

Investigation of a Two-Stage Aqueous Reactor Design for Carbon Dioxide Sequestration Using Steelmaking Slag

S.N. LEKAKH, D.G.C. ROBERTSON, C.H. RAWLINS, V.L. RICHARDS,
and K.D. PEASLEE

Hydrous carbonate sequestration of carbon dioxide using steelmaking slag was studied using a METSIM process model to analyze experimental data and estimate the reactor operating results. Several scenarios of a two-stage system with water/slag contact in reactor 1 and leachate/carbon dioxide contact in reactor 2 were investigated. These scenarios included batch vs continuous processing and fresh water input vs water recirculation. The METSIM leaching and carbonation models were verified with results obtained from previous slag sequestration experiments. Fresh water additions to reactor 1 allowed the highest leaching efficiency and resulted in excellent carbonation in reactor 2, but a continuous system has a high water demand. Recirculation of the spent leachate minimizes the fresh water addition required, but inhibits the leaching process by producing a calcium carbonate product layer on the slag particles in reactor 1. Increasing the slag surface area, slag/solution ratio, or reactor residence time partially overcomes product layer “blinding.” Optimal residence times were defined for different process parameters and slag particle sizes.

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I. INTRODUCTION

STEELMAKING slag contains a high fraction of alkaline-earth oxides that exothermically form carbonates, making this material an excellent vehicle for sequestering carbon dioxide. It has the potential to sequester 35 to 45 pct of the carbon dioxide generated from electric arc furnace production and 6 to 11 pct of the carbon dioxide generated from basic oxygen furnace production.^[1] Extraction of carbon dioxide from steel manufacturing off gas using steelmaking slag was studied by quantifying the extent and rate of carbonate formation under near-atmospheric aqueous conditions.^[2] Because the natural carbonate formation kinetics are very slow, fine grinding to increase slag surface area, increasing pCO₂, increasing temperature, and aqueous catalysis are being investigated as a means of increasing the reaction rate to a level suitable for industrial use.^[3] The goal of this research is to design a reactor for aqueous-based carbonation of steelmaking slag.

Several research groups have investigated the design of an aqueous reactor system for sequestration of carbon dioxide using steelmaking slag. Huijgen *et al.*,^[4] Eloneva *et al.*,^[5] and Stolaroff *et al.*^[6] have worked with leaching and carbonation of steelmaking slag under various

conditions. Each of their studies found that the rate and extent of aqueous leaching and carbonation were inversely related to particle size as the primary factor, while pH, temperature, and pCO₂ had milder effects on Ca conversion. In comparison to naturally occurring wollastonite (CaSiO₃), 11 times more carbon dioxide could be sequestered from steel slag at ambient temperatures. Other groups have actively researched methods of large-scale mineral-based carbon dioxide sequestration. O'Connor *et al.* conducted research in an effort to optimize the process conditions for direct aqueous carbonation of silicate minerals.^[7-9] Pretreatment of serpentine or olivine through acid leaching, fine grinding, or heat treatment was necessary to achieve high carbonation levels. Additions of NaHCO₃ and NaCl to the mineral suspension were found to catalyze the reaction. Park *et al.* investigated carbonation of olivine and serpentine in a manner similar to the work of O'Connor *et al.*^[10] Aqueous carbonation studies revealed that increasing the reactor temperature, pCO₂, and NaHCO₃/NaCl concentration increased the carbonation rate. Fernandez *et al.* found that the reactivity of magnesite slurries for carbonation increases with pCO₂, temperature, and solid-liquid ratio and decreases with particle size.^[11]

The current study capitalizes on the findings of many of these researchers, as well as current experimental work, to model the design of a reactor for aqueous-based sequestration of carbon dioxide using steelmaking slag. The current process uses a two-stage system to decouple the competing leaching and carbonation mechanisms that may occur simultaneously in a one-stage reactor. The reaction rate of calcium leaching from slag and the direct carbonation of slag particles were investigated separately in an effort to understand the

S.N. LEKAKH, Research Associate Professor, D.G.C. ROBERTSON, Professor of Metallurgical Engineering, C.H. RAWLINS, Graduate Researcher, V.L. RICHARDS, Robert W. Wolf Professor of Metallurgical Engineering, and K.D. PEASLEE, F. Kenneth Iverson Steelmaking Chair of Metallurgical Engineering, are with the Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409-0330. Contact e-mail: chrnr9@mst.edu

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limiting mechanisms for the overall sequestration process. The parameters modeled in this investigation include particle size, reactor residence time, reaction time, and reactor flow sequencing.

II. REACTOR DESIGN AND MODELING PROCEDURE

A. Carbon Dioxide Sequestration Reactions

Carbon sequestration *via* an aqueous-based reaction of carbon dioxide in off gas with lime in steelmaking slag may follow several possible reaction steps. A list of the key competing reactions considered is given in Table I. The thermodynamic and kinetic parameters of aqueous carbon dioxide dissolution (reactions 1 through 3) and the reaction of carbonate ions and calcium ions to precipitate solid calcium carbonate (reaction 5) have been previously described.^[12,15] Among the reactions in Table I, other investigators^[15,16] have shown that the rate controlling steps are carbon dioxide hydration (reaction 1) and carbonate precipitation (reaction 5). However, compared to the direct slag-solution reactions (reactions 4 and 6), the gas-liquid reactions are relatively rapid^[3] and are not critical in determining the overall reactor rate.

