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Research Article

Stochastic Dynamic Model of Sulfate Corrosion Reactions in Concrete Materials considering the Effects of Colored Gaussian Noises

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The corrosion reactions in concrete materials subjected to external environment attack can lead to the deterioration of concrete. However, the effects of internal fluctuations on the corrosion reaction process have not been reported in current studies on damage of concrete materials. To comprehensively describe the effects of internal fluctuations, the stochastic dynamic model of corrosion reactions in concrete materials subjected to sulfate attack is established based on the law of mass conservation and random process theory, in which internal fluctuations and the parameters of the chemical system are, respectively, regarded as colored Gaussian noises and a series of random variables. An experiment of sulfate corrosion reactions in concrete material is carried out to verify the effectiveness of the proposed method. Furthermore, the effects of variations of the initial reactant concentrations on the concentration evolution processes of the corrosion products are investigated. Results show that the stochastic dynamical responses of the corrosion reactions in concrete can be comprehensively investigated by the proposed stochastic mathematical model; the probabilistic information of the corrosion products can also be obtained conveniently. The concentration evolution process of sulfate corrosion products is a random process. The experimental data are only some samples of the random process. Concentrations of the corrosion products in concrete materials significantly fluctuate with the variations of the initial reactant concentrations.

1. Introduction

Sulfate attack is one of the main factors inducing the deteriorations of concrete materials. A more consistent viewpoint is the growth and expansion of the corrosion products in concrete materials accelerate the cracks' development, leading to the deterioration of the mechanical properties of concrete materials [1–4]. Although researchers have made significant progress in the experimental studies on concrete deteriorations [5–8], it is still very difficult to quantitatively analyze the deterioration process because of the finiteness and variability of the experimental data. Alternatively, many researchers devote themselves to numerical studies in recent years. According to the different phases in the concrete deterioration process, the numerical studies mainly focus on three aspects, namely, (a) the transport process of sulfate ions [9–11]; (b) chemical reactions induced by sulfate attack [12–14]; (c) coupling effects of the chemical reactions and mechanical properties [15–17]. These numerical models can basically achieve the quantitative analysis on the different phases of concrete deteriorations. However, the variability of the experimental results still cannot be explained by these methods.

In fact, abundant internal fluctuations exist in chemical reaction systems, which enhance the nonlinear performances of the systems [18–21]. It can be considered that the effects of internal fluctuations in the corrosion reactions in concrete materials lead to the variations of the experimental results. For an elementary chemical reaction system, the internal fluctuation effects can be described by the chemical master equation (CME) [22],

the chemical Langevin equation (CLE) [23], and the chemical Fokker–Plank equation (CFPE) [24]. However, most chemical reactions in the engineering practice are composite reactions, which cannot be achieved by a single reaction step. The existing stochastic kinetic methods applied in elementary chemical reactions cannot be directly employed to investigate the stochastic dynamical behaviors of composite chemical reaction systems because of the different reaction mechanisms. Moreover, internal fluctuations described by the CLE and CFPE are generally considered as white Gaussian noise [25]. This assumption is only a simplified treatment of internal fluctuations. Without loss of generality, a random process should be regarded as a colored noise process rather than a white noise process. The colored noises can also be expressed by the spectral representation method [26–28], linear filter method [29–31], proper orthogonal decomposition method [32–34], and other simulation methods [35–37]. These simulation methods for general random process have been successfully applied in the analysis on stochastic dynamical responses of nonlinear systems [38–40].

As mentioned above, although the deterministic corrosion reaction process induced by sulfate attack can be investigated by the existing literature studies [12–14, 22], the stochastic characteristics of the corrosion reaction system in concrete cannot be reasonably described by these methods. Alternatively, the above stochastic kinetic equations [22–24] are employed to investigate the random evolution process of chemical constituents. However, these stochastic kinetic equations of chemical reaction systems cannot be directly used in complex reaction systems due to the difficulties in solving the CME and CFPK. Furthermore, since the foundation of the derivation for the CLE is elementary reactions, it is not suitable for complex reactions. In the paper, the stochastic dynamical behaviors of the corrosion reaction system in concrete under sulfate attack are investigated by the proposed stochastic kinetic equation for complex reactions (SKE-CR), where internal fluctuations in the corrosion reaction system are considered as a colored Gaussian noise. The numerical solutions of the SKE-CR can be conveniently obtained by the general stochastic differential method or the Monte Carlo method.

The paper is arranged as follows. In Section 2, the stochastic kinetic equation for a composite chemical system is derived, and the solving procedure is also presented. In Section 3, a stochastic kinetic model of corrosion reactions in concrete with the effects of colored Gaussian noise is proposed. Then, in Section 4, the calculation results are compared with the experimental data. The effectiveness of the proposed method is also comprehensively discussed. Finally, we summarize our work in Section 4.

2. Methodology

The stochastic dynamical behaviors of an elementary chemical reaction can be conveniently investigated by solving the CLE. However, for a composite reaction, this method cannot be directly used because the premise of the deviation of the CLE is limited to an elementary reaction system. It is known that internal noises do not change the essential motion law of a system. Therefore, our work begins from the deterministic rate equation of a composite chemical reaction system.

2.1. Deterministic Rate Equation of Molar Concentration for Composite Chemical Reactions. Here, a composite chemical reaction system is considered, which consists of $M \geq 1$ molecular spices $\{Q_1, Q_2, \ldots, Q_M\}$ inside some fixed volume V, through $S \geq 1$ composite reactions $\{R_1, R_2, \ldots, R_S\}$. The dynamical state of the system at time t is $\mathbf{X}(t) = (X_1(t), X_2(t), \ldots, X_M(t))$, where $X_i(t)$ is the number of molecules Q_i in the system $(i = 1, 2, \ldots, M)$. $\mathbf{X}(t)$ is denoted as

$$\begin{cases} \mathbf{X}(t_0) = x_0, \\ \mathbf{X}(t) = x_t. \end{cases} \tag{1}$$

The reaction R_j in the system can be expressed as follows:

$$-\gamma_{j,A_1} A_1 - \gamma_{j,A_2} A_2 - \cdots \xrightarrow{k_j} \gamma_{j,B_1} B_1 + \gamma_{j,B_2} B_2 + \cdots, \tag{2}$$

where γ_{j,A_1}, γ_{j,A_2}, γ_{j,B_1}, and γ_{j,B_2} are the stoichiometric coefficients of reaction R_j, corresponding to A_1, A_2, B_1, and B_2, respectively; A_1 and A_2 are the reactants of reaction R_j; B_1 and B_2 are the products of the same reaction; and k_j is the reaction rate constant of reaction R_j.

If the molar concentrations of the chemical constituents A_1, A_2, B_1, and B_2 of reaction R_j are denoted as $C_{j,A_1}(t)$, $C_{j,A_2}(t)$, $C_{j,B_1}(t)$, and $C_{j,B_2}(t)$, respectively, the reaction rate $v_j(\mathbf{X}(t))$ of this reaction channel satisfies the following equation [41]:

$$v_j(\mathbf{X}(t)) = k_j C_{j,A_1}^{n_{j,A_1}}(t) C_{j,A_2}^{n_{j,A_2}}(t) C_{j,B_1}^{n_{j,B_1}}(t) C_{j,B_2}^{n_{j,B_2}}(t) \cdots = k_j \prod_{i=1}^{M} C_{j,i}^{n_{j,i}}(t), \tag{3}$$

where n_{j,A_1}, n_{j,A_2}, n_{j,B_1}, and n_{j,B_2} are the reaction suborder of the chemical constituents A_1, A_2, B_1, and B_2, respectively (for a specified reaction order n, $n = n_{j,A} + n_{j,B} + n_{j,G} + n_{j,M}$); $n_{j,i}$ represents the suborder of the ith chemical constituent in reaction R_j; and $C_{j,i}(t)$ is the molar concentration of the ith chemical constituent in reaction R_j.

Based on the mass conservation law, the rate equation of the molar concentration can be given as [41]

$$\frac{\partial C_i}{\partial t} + \nabla\left(C_i \mathbf{v}^i\right) = \sum_{j=1}^{S} \gamma_{j,i} v_{j,i} k_j \prod_{i=1}^{M} C_{j,i}^{n_{j,i}}(t), \tag{4}$$

where $\mathbf{v}^i$ is the velocity of the ith constituent diffusing into an arbitrary field D_{fixed} of the reaction system; $\nabla(\cdot)$ is a symbol of divergence; and $v_{j,i}$ is the oriental parameter, equal to 1, -1, or 0 according to the number of molecules Q_i in reaction R_j increasing, decreasing, or unchanged, respectively.

If the chemical reaction system is a well-stirred mixture, the concentration of the ith constituent in each field D_{fixed} of the system can be considered as the same value. Thus, the

velocity $\mathbf{v}^i$ is approximately equal to 0. Accordingly, equation (4) becomes

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} k_j \prod_{i=1}^{M} C_{j,i}^{n_{j,i}}(t). \tag{5}$$

Equation (5) is the rate equation of the concentration for composite reaction R_j. For writing convenience, this equation is denoted as the deterministic rate equation for composite reactions (DRE-CR) in the paper.

2.2. Stochastic Kinetic Equation for Composite Chemical Reactions. When the effect of internal fluctuations in a composite chemical reaction system is not concerned by researchers and engineers, the DRE-CR could give some deterministic results of the concentration evolution of chemical constituents. However, these results always deviate from the experimental data. Actually, as mentioned above, internal fluctuations can enhance the nonlinear performance of the chemical system. Because of the uncertainty of internal fluctuations, the concentrations of chemical constituents at the same corrosion time obtained in different experiments are different from each other. To further consider the effects of internal fluctuations on a composite chemical reaction system, the evolution process of the constituent concentrations should be investigated from the aspect of the dynamical state $\mathbf{X}(t)$ of the system. According to the rate equation of molar concentrations, for a deterministic composite chemical reaction system, according to equation (5), the rate equation of the number of molecules Q_i can be given as

$$\frac{\mathrm{d}X_i(t)}{\mathrm{d}t} = \frac{\mathrm{d}[C_i(t) \cdot V]}{\mathrm{d}t} = \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} k_j \prod_{i=1}^{M} C_{j,i}^{n_{j,i}} V. \tag{6}$$

By substituting equation (3) into equation (6), we can get the following equation:

$$\frac{\mathrm{d}X_i(t)}{\mathrm{d}t} = \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{X}(t)) \cdot V = \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} \hat{\upsilon}_j(\mathbf{X}(t)), \tag{7}$$

where $\hat{\upsilon}_j(\mathbf{X}(t)) = \upsilon_j(\mathbf{X}(t)) \cdot V$ is denoted as the deterministic reaction rate of the total number of molecules Q_i in reaction R_j. Note that this reaction rate at time t is a constant determined by equation (3) because the concentrations $C_{j,i}(t)$, $i = 1, 2, \ldots, M$ in reaction R_j are some constants when time t is given.

