Reaction–Diffusion Model for Gasification of a Shrinking Single Carbon-Anode Particle

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ABSTRACT: The present work focuses on the gasification of a single carbon-anode particle with CO₂, using a detailed reaction-diffusion transport model based on the reaction intrinsic kinetics and transport of gaseous species. The model includes the mass conservation equations for the gas components and solid carbon particles, resulting in a set of nonlinear partial differential equations, being solved using numerical techniques. The model may predict the gas generation rate, the gas compositions, and the carbon consumption rate during the gasification of a carbon particle. Five kinetic models were compared to describe the gasification behavior of carbon particles. It was found that the random pore model (RPM) provided the best description of the reactivity of anode particles. The model also predicted the particle shrinkage during the gasification process. The model was validated using experimental results obtained with different particle size ranges, being gasified with CO₂ at 1233 K. The experiments were performed in a thermogravimetric analyzer (TGA). Good agreement between the model results and the experimental data showed that this approach could quantify with success the gasification kinetics and the gas distribution within the anode particle. In addition, the Langmuir–Hinshelwood (L–H) model is used in order to capture the inhibition effect of carbon monoxide on the gasification reaction. The effectiveness factor and Thiele modulus simulated for various particle sizes helped assess the evolution of the relative dominance of diffusion and chemical reactions during the gasification process.

1. INTRODUCTION
Carbon anode reactivity is of considerable concern for most aluminum smelters using the Hall–Héroult electrolysis process. In this process, anodes are partially submerged into the electrolyte solution, which is made up of molten cryolite. Molten aluminum is produced by the reduction of dissolved alumina in the cryolite, and the anode is electrochemically oxidized, generating CO₂. The stoichiometry of this overall electrolysis reaction is shown as eq 1. The generated CO₂ at the anode surface directly escapes to the electrolysis cell headspace. However, part of the generated CO₂ diffuses into the porous structure of the carbon anode due to the electrolyte hydrostatic head and the concentration gradient. Consequently, it reacts with the solid carbon through the Boudouard reaction.¹ The Boudouard reaction is not desirable because it results in an increase in the net carbon consumption and may contribute to the generation of carbon dust in the pots, which is an operational problem.¹,² The carbon dust is principally generated by selective burning of the anode components that are in contact with air or CO₂. For instance, it is believed that the binder matrix within the anode is preferentially burnt, causing detachment of the carbon particles from the anode surface, which then fall into the electrolyte bath.³

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2\( \text{Al}_2\text{O}_3\text{(diss)} + 3\text{C(s)} \rightarrow 4\text{Al(m)} + 3\text{CO}_2\text{(g)} \) (1)

The combustion reactions occur either at the anode surface or within the anode bulk. For a given anode formulation, the reaction rate is a function of temperature, pore structure, permeability, and intrinsic reactivity of the anode constituents.\(^{1,2,5}\) The minimum theoretical carbon consumption for aluminum electrolysis is 0.334 kg per kg of Al produced. However, since the cell efficiency is usually less than 100%, the real electrolytic consumption of carbon is around 0.41 kg per kg of Al produced. Keller et al. reported that the extra cost associated with the overconsumption of 1 kg anode per one ton of produced aluminum is around US$ 2. The overconsumption of a midsize smelter (producing 300,000 tons of aluminum per year, and needing 150,000 anodes per year), is approximately 40 kg per anode. Therefore, the estimated extra cost could be about US$ 12 million per year.\(^{6,23}\) Gasification of the anode by air and CO\(_2\) greatly contributes to this carbon consumption. The present work will mainly emphasize changes.\(^{8,10,14,18,22,26,27}\) In this latter approach, the problem is addressed by feeding the model with the anode mechanical properties or other experimental data. These models explicitly mention the solid microstructure changes during the reaction and the influence of the microstructure evolution on reactivity, but despite changes in the structure, the particle size during the process remains invariant. The literature abounds with simplified techniques to circumvent mathematical and computational difficulties. Jamshidi and Ale Ebrahim\(^{7,2,8,10,14,18,22,26,27}\) developed a semi-analytical, semi-numerical method, the Quantize Method (QM), with simplifying assumptions. Their model leads to acceptable results based on the experimental data, though without mentioning the effect of solid structural changes into the solid volume. Thus, the particle radius remained fixed during the gasification, that is, not truly representing the real gasification conditions.

In a non-catalytic carbon–CO\(_2\) reaction, it is essential to take into account the solid structural changes as the reaction progresses because the reaction rate is a function of both gas and solid concentrations.\(^{1,4,14,18,23,28,29}\) From a mathematical point of view, this aspect leads to coupling the gas–solid conservation equations within the model that increases the complexity of the problem. Researchers have extensively studied the computational aspects of these models, but there is only limited research data available on single-particle reactions, considering gas–solid conservation equations,\(^{18,22}\) and it is essential to develop models for such practical systems. An accurate model for a particle reaction could generate valuable insights for modeling the whole anode reaction in the future.

In this contribution, we attempted to reduce the gap between theory and experiment by providing a model that considers diffusion and pore growth during the reaction of an anode particle. Upon the gasification process, the anode particles are consumed, and the apparent radius of the carbon anode reduces gradually while the porosity of the particle also increases. Hence, the effect of shrinkage and particle porosity was considered in mathematical modeling. Therefore, suitable numerical methods were implemented in the mathematical model for solving the governing transfer equations. First, the intrinsic kinetics of CO\(_2\) gasification is experimentally investigated by using a thermogravimetric analysis. Then, a global reaction model was developed by considering all the abovementioned aspects. The suitability of the existing structural reaction models for our global reaction model was examined.

2. EXPERIMENTS

2.1. Materials and Method. 2.1.1. Materials. The carbon anode particles were obtained from the Deschambault aluminum smelting plant (Alcoa Corporation). Ball milling was used to mill large particles into fine fractions. To have various particle sizes of anodes, the particles were crushed and passed through various USA standard sieve trays (from 20 to 4380 \(\mu\)m).

