Study on the Shrinkage Behavior of the Cement Mortar with the Additives of the Nano-Kaolinite Clay

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Abstract. The effect of nano-kaolinite clay (NKC) on the early age cracking behavior of cement mortar was investigated. The restrained ring-test method was used to detect shrinkage crack tendency of cement mortar specimen. The cracking and strain on the surface of mortar ring for the ordinary and NKC mortar were monitored. The development of crack width and strain during the drying process were obtained. Finite element analysis is carried out to simulate the evolution of the crack in restrained concrete rings subject to circumferential drying. The results demonstrate that the addition of NKC increases the shrinkage cracking tendency of mortar at early age. It is found that the crack width is significantly increased in the mortar specimen added with 3% NKC replacement.

1. Introduction
In recent years, High Performance Concrete (HPC) has been widely used in structural engineering. It is found that the brittleness and the tendency to shrink and crack of HPC are more serious than normal concrete [1]. Early-age cracking of concrete is a common phenomenon in engineering, and the early age micro-cracks is regarded as the beginning of macro-cracking. Obviously, the early-age cracking seriously affects the durability and safety of concrete structures [2-5]. The plastic shrinkage cracking is an important part of early-age cracking of concrete, but the study on early-age shrinkage and cracking of HPC is limited in existing research [6-8]. Early-age shrinkage and cracking of concrete can accelerate the deterioration process of concrete, reduce the bearing capacity and decrease the safety and usability of structures. Based on the noteworthy shrinkage and cracking of concrete structures under constrained conditions, it is necessary to study the early-age shrinkage performance of concrete such as the cracking time, the cracking mechanism and the development law of cracks.

Shrinkage results in cracks in cement-based materials, so it has been a matter of great interest for the studies focusing on the use of NKC in the concrete structure. Free shrinkage and restrained shrinkage tests are the main methods to examine the shrinkage behavior of the cement-based materials. Therefore, it is important to diminish the rate of shrinkage strain. In the literature, there are some studies regarding the improvement of the shrinkage properties of concrete [9]. Shah et al. [10-11] used shrinkage reducing admixture (SRA) in concretes and performed. Their results showed that the addition of SRA significantly reduced free shrinkage and caused a considerable reduction in crack width of the restrained samples. In the studies of Al-Khaja and Jianyong and Yan, the effects of ultrafine mineral admixtures on shrinkage properties of the concrete were investigated. Al-Khaja reported that the shrinkage of plain concrete was considerable or moderately reduced with the incorporation of silica fume. Jianyong and Yan showed that the use of the ultrafine ground granulated
blast furnace slag resulted in a stronger structure and higher resistance to deformation caused by drying shrinkage.

The nano-kaolinite clay improves the hydration reaction degree of cement slurry and promotes the generation of hydration products. This process consumes a lot of water, resulting in the decrease of liquid humidity in the cementitious material matrix, which seriously affect its early-age shrinkage performance. Therefore, the restrained ring test was conducted in this study to analyze the early-age shrinkage performance of cement mortar with the additives of the nano-kaolinite clay including the cracking time, the strain change and the cracking mechanism on surfaces of cement mortar, which provided some experimental evidence for the application of nano-kaolinite clay in the practical civil engineering. In order to reveal the effect of nano-kaolinite clay on the early-age cracking performance of cementitious material, paste specimen with ordinary mortar (NM0) and 3% NKC mortar (NM3) were tested by the restrained ring-test method.

2. Experimental Programme

2.1. Materials
Ordinary Type 42.5R Portland cement was used in this study. A type of commercially available nano-kaolinite clay powder was employed in this study. The kaolinite clay has a crystalline structure and contains silicon, with a theoretical formula of \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) [12]. To clarify the microstructure of the NKC studied in this paper, X-ray Diffraction (XRD) analysis and Transmission Electron Microscopy (TEM) techniques were applied to the neat clay powder. The resulting TEM and XRD images of clay powder samples are presented in figure 1.