Nevertheless, if the effects of internal fluctuations in the system are considered, the reaction rate of the total number of molecules at time t will be a random variable rather than a constant. Therefore, the reaction rate $\upsilon_j(\mathbf{X}(t), \tau)$ of reaction R_j will be a random process according to the stochastic process theory, where τ is the time interval of two time points t_2 and t_1. As proposed in the literature [25], generally, the random process $\upsilon_j(\mathbf{X}(t), \tau)$ can be regarded as a Gaussian random process with the mean vector $\hat{\upsilon}_j(\mathbf{X}(t))$ and covariance function D_j.

Thus, in the time interval τ, the increment of the number of molecules Q_j in reaction R_j satisfies the following equation:

$$\Delta x_{j,i} = \int_t^{t+\tau} \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{x}_t, \tau) \mathrm{d}t'. \tag{8}$$

Noting that $\upsilon_j(\mathbf{x}_t, \tau)$ is only related to $\mathbf{x}_t$ and τ, equation (8) turns into

$$\Delta x_{j,i} = \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{x}_t, \tau) \int_t^{t+\tau} \mathrm{d}t' = \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{x}_t, \tau)\tau. \tag{9}$$

Thus, the number of molecules Q_i in reaction R_j at the time $(t + \tau)$ can be given as

$$X_{j,i}(t+\tau) = X_{j,i}(t) + \Delta x_{j,i} = X_{j,i}(t) + \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{x}_t, \tau)\tau. \tag{10}$$

Then the total number of molecules Q_i in the system can be obtained:

$$\begin{aligned} X_i(t+\tau) &= \sum_{j=1}^{R} X_{j,i}(t+\tau) = \sum_{j=1}^{S} \left(X_{j,i}(t) + \Delta x_{j,i} \right) \\ &= X_i(t) + \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} \upsilon_j(\mathbf{x}_t, \tau)\tau. \end{aligned} \tag{11}$$

Invoking the linear combination theory for a Gaussian random process [42], and noting that the mean vector of Gaussian random process $\upsilon_j(\mathbf{X}(t), \tau)$ is $\hat{\upsilon}_j(\mathbf{X}(t))$ (as shown in equation (1), the state $\mathbf{X}(t)$ of the system at time t can be denoted as $\mathbf{x}_t$), $\upsilon_j(\mathbf{X}(t), \tau)$ can be expressed as follows:

$$\upsilon_j(\mathbf{X}(t), \tau) = \hat{\upsilon}_j(\mathbf{X}(t)) + \omega_j(t), \tag{12}$$

where $\omega_j(t)$ is a Gaussian random process with zero mean vector and covariance function D_j.

Recalling that $\mathbf{x}_t$ stands for $\mathbf{X}(t)$, and substituting equation (12) into equation (11) and $\mathrm{d}t$ for τ, equation (11) can be rearranged as

$$\frac{\mathrm{d}X_i(t)}{\mathrm{d}t} = \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} \cdot \hat{\upsilon}_j(\mathbf{X}(t)) + \sum_{j=1}^{S} \gamma_{j,i} \nu_{j,i} \cdot \Gamma_j(t), \quad i = 1, \ldots, M, \tag{13}$$

where $\Gamma_j(t) = \omega_j(t)/\mathrm{d}t$. Considering that the derivative of a Gaussian random process is still a Gaussian process, naturally, $\Gamma_j(t)$ is still a Gaussian random process with zero mean and covariance function $D_j(\mathbf{x}_{t_1}, \mathbf{x}_{t_2})$ in equation (13). Noting that all reactions occur in a same chemical reaction system, we could assume that $\Gamma_j(t)$ in each reaction channel R_j has the same covariance function $D(\mathbf{x}_{t_1}, \mathbf{x}_{t_2})$. Thus, each $\Gamma_j(t)$ can be approximated by the same random process $\Gamma'(t)$, i.e., $\Gamma_1(t) = \Gamma_2(t) = \cdots = \Gamma_S(t) = \Gamma'(t)$.

Finally, recalling $X_j(t) = C_i(t) \cdot V$ and $\hat{\upsilon}_j(\mathbf{X}(t)) = \upsilon_j(\mathbf{X}(t)) \cdot V$, the stochastic kinetic equation for composite reactions (SKE-CR) is presented as follows:

$$\frac{\mathrm{d}C_i(t)}{\mathrm{d}t} = \sum_{j=1}^{S} \gamma_{j,i}\nu_{j,i}\xi_{k_j}\prod_{i=1}^{M} C_{j,i}^{n_{j,i}}(t) + \frac{\sum_{j=1}^{S}\gamma_{j,i}\nu_{j,i}}{\sqrt{V}}\Gamma(t), \quad i = 1,\ldots,M, \tag{14}$$

where ξ_{k_j} $(j = 1, 2, \ldots, S)$ are a set of independent random variables considering the variability of the reaction rate constant k_j in the composite reaction system and $\Gamma(t) = \sqrt{V}\cdot\Gamma'(t)$ is still a Gaussian random process because $\sqrt{V}$ is a constant for a given chemical reaction system. Generally, the reaction rate coefficients k_j are some ratio coefficients without relation to the concentrations of the chemical constituents. However, they are related to the temperature, solvent, and catalyst of the chemical system. Because of the variations of the parameters in the system, the reaction rate coefficients k_j should also be considered to be some random variables [36, 42].

2.3. Solution of the SKE-CR. $\Gamma(t)$ is a Gaussian random process with zero mean and covariance function $D(\mathbf{x}_{t_1}, \mathbf{x}_{t_2})$, namely, $\Gamma(t)$ is a colored Gaussian noise. According to the stochastic process theory, a colored Gaussian noise can be expanded into a linear combination of a series of random variables [42]. Generally, the Karhunen–Loeve decomposition can be employed to expand a colored Gaussian noise:

$$\Gamma(t) = \sum_{m=1}^{\infty} \delta_m\sqrt{\lambda_m}\phi_m, \tag{15}$$

where λ_m and ϕ_m are the mth eigenvalue and eigenvector of the covariance function $D(\mathbf{x}_{t_1}, \mathbf{x}_{t_2})$, respectively, and δ_m $(m = 1, 2, \ldots, \infty)$ are a set of independent standard random variables. The eigenvalues and eigenvectors can be calculated from the following Fredholm equation [42]:

$$\int_0^t D(\mathbf{x}_{t1}, \mathbf{x}_{t2}) f_m(\mathbf{x}_1) d(\mathbf{x}_1) = \lambda_m f_m(\mathbf{x}_{t2}). \tag{16}$$

The first N sets of eigenvalues and eigenvectors can be determined according to the 97% energy principle [42, 43]. Hence, $\Gamma(t)$ can be approximated as

$$\Gamma(t) \approx \sum_{m=1}^{N} \delta_m\sqrt{\lambda_m}\phi_m. \tag{17}$$

By substituting equation (17) into equation (14), we can get the following equation:

$$\frac{\mathrm{d}C_i(t)}{\mathrm{d}t} = \sum_{j=1}^{S} \gamma_{j,i}\nu_{j,i}\xi_{k_j}\prod_{i=1}^{M} C_{j,i}^{n_{j,i}}(t) + \frac{\sum_{j=1}^{S}\gamma_{j,i}\nu_{j,i}}{\sqrt{V}}\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\phi_m, \quad i = 1,\ldots,M. \tag{18}$$

Equation (18) is a stochastic kinetic equation consisting of $S + N$ random variables. This equation can be solved by the Monte Carlo simulation method (MCSM) [25], the general stochastic differential method (SDM) [23], and the probability density evolution method (PDEM) [39, 44]. Here, without loss of generality, the procedure of solving the SKE-CR by using the MCSM is presented:

(1) Expanding the random process $\Gamma(t)$ by the K-L decomposition method and determining N sets of eigenvalues and eigenvectors
(2) Randomly generating 10000 representative points representing the random variable space expanded by $(S + N)$ random variables
(4) Solving equation (18), where the random variables are determined by the above 10000 representative points randomly generated by a computer
(5) Analyzing the calculation results and obtaining the probabilistic information of the concentrations of chemical constituents

2.4. Stochastic Kinetic Model of Corrosion Reactions in Concrete. The chemical reactions occurring in concrete are very complicated when the concrete is subjected to external sulfate attack. The paths and results of these corrosion reactions will change with the different initial concentrations of sulfate and chemical constituents. In the literature, the chemical reactions in concrete under sulfate attack are summarized as following equations [2, 41, 45]:

$$\mathrm{Na_2SO_4 + 2H + CH} \xrightarrow{k_1} \mathrm{C\bar{S}H_2 + 2NaOH} \tag{19}$$

$$\mathrm{C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H} \xrightarrow{k_2} \mathrm{C_6AS_3H_{32}} \tag{20}$$

$$\mathrm{3C_4A\bar{S}H_{12} + 3Na_2SO_4 + 34H} \xrightarrow{k_3} \mathrm{6NaOH + 2Al(OH)_3 + 2C_6A\bar{S}_3H_{32}} \tag{21}$$

$$\mathrm{C_3A + 3C\bar{S}H_2 + 26H} \xrightarrow{k_4} \mathrm{C_6A\bar{S}_3H_{32}} \tag{22}$$

$$\mathrm{C_3AH_6 + 3C\bar{S}H_2 + 20H} \xrightarrow{k_5} \mathrm{C_6A\bar{S}_3H_{32}} \tag{23}$$

where, except for sodium hydroxide (NaOH) and aluminum hydroxide ($Al(OH)_3$), C denotes CaO, H denotes H_2O, A denotes Al_2O_3, and $\bar{S}$ denotes SO_3; calcium hydroxide (CH), tricalcium aluminate (C_3A), and calcium aluminosilicate hydroxide ($3C_4A\bar{S}H_{12}$) are the products of cement hydration; ettringite ($C_6A\bar{S}_3H_{32}$), gypsum ($C\bar{S}H_2$), sodium hydroxide, and aluminum hydroxide are the products of corrosion reactions. The volume expansion of the corrosion products, such as ettringite and gypsum, is the main reason leading to the deterioration of the mechanical properties of

concrete. Therefore, it is important to quantify the content of these corrosion products before we obtain the relationship between the expansion degree and concentration of the corrosion products. First, the deterministic dynamic model of sulfate corrosion reactions in concrete should be established.

