



CO₂ sequestration by carbonation of steelmaking slags in an autoclave reactor

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ABSTRACT

Carbon dioxide (CO₂) sequestration experiments using the accelerated carbonation of three types of steelmaking slags, i.e., ultra-fine (UF) slag, fly-ash (FA) slag, and blended hydraulic slag cement (BHC), were performed in an autoclave reactor. The effects of reaction time, liquid-to-solid ratio (L/S), temperature, CO₂ pressure, and initial pH on CO₂ sequestration were evaluated. Two different CO₂ pressures were chosen: the normal condition (700 psig) and the supercritical condition (1300 psig). The carbonation conversion was determined quantitatively by using thermo-gravimetric analysis (TGA). The major factors that affected the conversion were reaction time (5 min to 12 h) and temperature (40–160 °C). The BHC was found to have the highest carbonation conversion of approximately 68%, corresponding to a capacity of 0.283 kg CO₂/kg BHC, in 12 h at 700 psig and 160 °C. In addition, the carbonation products were confirmed to be mainly in CaCO₃, which was determined by using scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) to analyze samples before and after carbonation. Furthermore, reaction kinetics were expressed with a surface coverage model, and the carbon footprint of the developed technology in this investigation was calculated by a life cycle assessment (LCA).

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1. Introduction

Carbon sequestration is a promising option for reducing carbon dioxide (CO₂) emissions and alleviating global warming. Both CO₂ captured from emission sources and subsequent transport of the captured CO₂ to isolated reservoirs are essential for carbon sequestration. Carbon capture is affected by environmental factors, capacity, and cost. Mineral sequestration is a method of carbon capture that accelerates the natural weathering of silicate minerals, allowing them to react with CO₂ to form stable products, carbonate minerals, and silica for further usage or disposal [1]. In addition, carbonation is an exothermic reaction; thus, energy consumption and costs may be limited by its inherent properties [1,2]. In all cases, the sequestration chemicals must provide base ions such as monovalent sodium and potassium, or divalent calcium and magnesium ions to neutralize the carbonic acid. Other carbonate-forming elements such as iron carbonates are not practical due to their unique and precious features [3].

In addition to controlling the reaction conditions, choosing suitable mineral feedstocks and properly designing the reactor are crucial to achieving high CO₂ sequestration efficiencies.

One possible feedstock for CO₂ sequestration by accelerated carbonation is industrial solid waste, including steelmaking slags, combustion residues, and fly ash, which generally are alkaline and rich in calcium. The use of industrial waste is advantageous because of its low cost and widespread availability in industrial areas [4]. Interest in using industrial alkaline solid wastes as sources of calcium or magnesium oxide for CO₂ sequestration has arisen because these materials are readily available, cheap, and usually produced near large-emission sources of CO₂ [5]. In this study, carbonation reactions were performed primarily via the reaction of CO₂ with raw CaO-based materials, and calcium carbonate (CaCO₃) was observed to be the predominant carbonation product [6]. The use of this material simultaneously can reduce the amount of waste and neutralize a hazardous material.

The objectives of this study were to investigate the carbonation of several steelmaking slags, including ultra-fine (UF) slag, fly-ash (FA) slag, and blended hydraulic slag cement (BHC), in an autoclave reactor. The effects of the operational conditions, including the type of steelmaking slag, reaction time, liquid-to-solid ratio (L/S), temperature, CO₂ pressure, and initial pH, on the performance of the carbonation process were evaluated. In addition, reaction kinetics of the carbonation process were tested using a surface coverage model.

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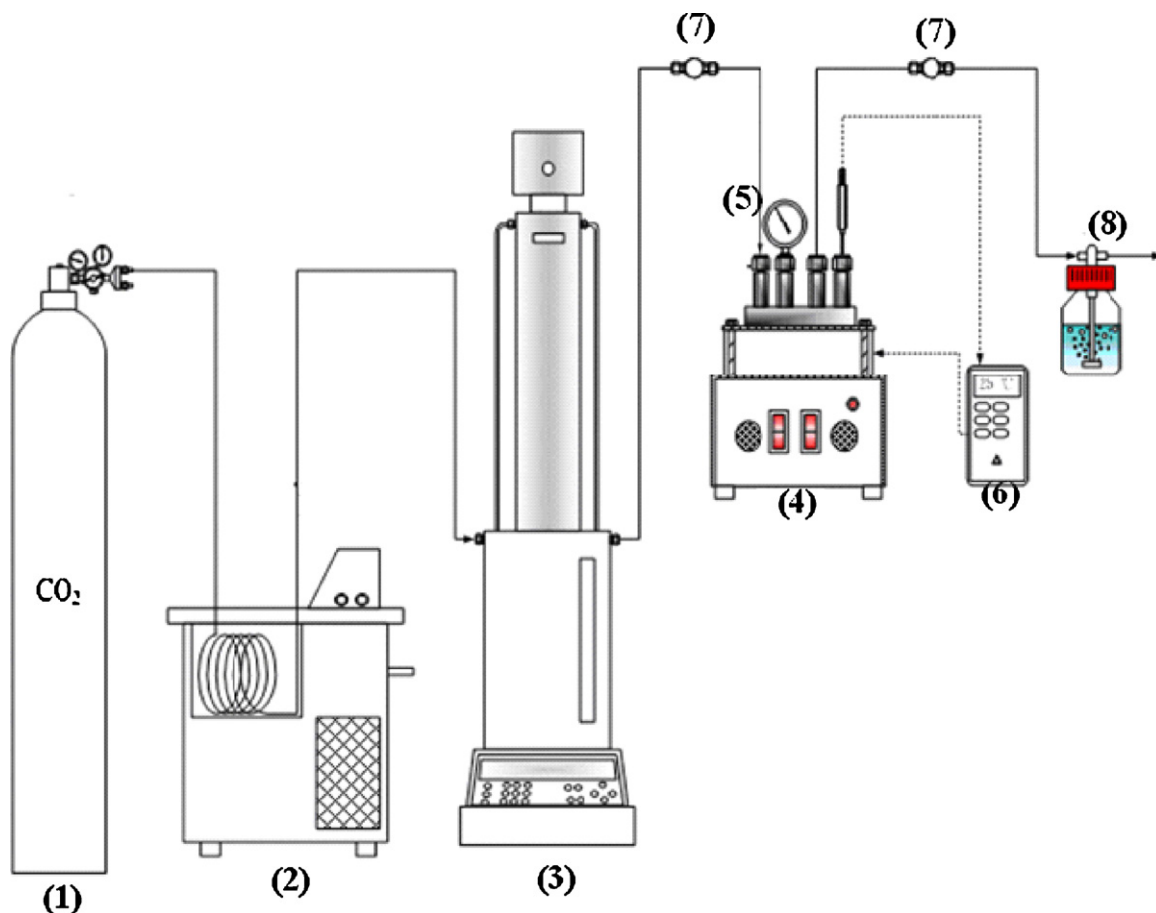


