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Multiple model approach to evaluation of accelerated carbonation for steelmaking slag in a slurry reactor

Shu-Yuan Pan [a], Hsing-Lu Liu [a], E.-E. Chang [b], Hyunook Kim [c], Yi-Hung Chen [d], Pen-Chi Chiang [a, e, *]

[a] *Graduate Institute of Environmental Engineering, National Taiwan University, Taiwan, ROC*
[b] *Department of Biochemistry, Taipei Medical University, Taiwan, ROC*
[c] *Department of Energy and Environmental System Engineering, University of Seoul, South Korea*
[d] *Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taiwan, ROC*
[e] *Carbon Cycle Research Center, National Taiwan University, Taiwan, ROC*

HIGHLIGHTS

- The effect of reaction time, temperature and L/S ratio on conversion was evaluated.
- CO_2 mass balance in slurry reactor was established with an error of less than 10%.
- Reaction kinetics and effective diffusivity for carbonation were determined by SCM.
- The maximum conversion was predicted by RSM via nonlinear mathematical programming.
- Applications and limitations of SCM and RSM for BOFS carbonation were illustrated.

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ABSTRACT

Basic oxygen furnace slag (BOFS) exhibits highly alkaline properties due to its high calcium content, which is beneficial to carbonation reaction. In this study, accelerated carbonation of BOFS was evaluated under different reaction times, temperatures, and liquid-to-solid (L/S) ratios in a slurry reactor. CO_2 mass balance within the slurry reactor was carried out to validate the technical feasibility of fixing gaseous CO_2 into solid precipitates. After that, a multiple model approach, i.e., theoretical kinetics and empirical surface model, for carbonation reaction was presented to determine the maximal carbonation conversion of BOFS in a slurry reactor. On one hand, the reaction kinetics of BOFS carbonation was evaluated by the shrinking core model (SCM). Calcite ($CaCO_3$) was identified as a reaction product through the scanning electronic microscopy and X-ray diffraction analyses, which provided the rationale of applying the SCM in this study. The rate-limiting step of carbonation was found to be ash-diffusion controlled, and the effective diffusivity for carbonation of BOFS in a slurry reactor were determined accordingly. On the other hand, the carbonation conversion of BOFS was predicted by the response surface methodology (RSM) via a nonlinear mathematical programming. According to the experimental data, the highest carbonation conversion of BOFS achieved was 57% under an L/S ratio of 20 mL g^{-1}, a CO_2 flow rate of 0.1 L min^{-1}, and a pressure of 101.3 kPa at 50 °C for 120 min. Furthermore, the applications and limitations of SCM and RSM were examined and exemplified by the carbonation of steelmaking slags.

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1. Introduction

Recently, scientists have found that an increase of greenhouse gas in the atmosphere enhances global warming (Cubasch et al., 2013). The global mean surface temperature rose 0.075 ± 0.013 °C per decade from 1901 to 2012, while the concentration of carbon dioxide (CO_2) in the atmosphere increased from 275 to 391 ppm

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* Corresponding author. Graduate Institute of Environmental Engineering, National Taiwan University, Taiwan, ROC.
E-mail addresses: d00541004@ntu.edu.tw (S.-Y. Pan), r98541126@ntu.edu.tw (H.-L. Liu), eechang@tmu.edu.tw (E.-E. Chang), h_kim@uos.ac.kr (H. Kim), yhchen1@ntut.edu.tw (Y.-H. Chen), pcchiang@ntu.edu.tw (P.-C. Chiang).

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over the past 250 years (Hartmann, 2013). Therefore, carbon capture, utilization and storage (CCUS) become one of the critical strategies that retard the rate of CO_2 discharge. There are numerous carbon capture methods developing by different groups, such as chemical and physical absorption (Yu et al., 2012), gas-separating membranes (Klemeš et al., 2007), and mineralization (Pan et al., 2012). Among CCUS methods, CO_2 mineralization appears to be an environmentally friendly alternative for both CO_2 capture and storage because it can not only reduce the CO_2 emission but also convert CO_2 to stable precipitates (Sanna et al., 2014). The energy for formation of gaseous CO_2 (i.e., -400 kJ mol^{-1}) can decrease to around -1100 kJ mol^{-1} as solid $CaCO_3$ precipitates (Brady, 1996). It has been demonstrated that the mineralization process using natural ores or industrial solid waste is superior in providing higher storage capacity and longer storage time (Seifritz, 1990; Lackner, 2003; Bobicki et al., 2012). According to the report by Lackner (2003), although there are natural ores on Earth to sequester the CO_2 emissions from all fossil fuels, cost-effective methods for accelerating carbonation are required to develop.

Industrial solid wastes, such as steelmaking slag, are relatively cheaper feedstock than natural ores. Therefore, CO_2 fixation capacity of steelmaking slag through carbonation process has been evaluated (Bonenfant et al., 2008; Teir, 2008; Pan et al., 2013b; Santos et al., 2013). Since steelmaking slag is chemically unstable with high calcium content, it can be readily hydrated and reacted with CO_2 to form carbonates (Lekakh et al., 2008). For instance, the fraction of calcium leaching from steelmaking slag was 97%, when acetic acid was used as extractant (Eloneva et al., 2012). In addition, a carbonation conversion of 80% was achieved by using steelmaking slag with a particle size less than 38 μm under a pressure of 1.0 MPa at 200 °C for 15 min (Huijgen et al., 2006). Beside the studies of leaching and carbonation behaviors for steelmaking slag, different novel approaches, such as two-step pH swing (Mattila et al., 2012), are developed to produce pure calcium carbonate precipitates for further utilization.

