Effect and Mechanism of Coral Powder on the Rheological Properties of Cementitious Materials

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Abstract. To study the effect and mechanism of micro coral powder on the flow behavior of fresh cement paste, the fluidity and rheological parameters of cement paste with fine coral powder of different dosages were investigated. The influence mechanism of coral powder on rheological properties was investigated by testing the water demand, the adsorption behavior and the zeta potential. Results show that with the increasing dosage of coral powder, the fluidity of the cement paste decreases and the torque of cement paste increases at the same rotation speed. The derived yield stress and plastic viscosity increase with the increasing dosage of coral powder. Because micro coral powder has higher volume and area than cement with the same mass, the water demand ratio of coral powder is very high, which is one of the reasons for the fluidity drop with the coral powder content. With the same dosage of polycarboxylate superplasticizer (PCE), the adsorption amount and the adsorption ratio of PCE by blended micro coral powder are much higher than that of cement particles. Therefore, compared to cement paste without PCE, the fluidity of cement paste with PCE decreased more significantly at the same coral powder content. In addition, competitive adsorption of Ca\(^{2+}\) between coral and cement particles reduces the positive charge density on the surface of cement particles, causing the decrease of the adsorption capacity of cement particles for PCE, thus affecting its rheological properties.

1. Introduction
With the development of the marine industry in recent years, such as aquaculture and island tourism, the construction of offshore islands far away from the land has become an important issue on a global scale. However, due to the natural conditions and geographical location, the lack of conventional building materials and the high cost of long-distance transportation make it urgent to develop low-cost, reliable alternatives close to marine islands for marine construction. Under the premise of not destroying the local ecological environment, the wasted coral deposits on the island can be used as concrete raw materials, which can not only save natural resources, reduce transportation costs, shorten construction period, but also effectively meet the increasing construction needs [1-4]. Recently, much attention has been paid on the application of coral aggregate in concrete project. In the process of preparing coral aggregate, a lot of micro coral powder is inevitably produced as a byproduct.

The main chemical composition of coral powder is CaCO\(_3\), with a content of up to more than 95%. Fine coral aggregate used in concrete mixing has been studied in recent research [1, 2, 5-16]. However, relatively little research is focused on the use of coral powder as a substitution of cement. The results [5-13] show that coral sand has a fineness from 1.68 to 2.94, low bulk density, high porosity, high water absorption rate, and high chloride content. When clastic coral is used, pre-wet treatment is generally used to ensure the workability of the fresh concrete [13]. Wang X. et al. [16] conducted a study on the preparation of ultra-high performance concrete (UHPC) using pre-wet micro coral.
powder (<0.075 mm) and fine coral powder (0.075~0.125 mm). When 15% coral powder and 30% coral sand are added, the compressive strength of concrete is not significantly reduced, but due to the porous effect of coral particles, the self-shrinkage of UHPC is effectively reduced. Moreover, the addition of coral particles (<0.125 mm) in UHPC can significantly enhance its resistance to chloride ion attack. Though coral powder has been used in the preparation of cementitious materials [14-16], its influence on the rheological properties of cement-based materials is still not clearly clarified. Therefore, this study is an attempt to study the effect of fine coral powder on the rheological properties of cementitious materials. Because different PCEs had a strong influence on the rheological behavior of cement paste [17], only one kind of PCE was used in this study. Together with water demand, fluidity, absorption of PCE and zeta potential tests results, the influence and mechanism of coral powder on fresh cement-based materials was discussed.

2. Experiments

2.1 Raw Materials

The cement used in this study is CEM I 42.5 with the specific surface area of 346 m²/kg and volume density of 3.10 g/cm³. The micro coral powder was made by grounding coral sand from South China Sea for one hour and then sieved through a 0.075 mm mesh. Its specific surface area is 1470 m²/kg and volume density 2.77 g/cm³.

Figure 1 shows the particle size of cement particles and micro coral powder. The d50 of cement particles is 13.2 μm and of micro coral powder is 19.8 μm. The SEM images of coral powder used in this study were shown in Figure 2.

Figure 1. Particle size distribution of cement particles and micro coral powder

Figure 2. The SEM images of coral powder.

The main mineral phases of coral powder are aragonite and high magnesium calcite, which is
consistent with the founding in [15-16]. The CaCO$_3$ and (Ca, Mg)CO$_3$ content in coral powder is more than 90%.

Polycarboxylate superplasticizer (PCE) with solid content 40 % were used for cement paste and mortar preparation.

### 2.2 Experimental

The determination of the fluidity of cement paste refers to the Chinese national standard GB/T 8077-2012 "Test Method for the Homogeneity of Concrete Admixtures", with the dosage of coral powder is 0, 5%, 10%, 15%, 20%, 25% and 30%, respectively. The water to binder ratio of cement paste without water reducer is 0.5. The dosage of PCE 0.10% by weight of binder for the cement paste with PCE and the water to binder ratio is 0.29.