In this study, experimental kinetic data about calcium leaching from slag (reaction 4) and direct carbonation of slag particles by dissolved carbon dioxide (reaction 6) were used in the process model. The solid-liquid reactions (4 and 6) in Table I are shown in simplified form for use in studying the kinetics of the overall process. The actual processes involving slag are more complicated, because most of the CaO is combined into complex oxide phases (*i.e.*, Ca₂SiO₄ or Ca₁₂Al₁₄O₃₃).^[2] The dissolution rate of metal oxides (*e.g.*, Ca, Mg, Al, Si, and Fe) depends on the degree of ionicity of the M-O bond.^[12] For simplification in the current study, the calcium-containing phases were designated as CaO, while the experimental leaching kinetic parameters^[3] were obtained from industrial steelmaking slags containing multiple mineral phases. The actual mechanism of direct slag carbonation may take several different reaction paths. To maintain simplicity in process modeling, reaction 6 was used as the direct carbonation reaction mechanism.

Table I. Reactions Occurring during Aqueous Slag-Carbon Dioxide Sequestration^[4,12]

Description	Reaction
Carbon dioxide dissolution	(1) $\text{CO}_{2(g)} \rightarrow \text{H}_2\text{CO}_{3(aq)}$
	(2) $\text{H}_2\text{CO}_{3(aq)} \rightarrow \text{H}^+ + \text{HCO}_3^-$
	(3) $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$
Calcium leaching Carbonate precipitation	(4) $\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Ca}^{2+} + 2(\text{OH}^-)$
	(5) $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_{3(s)}$
Calcium oxide direct carbonation	(6) $\text{CaO}_{(s)} + \text{H}_2\text{CO}_{3(aq)} \rightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}$

B. Carbon Dioxide Sequestration Reactor Design

The process design consists of two vessels connected by a pumped water stream, as shown in Figure 1. Each reactor vessel operates at ambient pressure and temperature. Water and slag particles are introduced into reactor 1, wherein calcium ions are dissolved to form an alkaline leachate. The leachate is pumped to reactor 2, through which gaseous carbon dioxide is bubbled. Carbon dioxide dissolves into the water to form carbonic acid ions that react with the calcium ions in solution or report to the surface of the slag particle. At the particle surface, several competing reactions take place to precipitate calcium carbonate. This process design allows investigation of several system scenarios for optimizing carbon dioxide capture.

- (1) Scenario 1: Fresh water is supplied into reactor 1 and the leachate containing calcium ions is pumped to reactor 2, where calcium carbonate precipitates. The spent leachate (containing residual dissolved carbon dioxide) is discharged.
- (2) Scenario 2: The design is the same as scenario 1, except that the water supplied to reactor 1 is recirculated from reactor 2 after complete degassing.
- (3) Scenario 3: Fresh water is supplied to reactor 2 for saturation with carbon dioxide, and then the saturated water is pumped to reactor 1 for direct reaction with slag. The spent water (containing residual dissolved carbon dioxide) is discarded.
- (4) Scenario 4: The water supplied to reactor 1 is recirculated from reactor 2 without degassing.

Experimental verification of the different scenarios was undertaken using a lab-scale apparatus consisting of two connected reactors (tanks). Recirculation of the aqueous stream took place both with and without partial degassing by argon bubbling. Reactor 1 contained 2 kg of slag mixed with 20 L of water. The leachate was pumped at varying rates to reactor 2, which was sized with a 2-L volume. Bottle grade carbon dioxide was bubbled through a diffuser in the bottom of reactor 2 to generate a fine gas bubble distribution, which allowed intimate mixing of the gas and alkaline solution. A multichannel pH meter was used to measure the pH level in both reactors. At the completion of each

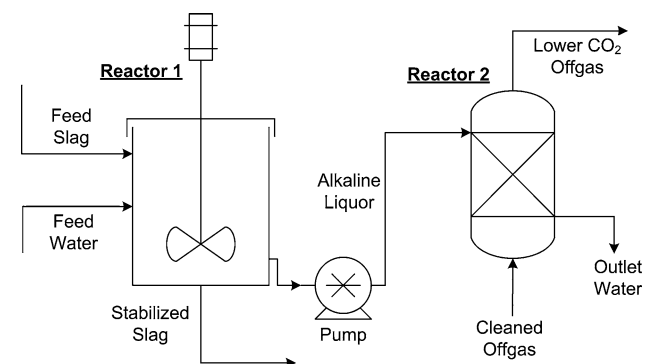


Fig. 1—Flow schematic of system for carbon dioxide sequestration with steelmaking slag.

test, a sample of the slurry from reactor 1 was filtered, dried, and analyzed for fraction carbonation, as described previously.^[3] Kinetic data from this earlier work was used to develop a process model with METSIM (version 15.07) process simulation software.

C. METSIM Modeling Procedure

An approach developed by Robertson^[13] for modeling the heterogeneous reaction kinetics of a non-steady-state process was used for the two-stage reactor system. A block diagram of the METSIM model is shown in Figure 2. The computer model consists of two blocks representing reactor 1 (Figure 2(a)) and reactor 2 (Figure 2(b)) and connected by streams 15/17 and 20/12. In reactor 1, the amount of input slag is defined by stream 10, which connects the mixer A and splitter C. In the same manner, the amount of aqueous solution is defined by stream 2, which connects the mixer B and splitter D. Slag leaching and direct carbonation reactions occur in splitters E and F, respectively. In reactor 2, carbon dioxide gas (stream 16) is mixed with the aqueous stream from reactor 1 (stream 12) in mixer F, while carbon dioxide dissolution to form carbonic acid ions takes place in splitter G. Carbonic acid ions react with calcium ions in splitter M, and precipitated calcium carbonate accumulates in the loop consisting of the mixer H and splitter L.

This model allows the flexibility of studying each of the four scenarios individually. For example, in scenario 1, fresh water is supplied by stream 9 to leach the slag in reactor 1. The leached calcium ions are pumped by stream 15/17 to reactor 2, where precipitated calcium carbonate accumulates in stream 26. The spent aqueous

stream is discarded by stream 22 without flowing back to reactor 1. Alternatively, in scenario 4, the aqueous solution is recirculated by streams 15/17 and 12/20 without fresh water input in reactor 1 or solution discharge from reactor 2. The model was used to calculate both a non-steady-state batch-type process in reactor 1 with no fresh slag input from stream 1 and no product discharge to stream 7 and a steady-state continuous-type process with fresh slag input and carbonate product output. Because the aqueous dissolution rate of carbon dioxide occurs more rapidly than slag leaching and carbonation, carbon dioxide dissolution was modeled using a fixed Henry constant^[12] and a reaction extent set to 1 (*e.g.*, equilibrium).