The real density of the anode particles was measured using a Helium-pycnometer (Micromeritics, AccucPyc II 1340, USA). Each analyzed sample (2 g) was weighed three times with an analytical balance (MS204S, Mettler Toledo, USA) and placed in a stainless-steel cell in the He pycnometer. The real density was obtained by dividing the mass of the sample to the volume obtained by the pycnometer.

To obtain the specific surface area, powder samples, with a given size, were first degassed under pure nitrogen (N\(_2\)) at 523 K for 5 h. Then, the samples were analyzed with a gas adsorption analyzer (Micromeritics, Tristar II 3020, USA). Nitrogen (Praxair, purity: 99.995%, USA) was used as the adsorbing gas at 97 K. The chemical composition was analyzed for all samples using an X-ray fluorescence spectrometer (Panalytical, USA). Characteristics of the anode particles with different sizes are presented by Chevarin et al.\(^{7,28,29}\) The amounts of sulfur, vanadium, nickel, and sodium are similar for all particle sizes. The increase in the amount of iron observed with decreasing particle size may be explained by the crushing and grinding of the particles, which resulted in potential iron contamination. The variability of silicon and calcium concentrations is difficult to explain.
2.1.2. Gasification Tests. A thermogravimetric analyzer (Netzsch STA 449 F3 Jupiter) was used for measuring the apparent reaction rate of anode particles at 1233 K by measuring the online weight loss of the samples. To remove moisture content, the samples were placed in an oven at 423 K for 15 h. Only one layer of dried particles was placed in the TGA sample holder (1.82 mm height and 6.45 mm diameter) to ensure the constant composition of the feeding gas near the surface of each particle. The temperature was gradually raised to 1233 K to the target reaction temperature (1233 K). Nitrogen (99.995%, 100 mL·min⁻¹) was used as a protecting gas during the heating step. After reaching the target temperature, the system was stabilized for 15 min under the flow of N₂. The flow rate of nitrogen was then steadily decreased to 20 mL·min⁻¹, while the flow of CO₂ gas (99.9%) was increased to 100 mL·min⁻¹, and the mass loss was recorded. At the end of the experiment, the CO₂ flow was cut off and substituted by N₂ flow, and the furnace was switched off to cool down to ambient temperature. Each experiment was stopped once no further mass loss was occurring, indicating complete gasification of the samples. The reaction time was indeed a function of the particle size. Equation 2 states the gasification conversion (X) of the carbon material to be used for expressing the apparent anode reactivity:

\[ X = \left(1 - \frac{m_t}{m_0}\right) \]

where \( m_0 \) is the initial mass of the anode particle sample and \( m_t \) is the instantaneous mass at time.

3. MATHEMATICAL MODELING

3.1. Gasification Models. The primary chemical reaction can be represented by eq 3:

\[ aA_{(g)} + bB_{(s)} \rightarrow C_{(g)} \]

where A and B are the gas and solid reactants, respectively, and C is the gaseous product while \( a \) and \( b \) are their corresponding stoichiometric coefficients. Some simplifying assumptions are used in this model as follows: the domain of the anode particle consists of a spherical reactive solid and the intra-particle porosity, which shelters the gaseous reactants and products. On account of the small size of the particles, it is safe to assume that both gas and solid phases are in an isothermal state. For simplicity, we assume the topochemical particle evolution preserving its sphericity during the gasification process. CO₂ in a spherical anode particle reacts with carbon according to the following reaction:

\[ CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \]

The local mass conversation equations for each species assuming spherical particle symmetry can thus be written as:

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{CO_2}}{\partial r} \right) + R_{CO_2} = \frac{\partial (\varepsilon C_{CO_2})}{\partial t} \]  

(5)

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_CO}{\partial r} \right) - 2R_{CO_2} = \frac{\partial (\varepsilon C_CO)}{\partial t} \]  

(6)

\[ R_C = - \frac{\partial C}{\partial t} = R_{CO_2} \]  

(7)

The boundary and initial conditions are:

\[ r = r_0: C_{CO_2} = C_{CO_2,0}, C_CO = 0 \]  

at

\[ r = 0: \frac{\partial C_{CO_2}}{\partial r} = 0, \frac{\partial C_CO}{\partial r} = 0 \]  

(9)

\[ C_{CO_2,0} = C_{CO_2,0}, C_CO = 0, C_{Cl} = 0 = C_C \]

(10)

where \( R_{CO_2} \) is the chemical reaction rate of CO₂, \( R_C \) is the rate of anode reactant consumption, \( C_C \) is the instantaneous concentration of anode, \( C_C,0 \) is the initial concentration of anode, \( C_{CO_2} \) is the concentration of the gaseous reactant, \( C_{CO_2,0} \) is the initial concentration of the gaseous reactant, \( D_1 \) is the effective molecular diffusivity, \( r \) is the local radial position within the anode particle, and \( r_0 \) is the initial particle radius. According to eq 7, both rates of gas consumption (\( R_{CO_2} \)) and carbon reactant consumption (\( R_C \)) are equal during gasification. The void fraction or the local porosity of the anode may change during reaction due to the consumption of the solid reactant and the difference between the volume of the solid reactant and product. The variation of local porosity can be modeled by eq 11 as follows:

\[ \varepsilon = \varepsilon_0 + (1 - \varepsilon_0)X \]

(11)

where \( \varepsilon_0 \) is the initial porosity of the anode. Equation 11 can be derived by means of a material balance based on the assumption that the bulk density of the ash remains constant and the local porosity satisfies a linear relation with conversion.

