



Article Roles of Mineralogical Phases in Aqueous Carbonation of Steelmaking Slag

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Abstract: Mineralogical phases of steelmaking slags have significant influences on the carbonation of the slags. In this paper, the effects of temperature and reaction time on the conversion of calcium-related phases and the carbonation degree of a slag sample were studied. The experimental conditions were a liquid-to-solid ratio of 20 mL/g, a carbon dioxide flow rate of 1 L/min and a slag particle size of 38–75 µm. The results show that the optimum carbonation temperature and reaction time are 60 °C and 90 min, respectively, and calcite phase content is about 26.78% while the conversion rates of Ca₃Al₂O₆, CaSiO₃, Ca₂SiO₄ and free CaO are about 40%, 42.46%, 51% and 100%, respectively, and the carbon dioxide sequestration efficiency is about 170 g/kg slag.

Keywords: steelmaking slag; mineralogical phase content; carbonation degree; conversion rate

1. Introduction

As known to us, the generation rate of steelmaking slag is about 10%–15% of crude steel production. In China, there are more than 100 million tons of steelmaking slags stored on the ground. Steelmaking slag has been accumulated for a long time without consideration. This not only wastes valuable resources, but also causes some threats. For example, heavy metal in slag can contaminate groundwater. Thus, the development of utilization technologies of steelmaking slag has garnered more attention recently.

The idea of slag carbonation comes from the mineral carbonation firstly proposed by Seifritz [1] and then developed by Lackner [2]. CO_2 is hardly released from carbonation products after mineralizing because they are thermodynamically stable [2,3]. Furthermore, steelmaking slag is rich in calcium and magnesium, and naturally, steelmaking slag can be a better CO_2 adsorption carrier. The utilization of slag has some advantages including lower cost and minimal environmental impacts through pH-adjustment [4,5].

The existing dominant slag carbonation process has three advantages. Firstly, greenhouse gas carbon dioxide can be sequestrated permanently. Secondly, the reaction process is helpful for improving the stability of slag for construction materials, because active mineralogical phases containing calcium stay stable in the form of calcium carbonate. Lastly, calcium carbonate precipitates in slag particles surface, and the coated surface after carbonation hinders the heavy metal leaching process.

In previous works, the effect of experimental parameters such as the ratio of liquid to solid (L/S ratio), temperature, particle size, stirring intensity, *etc.*, on carbonation efficiency and the slag carbonation mechanism were analyzed when slag was dissolved in water [6,7]. In order to improve the carbonation efficiency, conditions such as higher reaction pressure [8–12] and an acid leaching agent [13–15] are adopted. Previous researchers focused on the total carbonation degree of steelmaking slag in their research. The effects of mineralogical phases containing calcium on the carbonation degree were less referred to in literature. In order to analyze the CO₂-binding mineralogical phases' activity with carbon dioxide when slag is applied for carbon dioxide sequestration, in this paper the effects of the main mineralogical phases containing calcium on the carbonation degree have been studied by quantitative X-ray diffraction (XRD) collaborating with X-ray fluorescence spectroscopy (XFR) analysis, and the effects of temperature and time on the conversion rate of mineralogical phases have been analyzed.

2. Material and Methods

2.1. Sample Characterization

A steelmaking slag sample was taken from a Chinese steel plant (Baosteel, Shanghai, China). The steelmaking slag sample was ground in a ball mill. Chemical composition of the slag sample was analyzed and is presented in Table 1. It can be seen that calcium oxide content nearly counts for 55.3%, magnesium oxide content is less than 10%, silicon dioxide content of the steelmaking slag is more than 10%, and aluminum oxide is about 30%. Quantitative X-ray diffraction (XRD) test for steelmaking slag was conducted. XRD analysis in a Dron-3M diffractometer (Shimadzu Ltd., Tokyo, Japan) using Ni-filtered Cu-K α radiation, powdered non-oriented preparations was made. Diffractograms were digitally registered and analyzed by Sirquant code [16] using full-profile Rietveld analysis [17].

Table 1. Chemical composition of the slag sample, wt. %.

TFe	MFe	FeO	CaO	MgO	SiO ₂	Al ₂ O ₃	MnO
0.55	< 0.50	< 0.10	55.3	5.64	8.00	30.0	0.41

Specific surface area (SSA) was estimated with BET method at Quanta chrome instruments Autosorb (Automated Gas Sorption1-Win, Version 1.50, CostechMicroanalytical Ltd., Beijing, China), 0.5–1.5 g steelmaking slag with different particle sizes was applied for testing, Nitrogen gas was used for analyzing gas, and analyzing time was set for 200 min, outgas temperature was controlled at 350 °C, and liquid density was 8080 kg/m³. Scanning electron microscope (SEM) JSM-6301F (JEOL Ltd., Tokyo, Japan) was used for slag surface observations before and after carbonation process.

2.2. Experimental Setup

The carbonation degree of the steelmaking slag was investigated at room temperature and under normal atmosphere, and the experimental apparatus is displayed in Figure 1. The experimental apparatus includes measurement and control of temperature and pH measurement. The liquid-to-solid ratio was set up as 20 mL/g, and the sample weight was 5 g each time.