In a solid-liquid reaction system, the content of H_2O is always sufficient, namely, the concentration of water can be considered as 100%. Generally, these sulfate corrosion reactions are 2 order reactions because the reaction rate of each reaction is only related to two reactants. Here, we denote the suborders of the reactants and products as $n_{j,A_1} = n_{j,A_2} = 1$ and $n_{j,B_1} = n_{j,B_2} = \cdots = 0$, respectively. Then, the deterministic rate equations for sulfate corrosion reactions (DRE-SCR) in concrete can be established based on the DRE-CR:

$$\begin{cases} \dfrac{dx_1}{dt} = -k_1x_1x_2 - 3k_3x_1x_4, \\ \dfrac{dx_2}{dt} = -k_1x_1x_2, \\ \dfrac{dx_3}{dt} = k_1x_1x_2 - 2k_2x_3x_4 - 3k_4x_3x_5 - 3k_5x_3x_6, \\ \dfrac{dx_4}{dt} = -k_2x_3x_4 - 3k_3x_1x_4, \\ \dfrac{dx_5}{dt} = -k_4x_3x_5, \\ \dfrac{dx_6}{dt} = -k_5x_3x_6, \\ \dfrac{dx_7}{dt} = k_2x_3x_4 + 2k_3x_1x_4 + k_4x_3x_5 + k_5x_3x_6, \end{cases} \tag{24}$$

where x_i, $i = 1, 2, \ldots, 7$ represent the molar concentrations of the reactants and products in the reactions. Equation (24) is a set of ordinary differential equations which can be solved by the fourth-order Runge–Kutta method with some given initial conditions. The chemical constituents represented by x_i, $i = 1, 2, \ldots, 7$ can be found in Table 1.

Then, according to the SKE-CR (equation (18)), the stochastic kinetic equation for sulfate corrosion reactions (SKE-SCR) in concrete can be given as

$$\begin{cases} \dfrac{dx_1}{dt} = -\zeta_{k_1}x_1x_2 - 3\zeta_{k_3}x_1x_4 + \dfrac{(-1-3)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_2}{dt} = -\zeta_{k_1}x_1x_2 + \dfrac{(-1)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_3}{dt} = \zeta_{k_1}x_1x_2 - 2\zeta_{k_2}x_3x_4 - 3\zeta_{k_4}x_3x_5 - 3\zeta_{k_5}x_3x_6 \\ \qquad + \dfrac{(1-2-3-3)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_4}{dt} = -\zeta_{k_2}x_3x_4 - 3\zeta_{k_3}x_1x_4 + \dfrac{(-1-3)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_5}{dt} = -\zeta_{k_4}x_3x_5 + \dfrac{(-1)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_6}{dt} = -\zeta_{k_5}x_3x_6 + \dfrac{(-1)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_7}{dt} = \zeta_{k_2}x_3x_4 + 2\zeta_{k_3}x_1x_4 + \zeta_{k_4}x_3x_5 + \zeta_{k_5}x_3x_6 \\ \qquad + \dfrac{(1+2+1+1)}{\sqrt{V}}\displaystyle\sum_{m=1}^{N}\delta_m\sqrt{\lambda_m}\,\phi_m, \end{cases} \tag{25}$$

where random variables ζ_{k_j}, $j = 1, 2, \ldots, 5$ represent the reaction rate coefficients of five reactions obeying normal distributions with specific means and standard deviations (STDs). The equations can be solved according to the solving procedure introduced in Section 2.3.

3. Results and Discussion

To solve the DRE-SCR and SKE-SCR, the reaction rate constant k_j ($j = 1, 2, \ldots, 5$) should be determined. Generally, the reaction rate constant k_j proposed in the literature ranges from 1×10^{-11} mol/(m^3·s) to 1×10^{-2} mol/(m^3·s) [17, 46, 47]. It is very difficult for us to identify a set of appropriate parameters in such a large range. In this study, the experiment is carried out to determine the values of the reaction

Table 1: Chemical constituents represented by x_i, $i = 1, 2, \ldots, 7$ and their initial concentrations (mol/m^3).

Variable	x_1	x_2	x_3	x_4	x_5	x_6	x_7
Chemical constituent	Na_2SO_4	CH	$C\bar{S}H_2$	$C_4A\bar{S}H_{12}$	C_3A	C_3AH_6	$C_6A\bar{S}_3H_{32}$
S-1	140.85	3321.35	4.40	131.42	0	74.80	36.55
S-2	140.85	3277.48	4.09	131.42	0	74.80	29.22
S-3	140.85	3169.29	4.05	131.42	0	74.80	26.79
S-4	140.85	3157.41	3.50	131.42	0	74.80	21.99
Mean value	140.85	3253.13	4.01	131.42	0	74.80	28.64
CV	0.2	0.2	0.2	0	0	0	0.2

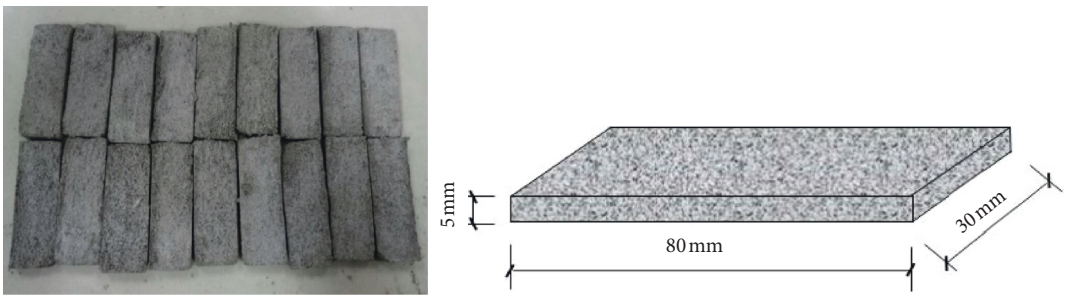
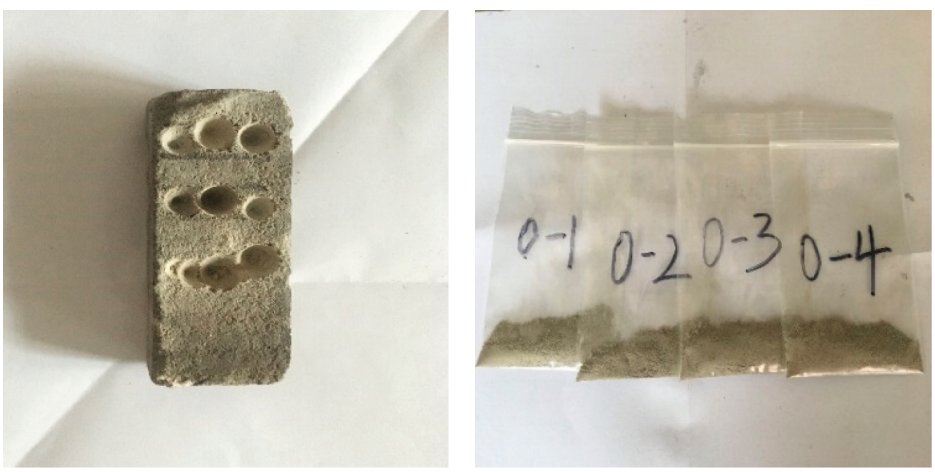


Figure 1: Specimens used in the experiment.



(a) (b)

Figure 2: Test powders used in DSC: (a) drilling in the specimen and (b) test powder mixed by drilling samplings at the beginning of the immersion.

rate coefficients of the sulfate reactions by minimizing the root-mean-square (rms) error between the theoretical results predicted by the DRE-SCR and the experimentally measured data.

3.1. Experimental Results. The concentrations of the chemical constituents in the sulfate corrosion reactions should be measured before we determine the reaction rate coefficients by the above method. In the experiment, Portland cement specimens were immersed in 2% sodium sulfate solution. To reasonably weaken the effects of the sulfate ions diffusion, the size of the specimens used in the experiment was 80 mm × 30 mm × 5 mm, as shown in Figure 1. Thus, equations (24) and (25) could be directly used to, respectively, describe the deterministic and stochastic concentration evolution process of the chemical constituents of concrete exposed to sulfate environment.

Four specimens were taken out of the solution at the end of 0, 2, 4, 8, 16, and 24 weeks from the time of immersion in sulfate solution. Then, these specimens had been immersed in an ethanol solution for two days to prevent them from hydration. After the specimens were naturally dried, the test powder was mixed by drilling sampling at different parts of the specimens, as shown in Figure 2. Afterwards, the concentrations of calcium hydroxide, gypsum, and ettringite were obtained by detecting the test powder with differential scanning calorimetry (DSC).

Concentrations of the chemical constituents at the end of 14 days were measured as the initial conditions. Four test powders are denoted as S-1, S-2, S-3, and S-4, respectively. The control temperature of the DSC is raised from room temperature to 550°C with the rate of 10°C/min. The peak temperature of the pure calcium hydroxide, gypsum, and ettringite was measured by DSC before the immersion. Peak temperatures of three

constituents were about 437°C, 170°C, and 130°C, respectively [48]. Figure 3 presents the typical DSC curve of the cement (measured at the end of 4 weeks), where peaks 1, 2, and 3, respectively, represent calcium hydroxide, gypsum, and ettringite.

The initial concentrations of calcium, gypsum, and ettringite are measured in the experiment; those of other chemical constituents are adopted according to the values proposed by Gouder [14]. The initial concentrations of the chemical constituents of four specimens are also given in Table 1, where CV represents the coefficient of variation.

3.2. Stochastic Dynamical Behaviors of the Sulfate Corrosion Reaction System in Concrete. In general, the concentrations of the corrosion products in concrete can be predicted by the deterministic rate equations based on the different rate constants k_j proposed in the literature [14, 49, 50]. However, people have to face the fact that the evolution process of corrosion product concentrations always changes with the different reaction rate coefficients. In this section, the reaction rate constant k_j is considered as a series of random variables with the given means and STDs. Thus, the SKE-SCR can be used to interpret the variability of experimental results.

3.2.1. Determination of the Reaction Rate Constant k_j. As mentioned above, the values of k_j for the four specimens were determined by minimizing the rms error between the theoretical results of the chemical constituents and the experimentally measured concentrations. Table 2 gives the values of reaction rate constant k_j in equations (19)–(23) calculated by the genetic algorithm with the above optimal objective. In the study, the initial concentrations of the constituents and five reaction rate coefficients are all considered as random variables following normal distributions. Their means and CVs are, respectively, presented in Tables 1 and 2.