D. Experimental Reaction Kinetics for METSIM Modeling

In the METSIM model, the reaction rate (F) is defined by Eq. [1]. The rate constant (K) is defined by the mass flow rate ($m_i/\Delta t$) from the mixer/splitter to the phase splitter, where the reaction occurs with the particular value of reaction extent (RE) at each time-step (Δt). The kinetic parameters for leaching and carbonation measured experimentally from earlier work^[3] were used to evaluate the factors in Eq. [1].

$$F = K \times (RE) \quad [1]$$

Heterogeneous direct aqueous carbonation of slag particles was modeled for the batch case of scenario 4 in order to validate the results with the experimental data. In this scenario, the reaction rate is limited by mass transfer through the carbonate product layer and decreases with time as a result of increasing thickness and density of carbonate layer.^[3] The reaction rate expression increases in complexity, because the porosity of the product layer decreases the core of unreacted slag (with radius r_c) in each particle (with initial radius R). Therefore, a modified shrinking core model was used assuming that diffusivity (D) decreases as the reaction proceeded. This model is defined by Eqs. [2] through [5], where J_A (moles/m²·s) is the flux of component A , dN_A/dt (moles/s) is the reaction rate, ρ_m (moles/m³) is the molar density, and the parameter k (m/s) was chosen to fit the experimental data.^[14]

$$-\frac{dN_A}{dt} = -4\pi r^2 J_A \quad [2]$$

$$J_A = -D \frac{dC_A}{dr} \quad [3]$$

$$dN_A = 4\pi \rho_m r_c^2 dr_c \quad [4]$$

$$D = D_0 - k(R - r_c) \quad [5]$$

In this system, Eq. [2] is the reaction rate as a function of surface area and flux, Eq. [3] is the diffusion flux as a function of diffusivity and concentration gradient, and

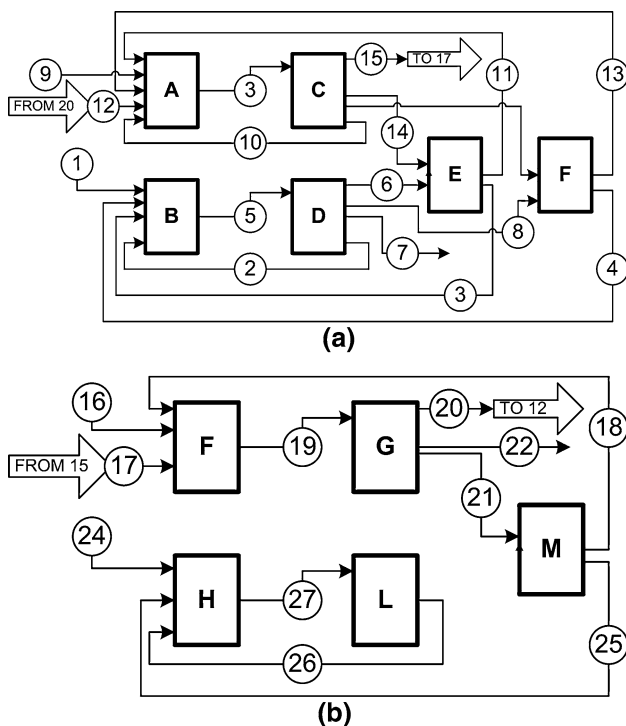


Fig. 2—Block diagrams of the METSIM model for (a) reactor 1 and (b) reactor 2, which are interconnected by streams 15/17 and 20/12.

Eq. [4] is the mass balance of component A .^[14] Equation [5] gives the diffusivity as a function of carbonate layer thickness. This system of equations was solved numerically for three incremental time-steps, each with changing diffusivity, in order to fit the experimental data for carbonation of an aluminum-killed ladle metallurgy furnace (LMF) slag with 49.9 wt pct CaO (slag 2, 420 to 590 μm). The experimental results are compared to those calculated from the modified shrinking core model using constant and decreasing diffusivity, as shown in Figure 3. The terms Ca_C and Ca_S are the respective fractions of calcium carbonated and calcium initially present in the slag.

For application in the METSIM model, the experimental kinetics of the carbonation reaction was approximated to be a function of time (t), as shown in Eq. [6]. A factor of $n = 1/3$ resulted in an appropriate fit for the reaction conversion (Ca_C/Ca_S) calculated from Eqs. [2] through [5] and the experimental data.

$$\ln\left(1 - \frac{\text{Ca}_C}{\text{Ca}_S}\right) = f(t)^n \quad [6]$$

For direct carbonation (Figure 4), the experimental data were fit to Eqs. [7] and [8], where d is the particle diameter (mm), t is the time (min), and the coefficient $A = 0.0012$ was taken from correlated experimental data (Figure 4(b)). Equation [8] is the first derivative form, which represents the reaction rate (F) and was the equation used in the METSIM model.

$$\text{Ca}_C = \text{Ca}_S \left(1 - \exp\left(-\frac{A}{d} t^{1/3}\right)\right) \quad [7]$$

$$F = \frac{d\text{Ca}_C}{dt} = \frac{A\text{Ca}_S}{3d} t^{-2/3} \exp\left(-\frac{A}{d} t^{1/3}\right) \quad [8]$$

