



Properties of coral waste-based mortar incorporating metakaolin: Part II. Chloride migration and binding behaviors

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HIGHLIGHTS

- Coral waste powder was used to prepare marine mortar and effect of metakaolin addition was investigated.
- Thermodynamic analysis was applied to uncover the mechanisms of hydrate conversion in chloride-rich environment.
- Carboaluminate has the high capacity to form Friedel's salt thermodynamically.

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ABSTRACT

This study investigated the mechanical properties, chloride migration and binding mechanisms of marine mortars with coral waste powder (CP) incorporating metakaolin. Due to the synergetic effect of carboaluminate formation and pozzolanic reaction, the compressive strength and chloride resistance of CP mortars are dramatically improved by metakaolin incorporation. When exposed to 0.5 M NaCl solution, more than 75% of the total bound chloride is bound by the hydrated mortars within 24 h. Friedel's salt (Fs) is the main chloride-uptaking phase and its X-ray diffraction peak area is well consistent with bound chloride content. The thermodynamic analyses indicate that carboaluminate has great capacity to form Fs, and SO₄-AFm can transform to Fs and release gypsum in temperatures below 21 °C. The released gypsum further reacts with SO₄-AFm to form additional SO₄-AFt after exposed to chloride solution. Besides, nearly linear relationship between bound chloride content and active alumina content in binder is found.

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1. Introduction

With the continuous exploitation of ocean, more and more marine engineering works that far from the coastline are in construction nowadays. Concrete is the main material used in marine construction due to its high reliability and low cost. Every year, millions of tons of Portland cement are shipped to the pelagic worksites to produce concrete. As a result, tremendous energy consumption and sharp increase in cost are resulted as well as remarkable CO₂ emission induced by transportation. According to the Green Building Challenge Handbuch [1], shipping one ton of raw materials per kilometer will lead to 0.13 MJ non-renewable energy cost and 0.0089 kg CO₂ emission. Besides, due to the fact that 5%–8% of global CO₂ emission results from cement industry, supplementary cementitious materials (SCMs), like fly ash (FA) and

ground granulated blast-furnace slag (GGBS), are now widely used in concrete to reduce the CO₂ emission and improve the properties of concrete, but such SCMs are also in short supply on pelagic areas. Therefore, it is of great significance to find some local materials to partially replace cement.

During marine engineering works such as dock construction and waterway dredging, large number of coral materials is actually dug up and abandoned on the islands. The mineral composition of the coral waste is mainly aragonite and small amount of calcite that rich in Mg [2,3], which is very similar to limestone. The early stage investigation of coral materials as concrete ingredient, mainly as aggregate, was carried out by the Naval Civil Engineering Laboratory of the U.S. in 1960 [4] and limited papers were published in the next few decades [5–8]. In recent years, with the increasing attention on the exploitation of ocean, using coral materials as construction materials draw great attentions again [3,9–14]. Cheng et al. [14] investigated the effects of FA, GGBS and metakaolin on the performance of coral sand concretes and found that

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mineral admixtures could improve the mechanical properties and durability-related properties including chloride resistance and drying shrinkage of coral sand concrete. Besides, Chen et al., [10–12] studied the properties of coral sand concretes and concluded that the coral sand concrete could achieve comparable compressive strength with river sand concrete involved in fresh water mixing and curing. However, almost all researchers only used coral materials as alternative aggregates. Due to the high CO₂ emission and energy consumption during cement producing and shipping, if these coral waste materials can be used as SCM through a local treatment, the construction on islands will be significantly more sustainable.

As aforementioned that the mineral composition of coral materials is rather similar with that of limestone, coral waste powder (CP) may possess the potential to play similar roles as limestone power (LP). The effects of LP on the Portland cement-based materials have been investigated by many researchers [15–20] and LP combined with some SCMs rich in alumina on the hydration and properties of cement-based materials were also discussed [19–23]. It can be generally concluded that LP can be considered as inert filler in cement-based materials, thus in most cases lower compressive strength and weaker durability-related properties are resulted in LP concrete. However, with the combined use of active SCMs rich in alumina, LP can be activated to form calcium carboaluminate with alumina, then the properties LP concrete are greatly improved due to the joint effects of pozzolanic reaction and the formation of carboaluminate. As CP shares similar mineral composition as LP, it may also reduce mechanical properties and durability, so some highly active SCMs rich in alumina may be suitable to improve the properties of CP concrete. Besides, as chloride corrosion is a major problem for marine concrete, the chloride resistance of coral waste-based mortar should be highly improved to meet it serving environment [24].

Metakaolin (MK) is a high-alumina pozzolanic material. Its high efficiency to improve the mechanical properties and prevent chloride ingress by refining the pore size of concrete has been well verified [14,25–29]. It is mainly attributed to its high pozzolanic activity and the filler effect. Moreover, the MK blended cement and MK-lime based mixtures show dramatically high chloride binding ability [30–34]. All these advantages highlight that MK is a promising material used in marine concrete reinforced by steel bar. Additionally, the great chemical compatibility between MK and limestone powder is also widely recognized. It is reported that the combined use of MK and LP can promote the formation of calcium carboaluminate and benefit the performance of concrete significantly [19,23,31,35]. Based on the overviews, as MK share the similar mineral composition with LP, using MK to enhance CP concrete serving in a marine environment has the following benefits: 1) High pozzolanic activity; 2) Increase the chloride binding capacity; 3) Activate carbonate materials to form calcium carboaluminate. Therefore, applying MK with CP for marine concrete production is promising in performance enhancement and sustainable development.