The reactor was sealed with preservation film for avoiding solution evaporation; the initial time is obtained when the temperature reached the target temperature. When experiments began, CO₂ gas at a predetermined flow rate was blown into the reactor. The experimental conditions are presented in Table 2. The temperature varied among 25 °C, 40 °C, 60 °C, and 90 °C, the reaction time changed among 30 min, 60 min, 90 min, 120 min and 180 min, and CO₂ flow rate was kept at 1 L/min.



Figure 1. Schematic diagram of steelmaking slag carbonation process: (1) temperature controller; (2) magnetic stirrer; (3) pH reader; (4) temperature electrode; (5) heated water; (6) leaching solution; (7) flow meter; (8) gas exit.

Test No.	Temp (°C)	Time (min)	Test No.	Temp (°C)	Time (min)
1	25	30	11	60	60
2	25	60	12	60	90
3	25	90	13	60	120
4	25	120	14	60	180
5	25	180	15	90	30
6	40	30	16	90	60
7	40	90	17	90	90
8	40	120	18	90	120
9	40	180	19	90	180
10	60	30	-	-	-

Table 2. Arrangement of carbonation experiment.

2.3. Evaluation of Carbonation Degree

In order to evaluate carbonation degree of steelmaking slag and efficiency of absorbing CO₂ by the slag, HCT-1/2 differential thermal analyzer (Henven Scientific Instument Factory, Beijing, China) was adopted. In the test, the crucible weighed m_0 , the weight of the crucible plus the slag sample was m_1 , and then weight of the slag sample was m_1 minus m_0 .

The end temperature for the TGA test was 1000 $^{\circ}$ C, and heating rate was 10 $^{\circ}$ C/min; after the end temperature was achieved, the sample was held at that temperature for 3 min. Because HJ thermal analysis software can record temperature, thermo-gravimetry and differential thermal analysis curve synchronously, it is convenient to determine the thermal characteristics of the slag.

Slag weight loss can be obtained from the thermogravimetric analysis curve, which mainly include three parts, free water evaporation in the temperature range of 25–105 °C, organic carbon loss and magnesium carbonate decomposition in the temperature scope of 105–500 °C, between 500 °C and 1000 °C, calcium carbonate decomposition occurs. Carbonation degree can be evaluated with the Equations (1) and (2) referred in literature [9].

$$\eta_{\rm CD} = \frac{\frac{\rm CO_2(wt.\%)}{1 - \rm CO_2(wt.\%)} \times \frac{MW_{\rm Ca}(kg/mol)}{MW_{\rm CO_2}(kg/mol)}}{\rm Ca_{\rm total}(kg/kg)} \times 100\%$$
(1)

$$CO_2(wt. \%) = \frac{\Delta m_{(500 \ ^\circ C - 1000 \ ^\circ C)}}{m_{105 \ ^\circ C}} \times 100\%$$
⁽²⁾

where Ca_{total} represents the content of element calcium in slag, %, $m_{105 \circ C}$ denotes the weight of slag when heated to 105 °C, mg, $\Delta m_{(500 \circ C-1000 \circ C)}$ denotes steelmaking slag weight loss when heated from 500 °C to 1000 °C, mg, η_{CD} denotes carbonation degree of slag, %.

3. Results and Discussion

3.1. Characteristics of Slag Sample

The slag sample contains 55.3% CaO, of which 10.6% is free CaO, 29.6% is a Ca-aluminate compound ($Ca_3Al_2O_6$) and 15.1% is Ca-silicates (5.7% CaSiO_3 and 9.4% Ca_2SiO_4).

Specific surface areas of the raw slag sample change from $0.51 \text{ m}^2/\text{g}$ to $1.57 \text{ m}^2/\text{g}$, depending on the particle sizes. The specific areas of carbonated slag samples vary from 7.56 m²/g to 12.78 m²/g with the carbonation time increasing at 25 °C. The results can be explained by the slag fragmentation model [18]; in other words, during the carbonation reaction process, carbonate calcium produced in slag surface area is peeling from the matrix by stirring, and causing increases of the initial slag surface area. SEM images of the steelmaking slag carbonated at different temperatures and reaction times are shown in Figure 2.



Figure 2. Steelmaking slag morphology before and after carbonation process: (**a**) before carbonation; (**b**) for 30 min at 60 °C; (**c**) 90 min at 60 °C; (**d**) 90 min at 90 °C.

3.2. Effect of Carbonation Time on Mineralogical Phases Containing Calcium

The effect of the carbonation time on the content of the main mineralogical phases in the slag sample is shown in Figure 3. Clearly, the peak intensity of the calcite phase increases when the carbonation time increases from 30 min to 60 min, but after that, if extending carbonation time, the peak intensity of the calcite phase decreases. The peak intensity of the calcium aluminate phase decreases

with the carbonation time increasing. This is because the calcium aluminate absorbs carbon dioxide dissolved in water, and the Ca-silicate phase, such as wollastonite, also reacts with carbon dioxide.



