Effect of coral powder on the properties of cement-based materials

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Abstract. In the construction of offshore engineering, a growing number of coral sand and coarse aggregate is used as concrete aggregates in the local construction. Thereupon, a lot of coral powder is left as a solid waste. This work is an attempt to study the potential of the coral powder replacing part of cement as supplementary cementitious materials. The flow properties of fresh cement paste with coral powder were studied, as well as the mechanical properties of hardened cement paste. Experimental results show that the fluidity of cement paste blended with coral powder decrease with the dosage of micro coral powder, due to its high water demand and high adsorption of polycarboxylate superplasticizer (PCE). Replacement of cement by coral powder have positive effects on the cement hydration and mechanical properties of cement paste at early ages. However, at the curing age of 7 days, the addition of coral powders deceases the strength of cement paste regardless of replacement levels.

1. Introduction
With the development of China’s marine economy and island construction, the demand for concrete projects for offshore island reef construction has gradually increased. Due to the environmental geography and location of offshore projects, there is a lack of qualified coarse aggregate. However, shipping from the mainland not only has high transportation costs, but also is limited by natural conditions such as wind and waves [1-2]. Therefore, the preparation of local materials without destroying the ecological environment of islands and reefs, and the use of coral reefs instead of normal aggregates for the preparation of concrete has important practical significance and application prospect. Thereupon, a lot of coral powder is left as a solid waste. The use of coral powder as an alternative resource in cement-based materials can not only effectively alleviate the shortage of offshore supplementary cementitious materials, but also take full use of the wasted coral powder produced by related industries.

The main mineral phases of coral powder are aragonite and high magnesium calcite and its main chemical composition is CaCO₃, the content of which is up to 96%. In the existing research, clastic coral granule is mostly used as a fine aggregate in cement-based materials [3-14]. Results [3-14] show that the hydration products of coral sand concrete are basically the same as ordinary river sand concrete at 28 days. Due to its special surface morphology, the bonding strength of coral sand and hydration products is higher than that of river sand. Compared with ordinary river sand concrete, the concrete made with coral sand has slightly lower compressive strength but nearly the same bending and tensile strength at 28 days. There is relatively little research on the use of coral powder as supplementary cementious materials.
Therefore, this study is an attempt to study the effect of micro coral powder on the rheological and mechanical properties of cement paste. The coral sand is ground to powder to form micro coral powder firstly. And then micro coral powder was added as a mineral admixture to partial replace cement. The influences of coral powder on the rheological and mechanical properties are comprehensively investigated in terms of fluidity test, water demand test, total organic carbon (TOC) analysis, hydration heat test and compressive strength test.

2. Experimental

2.1 Raw materials

The cement used in this study is P.I 42.5 Portland cement with the specific surface area of 350 m²/kg and volume density of 3.10 g/cm³. The micro coral powder is made from coral sand obtained from South China Sea by grounding in a laboratory ball mill for one hour and sieving through a 0.075 mm mesh. The specific surface area and volume density are 1470 m²/kg and 2.77 g/cm³, respectively. The chemical compositions of cement and coral powder are presented in Table 1.

| Material      | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃  | Na₂Oeq | LOI  |
|---------------|------|-------|-------|------|------|------|--------|------|
| Cement        | 25.10| 6.38  | 4.19  | 54.87| 2.61 | 2.66 | 0.56   | 2.18 |
| Coral powder  | 0.36 | 0.09  | 0.04  | 47.70| 2.48 | 0.68 | 1.96   | 44.79|

The particle size distribution of cement and coral powder is shown in Figure 1, and the d50 of cement and coral powder is 13.2 μm and 19.8 μm, respectively. Figure 2 presents the XRD pattern of coral powder. It can be seen that the main mineral phases of coral powder are CaCO₃ and (Ca, Mg)CO₃, which is consistent with the founding in [8]. The content of CaCO₃ ((Ca, Mg)CO₃ included) in coral powder from Table 1 is more than 90%. The water reducer used in this study is polycarboxylate superplasticizer (PCE) with solid content of 40%.

![Figure 1. Particle size distribution of cement and coral powder.](image1)

![Figure 2. XRD pattern of coral powder.](image2)

2.2 Experimental test

The fluidity of cement paste with addition of coral powder was determined by the mini-cone test in which a copper cone with a top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm was used according to the Chinese standard GB/T 8077-2012. After well mixed, the cement pasted was poured into the cone right away and the cone was then quickly lifted up. After the paste stopped flowing on the glass table, the average value of four crossing spread diameters of the pasted was recorded. Their mean was employed to compute the relative fluidity. The substitution rate of coral powder for cement is 0, 5%, 10%, 15%, 20%, 25% and 30%, respectively. The w/b ratio of cement paste without PCE is 0.5. The w/b ratio of cement paste with PCE is 0.3 and the dosage of PCE is 0.10%
by weight of binder.

The water demand ratio of coral powder was tested according to Chinese national standard GB/T 35164-2017 and GB/T 18736-2017. The substitution ratio of coral powder for cement is 30%. The water demand ratio is calculated from the water consumption that makes the tested mortar have the same fluidity (within 5 mm) with the reference mortar divided by the reference water consumption.