Identifying the effect of key operating factors on carbonation performance is crucial to reaction design and system optimization. There are several theoretical models available for evaluating the performance of carbonation using a CaO-based material, such as random pore model (Bhatia and Perlmutter, 1983), overlapping grain model (Liu et al., 2012), shrinking core model (Lekakh et al., 2008), and surface coverage model (Pan et al., 2014). For the sake of simplicity, different assumptions were made by each model to avoid complicate calculation. This study presents a multiple model approach, i.e., theoretical kinetics and empirical mathematical equation, to determining the maximal carbonation conversion of BOFS in a slurry reactor. The objectives of this research were (1) to evaluate the effect of various operating factors, i.e., reaction temperature, liquid-to-solid (L/S) ratio and reaction time, on the carbonation conversion of BOFS in a slurry reactor; (2) to determine the reaction kinetics and rate-limiting step by applying a shrinking core model (SCM); (3) to predict the carbonation performance by response surface methodology (RSM) using a nonlinear optimization program; and (4) to examine the applications and limitations of SCM and RSM exemplified by the carbonation of steelmaking slags.

2. Materials and methods

2.1. Materials

The ground BOFS was provided by the China Hi-ment Corporation (Kaohsiung, Taiwan). The ground BOFS was sieved by a standard sieve with mesh #325 (i.e., < 44 μm). After sieving, BOFS samples were placed in an oven at 105 °C to eliminate surface moisture and then collected in an air-tight bag. Deionized (DI) water (18.2 MΩ cm^{-1}) was produced by the Water Still Apparatus (Chemist, A4DL, Taiwan). In addition, high-pressure CO_2 with 99% purity was supplied by Ch'ing-Feng Gas Corporation (Taipei, Taiwan).

2.2. Experiment

Fig. S1 (see Supporting Information) shows a schematic diagram of the slurry reactor system used for the BOFS carbonation. The slurry reactor was a glass column 0.20 m in height and 0.08 m in diameter, and the sampling port was located 0.02 m above the bottom of the reactor. Different amounts of fresh BOFS samples were mixed with 250 mL of DI water in the slurry reactor. According to the previous study (Chang et al., 2011), the CO_2 flow rate was set at 0.1 L min^{-1} under atmospheric pressure by a mass flow controller (MC-1SLPM-D, Alicat Scientific Inc., USA) for providing sufficient mass transfer rate of CO_2 in the slurry within the similar size of reactor. The reaction temperature was automatically controlled by a stirring and heating plate (PC-420D, Corning, Mexico).

To evaluate the effect of operating factors on carbonation performance in a slurry reactor, a response surface was introduced using the response surface methodology (RSM) coded with Design Expert 8.0 software (Stat-Ease, Inc., USA). The operating factors for the slurry reactor system considered in this study include reaction temperature (i.e., 30, 40, 50, 60 and 70 °C), L/S ratio (i.e., 5, 10 and 20 mL g^{-1}), and reaction time (i.e., 5, 10, 20, 40, 60 and 120 min). These factors, i.e., temperature, L/S ratio, and reaction time, were coded as high ($+1$) and low (-1) levels in the RSM.

2.3. Characterization of BOFS

The composition of fresh BOFS was analyzed at the Chemistry Analysis Laboratory in China Hi-ment Corporation, Kaohsiung, Taiwan. Acetic acid and phosphoric acid were used for digesting various ingredients in BOFS samples. A micro-digestion method was applied at high temperature and pressure to ensure completely dissolution of BOFS samples. The concentrations of various metal ions in the extracted solution were measured by an inductively coupled plasma optical emission spectroscopy (ICP-OES).

After carbonation, the reacted BOFS slurry sample was filtered with a 0.45 μm membrane to separate the solid and liquid phases. The solid sample was then dried in an oven at 105 °C for 1 d to completely remove moisture. The dried BOFS samples were analyzed by thermogravimetric analysis (TGA), scanning electronic microscopy (SEM), and X-ray diffraction (XRD). In contrast, the concentrations of metal ions in the filtrate (i.e., liquid phase) were measured with an atomic absorption spectrometer (AAS, PerkinElmer AA800, USA). In addition, the concentration of total inorganic carbon (TIC) in the liquid phase was determined using an Aurora 1030W TIC Analyzer (O.I. Analytical, Canada).

The surface micro-structure of the BOFS samples before and after carbonation was analyzed by SEM (Hitachi S-800, Tokyo, Japan). In addition, XRD (X' Pert Pro, PANalytical, Almelo, The Netherlands) was applied to identify and characterize crystalline materials using monochromatic X-rays. The XRD patterns of a BOFS sample before and after the carbonation reaction were collected from 20° to 80° with a scanning time of 1 s per step.

2.4. Determination of carbonation conversion of BOFS using thermal analysis

TGA (TGA-51, Shimadzu, Kyoto, Japan) was used to determine the carbonation conversion of BOFS before and after carbonation. A modified TG-DTG interpretation method (Pan et al., 2016) was applied to determine the weight fraction of $CaCO_3$, expressed as CO_2 (wt.%) in Eq. (1):

$$CO_2(wt.\%) = \frac{m_{500^\circ C} - m_{850^\circ C}}{m_{t=0}} \times 100 \quad (1)$$

where $m_{500^\circ C}$ (mg) and $m_{850^\circ C}$ (mg) are the weight of the samples measured at 500 °C and 850 °C in TGA, respectively. The $m_{t=0}$ (mg) is the weight of the specimen measured at 105 °C.

It has been reported that $CaCO_3$ is the main product from the carbonation of Ca–Mg-bearing silicate mineral (Uibu et al., 2011; Chang et al., 2012; Pan et al., 2012). Due to the similar composition of BOFS, it was assumed that only calcium components would be carbonated during the carbonation process in the slurry reactor. Therefore, the carbonation conversions of BOFS (δ_{CaO}), i.e., the fraction between the CaO reacting with CO_2 and the original CaO in fresh BOFS, can be determined by Eq. (2):

$$\delta_{CaO}(-) = \frac{CO_2(wt.\%)}{1 - CO_2(wt.\%)} \times \frac{1}{MW_{CO_2}} \times \frac{MW_{CaO}}{CaO_{fresh}} \quad (2)$$

where MW_{CaO} and MW_{CO2} are the molecular weights of CaO (i.e., 56 g mol^{-1}) and CO_2 (i.e., 44 g mol^{-1}), respectively; and CaO_{fresh} is the CaO content of a fresh BOFS sample.