3.2.2. K-L Decomposition on Colored Gaussian Noise. In this section, the effects of internal fluctuation on dynamical behaviors of the corrosion reaction system in concrete subjected to external sulfate attack are investigated, where internal fluctuations are regarded as colored Gaussian noises. Generally, it is difficult to determine the covariance function of a colored Gaussian noise. Therefore, a simple form of the covariance function is employed to illustrate the effectiveness of the SKE-SCR. The covariance function of the colored Gaussian noise in the SKE-SCR is assumed as the form of $D(\mathbf{x}_{t_1}, \mathbf{x}_{t_2}) = \langle \Gamma(t_1)\Gamma(t_2)\rangle = \exp(-|t_2 - t_1|/l)$, where l is the correlation time of colored Gaussian noises because the analytic solution of the Fredholm equation can be conveniently obtained by using the above covariance function $D(\mathbf{x}_{t_1}, \mathbf{x}_{t_2})$ as the kernel function. The eigenvalues obtained by solving the Fredholm equation with different correlation times are presented in Figure 4.

As shown in Figure 4, the eigenvalues are gradually close to zero with their orders increasing. The numbers of the eigenvalues in a specific time interval change over the different correlation times. To decrease the number of the random variables, in general, the first several order

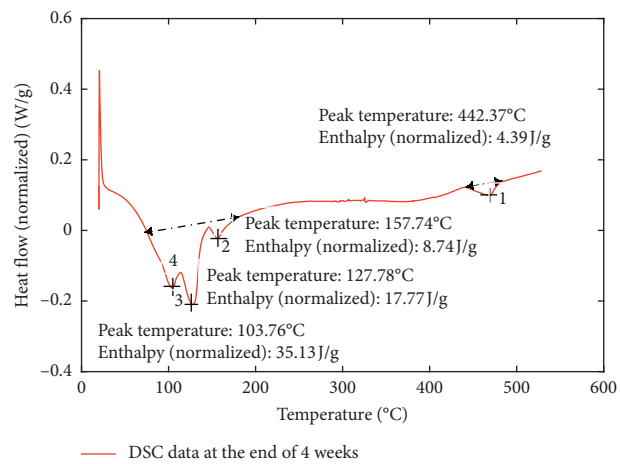


Figure 3: Typical DSC curve of specimens at the end of 4 weeks.

eigenvalues and eigenvectors are employed to represent the colored Gaussian noises. In this study, the correlation time is assumed as 2 weeks. The first 6 order eigenvalues and eigenvectors are determined to represent internal fluctuations because the latter eigenvalues are very close to zero. Accordingly, equation (25) becomes the following form:

$$\begin{cases} \dfrac{dx_1}{dt} = -\zeta_{k_1}x_1x_2 - 3\zeta_{k_3}x_1x_4 - \dfrac{4}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_2}{dt} = -\zeta_{k_1}x_1x_2 - \dfrac{1}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_3}{dt} = \zeta_{k_1}x_1x_2 - 2\zeta_{k_2}x_3x_4 - 3\zeta_{k_4}x_3x_5 - 3\zeta_{k_5}x_3x_6 \\ \qquad - \dfrac{7}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_4}{dt} = -\zeta_{k_2}x_3x_4 - 3\zeta_{k_3}x_1x_4 - \dfrac{4}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_5}{dt} = -\zeta_{k_4}x_3x_5 - \dfrac{1}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_6}{dt} = -\zeta_{k_5}x_3x_6 - \dfrac{1}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m, \\ \dfrac{dx_7}{dt} = \zeta_{k_2}x_3x_4 + 2\zeta_{k_3}x_1x_4 + \zeta_{k_4}x_3x_5 + \zeta_{k_5}x_3x_6 \\ \qquad + \dfrac{5}{\sqrt{V}}\displaystyle\sum_{m=1}^{6}\delta_m\sqrt{\lambda_m}\,\phi_m. \end{cases} \tag{26}$$

Considering the variation of reaction rate constant k_j, there are 11 random variables in equation (26) in total. They expand to an 11-dimensional random-variate space which can be represented by some specific representative points. The

Table 2: Values of reaction rate constant k_j (mol/(m^3·week)).

	k_1	k_2	k_3	k_4	k_5
S-1	5.85×10^{-3}	4.83×10^{-4}	5.32×10^{-3}	4.77×10^{-4}	2.41×10^{-5}
S-2	5.31×10^{-3}	2.93×10^{-4}	5.44×10^{-3}	5.58×10^{-4}	4.94×10^{-5}
S-3	5.31×10^{-3}	8.74×10^{-4}	5.33×10^{-3}	6.62×10^{-4}	6.65×10^{-5}
S-4	5.52×10^{-3}	6.82×10^{-4}	5.35×10^{-3}	4.74×10^{-4}	8.15×10^{-5}
Mean value	5.50×10^{-3}	5.83×10^{-4}	5.54×10^{-3}	5.43×10^{-4}	5.54×10^{-5}
CV	0.2	0.1	0.1	0.1	0.2

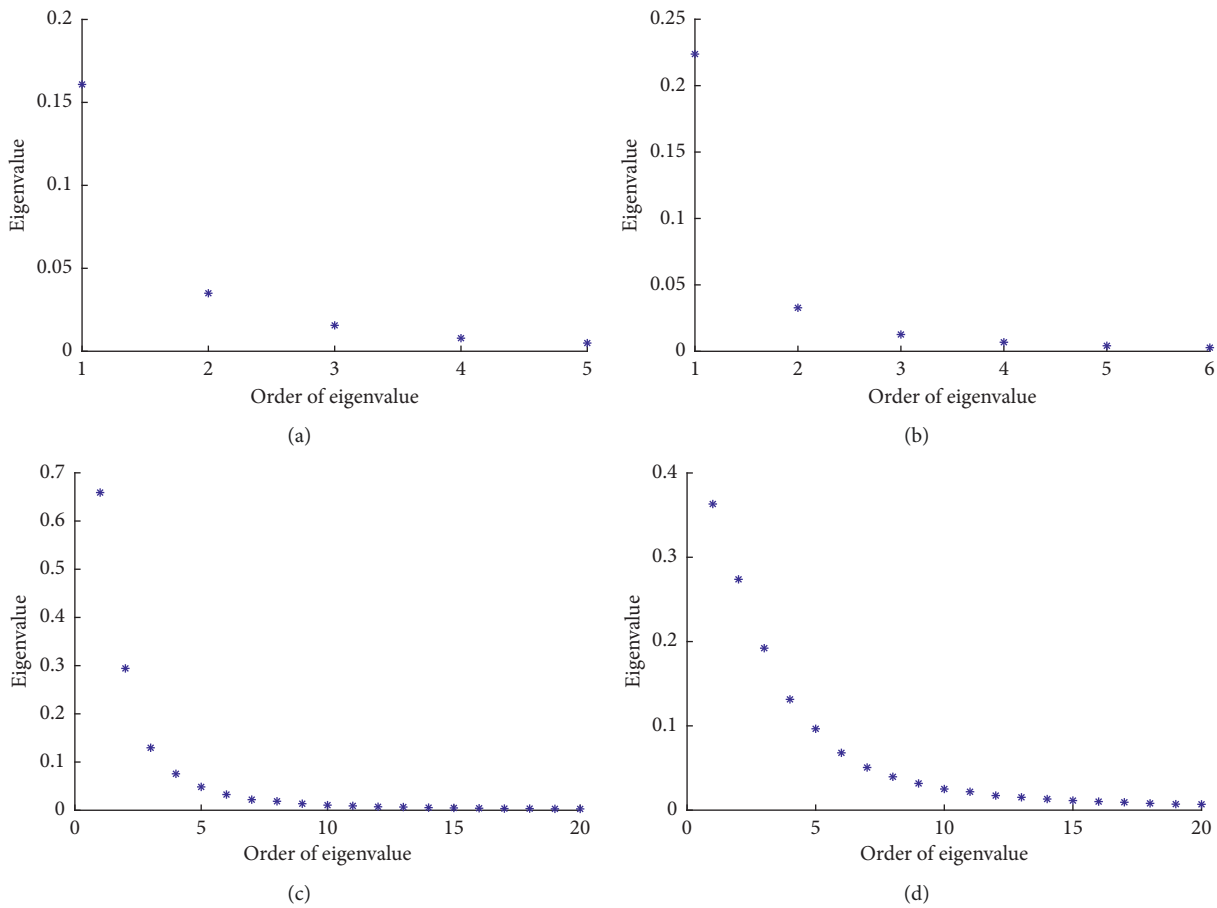


Figure 4: Eigenvalues calculated from the Fredholm equation with the different correlation times of (a) 4 weeks, (b) 2 weeks, (c) 0.5 weeks, and (d) 0.2 weeks.

MCSM is used to generate the representative points and solve the SKE-SCR. A computer randomly generates 10,000 representative points to represent the random-variate space expanded by 11 random variables. Figure 5 presents the values of the samples of random processes with different correlation times.

As shown in Figure 5, the amplitude and frequency of the colored Gaussian noise significantly change over the different correlation times. The fluctuation frequency of the colored noise increases with the correlation time increasing.

3.3. Result Analysis of the SKE-SCR. After each representative point in the representative point set is substituted into the SKE-SCR, equation (25) becomes a set of deterministic ordinary differential equations which can be conveniently solved by the fourth-order Runge–Kutta method. Figure 6 presents some samples of the concentration evolution process of calcium hydroxide, ettringite, and gypsum, where the black solid line represents the results calculated from the DRE-SCR; points 2132, 4311, 6657, and 7489 are some points randomly specified from the representative point sets. Each curve illustrates the calculation results of the SKE-SCR in which the values of the reaction rate coefficients and the samples of colored Gaussian noise are determined by the corresponding representative points.