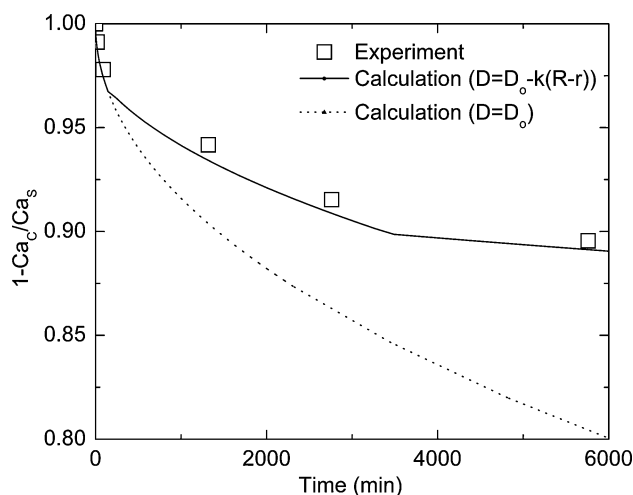


Fig. 3—Comparison of experimental data for slag carbonation with shrinking core model using constant ($D = D_0$) and decreasing ($D = D_0 - k(R - r)$) diffusivity of the product layer for slag with 49.9 wt pct CaO and 420- to 590- μm particle size.

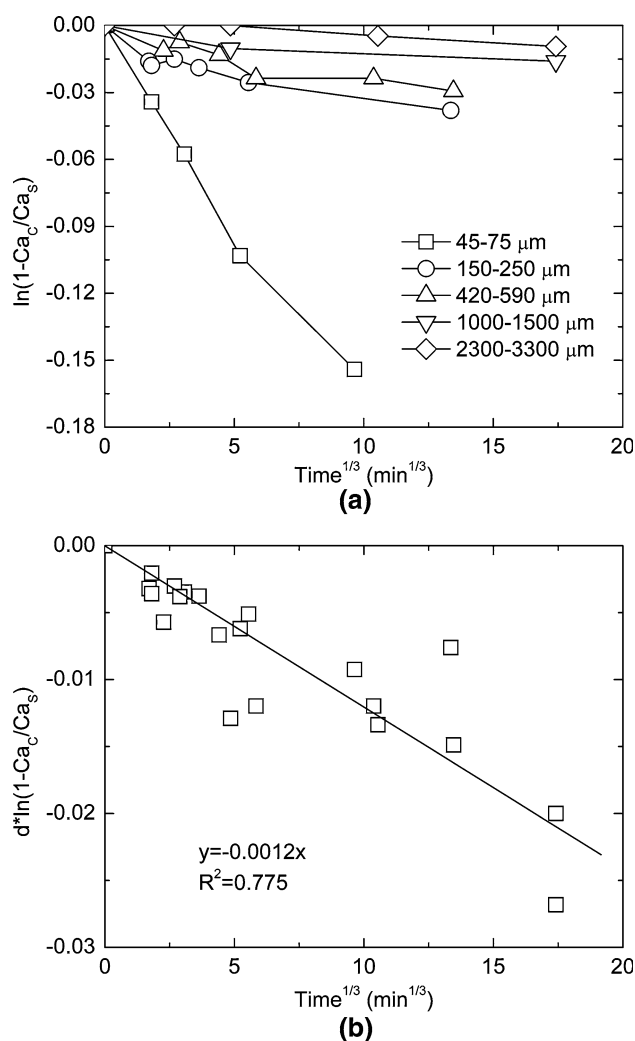


Fig. 4—Comparison of experimental data for slag carbonation with the parameters (a) $\ln(1 - \text{Ca}_C/\text{Ca}_S)$ and (b) $d \ln(1 - \text{Ca}_C/\text{Ca}_S)$ vs $\text{time}^{1/3}$.

A similar analysis of the calcium leaching process was undertaken using the set of reactions described in scenario 1. The reaction rate changes during the leaching process, because the initial chemical reaction limited mechanism is overtaken by diffusion through the porous surface layer developed during treatment.^[3] The difference in Eq. [9] between leaching and carbonation (Eq. [8]) arises from the necessity of taking into account the solution volume V (cm^3), the calcium saturation level C_{sat} (wt pct) for solution in equilibrium with solid $\text{Ca}(\text{OH})_2$, and the total surface area $S = 6W/\rho d$ (cm^2) of slag particles with diameter d (cm), density ρ (g/cm^3), and weight W (g) according to the batch test procedure. In Eq. [9], C_D is the concentration of dissolved calcium in solution (weight percent), and the coefficient $A = 0.0004$ was taken from the correlation of experimental data shown in Figure 5.

$$F = \frac{dC_D}{dt} = 1/3 V A C_{\text{sat}} S t^{-2/3} \exp(-A S t^{1/3}) \quad [9]$$

The extent of calcium leaching from slag depends on particle size and particle surface conditions. Calcium

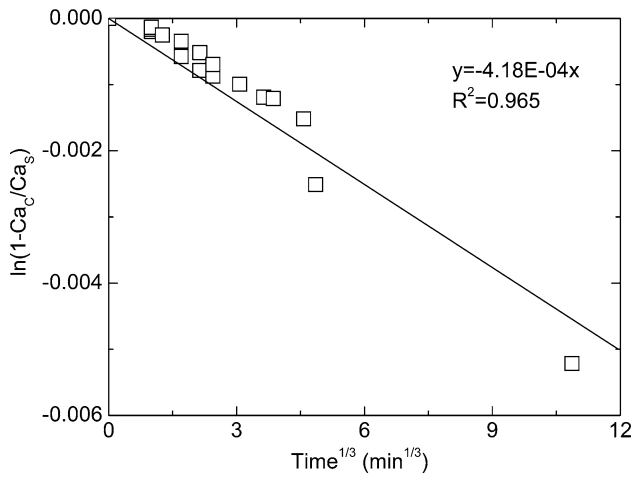


Fig. 5—Comparison of experimental data for slag leaching with the parameter $(1/S) \ln(1 - C_D/C_{sat})$ vs $time^{1/3}$.

leached in the fresh slag at twice the rate of carbonated slag leaching.^[3] Because leaching and carbonation may occur simultaneously, the leaching reaction rate (Eq. [9]) was linked to the amount of slag carbonation at each calculation step in scenario 4. The rate of calcium carbonate precipitation (reaction 5) was larger than the rate of leaching (reaction 4) or the rate of direct carbonation (reaction 6), as verified by comparing the slag leaching and carbonation experiments to the pure lime and carbon dioxide experiments. In the METSIM model, calcium and carbonate ions were assumed to have been completely consumed. Therefore, the extent of calcium carbonate precipitation was set to one.

