



# Interface and anti-corrosion properties of sea-sand concrete with fumed silica

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## HIGHLIGHTS

- Fumed silica has been used for preparation of concrete with dredged materials.
- The mechanism of Friedel's salt formation in the sea-sand concrete were discussed.
- The hydroxyl fumed silica can reduce the free chloride content of the concrete.

## ARTICLE INFO

### Article history:

Received 3 March 2018

Received in revised form 25 July 2018

Accepted 8 August 2018

### Keywords:

Sea-sand concrete  
Dredged aggregate  
Interface  
Fumed silica  
Friedel's salts

## ABSTRACT

The present study investigates the influence of fumed silica on the formation mechanism of Friedel's salt of the concrete made with dredged sea-sand, containing high chloride content. We have observed significant differences in the measured silicon and aluminum content, which changed the interfacial response of as-prepared concrete. The fumed silica was migrated from the cement matrix and diffused to the concrete interface, which induced  $H^+$  evolution reaction due to Al-OH groups. Hence, the enhanced compressive strength and lower porosity and ion permeability of modified concrete have been obtained. The fracture modes of concrete, with and without fumed silica have also been discussed. These results provide the possibility of using non-desalination dredged sea-sand, for concrete preparation and attain the optimized production efficiency and performance of sea-sand concrete. Furthermore, the choice of one-electron oxidized species of additives provide a mechanistic insight into the formation of Friedel's salt assisted sea-sand concrete production.

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## 1. Introduction

Sea-sand concrete technology [1], which is characterized by the dredged marine aggregate materials as the basic aggregate of concrete, can be applied to important port expansion projects and reclamation works [2]. The dredged materials are mainly obtained from sea-sand, coral reefs or other marine sediments. This technology can not only be beneficial in alleviating aggregate requirement of hill or river sand but also adapting to the demand of the sustainable development of marine organisms.

The technique has been valued by researchers worldwide since the 1960s [3–5]. In the beginning, the sea-sand needs to be desalinated before it can be used and the technology had been applied to the pavement, coastal breakwater, and other fields [6–8]. At this stage, there are still some constraint requirements, for example, the total replacement amount of sea-sand for river sand which

should be considered. Later some researchers pointed out that the presence of chloride ion from the salt water was unlikely to affect the properties of concrete beyond a mild acceleration of the setting times and hardening rate of concrete, especially, for the project without the use of reinforced concrete or replaced steel with carbon fiber and basalt fiber reinforcement [9–10]. In recent years, researchers have put forward the new connotation of this technology, “Coral seawater concrete technology” [11–13], highlighting the combination of the coral reef and sea-sand usage, whose goals are to further its application in concrete preparation technology. However, for the plain concrete without washing or decontaminating processes, salt should be as low as possible since it could affect the service environment of concrete which induce bacteria corrosion or accelerate loading coupling effect corrosion [14–18]. It is important to develop the methods of concrete preparation technology using dredged material which is beneficial in reducing the impacts of the presence of chloride.

To determine chloride content is an essential procedure. According to Roeder [19], unwashed sand with a typical 10%

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moisture content will contain about 0.3% NaCl. The condition of chloride ions should be indicated as one of the important evaluating factors that affect the service life of concrete structures [20–23]. The total chloride content can be determined by the acid soluble extraction, including the free chloride contents and Friedel's salt. The free chloride content can be determined by the distilled water soluble extraction. Normally speaking, the formation of a certain amount of Friedel's salt can mitigate chloride penetration of concrete to a certain degree. Nevertheless, Friedel's salt will change to free chloride ions in the case of the carbonation, sulfate, especially under the action of load. Apparently, a practical method that can not only lower the free chloride contents but also the total chloride is a more favorable choice. For this, we found that making the dredged marine aggregate concrete with a slight amount of fumed silica [24–26] whose surface was abundant with HO<sup>-</sup> can reduce both total chloride and free chloride of hardened concrete.

In this study, fumed silica has been applied for preparation of dredged marine aggregate concrete with high chloride content, effectively reducing the total chloride content of concrete and affecting the mechanisms of Friedel's salt formation. Besides, the addition of polypropylene fiber was also investigated.