When the effects of internal fluctuations and variability of the reaction rate coefficients are considered, as shown in Figure 6, the concentrations of calcium hydroxide, gypsum, and ettringite significantly fluctuate with the corrosion time increasing, which are different from the results obtained by

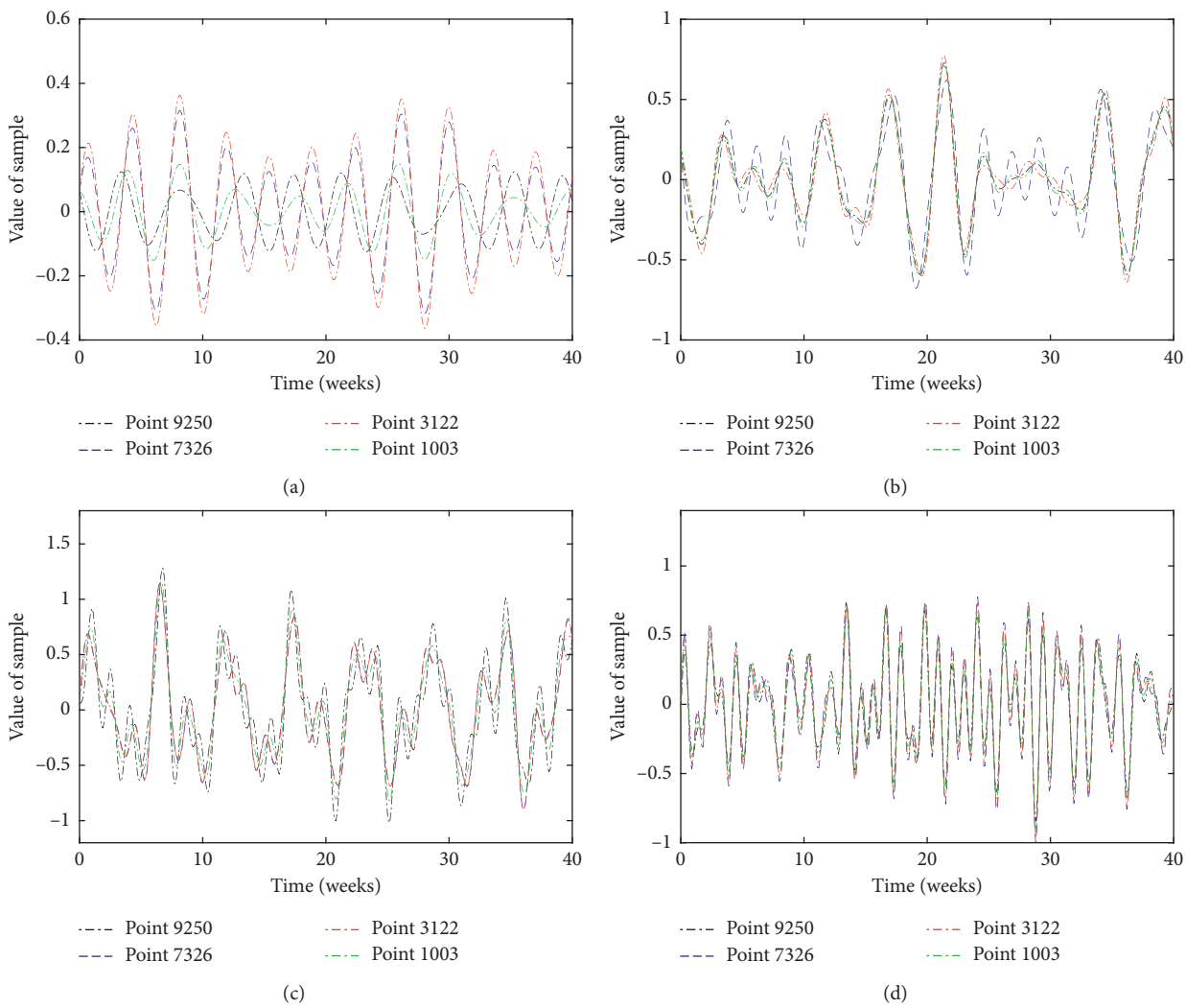


Figure 5: Samples of colored Gaussian noises with the correlation times of (a) 4 weeks, (b) 2 weeks, (c) 0.5 weeks, and (d) 0.2 weeks.

the DRE-SCR. The concentration evolution process of the corrosion products in concrete is no longer a deterministic result but a random process. Both the experimental data and theoretical predictions of the DRE-SCR can be regarded as some sample tracks of the random process. This conclusion can give the reason for the experimental data deviating from the theoretical results predicted by the DRE-SCR.

The means and STDs of the concentration of calcium hydroxide, gypsum, and ettringite can be found in Figure 7.

As shown in Figure 7, with the consideration of internal noises in the corrosion reaction system, the means of calcium hydroxide, gypsum, and ettringite at different times present large fluctuations. The STDs of three chemical constituents are far less than the means. This result indicates that the effects of internal fluctuations on the concentration means are greater than those on the concentration STDs. The STDs of the concentrations at the inchoate phase are more significant than those at the later phases. If the statistical properties of a random process change with time, this random process is called the nonstationary random process. In the study, the means and standard deviations of the concentration evolution processes of three constituents significantly fluctuate with the time increasing. Although the STD curves of calcium hydroxide, gypsum, and ettringite gradually become stable after 15th week, the concentration evolution processes of three constituents still belong to nonstationary random process because their means (the first-order moments) change against the corrosion times.

Figure 8 presents the comparison between the experimental data and the theoretical results predicted by the SKE-SCR. To demonstrate the distribution of the results obtained by the SKE-SCR, the predictions have been summarized as mean, mean ± STD, and mean ± 2 STDs, respectively. The experimental data of the concentration of each chemical constituent basically distribute between the curves of mean ± 2 STDs, with a few exceptions. The experimental data are the sample values of the concentration evolution process which should be considered as a random process. Meanwhile, it can be found by comparing Figures 8(a), 8(b), and 8(c) that the effects of internal fluctuations on the means of calcium hydroxide are smaller than those of the gypsum and ettringite, namely, the concentration evolution of

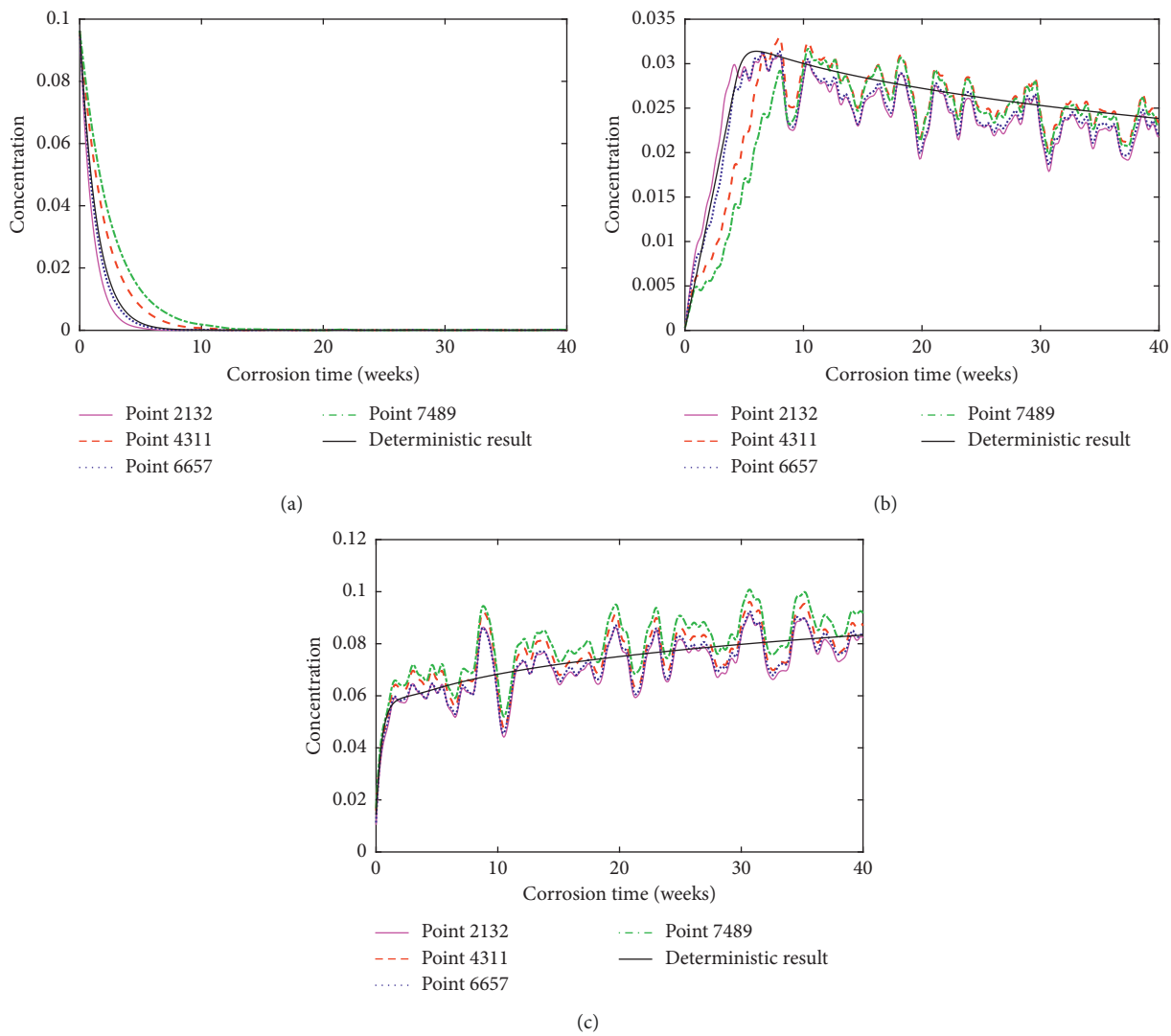


Figure 6: Samples of the concentration evolutions of (a) calcium hydroxide, (b) gypsum, and (c) ettringite.

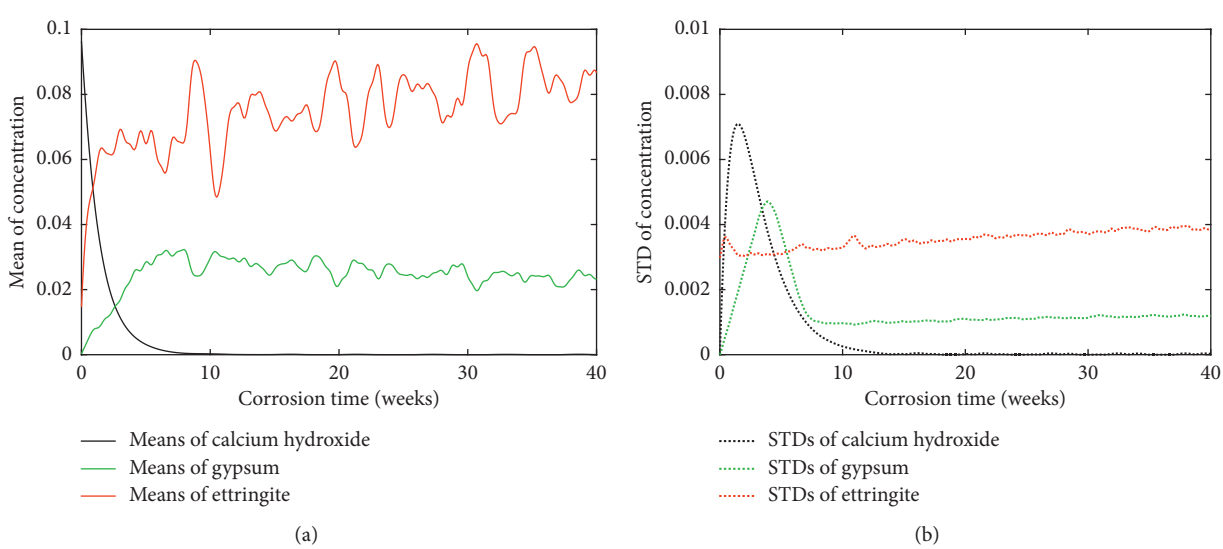


Figure 7: Means and STDs of the concentrations of three chemical constituents: (a) mean curve and (b) STD curve.