According to eqs 12–14, the partial differential eqs 5 and 6 with boundary and initial conditions (eqs 8–10) are solved to obtain the instantaneous \( C_{CO_2} \) and \( C_CO \) radial profiles. Then, \( C_C \) is calculated from the mass balance at each location by:

\[ C_C = C_{C,0} + (C_{CO_2} - C_{CO_2,0}) \]

(12)

The carbon conversion has been experimentally acquired and calculated by eq 2. Carbon conversion and porosity, which both are locally dependent, are calculated in the model as follows:

\[ X = 1 - \frac{C_C}{C_{C,0}} \]

(13)

\[ \varepsilon = \varepsilon_0 + (1 - \varepsilon_0)X = 1 - (1 - \varepsilon_0) \left(1 - \frac{C_C}{C_{C,0}}\right) \]

(14)

For the structural evolution of the particles during the gasification, different models have been proposed in the literature. For instance, RPM assumes that the pore structure of porous particles consists of cylindrical channels having different sizes and that the reaction takes place on the wall surfaces. According to this model, the relationship between the internal surface area of particle and its porosity can be given by:

\[ S(X) = S_0(1 - X)\sqrt{1 - \psi \ln(1 - X)} \]

(15)

where \( S_0 \) is the initial surface area, \( \psi \) is a dimensionless parameter indicating that the nature of the pore structure (i.e., RPM structural parameter) was calculated using equation 17.
and also other related parameters are determined by the following equations;

\[ S_0 = \frac{2}{(V_p + 1/\rho)} \int_0^\infty \frac{v_0(r)}{r} \, dr \]  
(16)

\[ \psi = \frac{4\pi L_0(1 - \varepsilon_0)}{S_0^2} \]  
(17)

\[ \varepsilon_0 = \frac{V_p}{V_p + 1/\rho} \]  
(18)

\[ V_p = \int_0^\infty v_0(r) \, dr \]  
(19)

\[ L_0 = \frac{1}{\pi(V_p + 1/\rho)} \int_0^\infty \frac{v_0(r)}{r^2} \, dr \]  
(20)

\[ \gamma = \frac{1}{V_p} \int_0^\infty v_0(r) \, dr \]  
(21)

where \( L_0 \), \( \varepsilon_0 \), and \( \rho_0 \) are the pore length, the porosity, and the density of the anode particle, respectively. The pore volume distribution function \( V_p(r) \) is obtained by eq 19. Equations 20 and 21 estimate the total pore length and the average pore radius, respectively.

Gas diffusion in a porous solid is affected by the porosity and the pore structure. Therefore, an effective diffusion coefficient is considered. The effective molecular diffusivity \( (D_f) \) of the gas in a porous particle is obtained by:

\[ D_f = \frac{D}{\tau} \]  
(22)

where \( D \) is the molecular diffusivity of the gaseous species, \( \tau \) is the tortuosity factor, and \( \varepsilon \) is the particle porosity. The binary diffusion coefficient of component \( (D_{ij}) \) at each temperature, for species \( I \) in reaction \( J \), is estimated by the correlation of Hirschfelder.33

\[ D_{ij} = \frac{0.0018587 T^{-1} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{0.5}}{P_{abs} \sigma_{ij}^2 \Omega_{ij}} \]  
(23)

where \( P_{abs} \) is the absolute pressure in atmospheres and \( M_i \) and \( M_j \) are the molecular weights of \( I \) and \( J \), respectively. \( \sigma_{ij} \) is the Lennard–Jones collision diameter in angstrom, and \( \Omega_{ij} \) is the collision integral for molecular diffusion.

Both the chemical reaction rate and diffusion rate may contribute to the overall reaction rate. At high diffusion rates, the chemical reaction could be a limiting factor, and reciprocally. The Thiele modulus is a dimensionless parameter that informs which phenomenon has the leading characteristic time.34 Here, a modified Thiele modulus (\( \lambda \)) is developed to account for the structural change undergone due to the consumption of the material during the particle’s gasification. For a first-order chemical reaction, a modified Thiele modulus is defined as:

\[ \lambda^2 = \varphi^2 \sqrt{1 + \psi \ln(1 - \varepsilon_0)} - \psi \ln(1 - \varepsilon) \times (1 - \varepsilon)/\varepsilon^2 \]  
(24)

in which \( \varphi \) is the Thiele modulus, defined as:

\[ \varphi = r_0 (k_0 S_0 D)^{1/2} \]  
(25)

where \( k \) is the reaction-rate constant, \( r_0 \) is the initial particle radius, \( \rho_0 \) is the density of the anode particle, \( S_0 \) is the initial surface area, and \( D \) is the effective diffusivity.

The effectiveness factor \( \eta \) can be calculated using the modified Thiele modulus by the following equation:

\[ \eta = \frac{1}{\lambda} \left( \frac{1}{\tanh(3\lambda)} - \frac{1}{3\lambda} \right) \]  
(26)

As the largest characteristic length scale of the pore structure is much smaller than the characteristic length associated with the concentration gradients, the reaction rate term in eqs 5–7 should be adequately defined. So, from a particle point of view, the reaction rate per unit volume must be formulated in a “structural” form. Thus, a function that summarizes the available reaction sites at a given time should be introduced. To incorporate this feature explicitly, we assume the following intrinsic kinetics at any location within the particle as:

\[ R = -r(C_{CO_2}) \cdot F(X) \]  
(27)

This reaction rate consists of two parts, \( r(C) \) and \( F(X) \). The first part stands for the influence of the gas phase components on the reaction rate, whereas the second part depicts the structural change brought by the reaction in the porous solid phase.31

In this work, to model \( CO_2 \) gasification of the anode particles, two types of equations are used to describe the gas phase reaction, \( r(C) \), a simple first-order form, and a Langmuir–Hinshelwood (L–H) form. The latter is preferred due to its ability to account for the species adsorption/desorption. In the L–H formulation, the adsorption coefficients of \( CO \) and \( CO_2 \) are assumed to be constant (\( k_1 \), \( k_2 \), and \( k_3 \)), and the following pathway is proposed for this process:

\[ C_\ell + CO_2 \rightarrow C(O) + CO \]  
(28)

\[ C(O) + CO \rightarrow C_\ell + CO_2 \]  
(29)

\[ C(O) \rightarrow CO + C_\ell \]  
(30)

where \( C_\ell \) is the active carbon site, \( k_1 \), \( k_2 \), and \( k_3 \) are the reaction rate constants, and \( C(O) \) represents the carbon–oxygen surface. The presence of \( CO \) results in lowering the steady-state concentration of \( C(O) \) by an inhibiting effect \( r(C) \) as described by eq 31:

\[ r(C) = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO_2} + k_3 P_{CO}} \]  
(31)