Fig. 1. Schematic diagram of the experimental set-up for the carbonation of steelmaking slag in an autoclave reactor. 1. CO₂ gas cylinder; 2. Circulating bath; 3. Syringe pump; 4. Magnetic stirrer and heater; 5. Reactor (autoclave); 6. Thermo couple; 7. Needle valve; 8. Vent to hood.

2. Materials and methods

2.1. Experiments

The aqueous carbonation of UF slag, FA slag, and BHC were conducted in an autoclave reactor that contained distilled water at a designated temperature of 40–160 °C. The UF slag, FA slag, and BHC with a diameter of approximately 1 cm were provided by the CHC

Resources Corporation (Kaohsiung, Taiwan). All slags were ground and sieved to less than 44 μm for all experiments. The BHC contains an intimate and uniform blend of Portland cement and fine granulated blast furnace (BF) slag. The BHC used in this investigation is classified as CEM III/C (~90% BF slag content) according to EN standards [7]. A schematic diagram demonstrating the carbonation of the steelmaking slag in an autoclave reactor is shown in Fig. 1. CO₂ was injected continuously into the reactor at a designated pressure and a constant flow rate.

The operational factors, including the reaction time (*t*), liquid-to-solid ratio (*L/S*), reaction temperature (*T*), CO₂ pressure (*P*), and initial pH, systematically were varied with the various feedstocks to minimize energy and chemical consumption. After the reaction, the samples of reacted slurry immediately were filtered through a PTFE membrane filter (Millipore, 45-μm pore size and 47 mm diameter), and then heated in an oven (105 °C) for use. The conversion of the carbonation products was determined quantitatively by thermogravimetric analysis (TGA) and qualitatively by X-ray diffraction (XRD) and scanning-electron microscopy (SEM).

2.2. Composition analysis

Prior to examining the capacity for CO₂ capture, the chemical compositions of steelmaking slags were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), after total digestion using aqua regia to dissolve the solid materials in the sample, by the chemistry analysis laboratory in the China Himent Corporation. However, SiO₂ was dissolved further by using hydrofluoric acid with increasing temperatures and pressures in a

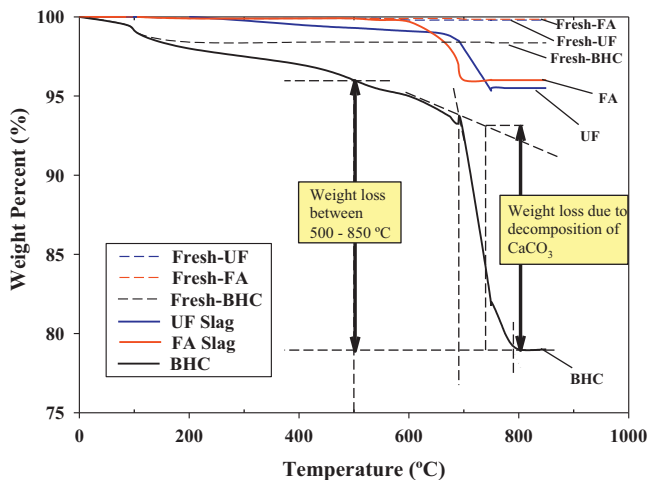


Fig. 2. TGA curves of fresh and carbonate of UF slag, FA slag, and BHC (Carbonation conditions: $P_{\text{CO}_2} = 650$ psig; $T = 60$ °C; $t = 1$ h; particle size < 44 μm; $L/S = 10$ mL g⁻¹).

microwave digestion. The contents of each metal in the extracted solution were measured by the ICP-AES method. Then, the content of metal oxide could be computed using the ICP-AES results.

2.3. TGA

The thermal characteristics of the slag before and after carbonation were examined using a thermo-gravimetric analyzer (TGA-51, Shimadzu); this analysis was performed to determine the weight loss using different temperatures for the selected samples. Three weight fractions corresponding to (1) moisture, (2) organic elemental carbon, calcium hydroxide, and $MgCO_3$, and (3) $CaCO_3$ content were determined mainly at the following temperature ranges: (1) 25–105 °C, (2) 105–500 °C, and (3) 500–850 °C. The weight loss between a temperature range of 500–850 °C is contributed mainly by the decomposition of $CaCO_3$ due to its release of CO_2 [6,8,9]. However, it has to be remarked that a continuous weight loss between temperatures of 105 and 1000 °C is due to the dehydration of calcium hydroxide, calcium silicate hydrates, calcium aluminate hydrates, and other minor hydrates [10]. In order to prevent overestimating the $CaCO_3$ content, the weight losses due to the dehydration of hydrates have been modified by a graphical technique and are illustrated in Fig. 2 [10]. Samples were heated linearly in the temperature range of 25–850 °C at a heating rate of 10 °C/min. The TGA weight fraction determined by means of a graphical technique, based on the dry weight, was assumed to be the $CaCO_3$ content, expressed in terms of CO_2 (wt%):

$$CO_2(\text{wt}\%) = \frac{\Delta m_{CaCO_3}}{m_{105^\circ C}} \quad (1)$$

The carbonation conversion (δ_{Ca}) was determined from the total calcium content of the carbonation product, assuming the initial carbonate content was negligible [8,11]:

$$\delta_{Ca}(\%) = [CO_2(\text{wt}\%)/100 - CO_2(\text{wt}\%)] \times [MW_{Ca}/MW_{CO_2}]/Ca_{\text{total}} \quad (2)$$

where δ_{Ca} is the carbonation conversion, MW_{Ca} and MW_{CO_2} are the molar weights of Ca and CO_2 , respectively, in kg/mol, and Ca_{total} is the total Ca content of the fresh sample in kg/kg.