2.5. Non-linear programming for maximization of carbonation conversion

A non-linear program was formulated to estimate the maximum carbonation conversion of BOFS in a slurry reactor. The carbonation conversion of BOFS (δ_{CaO}) should be a function of different operating parameters with interaction terms. According to the Weierstrass theorem (Weierstrass, 1885; Stone, 1948), δ_{CaO} has a global optimality in set S, if δ_{CaO} is continuous on feasible S, which is closed and bounded. Therefore, considering the objective of maximizing δ_{CaO} (X_1,X_2) subject to equality constraint h_i (X_1,X_2) converting from inequality constants s_i^2, it is convenient to write these conditions in terms of a Lagrange function defined as L (X_1,X_2, u) in Eq. (3):

$$L(X_1, X_2, u, s) = \delta_{RSM}(X_1, X_2) + \sum_{i=1} u_i h_i(X_1, X_2, s) \quad (3)$$

where X_1 and X_2 are the different operating factors. u_i (−) is the Lagrange multipliers, which can be either positive, negative, or zero. Therefore, the maximum δ_{CaO} (X_1,X_2) should be equal to maximum L (X_1,X_2, u, s) if the constraints were satisfied. Based on the necessary conditions of the Lagrange Multiplier Theorem, i.e., $L'(x^*) = 0$ and $L''(x^*) < 0$, respectively, the gradients of L (X_1,X_2, u, s) function were determined as follows:

$$\nabla L_{X_1}(x)|_{x=x^*} = \frac{\partial\delta(x^*)}{\partial X_1} + \sum_{i=1} u_i^* \frac{\partial h_i(x^*)}{\partial X_1} = 0 \quad (4)$$

$$\nabla L_{X_2}(x)|_{x=x^*} = \frac{\partial\delta(x^*)}{\partial X_2} + \sum_{i=1} u_i^* \frac{\partial h_i(x^*)}{\partial X_2} = 0 \quad (5)$$

$$\nabla L_u(x)|_{x=x^*} = h_i(x^*) = 0 \quad (6)$$

$$\nabla L_s(x)|_{x=x^*} = u_i^* \frac{\partial h_i(x^*)}{\partial s} = 0 \quad (7)$$

where x^* is the optimal solution set for the carbonation of BOFS. Any point that does not satisfy the conditions of the Lagrange Multiplier Theorem can not be a maximum point.

3. Results and discussion

3.1. Effect of reaction time, temperature and L/S ratio on carbonation conversion

Table 1 presents the physico-chemical properties of the BOFS used in this study and in the literature. The composition of BOFS varies from one experiment to another due to the different operating conditions applied to the steelmaking processes. In this study, the particle size distribution of the BOFS ranged from 25 to 125 μm, with a median diameter of 53 μm. The BOFS exhibits highly alkaline properties, where the pH value of the BOFS slurry was 12.0–12.6. According to the XRF analysis, the major elements in the BOFS included calcium, silicon, aluminum, iron, and magnesium. Based on the available methods for determining CO_2 fixation capacity in mortars/concrete and cement kiln dust reported by Steinour (1959) and Huntzinger et al. (2009), respectively, the theoretical CO_2 fixation capacity ($ThCO_2$, as a percentage of dry mass) of BOFS can be estimated *via* Eq. (8). It was assumed that all of the CaO content in the fresh BOFS, except that originally bound in $CaSO_4$ and $CaCO_3$ phases, will convert to $CaCO_3$ *via* the carbonation reaction. According to the physico-chemical properties of BOFS, the $ThCO_2$ of the BOFS was estimated to be 0.399 kg CO_2 per kg BOFS.

$$\%ThCO_2 = 0.785 \times (\%\,CaO - 0.56 \times \%\,CaCO_3 - 0.7 \times \%\,SO_3) \quad (8)$$

Aqueous carbonation is a neutralization reaction and occurs spontaneously. The affinity of each chemical element for the carbonate formation depends on its total content and solubility product constant. Therefore, prior to the carbonation experiment, the concentrations of dissolved reactive elements, such as calcium and magnesium that leached from the BOFS into solution were measured. Fig. S2 (see Supporting Information) shows the concentrations of calcium and magnesium in the filtered solution of BOFS slurry after 60 min mixing at various L/S ratios at 20 °C, without supplying CO_2 to the slurry reactor. The magnesium contents leached from BOFS was relatively much lower than that of calcium. Similarly, the leaching concentrations of other metal ions, such as iron and nickel, were significantly lower than calcium ions, where the amount of carbonate formation could be neglected (Pan et al., 2013a). The other components, such as SiO_2 and P_2O_5, in the fresh BOFS would not contribute to CO_2 fixation. It thus suggests that the calcium-bearing components should be the major components reacting with CO_2 in this study.

In the case of L/S = 2, the total calcium content from BOFS into solution should be 182.5 g/L, based on the XRF measurement in Table 1. However, the measured leaching concentration of calcium was about 890 ppm, equivalent to a fraction of calcium leaching from the BOFS = 0.5%, indicating an incomplete hydration of calcium-bearing compounds from the BOFS. In the case of L/S = 20, the fraction of calcium leaching from the BOFS slightly increased to 4.0%. If the solubility of pure calcium oxide (i.e., lime) at 20 °C was assumed to be 1.25 g/L (Zumdahl, 2009), the theoretical concentration of calcium ions in water should be 892.9 mg/L, which indicated that the content of lime might be essentially controlling the solubility of CaO-related species in BOFS. In other words, the calcium leaching should be a solubility-controlled step, as a result of equilibrium with specified mineral phases, thereby resulting in an almost constant concentration in solution irrespective of the L/S ratio.

The CO_2 mass balance was carried out in the slurry reactor by measuring the CO_2 loss in the gas phase as well as the increase of

Table 1
Physico-chemical properties of fresh BOFS used in this study and those in the literature.