![Figure 1. TEM and XRD spectra of neat nano-kaolinite clay powder: (a) TEM micrograph, (b) XRD results.](image)

2.2. Specimen Preparation
In order to quantify the effect of clay on the cracking behavior of mortar, ring tests were performed. The content of 3% nano clay by mass of cement was considered in this study. The clay was first dispersed in water by an ultrasonic dispersion method for 15mins. Then, the dispersed clay was mixed with cement and standard sand based on JTG E30-2005. The specimens were cast around a steel ring by using a PVC tube as the outside mold. Specimens with a 70mm thickness, 305mm internal diameter and 140mm height were cast around a rigid steel ring. To reduce the skin friction, a kind of lubricating oil was painted on the bottom and outer side of the steel ring. To ensure the compactness of the mortar specimen, the mortar slurry was poured into the ring layer by layer. The exterior mold was removed 24 h after casting. Three ring specimens were cast for each mortar mixture. Immediately after demolding, at 24 h, the top and bottom surface of the ring specimen was sealed with plastic film and sealant. This procedure creates a condition that allows drying only from the outer circumferential surface.
2.3. Restrained Shrinkage Test
In this study, the ring test was performed to evaluate the cracking behavior of the mortars in restrained shrinkage conditions according to ASTM C 1581-04. To measure the development of confining strains imposed by the mortar, four strain gauges were mounted on the internal circumferential surface of the steel ring. The applied strain gauge is BX 120-80AA, with a resistance of (120±0.1)Ω and a sensitivity coefficient of (2.12±1)% . The strain measurement of each steel ring was monitored from the demolding time by a 16 channels strain-meter from National Instrument, having sampling frequency of once a minute. The day at which the cracking starts was determined by the sharp drop in the confining strain-time curve. After the cracking of the mortar, the cracking widths were measured by a microscope. Since the cracking of the mortar restrained by a ring depends on the curing conditions, the temperature and humidity in the laboratory were monitored by the temperature and humidity sensor during the whole test. The recorded temperature is (23±2) °C, while the relative humidity is (50±4)%.

3. Results and Discussion

3.1. Cracking Development on the Surface of Mortar Ring
The crack width development of the NM0 and NM3 mortar rings are presented in figure 2. The results reported in this paper are the average of three measurements taken along the cracking length (top, center and bottom). In comparison with ordinary mortar (NM0), the NKC rings experienced a significant advance in cracking time by 72 h compared to the ordinary rings. 3% replacement of cement with NKC also led to an increase in crack width development, with a 110% increase in final crack width. Furthermore, NKC mortar showed lower cracking resistance than the ordinary mortar.

3.2. Strain on the Internal Surface of Steel Ring
The strain development in the internal surface of the steel ring during the test is shown in figure 3. It can be seen that from the beginning of casting, the shrinkage of NKC mortar rapidly increased the strain of the internal surface of the steel ring; the strain in the internal surface of the steel ring with the ordinary mortar changed gently in the first 4 days after casting, then increased rapidly until it is damaged.

![Figure 2. Crack width development of ring specimen.](image1)

![Figure 3. The measured strain in the steel ring.](image2)

Based on the shrinkage strain in the surface of the steel ring decreased suddenly, the NM3 and NM0 specimens have been cracked after being cured for 8 and 11 days, respectively. The above analysis indicates that the NKC decreases the cracking time of cement mortar rings, which is mainly because NKC with high pozzolanic activity produces the hydration reaction between cement particle and NKC. Meanwhile, NKC consumed a huge amount of free water to produce more hydration products, which result in the internal microstructure of cement matrix became denser. The large
shrinkage stress under the ring constraint aggravates the shrinkage trend of the cementious materials, which lead to earlier cracking.