2.4. SEM and XRD

SEM (JSM-6500F, JEOL) was used in this study to produce high-resolution three-dimensional images of the sample and to study the surface structure of the slag. SEM was useful particularly in identifying $CaCO_3$ formed on the surface of the slag in the carbonation reaction.

XRD (X' Pert Pro, PANalytical) was used to identify and characterize the $CaCO_3$ crystals in the carbonation products. Monochromatic X-rays were used to determine the interplanar spacing of the sample atoms using Cu as the anode material ($K\alpha-1$ wavelength = 1.540598 Å and $K\alpha-2$ wavelength = 1.544426 Å) at an angular step of 1° held for 1 s with 2θ spanning from 20° to 70°. When the Bragg conditions for constructive interference were obtained, a “reflection” was produced in which the relative peak height was proportional to the number of grains in a preferred orientation.

2.5. Aqueous carbonation

Theoretically, the extent of carbonation increases with reaction time. The aqueous carbonation experiments were conducted with reaction times of up to 720 min. The experimental procedures included the following three steps: aqueous CO_2 dissolution, Ca leaching, and $CaCO_3$ precipitation. Previous studies by Huijgen et al. [9] had indicated that the influence of the L/S ratio on carbonation was insignificant. Therefore, the L/S ratio was fixed at 10 mL g^{-1}

Table 1

Physico-chemical properties of UF slag, FA slag, and BHC (CHC Resources Corporation).

Parameters	UF slag	FA slag	BHC
Physical properties			
True density (g/cm^3)	2.89	2.78	2.94
Mean diameter (μm)	11.67	17.35	20.63
BET surface area (m^2/kg)	148	237	115
Total pore area (m^2/g)	1.76	1.32	1.13
Porosity	0.63	0.59	0.60
Chemical properties			
SiO_2 (%)	33.93	34.89	27.34
Al_2O_3 (%)	14.35	15.75	8.42
Fe_2O_3 (%)	0.35	1.97	2.71
CaO (%)	42.43	38.80	52.82
MgO (%)	6.42	5.59	4.66
S^{2-} (%)	0.24	–	–
SO_3 (%)	0.52	0.52	1.49
Total (%)	98.24	97.52	97.44

in this study. The conditions of the carbonation experiment were as follows: L/S ratio of 10 mL g^{-1} , a P_{CO_2} of 700 psig, particle size of less than 44 μm , and reaction time of 60 min, unless otherwise specified.

To assess the effective initial pH of the water samples for the carbonation conversion, the pH values of the water were prepared from 2 to 12 at a fixed reaction temperature of 100 °C, and a pressure of 700 psig. The initial pH value of solution was adjusted to the designed value using KOH and HNO_3 solutions. Then, different steelmaking slags were dispersed intensively in the prepared water at an L/S of 10 mL g^{-1} .

3. Results and discussion

3.1. Physico-chemical properties of steelmaking slags

The physico-chemical properties of the UF slag, FA slag, and BHC feedstocks are presented in Table 1, which shows that the major components of these three steelmaking slags were CaO: 42.43 wt%, 38.80 wt%, and 52.82 wt% for UF slag, FA slag, and BHC, respectively. Minor amounts of SiO_2 , Al_2O_3 , MgO, Fe_2O_3 , S^{2-} , and SO_3 , which do not contribute to CO_2 sequestration because the CO_2 -capturing capacity of the slag material is attributed mainly to the CaO components, are also listed in Table 1. A higher adsorption capacity of CO_2 on the slags was expected in the carbonation reaction, which was validated by the following experiments. Assuming that all CaO was converted to $CaCO_3$, the theoretical capacities of the UF slag, FA slag, and BHC were 0.333, 0.305 and 0.415 kg CO_2/kg dry solid, respectively.

Fig. 2 shows the weight variation of the fresh and carbonated specimen obtained by using TGA. According to the TGA results, the weight losses of the fresh UF slag, FA slag, and BHC between 500 and 850 °C was insignificant which indicated that the initial hydrate and carbonate contents of the three feedstocks were negligible. In addition, the TGA curves of carbonated specimen indicate that the CO_2 release at high temperatures (above 800 °C) can be neglected due to the lack of a peak at 800 °C in the TGA curves. The weight loss of the carbonated BHC was higher significantly than the carbonated UF and FA samples, which can be attributed to the greater CaO content and lower silicon dioxide content of the BHC. Therefore, the BHC conclusively captured a higher amount of CO_2 than the other two slags during the carbonation reaction.

