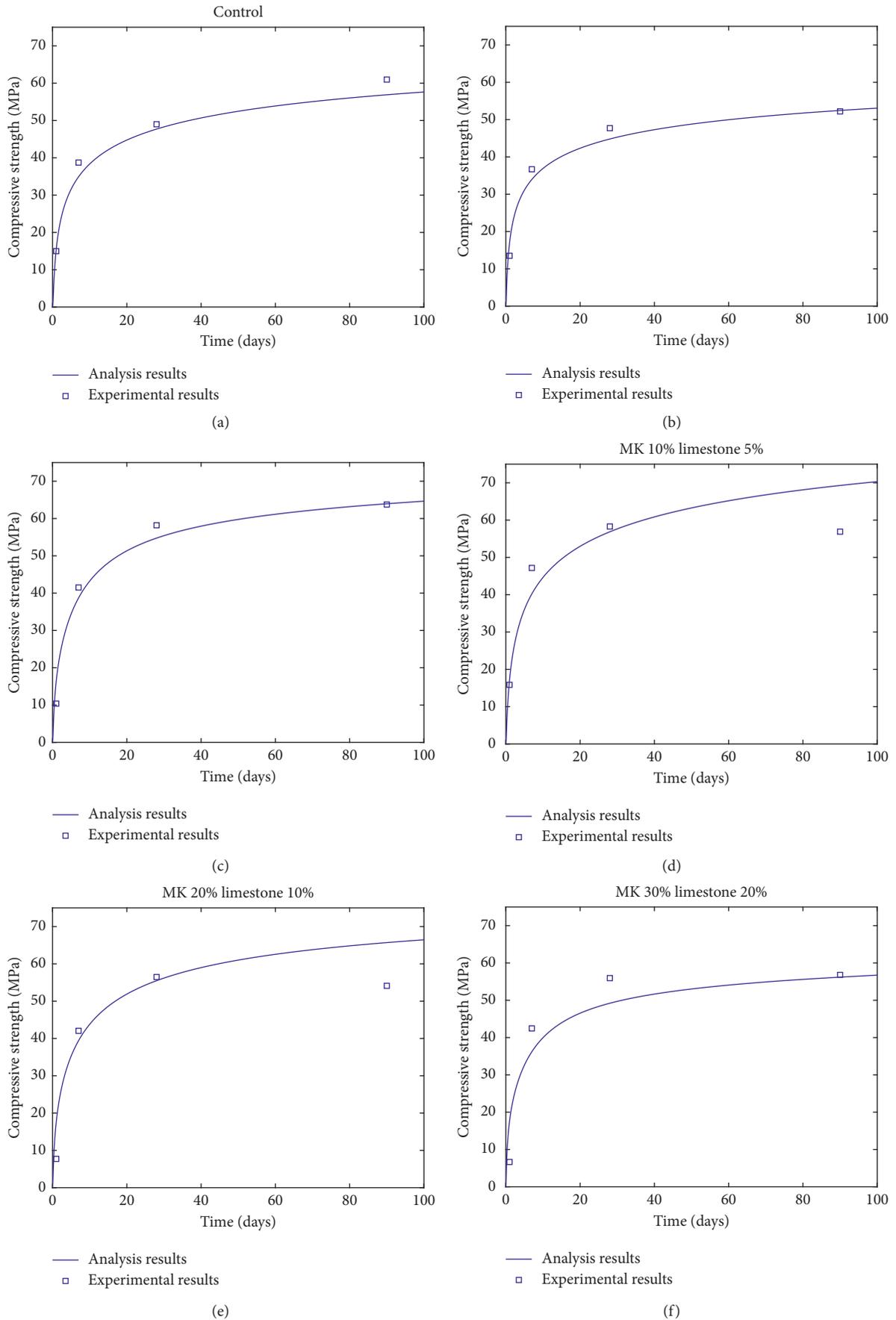


FIGURE 4: Continued.

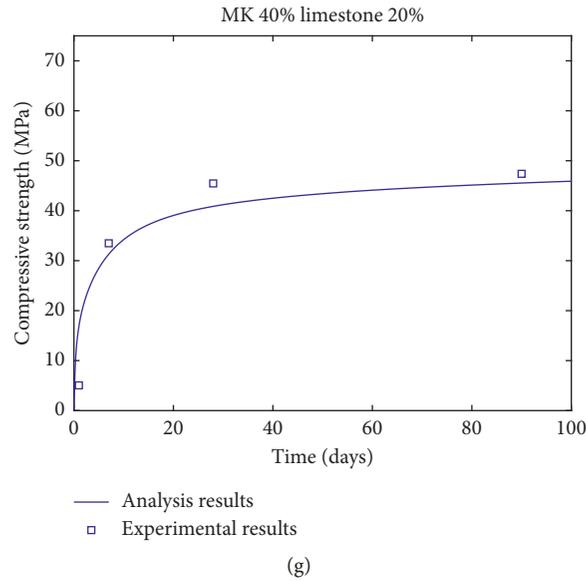


FIGURE 4: Analysis of compressive strength: (a) PC; (b) LS15; (c) MK30; (d) B15; (e) B30; (f) B45; (g) B60.

