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The effects of nano-calcined kaolinite clay on cement mortar exposed to acid deposits

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HIGHLIGHTS

- NKC has been successfully applied to improve the acid resistance of cement mortars.
- NKC reduces the CH content, and increase the CSH content in the cement pastes.
- The improvement of acid resistance resulted from the filling and pozzolanic effect.
- The effect of NKC on the acid resistance of cement mortars depends on its additives.

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ABSTRACT

This paper explores the effects of calcined nano-kaolinite clay (NKC) on cement mortar, when exposed to an acidic environment. Ordinary Portland cement was partially substituted with NKC in ratios of 0%, 1%, 3%, and 5% by weight. To simulate acid deposits, a sulfate and nitric acid solution with a pH level of 1.5 was employed in the cement mixture in our laboratory experiments. The fresh mortar pastes were first cured at 100% relative humidity for 24 h and then cured in water for 28 days. The prepared specimens were then submerged in the acid solution for 20, 40, and 60 days, respectively. We periodically evaluated the mass, compressive strength, and microstructure of the control mortar (no NKC addition) and the mortar with various dosages of NKC addition at the prescribed conditioning ages. Thermo gravimetric analysis, differential scanning calorimetry, backscattered scanning electron microscope and X-ray diffraction were performed to discover the microstructure evolution of the control and NKC modified mortar. The results showed that a substantial beneficial effects of NKC addition. After 28 days of curing, prior to acid exposure, the content of calcium hydroxide and volume of pores decrease with the incorporation of NKC. After 60 days of submersion in exposure acid solution, the loss of mass and the reduction in compressive strength were significantly less for specimens with the addition of NKC as compared to the control mortar specimens. The optimum dosage of NKC appears to be less than 3% by weight.

1. Introduction

Due to the rapid development of global industrialization and urbanization, atmospheric pollution has worsened. China has become the third largest acid rain area, following Europe and the United States of America [1]. For example, acid rainfall covers at least 30% of Chinese territory [2,3]. Acid rain typically has a pH value less than 5.7, which contains strongly aggressive agents (e.g. sulfuric acid, nitric acid, etc.) [4]. In Wheeling, West Virginia, researchers once measured rainfall with a pH value of 1.5 [5]. In cities around the world, many irreplaceable statues and buildings have been significantly damaged by acid deposits, resulting billions of dollars of damage per year [5]. Previous research has thoroughly discussed and reviewed the phenomenon of acid corrosion of cement-based materials [2,3,5–12]. The research results show that the deterioration of cement-based materials exposed to acid is mainly attributed to the combined actions of dissolving and expansion, which are induced by H^+ and SO_4^{2-}. Since the durability of concrete structures is greatly affected by the building materials, enhancing the acid resistance is an efficient way to increase the structural durability. Accordingly, civil engineers worldwide are interested in new ways to improve the resistance of cementitious materials to acid deposits.

A number of recent studies investigated the acid resistance of concrete made with supplementary cementitious materials (SCM)

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[13–29]. The results show that using SCM, such as slag [13], fly ash, silica fumes [14,15,17,23], rice husk ash (RHA), and cement kiln dust (CKD) [20] improves the acid resistance of the concrete. Aydin et al. [14] found that a 40% FA replacement level can improve the sulfuric acid resistance of steam-cured concrete. According to Chang's report [16], a 25% mass loss reduction of concrete can be achieved by adding 10% silica fumes and 60% fly ash (according to the mass of cement) after 56 days immersion in a 1% sulfuric acid solution. In a separate study, Hashem et al. [20] showed that a 5% addition of both rice husk ash (RHA) and cement kiln dust (CKD) or a 10% addition of pure RHA can increase the compressive strength of cement paste in a sulfuric acid solution with a pH of 1.0 at a curing temperature of 50 °C. Compared with the above traditional mineral admixtures, nano-materials possess fine particles, which result in activating the cement hydration process at early age and filling the pores and voids in the cement based materials. Multiple studies have shown that even small dosages of nanoclay with two dimensions below 100 nm can improve the physical and mechanical properties [30–33], chloride permeability [34,35], and microstructure [36,37] of cement-based materials. From the above studies, it can be derived the nanoclay particles could delay damage to cementitious materials exposed to acid deposits. However, until now, it was not clear exactly whether and how nanoclay would affect the acid resistance of cementitious materials.

The objective of this investigation was to identify the effects of NKC on mechanical behavior of cement mortar that has been exposed to acid. We examined the microstructure, mass change, and strength of the control group (ordinary Portland cement mortar with no NKC admixed) and the NKC-incorporated mortar specimens exposed to acid solution. Simulated acid rain was employed by creating a mixture of sulfate and nitric acid in the laboratory. The samples subjected to stronger artificial acid rain, which had a pH value of 1.5. The mortar specimens were immersed in the acid solution for over 60 days. During the immersion process, the mortar specimens were periodically inspected for visual surface deterioration, mass change, compressive strength, and evaluated using scanning electron microscopy (SEM). We then compared the physical and mechanical properties (for instance, appearance damage, mass loss, compressive strength, etc.) and the microstructure of the control samples and the NKC cement mortars, after being exposed to the acid.

