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Chloride resistance of concrete with metakaolin addition and seawater mixing: A comparative study



^a State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

^b Hubei Urban Construction Vocational and Technological College, Wuhan 430205, China

^c WUT-UC Berkeley Joint Laboratory on Concrete Science and Technology, Wuhan University of Technology, Wuhan 430070, China

^d School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

HIGHLIGHTS

• Chloride resistance of concrete with seawater and metakaolin was assessed.

- Combination of seawater and metakaolin increased chloride resistance of concrete.
- There is a correlation between total charge passed and chloride diffusion coefficient.
- Chloride in seawater and NaCl curing was immobilized by Friedel's salt.

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ABSTRACT

Chloride resistance of concrete with seawater mixing and metakaolin (MK) addition was evaluated by analytical techniques. With the combination of seawater mixing and NaCl solution curing, the compressive strength of concrete increased with MK content, which prevented the decrease of strength at 56 days. Both MK and seawater improved the chloride resistance which increased with MK content. The chloride ingress distance was reduced through the refinement of pore structure and immobilization of chloride by formation of Friedel's salt. The minerals after chloride attack were characterized. The microstructure analysis along ingress direction confirmed the improvement of chloride resistance by MK and seawater.

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1. Introduction

Metakaolin (MK) is a supplementary cementitious material with high pozzolanic activity, whose application in concrete can be traced back to 1960's during the construction of Jupia Dam in Brazil.

During the manufacture of MK, kaolin was heated up to 650–800 °C, where the long-range order of silicon–aluminium layer structure was deteriorated with structure deformation due to the loss of interlayer water and OH [1–10]. The pozzolanic activity was obtained by MK as amorphous mineral additive of concrete [5,8,11–15]. By addition of MK, the compressive strength of

concrete was improved, the porosity and permeability reduced and the pore structures was refined [8,16–21], due to the filler effect, acceleration of hydration and pozzolanic reaction of MK with calcium hydroxide formed during the cement hydration [22–26].

The chloride resistance of concrete mainly depends on the microstructure and hydration process of concrete. MK affects both the microstructure and hydration process of concrete so as to improve the chloride resistance. Previous studies on concrete with MK addition indicated the pore structure refinement, the formation of extra C–S–H gels through pozzolanic reaction and immobilization of chloride through formation of Friedel's salt [3,16,17,27–30].

The authors' previous study reported the combination of seawater mixing and 5 wt% (weight percentage) MK addition improved the compressive strength and refined the pore structure of concrete [31]. As a more expansive admixture comparing to fly ash and slag, low content of MK addition will reduce the cost of application in





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^{*} Corresponding author at: State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China.

E-mail address: Qiu-Li@whut.edu.cn (Q. Li).

¹ These authors contributed equally.

Table 1

Chemical composition and physical properties of cement (wt%).

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO₃	LOI
19.05	4.15	3.29	64.43	1.60	0.77	0.09	3.32	2.43
Specific surface area (m²/kg) Density (g/cm³)			437 3.05	Initial settin Final setting	ng (min) g (min)			128 220

Table 2	
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Chemical composition of metakaolin (wt%).

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	SO ₃	P_2O_5	Na ₂ O	MgO	LOI
38.63	57.37	0.77	0.03	0.49	0.40	0.15	0.61	0.39	0.07	1.04



Fig. 1. XRD results of MK.

construction. In this study, the chloride resistance of concrete with seawater mixing and 0–6 wt% MK addition was analysed by various methods of chloride resistance tests. And the effect of chloride attack on the compressive strength, hydration products and microstructure of concrete with seawater mixing and MK addition was analysed and compared with that of concrete with fresh water mixing and MK addition.

