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Study on the treatment of BOF slag to replace fine aggregate in concrete

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HIGHLIGHTS

- Scrubbing attrition and chelating reagent treatment were used to remove free lime from BOF slag.
- By reducing *f*-CaO through pretreated processes, BOF slag expansion rate can be reduced to 0.16%.
- The compressive strength of cement mortars using treated BOF slag can be reached 45.4 MPa.

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ABSTRACT

Excessive free lime in the BOF slag will react with water and causes serious expansion, and thus, results in its reutilization difficulty. In this study, scrubbing attrition and chelating reagent treatment were used to remove free lime from BOF slag. After removing free lime, the BOF slag was used as fine aggregate for making cement mortar. Under different curing periods, the specimens were characterized for their physical and mechanical properties, ultrasound conduction velocity, and volume expansion. By reducing free-calcium oxide through attrition and chelating processes, the expansion rate of specimen can be reduced to 0.16%. The compressive strength and flexural strength of cement mortars prepared with BOF slag can reach 45.4 MPa and 7.1 MPa, respectively. The test results suggested that the scrubbing and chelating treatments can effectively remove free-calcium oxide and improve expansion and strength development of concrete mortar.

1. Introduction

Due to the environmental concern and more restrict regulations, sand and gravel extraction are no long allowed in most rivers in Taiwan. However, >15 million tons natural aggregate resources such as gravel, limestone and other processed rocks are requested annually by civil construction industry. Therefore, the search for natural aggregate replacement has become an important and urgent issue.

BOF slag is a final waste material in the basic oxygen furnace steel making process. In basic furnace iron making, limestone (as fluxes) is added to react with the gangue minerals (iron ore and coke) to form iron slag [1]. 1.5 million tons of BOF slag was produced annually in Taiwan [2]. This larger quantity of waste may cause serious environmental problem if no feasible recycling and utilization methods are found. The engineering characteristics of BOF slag, such as Los Angeles abrasion, California bearing ratio, compressive strength, and Mohs' scale of hardness are better than natural aggregate. Because of its good mechanical properties, BOF slag can be a great source to replace natural aggregate. Toxicity Characteristic Leaching Procedure (TCLP) test show no toxic materials exist in BOF slag which can be classified as general industrial waste [3]. Many studies on steel slag use as aggregates in concrete and its advantageous properties have been widely reported [4–8]. However, the BOF slag contains hydratable oxides (CaO and/or MgO) that can result in volumetric instability (expansion) that must be dealt with through appropriate treatment [9,10]. The volume expansion can be attributed to the chemical composition of the BOF slag used. It was found that 5–15% of the CaO in the slag is free lime (*f*-CaO). This *f*-CaO can easily react with water and CO_2 to form calcium hydroxide and calcium carbonate, and result in volume expansion [11,12]. Reddy et al. (2006) and Mahieux et al. (2009) reported that 5 to 10% of volume expansion may occur and cause a mechanical strength reduction and even disintegration of concrete if it is used as a construction aggregate [13]. Singh et al. (2003) added 1–3% oxalic acid into cement mortar to improve the

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densification and mechanical properties of concrete [14]. In the case here, when chelating reagent of oxalic acid is added into BOF slag, the *f*-CaO in the solution will convert to $Ca(OH)_2$, which is basic enough to react with oxalic acid to form calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$) [15]. The solubility of calcium oxalate monohydrate is very low and insoluble at high pH and high calcium concentration condition [16]. The calcium oxalate produced is identical with the naturally occurring mineral whewellite, which is relatively insoluble and stable over a wide range of conditions [17].

In this study, chelating reagent and scrubbing attrition process was used as a pre-treatment to remove free lime attached on the surface of slag. After scrubbing attrition, chelating process were used to remove remaining free lime (hydratable CaO) from BOF slag. The treated slag was then used to prepare cement mortar followed by a series of chemical and mechanical tests to evaluate its potential of replacing natural aggregate.

2. Experimental

2.1. Raw material characterization

Two BOF slags with different free lime contents (SA: 8.7%, SB: 12.2%) were obtained from CHC Resources Corporation. ASTM C114, Standard Test Methods for Chemical Analysis of Hydraulic Cement, was used to analyze the free lime in the BOF slag. Table 1 shows the chemical compositions of the SA and SB slags used in this study. It is mainly composed of CaO, Fe_2O_3, SiO_2, Al_2O_3, MnO and MgO. It can be seen that except free lime, both slags have a very high MgO content. This can be a risk for long term (>1 year) expansion due to free-MgO may exist. The particle size distribution (as received) is between 0.15 mm and 9.5 mm with D_{50} at 0.76 mm. The BOF was sieved and the +100 mesh particles were collected and used for concrete mortar preparation according to CNS486.