III. RESULTS AND DISCUSSION

A. Model Validation with a Batch Reactor

Experimental data obtained from the batch reactor tests in the previous work^[3] were used to validate the METSIM model. The calcium leaching experiments were performed in a batch-type reactor under a protective argon atmosphere with unsaturated aqueous solutions, as described in scenario 1 for reactor 1. The METSIM modeling of the batch-type reactor was conducted by disconnecting reactor 1 from reactor 2 and disregarding the feed streams. Figure 6 compares the calculated and experimental results for the concentration of calcium leached (C_D) from LMF slag 2 (49.9 wt pct CaO) at two average particle sizes (60 and 200 μm). The calculated leaching results were in good agreement with the experimental data. Direct carbonation of the same slag was studied in a batch-type reactor using an aqueous solution saturated by carbonic acid at one atmosphere pressure.^[3] This process was modeled by connecting reactor 1 to reactor 2 and allowing carbon dioxide gas to saturate the aqueous solution. The transport of calcium ions from reactor 1 to reactor 2 was prohibited. This approach modeled the experimental conditions of scenario 3. Figure 7 shows that the experimental results for the amount of calcium

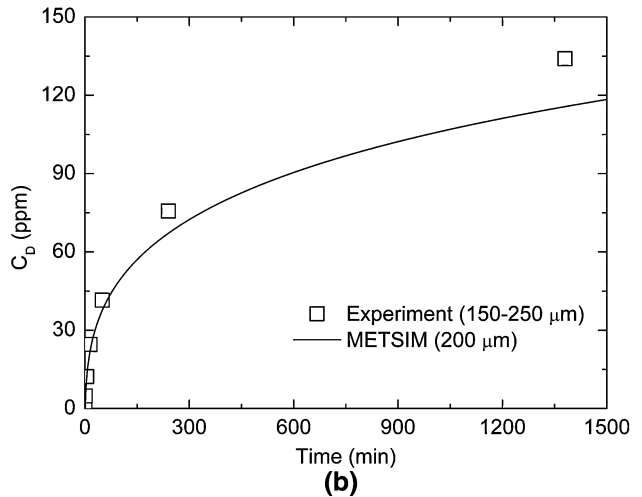
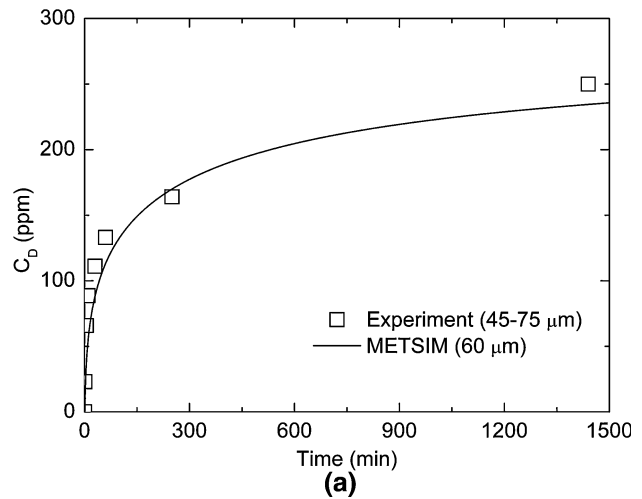


Fig. 6—Comparison of experimental and calculated concentration of leached calcium (C_D) for slag particles with (a) 60- μm and (b) 200- μm average diameter.

carbonated (Ca_C) were in good agreement with those predicted by the METSIM model for two different average particle sizes of LMF slag 2 (60 and 2800 μm).

B. Model Validation with Experimental Two-Stage Reactor

The experimental data obtained from the two-stage reactor tests of the previous work^[3] were used to validate the METSIM model calculated results. Scenario 4 (batch slag with recirculated nondegassed water) was modeled, and the results were compared to the experimental data for slag carbonation. Calcium leaching and direct slag particle carbonation were monitored simultaneously in both reactors. Reactor 1 contained 200 g LMF slag ($< 3.2 \text{ mm}$) in 20 L of water, while reactor 2 contained 2 L of solution through which 1.5 g/min carbon dioxide was bubbled. A solution exchange rate of 1 L/min was used to transfer the fluid between the two reactors. The experimental procedure included soaking the slag in reactor 1 for 20 minutes with solution recirculation and no carbon dioxide input into reactor 2. During the soak period, pH increased in both reactors as calcium