The adsorption of the PCE on surface of cement or coral grains was determined by the depletion method using a total organic carbon (TOC) analyzer (Multi N/C 2100 TOC, JENA, Germany), whose measurement range is from 50 ppt to 30000 ppm. The w/b ratio of the test cement paste is 4, with different PCE dosages from 0.1% to 2.0% (by weight of binder). After well mixed, the cement paste was immediately centrifuged at 4000 rpm for 10 min. The supernatant liquid after centrifugation was then carefully collected using a syringe filter with a pore diameter of 0.2 μm. Subsequently, the supernatant solution after filtered was diluted with deionized water to a suitable concentration for TOC test.

An 8-channel isothermal calorimeter (TAM Air; Thermometric AB, Sweden) was used to record the hydration heat evolution of cement paste blended with coral powder. 4 g of binder and 2 g of deionized water were mixed in a standard plastic bottle. The bottle was placed in the isothermal calorimeter immediately. Heat flow curves of paste were recorded at a constant temperature of 20 °C.

The compressive strength was tested according to ASTM C192.

3. Results and Discussion

3.1 Effects of coral powder on the flow properties of cement paste

The relationship between the amount of coral powder and the fluidity of cement paste is shown in Figure 3. It can be seen from the figure that whether PCE is added or not, the fluidity of cement paste gradually decreases with the increase of coral powder. For the cement paste with PCE, the effect of coral powder on the slurry fluidity is more significant. When the amount of coral powder is 30%, the fluidity of the PCE-free paste is reduced by 16.6%, and the fluidity of the PCE-added paste is reduced by 26.1%.

The tested water demand ratio of coral powder is 106.7%, indicating that the water consumption of coral powder is larger than that of cement. It is because that coral powder has a larger specific surface than cement, the replacement of cement particles by coral powder results in a significant increase in the total surface area of the solid particles. Therefore, the fluidity of cement paste without PCE decreases with the increase of coral powder content.

The adsorption behaviors of PCE on cement particles and coral powders are shown in Figure 4. Results show that with the increase of PCE dosage, the adsorption amount of PCE on cement particles and coral powder particles both increases. With the same PCE dosage, the adsorption amount of PCE by coral powder is much larger than that of cement particles. Because coral powder shows a stronger PCE adsorption capacity than cement, after partial replacement of cement particles by coral powder particles, the effective PCE concentration on cement particles decreases, macroscopically showing the decrease of the fluidity. Due to the higher water demand and adsorption capacity of PCE, the fluidity of blended cement paste with PCE decrease more significantly with the dosage of coral powder than that of blended cement paste without PCE.
3.2 Effects of coral powder on the cement hydration heat evolution
The influence of micro coral powder on the heat of hydration of cement is shown in Figure 5. From Figure 5, it can be seen that the addition of micro coral powder reduces the total hydration heat. The negative effect is significant with the increasing dosage of coral powder. The addition of micro coral powder increases the normalized heat flow of cement at early ages and the exothermic peak, i.e. acceleration period ends in advance. This is possibly attributed to the fact that the nucleation effect of fine coral powder and the replacement of cement by coral powder increases the effective water to cement ratio, thus stimulating nucleation and accelerating the hydration of cement. Besides, the shoulder perk right after the second heat peak also shifts forward. According to Shi’s research, it is caused by the reaction between C₃A and calcium carbonate in coral powder [8].
3.3 Effects of coral powder on the mechanical properties of cement paste

The effect of coral powder on the compressive strength of cement paste at different curing ages is shown in Figure 6. At the age of 3 days, 5% coral powder improves the compressive strength of cement paste and 15% and 25% coral powder decreases the compressive strength of cement paste. At the curing age of 7 days, the addition of coral powder decreases the compressive strength of cement paste.

In the coral powder-cement binary system, coral powder presents lower activity than cement. The addition of coral powder decreases the amount of cementitious materials and reduces the hydration products of per unit volume of binder accordingly, so the strength of cement paste decreases to some extent. However, at early ages (3 days), the reaction eliminate the strength loss caused by dilution effect of coral powder at relatively low replacement level, thus, the compressive strength of cement paste with 5% coral powder is higher than the reference one. For relatively high replacement level (25%), due to the low chemical activity of coral powder, the strength to cement paste with 25% coral powder is lower than the reference one.

Figure 5. Hydration heat and normalized heat flow curves of cement paste with different dosages of coral powder.

Figure 6. Compressive strength of cement paste blended with coral powder at 3 and 7 days.
4. Conclusions
The fluidity of blended cement paste with coral powder decreases with the increase of coral powder content, due to the higher water demand of coral powder. Coral powder shows a much stronger adsorption capacity of PCE than cement particle, so that the fluidity of cement paste with PCE decrease significantly with the dosage of coral powder than the cement paste without PCE. The addition of micro coral powder reduces the total hydration heat due to the dilution effect of coral powder in cement, but accelerates the early hydration of cement because of its nucleation effect. Low coral powder replacement level of 5% has a positive effect on the mechanical properties of cement paste at curing age of 3 days. But after 7 days, the addition of coral powder causes strength loss of cement paste.

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