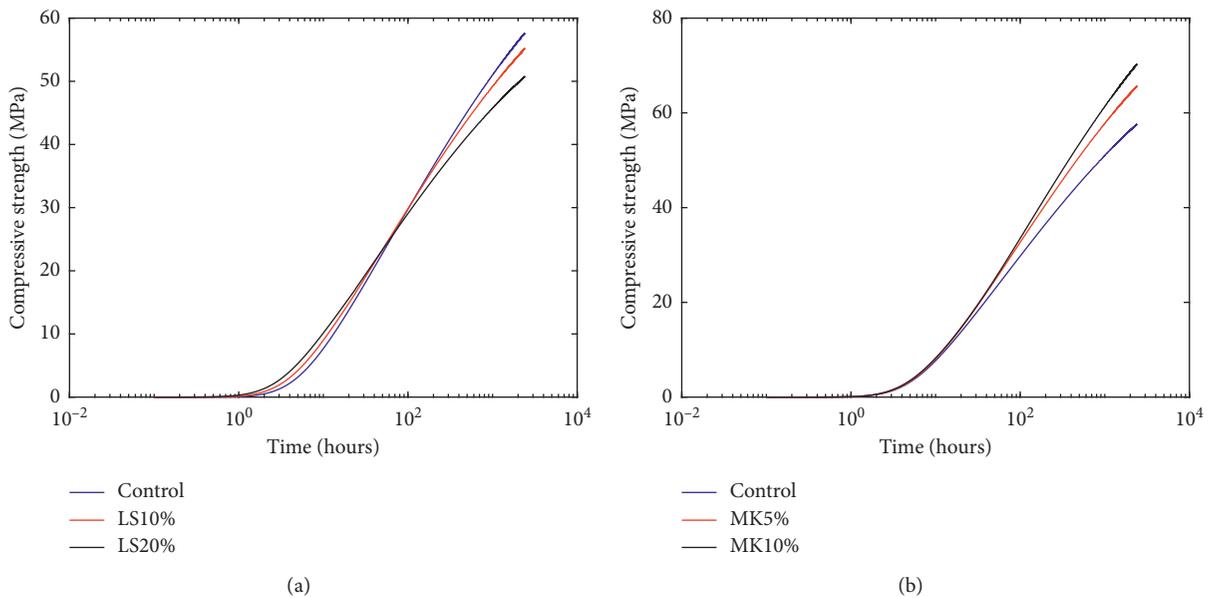


FIGURE 5: Effect of LS and MK on strength development: (a) cement-LS binary blends; (b) cement-MK binary blends.

(mk + limestone) ratios of 25%, 50%, 75%, and 100%, because the reaction of metakaolin can contribute to the strength, the strength of blended concrete is higher than base Portland cement.

At the age of 1.5 days, 3 days, 28 days, and 90 days, the optimum weight fractions of clay/(clay + limestone) are 25%, 50%, 75%, and 75%, respectively (shown in Figures 6(e)). Our analysis result about optimum weight fraction of clay/(clay + limestone) is similar to that of Damidot et al. [26] studies. In addition, our analysis shows that, at the ages of 1.5 days, 3 days, 28 days, and 90 days, the optimum weight fraction of limestone/(clay + limestone) is 75%, 50%, 25%, and 25%, respectively. It means that, at the early age, limestone is effective to improve the strength of concrete (this is because of

the nucleation effect of limestone), and at the late age, metakaolin is effective to improve the strength of concrete (this is because of the pozzolanic reaction of metakaolin).

In Figure 6, the sum of metakaolin and limestone is fixed as 30%. To find the optimum combinations of cement, metakaolin, and limestone, we make much wider parameter analysis. In this wider parameter analysis, the sum of metakaolin and limestone is not a fixed value. The contents of metakaolin vary from 0 to 30%, and the contents of limestone vary from 0 to 20%. The analysis results of isoline of strength are shown in Figures 7(a)–7(d). At the early age 1.5 days, the concrete with a higher limestone content and a lower metakaolin content has highest strength (shown in Figure 7(a)), while at the late