## 2. Materials and methods

With respect to the provenance of the dredged marine aggregate, coarse aggregate, and fine aggregate were obtained at the Port of Bohai Bay in China. The aggregates were not subjected to any washing process during this study. The maximum size and specific gravity of coarse aggregates were 37.5 mm and 2.6. The fineness modulus and specific gravity of sand used were 2.7 and 2.6, respectively. Portland cement 42.5 was used in all cementitious materials. Commercial hydroxy fumed silica additive, namely K-SP30, was bought from Xuan Cheng Jing Rui new material Co, Ltd. in Anhui Province. The manufacturers' reported properties of the fumed silica were as follows: an average primary particle size of 30 nm, corresponding to a surface area of 200 m<sup>2</sup>/g. Commercial polypropylene fiber PF-1A, with the average length of 12 mm, was bought from pioneer Co, Ltd. in Nanjing. The mix proportions of sample made by the method of BM11 that concrete prepared without any additives were listed in Table 1. On the basis of BM11, 1% fumed silica and 1% polypropylene fiber were added in samples made by the method of BM21 and BM31.

Samples of concrete's compressive strength test with the size of 150 × 150 × 150 mm were made in accordance with China's Standard GB50107-2010 and the average compression values can be seen in Table 2. All the samples prepared for microstructure and elemental analysis were taken from the samples of concrete compressive strength test which broke in the core part of the sample. For powder samples, they were scraped out at the interface between the C-S-H phase and the aggregate region, as close as possible to the aggregate surface position.

**Table 1**  
Mix proportions of sample made by the method of BM11.

Method	Sample content (kg/m <sup>3</sup> )			
	Water	Cement	Coarse aggregate	Sand
BM11	270	450	692	692

**Table 2**  
Comparison of compressive strength, porosity and ion permeation flux value.

Method	Sample crushed value /kN	Average compressive strength/MPa	Preferred sample	Porosity/%	Electric flux/C
BM11	B11-1	939.5	B11-1	15.1	15,032
	B11-2	894.1			
	B11-3	931.6			
BM21	B21-1	994.7	B21-2	10.2	11,343
	B21-2	1000.6			
	B21-3	994.9			
BM31	B31-1	742.1	B31-3	22.3	13,354
	B31-2	737.5			
	B31-3	735.1			

(For ease of description in the following text, 'B11-1' is abbreviated as 'B11', 'B21-2' is abbreviated as 'B21' and 'B31-3' is abbreviated as 'B31').

Rapid chloride permeability test was used to evaluate the ion permeability of concrete. Curing for 28 days, the concrete samples were cut into size of 50 mm thick and 100 mm diameter, and then treated by water saturation under vacuum conditions. The specimens were fixed to the sink, one sink with a solution of 3.0% NaCl and another with 0.3 mol/L NaOH. In the 60 V plus electric field, the total amount of electricity was calculated by the current curve of the function curve at 30-minute intervals for 6 h.

The chloride analyses were undertaken according to JGJT 322-2013 (Technical specification chloride ion content concrete), similar to ASTM C1152 (2004) and ASTM C1218 (2008) for free and total chloride contents, using the Volhard titration method (NT Build 208, 1996). The titration process was repeated three times and the data obtained were stable.

XRD analyses were performed for characterizing and chemical compositions physical phases of the power samples with an X-Ray Diffractometer, SHIMADZU. AutoPore IV 9500 Automatic Mercury Porosimeter was used for pore structure analysis. The samples in size of 40 mm × 40 mm × 160 mm were cured in standard condition for 40 days, then cut and sampled at the center. Freeze-dry the sample to terminate hydration before analysis. A Field-emission scanning electron microscope (SEM) Sirion and energy dispersive spectroscopy (EDS) were employed in the microstructural evaluation of concretes.

## 3. Results and discussions

### 3.1. Comparison of compressive strength, total porosity and ion permeation flux

It can be clearly seen that the average compressive strength of samples made by the method BM21 were obviously improved as shown in Table 2. The porosity and the electrical flux were reduced. However, the performance of samples made by the method BM31 with the addition of polypropylene fiber were not better.

In addition, fumed silica effectively improved the strength of the concrete specimen. Kumar et al. [27] have demonstrated that most of the existing models, relating the mechanical strength with the pore size distribution of cement-based material, are not suitable for concrete. Hence, microscopic structures should be investigated for the sea-sand concrete. The mercury intrusion method and the ion permeability method have been applied to assess the pore distribution. Furthermore, compositional analysis of the sea-sand concrete was studied by XRD and discussed in Chapter 3.2.

In the accumulative pore size distribution curve, the sum of the integral area under the curve reflects the total porosity and provides pore size distribution of concrete. As shown in Fig. 1, the cumulative B21 pore curve was below B11, whereas the cumulative B31 pore curve was above B11, which are in good agreement with total porosity results. Compared with B11 and B31, the B21 curve had shown a little back fold trend at the 10 nm pore distribution, which corresponds to the more solid and rougher surface of the sample taken from the B21 interface area. However, the return of this curve did not influence the pore size distribution estimation because mercury porosimetry results below 10 nm are not reliable.

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