



Accelerated carbonation of basic oxygen furnace slag and the effects on its mechanical properties



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HIGHLIGHTS

- Temperature, CO₂ content, and relative humidity all affect carbonation reactions.
- The appropriate carbonation conditions for BOF slag were found out in this study.
- Consumption of free CaO is highly related to decreases in pH value of BOF slag.
- The carbonated shell on BOF slag can be up to about 200 μm in thickness.
- Carbonation is beneficial to the mechanical performance of BOF slag.

ARTICLE INFO

Article history:

Received 29 August 2014

Received in revised form 28 July 2015

Accepted 9 August 2015

Available online 24 August 2015

Keywords:

Steel slags

Accelerated carbonation

Mechanical properties

Free CaO

Particle size

ABSTRACT

Basic oxygen furnace (BOF) slag, a byproduct of steel-making processes, is mainly composed of calcium compounds and thus has high potential for carbonation. The purpose of this study was to use an accelerated carbonation process to treat BOF slag and to examine the effects on the slag properties. Three BOF slags with different particle sizes (3.5–7 mm, 7–15 mm, and 15–25 mm) were tested, and the effects of carbonation temperature, CO₂ content, and relative humidity (RH) were investigated. It was found that the pH value of the BOF slag samples decreased after carbonation, a result which was mainly attributed to the transformation from CaO to CaCO₃. The appropriate carbonation conditions selected from this study were 200 °C of temperature, 40% of CO₂ content, and 60% of RH. The X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy analyses both demonstrated the formation of carbonates in the treated slag. By observing cross-sections of the carbonated slags with an optical microscope, it was revealed that the thickness of a carbonated shell on the BOF slags can achieve about 200 μm. The mechanical properties of BOF slag, including bearing strength and particle cylindrical crushing strength, were improved after carbonation, and this shows that the carbonation of BOF slag can not only capture CO₂ but also have benefits to its mechanical performance.

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1. Introduction

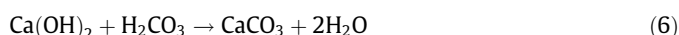
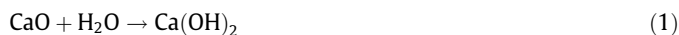
The manufacture of iron and steel is generally a fundamental industry for any country since it provides basic materials for infrastructures, vehicles, buildings, industrial facilities, and daily necessities. In addition to iron and steel products, the manufacturing processes generate many kinds of solid byproducts, which are discharged in the form of dust, sludge, ash, and slag. Basic oxygen furnace (BOF) slag is one of the byproducts from steel-making processes, and producing one ton of steel normally generates about 0.1–0.15 tons of BOF slag. In 2013, the annual output of BOF slag in

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Taiwan was about 1.5 million tons. BOF slag is mainly composed of calcium, silicon, and iron compounds, and it has high specific gravity, mechanical strength, and abrasion resistance [1–3]. Many studies have reported that BOF slag has potential for uses in cement production, road construction, asphalt concrete, and land reclamation in marine areas [4–6]. However, some research has indicated that the high free CaO content in BOF slag can cause volume expansion problems, thus reducing its applicability for construction materials [2,7].

Eqs. (1)–(6) present the chemical reactions in a CaO–H₂O–CO₂ system. When CaO reacts with H₂O to form Ca(OH)₂, the density decreases from 3.35 g/cm³ to 2.21 g/cm³, and the volume thus increases by about 100%. As Ca(OH)₂ converts to CaCO₃, the volume will further increase by 46%. Altun and Yilmaz [8] reported that the

free CaO in BOF slag can react with H₂O or CO₂ for up to several months under normal atmospheric conditions, so weathering the slag outdoors is a feasible method for improving its volume stability.



Although the outdoor weathering process is feasible, it normally takes a long time and requires a large amount of land space for slag piles, and these both increase the treatment costs of BOF slag. Many studies have shown that some artificial methods, such as steam aging, autoclaving, and carbonation technologies, are capable of accelerating the chemical reactions related to free CaO, and therefore improve the volume stability of steel slags and expand the possible applications [9–13]. In comparison to hydroxides, carbonates are more stable products of the conversion of free CaO, and accordingly carbonation methods should be better than steam aging or autoclaving. Santos et al. [13] used a hot-stage carbonation approach to treat BOF slag, and the results showed that this method can reduce the free CaO content and thus stabilize the slag volume. Bertos et al. [10] reported that steel slag can be reused as aggregates or armor stones after treatment with an accelerated carbonation technology.

Moreover, the CO₂ capture by calcium-based materials, such as steel slags, has been followed with interest in recent years because of their high CO₂ reactivity, high capacity, and low material cost [14]. Several researchers have studied the CO₂ capture of steel slags by using high-temperature sorption [13,15] or aqueous carbonation processes [16]. However, there is little information available on the changes in mechanical properties of the carbonated slag [17] and the influence on the subsequent slag utilization. Accordingly, the purpose of this study was to use an accelerated carbonation process to treat BOF slag and to investigate the effects of carbonation conditions, including temperature, CO₂ content, and relative humidity (RH), and the changes in the characteristics of the slags.

