An Overview: Reaction Mechanisms and Modelling of CO₂ Utilization via Mineralization

Shu-Yuan Pan1**, Tung-Chai Ling2, Ah-Hyung Alissa Park3,4, Pen-Chi Chiang1,5*

1 Carbon Cycle Research Center, National Taiwan University, Taipei 10672, Taiwan
2 Key Laboratory for Green and Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha 410082, China
3 Department of Chemical Engineering; Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA
4 Lenfest Center for Sustainable Energy, Columbia University, New York, NY 10027, USA
5 Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 10673, Taiwan

ABSTRACT

Accelerated carbonation using alkaline solid wastes has been considered an effective approach to mineralizing flue gas CO₂ from industries or power plants. Despite its recent progress, mechanistic understanding and modelling at interface levels are still needed to control the reactivity and equilibrium of the reaction system. This review focuses on several phenomenological models for accelerated carbonation that look at the solid-fluid interface. We first illustrate the principles of kinetic and mass transfer driven reactions for CO₂-mineral-water systems. Then, we provide an overview into the reaction mechanisms and modelling for CO₂ mineralization including leaching-precipitation model, shrinking core model and surface coverage model. Advanced models considering multiple mechanisms, such as two-layer diffusion model, are also discussed. Finally, the perspectives and prospects are provided to shine a light on future directions, including incorporation of structural and physical properties in phenomenological models, identification of dynamic speciation by in-situ high-resolution equipment, and integration of heat transfer in reaction modelling for system optimization.

Keywords: Mechanism; Diffusion; Kinetics; Shrinking core model; Surface coverage model.

INTRODUCTION

Numerous approaches to carbon capture, storage and utilization have been evaluated to mitigate rapid anthropogenic CO₂ emissions in the atmosphere, such as adsorption on modified carbon surfaces (Adelodun et al., 2017) or carbon aerogels (Xie et al., 2017), accelerated carbonation (Gadikota and Park, 2014), biological fixation (Su et al., 2017), chemical looping (Ku et al., 2017), assimilation by vegetation (Yu et al., 2017), and geological storage (Jean et al., 2016; Jen et al., 2017). Accelerated carbonation using alkaline solid wastes has been considered an effective approach to mineralizing flue gas CO₂ from industries or power plants (Li et al., 2016). Accelerated carbonation, originally proposed by Seifritz (1990), mimics and accelerates natural weathering to a timescale less than a few hours. It involves gaseous CO₂ reacting with metal-oxide bearing materials (mostly calcium and/or magnesium oxides) in the presence of moisture to form stable and insoluble carbonate precipitates. From the viewpoint of water chemistry, the affinity of metal oxides to form carbonate precipitates replies on (i) chemisorption strength to carbonate ions (or gaseous CO₂) at the fluid-solid interface, (ii) number of active basic sites at the surface of the particle, and (iii) solubility product constant (Ksp) in the case of aqueous carbonation. In general, CaO and MgO are the most favourable metal oxides in reacting with CO₂ (Pan et al., 2012).

Alkaline solid wastes are suitable feedstock for CO₂ mineralization via accelerated carbonation. These solid wastes are usually produced in a large amount from nearby CO₂ emission sources. Some examples of alkaline solid wastes as feedstock for CO₂ mineralization include blast furnace slag (Ukwattage et al., 2017), converter slag (Said et al., 2013), electric arc furnace slag (Pan et al., 2017),
Ca(OH)₂ and CaSiO₃, are the major phases participating in solution. In general, calcium-bearing minerals, such as CaO, Ca(OH)₂, and CaSiO₃, are the major phases participating in the accelerated carbonation reaction using alkaline solid wastes.

Despite recent progress on developing various types of processes for CO₂ mineralization, mechanistic understanding is still needed to unlock CO₂ mineralization at interface levels for controlling reaction pathways and rates. In this article, we review the reaction mechanism and coupled modelling for CO₂ mineralization via accelerated carbonation that are looking at the solid-fluid interfaces. We first illustrate the principles of kinetic and mass transfer driven reactions for CO₂-mineral-water systems, and then provide an overview into the reaction mechanisms and modelling for CO₂ mineralization. We review the progress of several commonly used classical models for the heterogeneous (CO₂-mineral-water) reactions, such as leaching-precipitation model, shrinking core model and surface coverage model. Several advanced models considering multiple mechanisms, such as two-layer diffusion model, are also discussed.

**KINETIC AND MASS TRANSFER DRIVEN REACTIONS FOR CO₂-MINERAL-WATER SYSTEMS**

The effect of key operating parameters on the performance of reaction kinetics and mass transfer for CO₂ mineralization is strategically important for system optimization. In general, CO₂ mineralization using alkaline solid wastes can be simply described by three simultaneous steps of reactions: (i) dissolution of gaseous CO₂ into a liquid phase; (ii) hydration and leaching of CO₂-reactive components from a solid phase; (iii) nucleation and growth of carbonate precipitates. In this section, we illustrate the theoretical considerations of kinetic and mass transfer driven reactions for CO₂-mineral-water systems.

**Tools for Modelling Equilibrium and Mechanisms**

The equilibrium of the heterogeneous (CO₂-mineral-water) reaction system depends on numerous factors and parameters, such as temperature, pressure, pH of the solution, and the mixing extent. The thermodynamic modelling can assess the saturation state of system, pH changes, and reaction rate with a complex chemistry and varying solid-fluid interfaces. A sophisticated numerical simulation on thermodynamics can be performed by a variety of codes, such as PHREEQC (Swanson et al., 2014; Mun et al., 2017), GEMS (Azad et al., 2016), Outokumpu HSC (Teir et al., 2007), and TOUGHREACT (André et al., 2015), to determine the equilibrium parameters of reaction system and thus improve the understanding of reaction mechanism.

Thermal analyses are commonly used as rapid methods for the quantification of the carbonate products, e.g., carbonation conversion, in the reacted samples. Due to the chemical complexity of alkaline wastes and various ways to interpret thermogravimetric curves, it is difficult to evaluate the carbonation conversion and capacity of different solid wastes in the literature on the same basis. Pan et al. (2016b) proposed an integrated thermal analysis for determining carbonation parameters (i.e., CO₂ uptake and carbonation conversion) in alkaline solid wastes based on thermogravimetric, derivative thermogravimetric, and differential scanning calorimetry. They modified the interpretation of thermal analysis by considering the consecutive weight loss of specimen between 200 and 900°C, which was attributed to the decomposition of hydrated compounds. This proposed methodology can effectively evaluate the CO₂ fixation capacity of alkaline solid wastes, thereby providing more accurate and precise data for subsequent system modelling and process assessment.

Advanced techniques on mineral solids, such as in-situ X-ray diffraction (Cizer et al., 2012), carbon (δ¹³C) and oxygen (δ₁⁸O) isotope (Gras et al., 2017), and nuclear magnetic resonance (Ashraf and Olek, 2018), can assist in characterizing the changes in physico-chemical properties during the reactions. Gras et al. (2017) performed an isotopic analysis for elucidating the mechanisms of in-situ natural weathering using waste rocks and mining tailings from the Dumont Nickel Project at Quebec. They proposed three major steps that control the rate of CO₂ uptake, as shown in Fig. 1: (i) diffusion of gaseous CO₂ into unsaturated phases such as the porous medium, (ii) dissolution of gaseous CO₂ in interstitial water, and (iii) precipitation of metal carbonates from the interstitial water. In general, natural weathering is controlled by diffusion of atmospheric CO₂ toward the center of the minerals due to low CO₂ concentration and moisture in the atmosphere, as well as insufficient advection Gras et al. (2017).

Similar finding was also found that the rate-limiting step in passive carbonation should be the dissolution of atmospheric CO₂ into interstitial water (Wilson et al., 2010). Other potential mechanisms influencing the compositions of interstitial water may include evaporation, bedrock carbonate dissolution, and microbial activities such as photosynthesis reactions (Gras et al., 2017). Liang et al. (2017) gave an intensive review on four major mechanisms that trap CO₂ in the pores of subsurface, namely (i) structural trapping, (ii) residual trapping, (iii) dissolution trapping, and (iv) mineral trapping, for modelling the CO₂-solid-fluid wettability. Both the structural and residual trapings are considered to be dominated by capillary action, and control by wettability in the porous media. In a well mixing system, the reaction with calcium should be the rate-limiting step (Mitchell et al., 2009).