Fig. 3 shows the SEM images of the fresh (Fig. 3a, c, e) and carbonated (Fig. 3b, d, f) UF slag, FA slag, and BHC, respectively. Comparisons of the SEM images of the feedstocks before and after carbonation showed that cubic particles adhered to the feedstocks

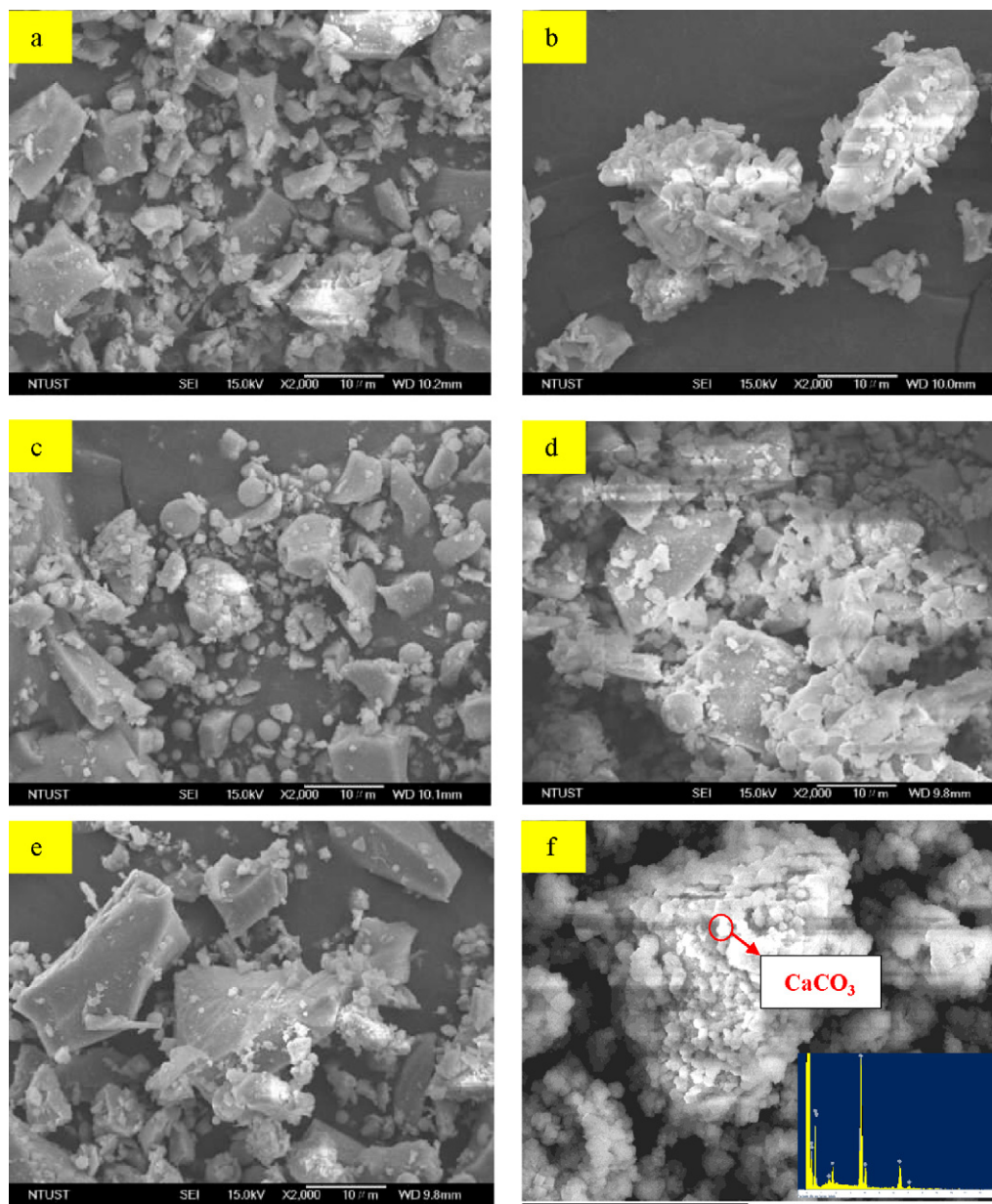


Fig. 3. Scanning electron micrographs (SEMs) of (a) fresh and (b) carbonated UF slags; (c) fresh and (d) carbonated FA slags; and (e) fresh and (f) carbonated BHC.

after carbonation. Based on the SEM images and qualitative analysis from XRD, it was determined that the cubic particles were composed of CaCO_3 and had diameters ranging from 1 to 2 μm , which is similar to the literature [4,11]. The dark cubic particles in the SEM images were found to be CaCO_3 which was confirmed by the EDX and XRD analyses.

The mineralogical characterizations of fresh and carbonated UF slag, FA slag, and BHC were performed based on the XRD patterns shown in Fig. 4a–c, respectively, which indicated that the main crystal phase of the fresh slags was CaO. In contrast to the XRD results from fresh BHC, CaCO_3 was identified as the primary phase in the reaction products. The peaks in the XRD analysis of the carbonated material appeared at 2θ values of 23.02°, 29.41°, 35.97°, 43.15°, 47.49°, 48.50°, 57.40°, 60.68°, and 64.68° (in red line), which are indicative of calcium carbonate. These results suggest that the steelmaking slags should be carbonated with CO_2 to form CaCO_3 in an autoclave reaction.

3.2. Effects of feedstocks and operating factors

The effect of reaction time on the conversion ratio of the three feedstocks at 160 °C and 700 psig is shown in Fig. 5, which indicates that the carbonation rate decreased as the reaction time increased. The reaction leveled off after 60 min, indicating that the carbonation reaction had a stationary phase due to the formation of a SiO_2 barrier, which strongly blocks the reactive surface sites and inhibits the release of calcium ions from the slag. These effects exhibit a limited conversion of CO_2 during the carbonation reaction, which is consistent with the findings suggested by Huijgen et al. [4]. Therefore, the maximum efficiencies in carbonation conversion (δ_{Ca}) after a reaction time of 720 min for the UF slag, FA slag, and BHC were found to be 38.1%, 34.7%, and 68.3%, respectively.