4. Numerical Simulation of the Early-Age Cracking Process of NKC Mortar under Uniform Drying Condition

The temperature stress, autogenous shrinkage and drying shrinkage are three main reasons for the cracking of cementious materials. The volume of the specimens decreases and shrinkage deformation occurs due to these three factors. The shrinkage deformation of cement mortar produces the tensile stress in the cementious material under constraint, and it can be cracked when the tensile stress exceeds its tensile strength. Based on the theory of internal humidity distribution of cementious materials and elastic mechanics, the cracking behavior of the cement mortar rings under uniform drying condition was analyzed using MATLAB software.

4.1. Calculation Model for the Humidity Field in Cement-Based Materials

4.1.1. Theory of Humidity Diffusion. The loss of pore water in the cementious material directly affects its early cracking behavior. The internal humidity field in the cementious materials is very complicated. The diffusion model of the cementious materials has a highly nonlinear relationship, which is affected by water-cement ratio, temperature, humidity and other factors. Therefore, the law of diffusion and mass conservation were used to describe the process of water migration in cementious materials.

In the process of calculating the internal humidity field of cementious materials, only the influence of concentration on water diffusion is taken into consideration. Assuming that \( N(x, y, z, t) \) is the substance concentration at point \( X \) in the space at time \( t \), the law of diffusion is expressed as,

\[
du = -D \frac{\partial N}{\partial t} dt
\]

Where, \( du \) is the diffusion amount in a differential element with an infinitesimal period. \( D \) is water diffusion coefficient. In any closed surface, the quantity of diffusion and substance in the closed surface must meet the conservation of mass. Thus, the quantity of substance diffusion in any time period is expressed as \( u_2 = \iiint_V (N_1 - N_2) dV \).

Water diffusion and cement hydration reaction consumes the internal pore water in the cementious materials at early age. Assuming that the consumption rate of water is \( f(x, y, z, t) \), the total consumption of water in the space for a period of time can be written as \( u_3 = \iiint_V f(x, y, z, t) dV dt \). According to the law of mass conservation, it can be derived that \( u_2 = u_1 + u_3 \). For any \( t \) and \( V \), there is,

\[
\frac{\partial N}{\partial t} = DN^2 + f \]

Obviously, humidity consumption caused by outward diffusion of water is much greater than that of cement hydration. Therefore, humidity consumption caused by the hydration of cement are always neglected. The Diffusion control equation is further written as,

\[
\frac{\partial N}{\partial t} = DN^2
\]

4.1.2. Humidity Diffusion Coefficient. To solve the humidity diffusion equation, it is crucial to determine the value of \( D \). In the previous studies, linear equation is widely accepted as the diffusion equation. That is, \( D \) is assumed to be a constant, with a range of \( 10^{-10} \) to \( 10^{-12} \)m²/s. Actually, the humidity diffusion coefficient \( D \) is not constant, which has a close relation with the humidity,
temperature and water-cement ratio. According to CEB-FIP [13], $D$ is expressed as the function of humidity under the constant temperature condition herein, 

\[
\frac{D}{D_{\text{sat}}} = \alpha_0 + \frac{1-\alpha_0}{1+\left(\frac{1-h}{1-h_c}\right)^n},
\]

humidity diffusion coefficient at the relative humidity of $h$. $D_{\text{sat}}$ is the diffusion coefficient when the relative humidity $h$ is saturated; $\alpha_0$, $h_c$ and $n$ are empirical coefficients, which are recommend to be 0.05, 15 and 0.8 in the current code. According to CEB-FIP, $D_{\text{sat}}$ can be calculated by the following expression, 

\[
D_{\text{sat}} = \frac{D_{1,0}}{f_{cm}/f_{ck0}},
\]

Where, $D_{1,0}$ is $3.6 \times 10^{-6}$ m$^2$/h; $f_{ck0}$ is 10MPa; $f_{ck}$ is $f_{cm}$-8, and $f_{cm}$ is the compressive strength.