**Molecular Diffusion at Interface Levels**

The non-catalytic heterogeneous reaction with porous particles is a complex system, which involves a number of physical (e.g., mass transfer and diffusion through interfaces)
Fig. 1. A process-based conceptual model for carbonation reaction using waste rocks and mineral processing tailings with the isotope fractionation. Field experiments were conducted at the Dumont Nickel Project (Abitibi, Quebec) site. Adapted from the literature (Gras et al., 2017).

and chemical (e.g., reaction) phenomena. Although the porous network could be complex, Benedetti (2014) suggests that the pore size distribution of particles during reaction should be considered in determining the reaction kinetics. It may also be necessary to consider the effects of heat transfer (e.g., exothermic or endothermic reactions) in the surrounding fluid or in the interior of the porous particle. For aqueous carbonation using alkaline solid wastes, there are four major resistances to molecular diffusion (Fig. 2):

- Bulk diffusion: mass transfer of CO₂ from the bulk flow (i.e., the gas phase) to the liquid film
- Inter-particle diffusion: the CO₂-related species diffuse within the liquid film through molecular diffusion among each particle
- Intra-particle diffusion: the CO₂-related species diffuse inside the pore network of the particle
- Product layer diffusion: during the reaction, a layer of carbonate products is formed on the surface of unreacted solid matrix.

One of the technical challenges in CO₂ mineralization is the slow dissolution rate of gaseous CO₂ into the liquid phase (Pei et al., 2017). Therefore, sufficient mass transfer among phases is a strategical key to effective carbonation for CO₂ mineralization. Accelerated carbonation is usually regarded as a diffusion controlled reaction (Chang et al., 2012b; Pan et al., 2012). Mattila et al. (2012) found that effective mixing would significantly reduce the reaction time to reach equilibrium. In most cases of carbonation, the resistance of the product layer increases with the thickness of the product layer on the surface of the particle. Due to the inherent properties of the carbonation reaction, a well-designed reactor with efficient mass transfer between the gas and liquid phases are required to achieve cost effectiveness.

AN OVERVIEW INTO REACTION MECHANISM AND MODELING FOR CO₂ MINERALIZATION

Prior to the process scale-up and optimization, it is imperative to obtain the key process data for reactor design, such as reaction kinetics, diffusivity of the reactant and mass transfer coefficient. Kinetic analyses can effectively characterize the mechanistic factors that control the reactivity and equilibrium of the reaction system. For the sake of simplicity, a number of reasonable assumptions is typically considered to avoid complicated calculations. Benedetti (2014) reviewed the kinetic models for non-catalytic fluid-solid reactions, including the grain model (i.e., assuming non-porous spherical grains) and the random pore model (i.e., considering particle porosity). In the grain model, it is assumed that the solid particle consists of a matrix of dense and porous grains with shapes of a sphere, a cylinder or a flat plate. In contrast, the pore model describes the pore network by a collection of capillaries with a cylindrical shape, which may overlap in the course of reaction. Several studies have applied the classical (theoretical) models (e.g., random pore model (Bhatia and Perlmutter, 1983), surface coverage model (Pan et al., 2014)) and/or the grain models (e.g., crackling core model (Farhang et al., 2017) and shrinking core model (Lekakh et al., 2008; Chang et al., 2012a)), for evaluating the performance of leaching and/or carbonation steps for CO₂.
mineralization. Several advanced computational approaches, such as saturation state model (Zeebe and Westbroek, 2003), dissolution-precipitation model (Lagasa, 1995), and moving-sharp-interface model (Muntean et al., 2011), have also been developed for determining the kinetics of CO2 mineralization. In this section, we illustrate two theoretical approaches to evaluating reaction kinetics, including solid-state-reaction approach and transition-state-theory approach.

Solid-State-Reaction Approach

CO2 mineralization using alkaline solid wastes via accelerated carbonation is a heterogeneous and irreversible fluid-particle reaction. CO2-bearing compounds diffused from the bulk fluid phase and then either (i) permeated into the mineral matrix through micropores and reacted with reactive components, or (ii) directly reacted with reactive components leached out from the mineral matrix at water (fluid)-mineral (solid) interfaces. In this case, the external mass transfer from bulk gas phase was neglected. The reaction kinetics of a general solid-state reaction can be described by the law of mass action, as shown in Eq. (1), associated with Arrhenius theory.

\[
\frac{dX}{dt} = k \cdot f(X)
\]  

(1)

where \(X\) is the carbonation conversion of solid wastes (-), \(t\) is the reaction time (s), \(k\) is the reaction rate constant, and \(f(X)\) is an algebraic function determined by reaction mechanisms. The reaction rate constant \((k)\) is dependent on the reaction temperature according to the Arrhenius’s equation (Eq. (2)):

\[
k = A \cdot \exp((-E_a)/RT)
\]

(2)

where \(A\), known as the pre-exponential factor, represents the frequency of collisions in the correct orientation (s^-1), \(E_a\) is the apparent activation energy for the reaction (kJ mol^-1), \(T\) is the reaction temperature (K), and \(R\) is the universal gas constant (i.e., 8.314 J K^-1 mol^-1).

The function \(f(X)\) can be generally expressed by Eq. (3):

\[
f(X) = C \cdot X^m (1 - X)^n [-\ln(1 - X)]^p
\]

(3)

where \(m\), \(n\), and \(p\) are empirically obtained exponent factors depending on the reaction mechanism, and one of them should always be zero. Eq. (1) can be solved and expressed by Eq. (4), in terms of an algebraic function of \(g(X)\).

\[
g(X) = kt
\]

(4)

Table 1 summarizes several commonly employed functions of solid-state reactions with their associated mechanisms. Several studies on mineral carbonation have applied the classic solid-state reactions to describe the reaction behaviours, such as wet carbonation (Um and Ahn, 2017) and carbonation curing (Wang et al., 2017). For instance, the experimental data of accelerated carbonation can fit the theoretical functions derived from Eq. (5). By taking the logarithmic form, the obtained equation shows a linear relationship of \(\ln[(1 - (1 - X)^{1/3})\] and \(\ln t\), as indicated by Eq. (6). When the \(n\) value equals one, the chemical reaction at the phase boundary (such as the unreacted core surface) is the rate-limiting step. Whereas the \(n\) value equals two, the diffusion through the product layer of the particle becomes the rate-determining step.

\[
[1 - (1 - X)^{1/3}] = k \cdot t
\]

(5)

\[
\ln[1 - (1 - X)^{1/3}] = \left(\frac{1}{n}\right) \ln t + \left(\frac{1}{n}\right) \ln k
\]

(6)

Um and Ahn (2017) applied the theoretical functions to evaluate the kinetics of wet carbonation reaction for bottom ash. They found that, during the initial 20 min of carbonation, the rate-limiting step should be the phase-boundary reaction controlled mechanism at the interfaces of water film and the surface of bottom ash. As the reaction proceeded, the rate-limiting step switched to the diffusion-controlled mechanism through the product layer.
Table 1. Kinetic Functions of Solid-State Reactions and their Associated Mechanism.