	Item	Unit	This study	Chiou et al. (2006)	Pan et al. (2012)	Belhadj et al. (2012)
Physical properties	Density	g/cm^3	3.00	–	–	3.70
	BET surface area	m^2/g	3.10	–	–	0.38
	Mean diameter	μm	53.0	–	–	8.5
	Molar weight	g/mol CaO	109.6	108–124	100–121	124.4
Chemical properties	pH	–	11.9–12.5	–	11.5–12.4	–
	δ_{CaO}[a]	%	2.2	–	–	2.9
	LOI[b]	%	–	–	–	1.1
	Free-lime	%	5.2	–	–	6.8
XRF analysis	SiO_2	%	11.2	13–16	9.3–12.9	10.8
	Al_2O_3	%	1.2	0.9–1.7	1.1–2.0	1.9
	Fe_2O_3	%	24.0	6–28	22.7–25.3	32.0
	CaO	%	51.1	45–52	46.3–55.9	45.0
	MgO	%	4.2	4–6	2.1–6.3	4.5
	MnO	%	–	4–7	–	2.6
	P_2O_5	%	–	1.6–2.1	–	1.4
	SO_3	%	0.4	0.1–0.2	0–0.7	0.4
	TiO_2	%	–	0.4–0.9	–	0.5

[a] Carbonation conversions of BOFS.
[b] LOI = loss of ignition.

inorganic carbon content in both the liquid (i.e., TIC concentration) and solid phases (i.e., $CaCO_3$ content). Since the CO_2 concentration in the input and output should be 99.9%, the amounts of CO_2 fixed by the slurry reactor can be determined by the difference in the volumes of the gas flows measured at the inlet and outlet of the slurry reactor. The results of the CO_2 mass balance for the slurry reactor are shown in Fig. 1, which clearly indicates that the CO_2 can be effectively fixed by the carbonation reaction of BOFS, with an error of less than 10%. It was noted that most of the gaseous CO_2 should be fixed as $CaCO_3$ precipitate (i.e., solid phase) in aqueous carbonation using steelmaking slag (Pan et al., 2013b).

Fig. 2a–2c show the effects of the reaction time and temperature on the carbonation conversion at L/S ratios of 5, 10 and 20 mL g^{-1}, respectively. A rapid reaction was observed in the first 20 min, and the reaction equilibrium could be reached within 40 min. After 120 min, the CO_2–H_2O-BOFS system reached stable pH values of 6.3–6.5, which is the pH value of pure water in equilibrium with atmospheric CO_2. The highest BOFS carbonation conversion of 57% could be achieved at an L/S ratio of 20 mL g^{-1}, a reaction temperature of 50 °C and a reaction time of 120 min in a slurry reactor. However, similar levels of carbonation conversion were observed for all tested L/S ratios. A relatively higher carbonation conversion was observed at a higher L/S ratio of 20. However, the effect of L/S ratio on the carbonation conversion of BOFS at equilibrium in a slurry reactor was not significant, which should be attributed to the solubility -controlled release of reactive elements from the BOFS.

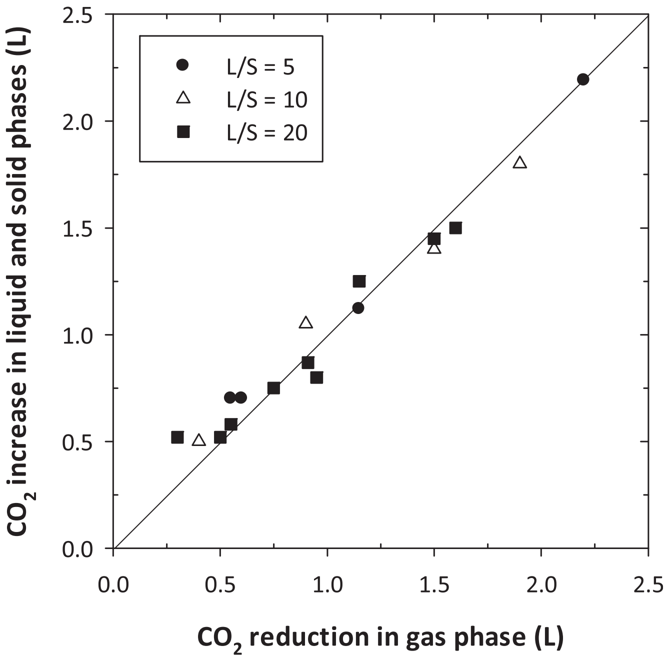

Fig. 1. CO_2 mass balance among the gas, liquid and solid phases in the slurry reactor (carbonation conditions: $P_{CO2} = 14.7$ psia; CO_2 flow rate = 0.1 L min^{-1}).

3.2. *Carbonation kinetics: shrinking core model (SCM)*

Shrinking core model (SCM), developed by Sohn and Szekely (1973), has been applied for kinetic analysis of heterogeneous reactions such as the carbonation reactions of solid particles (Lekakh et al., 2008; Chang et al., 2011). The governing equations of possible rate-determining steps, including chemical reaction (C-mechanism), ash-layer diffusion (A-mechanism), and fluid-film diffusion (F-mechanism) were described in the SCM. It was assumed that the reaction occurs first at the outer layer of the BOFS and then proceeds into the inside of the BOFS, leaving behind the completely reacted product and the reactive-species-depleted (i.e., "ash" or "product") layer (Lekakh et al., 2008; Chang et al., 2011, 2013).