Equation 27 becomes eq 32 by substitution of \( -r(C) \) (eq 31):

\[ R = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO_2} + k_3 P_{CO}} F(X) \]  
(32)

An Arrhenius-type of temperature dependence is assumed for \( k \):

\[ k = k_0 \exp\left(-\frac{E}{R \cdot m \cdot T}\right) \]  
(33)
where $E$ is the activation energy, $k_0$ is the pre-exponential factor (atm“s$^{-1}$), and $R_m$ is the ideal gas constant (kJ·mol$^{-1}$·K$^{-1}$).

There are also various models to cast the kinetics of the gasification reaction for the porous solid phase $F(X)$. In general, different kinetic models can be applied to the structure part of eq 27, among which, the shrinking core model, the volumetric reaction model, the modified volumetric model, and the random pore model are widely used by researchers$^{14,15,17,18,35,36}$ (Table 1). To evaluate these different models, a set of experimental data is used. The carbon conversion is calculated by using various kinetic models, and the solved set of equations is compared with the experimental data. Models that account for particle shrinking-core behavior usually assume that the external layer of the particles is removed with time, which is referred to the exposed shrinking-core model (CM). Therefore, in these models, the external mass transfer and intrinsic kinetics in the external surface are considered. In addition, the reacting particles are assumed to preserve their spherical shape during gasification, as stated earlier. The reaction between the particle and gas reactants is started on the interface of the particle and gas. As the external surface is consumed, the reaction front moves gradually to the particle’s interior. This results in decreasing the particle’s radius during the gasification reaction progress. However, this model cannot capture the structural changes inside the particle since the gasification takes place only on the external surface of the particle.

On the other hand, in the volumetric model (VM), it is assumed that a homogeneous reaction occurs.$^{10,14,15,32}$ It results in a linear decrease of the surface area with conversion during the reaction. In the RPM model, from a practical standpoint, while $S_0$ and $e_0$ are accessible experimentally, $L_0$ cannot be measured.$^{14,15}$ $\psi$ is a free parameter that is adjusted using experimental data. The value of $\psi$ is related to the solid material and the formation condition.$^{16,37,38}$ Moreover, the modified random pore model (MRPM) is the improved pore structure model to simulate the evolution of the superficial area of carbon particles during CO$_2$ reaction. Different forms of MRPM have been proposed in the literature by introducing a new conversion term and a time function with two or three dimensionless parameters into the original random pore model.$^{14,39-42}$ We used the equation, which is proposed by Gómez-Barea and Ollero$^{47}$ in which the new conversion term and time function have a linear relation with time. It simplifies the equations and lets us find the analytical solution with reasonable results. The influencing factors, such as pore characteristics and the superficial area of porous particles during gasification are taken into account.$^{39,43,44}$ In MRPM the gasification time, and $\psi$ and $\omega$ are the structural parameter and the power-law constant, respectively. $\omega$ is the power-law constant that can be positive or negative that shows the effects of time on $k_s$ that is defined by $[1 + (\omega + 1)(\alpha t)]$. The negative value of $\omega$ means that the reaction rate is constant. The higher value of $\omega$ ($>5$) shows the higher impact of time on the reaction rate. In this case, MRPM can deliver reliable results comparing to RPM. $\alpha$ is a discreteness parameter. When $\alpha$ goes to zero, the results of RPM and MRPM are the same. The parameter $\alpha$ is related to the structural parameters of particles such as initial porosity and specific surface area. With an increase in $\alpha$, the value of the surface area is reduced.

Several equations were applied to obtain the effective diffusion coefficient, which depends on both porosity and tortuosity (eq 22). Comiti and co-workers$^{46,47}$ defined the tortuosity of spheres based on the theoretical tortuosity–porosity relations. Their equations are used by numerous researchers, especially for porous carbon materials.$^{45,49}$ Akkani et al. investigated different practical equations to calculate the tortuosity value, and their results showed that the effective diffusion could be related to the particle size, shrinkage, and the pore size of the particle.$^{49}$ In this work, we applied various tortuosity equations proposed in the literature to obtain the one best representing the anode particle behavior. To do so, the model was run using different models, and the simulated results were compared to the experimental gasification tests. The experiments were carried out at different particle sizes of 0.05, 1, and 3 mm to cover the diffusion effect from low to high, respectively. The results, summarized in Table 2, reveal

| Table 1. Main Structural Reaction Models for the Gasification Rate$^{14,31,45}$ |
|----------------------|-----------------------------|
| model                | equation ($F(X)$)           |
| volumetric model (VM)| $(1 - X)$                   |
| shrinking core model (CM)| $(1 - X)^{1/3}$            |
| random pore model (RPM)| $(1 - X)^{\sqrt{1 - \psi \ln(1 - X)}}$ |
| modified random pore model (MRPM)$^a$| $[1 + (\omega + 1)(\alpha t)](1 - X)^{\sqrt{1 - \psi \ln(1 - X)}}$ |
| traditional (TM)     | $(1 - X)^{\alpha}$         |

$^a$: modified random pore model constant, $(s^{-1})$, $\omega$: power-law constant, $(\approx)$.