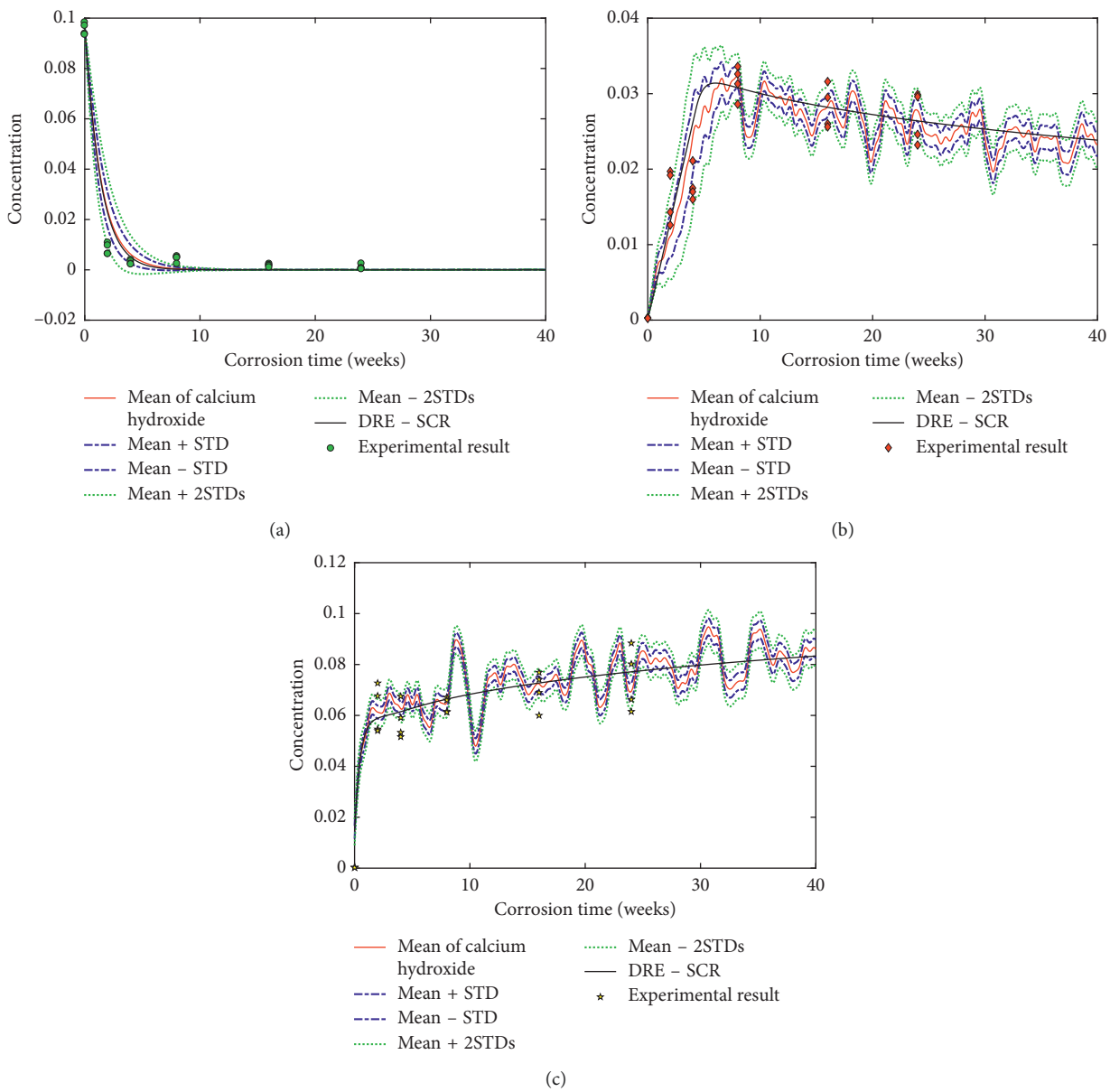


Figure 8: Comparison of the experimental data and the predictions of the SKE-SCR for (a) calcium hydroxide, (b) gypsum, and (c) ettringite.

calcium hydroxide can be little affective by internal fluctuations in the corrosion reaction system. The concentrations of calcium hydroxide are gradually close to zero with the corrosion time increasing. Therefore, the effects of internal fluctuations on the concentrations of calcium hydroxide can be approximately ignored. For convenience, in the following parts of the paper, we only discuss the effects of internal noises on the concentration evolution processes of gypsum and ettringite.

The probability density functions (PDFs) of the concentrations of calcium hydroxide, gypsum, and ettringite at the specific time steps are presented in Figure 9, where the blue dots represent the experimental results at the end of 16 weeks.

Figure 9 shows that the concentration of the sulfate corrosion products at each time step satisfies a certain distribution. However, the concentration distribution of the corrosion products does not follow the Gaussian distribution even though the random variables in the SKE-SCR are all assumed as independent Gaussian random variables. Meanwhile, the probabilities for the appearances of experimental results can be calculated by analyzing the concentration PDFs of the chemical constituents at a specific time step.

Figures 10 and 11, respectively, depict the PDF surfaces and probability contours of the concentrations of gypsum and ettringite. As shown in Figure 10, the PDF surfaces of the concentrations of the corrosion products significantly change with the corrosion times. This means that the concentration evolution processes of gypsum and ettringite are nonstationable random process because their means and STDs are all change against the corrosion time.

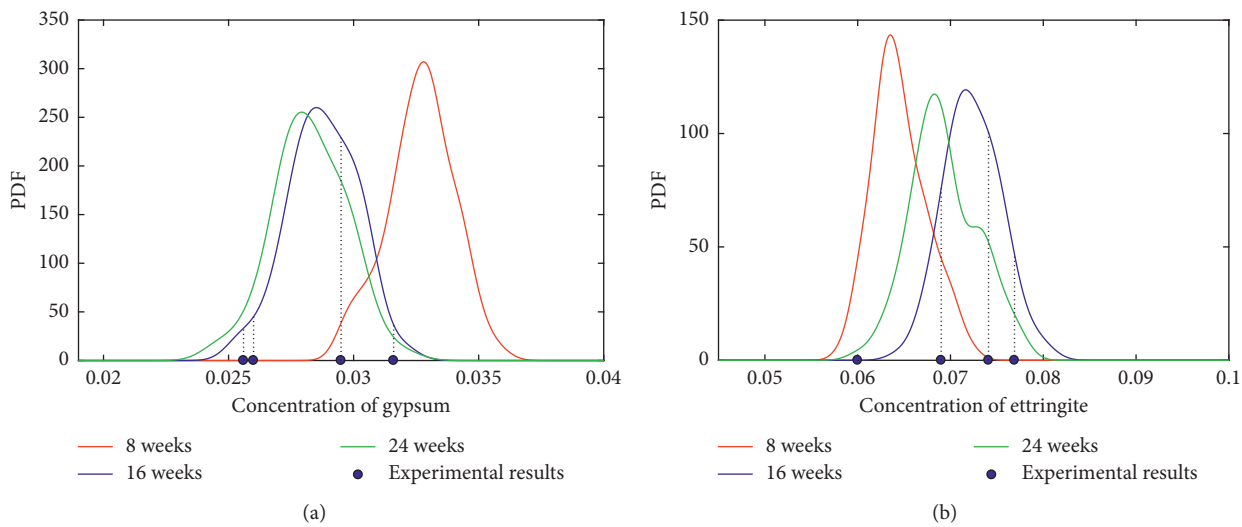


Figure 9: PDF curves of the concentrations of (a) gypsum and (b) ettringite.

The probability contours presented in Figure 11 give the distribution trends of the concentrations of gypsum and ettringite. Generally, the distribution range of the probability at a specific time step can reflect the degree of variability. The larger the range of the probability distributes, the higher the degree of variability is. It is found that the concentration range of gypsum at the early corrosion phase is wider than that at the medium and later phases. This result shows that the concentration variation of the former is larger than that of the later. However, it is not the case for ettringite. The variation of ettringite concentration is relatively more stable compared with those of the gypsum.

3.4. Sensitivity Analysis of the Initial Conditions to the Stochastic Dynamical Behaviors of Sulfate Corrosion Reaction System. The effects of variability of reaction rate constant k_j on the stochastic behaviors of the corrosion reaction system in concrete subjected to external sulfate attack are investigated in Section 4.2. In this section, the effects of variability of the initial concentrations on the corrosion reaction process are studied. The means and CVs of the initial concentrations of the chemical constituents can be found in Table 1. In order to illustrate the sensitivities of the initial concentrations to evolution processes of sulfate corrosion reactions, different variable coefficients are employed. The CVs of 0, 0.2, and 0.3 for sodium sulfate, gypsum, and ettringite are, respectively, considered in the initial conditions. It is worth noting that the gypsum and ettringite exist in both reactants and corrosion products. Figure 12 presents the different effects of CVs of the reactants in the initial conditions on the concentration means of gypsum and ettringite in the corrosion products. The variations of the initial values of sodium sulfate, gypsum, and ettringite, which are the hydration products of cements before the specimens were immersed in the sodium sulfate solution, have the smaller effects on the concentration means of gypsum and ettringite in the corrosion products. It can approximately think that the concentration means of gypsum and ettringite in the corrosion products are not affected by the variations of the initial concentrations of reactants.

The effects of the initial concentration variations of sodium sulfate, gypsum, and ettringite on the concentration STDs of the corrosion products are given in Figure 13. It is different from the effects on the concentration means of two corrosion products that the concentration STDs of gypsum and ettringite in the corrosion products change with the variations of the initial conditions. The concentration STDs of gypsum in the corrosion products are significantly affected by the variation of the initial concentration of sodium sulfate, however, less fluctuating with the increasing CVs of the initial concentrations of gypsum and ettringite. Accordingly, variations of the initial concentrations of sodium sulfate and ettringite all have relatively large effects on the concentration STDs of ettringite in the corrosion products. The increasing CVs of the initial concentration of gypsum have a few effects on the concentration STDs of ettringite in the corrosion products.

