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Influence of kaolinite clay on the chloride diffusion property of cement-based materials

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ABSTRACT

To constitute blended cement concrete with high chloride diffusion resistivity, the effects of kaolinite clay on the mechanical properties and chloride diffusivity of cement paste, mortar and concrete were investigated. Ordinary Portland cement was partially replaced by kaolinite clay at 0%, 1%, 3%, 5%, 7% and 9% by weight of cement. All blended cement-based samples were prepared using a w/c ratio of 0.5. The microstructure, workability, early-age and long-term flexural strength of pastes were tested. The chloride diffusivity of mortars was measured. And the compressive strength and chloride diffusivity of concrete were measured. Mercury Intrusion Porosimetry (MIP) was employed to evaluate porosity characteristics. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectra (EDS) were applied to investigate the micro morphology and chemical element distribution inside the cement matrix, and the rapid chloride migration (RCM) method was applied to test chloride diffusivity. The MIP test results show that the addition of clay improves the micro-pore structure in the cement paste and limits the introduction of chloride ions. SEM imaging suggests that the kaolinite clay is acting as both filler and accelerator of cement hydration. It is found that the addition of clay alters the water requirement of normal consistency and the setting time of cement, whereas it has little influence on the soundness. Compared to the control, the flexural strength of cement paste with 1% kaolinite clay increased by 30.41%, 39.04%, 36.27% and 38.32% at 1, 3, 7 and 90 days, respectively. The 28-day flexural strength only increased slightly. It is observed that the cement mortar with clay has lower chloride diffusion coefficient values compared to the plain mortar, the 28-day diffusion coefficient of chloride ion (D_{Cl}^{-}) of cement mortar is decreased by 53.03% with 5% clay. The increase in compressive strength of the cement concrete with clay is 12%, 13.5%, and 28.4% compared to the control at 1%, 3% and 5% addition, respectively. The chloride diffusion coefficient of cement concrete decreases exponentially with the clay addition. The reduction of chloride diffusion coefficient of cement concrete is 8.68% and 18.87% at 1% and 5% clay, respectively. The 28-day compressive strength increases linearly with the chloride diffusion coefficient of the concrete.

1. Introduction

It is well known that concrete is a porous material, which makes it susceptible to attack by chloride ions in seawater and deicing environments. Penetration of chloride ions through the connected pore network promotes corrosion of steel reinforcement, potentially leading to early deterioration of the structure. During the past decades, many concrete structures in service within chloride environments (e.g. seawater, deicing salt, chemical plant, etc.) were damaged much earlier than their target service lives. Developing construction materials with high chloride penetration resistance would be an efficient and fundamental way to extend the service life, and subsequently increase the sustainability of concrete structures.

Chloride diffusivity through concrete and cement paste is influenced by many factors, including water cement ratio, the type of cement and other mix constituents, concrete mix proportions, compaction and curing condition. To reduce the chloride permeability of concrete in practice, various types of plasticizers are used, but the strength or ductility is not always satisfactory. With the application of nanotechnology in civil engineering, the incorporation of nanoparticles in cement-based materials has been demonstrated to improve the properties of concrete. In previous studies, additives such as nano SiO_2, nano TiO_2, Fe_2O_3, Al_2O_3, and clays were found to improve material strength and fatigue characteristics while enhancing ductility and other durability properties of engineering materials [1–4]. However, there are only a limited number of studies on the use of nanoparticles to enhance the

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durability of cement-based materials. It is reported that for cement mortars with nanoparticles (Fe_2O_3, Al_2O_3, TiO_2, and SiO_2) and nanomontmorillonite at 1% by weight of cement, the reduction of 28-day D_{Cl^-} was in the order of Clay (montmorillonite) > SiO_2 > TiO_2 > Al_2O_3 > Fe_2O_3 [5]. Considering the low cost of clay, the use of clay in concrete to reduce chloride permeability seems to be promising. Since the two-layer structure of kaolinite clay resists water molecules from going through the sheets, the addition of clay in concrete can take an active effect on lowering the permeability of cement mortar [6,7]. However, the early age and long term properties of the cement concrete with clay are still unclear and needs further investigation. To realize the application of clay-modified cement-based materials in practical engineering, it is necessary to explore their mechanical and durability behavior.

The objective of this research is to investigate the effect of kaolinite clay on the workability, strength and chloride diffusion coefficient of cement-based mixtures (i.e. cement, mortar, and concrete). The effects of addition amount and dispersion method on the porosity characteristics of cement paste are studied. The porosity and microstructure are evaluated through Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscope (SEM) and Energy Dispersive Spectra (EDS) methods.