Table 2. Summarized Model Results for Different Tortuosity Equations for Three Anode Particle Sizes$^{39,50}$

| theoretical tortuosity–porosity relations | error     | $R = 0.05$ mm | $R = 1$ mm | $R = 3$ mm | remarks                   |
|------------------------------------------|-----------|---------------|------------|------------|--------------------------|
| $\tau = (3 - \epsilon)/2$               | 0.04      | 0.01          | 0.05       | packing$^{39}$        |
| $\tau = 0.8(1 - \epsilon)$ + 1         | 0.08      | 0.03          | 0.07       | laboratory contaminant diffusion$^{41}$ |
| $\tau = \epsilon^{-1/2}$                | 0.07      | 0.20          | 0.06       | spherical particle$^{30}$ |
| $\tau = 1 - 0.5 \ln \epsilon$          | 0.09      | 0.03          | 0.11       | sand-spherical particle$^{49}$ |
| $\tau = \epsilon^{-2}$                  | 0.04      | 0.03          | 0.05       | overlapping spheres$^{49}$ |

That using the tortuosity expression in the first row is the most suitable one for anode particles ranging between 0.05 and 3 mm for which the fitted tortuosity led to the least error among all the tested tortuosity models.

3.2. Particle Shrinkage. Understanding the structural features of anode particles and their evolution during gasification provides useful information for the development of gasification-based systems. During the gasification process, the anode particle starts to shrink, and the apparent radius of the anode particle ($r_{ap}$) decreases gradually. In this step, the outer layer of the solid is fragmented.$^{17}$ In the developed model, the fragmentation occurs when 100% of an imaginary external layer is consumed. This imaginary external layer may have a finite thickness, which could be defined depending on the resolution of the calculations. In our model, the apparent radius is kept unchanged until the conversion at the outer surface layer reaches 100%. On the other hand, at this step, the
thin outer layer of particle reaches to a conversion of \( X(r_{ap}) = 1 \). After consuming the outer layer, a new updated outer layer is defined, and the radius of the particle is now smaller by the thickness of the removed outer layer.\(^{32} \) According to this description, the change in the anode particle radius during the process can mathematically be represented employing a moving boundary condition as follows:

\[
\frac{\partial r_{ap}}{\partial t} = \begin{cases} 
0 & X(r_{ap}) \text{outer layer} < 1 \\
\frac{\partial X_{ap}}{\partial r} & X(r_{ap}) \text{outer layer} = 1 
\end{cases}
\] (34)

When 100% of an imaginary external layer is consumed, the start point shrinkage conversion \( (X_{ap}) \) will be obtained by solving the second condition term of eq 34. The schematic of gasification inside an anode particle is illustrated in Figure 1. At the center of the particle, the apparent radius equals 0, and at the outer layer of the particle, the apparent radius and related anode conversion equal \( r_{ap} \) and \( X(r_{ap}) \), respectively.

3.3. Numerical Method. In the developed model, the anode conversion \( (X) \) is the target variable to be computed. In this model, after reaching a critical carbon conversion rate, the apparent radius of the anode particle decreases until it eventually leads to particle vanishment (depending on the ash content of the particle, complete disappearance of this latter may not occur experimentally). Thus, it is essential to consider the moving boundary method for solving the proposed model. The model includes certain nonlinear partial differential equations (PDEs), which are also time-dependent equations. Since the numerical method of lines is a proper technique for solving the time-dependent partial differential equations, the sets of PDEs of this model can be solved using this method.\(^{31} \) In the method of lines, all the derivatives are substituted by the finite difference method, but the time derivatives remain with no change. It is assumed that the variables \( C \) and \( X \) are related to \((z, \tau)\) but are independent on \((z, i, j, \tau)\) or \((z, r, \tau, j)\). Here, \( i \) and \( j \) indicate the indices of a computational grid node; \( index \) defines the position and \( \tau \) the time instant. The grid number in the \( r \) direction equals 10,000 for a particle with a 1 mm radius. The model is an explicit time step of a finite difference algorithm in which the time step is automatically defined, and it is compatible with the ODE solver. Therefore, PDEs are converted into a system of ODEs. This package is written in MATLAB software in three-layers of calculations. All the input data are imported to the first layer; an appropriate model is defined; at the end of calculations, the results are returned to this layer. The second layer is a transporter layer in which all the required data are transported to the solver of the model. Besides, the results of the modeling are reflected from the calculation core to the upper layer by this part. The third layer (calculation core) is the ODE solver. In this package, the ODE solver consists of ODE23tb that accurately calculates rigid systems using raw error tolerances. This solver is an implicit Runge–Kutta method. All unknown variables must be solved simultaneously in one system of ODEs. The model outputs are the carbon conversion \( (X) \) versus time. The model constants can be calculated using the experimental results.

Originally, \( X \) is a local value, but to compare it with the experimental value, \( X \) must be averaged over the particle volume at each time instant as follows:

\[
X_{ave}(t) = \frac{3}{r_0} \int_0^{r_0} X(r, t) r^2 \, dr
\] (35)

We defined eq 36 as a cost function for identification of the model constants, including the chemical reaction rate constant and adjustable parameters in the function of \( F(x) \) such as \( \psi \) for RPM, \( w \) and \( \alpha \) for MRPM, and \( n \) for the TM equation.

\[
\min f = \sum_{j=1}^{H} (X_{ave}(t) - X_{exp}(t))^2
\] (36)

where \( H \) is the number of experimental time points.

4. RESULTS AND DISCUSSION

Figure 2 shows the conversion of the anode particle as a function of time both in terms of model predictions and the experimentally determined one. Particles with an average size of 1 mm were used to generate experimental data, and the spherical particles of diameter 1 mm were used for simulation. In the model, we integrated different structural kinetic models presented in Table 2 to verify their suitability for the gasification of anode particles. The results exhibited good agreement between experiments and three models (RPM, MRPM, CM). The errors between experimental and simulated results are presented in Table 3. As the RPM model showed the reasonable outcome with the low error and number of parameters; thus, we used hereafter the RPM model to simulate the gasification of anode particles under varying conditions.