<table>
<thead>
<tr>
<th>Controlled step</th>
<th>Mechanism</th>
<th>Symbol</th>
<th>Function $f(\alpha)$ in Eq. (1)</th>
<th>$g(\alpha) = kt$ in Eq. (2)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random nucleation and nuclei growth</td>
<td>First order random nucleation</td>
<td>F1, A1</td>
<td>$(1 - X)$</td>
<td>$- \ln (1 - X)$</td>
<td></td>
</tr>
<tr>
<td>Random nucleation</td>
<td>A3/2</td>
<td>$(3/2) (1 - X) [ - \ln (1 - X)]^{1/3}$</td>
<td>$(- \ln (1 - X))^{2/3}$</td>
<td>Avrami-Erofev eq.</td>
<td></td>
</tr>
<tr>
<td>Bi-dimensional nucleation</td>
<td>A2</td>
<td>$2 (1 - X) [ - \ln (1 - X)]^{2/3}$</td>
<td>$(- \ln (1 - X))^{1/3}$</td>
<td>Avrami-Erofev eq.</td>
<td></td>
</tr>
<tr>
<td>Three-dimensional nucleation</td>
<td>A3</td>
<td>$3 (1 - X) [ - \ln (1 - X)]^{2/3}$</td>
<td>$(- \ln (1 - X))^{1/3}$</td>
<td>Avrami-Erofev eq.</td>
<td></td>
</tr>
<tr>
<td>Branching nuclei</td>
<td>Au</td>
<td>$X (1 - X)$</td>
<td>$\ln (X / (1 - X))$</td>
<td>Prout-Tomkins eq.</td>
<td></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>One and a half order</td>
<td>F3/2</td>
<td>$2 (1 - X)^{3/2}$</td>
<td>$(1 - X)^{3/2} - 1$</td>
<td></td>
</tr>
<tr>
<td>Second-order random nucleation</td>
<td>F2</td>
<td>$(1 - X)^2$</td>
<td>$(1 - X)^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third-order random nucleation</td>
<td>F3</td>
<td>$(1/2)(1 - X)^3$</td>
<td>$(1 - X)^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nucleation (Accelerated X-t curve)</td>
<td>Nucleation</td>
<td>E1</td>
<td>$X$</td>
<td>$\ln X$</td>
<td>Exponential law</td>
</tr>
<tr>
<td>Nucleation</td>
<td>P3/2</td>
<td>$(2/3)X^{1/2}$</td>
<td>$X^{1/2}$</td>
<td>Mampel Power law</td>
<td></td>
</tr>
<tr>
<td>Nucleation</td>
<td>P1/2</td>
<td>$2X^{1/2}$</td>
<td>$X^{1/2}$</td>
<td>Mampel Power law</td>
<td></td>
</tr>
<tr>
<td>Nucleation</td>
<td>P1/3</td>
<td>$3X^{1/3}$</td>
<td>$X^{1/3}$</td>
<td>Mampel Power law</td>
<td></td>
</tr>
<tr>
<td>Phase boundary (surface reaction)</td>
<td>Contracting disk</td>
<td>R1 (P1, F0)</td>
<td>$(1 - X)^0$</td>
<td>$X$</td>
<td>Power law</td>
</tr>
<tr>
<td>Contracting cylinder</td>
<td>R2</td>
<td>$2 (1 - X)^{1/2}$</td>
<td>$1 - (1 - X)^{1/2}$</td>
<td>Power law</td>
<td></td>
</tr>
<tr>
<td>Contracting sphere</td>
<td>R3 (F2/3)</td>
<td>$3 (1 - X)^{2/3}$</td>
<td>$1 - (1 - X)^{1/3}$</td>
<td>Power law</td>
<td></td>
</tr>
<tr>
<td>Diffusion (Deceleratory X-t curve)</td>
<td>One-dimensional diffusion</td>
<td>D1</td>
<td>$(1/2)X$</td>
<td>$X^2$</td>
<td>Parabola eq.</td>
</tr>
<tr>
<td>Two-dimensional diffusion</td>
<td>D2</td>
<td>$[- \ln (1 - X)]^4$</td>
<td>$(1 - X) \ln (1 - X)$</td>
<td>Valensi eq.</td>
<td></td>
</tr>
<tr>
<td>Three-dimensional diffusion</td>
<td>D3</td>
<td>$(3/2) (1 - X)^3 [1 - (1 - X)^{1/3}]^{-1}$</td>
<td>$[1 - (1 - X)^{1/3}]^3$</td>
<td>Jander eq.</td>
<td></td>
</tr>
</tbody>
</table>

The term X represents the carbonation conversion of alkaline solid wastes, typically determined by thermogravimetric analysis.
Transition-state-Theory Derived Approach

Transition-state-theory, known as activated-complex theory, provides an approach to describing the concentration dependence of the kinetic rate law for elementary chemical reactions. The theory assumes a quasi-equilibrium between reactants and activated transition state complexes. Using a simplified form of the general transition-state-theory derived model is a common approach to modelling the kinetics of both leaching and precipitation reactions. It is assumed that the heterogeneous leaching-precipitation reactions occur at the surface of a particle (Lagasa, 1995). The governing equation of the reaction kinetics \( r, \text{mol} \cdot s^{-1} \) is shown as follows:

\[
r = k \cdot A_i \cdot \exp \left( -\frac{E_a}{RT} \right) \cdot a_i^{n_i} \cdot \prod_i a_i^{n_i} \cdot f(\Delta G_\beta) \cdot g(1) \tag{7}
\]

where \( k \) is the rate constant of the forward reaction \( \text{mol} \cdot m^{-2} \cdot s^{-1} \), \( A_i \) is the reactive surface area of the particle \( \text{m}^2 \), \( a_i^{n_i} \) is the pH dependence of the rate for the reaction, and \( a_i^{n_i} \) represents catalytic or inhibitory effects due to the presence of other solutions. The terms \( f(\Delta G_\beta) \) and \( g(1) \) denote the dependence of the rate on the thermodynamic driving force and ionic strength \( I \) of the aqueous solution, respectively. The thermodynamic driving force, \( f(\Delta G_\beta) \), can be simplified to Eq. (8):

\[
f(\Delta G_\beta) = 1 - \exp \left( \frac{\Delta G_\beta}{RT} \right) \tag{8}
\]

where \( \Delta G_\beta \) is the free energy of the reaction. The transition-state-theory approach can well describe the reaction system when it is below saturation. To better evaluate the mineral formation rates, Pham et al. (2011) combined the Burton-Cabrera-Frank growth equation with a simplified form of the classical nucleation theory. This integrated model was successfully applied to assess the supersaturation reaction system, while the transition-state-theory approach was used for states below saturation levels.

LEACHING-PRECIPITATION MODEL

Accelerated carbonation reaction is a heterogeneous system containing two dynamic interfaces, i.e., the gas-liquid interface and the liquid-solid interface. The overall reaction can be generally simplified into three simultaneous steps: (1) dissolution of \( \text{CO}_2 \) in bulk solution through the gas-liquid interface, (2) leaching of reactive components (e.g., \( \text{Ca}^{2+} \)) from solid matrix into solution which typically occurs at the liquid-solid interface, and (3) precipitation of carbonate (e.g., \( \text{CaCO}_3 \)) crystals in the bulk liquid phase or at the liquid-solid interface. Gaseous \( \text{CO}_2 \) dissolution is usually considered as a diffusion-limited step, where the mass transfer between the gas and liquid phases plays an important role on reaction kinetics. Several simulation models on evaluating the dissolution behaviors of gaseous \( \text{CO}_2 \) into the aqueous phase are available (Legendre and Zevenhoven, 2016, 2017). For instance, Legendre and Zevenhoven (2016) established a numerical model by incorporating mass transfer boundary layer with bubble force. This model was developed by the mass time derivative of the dissolving bubbles as the function of local dimensionless numbers such as Re, Sc and Sh. However, if we look at the solid-fluid interfaces by neglecting the external mass transfer of gaseous \( \text{CO}_2 \) dissolution, several kinetic models regarding the leaching and precipitation reactions can be applied for accelerated carbonation.