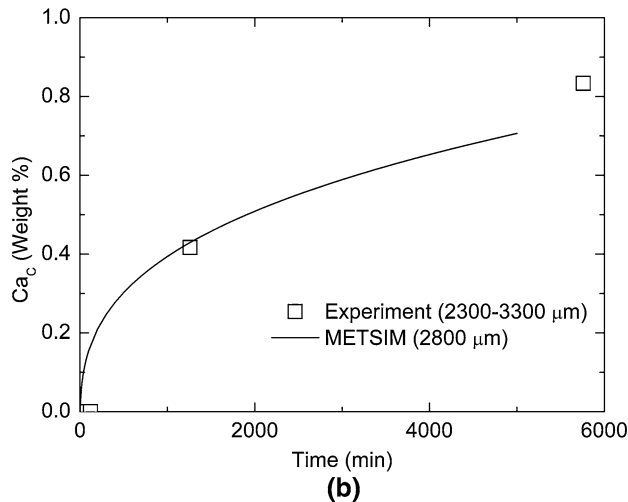
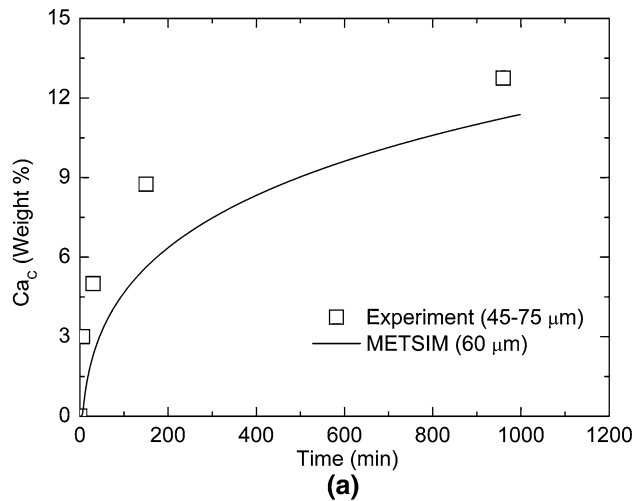


Fig. 7—Comparison of experimental and calculated results for slag carbonation (Ca_C) with (a) 60- μm and (b) 2800- μm average diameter particles.

hydroxide was formed. Upon introduction of carbon dioxide into reactor 2, the concentration of calcium ions in solution began to decrease while the concentration of carbonic acid began to increase. The rate of pH decrease (Figure 8) depended on the solution residence time in reactor 1 (20 minutes) and reactor 2 (2 minutes). Equilibrium carbon dioxide dissolution in reactor 2 of the METSIM model results in a pH neutralization time that is less than experimentally measured. Actual conditions deviate from ideal (equilibrium), because the carbon dioxide gas is incompletely dissolved in reactor 2. However, after completion of the neutralization period, the equilibrium carbon dioxide approximation does not affect the process model results.

The reaction was allowed to proceed for 20 hours, after which the product was dried, sieved, and analyzed for calcium carbonation. The prevailing reaction was direct slag particle carbonation in reactor 1, while a minor amount of residual precipitated carbonates was found in reactor 2. A similar result was achieved using the METSIM simulation. The model predicted

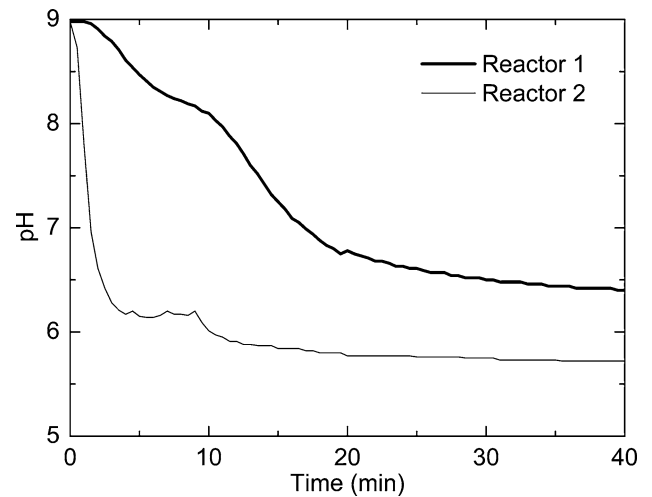


Fig. 8—Changing pH of aqueous solutions in reactors during carbonation (200 g of crushed < 3.2 mm LMF slag 2, 1.5 g/min flow rate carbon dioxide) based on start of carbon dioxide flow.

carbonate precipitation in reactor 2 immediately after introducing carbon dioxide, after which direct carbonation of the slag in reactor 1 was predicted to predominate. As the particle size decreased, the amount of slag carbonate product increased, as shown in the model results in Figure 9(a). A 1000- μm particle size resulted in 2 pct calcium carbonate at 20 hours (1200 minutes), while decreasing the particle size by an order of magnitude to 100 μm resulted in 8 pct calcium carbonate at the same time. Decreasing the particle size another half order of magnitude to 20 μm resulted in 23 pct calcium carbonate. A comparison of the experimental results (Figure 9(b)) and modeled results (Figure 9(a)) for five particle sizes shows good agreement.

C. Industrial Process Modeling

The validated METSIM process model was used to study the four scenarios defined for the purpose of reactor flow schematic optimization.

Scenario 1: The goal of scenario 1 was to analyze the influence of slag/solution ratio and solution residence time in reactor 1 on the extent of leaching only. In this model, slag was leached in reactor 1 and the alkaline leachate was carbonated in reactor 2. LMF slag 2 with 49.9 wt pct CaO and a monosize 200- μm distribution was used. During continuous operation, fresh water that contained a fixed amount of slag was input into reactor 1, while the spent leachate was discharged at the same rate from reactor 2. No water was recirculated to reactor 1. For comparison, a batch operation using a fixed starting volume of water and slag in reactor 1 and with no water input or output was studied.