Figure 3 demonstrates the time required for full consumption of the particles with different sizes as a function of...
their initial radius. The results revealed that a good agreement exists between predicted (continuous red line) and measured (solid circles) data. As expected, the smaller particles are consumed faster due to both a higher specific external area and smaller quantity of material to be consumed.

Figure 4 shows the simulated plots of anode particle conversion versus time for different particle sizes. The experimental data points for the particle size of 1 mm were also presented for comparison. Figure 4 reveal that the model validated by one set of experiment data (particle size = 1 mm) and other particle sizes were obtained by model prediction not just validation and data fitting. The results suggest that the particle size significantly affects the reaction rate of the particle gasification (as reflected by the slope of the curves). As the particle size decreases, the reaction rate increases, and full consumption is reached in a shorter time. Particles with a radius larger than 1 mm did not achieve total consumption after 10 h of reaction. This could be attributed to the larger external surface area of the fine particles compared to that of the coarser ones. This also indicates the diffusion-inhibited reaction rate for the coarser particles, the same as the observations reported by Gomez-Barea and Ollero. As expected, the conversion rate holds a direct relationship with the reaction time but an inverse relationship with the particle size.

The CO₂ mole fraction inside a reacting particle, predicted by the model during the gasification time, is shown in Figure 5 for eqs 5 and 6 solved for the central position (r = 0) of the anode particle for different particle sizes. Initially, CO₂ reactive gas is introduced into the pores. Therefore, the CO₂ mole fraction is near one within the pores and at the surface of the particles (Figure 5a). When the reactions start, CO₂ is consumed and CO is generated, resulting in a gradual increase of CO concentration at the expense of that of CO₂. The graph (Figure 4b) shows that the CO₂ concentration at the center of the particle decreases first to reach a minimum at (t = 1 × 10⁴ s), and then it increases gradually until the particle is fully consumed. This peak of CO₂ is attributed to the quick consumption of active carbon at the beginning of the reaction. In fact, not all carbon sites have the same activity with respect to CO₂, and some of them are more reactive, as reported earlier. In these areas, carbon is consumed quickly when they come in contact with CO₂. Therefore, in the beginning (Figure 5a), the rate of reaction is high due to the presence of active carbon sites, resulting in a quick depletion of CO₂ concentration over the first 25 s. Then, the rate of CO₂ reaction with carbon decreases as the active sites are consumed. At the same time, the presence of CO₂ results also in a decrease of CO₂ reaction with carbon. These two phenomena result in a balance between the consumption rate of CO₂ and its diffusion rate from the surface at around t = 1 × 10⁴ s. By progressing the reaction, the porosity of the particle increases, so is its permeability, leading to the increase of the CO₂ diffusion from the surface and its mole fraction at the center of the particle. The reaction rate with CO₂ for all particle sizes follows the same trends. Another observation is that the CO₂ fraction at the center of large particles is always smaller than that of the fine particles, mainly due to higher diffusion distance.

4.1. Structural Evolution of Anode Particle during Gasification. Figure 6 is demonstrating RPM predictions of carbon consumption as a function of time for particles with a radius of 1 mm for different initial porosity. The rate of solid consumption (slope of curves in Figure 6) in the first stage of the reaction is steep, and then it reduces gradually at a later stage. The monotonic reduction of reaction rate is presumably ascribed to the lesser amount of residual solid to react as reaction progresses. Therefore, the porous samples will vanish in a shorter process time. The difference between slopes increases by increasing the porosity. As expected, for the samples with higher porosity (ε ≥ 0.5 and more), the slope of the curves at the first stage is steeper since the diffusion rate is higher at higher porosity levels and conversely, for the sample size.
Figure 5. Mole fractions of CO$_2$ inside the reacting anode particle (at $r = 0$) versus time for various initial particle sizes and $T = 1233$ K and different time scales: (a) the first 25 s and (b) the rest of the process time.

Figure 6. Effects of initial porosity on the conversion of carbon versus time; initial particle radius is 1 mm, $T = 1233$ K.

with lower porosity ($\epsilon \leq 0.2$ and less), the difference between two stages is not significant.

Experimentally, Figure 7 shows the pore volume distributions measured by mercury intrusion (Auto Pore IV, Micromeritics, Norcross, GA, USA) as a function of the pore size for anode particles gasified under CO$_2$ at 1233 K and at gasification levels of 0, and 50 wt % for two particle sizes (1 mm and 2 mm). As can be seen in Figure 7 the pore interval (0.1−40 μm) has the largest pore volume for both particle sizes, and these pore sizes increase strongly with the increase in the percentage of gasification. A broader peak for the pore size range larger than approximately 80 μm is observed that is associated with the voids between the particles.

Over the gasification process, the model includes both effects of transport of gaseous species and intrinsic reaction rates. Due to the diffusion resistance, it is expected that the reaction on the particle surface be faster than that inside the particle. This description conforms to simulation outcomes for the anode particle gasification at 1233 K, as shown in Figure 8. This figure presents the consumption of carbon (mole fraction) as a function of time at three different locations of the particles: at the external layer, at the middle radial position, and at the center of the particle. As Figure 8a,b shows, the anode particle on the external surface layer will be consumed faster than on other positions within the anode particle. This difference is getting larger when the size of the particle increases. The shorter consumption time at the surface confirms the particle shrinkage over the gasification process.

Figure 9a shows the change of the relative particle radius ($r/ r_0$) as a function of reaction time. It can be seen that the relative radius of all samples remains unchanged within the first $1 \times 10^4$ s of reaction. After this period, the particles start to shrink. According to Figure 4, this reaction time corresponds to almost full consumption of small particles ($r = 0.05$ mm) and 33% of consumption for the largest particles ($r = 5$ mm). It is interesting to see which fraction of a particle is consumed when it starts to shrink. Thus, we plotted the shrinkage conversion, corresponding to the conversion of the particle at a shrinkage starting point ($X_{sh}$) as a function of particle radius (Figure 9b). We can see that $X_{sh}$ decreases sharply with increasing particle size. In other words, as the particle radius increases, inception of shrinkage occurs at the smaller conversions, $X_{sh}$, e.g., 45, 33, 25, 18, and 12% for $r_0 = 1, 2, 3, 5$ mm, respectively.

