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On the use of blast furnace slag and steel slag in the preparation of green artificial reef concrete

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HIGHLIGHTS

- Development of artificial reef concrete with industrial wastes was proposed.
- 98% of the solid raw materials in the developed concrete are industrial wastes.
- Physical property, compressive strength and hydration products were investigated.
- No considerable amount of portlandite was detected in the developed concrete.
- The developed concrete is suitable for the attachment growth of algae in the sea.

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ABSTRACT

This study is motivated by the need for the development of green artificial reef concrete (GARC) and the reuse of granulated blast furnace slag (GBFS) and steel slag (SS) from the steel manufacturers located near coastline. GARC was developed with industrial waste including GBFS, SS and flue gas desulfurization gypsum as the major raw materials. Physical properties and compressive strength development of the prepared GARC were examined. Hydration products of GARC paste were investigated through X-ray diffraction, differential scanning calorimetry and scanning electron microscope techniques. The developed GARC shows a 28-day compressive strength of 71.4 MPa and a density of 2765.5 kg/m^3, which contains industrial waste accounting for 98% by weight of its total solid raw materials. Investigation of hydration products in GARC paste reveals that the major hydration products are ettringite and C–S–H gel with a very dense microstructure, without considerable amount of portlandite that is commonly found in traditional concrete. The absence of portlandite is favorable for lowering the pH valve of artificial reefs, which would be benefit for avoiding the accumulation of fouling organisms like barnacles on the surface of concrete artificial reefs. An experimental-scale deployment of GARC specimens in the sea preliminarily demonstrates that GARC is suitable for the attachment growth of algae. The successful development of GARC mainly composed of GBFS and SS could potentially offer great benefits in promoting the sustainable development of steel manufacturers closely located to coastline as well as fishery industry.

1. Introduction

Artificial reefs are man-made underwater structures that provide habitants for marine plants and animals resources [1]. Artificial reefs have been applied in at least 40 countries to increase commercial fishery production, restore marine ecological environment and fishing ground, improve recreational activity and prevent trawlers from destroying seabed, bringing substantial economic and environmental benefits [2–4]. Concrete is the most widely used material for building artificial reefs as concrete can be easily used to make complex shapes and big hollow-shaped structures [5]. To reduce the material cost and increase the material greenness of artificial reef concrete, it is very important to use locally available industrial waste as raw materials.

Granulated blast furnace slag (GBFS) and steel slag (SS) are the major solid waste generated by steel manufacturers. GBFS has been widely used as mineral admixture in the production of concrete in China as well as other countries. As for SS, the annual output of SS reaches 93 million tons in 2013 [6] in China. However, its current utilization rate of SS is less than 30%, far below that in developed countries [6]. The stockpile of huge amounts of SS causes severe environmental problems and economic losses, demanding more approaches of economical reuse and treatment.

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Steel manufacturers that accumulate nearly 30% of the national production capacity are located near the sea coast or river in China. This is natural as more than 50% of raw iron ore are imported in this country [7]. For some other countries like Korean and Japan, all the steel manufacturers are built near coastline. Naturally, the potential use of SS and GBFS from such steel manufacturers that are located close to coastline in the preparation of green artificial reefs concrete as raw materials would benefit the sustainable development of both steel industry and fishery industry, as it would consume solid waste, save natural resource and reduce material cost.

This study investigates the use of SS and GBFS as the major raw materials in the preparation of green artificial reef concrete (GARC). GBFS powder, ground SS power, cement clinker and flue gas desulfurization (FGD) gypsum are used as binder; SS are used as fine and coarse aggregates. Physical properties and compressive strength development of the prepared GARC were evaluated. Hydration products of the GARC paste were investigated by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscope (SEM) techniques. To preliminarily investigate the accumulation of marine lives on the developed GARC, an experimental-scale deployment of GARC in the sea was conducted.

2. Materials and methods

2.1. Materials

The materials used in this study include SS, GBFS, FGD gypsum, cement clinker, tap water and polycarboxylate superplasticizer. Chemical and physical properties of SS, GBFS, cement clinker and FGD gypsum are given in Table 1.

SS in this study is a basic oxygen furnace slag that is cooled through a heat pyrolytic pulverization technology [8]. Such technology enables free calcium oxide (f-CaO) and free magnesium oxide (f-CaO) to turn into $Ca(OH)_2$ and $Mg(OH)_2$, therefore eliminating the volume instability of SS. The content of residual f-CaO in SS is only 1.23%, which meets the specification of Chinese national standard GB/T20491-2006 "Steel slag powder used for cement and concrete" that requires f-CaO content of steel slag shall be no more than 3% when used in the preparation of cement and concrete [9]. The content of residual f-MgO in SS is only 0.81%. Also, it should be noted that SS contains relatively high content of Fe (Table 1), which is potentially desirable for artificial reefs, as it has been demonstrated that Fe element is benefit for the attachment growth of marine plants [10]. The major minerals in SS include C_3S (Ca_3SiO_5), β-C_2S (β-Ca_2SiO_5), C_2F ($Ca_2Fe_2O_5$) and RO phases [11].

GBFS powder, SS powder, FGD gypsum and cement clinker are used as cementitious materials. The Blaine finenesses of these materials are given in Table 1. GBFS powder from the same plant as SS is a commercial product that is finely ground. SS powder was obtained by grinding SS with particle size of 0–4.75 mm in a laboratory scale ball mill. FGD gypsum is the by-product from a power generation plant. The major composition of FGD gypsum is $CaSO_4{\cdot}2H_2O$. Cement clinker is typical Portland cement clinker.