The results from this scenario are presented in Figure 10. They show that increasing the slag/solution ratio and the solution residence time in reactor 1 produced a higher concentration of calcium ions in solution. Increasing the slag/solution ratio with zero water throughput (*i.e.*, in batch mode) provided a diminishing increase in calcium ions in solution due to

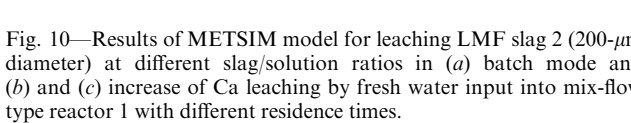
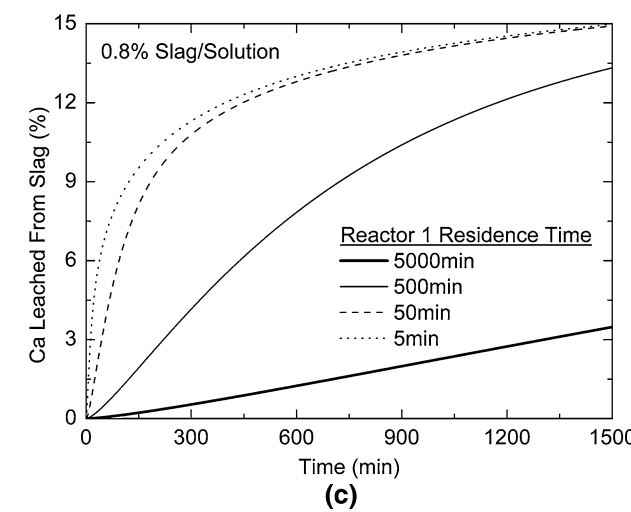
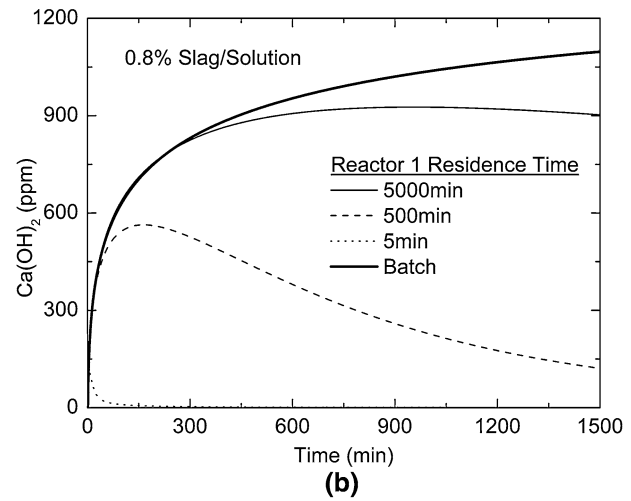
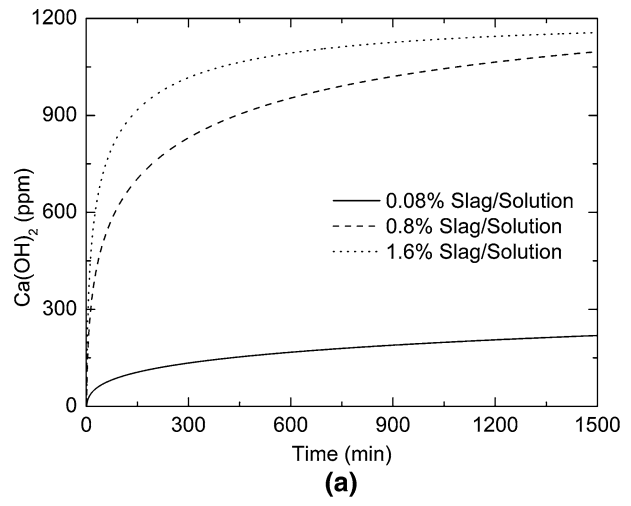
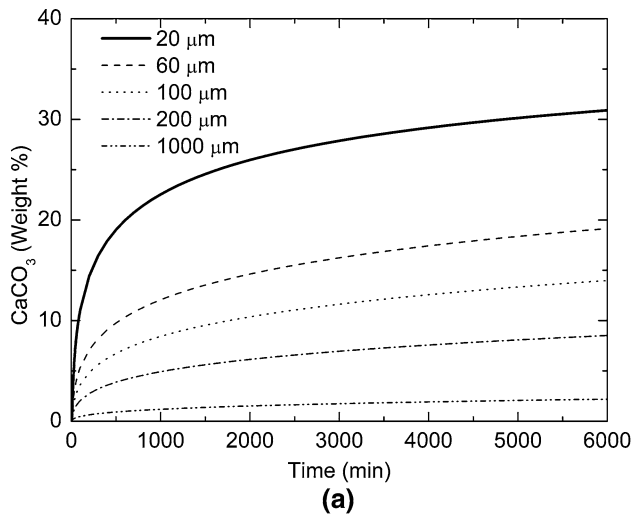


Fig. 9—METSIM calculated kinetics of (a) LMF slag carbonation for several particle sizes and (b) comparison of calculated and experimentally measured calcium carbonate content after 20 h reaction.

saturation of the aqueous phase (Figure 10(a)). For example, increasing the slag solution ratio by an order of magnitude from 0.08 to 0.8 pct resulted in an increase of calcium hydroxide from 150 to 950 ppm at 10 hours, while a further doubling of the slag/solution ratio to 1.6 pct resulted in a corresponding increase to 1100 ppm at the same time. To overcome saturation of the aqueous phase, the feed water throughput in reactor 1 can be increased, which causes a corresponding decrease in residence time (Figure 10(b)). At a fixed slag/solution ratio of 0.8 pct, a 5000-minute residence time approaches the response of a batch system, which has a theoretical infinite residence time. As the residence time decreases, the resulting solution becomes less saturated, and at 5 minutes, the leachate is undersaturated. While minimizing the solution saturation provides an increased driving force for Ca dissolution, it also requires a significant increase in feed water. The total fraction of calcium leached from the slag (ordinate axis of Figure 10(c)) is equal to the concentration of calcium

Fig. 10—Results of METSIM model for leaching LMF slag 2 (200- μ m diameter) at different slag/solution ratios in (a) batch mode and (b) and (c) increase of Ca leaching by fresh water input into mix-flow type reactor 1 with different residence times.

in solution multiplied by the solution volume. The optimal residence time is, therefore, a balance between maximizing the amount leached and minimizing fresh

water input. For slag with 200- μm particle diameter (monosize) and 0.8 pct slag/solution ratio, the optimal residence time is near 1 hour (Figure 10(c)).