The relatively higher conversion of the BHC also could be explained by the chemical compositions of the slags shown in Table 1, indicating that the CaO content of the BHC was (52.82 wt%) and thus higher than that of the UF (42.43 wt%) and FA (38.80 wt%)

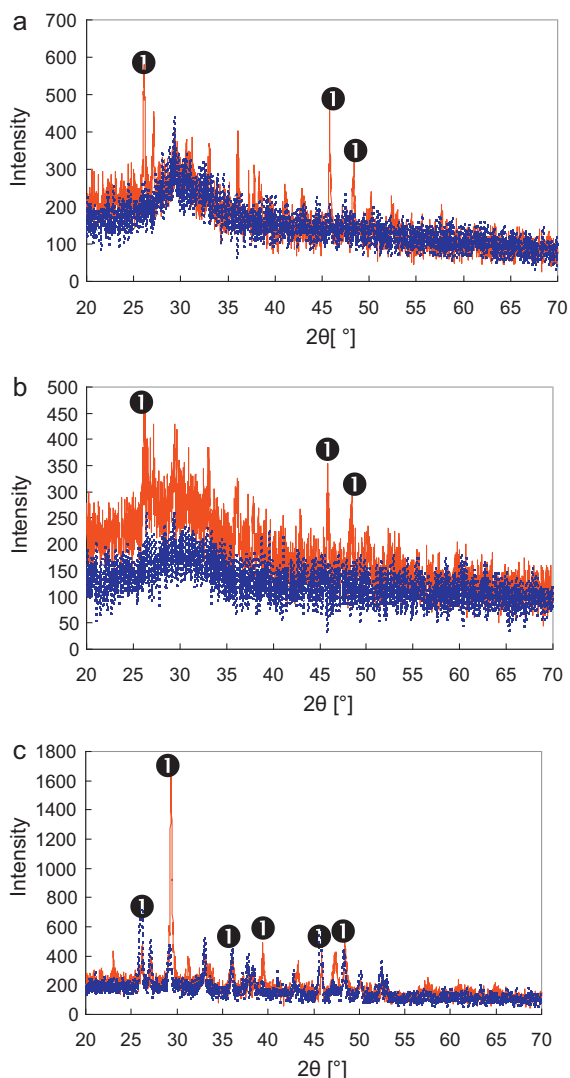


Fig. 4. XRD spectra of fresh (in blue line) and carbonated (in red line) slag with peak identifications (1 = CaCO_3); (a) UF slag; (b) FA slag; and (c) BHC (Carbonation conditions: 700 psig, 160 °C, and 2 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

slags. The actual CO_2 capture capacities per gram of dry solid were 0.127, 0.107, and 0.283 kg CO_2 for the UF slag, FA slag, and BHC, respectively.

The L/S ratio represents the weight ratio of water-to-waste in the slurry used in the aqueous carbonation. The L/S ratios of the three solid wastes in this study ranged from 0 to 100 mL g^{-1} . The particle size was controlled to be less than 44 μm , the reaction temperature was maintained at 100 °C, and the reaction pressure was set at 700 psig. As shown in Fig. 6, the conversions of the UF slag, FA slag, and BHC were quite low in the absence of water (L/S = 0) because of the slow reaction kinetics of dry carbonation, which is reflective of the natural carbonation of minerals in the environment.

When the L/S ratio was increased to 10 mL g^{-1} , the conversions were improved to be 18.3%, 13.9%, and 57.5% for the UF slag, FA slag, and BHC, respectively, because the aqueous carbonation process was dominant. As the L/S ratio further increased, the conversions were not increased significantly because the presence of excessive water formed a mass transfer barrier, lowered the ionic strength, and resulted in decreasing the dissolution rate of Ca^{2+} . The L/S ratio was held from 10 to 20 for these three feedstocks, which implies

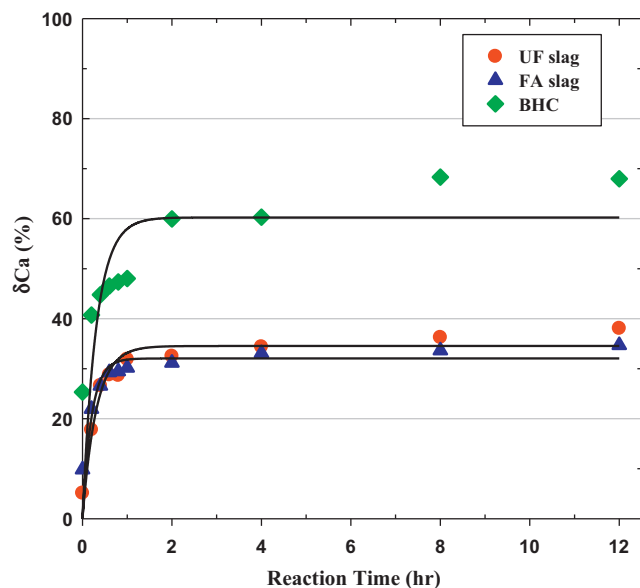


Fig. 5. The influence of reaction time on carbonation conversion of steelmaking slags (carbonation conditions: P_{CO_2} = 700 psig; T = 160 °C; particle size <44 μm ; L/S = 10 mL g^{-1}).

that the use of a large amount of water in the sequestration process could inhibit the carbonation reaction.

From a thermodynamic equilibrium perspective, the actual concentration of CO_3^{2-} significantly was smaller than the concentration of Ca^{2+} , even at high partial pressures of CO_2 . The solution became strongly alkaline (pH 11.8) before carbonation, whereas the pH of the suspension slurry dropped rapidly after the introduction of pure CO_2 gas into the system. The solution ultimately stabilized at a pH of approximately 6.3. This reaction suggests that the carbonation process should eliminate the alkalinity, which was in agreement with the literature [11,12].