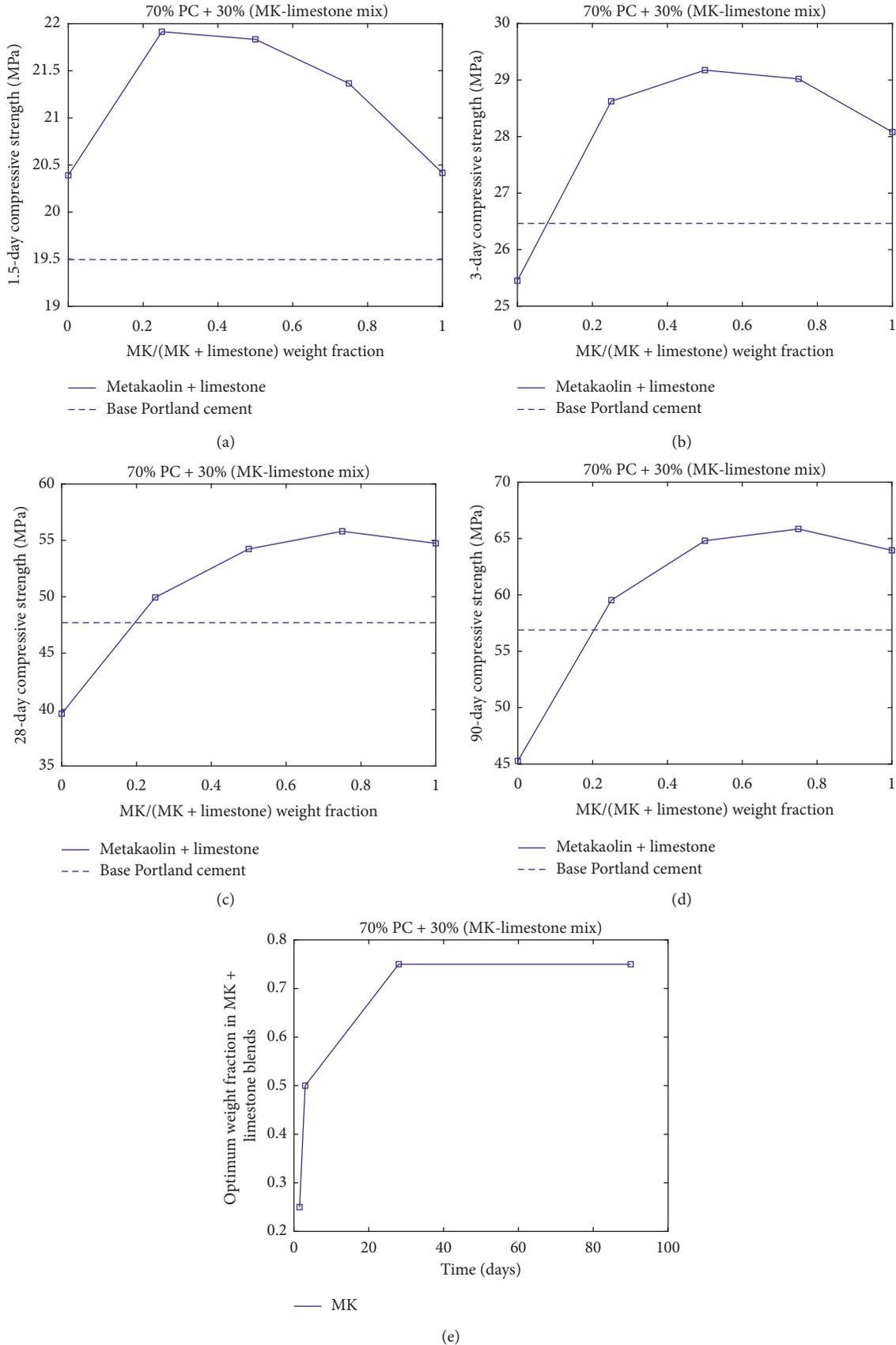


FIGURE 6: Synergetic effect of cement-MK-LS ternary blends (MK + LS = 30%): (a) 1.5 days; (b) 3 days; (c) 28 days; (d) 90 days, (e) optimum fractions of MK.