Figure 14 depicts the effects of initial concentration variations of both sodium sulfate and ettringite on the stochastic dynamical behaviors of the corrosion products, where the initial concentration variation of gypsum is not considered because of its less effect on the concentration means and STDs of the corrosion products, as shown in Figures 12 and 13. Therefore, there are 13 random variables in total in the SKE-SCR. The CVs of the initial concentrations of sodium sulfate and ettringite are all 0.2. Similarly, in order to illustrate the effects of variations of the initial conditions, the concentration means, means ± STDs, means ± 2 STDs, and experimental data of gypsum and ettringite are presented in Figure 14, respectively.

Figure 14 demonstrates that the concentration evolution processes of the corrosion products in concrete under the external sulfate attack can be conveniently obtained by solving the SKE when the variations of the initial conditions, reaction rate coefficients, and the internal fluctuations are considered together. Furthermore, comparing with Figure 8,

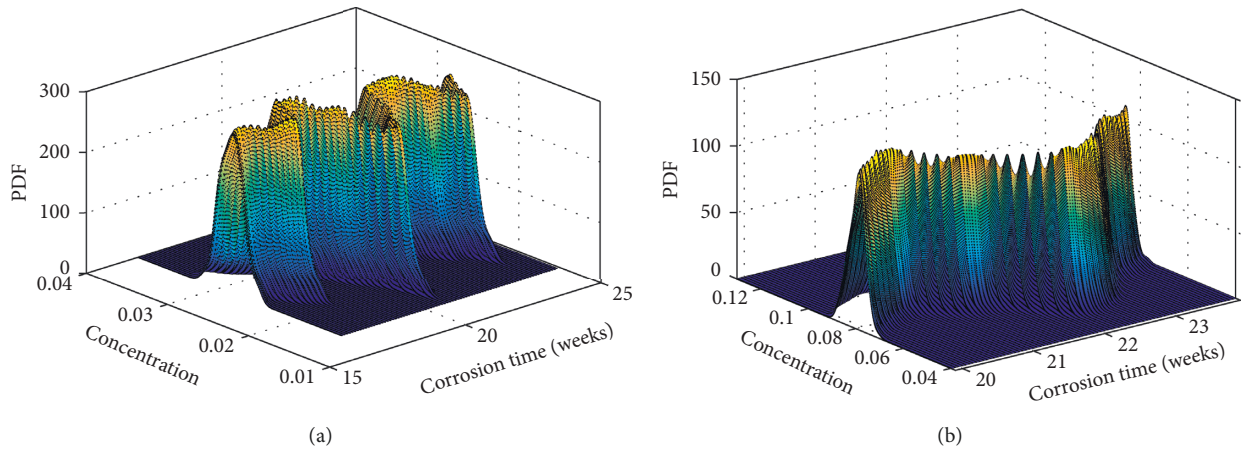


Figure 10: PDF surface of the concentrations of (a) gypsum and (b) ettringite.

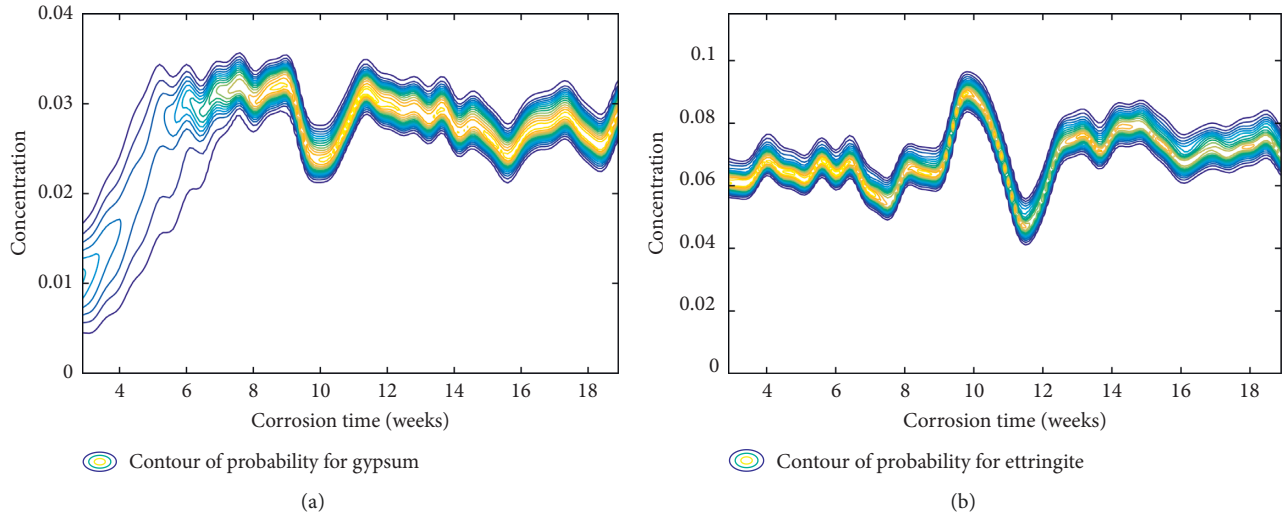


Figure 11: Probability contours of the concentrations of (a) gypsum and (b) ettringite.

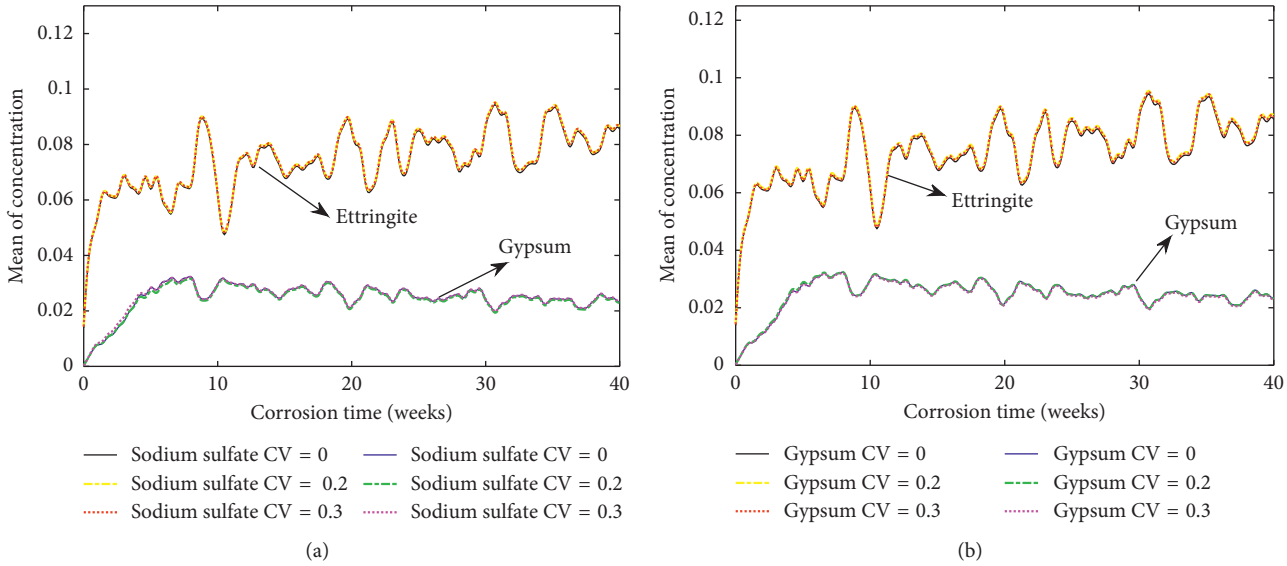
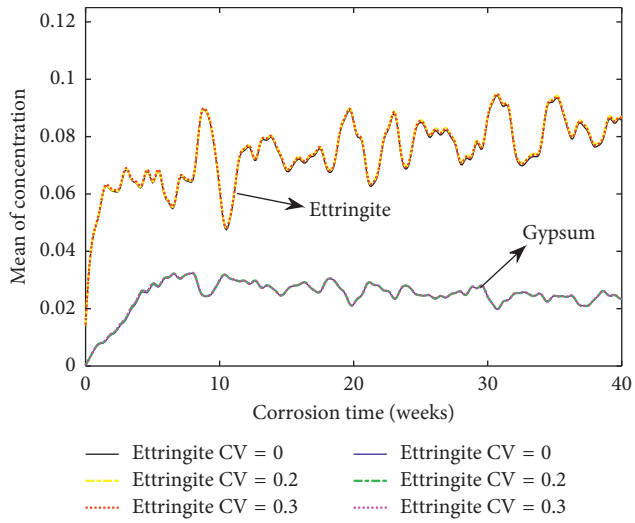
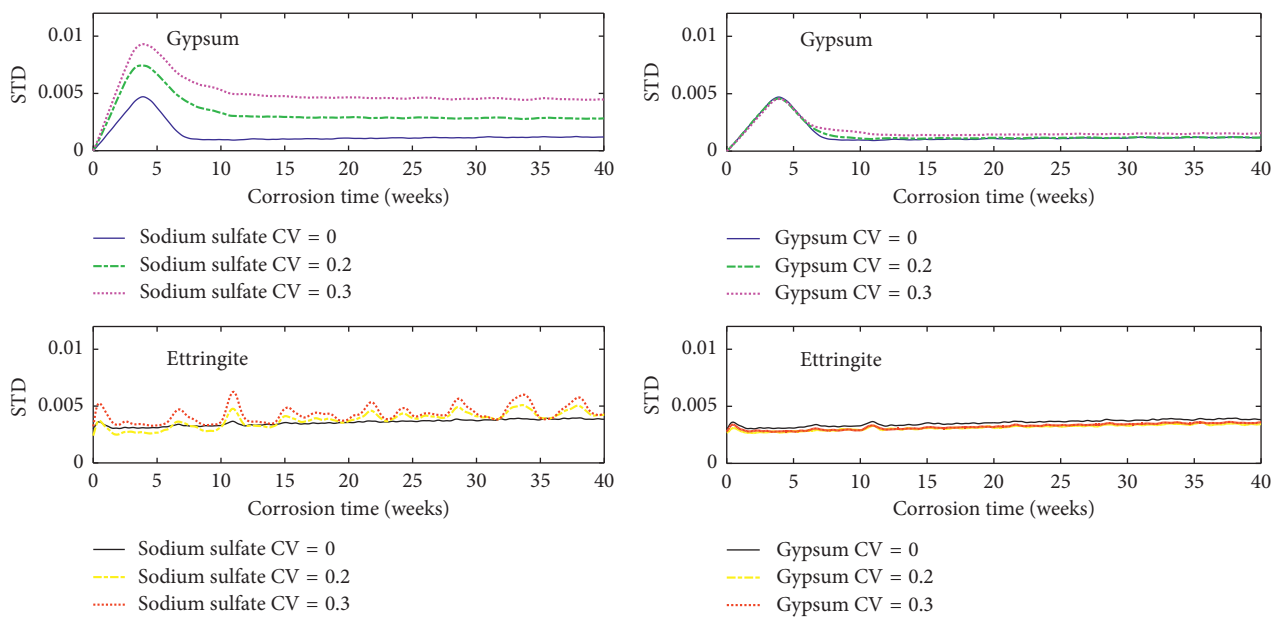


Figure 12: Continued.