The effect of temperature on the feedstocks was assessed by varying the temperature from 40 °C to 160 °C, with a fixed reaction time of 60 min and a CO_2 pressure of 700 psig. The conversion increased with increasing temperature (Fig. 7) due to the higher leaching rate of calcium at higher temperatures. However, in the

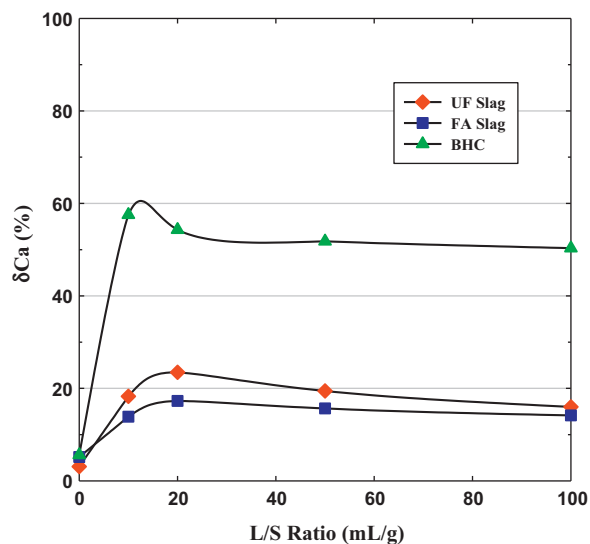


Fig. 6. The influence of liquid-to-solid ratio (L/S) on carbonation conversion of steelmaking slags (carbonation conditions: P_{CO_2} = 700 psig; T = 100 °C; t = 1 h; particle size <44 μm).

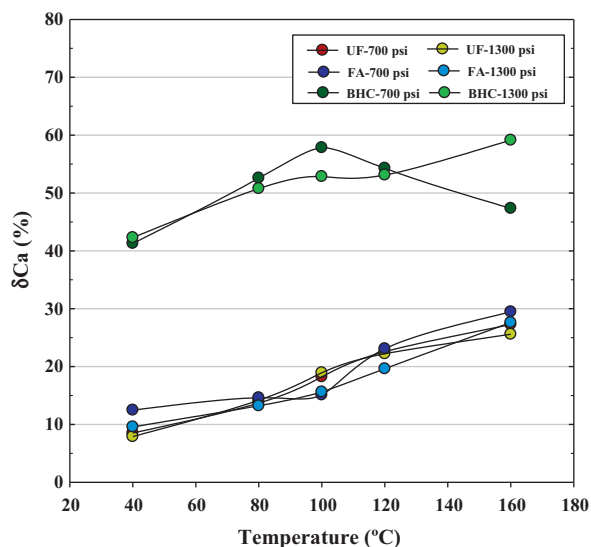


Fig. 7. The influence of reaction temperature and pressure on carbonation conversion of (a) UF slag, (b) FA slag; and (c) BHC (carbonation conditions: $t = 1$ h; particle size $<44 \mu\text{m}$; $L/S = 10 \text{ mL g}^{-1}$).

BHC case, the conversion started to decrease at temperatures over 120°C if the pressure was set at 700 psig. The above evidence may be caused by the reduction of the CO_2 dissolution as temperatures increased. These observations were similar to a previous study [11] which found that the CO_2 solubility could be the key factor affecting the carbonation conversion at higher temperatures in BHC case. In contrast to the supercritical condition (1300 psig), under which the CO_2 fluid has a relatively higher solubility of liquid and lower dynamic viscosity of gas, the conversion of BHC increases due to its superior CO_2 solubility at higher temperatures. It was concluded that the temperature significantly influenced the conversion of the carbonation reaction, with increasing temperatures resulting in higher conversions.

The CO_2 pressure was varied between two types of conditions: a normal condition (700 psig) and a supercritical condition (1300 psig). The conversion of supercritical CO_2 was slightly less than that of normal CO_2 (Fig. 7), due to the inhibition of CaCO_3 crystal growth under this supercritical pressure. However, in general, a sufficiently high pressure increases the rate of the carbonation reac-

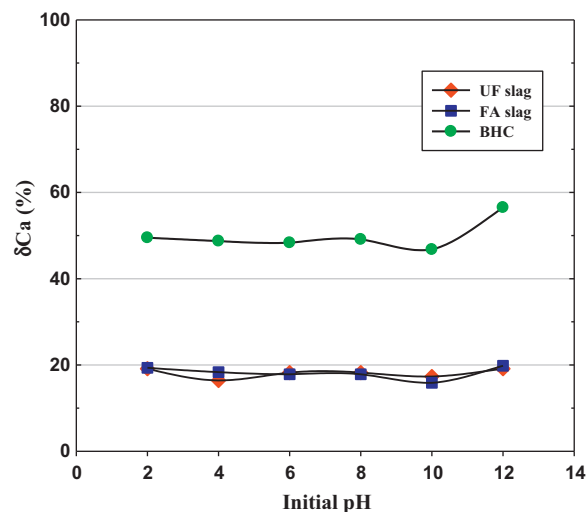


Fig. 8. The influence of initial pH on carbonation conversion of steelmaking slags (carbonation conditions: $t = 1$ h; particle size $<44 \mu\text{m}$; $L/S = 100 \text{ mL g}^{-1}$).

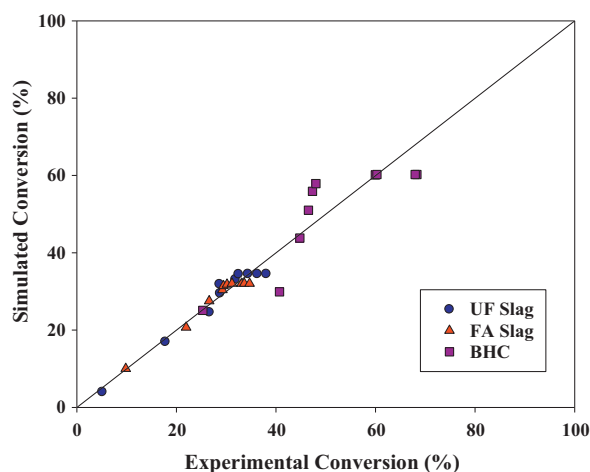


Fig. 9. Comparison of simulated and experimental conversion values for the carbonation of UF slag, FA slag, and BHC.

tion, which precludes the formation of CaCO_3 crystals and inhibits the reaction.