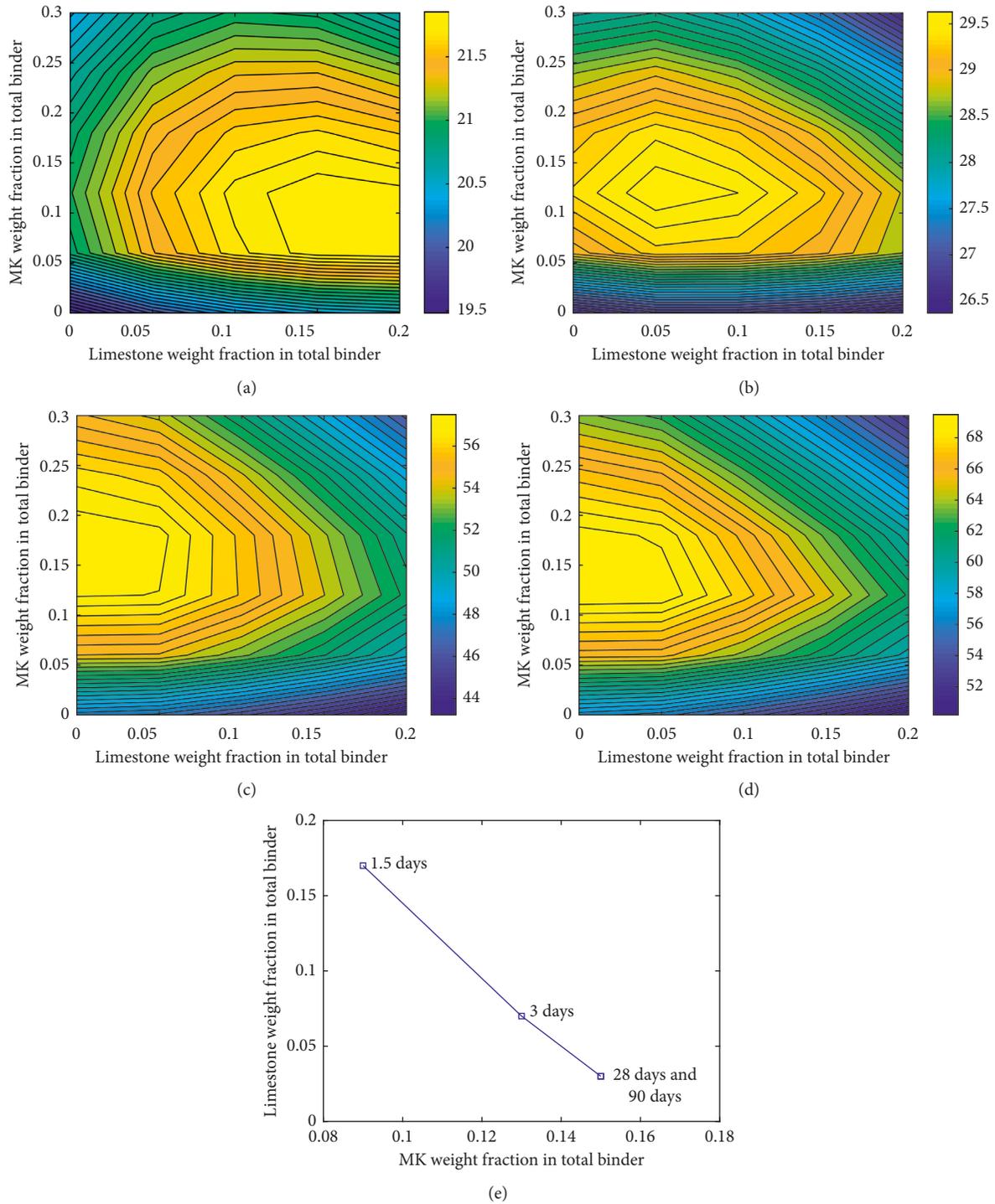


FIGURE 7: Analysis of optimum MK and LS combinations: (a) 1.5 days; (b) 3 days; (c) 28 days; (d) 90 days; (e) optimum MK and LS combinations at different ages.

age of 90 days, the concrete with a higher metakaolin content and a lower limestone content has highest strength (shown in Figure 7(d)). In other words, to achieve the highest strength of cement-metakaolin-limestone ternary blends, the optimum combination of metakaolin and limestone is dependent on ages. From the early age to late age, the optimum combinations change

shift from high limestone-low metakaolin zone to low limestone-high metakaolin zone (shown in Figure 7(e)).

#### 4. Conclusions

This study presents an integrated hydration-strength model for cement-limestone-metakaolin ternary blends.

First, a cement hydration model, a metakaolin reaction model, and a limestone reaction model are proposed in the ternary-blended hydration model. Pozzolanic reaction of metakaolin, chemical and physics effect of limestone, and synergetic effect between metakaolin and limestone are detailed considered in the ternary-blended hydration model. Moreover, the interactions among cement hydration, limestone reaction, and metakaolin reaction are considered through the contents of calcium hydroxide and capillary water. The coefficients of the hydration model do not change for various concrete mixtures.

Second, based on the hydration model, the gel-space ratio of hydrating blends is calculated considering the contributions from the reactions of cement, metakaolin, and limestone. Furthermore, the strength development of ternary blends is evaluated using the gel-space ratio. The coefficients of the strength model do not change for various concrete mixtures. Based on parameter analysis, the synergetic effect on strength development is shown, and the optimal combinations of cement-limestone-metakaolin ternary blends are determined. From the early age to late age, the optimum combinations of ternary blends shift from high limestone-low metakaolin zone to low limestone-high metakaolin zone.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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