Construction and Building Materials 150 (2017) 66–76

Contents lists available at ScienceDirect

Construction and Building Materials

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

Use of grounded iron ore tailings (GIOTs) and $BaCO_3$ to improve sulfate resistance of pastes

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HIGHLIGHTS

- Novel methods are explored to improve sulfate resistance for cement pastes.
- Grounded iron ore tailings (GIOTs) are used to improve sulfate resistance for pastes.
- Influence of $BaCO_3$ on deterioration of pastes under sulfate attack was studied.
- Interaction of GIOTs and $BaCO_3$ in improving paste sulfate resistance was studied.
- Mechanisms of improvements in sulfate resistance for pastes were analyzed.

ARTICLE INFO

Article history:
Received 5 February 2017
Received in revised form 22 May 2017
Accepted 26 May 2017

Keywords:
Paste
Sulfate attack
Sulfate resistance
Grounded iron ore tailings
$BaCO_3$

ABSTRACT

Novel methods are explored to improve sulfate resistance for cement pastes by using grounded iron ore tailings (GIOTs), $BaCO_3$ and both of them. Experiments were conducted on a plain cement paste and six blended cement pastes with different contents of GIOTs and $BaCO_3$. All the pastes were exposed to two kinds of external sulfate attacks (a 5 wt.% Na_2SO_4 solution and a 5 wt.% $MgSO_4$ solution). The effect of additions on the sulfate resistance of pastes was assessed by compressive strength, expansion and Vickers hardness. Mercury Intrusion Porosimetry (MIP), X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) were performed to clarify mechanisms of $BaCO_3$ and GIOTs on sulfate resistance of pastes. As the results shown, both $BaCO_3$ and GOITs can improve the capacity of pastes against to external sulfate attack. Pastes with interaction of $BaCO_3$ and GIOTs present the highest sulfate resistance level under the both sulfate attacks.

1. Introduction

Iron ore tailing (IOT) is a kind of industrial waste generated during productive process of iron mine factories. With increase of construction industry demands and the rapid development of iron and steel industry, millions of tons of IOTs are being produced annually. IOTs are powder particles with quite small sizes that cause various environmental problems, such as the haze, dust storm, river pollution and so on, when discharged arbitrarily [1–3]. Therefore, the proper treatment of IOTs is very important to alleviate environmental pollutions and also to save landfill space [4]. One way of disposing of IOTs is to utilize them as the replacement of clinker or aggregates to produce high performance concrete in civil industries [5,6]. In previous studies, it has been noted that concrete containing IOTs consistently showed higher mechanical properties and lower drying shrinkage than the reference concretes [7–10]. This indicates that the comprehensive utilization of IOTs is scientific and feasible in concrete technology. Nevertheless, rare studies have been conducted on the capacity of resistance to aggressive conditions of IOTs-containing concrete.

Concrete is a kind of widely used building material that can be easily attacked owing to its porosity and alkaline component. Sulfate attack is one of the causes that reduce the durability of concrete when exposed to sulfate-containing environments. Extensive research has been done regarding this hot topic [11,12]. The well known damage mechanisms of concrete under sulfate attack primarily include ettringite, gypsum, mirabilite, thaumasite, etc [13–17].

Conventional methods to restrain sulfate attacks include the use of sulfate-resistant cement with a lower content of C_3A [18–20] and the reduction of penetrability in mortar or concrete. The other way is the reduction of $Ca(OH)_2$ in concrete by adding mineral admixtures with a lower CaO content [21] or adding materials

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http://dx.doi.org/10.1016/j.conbuildmat.2017.05.209
0950-0618/

that can consume $Ca(OH)_2$ in pozzolanic reactions [22]. IOTs are a kind of mineral materials containing a low content of CaO and a certain content of active substances [1,4]. Lower content of CaO means lower content of $Ca(OH)_2$ in hardened paste, which can reduce the formation of gypsum and further ettringite. The active substances react with $Ca(OH)_2$ in pastes, filling voids and retarding the ingress of sulfate [23,24]. Therefore, concrete with IOTs can theoretically get a higher level of sulfate resistance. Nevertheless, further experimental evidences are needed in order to confirm this hypothesis.

Another way to inhibit sulfate attacks is the use of limestone for their impact on paste porosity [25,26]. According to Schmidt et al. [27], the addition of 5 wt.% limestone in Portland cement systems led to a decrease in sulfate uptake due to its lower initial capillary porosity. However, under certain conditions, the presence of carbonate and sulfate can lead to the formation of thaumasite, prior the formation of ettringite, which is another kind of sulfate attack [28,29]. In consequence, $BaCO_3$ (witherite) has been used to improve sulfate resistance for concrete in view of the capacity of Ba to immobilise sulfates [30–32]. Some experimental conclusions, including the influences of $BaCO_3$ on cement hydration [33–35] and ettringite decomposition in the presence of $BaCO_3$ [36], have been obtained by researchers. However, few studies have been conducted on the influences of $BaCO_3$ on mechanical properties, pore structures and deterioration process of concrete under sulfate attack.