To assess the effective initial pH for the carbonation of the three feedstocks, the initial pH values of the water samples were varied from 2 to 12 at a fixed reaction temperature of 100°C , a pressure of 700 psig, and an L/S of 10 mL g^{-1} . As shown in Fig. 8, the conversion of the BHC was higher than the other two at all pH values due to its higher CaO content. It also was observed that the three feedstocks had the highest conversions at pH 12 because there were large amounts of CO_3^{2-} in the slurry, which enhanced the carbonation process. The conversions of all three feedstocks were lower when the pH ranged from 6 to 10. However, when the pH was lower than 4, the conversions of the three feedstocks increased because the Ca^{2+} dissolved thoroughly. Furthermore, in UF slag case, the trace S^{2-} content ($\sim 0.24 \text{ wt}\%$) may cause a potential problem of H_2S emissions if the operational pH value was lower than 4 [13]. Therefore, it is required to control experiments at a higher pH (e.g., 10) to increase the degree of aqueous carbonation and prevent an environmental issue.

3.3. Kinetic modeling of the carbonation reaction

A surface coverage model, which was originally developed by considering the carbonation of hydrated lime [14], was chosen to determine the kinetics of the carbonation reactions in this study.

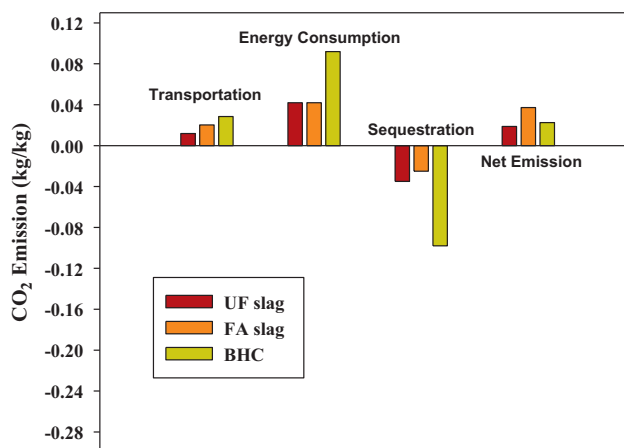


Fig. 10. Comparison of CO_2 emissions including transportation, energy consumption, and sequestration for various steelmaking slags.

Table 2
Surface coverage model and LCA results for the UF slag, FA slag, and BHC.

Item	Unit	UF slag	FA slag	BHC
Surface coverage model results				
S_g	(m ² /g)	0.15	0.24	0.12
M	(g/mol)	61.24	61.83	60.21
k_s	(mol/h/m ²)	12.11	10.69	27.28
k_p	(m ² /mol)	0.27	0.46	0.12
k_1	(1/h)	111.2	158.7	197.01
k_2	(-)	0.0290	0.0312	0.0167
Life cycle assessment results				
CO ₂ (Emission) ^a	(kg CO ₂ /kg solid)	0.054	0.062	0.13
CO ₂ (Sequestration)	(kg CO ₂ /kg solid)	0.035	0.025	0.098
CO ₂ (Net) ^b	(kg CO ₂ /kg solid)	0.019	0.037	0.023

^a Sum of CO₂ emission during transportation and energy consumption.

^b Net = CO₂ emission – CO₂ sequestration.

The measurements of the fresh and carbonated materials by SEM in conjunction with XRD provided evidence that indicated the suitability of using the surface coverage model in this investigation. The surface composition and molecular structure changed during the course of carbonation. The small CaCO₃ particles formed on the surface of slags, which indicated that the carbonation reaction occurred on the surface of slags and formed a protective layer around the reacting particles, thus inhibiting further reaction.

Assume that the rate-determining step of carbonation is the surface reaction, which occurs only at unreacted surface sites not covered by product, then the carbonation reaction rate per initial surface area of the solid can be expressed by Eq. (3):

$$r_s = k_s \Phi \quad (3)$$

where k_s is the rate constant (mol/h/m²) which is a function of temperature, the concentrations of reacting species, and the relative humidity; and Φ is the fraction of surface sites (or area) still active and not covered by the reaction product.

The rate of conversion, δ_{Ca} (%), can then be expressed by Eq. (4):

$$\frac{d\delta}{dt} = S_g M r_s = S_g M k_s \Phi \quad (4)$$

where S_g (m²/g) is the initial specific surface area of the solid waste, and M (g/mol) is the weight of solid waste per mole. Φ is a function of time and is indicative of the manner in which the product is deposited on the surface. Hence, Φ changes with reaction time and is dependent on the reaction rate, and one may assume that Φ can be expressed by the following equation:

$$\frac{-d\Phi}{dt} = k_p r_s = k_p k_s \Phi \quad (5)$$

where k_p (m²/mol), a function of temperature, the concentrations of reacting species, and the relative humidity, is a proportional constant that reflects the fraction of the surface that is reactive and not covered by the reaction product. Integration of Eq. (5) enables Φ to be expressed as a function of time, as shown in Eq. (6), and assuming that $k_1 = k_s S_g M$ and $k_2 = k_p / (S_g M)$

$$\Phi = \exp(-k_1 k_2 t) \quad (6)$$

By substituting Eq. (6) into Eq. (4), the integration of Eq. (4) can be used to describe the relationship between the conversion and reaction times:

$$\delta = \frac{[1 - \exp(-k_1 k_2 t)]}{k_2} \quad (7)$$

Table 2 shows the values of S_g , M , k_s , k_p , k_1 , and k_2 determined by non-linear regressions for each of the three materials based on the data obtained from experiments conducted at 160 °C, which indicated that the BHC had the fastest reaction rate (k_s) due to its higher CaO content and lower SiO₂ content. However, the FA slag

resulted in the largest k_p , which suggested that the product was deposited on its surface faster than it was on the other materials because of its higher SiO₂ content. It was concluded that the BHC was the most reactive material for carbonation among the three feedstocks tested.

Fig. 9 presents the relationship between the experimental and model values and indicates that the experimental values were consistent with the model values, which suggests that the surface coverage model is suitable to describe the carbonation of the steel-making slag. The standard errors (%) between the experimental and model values of the UF slag, FA slag, and BHC were 5%, 6%, and 7%, respectively, indicating that the surface coverage model could simulate successfully the carbonation reaction of these slag materials.

