Primary Chemical - Physical Properties of Marine Cement-Based Materials

YAN Qian1,2, WANG Ya-jun2*, LIU Tao2, WU Di2, XU Yan-jie3, GAN Xiao-qing4, DONG Zhi-hong4

1CHINA MCC5 GROUP CORP.LTD, ChenDu 316002, China;
2School of Maritime and Civil Engineering, Zhejiang Ocean University, Zhoushan 316002, China;
3Key Laboratory of Hydroscience and Hydraulic Engineering, Tsinghua University, Beijing 100084, China;
4Yangtze River Scientific Research Institute, Wuhan, 430010, China

*E-mail: 644594016@qq.com

Abstract: The uniaxial pressure experiment was carried out on the whole-age marine cement-based materials. By analyzing this type of material, there is obvious early strength and late strength decay. The X-ray diffraction experiment was carried out on the sample before the pressure test. After the crushing, the characteristic samples were taken for multi-scale electron microscopy. The microstructure of the material was divided into the strengthening region and the weak region, and the microscopic damage process was summarized.

1. Introduction
Under the background of the transformation of the great power of the motherland into a maritime power, the exploitation of marine building materials resources has become a hot research direction for the global construction of raw material resources [1]. At the same time, with the expansion of the marine economic circle, the booming tourism industry, the increase in the number of migrants and the increase in infrastructure, the demand for sand and gravel fresh water continues to increase, and the contradiction between supply and demand will become more and more prominent [2]. There are no large rivers and rivers in the area. If natural seawater sea sand can be used directly as engineering materials, it will inevitably save cost resources. However, there are obvious differences between seawater and sea sand. Compared with fresh water and river sand, different chemical composition and mineral composition make the marine cement-based materials have different performances compared with conventional cement-based materials. Therefore, the analysis of physical and chemical composition and microscopic macrostructure of seawater and sea sand in Zhoushan area has far-reaching significance for the construction of marine infrastructure.

2. Materials and Methods
2.1 Goal Materials
Sand: The sea sand of the sample is taken from the main physical properties of the sea sand in the Nansha
beach of Putuo District, Zhoushan. As shown in Table 1.

Table 1. Main Physical Performance Indicators of Sea Sand

| Sea sand sample | Apparent density (kg/m³) | Bulk density (kg/m³) | MB value (g/kg) | Shell content (%) | Mud content (%) |
|-----------------|--------------------------|----------------------|----------------|------------------|-----------------|
|                 | 2652                     | 1370.3               | 1.4            | 0.23             | 0.27            |

Figure 1. River sand particle size distribution and sea sand laser particle size test

The sample sea sand has the advantages of shellfish content and low mud content, but at the same time, the bulk density does not meet the requirements for use, and the large MB value belongs to the problem of just passing the qualification. According to the Malvern laser particle size analyzer test, the specific surface area of Nansha sea sand is 30.12m²/kg, and the large specific surface area has an adverse effect on the fluidity of concrete. The median diameter is 210.492μm, and the volume average particle size is D(4,3). The average surface area of 218.566μm is 199.233μm, and the difference between D(4,3) and D(3,2) is relatively small. The sea sand is more regular and the particle size distribution is more concentrated.

Mixing water: The sample is taken from the Zhoushan District of Zhoushan, about 1 km away from the island. The annex has no sewage from the river. Because of the large amount of seawater in the area, the precipitation phenomenon after retrieving must be quenched evenly before testing. Several kinds of ions and salt components that have a great influence on the hydration reaction are tested by laboratory internal test method.

Figure 2. Seawater Ion Distribution
2.2 Experimental Program

(1) Stirring with a JJ-5 cement mortar mixer, the size of the cube test piece is 70.7mm×0.7mm×0.7mm, and the standard maintenance setting of the test block is 3 days, 28 days, 90 days, 180 days, 240 days. A single-axis loading experiment was performed at the age of the experiment. At the age of age, the uniaxially loaded sample is sampled by the quartering method, and the sample is subjected to X-ray energy spectrum test.

