Construction and Building Materials 114 (2016) 162–171

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

ITZ properties of concrete with carbonated steel slag aggregate in salty freeze-thaw environment

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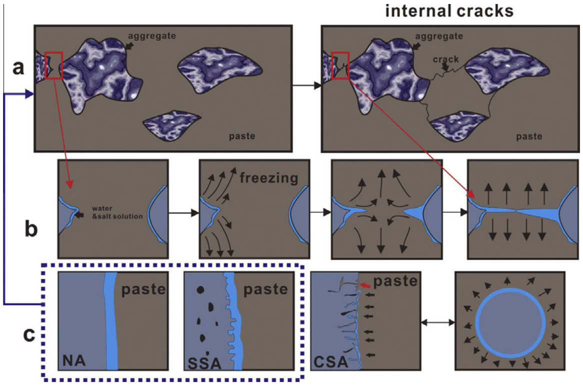
HIGHLIGHTS

- Carbonated steel slag aggregate (CSA) was used as fully replacement of normal aggregate (NA).
- Freeze-thaw resistance of concrete with NA, SSA and CSA were investigated.
- The ITZ was investigated and presented by Vickers hardness, Ca/Si ratios and microcosmic morphology.
- The effects of resistance on freezing and thawing of concrete were explained by ITZ properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 May 2015
Received in revised form 17 March 2016
Accepted 29 March 2016
Available online 1 April 2016

Keywords:
Carbonation
Steel slag
Freeze-thaw
Salt
ITZ

ABSTRACT

The concrete samples with carbonated steel slag aggregate (CSA), normal aggregate (NA) and crushed steel slag aggregate (SSA) with W/C of 0.42 were prepared. The properties of the resistance on freezing and thawing were investigated and compared by freeze-thaw test with the condition of fresh-water and salt-water. The rapid chloride migration test (RCM) and coulomb electric flux test (CEF) were made in order to test the resistance of the concrete to chloride ion penetration. The ITZ properties and freeze thaw resistance of concrete were investigated by micro hardness tests, SEM, Ca/Si ratios, weight loss and relative dynamic elastic modulus test. The results show that using CSA instead of NA increased the freeze-thaw cycles from about 30 cycles to 175 cycles in salt-water condition and from about 150 cycles to 300 cycles in fresh-water condition. The average value of the hardness of ITZ around CSA is more than 43, which may due to the low W/C ratio caused by high water absorption of the CSA. The range of interfacial transition zone (ITZ) of CSA from SEM and EDS is larger but denser than NA and SSA, and fewer cracks are observed. The resistance to freeze and thaw will be improved by the hydration of steel slag to bond cement matrix. The cambered surfaces of CSA are less likely to occur stress concentration.

1. Introduction

The annual production of steel slag in China is about 30 Mt, however, the utilization rate of steel slag is only about 22%. Deposition of steel slag leads to the occupation of farm lands and pollution to the environment [1].

Abbreviations: CSA, carbonated granulated steel slag aggregates; NA, natural aggregates; SSA, steel slag aggregate (crushed steel slag); CSC, carbonated granulated steel slag concrete, which is concrete made with CSA; NAC, natural aggregates concrete, which is concrete made with NA; SSC, steel slag concrete, which is concrete made with SSA.

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http://dx.doi.org/10.1016/j.conbuildmat.2016.03.168
0950-0618/

Steel slag contains about 50 wt.% of CaO (wherein more than 5 wt.% of free CaO) and about 10 wt.% of MgO. The formation of $Ca(OH)_2$ and $Mg(OH)_2$ will cause volume expansion of 98% and 148% respectively. Besides, the uneven distribution of the RO phase (the phase with the maximum density and hardness in steel slag which account for about 20–30%wt. of steel slag) introduces defects in concrete structure [1,2]. Thus, directly using crashed steel slag as aggregate can result in unstable service of hardened concrete.

Carbonation is an effective way to transform calcium and magnesium into carbonate minerals, therefore the strength and durability are further enhanced. Additionally, carbonate minerals like shell structure of shellfish maintain sufficient stability as well as biocompatibility [3]. The artificial reefs which are mainly consisted by $CaCO_3$, e.g. shells and corals show a high stability in seawater and act as great breeding habitats for seaweeds and corals [1].

Many cases have demonstrated the stability of marine construction with steel slag. In Germany, about 400,000 tons of steel slag has been used in reinforcement of bed and bank to resist the erosion of sea water at an annual rate [4]. JFE iron and steel enterprise has investigated the possibility of using the steel slag as an engineering material in harbor and coast from 1993, and the artificial fish reefs made from carbonated steel slag have exhibited an excellent durability to chloride environment and a good biocompatibility to other marine algae and coral [5]. In China, Xu et al. [6] has used steel slag partially replacing natural river sand to build coastal projects like coastal slope and retaining plate. Besides, similar construction has been used in the reclamation such as Luchao port project in the East Sea of China. Thus, accelerated carbonation may be an efficient way to make largely apply steel slag in concrete as aggregate possible.

Laboratory tests and observations show that internal cracking and surface scaling are treated as the classical damages of concrete in freeze-thaw condition which generate great damages on concrete pavement of highway, bridge etc. The internal cracking decreases the material dynamic modulus and increases the porosity [7] while the surface scaling leads to material surface removal (such as exfoliations) with a solute pessimum concentration around 3% [8,9]. The salt condition consisted of NaCl, CaCl and MgCl etc. can reduce the expansion rate of ice to about 9%, the saturation degree of concrete, however, will reach or exceed the critical degree of saturation of the concrete (the percentage of concrete pores filled with water in a certain condition) [10]. Therefore, the concrete in salt condition is subjected to tensile stress from freeze-thaw cycles and crack to damage and break eventually.