The torque-shear rate experiment of cement paste was carried out using a concrete rheometer in a room with ambient temperature 25 °C. The water to binder ratio of cement pastes is 0.3 and the dosage of PCE is 0.10% by weight of binder. The amount of coral powder (replacement of cement) is 0, 5%, 10% and 15%, respectively.

The mix proportion for the water demand test is listed in Table 1. The water demand of coral powder was calculated according to Chinese national standard GB/T 35146-2017.

| Table 1. Mix proportion of the test mortar and reference mortar (g) |
|---------------------------------------------------------------|
| No. | Water | Cement | Coral powder | ISO sand |
|------|-------|--------|---------------|----------|
| Reference mortar | 225 | 450 | 0 | 1350 |
| Tested mortar | $w_c$ | 315 | 135 | 1350 |

The adsorption capacity of the cement and coral powder of PCE is tested using total organic carbon TOC (multi N/C 2100/2100S, Jena, Germany). The adsorption amount is determined by the depletion method. First, prepare PCE solutions of different concentrations from 0.1% to 2.0% by weight of binder. After standing for a certain period of time, take a small amount of supernatant and filter with 0.2 μm filter membrane, then dilute to a certain concentration with deionized water to make the solution suitable for TOC test. The adsorption amount (T) and the adsorption ratio (P) was calculated by Equation (1) and (2), respectively.

$$T = \frac{V \times (C_0 - C_1)}{m}$$  \hspace{1cm} (1)

$$P = \frac{C_0 - C_1}{C_0} \times 100\%$$  \hspace{1cm} (2)

Where $C_0$, $C_1$ are the total content of organic carbon before and after adsorption, respectively; $V$ is the volume of PCE solution; $m$ is the mass of powder.

Zeta potential of cement and coral powder suspension was measured using zeta potential analyzer (DT 300, America). The solid content of the suspension was 20%.

### 3. Results and Discussion

#### 3.1 Effects of Coral Powder on the Rheological Properties of Cement Paste

##### 3.1.1 Fluidity of cement paste blended with coral powder

Figure 3 shows the relationship between the dosage of coral powder and the fluidity of cement paste. Form the figure we can see that the fluidity of cement paste decreases gradually with the dosage of coral powder both in the paste with and without PCE. The influence of coral powder on the fluidity drop in the cement paste with PCE is more significant than without PCE. When the dosage of coral powder is up to 30%, the fluidity of the cement paste without PCE is reduced from 165 mm to 140
mm, with a drop of 16.6%, 245 mm to 180 mm, and the fluidity of the cement paste with PCE is reduced from 245 mm to 180 mm with a drop of 26.1%.

**Figure 3.** Effect of coral powder on the fluidity of cement paste with and without PCE

### 3.1.2 Rheological parameters of cement paste with different amount of coral powder

Figure 4 shows the relationship between the torque and the rotation speed of the cement paste blended with coral powder. If the commonly used Bingham fluid model is used for fitting, the yield stress (Y-axis intercept) will be negative, and the rheological parameters of the pastes cannot be correctly characterized and reflected. Therefore, the modified Bingham fluid model [17] was used in this study. The derived parameters from the torque-rotation speed curves are also shown in Figure 4.

It can be found that at the same rotation speed, the torque of the cement paste mixed with the coral powder gradually increases with coral powder dosage, indicating that the viscosity of the paste system is increased by the addition of the coral powder. Within the experimental range, the higher the amount of coral powder, the greater the viscosity of the paste. It can be seen from the modified Bingham fluid model fitting data that the slurry exhibits shear thickening (reflected by the quadratic coefficients), but the difference among them is not obvious. When the amount of coral powder increased from 0 to 15%, the yield stress τ₀ of the system (reflected by the Y-intercept) gradually increased from 1.20 to 3.71 Pa, with an increase of 208.1%, and the plastic viscosity μ of the pastes (reflected by the linear term) also gradually increases from 0.21 to 0.74, with an increase of 243.3%.

**Figure 4.** Evolution of torque with rotation speed of cement paste with coral powder

**Figure 5.** Evolution of yield stress and plastic viscosity of cement paste with coral powder

The extended Reiner-Rivlin equation for the modified Bingham model[17] was used to estimate
the yield stress and plastic viscosity of cement paste with coral powder. The yield stress and plastic viscosity of cement paste without coral powder is 0.301 Pa and 0.054 Pa•s, respectively. To illustrate the influence of the added coral powder on the rheological properties on cement pasted, the relative yield stress and the relative plastic viscosity (the ratio of corresponding parameter to the reference one) were calculated, as shown in Figure 5. It can be seen from Figure 5 that the yield stress and plastic viscosity increase with the increasing dosage of coral powder. The analysis of rheological data proves that the addition of coral powder increases the yield stress and plastic viscosity of cement paste, which affects the rheological properties of cementitious materials.