2. Materials and methods

2.1. Material properties

Ordinary Portland cement of Type 42.5R was used in all mixes. A commercially available kaolinite clay powder was used in this study. The kaolinite clay has a crystalline structure and contains silicon. The relative density, average size, and pH value of the clay is 2.58, 370 and 7.9 nm. Its theoretical formula is $Al_2Si_2O_5(OH)_4$ [8]. The chemical composition of the cement and clay are listed in Table 1. To clarify its microstructure, X-ray diffraction (XRD) analysis and SEM/EDS techniques were carried out on the neat clay powder. The resulting XRD and SEM/EDS images of the clay are shown in Fig. 1. From the EDS spectra shown in Fig. 1b.

Table 1
Chemical composition of PO42.5R cement and clay (wt.%).

Compound (%)	Cement	Clay
CaO	59.30	0.28
SiO_2	21.91	47.80
Al_2O_3	6.27	41.80
Fe_2O_3	3.78	0.30
MgO	1.64	0.03
SO_3	2.41	–
K_2O	–	0.58
TiO_2	–	0.02
Na_2O	–	0.06

2.2. Specimen fabrication

To prepare the paste samples, 1%, 3%, 5%, 7% and 9% of cement by weight was replaced by kaolinite clay. An effective water-to-binder ratio of 0.5 was maintained in all mixes. ISO standard sand was applied. For mortar, the cement-sand ratio was 1:3 by weight. For concrete, the cement: water: sand: aggregate ratio was 350:175:619:1256.

To achieve a good dispersion of the clay in pastes and mortars, the clay was first dispersed in water in a rotary mixer at high speed for 5 mins. The mixing protocols for cement paste and mortar are listed in Table 2, respectively. In the case of concrete, the clay was first dispersed in water by an ultrasonic dispersion method. Then, the dispersed clays were mixed with fine and coarse aggregate.

For paste, the mix is poured into oiled molds to form prisms of size 40 mm × 40 mm × 160 mm, to be used for compressive strength testing. For mortar and concrete, the mix is poured into oiled molds to form cubes of size 150 mm × 150 mm × 150 mm and cylinders of size Φ100 mm × 50 mm to be used for compressive strength and permeability testing, respectively. The fabricated samples 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%) until the prescribed period. For all mixes at each age, three specimens were fabricated and tested to ensure the statistical reliability of test results.

2.3. Methods

2.3.1. Mercury Intrusion Porosimetry (MIP)

The chloride resistance of cement and concrete is highly dependent on the porosity of the material in terms of pore size, pore distribution and interconnectivity of the pore system [9]. The inclusion of nanoparticles will lead to a change in the pore size distribution of concrete. Therefore it is necessary to understand the influence of different nanoparticle additions on the porosity characteristics of the cement matrix. The water vapor adsorption test, nitrogen adsorption test, and MIP test are the most popular methods to examine the porosity characteristics of cement-based material [10,11].

In this study, the MIP test was implemented to investigate the effect of kaolinite clay on the pore size distribution of cement pastes. The porosity of hardened cement paste was measured using high-pressure porosimeter Micrometrics Auto-Pore II9200 (with pressure range up to 400 MPa).

2.3.2. Scanning Electron Microscopy (SEM)

SEM is a well-established method that can offer useful information concerning the structure of material [12]. To better understand the evolution of the microstructure of cement paste samples with clay addition, they were observed by a JSM-6360LV

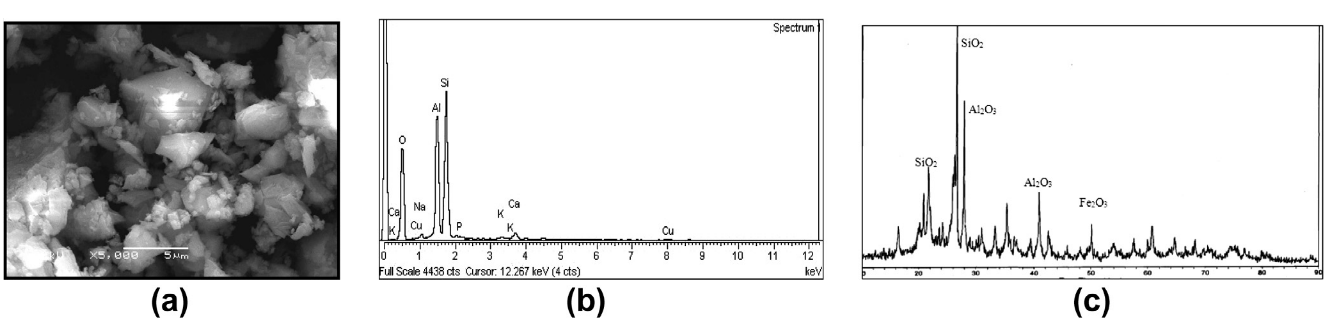

Fig. 1. SEM/EDS and XRD spectra of neat clay powder. (a) SEM micrograph. (b) EDS result. (c) XRD result.