Both fine and coarse aggregates are made of SS. SS was crushed and sieved before using as aggregate. SS with particle size of 0–4.75 mm are used as fine aggregates. SS with particle size of 4.75–19 mm are used as coarse aggregate whose particle size distribution was optimized according to Fuller's curve to obtain a dense packing. Particle size distributions of both fine and coarse aggregates are shown in Table 2, which were optimized in a previous research [12]. The fineness modulus of fine aggregate is 3.1 measured according to Chinese standard [13].

Table 1
Chemical and physical properties of SS, GBFS, Cement clinker and FGD gypsum.

Materials		GBFS	SS	Cement clinker	FGD gypsum
Chemical composition (%)	CaO	41.41	35.82	66.3	33.38
	SiO_2	36.97	12.22	22.5	3.16
	Al_2O_3	11.6	6.84	4.86	1.35
	Fe_2O_3	0.3	14.53	3.43	0.47
	FeO	0.33	11.83	–	0.09
	MgO	4.24	11	0.83	7.49
	SO_3	2.03	5.04	0.31	45.7
	Na_2O	0.34	0.23	–	0.13
	K_2O	0.53	0.08	1.47	0.18
	TiO_2	0.51	0.5	0.81	–
	P_2O_5	0.25	0.67	–	0.13
	MnO	0.39	1.54	–	–
	L.O.I	0.3	0.43	0.96	8.28
Blaine fineness (m^2/kg)		530	550	420	320
Specific gravity		2.89	3.39	3.19	1.87

2.2. Mixture proportion

Mix proportion is given in Table 3, which was optimized on the basis of strength performance in a previous study [12]. The addition of superplasticizer is 1.64 kg/m^3. As shown in Table 3, GARC mixture contains only 54.5 kg/m^3 of cement clinker that accounts for 2% of total solid raw materials. All the rest solid materials accounting for 98% by weight are industrial waste. The addition of SS and GBFS are 2170.7 kg/m^3 and 381.4 kg/m^3, respectively. Slump and spread of the fresh mixture are 22 cm and 370 mm, respectively, which were tested according to Chinese national standard GB/T50080-2002 "Standard for test method of performance on ordinary fresh concrete" [14].

2.3. Specimen preparation and testing

All the materials were thoroughly mixed according to the mixture proportion in Table 3. Slump and spread were measured afterwards. Then, the fresh mixture is cast. Cube specimens measuring 100 × 100 × 100 mm^3 were prepared for compressive test at various ages. All the specimens were demolded at 24 h.

Cube specimens were firstly cured in a standard curing chamber (at temperature of 20 ± 2 °C and humidity of 90 ± 2%) until 28 days after demolding. Parts of cube specimens were then cured in artificial sea water at 20 ± 2 °C until 240 days. The chemical composition of artificial sea water is given in Table 4 [15]. Three specimens were used for testing at each age. Density of GARC was measured at 28 days. Compressive strength tests were performed on a 2000 kN compression testing machine.

GARC paste without aggregates according to the mix proportion in Table 3 was prepared to investigate the hydration products through XRD, DSC and SEM analyses. For comparison, typical Portland cement paste was also prepared with identical dosage of water and superplasticizer as GARC paste contains. Both GARC paste and cement paste specimens are cured in a standard chamber as mentioned in the above paragraph. The hydration of GARC and cement paste at testing ages was stopped by ethyl alcohol.

XRD analyses were performed on a D/Max-RC diffractometer with copper Kα radiation at 30 mA and 50 kV. A step interval of 0.02° was selected in a 2θ range of 5–70°. DSC analyses were done with apparatus type STA 409C/CD by heating from room temperature to 1000 °C in nitrogen atmosphere with a step size of 20 °C/min. The microstructure of GARC paste and GARC was observed with a SUPRA™ 55 field emission scanning electron microscope. The fractured surfaces of the samples were coated with carbon prior to examination.

In order to preliminarily investigate the effectiveness of accumulation of marine lives organisms on the surface of the developed GARC, nine plate specimens measuring 300 × 300 × 50 mm^3 were prepared according to the mixture proportion in Table 3. Plate specimens were placed at an intertidal zone in Heishijiao costal area (Dalian, China) near natural reefs after curing for 28 days at room temperature in a plastic bag. The specimens were fixed by a steel frame to prevent washing away by wave action. After 8-month in the sea, the specimens were taken out, and the marine lives attached on the specimens were observed and recorded.

3. Results and discussion

3.1. Density

The average density of developed GARC measured at 28 days is 2765.5 kg/m^3, which is roughly 15% higher than that of normal concrete with a typical density of 2400 kg/m^3. The higher density of GARC is due to the incorporation of steel slag as aggregate that has higher specific gravity than sand and gravel used in normal concrete. The specific gravity of steel slag is 3.39 compared to 2.4–2.9 of sand and gravel. High density of GARC means that the

Table 2
Particle size distribution of fine and coarse aggregates.

Coarse aggregate		Fine aggregate	
Size (mm)	Mass percent (%)	Size (mm)	Mass percent (%)
16 ∼ 19	16.5	4.75–2.36	26
9.5 ∼ 16	42.1	2.36–1.18	18
4.75 ∼ 9.5	41.3	1.18–0.60	14
		0.60–0.30	24
		0.30–0.15	16
		−0.15	2