When the chemical reaction between reactants is the rate-limiting step, Eq. (9) shows the relationship between the carbonation conversion of BOFS (δ_{CaO}) and reaction time (t, sec)

$$t = \tau_C \times \left[1 - (1 - \delta_{CaO})^{1/3}\right] \tag{9}$$

When the diffusion of carbonate ions (i.e., reactant) through the ash layer is the rate-limiting step, the relationship between the conversion and reaction time can be illustrated by Eq. (10):

$$t = \tau_A \times \left[1 - 3(1 - \delta_{CaO})^{2/3} + 2(1 - \delta_{CaO})\right] \tag{10}$$

When the mass transfer of the reactants through the boundary layer at the liquid–solid interface is the rate-limiting step, Eq. (11) shows the dependence of the reaction time on the conversion:

$$t = \tau_F \times \delta_{CaO} \tag{11}$$

where τ_C, τ_A, and τ_F (min) are the time required for complete

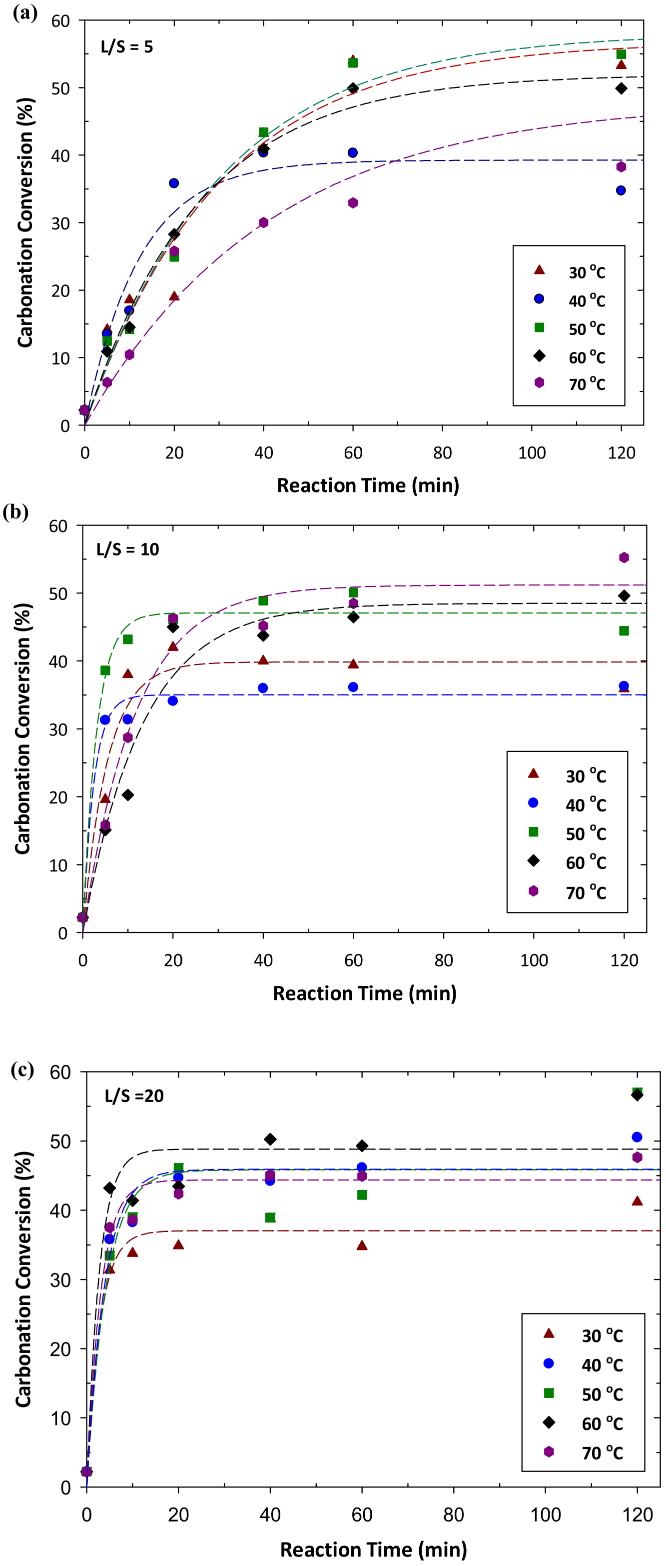

Fig. 2. Influence of reaction time and temperature on the carbonation conversion with an L/S ratio of (a) 5, (b) 10 and (c) 20 mL g^{-1} (carbonation conditions: $P_{CO2} = 14.7$ psia CO_2; CO_2 flow rate = 0.1 L min^{-1}). The carbonation conversion of fresh BOFS was approximately 2.2%, as indicated at t = 0 min. The models of interpolating lines for experimental data were based on the shrinking core model.

conversion of BOFS to product, i.e., $\delta_{CaO} = 1$, for the mechanisms of chemical reaction, ash-layer diffusion, and film diffusion, respectively.

The results indicated that the ash-layer diffusion was identified as the rate-determining step [Eq. (10)] for carbonation in a slurry reactor, based on the R^2 value of regression. Therefore, for this mechanism, the relationship of τ_A and the effective diffusivity of the reactant through the ash layer (D_e, $cm^2\ s^{-1}$) can be determined by Eq. (12):

$$\tau_A = \frac{\rho_B R_p^2}{6bD_eC_{Ag}} \qquad (12)$$

where R_p (cm) is the radius of the BOFS particles. b (−) is stoichiometric coefficient of a fluid-solid reaction, which was assigned as one in this study. ρ_B (mol cm^{-3}) is the molar density of BOFS. C_{Ag} (mol cm^{-3}) is the concentration of CO_2 in the solution. Fig. 3 shows the effect of L/S ratio and reaction temperature on the D_e values according to the SCM results. In general, the D_e value increased as the reaction temperature and L/S ratio increased. The D_e values for carbonation of BOFS at an L/S ratio of 20 ranged from 1.4×10^{-6} to 2.8×10^{-5} $cm^2\ min^{-1}$ at temperatures of 30–70 °C.