4.1.3. Humidity Diffusion Simulation. The humidity diffusion equation $D_{\text{sat}}$ is a partial differential equation with complex boundary conditions, which is difficult to solving directly. Therefore, the difference method and finite element methods (FEM) is often used to solve it conveniently. Based on the temperature and humidity curve from this experiment (figure 2), the internal temperature of mortar rings was calculated with humidity is 55% and temperature is 25 ℃. Consulting the empirical coefficient recommend by CEB-FIP, the humidity diffusion coefficient in the NKC mortar was determined as $3.89 \times 10^{-6}$ m$^2$/h.

Based on the mortar rings, the humidity diffusion model was built. In experimental process, the internal water of the cement mortar ring only diffuses from the side surface, therefore the two-dimensional model can be used to calculate the loss process of water inside the mortar. Due to the mortar ring only holds moisture diffusion on the outside surface, the outside and inside boundary can be set as Dirichlet boundary condition and Neumann boundary conditions.

Humidity distributions of cement mortar rings were calculated for 8, 24, 48, 72, 96 and 120 hours by using the MATLAB software. Humidity distributions in the mortar ring during the drying age are shown in figure 4.

![Figure 4. Humidity distribution in the mortar ring during the drying age.](image-url)
24 hours and 48 hours, respectively. It can be observed that drying rate decreased with time increased: the rate of descent was fast, then became slow. After 48 hours, the relative humidity difference between the inside and outside of the early-age mortar was approximately 40%, and the relative humidity difference was only approximately 15%. After 120 hours, humidity between the inside and outside of the early-age mortar became balance.

4.2. Calculation Method of Internal Restraint Stress of Cement Mortar

The steel ring is exactly symmetrical. Uniform compressive stress distributed on outer surface, while the internal surface is free. Hence, the calculation of internal restraint stress can be simplified as a plane problem [14]. Based on the theory of elastic mechanics, the exact solution of stress can be calculated as, 

\[ \delta_r = \frac{1-a^2}{b^2-a^2} q(<0), \quad \delta_\theta = \frac{a^2}{b^2-a^2} q(<0), \quad u_r = \frac{1}{E} \left[ -(1+\mu) \frac{A}{r} + 2(1-\mu)Cr \right], \]

\[ A = \left( \frac{ab}{b^2-a^2} \right)^2, \quad 2C = -\frac{q}{b^2-a^2}. \]

Where, \( a \) and \( b \) are the internal and outside radius of the ring. \( Q \) is the lateral compressive stress, \( \mu \) is the Poisson’s ratio of steel ring. Based on the test data of the shrinkage strain \( \varepsilon_a \), it can be derived that, \( u_a = a - a_1, \quad \varepsilon_a = \frac{a-\varepsilon_d}{a} = \frac{a-a_1}{a} \). Where, \( a_1 \) is the internal diameter of the deformed steel ring after being compressed. \( \varepsilon_a \) is the compressive strain in the internal surface of the steel ring, which is obtained during the ring test.

Based on the above equations, the inside displacement of steel ring was \( u_a \), which is equals to \( \varepsilon_d a \). The drying shrinkage of cementitious materials is mainly affected by the difference of internal and external humidity, and the shrinkage of internal and external matrix (drying shrinkage and self-shrinkage) is different. The outside surface contact is large, meanwhile the inside surface contact is small, and the distribution is continuous. In order to study the internal shrinkage stress of cementious materials, it is assumed that the non-stress shrinkage deformation presents a linear distribution from outside to inside. Thus, mortar ring is simplified as a plane stress problem, which can be described as,

\[ \varepsilon_r = \frac{1}{E} (\delta_r - \mu \delta_\theta) + \varepsilon_T, \quad \varepsilon_\theta = \frac{1}{E} (\delta_\theta - \mu \delta_r) + \varepsilon_T, \quad \gamma_r\theta = \frac{2(1+\mu)}{E} \tau_r\theta. \]