Leaching Kinetics

In \( \text{CO}_2 \) mineralization, leaching is the process of dissolving and releasing metal ions from the solid matrix (e.g., steel slag or fly ash) to the aqueous solution. The rate of metal ion leaching depends on the mineralogy of metal oxides in the solid matrix and their affinity to the solution speciation and pore water. A simple kinetic formulation for weathering of natural ores, such as wollastonite and serpentine, can be applied to describe the leaching rate of certain components \( r_i \) from alkaline solid wastes (De Windt et al., 2011), as indicated by Eq. (9).

\[
r_i = \frac{d}{dt}[M_i] = k_i \cdot A_i \cdot (\Omega_i - 1) = k_i \cdot A_i \cdot \left( \frac{Q_i}{K_i} - 1 \right) \tag{9}
\]

where \( M_i \) stands for the mineral phase that contributes to leaching, \( k_i \) is the intrinsic rate constant, \( A_i \) is the mineral surface area, \( \Omega_i \) is the saturation state of solution with respect to the mineral phase \( i \), \( Q_i \) is the ion activity product, and \( K_i \) is the thermodynamic formation constant. The thermodynamic equilibrium constant of calcite (\( \text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+ \)) at 25°C is approximately \( 10^{-1.85} \) (De Windt et al., 2011). When \( \Omega_i \) equals to one, the solution is exactly in equilibrium or saturation with respect to the mineral phase, i.e., the term \( (Q_i/K_i - 1) \) becomes zero and the mineral phase \( i \) does not dissolve afterwards.

A mass conservation approach is also commonly applied to determine the leaching kinetics of metal ions in solution. The metal ions are usually leached out rapidly in the beginning, and then gradually approach a maximum concentration in solution \( C_{i, \text{max}} \). By the mass-loss based approach, the kinetics of the leaching reaction can be described in Eq. (10):

\[
r_i = \frac{d}{dt} C_i = k_i \cdot [C_{i, \text{max}} - C_i]^{n_i} \tag{10}
\]

where \( C_i \) is the leaching concentration of metal ions, and \( n_i \) is the order of the leaching reaction. The values of \( C_{i, \text{max}} \) and \( k_i \) constants should generally increase as the particle size of solid waste decreases. Eq. (10) can be integrated into Eq. (11a) in the case of \( n = 1 \), or Eq. (11b) in the case of \( n \neq 1 \).

\[
C_i = C_{i, \text{max}} \left[ 1 - e^{-k_i t} \right], \quad \text{for } n = 1 \tag{11a}
\]

\[
C_i = C_{i, \text{max}} \left[ C_{i, \text{max}}^{1-n} - (1-n)k_i t \right]^{(1-n)}, \quad \text{for } n \neq 1 \tag{11b}
\]
Pan et al. (2013) found that the leaching of Ca, Na and K ions from steel slags were more sensitive to the concentration driving force in comparison to other ions. In most curriculum, the release of Mg ions from steel slag was quite low compared to Ca release (Chang et al., 2012a). Several factors could increase the leaching concentration of calcium ions from the solid matrix (Park et al., 2003; Iizuka et al., 2004; Alexander et al., 2005): (i) high porosity and fine particle size of alkaline solid wastes; (ii) high temperature and low pH value in solution; and (iii) sufficient mixing between the solid and liquid phases to avoid severe agglomeration. The leaching of calcium ions is probably determined by the diffusion through the Ca-depleted silicate rim inside the solid matrix (O’Connor et al., 2002; Santos et al., 2009), rather than by the surface reaction at the phase boundary (i.e., the solid-liquid interface) which usually is the rate-limiting step in the beginning of aqueous carbonation.

Aside from the conventional mass conservation method, several approaches are developed for evaluating the leaching behaviors of solid particles. For example, Hariharan et al. (2014a) developed a non-steady state dissolution kinetic model for lizardite particles by considering the dynamics of the pH value during the reaction. This model can accurately describe the non-stoichiometric concentration profiles of magnesium and silica ions in the solution. Similar approaches have also been applied for other solid particles, such as thermally activated serpentine (Hariharan et al., 2014b).

**Precipitation Kinetics**

Contact between calcium and carbonate ions would lead to the formation of calcium carbonate precipitates. Calcium carbonate is almost insoluble in water at the pH above 9 (Chiang and Pan, 2017b). The reaction of calcium ions with carbonate ions is fast and usually related to the carbonate ion concentration in the liquid phase. Ishida and Maekawa (2000) suggested that the precipitation of calcium carbonates should be a first-order reaction with respect to the concentrations of Ca\(^{2+}\) and CO\(_3^{2-}\) ions, as described by Eq. (12):

\[
\frac{dr}{dt} = k \left[ Ca^{2+} \right] \left[ CO_3^{2-} \right]
\]  

(12)

The formation of calcium carbonate precipitates occurs when the precipitation kinetics is not equal to dissolution kinetics (i.e., not equilibrium). The balance between leaching and precipitation reactions depends on their reaction kinetics and solubility of the feedstock and reaction products (e.g., the solubility of CaCO\(_3\) is about 0.15 mmol L\(^{-1}\) at 298 K). As the calcium ions in solution are consumed to form precipitates, more calcium-bearing components in the solid phase dissolve to equalize the difference in calcium ion concentration.

**Applications in CO\(_2\) Mineralization**

CO\(_2\) mineralization via accelerated carbonation proceeds via dissolution and precipitation reactions in which the aqueous solution plays a critical role on reaction kinetics. Gadikota et al. (2014c) developed a systematic framework on experimental design and data analysis for accurate evaluation of dissolution and carbonation behaviors. Harrison et al. (2017) applied the transmitted light and backscattered electron micrographs to evaluate the mechanism of brucite [Mg(OH)\(_2\)] carbonation at the pore scale. They found that brucite in dry pores remained visibly unreacted, whereas hydrated carbonate precipitates (e.g., nesquehonite [MgCO\(_3\)-3H\(_2\)O]) were abundant in water filled pores, as shown in Figs. 3(a)-3(b). This reveals that the gas-mineral interface is relatively unreactive. As the reaction proceeds, the magnitude of the solid-fluid interfaces is significantly dynamic due to the water loss and the entrapment of reactive minerals by the moving gas-water interfaces, as illustrated by Figs. 3(c)-3(e).

Cizer et al. (2012) evaluated the reaction mechanisms of carbonation of lime pastes with an in-situ X-ray diffraction determining the dynamic changes in mineralogy including portlandite and calcite. The results revealed that the reaction first was chemically controlled at the exposed surface with a strong CO\(_2\) diffusion resistance, and then followed by a transition to a CO\(_2\)-diffusion controlled regime through the carbonate product layer (Cizer et al., 2012). Ashraf and Olek (2018) conducted a multi-technique approach to elucidating accelerated carbonation products of calcium silicates, as shown in Fig. 3(f). They found that the presence of agglomerations of silica gel clusters on the surfaces of amorphous calcium carbonate would result in a lower inter-cluster porosity for carbonated matrixes. The small portion of gel pores in carbonated matrix of monocalkaline silicate (CaO-SiO\(_2\)) may be formed between the partial agglomerates of silica gel clusters.

**SHRINKING CORE MODEL**

For the noncatalytic reaction of solids with surrounding fluid (i.e., heterogeneous reactions), the shrinking core model can be used to determine its reaction kinetics and rate-determining step. The features of the shrinking core model include (Benedetti, 2014):

- Applicable to each grain, but not to the particle as a whole
- Suitable for explaining data where the conversion is less than 100%
- There is a non-porous passivated product layer around the grain reactive surfaces

In the shrinking core model, it is assumed that an unreacted core of material always exists before complete conversion of particle to product. The reaction occurs at the surface of the unreacted core (i.e., typically a sharp interface for non-porous grains) and then proceeds into the inside of the core, leaving behind the reacted rims (known as an ash layer). In other words, the size of the unreacted core gradually shrinks during the reaction. Shrinking core model exhibits inherent limitations to the reactions with a porous particle. Ahn and Choi (2017) indicated that the shrinking core model for a porous pellet would become
Fig. 3. (a) Nesquehonite precipitates in water-filled area with lateral growth limited by the gas-water interface. Green color indicates the gas-filled areas. Adapted from the literature (Harrison et al., 2017). (b) Backscattered electron micrograph of reaction products from brucite carbonation. Adapted from the literature (Harrison et al., 2015). (c–e) Time series of light micrographs illustrating the entrainment of brucite particles by the retreating gas-fluid interface. Micrographs captured at (c) 250 min, (d) 355 min, and (e) 360 min. Adapted from the literature (Harrison et al., 2017). (f) Distribution of the pores smaller than 10 nm in carbonated calcium silicate matrices in the presence of amorphous calcium carbonate (ACC). Adapted from the literature (Ashraf and Olek, 2018).
valid only when the reaction was controlled by inward diffusion (i.e., the reaction proceeded with the core-shell structure).