Fig. 4a and 4b show the SEM images of the BOFS before and after carbonation, respectively. After carbonation, crystal precipitates of small $CaCO_3$ particles were formed on the surface of the BOFS. Parts of the $CaCO_3$ product appear to be isolated and separated, with a size of 1–3 μm, which was similar to the findings in the literature (Chang et al., 2012). Combined with the results of XRD, the reaction products coating the BOFS surface was identified as pure calcite, as shown in Fig. S3 (see Supporting Information), which is evident that the calcite precipitate was formed a protective layer around the particles, indicating the rationale for applying the SCM in this study. The above phenomena were in good agreement with the literature (Fernandez Bertos et al., 2004), where the carbonation reaction would lead the reacted solid with a lower porosity, tortuosity, and pore area due to the formation of calcite. It thus suggests that the carbonation of BOFS in a slurry reactor should be controlled by ash diffusion, which was verified through the SEM images of the BOFS surface structure taken during the carbonation.

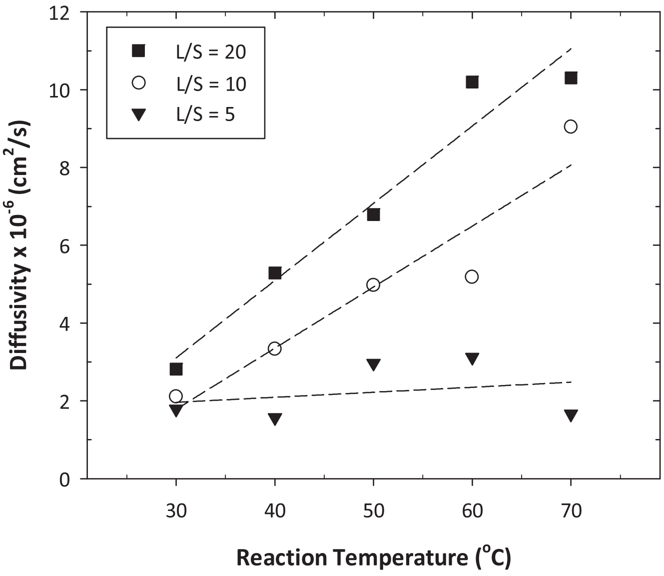

Fig. 3. Effective diffusion coefficients obtained from SCM at different temperatures and L/S ratios (carbonation conditions: CO_2 pressure = 14.7 psia; CO_2 flow rate = 0.1 L min^{-1}).

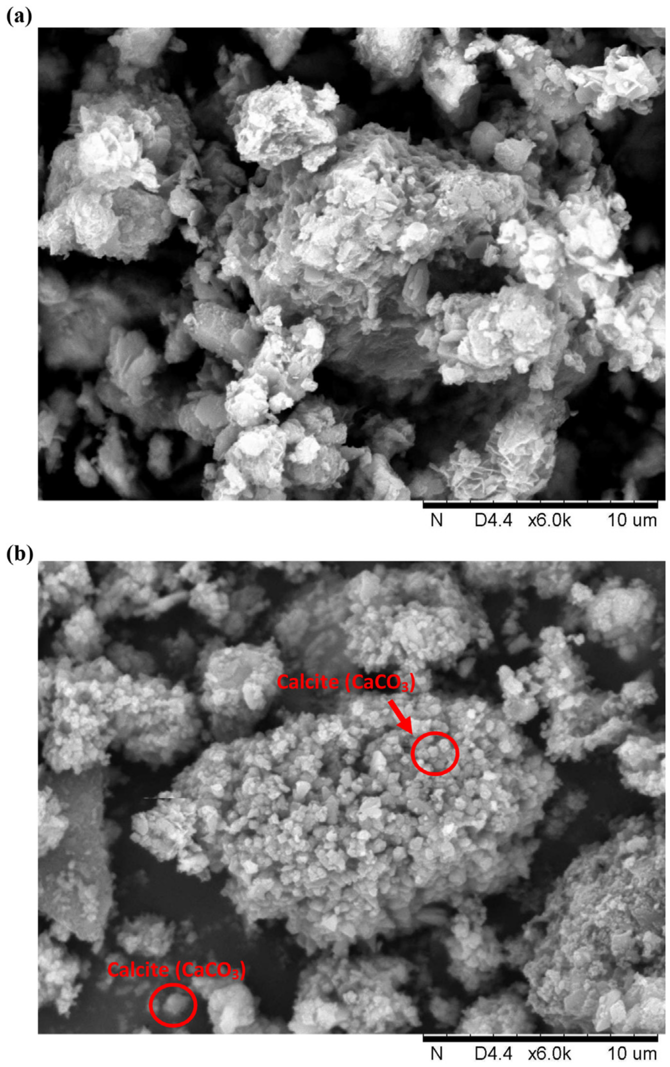

Fig. 4. SEM images of BOFS (a) before and (b) after carbonation in 10,000X (carbonation conditions: CO_2 pressure = 14.7 psia; L/S = 10; reaction time = 60 min; 50 °C).

3.3. Maximal carbonation conversion: response surface model (RSM)

In addition to the theoretical kinetic model using SCM, the RSM, from the statistics point of view, was also introduced to evaluate the effect of the relating operational parameters, including reaction time, temperature, and L/S ratio on the carbonation conversion of BOFS. The carbonation conversion of BOFS in a slurry reactor predicted by the developed response surface mode (δ_{RSM}) can be expressed as Eq. (13):

$$\delta_{RSM,coded}(\%) = 47.87 + 5.39A - 0.1B + 16.88C - 2.55AB + 3.58AC + 6.55\,BC - 5.36A^2 - 0.91B^2 - 19.19C^2 \tag{13}$$

where A (coded) is the reaction temperature, B (coded) is the L/S ratio, and C (coded) is the reaction time. A quadratic model was found to be the best fitted one because the p-value of model was less than 0.0001. Table S1 (see Supporting Information) presents the ANOVA results of the developed response surface, which indicate that the standard deviation and the mean value of the RSM were 6.1 and 37.0, respectively, with R^2 of 0.91. Fig. 5a presents the comparison of predicted conversion by the developed RSM with experimental data. The result indicates that the experimental data can be well described by the RSM. The reaction time was found to be the most significant factor affecting the carbonation conversion of BOFS in a slurry reactor. Compared to the L/S ratio, the reaction temperature exhibits relatively more influence on the carbonation conversion of BOFS.