(2) Marine cement-based mortar mix as shown in Table 2

| Numbering | W/C | Cement(kg·m⁻³) | water(kg·m⁻³) | Sand(kg·m⁻³) |
|-----------|-----|---------------|---------------|-------------|
| 1         | 0.67| 1061          | 486           | 803         |

3. Experiments Results

3.1 Analysis of Uniaxial Compressive Strength of Variable Age

Marine cement-based materials showed significant early strength and grew rapidly 28 days ago. The reason for this phenomenon is that the inorganic salt ions in the seawater accelerate the progress of the hydration reaction, and the material strength no longer increases to a maximum after reaching 180 days. The first group and the second group showed the intensity decay phenomenon. The microscopic structure of the marine cement-based material was obtained by microscopic analysis of the sample to find that the calcium-vanadium and the Friedel salt were higher than the conventional cement-based materials in the later stage. The voids and internal cracks change.

3.2 Micro-Macro Cracking Analysis

Figure 3. Peak uniaxial pressure at multi-age

Figure 4: Diffraction Analysis of Marine Cement-based Samples
In addition to calcium hydroxide, calcium silicate hydrate, monosulfide hydrated calcium aluminate and trisulfide hydrated calcium aluminate produced by conventional hydration reactions, a large amount of inorganic salt ions in seawater participate in the hydration reaction or further reaction with the hydration product produces a new substance. These include: chloride ions participate in the hydration reaction to form monochloroaluminum chloroaluminate, and when the C₃A content is lowered in the later stage of the reaction, the latter combines to form trichloroaluminum chloroaluminate. The simultaneously produced C-S-H reacts with magnesium chloride to form magnesium hydroxide, which in combination with silica forms M-S-H. The increase in the content of calcium vanadium in the presence of sulfate ions increases compared with conventional concrete. The three minerals in the seawater are not produced in the hydration reaction and are well preserved in the material.

The marine cement-based materials were microscopically tested after being crushed at a full age, and some high-resolution images are shown in Fig. 5, and micro-fine-macro photos were taken for analysis.

![Multi-age Multi-scale Damage Rupture Diagram](image)

Based on the test and analysis of the whole age of Marine cement-based materials, the location of the cement-based material strengthening point and the loss of loss are attributed to the following positions: Cement-based interphase adhesion is mainly provided by small hydrated calcium silicate, M-S-H, calcium sulphoaluminate and calcium aluminate hydrate. It is often difficult to cause losses in the area where the above substances are concentrated and at the intersection of sand and other materials, and it is a point of reinforcement for such materials.

Through the test of the whole age of Marine cement-based materials, the weak point or damage germination point of microscopic damage of cement-based materials is summarized as follows:

1. There is an inverse relationship between the porosity and the strength of marine cement-based materials. The main sources of pores in the material are cement particle raw materials that are not involved in the hydration reaction, interlayer pores of hydrated calcium silicate, pores mixed during material preparation, and water capillary pores in the cement slurry.

2. Micro-cracks have an enormous impact on the strength of marine cement-based materials. In the
bulk calcium hydroxide, large volume of calcium vanadium, monochloroaluminum chloroaluminate, and calcium trichloroaluminate crystals, it is a weak link and it is extremely prone to micro cracks in this area.

4. Conclusions

Through the full-scale compressive strength test and micro-physical and chemical analysis of the whole age marine cement-based materials, the following conclusions can be drawn:

The strength of marine cement-based materials showed obvious early strength in the early stage, and began to stop growing after 180 days, and then weakened in the later stage.

In addition to the formation of conventional substances in the hydration reaction process, monochloro-type calcium chloroaluminate, M-S-H, and calcium vanadium with a large content are also formed.

The cement-based material strengthening point and the position where the loss is not easy are attributed to: Cement-based interphase adhesion is mainly provided by small hydrated calcium silicate, M-S-H, calcium sulphoaluminate and calcium aluminate hydrate, it is often difficult to cause losses in the area where the above substances are concentrated and at the intersection of sand and other materials, and it is a point of reinforcement for such materials. The micro-damage weak point or damage germination point of cement-based materials is attributed to: cement particle raw material not involved in hydration reaction, interlayer hole of hydrated calcium silicate, pores mixed during material preparation, and water capillary pore water in cement slurry. And in the bulk calcium hydroxide, large volume of calcium vanadium, monochloro type calcium chloroaluminate, calcium chloride chloroaluminate crystal, it is extremely vulnerable to micro cracks in this area.

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