**Governing Equations**

According to the definition of a fluid-solid reaction in shrinking core model, accelerated carbonation can be simply expressed by Eq. (13):

$$\text{CO}_2(\text{fluid}) + b \ \text{CaO}(\text{solid}) \rightarrow \text{CaCO}_3(s) \quad (13)$$

where $b$ is the stoichiometric coefficient for carbonation reaction (-). For this reaction, three possible rate-determining steps can be considered in the shrinking core model (Fig. 4): fluid-film diffusion (F-mechanism), ash-layer diffusion (D-mechanism), and chemical reaction at the unreacted core surface (C-mechanism).

In the classic shrinking core model, it is assumed that the particle size ($R$) remains constant during the reaction. The characteristic time ($\tau$) for complete conversion of particle to product with respect to three rate-determining steps can be obtained via the governing equations:

**Fluid-film Diffusion (F-mechanism)**

When the diffusion of the carbonate ions through the boundary layer at the fluid–particle interfaces is the rate-determining step, the carbonation conversion of solid particles ($X$, dimensionless) can be described as the function of reaction time ($t$, sec) by Eq. (14):

$$k_F \cdot t = X \quad (14)$$

where $k_F$ is the apparent reaction rate constant (s$^{-1}$) for the fluid-film diffusion control mechanism. The characteristic time for the fluid-film diffusion control mechanism ($\tau_F$) can be determined by Eq. (15):

$$\tau_F = \frac{1}{k_F} = \frac{\rho_b R}{3b_k C_{Ag}} \quad (15)$$

where $\rho_b$ is the molar density of the particles, $R$ is the radius of the particles, $k_b$ is the mass-transfer coefficient, and $C_{Ag}$ is the molar concentration of CO$_2$ in the bulk fluid.

**Ash-layer Diffusion (D-mechanism)**

When the diffusion of the carbonate ions through the ash layer is the rate-determining step, the governing equation can be described by Eq. (16):

$$k_D \cdot t = [1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)] \quad (16)$$

where $k_D$ is the apparent reaction rate constant (s$^{-1}$) for the ash-layer diffusion control mechanism. The characteristic time for the ash-layer diffusion control mechanism ($\tau_D$) is shown as Eq. (17):

$$\tau_D = \frac{1}{k_D} = \frac{\rho_b R^2}{6b_D C_{Ag}} \quad (17)$$

where $D_e$ is the effective diffusivity of carbonate ions through the ash layer.

**Chemical Reaction at the Unreacted Core Surface (C-mechanism)**

When the chemical reaction at the phase boundary (such as the unreacted core surface) is the rate-determining step, the carbonation conversion of solid particles can be expressed by Eq. (18):

$$k_C \cdot t = [1 - (1 - X)^{\frac{1}{3}}] \quad (18)$$

where $k_C$ is the apparent reaction rate constant (s$^{-1}$) for the
reaction control mechanism. The characteristic time for the reaction control mechanism \((\tau_c)\) is shown as Eq. (19):

\[
\tau_c = \frac{1}{k'} = \frac{\rho_g R}{bk' C_{ag}}
\]  

(19)

where \(k'\) is the first-order rate constant for the surface reaction.

**Combination of Mechanisms**

In actuality, the relative importance of the above single mechanism varies as the reaction proceeds due to the dynamical changes in several factors such as mineralogical compositions, particle size, and pore blockage. To consider the simultaneous action of the above three mechanisms, the time to reach any stage of conversion \((\tau_{total})\) can be determined by the sum of the times needed if each resistance acted alone, as shown in Eq. (20):

\[
\tau_{total} = \tau_F + \tau_D + \tau_c
\]  

(20)

Farhang et al. (2017) applied the crackling core model, which is an extension to the shrinking core model by involving two parameters of step reactions \((\tau_c\) and \(\tau_{gp}\)), to evaluate the dissolution kinetics of magnesium ions from serpentine. \(\tau_c\) and \(\tau_{gp}\) are the characteristic times for being completely converted to grainy porous solid and for complete conversion of a grain, respectively. They found the formation of meso-pores in the particles along the leaching process (Farhang et al., 2017). For accelerated carbonation, initial operating parameters such as liquid-to-solid ratios will result in different buffering capacities and reactant concentrations \((C_{ag})\) in solution (Pan et al., 2016c). Also, the release of reaction heat from accelerated carbonation may cause local temperature gradients within the particles or between particle and the bulk fluid. The heat transfer phenomena may cause local temperature gradients within the particles or between particle and the bulk fluid. The heat transfer phenomena may affect the importance of the chemical reaction control mechanism at the unreacted core surface. One of the technical challenge in CO2 mineralization is to accelerate the reaction while exploiting the heat of reaction to minimize the energy use (Bobicki et al., 2012).

Carbonation fronts at the solid-fluid interface are dynamic during the reaction. The changing solid-fluid interface is dependent on the rate of dissolution/precipitation at the mineral surface (i.e., the reaction-controlled mechanism) and the rate of reactant/product transport (i.e., the transport-controlled mechanism). The Damköhler \((Da)\) number has been typically used to distinguish between the regimes of mechanisms in mineral systems (Steefel and Maher, 2009; Deng et al., 2018). The Da number represents the ratio of the characteristic time of transport \((\tau_D)\) to that of reaction \((\tau_c)\), as shown in Eq. (21):

\[
Da = \frac{\tau_D}{\tau_c} = \left(\frac{I_{adv}}{k' I_{SFR}}\right)
\]  

(21)

where \(I_{adv}\) is the advection time (or residence time) of the bulk fluid, \(k\) is the dissolution rate constant (mol s \(^{-1}\) m \(^{-2}\) mineral), \(S_{eq}\) is the solubility of the mineral phase (mol m \(^{-3}\) fluid), and \(I_{SFR}\) is the solid-fluid interfacial area in units of m \(^{2}\) mineral per m \(^{3}\) fluid.

Harrison et al. (2017) suggest that the particle movement could shift the overall control of the carbonation since Da number is proportional to the solid-fluid interfacial area \((I_{SFR})\). In general, a Da value less than one indicates a kinetics-limited system, while a Da value higher than one refers to mixing-limited conditions. Deng et al. (2018) proposed a multireaction Da number to evaluate multiminerals systems with differing reactivity of minerals. However, they still mentioned several limitations for this framework, e.g., the mineral spatial heterogeneity was not considered.

**Considering Particle Size Changes with Reaction**

In practice, the particle size would change in the course of reaction due to the formation of ash and/or product layers. This would affect the diffusivity of the reactant in the ash and/or product layers. It is observed that the thickness of the product layer (precipitated calcium carbonate) on the surface of the steel slag ranges from 1 to 3 µm (Chang et al., 2012a). To consider the effect of particle size distribution, several factors can be included to modify the relationship between the carbonation conversion and reaction time.

**Z Factor**

A “Z factor” (Sohn, 2004) can be introduced to modify the governing equation for ash layer diffusion control in the classic shrinking core model, as shown in Eq. (22):

\[
t = \tau_D \times \left[ \frac{Z - (Z - (Z - 1)(1 - X))^{2/3}}{(Z - 1)^{1/3}} - 3(1 - X)^{2/3} \right]
\]  

(22)

where the Z factor represents the ratio of the volume of product solid to the volume of original solid (both including pore volumes). A Z value of one indicates the volume of the product solid remains the same as that of the original solid reactant, i.e., the particle size is unchanged in the course of reaction. In this case, Eq. (22) can be simplified to Eq. (16) by applying L’ Hospital’s rule.