2. Materials and methods

2.1. Materials

All mixes contained ordinary Portland cement, Type 42.5R. A commercially available nano-calcined kaolinite clay powder was used in this study. The raw kaolinite clay were heated at 800 °C for 2 h, and obtained by intercalation method [38]. Its theoretical formula is $Al_2Si_2O_5(OH)_4$ [39]. The chemical composition of the cement is presented in Table 1. The physical properties and chemical element composition of the nano-calcined kaolinite clay used in this study are presented in Tables 2 and 3, respectively. We carried out TEM techniques to clarify the NKC powder's morphology and particle size. From the TEM images of the NKC (shown in Fig. 1), it can be seen that the flake thickness of the NKC is about 18–40 nm, which is in agreement with the data given in Table 2.

2.2. Specimen preparation

Based on the former research [35], it was obtained that the chloride diffusion coefficient of cement mortar ($D_{\bar{Cl}}$) with 1% clay is decreased by 29.03% and 20.80% at 28 and 56 curing days, while the 28-day $D_{\bar{Cl}}$ of cement mortar with 5% clay is decreased by 53.03%. To detect the effect of NKC on the acid resistance of the cement mortar, we replaced 1%, 3%, and 5% of the cement by weight with a NKC addition when preparing the mortar specimens. An effective water-to-binder ratio of 0.5 was maintained. ISO standard sand was applied, using a cement-sand ratio of 1:3 by weight. To achieve an equal dispersion of nano-calcined kaolinite clay, we first dispersed the NKC powder in water, using a mixing machine set at high speed for 15 min. Then, we mixed the dispersed NKC with the cement paste in the mixing machine. The mixing protocol for cement mortar is listed in Table 4. Next, we poured the mixed cement mortar matrix into oiled molds to form the cylinders of 100 mm diameter and 100 mm height used for the compressive strength and accelerated corrosion tests. NC0, NC1, NC3, NC5 denote the mortar containing NKC in the amount of 0%, 1%, 3%, 5% by weight of cement, respectively, and NC0 is regarded as the control sample. The fabricated specimens were demolded after 24 h and then cured in the standard curing condition (at a temperature of 20 ± 3 °C and a relative humidity of 95%) for the prescribed period. We created three specimens to ensure the statistical reliability of the test results for the control specimens and the specimens with the NKC additive. The crushed specimens from the compressive strength tests were then ground up for the microstructure analyses.

Table 1
Chemical composition of cement.

Chemical components	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
Content/%	59.30	21.91	6.27	3.78	1.64	2.41

Table 2
Physical index of the nano-calcined kaolinite clay.

Average flake diameter/nm	Average flake thickness/nm	Specific surface area/m^2/g	Density g/cm^3	pH value
300–500	20–50	30	0.6	7.9

Table 3
Chemical composition of nano-calcined kaolinite clay.

Chemical components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	Na_2O
Content/%	47.80	41.80	0.30	0.28	0.03	0.58	0.02	0.06

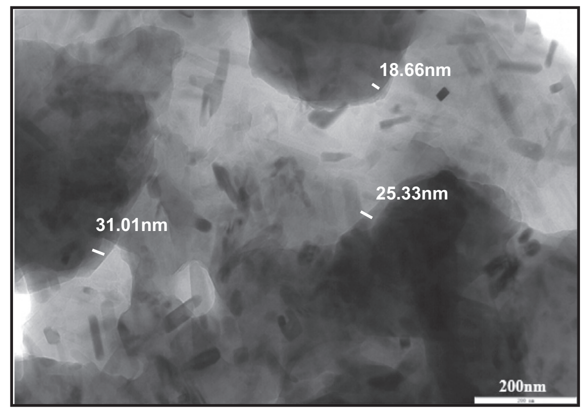

Fig. 1. TEM micrograph of neat NKC powder (magnification is 50,000).

2.3. Experimental methods and procedures

2.3.1. TG/DSC test of cement pastes with and without NKC

In the previous studies, the TG (thermo gravimetric analysis) and DSC (differential scanning calorimetry) have proven to be a valuable tool for evaluating the nature of hydration products according to different stages of cement hydration, as well as to quantify the different phases [40–42].

To investigate the activity of NKC, the cement paste with NKC as cement replacement was monitored by TG–DSC equipment, STA 409, at a heating rate 15 °C/min from 30 °C to 950 °C under an argon flow of 100 mL/min. At 28 days of

Table 4
Mix protocol for cement mortar.

Time/min	Procedure
0:00	Disperse the NKC in water
15:00	Add dry cement ingredients, mixing on low speed
17:15	Add sand in 30 s, and then mixing on low speed
20:00	Stop mixing, scrap edges of mixer
21:00	Mix on high speed
26:00	End of mixing