Scenario 2: In this scenario, fresh water input into the system is minimized by recirculating the leachate from reactor 2 to reactor 1. However, for this scenario to work properly, the recirculated leachate must be fully degassed to prevent carbonic acid from reporting to reactor 1. Preliminary experiments with degassing the leachate by argon bubbling showed that full leachate degassing is difficult to achieve and the residual content of carbonic acid will provide direct carbonation of the slag particles in reactor 1. This problem is addressed in scenario 4.

Scenario 3: In this scenario, fresh water is input into reactor 2 for saturation with carbon dioxide, and then the saturated water is pumped to reactor 1 for direct reaction with slag. Because this scenario requires a significant quantity of fresh water input, it was not modeled in this analysis.

Scenario 4: For scaleup to an industrial process of carbon dioxide sequestration, continuous processing of slag through the system is required. To meet this criteria, a steady-state METSIM model was set up to allow continuous feed of fresh slag to reactor 1 at the same rate as carbonated product was discharged from reactor 2. Carbon dioxide was introduced into reactor 2 and the aqueous solution was recirculated from reactor 2 to reactor 1. As a first approximation, reactor 1 was assumed to operate in back-mix mode with the composition of the discharged stream as an average for reactor 1. The steady-state model and the batch processing model, both of which used fresh slag (LMF slag 2 with 49.9 wt pct CaO), were compared.

In batch processing mode, the amount of slag carbonation increased steadily with reaction time, as shown in Figure 11(a). At 7 days (10,800 minutes) of processing in batch mode, ~8 pct carbonation was achieved using 200- μm particles. In the steady-state processing mode and with a constant amount of slag throughput, the overall amount of carbonation depended on reactor 1 slag residence time and particle size (Figure 11(b)). A 200- μm particle at 7 days residence time achieved ~8 pct carbonation, while a 20- μm particle achieved ~22.5 pct carbonation at the same residence time, showing that particle size is critical. A 1000- μm particle achieved only ~2 pct carbonation at the same residence time. Increasing the slag residence time of reactor 1 produces more carbonation. For a 200- μm particle, a 2-day residence time enabled ~5 pct carbonation, while a 20-day residence time allowed ~12 pct carbonation. While increasing the slag residence time in reactor 1 results in more carbonation, it also requires a larger reactor volume. Decreasing the slag residence time makes it possible to minimize the volume of reactor 1, but results in a simultaneous decrease in the level of slag carbonation in the discharged product. A balance can be realized between particle size and reactor residence time. When working to achieve a specific amount of carbonation, reducing the slag particle size allows for reduction in reactor residence time.

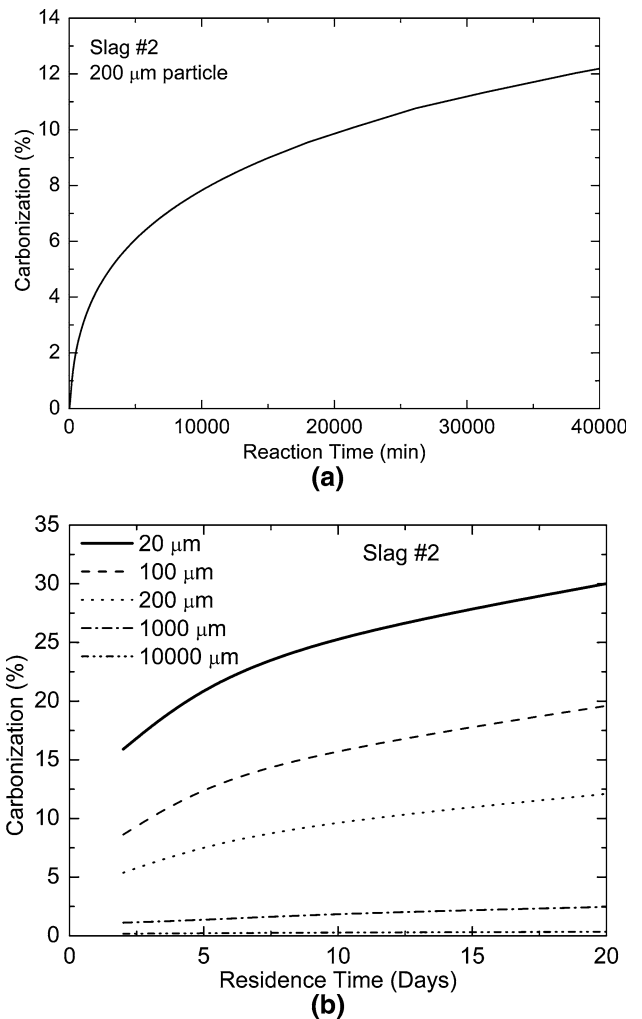


Fig. 11—Comparison of (a) batch carbonation in a 200- μm particle and (b) steady-state continuous carbonation using varying particle size of LMF slag 2 in reactor 1.

IV. CONCLUSIONS

The METSIM process simulation software was used to model several reactor design scenarios for hydrous carbonate sequestration of carbon dioxide using steel-making slag. A two-stage reactor design was modeled in batch and continuous modes. The process allowed the introduction of water and slag into the first reactor and carbon dioxide into the second reactor, along with the possibility of recirculating the solution. A comparison of the scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles, which could reduce the leaching efficiency. However, the water requirement in a continuous system is much higher than a recirculated system. To minimize the fresh water makeup, the spent leachate from the second reactor can be recirculated to the first reactor. This system's main drawback is that the residual absorbed carbon dioxide in the recirculated water results in the formation of a calcium carbonate layer on the slag particles, which inhibits leaching of

calcium ions. The product layer blinding effect can be partially overcome by increasing the slag surface area (*i.e.*, decreasing the particle size) and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly affected the amount of calcium carbonated. The METSIM model was shown to be a useful tool for designing and optimizing carbon dioxide sequestration reactor systems based on different slag fractions and compositions.

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