**λ Factor**

Li et al. (2015) applied fractal geometry principles, i.e., a “λ factor”, for considering the changes in the surface area and volume of the solid particles during the liquid-solid reaction between acid and minerals. In the shrinking core model, the λ factor can be used to modify the conversion \((X)\) with the changes of particle size \((R)\) in the course of reaction, as shown in Eq. (23):

\[
X = 1 - \int_{R_0}^{R} \left( \frac{t}{\lambda} + R^{\eta-\lambda} \right)^{\frac{\eta-\lambda}{\eta}} f(R) dR
\]  

(23)
where the term $D$ represents the fractal dimension of the external surface area of a particle. The value of $\eta$ is defined as Eq. (24):

$$\eta = \frac{4(D - 2)}{D}$$

For a spherical particle, the $D$ and $\eta$ values can be assigned to be two and three, respectively. It is noted that this modification factor can be used for determining the reaction kinetics of acid extraction for solid wastes that is controlled at the surface reaction stage.

**Applications in Leaching and Carbonation Reactions for CO$_2$ Mineralization**

Shrinking core model has been commonly applied in evaluating the unit processes and reactions for accelerate carbonation, such as the dissolution of Mg(OH)$_2$ (Bharadwaj et al., 2013), the extraction of calcium ions by dicarboxylic acids (Balduga et al., 2011), and calcium leaching from steel slags (Lekakh et al., 2008). The leaching of calcium ions from the solid particles by aqueous carbonation is much faster compared to that by natural weathering (Costa, 2009). However, Davel et al. (2009) noticed that the calcium leaching should be the primary rate-limiting step with respect to the entire accelerated carbonation reaction. The leaching of calcium and/or magnesium ions would result in a metal-depleted rim (e.g., SiO$_2$) around the surface of the unreacted core (Park and Fan, 2004). In particular, the rate-determining step for the initial stage of calcium leaching from steel slags (i.e., < 30% conversion) should be reaction controlled mechanism, while the later stage was controlled by molecular diffusion (Lekakh et al., 2008).

If we consider both the leaching and carbonation steps as a whole reaction, the ash-diffusion mechanism is found to be the rate-limiting step. Table 2 summarizes the effective diffusivity ($D_e$) of reactant for CO$_2$ mineralization via accelerated carbonation based on shrinking core model. The diffusivity varies remarkably among the types of feedstock and reactors, and operating conditions. In general, the effective diffusivity is highly dependent on the reaction temperatures, i.e., it increases as the temperature increases. Therefore, at similar levels of operating temperatures, the diffusivities in a slurry reactor and in a rotating packed bed were found to be at the similar magnitude of $\sim 10^{-7}$ cm$^2$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>CO$_2$ stream</th>
<th>Solid waste</th>
<th>Liquid agent</th>
<th>Operating time (s)</th>
<th>Diffusivity ($10^{-7}$ cm$^2$ s$^{-1}$)</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPB</td>
<td>~99%</td>
<td>~1</td>
<td>BOFS</td>
<td>298</td>
<td>4.82–9.18</td>
<td>318</td>
<td>Chang et al., 2012a</td>
</tr>
<tr>
<td>SR</td>
<td>~99%</td>
<td>~1</td>
<td>2.5</td>
<td>5.47–11.0</td>
<td>5.38–11.0</td>
<td>338</td>
<td>Chang et al., 2012a</td>
</tr>
<tr>
<td>SR</td>
<td>~99%</td>
<td>~1</td>
<td>0.1</td>
<td>1.72–28.2</td>
<td>1.72–28.2</td>
<td>303</td>
<td>Pan et al., 2016c</td>
</tr>
<tr>
<td>SR</td>
<td>~99%</td>
<td>~1</td>
<td>MSWI-BA</td>
<td>67.9–102.0</td>
<td>67.9–102.0</td>
<td>343</td>
<td>Chang et al., 2015</td>
</tr>
</tbody>
</table>

$^a$ RPB: rotating packed bed; SR: slurry reactor. $^b$ Concn.: CO$_2$ concentration in the feed stream (%); $^c$ Pressure (bar); $^d$ Liquid-to-solid ratio (mL g$^{-1}$).
the surface of the unreacted core would limit further diffusion of the reactants from inside the solid matrix into solution, thereby resulting in a dynamic equilibrium. The effect of the coverage of the product layer on the reaction kinetics is considered in the surface coverage model, which is illustrated in the next section.

SURFACE COVERAGE MODEL

The surface coverage model was first developed by Shih et al. (1999) for evaluating the kinetics of carbonation and desulfurization of hydrated lime (Ca(OH)₂) at low temperatures. Because of the similar behaviors to these heterogeneous reactions, the surface coverage model has been utilized to evaluate the kinetics of accelerated carbonation for alkaline solid wastes (Chang et al., 2011b, 2013b).

Governing Equations

In the surface coverage model, the reaction occurs only at the unsaturated sites of particles that are not covered by any reaction product (Φ). Then the product is coated on the particle surface (multi-layer coverage) at the solid-fluid interface. As the reaction proceeds, the solid particle will reach a maximum carbonation conversion (Xmax). It is assumed that the surface of the reactant is homogeneous and all sites are equivalent. In the surface coverage model, the governing equation of carbonation reaction rate per initial surface area of particles (r, mole min⁻¹ m⁻²) can be described by Eq. (25):

\[ r_s = k_s \Phi = \frac{1}{S_g M} \frac{dX}{dt} \]  

(25)

where \( k_s \) (mole min⁻¹ m⁻²) is the apparent reaction rate constant, \( \Phi \) (-) represents the fraction of the active surface sites without being covered by reaction products, \( S_g \) (m² g⁻¹) is the initial specific surface area of particles, \( M \) (g mol⁻¹) is the weight of solid particles per mole of calcium oxide, \( X \) (-) is the carbonation conversion of particles, and \( t \) (min) is the reaction time. It is noted that, in the above governing equation, only the calcium-bearing components are considered to be the major reactive species for accelerated carbonation.

The fraction of the active surface sites (Φ) should gradually reduce with the progress of the reaction depending on the reaction rate, which can be illustrated by Eq. (26):

\[ -\frac{d\Phi}{dt} = k_p \Phi^{n-1} \cdot r_s = k_p \cdot k_s \Phi^n \]  

(26)

where \( k_p \) (m² mol⁻¹) represents a coefficient indicating the availability of the active surface sites. Shih et al. (1999) found that the \( n \) value of 1.7 was the best fitting value for the carbonation of Ca(OH)₂.

We can simplify the above kinetic rate constants by designating the terms \( k_1 \) (min⁻¹) and \( k_2 \) (-), as shown in Eqs. (27) and (28), respectively:

\[ k_1 = k_s S_g M \]  

(27)

\[ k_2 = k_p (S_g M) \]  

(28)

By assigning the \( n \) value to be one for simplicity, the carbonation conversion of the particle (X), in terms of \( k_1 \) and \( k_2 \), can be expressed by Eq. (29):

\[ X = \frac{[1 - \exp(-k_1 k_2 t)]}{k_2} \]  

(29)

In the model, the reactant particles would eventually reach a maximum carbonation conversion (Xmax) when the system is under the equilibrium conditions. Thus, we can convert Eq. (29) to be Eq. (30) in terms of Xmax:

\[ X = X_{max}[1 - \exp(-k_5 k_p t)] \]  

(30)

where \( X_{max} \) equals to the value of the reciprocal of \( k_2 \).

Applications in CO₂ Mineralization

In the surface coverage model, the reaction products continuously deposit on the active surface of solid particles in the course of carbonation. The surface structure of the reacted particles also changes with the reaction. Due to the formation of the product layer, the diffusion of reactants from the inside unreacted particles through the product layer would be the rate-determining step as the reaction proceeds. This would hinder the solid particles from further reaction, thereby reaching a maximum conversion. Hariharan and Mazzotti (2017) found that the passivation behaviors by amorphous silica precipitation on the dissolving particle increased with temperature (30–60°C). The inhibitory effect would significantly reduce the rates of the magnesium ion release from the solid matrix.