The present work aims to investigate the effects of MK on the compressive strength, chloride migration and binding of CP blended concrete. To cut the work load, blended mortar was prepared instead of concrete. The replacement level of CP was 10 wt%, 20 wt%, 30 wt% and that of MK was 5 wt% and 10 wt%. The mechanisms of how MK influences the mechanical properties, chloride migration and binding behaviors of CP blended mortar were uncovered.

2. Materials and experiment

2.1. Materials

In this study, the ordinary Portland cement of grade 42.5 purchased from Huaxin Cement Co. Ltd. of China was used. Metakaolin and coral waste powder (CP) were used as SCMs. Aggregate used in this study is ISO standard sand. Polycar-

boxylate water-reducer (PCE) with the solid concentration of 40 wt% was used to adjust the workability. The metakaolin was provided by Maoming Kaolin Science and Technology Co. Ltd. of Guangdong Province of China. The CP was ground from coral waste detritus collected from an island. The coral detritus is very porous as the Scanning Electronic Microscopic (SEM) image shown in Fig. 1. The chemical composition and physical properties of materials are shown in Table 1. The X-ray diffraction (XRD) pattern of CP is presented in Fig. 2. It reveals that the mineral composition of CP is Aragonite, Calcite rich in Mg and very small amount of Halite. This is consistent with the chemical composition of CP (by X ray fluorescence analysis) as shown in Table 1.

2.2. Specimen preparation and curing

Mix proportion of mortars and pastes are presented in Table 2. As for mortars, the replacement of cement with CP is 10 wt%, 20 wt% and that of MK is 5 wt% and 10 wt%. The water to binder ratio of mortar is 0.5 by mass and the binder to sand ratio is 1/3 by mass. To maintain the comparable workability with plain mortar, certain amount of PCE is added. As for paste, the replacement level of CP is 30 wt% and that of MK is 5 wt% and 10 wt%. The water to binder ratio is 0.45 by mass. The mortars were cast into 40 mm*40 mm*160 mm and ϕ 100 mm*50 mm steel mould. The mortar specimens were cured under 20 °C and 98% relative humidity for 24 h, and then they were demoulded and cured in lime-saturated water at 20 ± 1 °C. The paste specimens were cast in 40 mm*40 mm*40 mm steel mould and cured under the same condition as mortars.

2.3. Flowability and compressive strength

Only the flowability of the plain mortar and three CP mortars were tested, because other mortars include some PCE. The method was complied with the Chinese standard GB/T 2419 and the spread diameter was determined to evaluate the

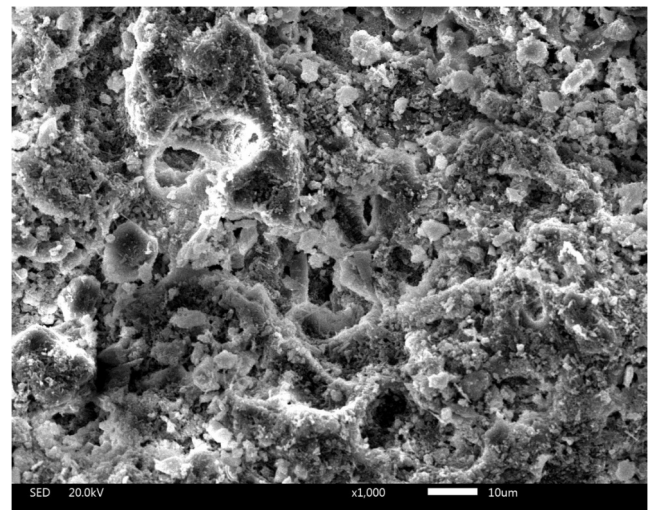


Fig. 1. SEM image of coral detritus.

Table 1
Chemical composition and physical properties of cement, MK and CP.

| | Cement | MK | CP |
|---------------------------------------|--------|-------|-------|
| CaO | 59.82 | 0.03 | 49.02 |
| SiO ₂ | 21.50 | 54.06 | 0.31 |
| Al ₂ O ₃ | 5.86 | 41.98 | 0.12 |
| Na ₂ O | 0.20 | 0.33 | 1.34 |
| K ₂ O | 0.67 | 0.56 | 0.56 |
| Fe ₂ O ₃ | 2.78 | 0.76 | 0.08 |
| SO ₃ | 2.01 | 0.13 | 0.31 |
| MgO | 2.18 | 0.09 | 2.97 |
| P ₂ O ₅ | 0.09 | 0.57 | – |
| Cl [–] | – | – | 0.09 |
| L.O.I | 3.85 | 1.09 | 44.75 |
| Mean particle size (μm) | 12.96 | 3.45 | 8.52 |
| BET fineness (m ² /g) | 0.437 | 33.48 | – |
| Specific gravity (g/cm ³) | 3.05 | 2.52 | 2.68 |

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