The boundary condition is described as, \( \delta_r (r=b) = -q, \delta_r (r=c) = 0 \). Hence,

\[
\begin{aligned}
\delta_r &= -\frac{Em}{3} r - \frac{b^2c^2}{b+c} \left( \frac{Em}{3} + q \right) \frac{1}{r^2} + \left( \frac{Em}{3} \frac{b^2+bc+c^2}{b+c} + q \frac{gb^2}{c^2-b^2} \right), \\
\delta_\theta &= -\frac{2Em}{3} r + \frac{b^2c^2}{b+c} \left( \frac{Em}{3} + q \right) \frac{1}{r^2} + \left( \frac{Em}{3} \frac{b^2+bc+c^2}{b+c} + q \frac{gb^2}{c^2-b^2} \right)
\end{aligned}
\]

where, \( c \) is the external diameter of the deformed steel ring after being compressed. \( \varepsilon_r \) is the compressive strain in the internal surface of the steel ring, which is obtained during the ring test.

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\[
\begin{aligned}
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\delta_\theta &= -\frac{2Em}{3} r + \frac{b^2c^2}{b+c} \left( \frac{Em}{3} + q \right) \frac{1}{r^2} + \left( \frac{Em}{3} \frac{b^2+bc+c^2}{b+c} + q \frac{gb^2}{c^2-b^2} \right)
\end{aligned}
\]
4.3. The Calculated Restrained Stress in the Cement Mortar

Assuming that the mortar was in the elastic state before cracking, \( \frac{\partial N}{\partial t} = D N^2 + f \) was used to calculate the circumferential stress caused by the restrained ring. An empirical coefficient of 0.01 was taken for \( m \). \( E(t) \) is the elastic modulus at dry for \( t \) days, and it can be determined by the following equation, \( E_0(t) = 15 + 0.5t \) and \( E_{3\%}(t) = 20 + 0.5t \) \( (0 \leq t \leq 20) \). The calculated circumferential stress on the outside of cement mortar ring was shown in figure 5.

![Figure 5. The calculated circumferential stress on the outside of cement mortar ring.](image)

It can be observed that the calculated circumferential stress on the outside of NKC mortar specimen increased fast, lead to big shrinkage stress which is higher than that of NM0 specimen. The calculated circumferential stress on the outside of NKC mortar specimen is 36.11% higher than that of NM0 specimen, increasing the early-age cracking risk of cement mortar.

Based on the MATLAB software, the circumferential stress in the NM0 and NM3 cement mortar specimen are shown in figure 6. As can be seen from the figure 6, the considerable theoretical calculation tensile stress was big in the internal direction of mortar ring, but the mortar did not damaged from inside. The main reason is that the error of \( m \) and \( E(t) \), meanwhile the uniform shrinkage theory cannot completely simulate the actual shrinkage of mortar. Moreover, the radial compressive stress inside the mortar perpendicular to the direction of the ring decreased the risk of the mortar inside which could be pulled and damaged. Comparing the calculation results in the figure, the cracking stress of NM3 mortar specimen is higher than that of NM0 mortar specimen. From the above analysis, it can be concluded that nano-kaolinite clay increases the internal shrinkage stress of cementious materials at early-age and increases the risk of shrinkage cracking of cementious materials, but is not conducive to the development of its early-age durability.
Figure 6. The circumferential stress in the cement mortar: (a) common mortar; (b) NKC mortar.

5. Conclusions
In this study, the early-age shrinkage performance of nano-kaolinite cement mortar was performed by the ring test. The internal constraints humidity and stress of annular cement mortar were examined by the numerical simulation and theoretical analysis. Under the condition of ring constraint, it is revealed that the crack time of nanometer kaolinite cement mortar is advanced, and the surface strain increases rapidly. The calculated results are consistent with the experimental results. The results show that the theoretical stress on the outer surface of the nanometer kaolinite mortar ring is 36.11% higher than that of ordinary mortar, and the risk of cracking at early age increases.

Acknowledgments
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