Table 3 summarizes the kinetic parameters of accelerated carbonation determined by the surface coverage model. A higher \( k_s \) value indicates a more rapid carbonation reaction rate with a higher carbonation conversion. As shown in Table 3, the rate of the carbonation reaction using inorganic wastewater (such as cold-rolling wastewater) is found to be generally higher than that using pure-water (such as deionized water). The maximum carbonation conversion (Xmax) in the high-gravity carbonation process is generally greater than that in the auto clave reactor and the slurry reactor. However, a high \( k_s \) value would also lead to a large quantity of reaction product deposited on the surface of particles at the beginning of the reaction. This might inhibit further leaching of reactive species from the inside unreacted particles into the bulk solution (Pan et al., 2014). Therefore, in addition to the \( k_s \) value, the \( k_p \) value is another important kinetic parameter in reactor design. A higher \( k_p \) value implies that the product would cover the active surface of particles more uniformly. The fresh solid particle usually has a smooth morphology before the reaction, while exhibiting characteristic precipitates (e.g., in the shapes of needle-like, rhombohedral, or cubic crystals) on the surface of particles after the reaction (Pan et al., 2014).

The limitation of the surface coverage model is that only a single layer of the diffusion-limited rim around the
Table 3. Comparison of kinetic parameters for CO₂ mineralization via accelerated carbonation based on surface coverage model.

<table>
<thead>
<tr>
<th>Reactor&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solid waste&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Liquid agent&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Experimental data&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Model parameters (mean value)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chang et al., 2011b)</td>
</tr>
<tr>
<td>AR</td>
<td>BHC</td>
<td>DW</td>
<td>0.68</td>
<td>433</td>
<td>106.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chang et al., 2011b)</td>
</tr>
<tr>
<td></td>
<td>FAS</td>
<td></td>
<td>0.35</td>
<td>433</td>
<td>144.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chang et al., 2013b)</td>
</tr>
<tr>
<td></td>
<td>UFS</td>
<td></td>
<td>0.38</td>
<td>433</td>
<td>132.0</td>
</tr>
<tr>
<td>SR</td>
<td>BOFS</td>
<td>DW</td>
<td>0.80</td>
<td>298</td>
<td>136.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chang et al., 2013b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EW</td>
<td>0.78</td>
<td>298</td>
<td>136.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CRW</td>
<td>0.89</td>
<td>298</td>
<td>136.1</td>
</tr>
<tr>
<td>RPB</td>
<td>BOFS</td>
<td>TW</td>
<td>0.52</td>
<td>303</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chen et al., 2016)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CRW</td>
<td>0.58</td>
<td>333</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chen et al., 2016)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.87</td>
<td>298</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Chen et al., 2016)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.95</td>
<td>338</td>
<td>130.0</td>
</tr>
<tr>
<td>RPB</td>
<td>BOFS</td>
<td>TW</td>
<td>0.86</td>
<td>298</td>
<td>117.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Pan et al., 2014)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CRW</td>
<td>0.92</td>
<td>338</td>
<td>117.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Pan et al., 2014)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td>293</td>
<td>95.0</td>
</tr>
<tr>
<td>RPB</td>
<td>EAFS</td>
<td>DW</td>
<td>0.61</td>
<td>333</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Pan et al., 2018)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.31</td>
<td>313</td>
<td>89.0</td>
</tr>
<tr>
<td>AR</td>
<td>FA</td>
<td>DW</td>
<td>0.23</td>
<td>343</td>
<td>89.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>AR: autoclave reactor; RPB: rotating packed bed; SR: slurry reactor.  
<sup>b</sup>FAS: fly-ash slag; UFS: ultra-fine slag; BOFS: basic oxygen furnace slag; EAFS: electric arc furnace slag; FA: fly ash.  
<sup>c</sup>DW: deionized water; TW: tap water; EW: effluent water from wastewater treatment plant; CRW: cold-rolling wastewater.  
<sup>d</sup>X<sub>CaO</sub>: carbonation conversion determined by thermogravimetric analysis (-); T: temperature (K); M (g mol<sup>-1</sup>); S<sub>G</sub> (m<sup>2</sup> g<sup>-1</sup>).
particle is considered. In real circumstances, the coverage at the solid-fluid interface may not always be a mono-layer. Also, the product layer and the reactive-species-depleted layer (i.e., the ash layer in the shrinking core model) may co-exist during the carbonation. Therefore, the determined parameters of modelling should be seen as the apparent (global) reaction rate, which can not clearly distinguish the effect of the aforementioned mechanisms. In any case, by applying the surface coverage model, preliminary information on the order of reaction rate can be obtained for evaluating various types of processes and/or feedstocks.

ADVANCED MODELS CONSIDERING MULTIPLE MECHANISMS

Classical kinetic models are usually developed based on a single resistance for the sake of simplicity. In real situations, the interplay among various resistances on the reaction kinetics is complex due to the dynamical changes in chemical (e.g., mineralogy of solid reactants and alkalinity of bulk solution) and physical (e.g., particle size and pore volume) properties. This section provides an overview on several advanced models that consider multiple mechanisms in evaluating the reaction kinetics of accelerated carbonation, including integrated reaction-diffusion model, two-layer diffusion model and integrated transport-reaction model.

Integrated Reaction-diffusion Model

Lee and Koon (2009) coupled the chemical reaction mechanism in the shrinking core model with diffusion mechanism to predict the kinetics of the desulfurization reaction. The concept of desulfurization (if a dry process) is introducing CaO-based sorbents into the flue gas, where the flue gas SO₂ would react with CaO in the sorbents to form CaSO₄ precipitates. This is basically a non-catalytic solid-gas (solid-fluid) reaction at low temperature. As a result, the phenominalogical kinetic model of desulfurization could be applicable to accelerated carbonation. The rate of the desulpharation reaction was normally considered to be controlled by particle pore diffusion and product layer diffusion (Han et al., 2005). In other cases, Christopher-Chia et al. (2005) presumed that the non-catalytic reaction between gaseous SO₂ and solid reactants is either a reaction-controlled or diffusion-controlled mechanism. They developed a global reaction rate model with the aim to incorporate both the reaction and diffusion controlling step for the desulfurization reaction.

Considering both chemical reaction and diffusion as the rate-determining step, the change of conversion (X) in the solid phase with time (t) is shown in Eq. (31). A surface coverage effect, i.e., \( f(\theta) \), is included in the original shrinking core model with chemical reaction mechanism.

\[
\frac{\partial X}{\partial t} = f(\theta) \cdot \frac{3b \cdot C \cdot Y}{\rho_p \cdot r} \cdot k(1 - X)^{2/3}
\]

(31)

where \( b \) is the stoichiometric coefficient (the molar ratio of solid reactant to gas reactant), \( Y \) is the dimensionless concentration of reacting gas (e.g., CO₂) with a function of time, \( C \) is the initial reacting gas concentration (mol m⁻³), \( \rho_p \) is the density of the particle (mol m⁻³), and \( r \) is the radius of unreacted core (m). The surface coverage effect, i.e., \( f(\theta) \), can be expressed by conversion of the solid phase, as shown in Eq. (32):

\[
f(\theta) = \alpha e^{\theta^2 - C \cdot (1 - bX)^d}
\]

(32)

where \( \alpha \) is the pre-exponential constant (-), \( T \) is the reaction temperature (K), and \( a, c \) and \( d \) are the order for the effect of the respective operating parameters on the surface coverage.

Two-layer Diffusion Model

In the classic shrinking core model, the product layer diffusion is not considered in the ash-diffusion controlled mechanism. In real circumstances, three distinguishable layers in a solid particle may exist during the carbonation: (i) the unreacted core, (ii) the ash layer containing the calcium-depleted zones, and (iii) the product layer with carbonate precipitates such as calcite. Several studies applied the shrinking core model and identified that the ash-layer diffusion is the rate limiting step for accelerated carbonation (Lekakh et al., 2008; Chang et al., 2011a). In other cases, the resistance from the product layer may also be the rate-determining step for the carbonation reaction. For instance, Min et al. (2017) observed a layer of amorphous silica and calcite products surrounded the solid particles after aqueous carbonation with supercritical CO₂, where the product layer could act as a diffusion barrier to the reaction. In other words, the diffusion resistances from both the ash and product layers are perhaps considerably important.