Actually, all the methods themselves have limitations on sulfate resistance for concrete owing to the variety of sulfate attack depending on sulfate salt types, exposure conditions and the features of concrete itself. For instance, ettringite attack can be prevented by using the cement with a low C_3A content. But this method cannot inhibit gypsum or thaumasite [37,38]. Therefore, combination of two or more methods usually behaves better in improving sulfate resistance for concrete or mortar [39]. In the present study, grounded iron ore tailings (GIOTs), $BaCO_3$ and both of them were used as replacement of cement to improve sulfate resistance for pastes. The improvement mechanisms were assessed and analyzed by experimental procedures.

2. Materials and methods

2.1. Raw materials

The materials used in this study were Portland cement P.II 42.5, $BaCO_3$, and GIOTs. The chemical composition of the cement and GIOTs was determined by X-ray fluorescence (XRF), respectively shown in Table 1 and Table 2. The mineralogical composition of the cement was calculated using the Bogue method. The GIOTs has a density of 2950 kg/m^3. The fineness (particle size) of GIOTs is 8.5 wt.% residues after pass 45 μm square hole sieve. The loss on ignition of the GIOTs is 7.34 wt.%. The content of SiO_2 in GIOTs is 51.89 wt.%. The purity of $BaCO_3$ is AR 99% with a particle size of D50 0.5–1.5 μm.

2.2. Mixtures

To investigate the sulfate resistance of pastes with different concentrations of $BaCO_3$ and GIOTs, seven mixtures labeled PC, PB5, PB10, PG15, PG30, PB5G15 and PB10G30 with different proportions of cement, $BaCO_3$ and GIOTs were prepared, as detailed in Table 3. The PC mixture was considered as a reference sample. The other mixtures were designed to study the inhibiting effects of adding compounds in degradation of paste due to sulfate attack. It should be stated that the Table 3 was designed keeping the binder (PC + $BaCO_3$ + GIOTs) weight constant. For all the mixtures, the water to binder ratio (w/b) was 0.45. The addition of $BaCO_3$ has little impact on the workability of fresh pastes with the same w/b, while the addition of GIOTs leads to a lower mobility for the pastes. This is mainly due to the water absorption of some porous minerals consisting in GIOTs during the preparation of pastes.

Table 2
Chemical and physical analysis of GIOTs.

Chemical composition	(%)	Physical properties	(%)
SiO_2	51.89	Fineness (Residue 45 μm square hole sieve, %)	8.5
Al_2O_3	5.39	Density (kg/m^3)	2950
Fe_2O_3	13.45	Loss on ignition (%)	7.34
CaO	23.31		
MgO	1.93		
SO_3	0.56		
Na_2O	0.57		
K_2O	0.41		

2.3. Specimens preparation and exposure conditions

For all the mixtures, $\phi 50 \times 100$ mm^3 circular cylinder specimens and $20 \times 20 \times 280$ mm^3 prismatic specimens were cast. Then all the specimens were cured for 28, 60 and 91 days in saturated limewater. To ensure that there was only one direction for sulfate migration when the samples were immersed in the solutions, the two end surfaces of the cylinder specimens were coated with epoxy resin before exposure. To accelerate test procedures, all the specimens were cyclically immersed in both a 5 wt.% Na_2SO_4 solution and a 5 wt.% $MgSO_4$ solution: exposure in the solution for two days and in air for three days. The cyclic exposure durations are 30, 90, 180, 270 and 360 days. The sulfate solutions were refreshed once a month. The air condition in the lab was kept with T = 20 °C and RH = 60%.

2.4. Compressive strength

Compressive strength of specimens was determined on subsamples with a size of $\phi 50 \times 50$ mm^3 cut from the $\phi 50 \times 100$ mm^3 specimens in limewater for 28, 60 and 91 days and after cyclic sulfate exposure for 30, 90, 180, 270 and 360 days. The compressive tests were carried out on an Electric Universal Testing Machine with a maximum capacity of 100 kN. The loading force was perpendicular to the sulfate migration direction. The final compressive strength data was the average of three parallel subsamples.

2.5. Expansion

After curing in limewater for 91 days, the initial length of the $20 \times 20 \times 280$ mm^3 prismatic specimens were measured and denoted by l_0. Then, after cyclic exposure in sulfate solutions for 30, 90, 180, 270 and 360 days, the length of the specimens was monitored by a length comparator with a dial indicator, denoted by l_t. The linear expansion was calculated by the following equation.

$$\varepsilon_l(t) = \frac{l_t - l_0}{l_0} \times 100\% \quad (1)$$

where $\varepsilon_l(t)$ was the linear expansion of t day. The final expansion data was the average of three parallel specimens.

Table 1
Chemical and physical analysis of the P.II 42.5 cement.

Chemical composition	(%)	Mineralogical composition	(%)	Physical properties	
SiO_2	20.74	C_3S	67.94	Specific surface (m^2/kg)	320
Al_2O_3	4.92	C_2S	11.65	Density (kg/m^3)	3100
Fe_2O_3	3.21	C_3A	7.61	3 day strength (MPa)	27.5
CaO	64.62	C_4AF	9.76	28 day strength (MPa)	52.3
MgO	1.64			Loss on ignition (%)	1.63
SO_3	1.53				
Na_2O	0.51				
K_2O	0.67				