Carbonation of basic oxygen furnace slag with metalworking wastewater in a slurry reactor

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ABSTRACT

CO_2 capture by accelerated carbonation of basic oxygen furnace (BOF) slag in a slurry reactor containing metalworking wastewater was investigated in this study. Two types of metalworking wastewater provided by China Steel Corp. (Kaohsiung, Taiwan) were used: cold-rolling wastewater (CRW) and effluent from a metalworking wastewater treatment plant (EW). The effect of operational conditions including the type of metalworking wastewater, reaction time, liquid-to-solid (L/S) ratio, CO_2 flow rate, and slurry volume on the CO_2 fixation process was evaluated. The results indicated that BOF slag in CRW provided the highest degree of carbonation, 89.4%, with a reaction time of 120 min, an L/S ratio of 20:1, and a CO_2 flow rate of 1 L min^{-1} at ambient temperature and pressure. In addition, the kinetics of the aqueous carbonation was evaluated using the surface coverage model. This study provided a promising alternative for CO_2 capture from the flue gas in steelmaking process by reusing the metalworking wastewater and steelmaking slag as feedstock, which could reduce the use of water resources as well as the total cost. Compared with other studies in the literature, this study showed a higher carbonation conversion with less consumption of energy and resources.

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1. Introduction

The global average CO_2 concentration in the atmosphere has steadily increased in the past thirty years, and the global greenhouse gas (GHG) emissions due to human activities increased 70% between 1970 and 2004, which is likely to cause further warming and induce many changes in the global climate system (IPCC, 2007). Options for mitigating climate change include the adoption of higher energy-efficiency standards, the use of renewable energy, the substitution of natural gas for coal, and the carbon capture and storage (CCS) technologies (IPCC, 2005). CCS are a group of technologies for effectively capturing CO_2 from emission sources, transporting it, and then storing it into a suitable and permanent geological sites. CO_2 capture processes include physical and chemical absorption, industrial solid wastes adsorption, low-temperature distillation, and membrane separation (Tan and Chen, 2006; Chang et al., 2011a).

However, recent year, extending CCS technology to incorporate "utilization" has received dramatically global attention, which has been considered as one of a portfolio of options for reducing CO_2 emissions (CSLF, 2011; Styring et al., 2011). The utilization routes of the captured CO_2 include enhanced fuel recovery (i.e., EOR and EGR), biological conversion (i.e., algae), food industry, chemicals (i.e., fertilizer and liquid fuel), refrigerant, inerting agents, fire suppression, plastics, and mineralization as carbonates (i.e., precipitation calcium carbonates (PCC) and construction materials). Since the concentration of CO_2 obtained from capture processes would reach more than 90%, it is suitable for the utilization in mineralization (aqueous carbonation) of alkaline solids to accelerate the reaction down to a time scale of a minute. As a result, the gaseous CO_2 would be captured and stored permanently in the alkaline solid as carbonate precipitation, which could be considered as construction material for further utilization. The challenges encountered are to increase the reaction efficiency, decrease the energy consumption, and improve the material properties for utilization due to the tendency of fresh slag to have high water absorption and expansion properties (the presence of CaO_f and $Ca(OH)_2$ in solid wastes). It is thus concluded that carbon capture, utilization and storage (CCUS) cannot only permanently store CO_2 but also provide environmental and economic benefits for further use of CO_2. It also suggests that CCUS technology by the accelerated carbonation of alkaline

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solids such as natural ores and industrial solid wastes should be a promising option in the future.

The concept of mineral carbonation was first introduced by Seifritz (1990) and then developed by Lackner et al. (1995). CO_2 is rarely released from carbonation products after mineralization because they are thermodynamically stable and require significant amounts of energy to cause the release of CO_2 from the carbonate minerals (Lackner et al., 1995; Huijgen and Comans, 2003). Industrial solid wastes such as steelmaking slag which are typically inorganic and rich in calcium and magnesium may be an alternative feedstock for CO_2 capture. The utilization of alkaline solid wastes has several advantages including a low cost of sequestration, close proximity to energy and industrial sites where CO_2 is emitted, ready access in a fine particle size (Fauth et al., 2002), and minimal environmental impacts through the resulting pH-neutralization (Huijgen and Comans, 2003). Moreover, alkaline solid wastes tend to be more reactive with CO_2 than natural minerals due to their chemical instability.

Basically, the carbonation reaction included the following three steps: calcium leaching from alkaline solid matrix into solution, CO_2 dissolution, and calcium carbonate precipitation. The mass transfer steps, i.e., CO_2 dissolution into solution and the diffusion of reactants in solid matrix, are considered to be the rate-limiting step (Chang et al., 2011a). Therefore, it is essential to improve the mass transfer phenomena in order to achieve a rapid carbonation reaction. A slurry reactor, which contains fine solid particles suspended in a liquid, is frequently used in the chemical and biochemical industry due to its ability to enhance mass transfer (Alper et al., 1980). The first application of the two-phase fluidization system was made by Winkler in 1922, and then the gas–liquid–particle three-phase system was developed, which seems to be a more efficient tool for chemical reactor (Ostergaard, 1968).