Figure 3. Effect of carbonation time on mineralogy phases containing calcium.

Quantitative XRD analysis of the slag has a better correlation with chemical test results [16]. Figure 4 describes the effect of reaction time on the carbonation degree contribution rate for calcium-related phases. It is apparent that the calcite content in slag increases from 15.34% to 25.47% when the carbonation time increases from 30 min to 90 min. The calcite content in slag increases to 26.78% when expanding to an additional 90 min, and the optimum reaction time can take place at 90 min. The carbonation time is less than 90 min, and the carbonation reaction cannot be allowed to complete. If the carbonation time is more than 90 min, the reaction kinetic condition is worse because the carbonate calcium production is coated on the surface of the slag, which hinders the carbonation degree from increasing after 90 min.



Figure 4. Effect of carbonation time on mineralogical phase content of slag carbonated at 60 °C.

From Figure 4, one can see that the content of $Ca_3Al_2O_6$ in the slag decreases from 29.6% to 17.79% when the slag is carbonated for 30 min. When the carbonation time increases from 90 min to 180 min, the content decreases from 12.51% to 11.49%. Clearly, almost 40% of the $Ca_3Al_2O_6$ can be carbonated in the first 30 min, and 8.15% of the $Ca_3Al_2O_6$ will be carbonated in the next 60 min. As for the calcium-silicate phase, the $CaSiO_3$ content sharply decreases from 5.7% to 3.28% when the slag is carbonated for 90 min, and further decreases to 3.14% after an additional 90 min; the $CaSiO_3$ conversion rate is 42.46% in the first 90 min, and only 4.3% in the additional 90 min carbonation time. Ca_2SiO_4 has similar carbonation behavior to $CaSiO_3$. In the first 30 min of carbonation time, the content of Ca_2SiO_4 in the slag decreases from 9.4% to 4.6%; when the carbonation time increases from 90 min to 180 min, the phase content decreases from 2.45% to 2.02%. In the first 30 min of carbonation. For free lime in the raw slag sample, after 60 min of carbonation all initial 10.6% of free lime is carbonated.

3.3. Effect of Carbonation Temperature on Mineralogical Phases Containing Calcium

In order to analyze the effect of carbonation temperature on the carbonation degree and slag phase conversion, TGA-DSC (Netzsch, Gerätebau, Germany) tests were conducted on the slag carbonated, and TGA analysis results at different reaction temperatures are shown in Figure 5.



Figure 5. Effect of temperature on carbonation degree for steelmaking slag carbonated for 90 min.

First, 7.95 g of steelmaking slag after 90 min of carbonation at 25 °C was analyzed. The weight loss of the sample is 10.1% when the heating temperature increases from 500 °C to 1000 °C; the carbonation degree calculated by Equation (1) is then 18.5% at 25 °C. The weight loss at 40 °C is 14.5%, and the carbonation degree is 27.9%, and the weight loss at 60 °C is 17.2%, and the carbonation degree is 33.4%. The weight loss at 90 °C is 15.2%, and carbonation degree is 29.5%. It can be concluded that the optimum temperature for maximum carbonation efficiency is about 60 °C, due to the contradicting effects of temperature on the carbonation kinetics and solubility of calcium-related minerals in the water.

Obviously, at ambient reaction temperature and with 90 min of reaction time, the contents of calcite, $Ca_3Al_2O_6$, $CaSiO_3$ and Ca_2SiO_4 in the slag are 16.8%, 18.9%, 4.3% and 6.3%, respectively in Figure 6. Calcite in the slag increases from 22.68% to 25.47% when the reaction temperature increases from 40 °C to 60 °C. The calcite content increases to 25.79% when the carbonation temperature rises to 90 °C. The Ca₃Al₂O₆ content in slag decreases from 14.8% to 12.49% when the carbonation temperature

increases from 40 °C to 60 °C, but it increases to 13.75% when the reaction temperature rises to 90 °C. This is because there is a reversal relationship between CO_2 solubility in water and the reaction temperature. $Ca_3Al_2O_6$ has a lower conversion rate with a lower carbon dioxide solubility at a higher carbonation temperature. The contents of $CaSiO_3$ and Ca_2SiO_4 decrease from 2.9% to 2.72% and 5.1% to 3.48%, respectively. When the carbonation temperature increases from 40 °C to 60 °C, the contents of the two phases increase to 3.11% and 5.18%, respectively.



Figure 6. Effect of temperature on content of mineralogical phases of slag carbonated for 90 min.

4. Conclusions

The carbonation process was experimentally tested on a steelmaking slag sample under the conditions of a ratio of liquid to solid at 20 mL/g, a 5 g sample weight and particle sizes from 38 μ m to 75 μ m. The optimum carbonation temperature and reaction time are 60 °C and 90 min, respectively. The maximum carbonation degree is about 26.78%. The conversion rates of Ca₃Al₂O₆ phase, CaSiO₃, Ca₂SiO₄ and free CaO are about 40%, 42.46%, 51% and 100%, respectively.

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Conflicts of Interest: The authors declare no conflict of interest.

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