The interfacial transition zone (ITZ) is commonly identified as the weakness in strength of concrete because of the higher porosity and more defects, which further decrease the durability properties e.g. freeze–thaw resistance. Evdon Sicat et al. [11] have carried out an investigation, which showed that the ITZ exhibited higher deformation than the matrix and aggregate due to its higher porosity and weaker strength. The findings verify that aggregate is insignificantly affected by freeze-thaw cycles. Therefore, ITZ of concrete is vulnerable for the invasion of solution, which leads to performance degradation between the aggregate and the cement matrix. This situation is aggravated especially at the presence of salt solution.

The resistance to chloride ion penetration of the concrete and the stability of concrete on chloride will directly affect the damage of freeze-thaw cycles on concrete. The higher salt content in concrete, the higher degree of water retention value will get in pores and voids, and the freezing pressure in concrete can be increased to more than a few times or even dozens of times in winter [12,13].

In our previous study [14,15], the concrete with CSA has showed a stable durability in alkaline condition and relatively higher strength than that of concrete with NA and SSA. In this study, the durability properties of concrete with CSA, NA and SSA exposed to salt and freshwater freeze-thaw condition and the ability to resist the chloride ion penetration will be investigated and further discussed from ITZ aspect and the internal structure of aggregate.

2. Materials and test methods

2.1. Materials

Portland cement with the Chinese National Standard GB 175-1999 was used. The Blaine fineness was 311 m^2/kg.

The Basic Oxygen Furnace (BOF) slag provided by Jinan Iron and Steel Works Company (ground by a lab ball mill for 30 min and then sieved through a sieve of 600 μm) was used as raw materials for preparing CSA. The chemical composition of the cement and steel slag are listed in Table 1.

The normal aggregate (NA), which were a kind of coarse crushed limestone (4.2–18 mm size fraction) and natural river sands (0–4 mm size fraction, fineness of 2.95) were used in the normal aggregate concrete (NAC). The crushed steel slag aggregate (SSA) were sieved into different sizes to prepare steel slag concrete (SSC). Some physical properties of NA and SSA are shown in Table 2.

2.2. Preparation of CSA

2.2.1. Pelletization

The water was sprayed on the steel slag powder mixture by pelletizer. The formation of pellets occurred between 10 and 12 min in trial productions. The total pelletization time was determined as 20 min for the compaction of fresh pellets.

2.2.2. Carbonation

The untreated CSA was carbonated in a carbonation chamber. The chamber was heated up to 70 °C and vacuumed to −0.03 MPa before carbonation. Then CO_2 was introduced into the reactor until the pressure reached 0.3 MPa. The carbonation time was 4 h and the technological process is shown in Fig. 1.

The compacted density (dry-rodded unit weight) of the aggregates was determined by following ASTM C 29. The Specific gravity and water absorption of the aggregates were measured using ASTM C 127 and ASTM C 128, respectively. The properties of all the CSA were illustrated in Table 2, which shown that the coarse CSA has the higher water absorption than the other two. Thus, it was necessary to study the pore types inside. Conversely, the fine CSAs had the least absorption, and it was due to the less powder content which affected the water absorption of aggregates and, further, the workability of concrete. The ratio of specific gravity of coarse SSA and CSA was 1.2 while the one of the rodded bulk density was only about 1.12, and which was an effective illustration of the effect of closely packed spherical aggregates of CSA.

2.3. Mix proportion

In order to minimize the influence of water absorption of aggregate on fluidity and W/C ratio, cement and water were mixed uniformly for 3 min in advance before all the aggregate was added into the mixtures. The mixture proportions of concrete were illustrated in Table 3.

2.4. Test methods

The resistance grade to freezing-thawing of concrete and the chloride ion penetration (test method for rapid chloride ions migration coefficient (RCM) and test method for coulomb electric flux) were following GB/T 50082-2009 which was the standard for test methods of long-term performance and durability of ordinary concrete.

2.4.1. Resistance of freezing and thawing

2.4.1.1. Rapid freeze-thaw cycles. The resistance of freeze-thaw condition of the concrete was tested in salt and fresh-water condition respectively to evaluate the freezing damage on concrete structure, additionally, to investigate the extent of salt solution on aggravating the deterioration and cracking of concrete. For salty freeze-thaw destruction, the most typical one was the low salinity whose salt concentration was about 3 wt.% in previous papers [8,16,17]. Besides, whatever the components of the salts were, there was no significant difference in the extent of the damage on concrete. In order to simulated the environment of deicing salt and sea water, the distilled water and chloride solution with 3 wt.% (NaCl:MgCl:CaCl = 8:1:1) salt concentration were used. Concrete specimens with dimensions of ø100 mm × 50 mm were manufactured and cured at 21 °C with an RH of 90% for 24 days, and were taken into (20 ± 1) °C water for 4 days to saturate the specimens. Then, the specimens were cleaned, weighted, numbered and measured by the relative dynamic elastic modulus test (tested by acoustic resonance and specific method is shown in Fig. 2), and then put into rapid freezing and thawing test cham-