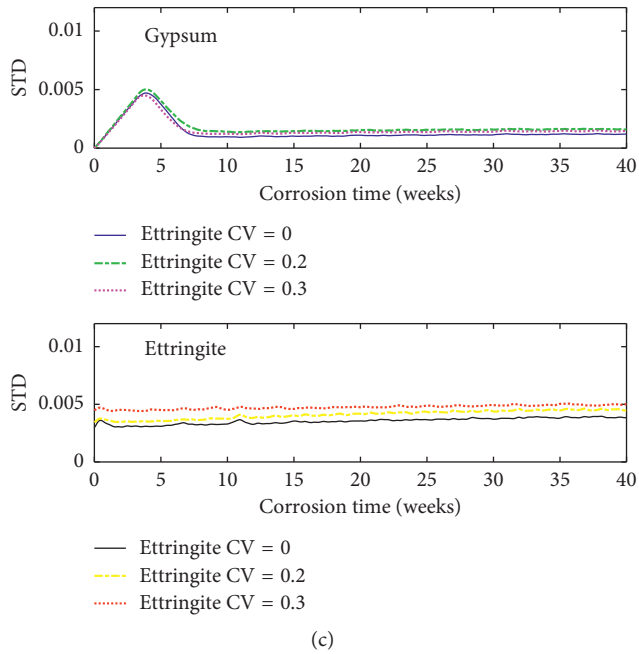
(c)

Figure 12: Concentration means of the corrosion products affected by the initial concentration variations of (a) sodium sulfate, (b) gypsum, and (c) ettringite.



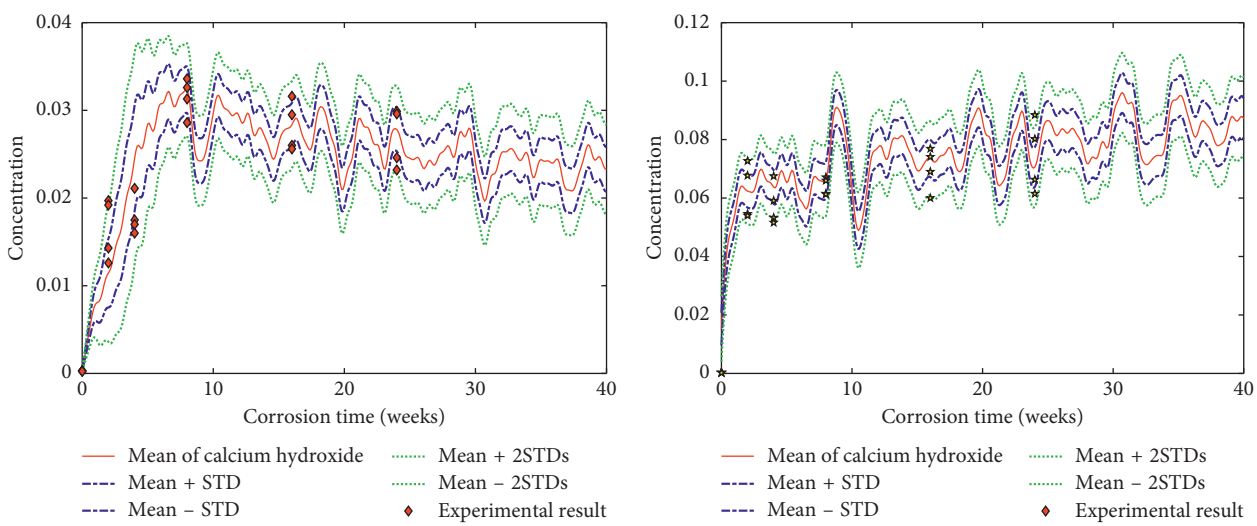
(a) (b)

Figure 13: Continued.



(c)

Figure 13: Concentration STDs of the corrosion products affected by the variations of the initial concentrations of (a) sodium sulfate, (b) gypsum, and (c) ettringite.



(a) (b)

Figure 14: Comparison of the theoretical predictions and experimental data of (a) gypsum and (b) ettringite in corrosion products, where variations of the initial concentrations of sodium sulfate and ettringite are also considered in the SKE-SCR.

the concentration evolution processes of the corrosion products present more remarkable fluctuations. Although the experimental data measured at the same time are different from each other, they are still within the range predicted by the SKE-SCR. Each point of the experiment data is only a sample of the random event, and it will appear with a certain probability. The PDFs of the concentrations of gypsum and ettringite are shown in Figure 15, where variations of all parameters in the SKE-SCR are considered.

Figure 15 further indicates that the concentrations of the corrosion products at each time step satisfy a certain probability distribution. We can obtain the probability of each experimental data point. The cumulative probability densities (CDFs) can also be attained by analyzing the theoretical results calculated by the SKE-SCR. Table 3 presents the CDFs of the experimental data at different corrosion times. In general, it can be regarded as a small probability event if the CDF value of the experimental data point is close to 0 or 1. Therefore, in this case, we can think

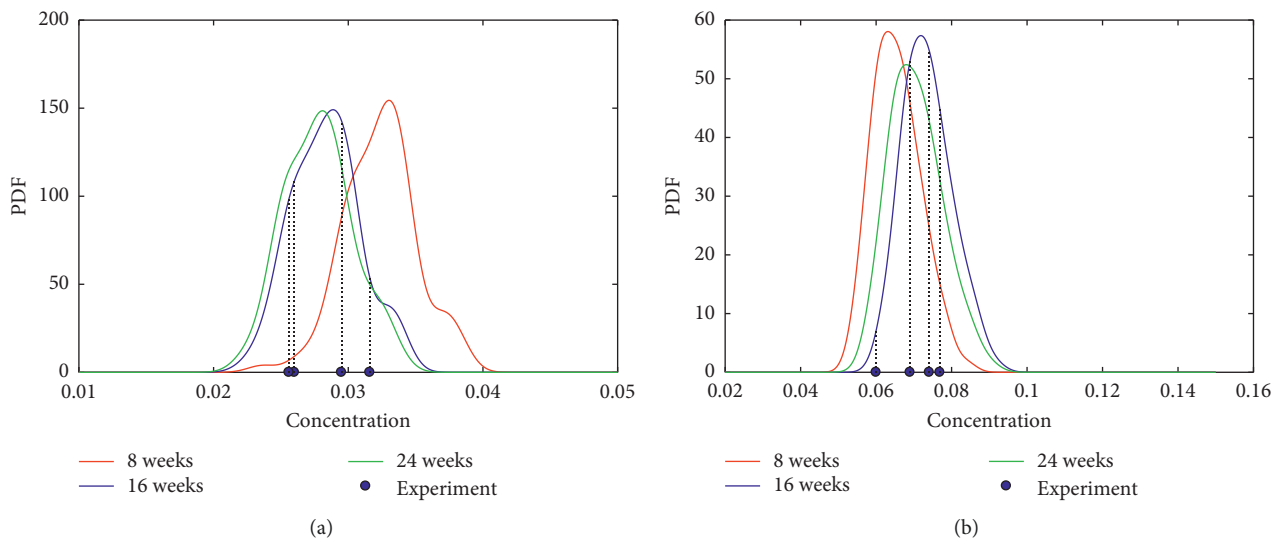


Figure 15: PDFs of the concentration of (a) gypsum and (b) ettringite, obtained by solving the SKE-SCR with 13 random variables.

Table 3: CDFs of experimentally obtained concentrations of the corrosion products at different times.

CDF	Time (weeks)	S-1	S-2	S-3	S-4
Gypsum	4	0.3147	0.1482	0.1306	0.1025
	8	0.6790	0. 5287	0.3489	0.0833
	16	0.8768	0.6713	0.2006	0.1590
	24	0.7875	0.7557	0.1165	0.0351
Ettringite	4	0.7304	0.2476	0.0344	**0.0134**
	8	0.6162	0.5567	0.2990	0.2878
	16	0.7004	0.5598	0.2732	**0.0131**
	24	**0.9869**	0.8903	0.3073	0.1024

that the values of these experimental data points are insufficiently accurate. The CDFs of the data with the smaller CDFs are marked in red boldface, as shown in Table 3.

4. Conclusion

The stochastic kinetic equation for composite reactions (SKE-CR) is derived based on the mass conversation law and random process theory. In the SKE-CR, internal fluctuations of composite reactions are considered as colored Gaussian noises. The stochastic dynamical behaviors of the sulfate corrosion reaction system in concrete are comprehensively investigated by the SKE-SCR which is proposed according to the SKE-CR and the actual corrosion reactions occurring in the concrete subjected to external sulfate attack. By comparison with the experimental results, it is found that the concentration evolution processes of the corrosion products can be reasonably predicted by the SKE-SCR. The concentration variations of the experimental data come from the excitations of internal fluctuations, and the variations of the reaction rate coefficients, and the initial concentrations of the reactants. The effects of variations of the initial concentration of sodium sulfate and ettringite on the variations of the concentrations of the corrosion products are more remarkable than that of gypsum. To effectively control the variations of the corrosion products, therefore, one should minimize the variations of the initial concentrations of sodium sulfate and ettringite. Furthermore, the probabilistic information of the concentration evolutions of the corrosion products can also be obtained by analyzing the calculation results of the SKE-SCR. The appearance of each experimental data has a certain probability.

In the paper, internal fluctuations are considered as a colored Gaussian noise with a specific covariance function $\exp(-(|t_2 - t_1|/l))$ because the analysis solution of the Fredholm equation can only be attained by using this kind of function as the core function. However, this assumption is a special example indeed, which cannot be applied in general cases. Therefore, the exact form of the covariance function of internal fluctuations in sulfate corrosion reaction systems should be further investigated.

Data Availability

The datasets analyzed during the current study are available in the (Baidu Netdisk) repository (https://pan.baidu.com/s/1Pqi2n5gyFjy1Rl2szQfuOw), with the access codes: mlwj.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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