Gopinath and Mehra (2016) modified the classic shrinking core model and proposed a novel two-layer diffusion model. As shown in Fig. 5, the kinetic model simultaneously considers two layers outside the unreacted core of a solid particle, i.e., the ash layer (calcium-depleted rim) and the product layer (calcium carbonate product). Thus, it describes the aqueous carbonation reaction with two moving boundaries, i.e., the product-ash interface \( (r_c) \) and the ash-core layer \( (r_r) \). The kinetic resistance of calcium leaching from alkaline solid wastes is also incorporated into the model.

It is assumed that (i) the calcium oxide forms carbonate instantaneously, and (ii) the carbonation reaction results in little CaCO₃ precipitates within the pores of the ash layer. The kinetics of carbonation with respect to the carbonation boundary \( (r_c) \) are expressed in Eq. (33):

\[
r = \rho_c A_0 \frac{dr}{dt} = \frac{-q[H^+]}{D_{\Phi}[D_{\Phi}A_{\Phi} + r_A + 1]}
\]

(33)

where \( \rho_c \) is the molar density of reactive calcium species in the fresh solid particle, \( A_0 \) is the superficial specific area of cross section, \( A_s \) is the total cross area of the pores in the ash layer, \( A_p \) is the specific surface area of the product layer, \( A_z \) is the initial surface area of the core, \( r_o \) is the
DI water in a slurry reactor (i.e., CO2 pressure ~0.1 MPa at 10–5 and 8.97 × 10 –5 cm 2 s –1, respectively. These results revealed that the diffusion through the ash layer should be the dominant rate-limiting step in comparison to the diffusion through the product layer.

Incorporated Mass Transfer with Reaction Kinetics

To include the effect of mass transport, the kinetics of the carbonation reaction can be developed based on the classical mass transfer model such as two-film theory. The diffusion control mechanism implies the relative importance of mass transfer phenomena, which involves the movement of a single mass molecular from one phase into another. In the carbonation reaction, the mass transfer of CO2 between the gas and liquid phases should be significant. Chang et al. (2013a) developed an apparent kinetic model of aqueous carbonation based on a shell mass balance, as shown in Eq. (34). The CO2 (gas phase) is characterized by convection behaviors between the inlet and outlet streams. It is also assumed that the mass transfer between the liquid and solid phases can be neglected.

\[
\rho_v V_g \frac{dC_{CO_2}}{dt} = \rho_v (Q_g, C_{CO_2} - Q_{g,o}C_{CO_2}) - k_{l,a} V_L (P_{CO_2} H_{CO_2} - C_{TC}) \tag{34}
\]

where \( \rho_v \) (mol cm–3) is the density of CO2 gas, \( V_g \) (cm3) and \( V_l \) (cm3) are the volume of gas and liquid, \( C_{CO_2} \) (mol cm–3) is the CO2 concentration in exhaust gas, \( k_l \) (cm s–1) represents the mass transfer coefficient on the liquid side, \( a_p \) (cm2 cm–3) is the specific surface area of packing materials, \( H_{CO_2} \) (mol cm–3 atm–1) refers to the Henry’s law constant of gaseous CO2 in water, and \( C_{TC} \) (mol cm–3) is total inorganic carbon in the bulk liquid solution.

For the bulk liquid, the rate of total inorganic carbon consumption during the reaction can be described by Eq. (35). Assuming the carbonation reaction is at the steady-state conditions, the concentration of total inorganic carbon would remain relatively unchanged during the carbonation.

\[
V_l \frac{dC_T}{dt} = k_{l,a} V_L (P_{CO_2} H_{CO_2} - C_{TC}) + k_s C_{TC} V_l \tag{35}
\]

where \( k_s \) (mol cm–3 atm–1) is the reaction rate constant, and \( C_s \) (mol cm–3) is the CaO concentration of solid particles. Similarly, the rate of the solid concentration can be expressed by Eq. (36):

\[
V_s \frac{dC_s}{dt} = k_{l,a} P_{CO_2} H_{CO_2} - C_{TC} \tag{36}
\]

where \( k_{l,a} \) value for the reaction using wastewater with steel slag was about 9.23 × 10–4 s–1, while the corresponding \( k_s \) value was ~216.9 cm3 mol–1 s–1. It was also noted that the reaction rate using wastewater (188–217 cm2 mol–1 s–1) was higher than that using DI water (160–195 cm2 mol–1 s–1).

PERSPECTIVES AND PROSPECTS

This article provides an overview on the phenomenological modelling at the solid-fluid interfaces for CO2 mineralization via accelerated carbonation. To improve the understanding of CO2 mineralization at interface levels, three priority research directions, including (1) incorporation of structural and physical properties in phenomenological models, (2)
identification of dynamic speciation by in-situ high-resolution equipment, and (3) integration of heat transfer in reaction modelling for system optimization, should be focused.

**Incorporation of Structural and Physical Properties in Phenomenological Models**

For CO$_2$ mineralization, transport phenomena such as carbonate- and calcium-ions diffusion to/from reaction sites are normally found to be the rate-limiting steps. Boundary layers would directly affect the reaction rate and CO$_2$ fixation capacity of accelerated carbonation, such as diffusion across precipitate coatings on particles, pore blockage in the ash layer, or dissolution of reactive components from solid matrix at the particle surface. Especially for the non-catalytic systems, the pore structure of the solid particle changes during the reaction. Therefore, in addition to the chemical reaction at the interface, the phenomenological models should consider the reaction dynamics in terms of structural and physical properties, e.g., the pore size and surface area (both internal and external) of particles, the thickness of product layer, and the extent of pore overlapping.

**Identification of Dynamic Speciation by in-situ High-resolution Equipment**

Determining the dynamic speciation and product properties in the heterogeneous system (i.e., CO$_2$ gas, liquid, and solid particles) plays a key role in controlling reaction pathways and rates. This requires the development and application of in-situ high-resolution investigative equipment for measuring local mass transfer and identifying phase characteristics at the molecular level. For different types of processes and/or feedstocks, broad-spectrum collection of thermodynamic and kinetic information, especially focusing on mass transfer and reaction rate at the solid-fluid interfaces, should be the priority research directions.

**Integration of Heat transfer in Reaction Modelling for System Optimization**

In practice, process heat integration is a necessary component for system optimization. It would also provide opportunities on increasing process energy efficiency that is required for achieving the positive carbon fixation. Björklöf and Zevenhoven (2012) suggest that a thermodynamic efficiency analysis from the perspective of exergy should be conducted to evaluate the overall thermal/energy efficiency of CO$_2$ mineralization processes. CO$_2$ mineralization by accelerated carbonation is an exothermic reaction, where the heat of reaction could be utilized as a source of energy input. From the viewpoint of a plant, the actual reaction temperature is related to the heat of carbonation reaction, the heat loss from reactors, and the energy recovered in heat exchangers. To realize the system optimization, the heat transfer at interface levels should be considered in the phenomenological models.

**CONCLUSIONS**

CO$_2$ mineralization using alkaline solid wastes has been considered one of the most promising potential technologies to combat anthropogenic CO$_2$ emissions. Classical models such as shrinking core model and surface coverage model can provide a rapid assessment on the reaction kinetics. However, in practice, multiple mechanisms should be considered in evaluating the reaction kinetics of CO$_2$ mineralization due to the dynamical changes in chemical (e.g., mineralogy of solid reactants) and physical (e.g., particle size and pore volume of reactant particles) properties. Future priority research directions on phenomenological modelling include incorporation of structural and physical properties, identification of dynamic speciation by in-situ high-resolution equipment, and integration of heat transfer for system optimization.

**ACKNOWLEDGMENTS**

This study was supported by the Ministry of Science and Technology (MOST), Taiwan (ROC) under Grant No. MOST-107-3113-E-007-002 and 107-2917-I-564-043. We also thank Dr. Mengyao Gao from Department of Chemical Engineering, National Taiwan University for her technical assistance on preparing figures.

**REFERENCES**


Received for review, March 14, 2018

Revised, March 20, 2018

Accepted, March 20, 2018