A non-linear program (see details in Section 2.5) was formulated to evaluate the developed response surface model for carbonation conversion of BOFS (δ_{RSM}) in a slurry reactor. To maximize the objective function of δ_{RSM} (A,B,C), the Lagrange function of L (A, B, C, u, s) can be expressed as Eq. (14):

$$L(A, B, C,\ u, s) = \delta_{RSM}(A, B, C) + \sum_{i=1} u_i \cdot h_i(A, B, C, s) \tag{14}$$

where A, B and C are the coded operating factors for temperature, L/S ratio and reaction time in the response surface model, respectively. In the following analysis, the reaction time was designated to be 120 min, i.e., C = 1 in Eq. (14) because the carbonation conversion normally increases with the increase of reaction time. Based on the necessary conditions of the Lagrange Multiplier Theorem [Eqs. (4) to (7)], eight candidate points may be obtained as a solution. In the case of $h_1 = 0$, for instance, the conditions can be determined by Eqs. (15) to (17):

$$\nabla L_{A,B}(x)|_{x=x^*} = \begin{bmatrix} \frac{\partial L}{\partial A} \\ \frac{\partial L}{\partial B} \end{bmatrix}_{x=x^*} = \begin{bmatrix} -10.72A - 2.55B + 8.97 \\ -2.55A - 1.82B + 6.45 + u_1 \end{bmatrix}_{x=x^*} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{15}$$

$$\nabla L_u(x)|_{x=x^*} = \frac{\partial L}{\partial u_1} = B - 1 + s_1^2 = 0 \tag{16}$$

$$\nabla L_s(x)|_{x=x^*} = \frac{\partial L}{\partial s_1} = 2u_1 s_2 = 0 \tag{17}$$

The temperature and L/S ratio for optimality were determined to be 62 °C (i.e., A = 0.6) and 20 mL g^{-1} (i.e., B = 1.0), respectively, where the s_1 and u_1 values were 0 and −3.1, respectively. The obtained results should meet the sufficient conditions of optimality by taking the Hessian matrix of Eq. (14), as shown in Eq. (18):

$$H(x)|_{x=x^*} = \begin{bmatrix} \frac{\partial^2 L}{\partial A^2} & \frac{\partial^2 L}{\partial A \partial B} \\ \frac{\partial^2 L}{\partial B \partial A} & \frac{\partial^2 L}{\partial B^2} \end{bmatrix} = \begin{bmatrix} -1.82 & -2.55 \\ -2.55 & -10.72 \end{bmatrix} < 0 \tag{18}$$

Since the function of carbonation conversion was found to be negative definite, the determined condition of Eq. (14) resulted in the maximal value. It was predicted that the maximum carbonation conversion of BOFS in a slurry reactor for 120 min should be 53.0%, as shown in Fig. 5b. It was noted that higher carbonation conversion of BOFS could be achieved if the alkaline wastewater was introduced as a liquid agent due to the sodium and chloride ions present in the wastewater (Krevor and Lackner, 2011; Pan et al., 2013a).

3.4. Integration of SCM and RSM: applications and limitations

In this study, two different approaches, i.e., SCM (from the kinetic point of view) and RSM (from the statistics point of view),