3.4. Comparison of various carbonation processes

CCS (carbon capture and storage) is an energy-intensive process; thus, it may consume additional energy, leading to further CO₂ emissions compared to the non-CCS treatment process. However, the consumption of energy for accelerated sequestration has decreased with recent technology developments. The factors that affected the system operation were reaction temperature, initial pH with various feedstocks, and CO₂ pressure. Many researchers have attempted to capture CO₂ with lower power consumption and less chemical usage. In this study, the highest conversion (δ_{Ca}) for the BHC was 68%, when the aqueous carbonation was conducted at an L/S of 10 mL g⁻¹, a partial pressure of CO₂ of 700 psig, and a temperature of 160 °C, with a reaction time of 12 h in an autoclave reactor.

Table 3 shows a comparison of the experimental results in this study with others reported in literature. In a previous investigation [11], the highest conversion for the BHC was 48%, in a reaction conducted at 101.3 kPa and 60 °C in a slurry reactor. A similar study by Huijgen et al. [9] on accelerated carbonation experiments using wollastonite in an autoclave was conducted with a reaction time of 15 min at 200 °C, CO₂ partial pressure of 20 bar and a particle size <38 μm, which resulted in a maximum conversion of 70%. In addition, the BF slag conversion by the pH-swing method from Kodama et al. [15] was 80% at a relatively low temperature of 40 °C and pressure of 1.9 psig. However, previous studies using the pH-swing method consumed great amounts of base and acid solvents, which could result in adverse effects on the environment. Furthermore, O'Connor et al. [16] and Lackner et al. [17] demonstrated that an extremely high carbonation conversion (91–100%) could be achieved at higher temperatures (185–500 °C) and pressures (1682–4930 psig). It was concluded that this investigation exhibited a higher BHC carbonation conversion (68.3%) at relatively a lower temperature (160 °C) and pressure (600 psig).

Table 3
Comparison of experimental results among the literature and this study.

Material type	Method	CO ₂ conc.	Pressure	Temperature	Particle size (μm)	Time	Conversion	Reference
Wollastonite	Aqueous carbonation	100 vol%	20 bar	200 °C	<38	15 min	70%	Huijgen et al. [9]
Olivine	Aqueous carbonation	100 vol%	1682 psig	185 °C	<37	1 day	91%	O'Connor et al., [16]
Mg(OH) ₂	Direct carbonation	100 vol%	4930 psig	500 °C	<20	2 h	100%	Lackner et al., [17]
Converter slag	pH-swing	13 vol%	1.9 psig	40 °C	<63	1 h	80%	Kodama et al., [15]
Blast furnace slag	pH-swing	100 vol%	14.7 psig	30 °C	<10	15 min	72.5%	Eloneva et al., [2]
APC Residues	Aqueous carbonation	100 vol%	3 bar	30 °C	Not specified	5 h	67%	Baclocchi et al., [18]
CKD	Direct carbonation	35,600 ppm	Atmospheric	Ambient	Not specified	12 days	70.6%	Huntzinger et al., [6]
BHC	Aqueous carbonation	100 vol%	14.7 psig	60 °C	<44	1 h	47.5%	Chang et al., [11]
BHC	Aqueous carbonation	100 vol%	700 psig	160 °C	<44	12 h	68.3%	This study
	carbonation		1300 psig	160 °C	<44	1 h	59.2%	

Life cycle assessment (LCA) is a method in which the energy and raw material consumptions, types of emissions, and other important issues related to a specific product are measured, analyzed, and evaluated from an environmental point of view. In this investigation, LCA was utilized to determine the CO₂ emission including transportation, energy consumption, and sequestration (Fig. 10). The transportation and energy consumptions including grinding, sieving, heating, and pressuring, could lead to additional CO₂ emissions. In addition, although BHC contains cement as small as 10% (CEM III/C), the process of limestone decomposition alone produces CO₂ for about 0.05 kg/kg BHC during the cement manufacturing process. Therefore, in case of BHC, the amounts of CO₂ emission from cement manufacturing also were taken into account. The calculated net CO₂ emission and sequestration are shown in Table 2, which indicates that the net CO₂ emissions of the UF slag, FA slag, and BHC were 0.019, 0.037, and 0.023 kg CO₂/kg solid, respectively. The heating process was the most energy intensive throughout all systems, which accounts for 92.6% of total energy consumption. In commercial operation, however, this problem could be improved by utilizing the waste heat from the industrial process to minimize the additional energy consumption. Therefore, it suggests that the BHC should be a feasible feedstock to sequester CO₂ through the carbonation according to the preliminary results of LCA.

4. Conclusions

UF slag, FA slag, and BHC were selected as feedstocks for the aqueous carbonation process in this study. The initial carbonation levels of the fresh slags were found to be negligible based on the TGA curves. The three feedstocks were alkaline, calcium-rich particles that reacted with CO₂ dissolved in the aqueous slurry to form CaCO₃ coating on the surface of the slag. In this study, the highest conversion (δ_{Ca}), 68.3%, for BHC was achieved when the aqueous carbonation was conducted at an L/S of 10 mL g⁻¹, a CO₂ partial pressure of 700 psig, and a temperature of 160 °C, with a reaction time of 12 h in an autoclave reactor. In comparison with a previous report, the BHC exhibited a better performance at a lower temperature (160 °C) and pressure (700 psig). Most of the carbonation reaction occurred within the first hour of reaction time, and the conversion efficiency was lower significantly after 12 hr of reaction time. In addition, it is required to control experiments at a higher pH (e.g., 10) to increase the degree of aqueous carbonation and prevent an environmental issue.

Kinetics of this reaction were described using a surface coverage model, in which the experimental data were shown to be consistent with the predicted values. The CaCO₃ product formed was identified as crystallized calcite, and the surface composition and molecular structure were found to be varied in the course of carbonation based on SEM and XRD measurements. Conclusively,

the aqueous carbonation of these steelmaking slags, including UF slag, FA slag, and BHC, in an autoclave reactor is feasible and results in a high conversion.

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