3.2 Mechanism of Coral Powder on the Rheological Properties of Cementitious Materials

3.2.1 Water demand of coral powder

The partial substitution of cement particles by micro coral powder can significantly reduce the fluidity of the paste. One of the possible reasons is that the water demand of the micro coral powder is much higher than cement, so that the in the cement paste blended with coral powder, the effective water-cement ratio is reduced. Therefore, the fluidity of cement paste shows an obvious decreasing with the substitution rate of coral powder. The tested water demand ratio of mortar with 30% of coral powder is 106.7, indicating that when the coral powder is mixed with water it need more water to get the same fluidity compared to the cement particle. In addition, the test results of raw materials show that the density of coral powder is much smaller than the density of cement particles. Under the condition of substitution of cement particles by coral powder with the same mass, the volume fraction of solid particles in the tested system is larger than that in the pure cement paste system, which causes the higher friction between solid particles. When the same amount of cement particles is replaced by micro coral powder, the total surface of the solid particles increases significantly, causing a significant increase of the water demand of the tested system. The comprehensive effect of higher water demand, higher volume fraction of solid particles and higher surface area makes the incensement of shear stress at the same rotation speed. Therefore, the plastic viscosity and yield stress of the cement paste blended with micro coral powder increase with the content of coral powder.

3.2.2 Competitive adsorption of PCE between coral powder and cement grains

Figure 6 shows the adsorption amount and adsorption ratio of cement and coral powder particle to PCE at different solution with different PCE concentration. It can be seen from the figure that the adsorption amount of PCE on cement particles and coral powder particles both increases with the increasing PCE content. Coral powder shown a stronger adsorption capacity than cement particle at the same PCE dosage. With the incensement of PCE concentration, the adsorption ratio of PCE on both cement particles and coral powder particles shows a downward trend.

![Figure 6](image)

**Figure 6.** Evolution of the adsorption amount (a) and adsorption ratio (b) with the dosage of PCE

Since the specific surface area of coral powder is larger than cement particles and the density of
coral powder is smaller than cement, the volume and total surface area of solid particle in the coral powder slurry are much higher than those in the cement paste. Therefore, the coral powder shows a stronger PCE adsorption capacity than cement, and this also explains the test results in Figure 3 to Figure 5. The test results of adsorption amount and adsorption ratio validates that the stronger PCE adsorption capacity of coral powder is another reason to reduce the fluidity and rheological properties of cement-coral powder paste system.

The zeta potential was used to characterize the surface electrical properties and the stability of the cement paste and coral paste. Since the zeta potential is not the real potential of the particle interface, but the potential outside the adsorption layer, the level of the zeta potential reflects the surface electrical properties of the particles in the aqueous solution to some extent. The zeta potentials of the cement and coral powder suspensions without PCE was 3.58 mV and -1.54 mV, respectively, indicating that the coral powder shows a weak negative charge on the surface. After water is added into cement, the hydration reaction occurs, Ca\(^{2+}\) and OH\(^{-}\) are generated and dissolved into the solution, so that a silicon-rich layer is formed on the surface of the cement mineral. The generated Ca\(^{2+}\) is then adsorbed to the surface of the particle, so that the surface of the cement particle carries a certain amount of positive charge. PCE is an anionic surfactant with a comb-shaped branched structure, which is easily adsorbed on the surface of positively charged particles to form an electric double layer structure, causing electrostatic repulsion between cement particles. In addition, the hydrophilic side chain of PCE molecules extends in the liquid phase, resulting in a steric hindrance effect among adjacent cement grains. The more PCE adsorbed on the surface of cement particles, the more obvious the electrostatic repulsion and steric hindrance effect, and the better the dispersion effect on cement particles. In the cement paste blended with coral powder, due to the weak negative charge of coral powder, it is easier to adsorb Ca\(^{2+}\) generated by cement hydration. This part of Ca\(^{2+}\) shows a further bridging effect for the adsorption of negatively charged PCE molecules. On the other hand, since Ca\(^{2+}\) is more easily adsorbed onto the surface of coral powder particles, the positive charge density on the surface of cement particles is significantly reduced, resulting in a decrease adsorption capacity of negatively charged PCE molecules on cement particles. Therefore, the competitive adsorption of Ca\(^{2+}\) between coral and cement grains affects the further adsorption of PCE. Due to the combined effects mentioned above, coral powder is in a dominant position in the competitive adsorption of PCE in the blended paste, so the plastic viscosity and yield stress of the blended paste increased with the dosage of coral powder, and the fluidity decrease with the increase of coral powder.

4. Conclusion
The fluidity of cement-micro coral powder paste system decreases with the amount of coral powder content. The plastic viscosity and yield stress of the cement paste blended with micro coral powder increase with the content of coral powder.

The water demand ratio of mortar with 30% of coral powder is 106%, due to its higher volume and total area than cement with the same mass, so that the fluidity of the cement-micro coral powder paste drops with the increasing amount of coral powder in PCE-free cement paste.

With the same PCE dosage, coral powder shows a much stronger adsorption capacity of PCE than cement particle. In addition, the competitive adsorption of Ca\(^{2+}\) between coral powder and cement particle further weakens the adsorption of PCE on cement particles. Therefore, the fluidity and rheological properties of blended cement paste with coral powder with PCE decrease more significantly with the increase of coral powder content than the PCE-free blended paste.

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