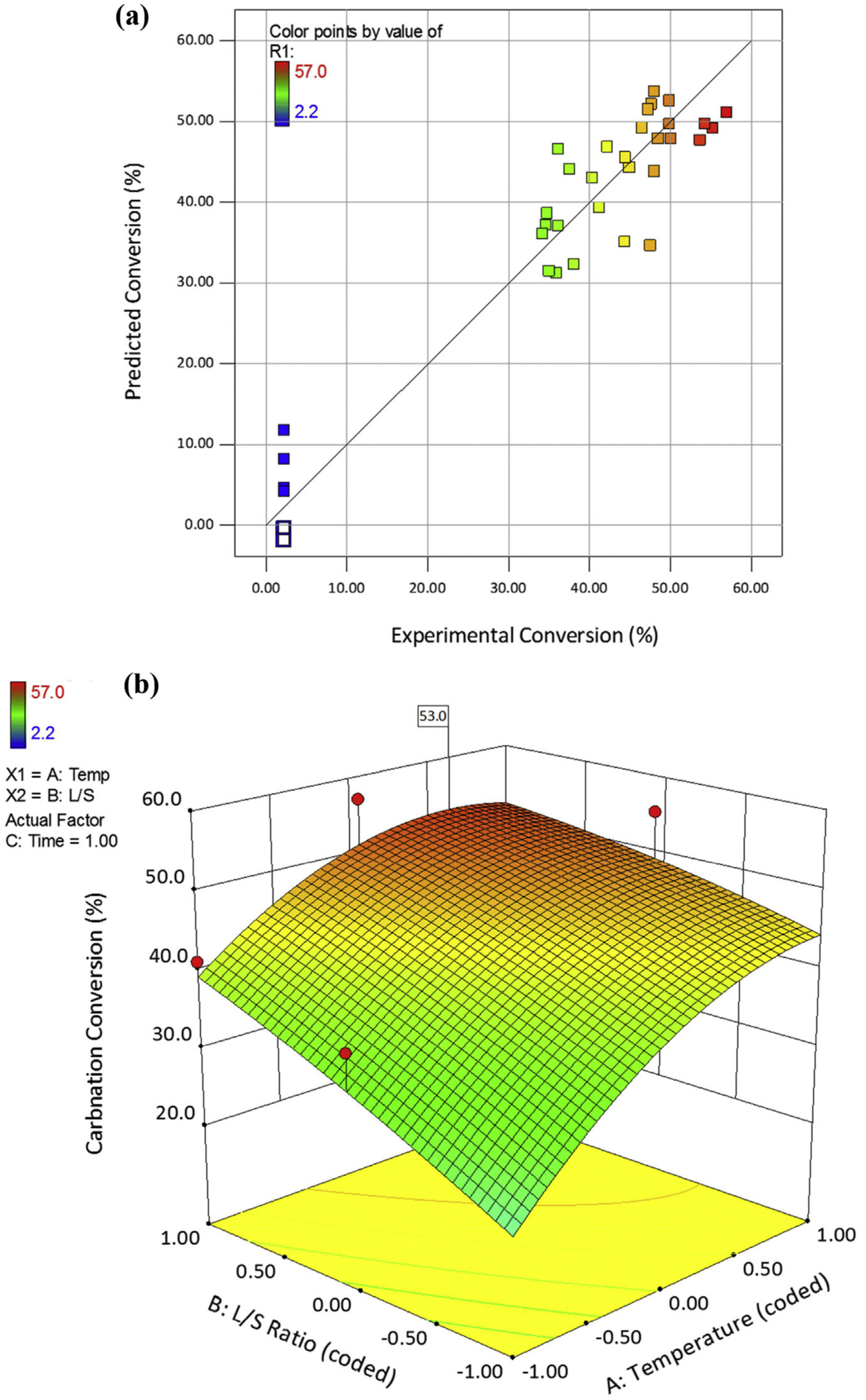

Fig. 5. (a) Comparison of predicted value by response surface model and experimental data; and (b) 3D response surface plot of various operating factors and conversion of BOFS in a slurry reactor.

were utilized to evaluate the effect of operating factors on carbonation conversion of BOFS. SCM has been used to determine the rate-limiting step in a heterogeneous reaction because of its conceptual and mathematical simplicity. The additional contribution of the SCM is that the key design parameter of reactor, i.e., diffusivity of the reactant, can be obtained for process scale-up and system optimization. Likewise, RSM is developed based on the experimental design from the statistics point of view to predict the maximal response of system performance. In this study, based on the developed RSM, several candidates were revealed to determine the maximum carbonation conversion, which indicated that the conversions predicted by the RSM were in good agreement with the experimental data. However, using the same operating conditions of candidates as suggested by the RSM, the predicted carbonation conversions of BOFS by the SCM were slightly lower than that by the RSM, as shown in Fig. S4 (see Supporting Information). As a result, the empirical RSM model was found to be much closer to the real behavior and performance of carbonation, compared to the SCM.

In the SCM, there is an inherent assumption that complete carbonation conversion of BOFS should be eventually reached. However, from the experimental data in a slurry reactor, it was observed that the full carbonation conversion of BOFS will never occur, with increasing time. This implies that other factors, such as mineralogy of particles, particle size changes, and pore blockage should be considered in addition to the diffusion limit of reactants into the BOFS. For instance, the mineralogical composition of BOFS are complex (Costa, 2009), where some of minerals do not react during carbonation. In addition, to consider the particle size distribution, both "Z factor [Eq. (19)]" (Sohn, 2004) and a "λ factor [Eq. (20)]" (Li et al., 2015) were introduced to describe the relationship between the modified particle conversion (δ_{CaO}) and reaction time (t).

$$t = \tau_A \times \left[\frac{Z - (Z - (Z - 1)(1 - \delta_{CaO}))^{2/3}}{(Z - 1)/3} - 3\,(1 - \delta_{CaO})^{2/3}\right] \tag{19}$$

$$\delta_{CaO} = 1 - \int_{\left(\frac{t}{-\lambda}\right)^{\frac{1}{\eta - D}}}^{r_{0,\,max}} \frac{\left(\frac{t}{\lambda} + r^{\eta - D}\right)^{\frac{\eta}{\eta - D}}}{r^{\eta}} f(r)dr \tag{20}$$

where Z is the volume of product solid formed from a unit volume of reactant solid, r is the particle size, D is the fractal dimension of the particle external surface (i.e., $D \in [2, 3]$), η is a function of fractal dimension. It was noted that if the particle sizes remained unchanged in the course of reaction, then these modified models should be identical to the traditional SCM.

Furthermore, the buffering capacity of the BOFS slurry will change with the different L/S ratios and reaction times, thereby resulting in different reactant concentrations (C_{Ag}) in solution because the C_{Ag} also changes as a function of pH. This implies that the diffusion coefficient should be time-dependent since the diffusion rate is a function of concentration gradient. On the other hand, from the application of RSM, the operating factor used in the experiments (i.e., L/S ratio) determined as the optimum conditions might be peripheral, which means that the model does not predict the values outside the assigned experimental ranges. Therefore, to improve the accuracy and precision of both SCM and RSM for accelerated carbonation of alkaline wastes, the above limitations should be critically accounted for in the future.

4. Conclusions

In this study, different operating factors, including temperature, L/S ratio and reaction time, were evaluated for CO_2 capture by aqueous carbonation of BOFS in a slurry reactor. The results showed that the CO_2 mass balance determined for the slurry reactor was accurate and the relative percent differences was less than 10%, indicating that CO_2 was effectively fixed and removed by the carbonation. The fraction of calcium leaching from the BOFS into water was approximately 4%, indicating an incomplete hydration of calcium-bearing compounds from the BOFS. In addition, the highest carbonation conversion of BOFS in a slurry reactor was experimentally found to be 57% with an L/S ratio of 20 mL g^{-1} at 50 °C for 120 min. Based on the observations of SEM and XRD, the reaction product formed on the surface of BOFS particles was identified as pure calcite ($CaCO_3$). According to the shrinking core model (SCM) results, the rate-limiting step of the aqueous carbonation of BOFS in a slurry reactor was found to be the diffusion of carbonate ions through the ash layer. Furthermore, the maximum carbonation conversion of BOFS was determined by the response surface model with a non-linear optimization program. The maximum carbonation conversion of BOFS was predicted to be 53.0%, indicating that the predicted results were in good agreement with the experimental data. Whereas, for system optimization, the key performance indicators, such as reactor capacity, processing costs, and environmental impacts and benefits, from the 3E (Engineering, Environmental, and Economic) perspectives should be considered in our future research.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.03.093.

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