4.2. Modified Thiele Module and Effectiveness Factor. The modified Thiele modulus, $\lambda$, describes the relationship between diffusion and the reaction rate in porous particles with no mass transfer limitations 34 (eq 24). The effectiveness factor, $\eta$, is a measure indicating that the diffusion resistance neutralizes the intrinsic reaction rate (eq 26). An effectiveness factor approaching unity indicates that the reaction controls the process. The results of the kinetic model show that, depending on particle size and the mass conversion of the anode, the intrinsic reaction and diffusion can be significant parameters in determining the overall gasification process. Achieved by RPM expression at multiple carbon conversions, the effectiveness factors, $\eta$, and modified Thiele module, $\lambda$, are shown in Table 4 for both first-order and L−H kinetic models. By increasing the particle size, the modified Thiele modulus increases whereas the effectiveness factor decreases. It means that, as expected, the diffusion resistance increases with the particle size, resulting in a reduction in the effectiveness factor. 23

For all samples, the effectiveness factor increases by conversion, approaching 1 at 80% of conversion. When the carbon conversion does not exceed 60%, the results reveal that both reaction and diffusion control the reaction. By further increasing in the anode conversion, the reaction becomes more dominant due to the particle shrinkage during the gasification process.

For small particles ($r = 0.035$ mm) the low values of the modified Thiele modulus ($<2$) demonstrate that reactant is homogeneous distributed inside of the anode, and therefore, the diffusion resistance is negligible. Inversely, for the larger particles (2.2 mm), especially for the initial conversion, high
values of the modified Thiele modulus (>3) confirm that the diffusion significantly resists against the gasification for large particles. By starting the gasification process and anode particle conversion, the modified Thiele modulus decreases and approached one at 80% of conversion. Because at the early stages, the reactant gas cannot easily penetrate inside the particle and the diffusion is dominant for larger particles.11

4.3. Specific Surface Area. The model allows capturing the evolution of the specific surface area during the gasification process. Figure 10a shows the evolution of the surface area versus the gasification conversion for four different particle sizes. For ease of comparison in a single graph, we used the relative specific surface area, obtained by dividing the actual specific surface area of the sample (S) into its initial specific surface area (S₀) to make a dimensionless parameter for the specific surface area. It can be seen that the specific surface area increases at the early stages of the gasification, reaching a maximum, and then declining until vanishing. By computing the derivative of the curves and plotting it against the gasification conversion (X), the maximum of the curves can be better visualized. These maxima can be seen in Figure 10b, where the curves cross the zero line. We can see that the maximum specific surface area for the smallest sample (r = 0.05 mm) occurs after 25% of gasification. By increasing the particle
size, the maximum is shifted toward lower gasification levels. For instance, this maximum occurs at 4% gasification for the largest sample (r = 3 mm). In other words, the conversion at which the maximum surface area occurs depends on the particle size and it decreases drastically by increasing the particle size. For all particle sizes, the specific surface area increases at the early stage of conversion. This is attributed to pore enlargement. However, with the progress of gasification, the overlapping of the multiple capillaries and the coalescence of neighboring pores take place (mostly through disappearing inter-walls), thus decreasing the specific surface area. For the small particles, there is not a big difference between the reaction rates at the internal and external layers (Figure 8a); however, this difference becomes significant as the particle size increases (Figure 8b). The delay of the reaction in the internal layers mitigates the increase of the specific surface area. That is, when the internal layer reaches its maximum specific surface area, the surface area of the external layers is already in a declining phase. Therefore, the maximum is barely seen for the largest particle.

Table 4. Modified Thiele Moduli and Effectiveness Factor for Different Particle Sizes and Carbon Conversions

| radius (mm) | reaction rate | definition | carbon conversion % | 0 | 20 | 40 | 60 | 80 |
|-------------|---------------|------------|----------------------|---|----|----|----|----|
| 0.035       | first order   | modified Thieles | 0.81 | 0.85 | 0.89 | 0.94 | 0.98 |
| L−H         | effectiveness factor | modified Thieles | 0.75 | 0.79 | 0.86 | 0.93 | 0.97 |
| 0.7         | first order   | modified Thieles | 1.94 | 1.82 | 1.45 | 1.15 | 0.43 |
| L−H         | effectiveness factor | modified Thieles | 0.49 | 0.64 | 0.79 | 0.88 | 0.94 |
| 1.0         | first order   | modified Thieles | 4.98 | 3.22 | 2.37 | 1.50 | 1.01 |
| L−H         | effectiveness factor | modified Thieles | 0.44 | 0.60 | 0.75 | 0.86 | 0.93 |
| 2.2         | first order   | modified Thieles | 5.41 | 3.41 | 2.56 | 1.59 | 1.06 |
| L−H         | effectiveness factor | modified Thieles | 5.47 | 3.25 | 2.46 | 1.54 | 1.04 |

Figure 9. (a) Relative radius \((r/r_0)\) versus processing time for different anode particle radii. (b) \(X_{ta}\) versus initial particle radius.