2. Materials and experimental

2.1. Materials

Commercial ordinary Portland cement (OPC) from Huaxin Cement Co. Ltd., China was used in this study. The physical properties and chemical composition of OPC are shown in Table 1. Chemical composition of commercial MK (Maoming Kaolin Science and Technology Co. Ltd., China) is shown in Table 2, with a specific surface area of $2800 \text{ m}^2/\text{kg}$. MK was manufactured by calcining kaolin at $800 \text{ }^\circ\text{C}$ for one hour in a rotary kiln. According to X-ray diffraction (XRD) result in Fig. 1 which was conducted by the authors, MK is amorphous with small amount of quartz. Artificial seawater was prepared according to ASTM D1141-1998 (2008) [32], and the chemical composition is shown in Table 3. Fine aggregate is natural sand with an apparent density of 2640 kg/m^3 , stacking density of 1458 kg/m^3 and fineness modulus of 2.91.

2.2. Experimental details

2.2.1. Mix design and curing conditions

The mix design of concretes is shown in Table 4. OPC was substituted by 0–6 wt % MK in the concrete. The water/binder ratio was 0.45 for all concrete mixes.

Table 3

Chemical composition of artificial seawater^{a,b} (g/L).

NaCl	MgCl ₂	Na_2SO_4	$CaCl_2$	KCl	KBr	H_3BO_3	NaF
24.53	5.20	4.09	1.16	0.695	0.101	0.027	0.003

^a Chlorinity of the artificial seawater is 19.38.

^b pH value is 8.2 after adjustment with 0.1 M NaOH solution.

Two types of mixing water were used in this study. One is fresh water, the other is artificial seawater. For compressive strength test, two types of curing conditions for each concrete mix in Table 4 were employed in this study. One was standard curing condition, where specimens were demoulded at 1 day and cured under temperature of $20 \,^{\circ}$ C and relative humidity above 90%. The other was chloride curing condition, where specimens were demoulded at 1 day, cured another 2 days under standard curing condition, and then cured in saturated Ca(OH)₂ solution with 5 wt% NaCl addition at $20 \,^{\circ}$ C. The solution was renewed every week. The specimens under standard curing condition were named as CMKN for fresh water mixing and SCMKN for seawater mixing and SCMKC for seawater mixing.

2.2.2. Compressive strength test

For compressive strength test, the concrete specimens were cast into the size of 100 mm \times 100 mm \times 100 mm. Nine specimens were used for each batch. The compressive strength test was performed at 28 and 56 days for all mixes under both curing conditions according to GB/T 50081-2002 [33].

2.2.3. Chloride resistance

Three analytical techniques were employed in this study to characterize the chloride resistance of concrete, namely Rapid Chloride Penetration Test (RCPT), Rapid Chloride Migration (RCM) test and free chloride content profile test.

RCPT was conducted in accordance to ASTM C1202-10 (2010) at 28, 56 and 70 days for all mixes [34]. Three specimens in size of 100 mm in diameter and 50 mm in thickness were conditioned accordingly and then subjected to 60 V potential for 6 h. The total charge passed through the specimens was determined to evaluate the chloride permeability of concrete.

RCM test was conducted according to NT Build 492 at 28, 56 and 90 days for mixes with fresh water because the chloride in seawater will interfere with the accuracy of results of mixes with seawater. Three specimens were used for each batch. In RCM test, a vacuum-saturated specimen of 100 mm in diameter and 30 mm in thickness was used. The distance of chloride ingress in the specimen was determined and the chloride diffusion coefficient was calculated accordingly [35].

Free chloride content profile test along the direction of chloride ingress was performed according to the procedure similar to AASHTO T259-02 (2006) but with modification [36]. In this test, specimens of 100 mm in diameter and 50 mm in thickness were vacuum saturated in water and sealed with epoxy on all sides except the test face after three days curing. Then the specimens were immersed in saturated Ca(OH)₂ with 5 wt% NaCl solution in sealed containers. After 56 days immersion, the specimens were removed from solution and profile ground on a milling machine. About seven layers of 2–3 mm thickness were collected at various depths up to 24 mm. Because the mixes with seawater incorporated chloride from seawater which will influence the results in the case of acid dissolution, the collected powder was immersed in distilled water, then the leachate was filtered and analysed by silver-nitrate titration to determine the free chloride content in various depths.

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