Accelerated carbonation of basic oxygen furnace (BOF) slag in a slurry reactor containing metalworking wastewater was investigated in this study. Various operational parameters including the type of metalworking wastewater, reaction time (t), liquid-to-solid (L/S) ratio, gas flow rate (Q), and slurry volume (V) on performance of CO_2 capture were evaluated. In addition, experimental data was used to evaluate the kinetics of the carbonation reaction by a surface coverage model.

2. Materials and methods

2.1. Materials

The BOF slag was ground and provided by CHC Resources Corporation (Kaohsiung, Taiwan). The ground BOF slag was sieved to yield powders with a size of less than 44 μm and then preheated to 850 °C in an oven to decompose calcium carbonate into pure calcium oxide. De-ionized water (DW), cold-rolling wastewater (CRW), and effluents from a wastewater treatment plant (EW) were used as liquid agents. The metalworking wastewater including CRW and EW was provided by China Steel Corp. (Kaohsiung, Taiwan).

The chemical compositions of the fresh BOF slag were measured in accordance with ASTM method C114 for concrete using XRF (PW2430, Phillips). The physical properties of BOF slag including particle size distribution, density, and BET surface area also were analyzed. The density of the samples was analyzed with a Micrometrics Accupyc1340 pycnometer. The BET surface area of BOF slag was determined using a low-temperature N_2 adsorption BET apparatus (Micrometrics ASAP2010). The particle size distribution (PSD) of the slag in tap water was obtained by laser diffraction (Malvern, Hydro 2000MU), adapted from the ISO 13320-1 method with a range of 0.02–2000 μm. The carbonated samples were determined quantitatively by thermogravimetric analyzer (TGA) and

qualitatively by an X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2.2. Aqueous carbonation experiments

Fig. 1 shows a schematic of the experimental apparatus. The slurry reactor was a glass column 0.5 m in height and 0.08 m in diameter, and the sampling port was located 0.04 m above the bottom of the reactor. A gas distributor made of 0.3 cm-thick Perspex plate was placed at the bottom of the glass column. All experiments were conducted with a batch of slurry containing wastewater and a fixed amount of BOF slag at a given L/S ratio. CO_2 was injected from the bottom of the reactor continuously at 101.3 kPa and a specific constant flow rate. All experiments were conducted with a reaction time of 120 min. The effects of the operational factors including the different types of wastewater, reaction time (t), L/S ratio, slurry volume (V), and gas flow rate (Q) on the carbonation conversion were evaluated.

2.3. TGA, XRD, and SEM

The thermal characteristics of the BOF slag before and after carbonation were examined with a thermogravimetric analyzer (TGA-51, Shimadzu), which determines the sample weight loss at different temperatures. Approximately 15–20 mg aliquots of the BOF samples were placed inside a platinum crucible, and then the samples were heated linearly in the temperature range 25–850 °C at a heating rate of 10 °C/min in an inert atmosphere with a nitrogen flow rate of 50 mL/min. In general, calcium carbonate will typically decompose into calcium oxide and CO_2 in the 500–850 °C temperature range based on Eq. (1) (Huijgen and Comans, 2003; Chang et al., 2011a). Other weight-loss fractions are related to the loss of moisture (<105 °C) and the decomposition of gypsum (110–180 °C) and portlandite (300–500 °C), respectively.

$$CaCO_{3(s)} \xrightarrow{heat} CaO_{(s)} + CO_{2(g)} \uparrow \tag{1}$$

The weight loss (Δm_{CO_2}) that occurred in the 500–850 °C temperatures range is mainly caused by the release of CO_2. Thus, the fraction of actual CO_2-captured weight in the dry mass of BOF slag by the carbonation was expressed as shown in Eq. (2):

$$CO_2(-) = \frac{\Delta m_{CO_2}}{m_{105\,°C} - \Delta m_{CO_2}} \tag{2}$$

The carbonation conversion of BOF slags (δ_{CaO}, dimensionless) was defined as the amount of CO_2 actually captured in the dry mass of each sample compared with the calculated theoretical extent of carbonation based on the reactive-oxide content of the BOF slag. It was suggested that calcium-bearing compound should be the major chemical components in the accelerated carbonation reaction (Chang et al., 2011b). In other words, the carbonation conversion is defined to be the CaO conversion of the BOF slag due to carbonation reaction. Therefore, the carbonation conversion was estimated by using Eq. (3):

$$\delta_{CaO}(-) = \frac{CO_2(-)}{CaO_{total}(g/g) \times (MW_{CO_2}(g/mol)/MW_{CaO}(g/mol))} \tag{3}$$

where MW_{CO_2} (g/mol) is the molecular weight of CO_2; MW_{CaO} (g/mol) is the molecular weights of CaO; and CaO_{total} (g/g) is the weight fraction of CaO in the fresh sample (i.e., 0.4115), represented in percent dry mass.

X-ray powder diffraction (XPRD) (X' Pert Pro, PANalytical) is the analytical technique used herein to identify and characterize $CaCO_3$ crystals in the carbonation products. Monochromatic X-rays are used to determine the interplanar spacing of the sample atoms with Cu Kα radiation and 2θ scanning, ranging between 20° and