2.2. Scrubbing attrition process

In order to remove the free lime from the BOF slag surface, a high-speed stirrer can be used as an attrition machine for particle surface attrition. Under high speed stirring and having a certain solid-liquid ratio, the particles may collide with each other and the container wall, and thus, remove the impurities exist on the surface [18,19]. The attrition process has been successfully used in the decontamination of storm water sediments [20]. Other studies also employed attrition as a process to remove contaminants from soil and sand surfaces [21–23].

A laboratory-type stirrer with a single axis and six pairs of arms was used in this study. The slag slurry with 50% pulp density was prepared and stirred at a rotation speed of 1200 rpm for one minute to remove the free calcium oxide off the surface of the slag.

2.3. Chelating process

After BOF slag treated by chelating process. The chelating reagent will remain on the slag surface. If water penetrating from slag crack, it will cause chelating reagent react with inside free lime, and thus prevent expansion occurs. The chelating reaction of oxalic acid and *f*-CaO can be written as follows

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2 + H_2C_2O_4 \rightarrow CaC_2O_4 + 2H_2O \quad (2)$$

2.4. Experimental procedures

The experimental flow charts are shown in Fig. 1. Because of its high *f*-CaO content, SB slag was first subjected to attrition treatment (1200 rpm for 1 min.) followed by chelating process. To evaluate the potential of using slag as construction aggregate, the treated +100 mesh slag was mixed with Portland cement at 3:1 ratio to prepare cement mortar with a 0.75 water/cement ratio. Because the grading of as received BOF was poor, in order to increased workability, a higher w/c ratio was chosen. After 24 h of setting, concrete specimens were removed from the molds and cured in water followed by a series of chemical and mechanical tests to evaluate its potential of replacing natural aggregate. Physical and Mechanical Properties test methods for slag cement mortar are shown in Table 2, including slag expansion and autoclave expansion tests, setting time of slag cement mortar and compressive/flexural strength tests. The expansion test is to determine the potential volume expansion of slag that contains components susceptible to hydration and consequent volume increase. Autoclave expansion test method is to evaluate the influence of slag on the expansion of slag cement mortar.

3. Results and discussions

The effects of the attrition and oxalic acid treatments on the stability of BOF slag are discussed through various analysis and test results. The stabilized BOF slag was used as fine aggregate to prepare cement mortar. Volume expansion, XRD analysis, morphology, setting time, and compressive and flexural strengths were analyzed and measured to evaluate the possibility of using slag to replace natural aggregate for construction applications. Table 3 lists the BOF slags that were treated with different processes. BOF-A slag only subjected to chelation treatment with oxalic acid. BOF-B slag subjected to attrition first followed by chelation treatment.

3.1. Expansion test of BOF slag

Original SA and SB slags with free lime contents of 8.7% and 12.2% were tested for their volume expansion. The volume expansion of SA and SB were measured as 4.7% and 5.4%, respectively. It is obvious that the higher the free lime content, the higher the expansion rate of the slag. This is because free lime has a specific gravity of 3.34 which can react with water to produce $Ca(OH)_2$, with a specific gravity of 2.23, and thus, results in volume increase [24,25] .

For stabilizing free lime in SA slag, 3.0 N oxalic acid as chelating agent was added into the SA slag slurry prepared at 1.0, 2.0, and 4.0 solid/liquid weight ratios. As shown in Fig. 2, the volume expansion of the slag reduced from 4.7% (original slag) to 2.8% and 1.7% for slags prepared with 2.0 and 1.0 solid/liquid ratios, respectively, which is about 40% and 66% reductions in volume expansion respectively. The influence of oxalic acid concentration on the chelation treatment of SA slag is shown in Fig. 3. According to JIS

Table 1
Chemical composition of BOF slag.

wt%	CaO	*f*-CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	MnO	Na_2O
SA	40.1	8.7	12.9	1.8	8.7	26.2	3.2	2.1
SB	36.9	12.2	9.6	2.3	11.2	29.1	2.7	1.7