2. Materials and methods

2.1. Materials

The BOF slag used in this study was generated from a steel mill in southern Taiwan, and the slags was crushed and sieved to four particle sizes, i.e. <3.5 mm, 3.5–7 mm, 7–15 mm, and 15–25 mm, which approximately accounted for 51.3 wt.%, 6.4 wt.%, 24.3 wt.%, and 18.0 wt.%, respectively. The <3.5 mm BOF slag normally is recycled as a raw material for iron-making, and therefore the other three particle sizes of slags were used as research subjects in this study. The specific gravity, pH value, moisture, and free CaO content of the BOF slags with different particle sizes were analyzed immediately. After drying to constant weight in an 105 °C oven, the chemical compositions of the BOF slags were determined by using an alkaline digestion process with lithium tetraborate (Li₂B₄O₇) in platinum melting pots at 1100 °C, followed by dissolving the molten material in hydrochloric acid (HCl) solution and measuring the element concentrations with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Seiko Instruments Inc., SPS 7800).

2.2. Accelerated carbonation process

Fig. 1 shows the schematic diagram of the accelerated carbonation devices used in this study. A rotary kiln made of stainless steel was employed as a carbonation reactor, whose operating temperature range is from ambient temperature to ~450 °C. Compared to static reactors, it was posited that using this rotary kiln should improve the level of contact between the gas and solid phases. In order to control the gas composition, a gas mixing chamber was installed in front of the rotary kiln, and three kinds of gases, namely air, CO_{2(g)}, and H₂O_(g), were mixed together in specific proportions and subsequently introduced into the kiln. To prevent H₂O_(g) from condensing into droplets, the gas mixing chamber was heated as hot as the rotary kiln. During the carbonation process, the weighed BOF slag samples were put into the rotary kiln, and the retention time was set at 24 h to provide sufficient reaction time. In this study, three carbonation conditions, i.e. kiln temperature (25–250 °C), CO₂ content (0–40%), and RH (0–80%), were controlled to examine their effects on the characteristics of the BOF slags with different particle sizes.

2.3. Material testing and analyses

To determine the pH value of the BOF slags, deionized water was mixed with a slag sample at a liquid-to-solid ratio of 1.0 L/kg, and after stirring for 20 min, the mixture was tested with a pH electrode. The free CaO content of the BOF slags was determined by the chemical extraction method described in ASTM C 114 [18]. A slag sample was extracted with a boiled glycerin-ethanol solvent first, and the extract was titrated with a standard ammonium acetate (CH₃COONH₄) solution equivalent to 0.005 g CaO/mL. To analyze the mineralogical compositions of the original and carbonated BOF slags, the X-ray diffraction (XRD) method was conducted by using an X-ray diffractometer (Rigaku, D-MAX 2000) with Cu K α radiation. The XRD patterns were recorded and compared with the standard diffraction cards from the International Centre for Diffraction Data-Powder Diffraction File (ICDD-PDF) to identify which compounds were present in the slags. A Fourier transform infrared spectroscope (FT-IR, Bruker, Vector 22) was used to examine the mineral structures of the carbonated BOF slags. The FT-IR analysis was performed in a wavenumber range of 4000–400 cm⁻¹ with a spectral resolution of 1 cm⁻¹. The slag samples were further immersed in epoxy resin to prepare the specimens for microstructure observation. After the epoxy resin solidified, the specimens containing slags were cut open, and the cross-sections were polished and then investigated with an optical microscope. To test the mechanical properties

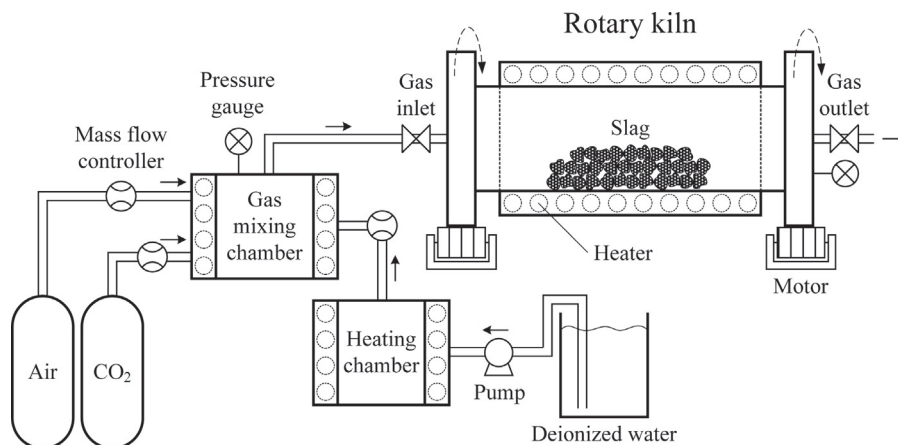


Fig. 1. Schematic diagram of the accelerated carbonation devices.

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