Figure 10. (a) Prediction of the surface area of the particle during the gasification. (b) Differentiation of surface area versus carbon conversion \((T = 1233 K, r = 3.0, 2.0, 1.0, and 0.05 \text{ mm})\).
4.4. Inhibition Effect of CO in Anode Gasification. The presence of CO in the internal anode pores can play an inhibition role on the carbon gasification reaction, which could explain the lower observed reaction rate compared to the expected one. To describe these observations, the inhibition effect caused by CO should be modeled by a reasonable kinetic expression to understand its effect. A Langmuir–Hinshelwood model can adequately separate the inhibition effect of CO (chemical limitation) from purely diffusional effects (physical limitation). It is believed that adsorption of CO2 on the surface of the anode followed by desorption of CO are the main steps determining the gasification rate (eqs 28–30). Adsorption of CO on the carbon sites may decrease the rate of adsorption of CO2 by occupying the active sites, thus inhibiting the reaction rate. To assess this effect, we ran the reaction with three different CO concentrations in the inlet gas. Figure 11 shows the conversion in mole fraction at the center of a particle (r = 1 mm) as a function of time for three different inlet gas compositions. Table 5 shows the experimental data and the corresponding values obtained from the model for different values of initial P\(_{\text{CO}}\) as well as their temperature dependence by means of its Arrhenius coefficients. The results show good agreement between calculated data and experimental data for \(k_1\) and \(k_2\), but there is a high level of uncertainty and discrepancy for \(k_3\) particularly at the start and the end partial pressure ratio ranges (\(\frac{P_{\text{CO}}}{P_{\text{CO2}}} = 0\) and 1). These values confirm the stronger CO inhibition effect in the anode-CO2 gasification in comparison with that obtained with pure CO2 in the inlet gas. As a result of this mechanism, any increase in the CO amount at the inlet gas causes a decrease in the conversion of anode particles during the gasification process.

Figure 12 shows the rate of gasification reaction as a function of time for three different gas compositions in the inlet gas. It can be seen that the rate of reaction at the beginning of the reaction is much smaller for higher CO concentrations. As discussed above, all reactions reach a maximum rate after a while, which is due to the fast reaction of the more active carbon sites. However, this maximum occurs earlier for pure CO2. The inhibition effect of CO delays the occurrence of this maximum and decreases the maximum value of the reaction rate. After about 1 \(\times 10^4\) s, it seems that the reaction rate for the samples with pure CO2 becomes smaller than those with CO in the inlet gas. This is basically due to the lower amount of remaining solid carbon in the former case at the same reaction time. For instance, at \(t = 1 \times 10^4\) s 60% of the sample is consumed under pure CO2, while only 42% is consumed under 50% CO2.

According to the L–H mechanism, it is possible to use the values of activation energies (\(E_1\), \(E_2\), and \(E_3\)) respectively corresponding to \(k_1\), \(k_2\), and \(k_3\) to illustrate how the various activation energies are involved in the C–CO2 reaction. The amount of activation energy was calculated by the Arrhenius type of temperature dependence (eq 33) for each L–H mechanism step. The activation energies of 59, 17, and 187 kJ-

![Figure 11](https://example.com/fig11.png)

**Figure 11.** Anode particle conversion versus process time at different ratios of the partial pressure of CO2 and CO in the inlet gas (\(T = 1233\) K, \(r_0 = 1.0\) mm).

![Figure 12](https://example.com/fig12.png)

**Figure 12.** Simulation of the anode particle gasification rate at different ratios of the partial pressure of CO2 and CO in the inlet gas (\(T = 1233\) K, \(r_0 = 1.0\) mm).

| temperature (K) | \(\frac{P_{\text{CO}}}{P_{\text{CO2}}}\) | model results \(k_1\) | \(k_2 \times 10^3\) | \(k_3 \times 10^3\) | \(R^2\) | experiment result \(k_1\) | \(k_2 \times 10^3\) | \(k_3 \times 10^3\) |
|-----------------|-------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 1233            | 0.00                          | 100.6                | 66                   | 96.8                 | 101.5                | 97.9                 | 99.6                 | 101                  |
| 1233            | 0.25                          | 96.6                 | 64                   | 98.6                 | 97.9                 | 102                  | 102                  | 63                   |
| 1233            | 0.50                          | 95.3                 | 63                   | 99.4                 | 95.8                 | 102                  | 102                  | 64                   |
| 1233            | 0.75                          | 91.2                 | 64                   | 98.8                 | 90.8                 | 102                  | 102                  | 63                   |
| 1233            | 1.00                          | 84.9                 | 63                   | 96.5                 | 84.4                 | 103                  | 103                  | 62                   |
| 1193            | 1.00                          | 82.8                 | 62                   | 97.9                 | 85.0                 | 95                   | 95                   | 63                   |
| 1273            | 1.00                          | 86.7                 | 64                   | 98.4                 | 85.7                 | 99                   | 99                   | 64                   |
mol\(^{-1}\), were obtained for three steps of the reaction, respectively. Higher partial pressure of carbon monoxide leads to a decreasing gasification rate, which is reflected by the \(k_3\) reaction rate constant of L−H eq 31.\(^{39-11,25,53}\) Results are in accordance with those obtained in most studies and showing that the activation energy of step 3 (\(E_3\)) is higher than that of step 1 (\(E_1\)). This means that the third step (eq 30) is the limiting step of the reaction rate.\(^{54}\)

**5. CONCLUSIONS**

A diffusion−reaction model was developed for the gasification reaction of aluminum-industry anode particles, involving different kinetic models. The model assumed spherical symmetry and included the most notable chemical reactions, e.g., Boudouard reaction, intra-particle mass transfer resistance, mass conservation and anode structural characteristics such as porosity, permeability and shrinkage. The heat transfer was not included since the size of the anode particles was small enough to assume insignificant temperature gradient across the particle. A numerical method was used to solve the model. Model parameters were obtained experimentally by reacting monolayer anode particles in TGA. According to the experimental and simulated results, we concluded that the random pore model (RPM) is best describing the anode reaction behavior. Thus, this model was chosen among 5 models tested in this study.

The model outputs allow tracking the particle consumption rate and the distribution of gas composition inside the reacting particle. In addition, due to the moving boundary condition for the external gasification, it is also possible to track the shrinkage and structural evolution of the particle during the gasification process. These data, mostly impossible to obtain experimentally, allow better interpretation of the reaction behavior. As such, the evolution of different parameters such as particle size, processing time, porosity, and surface area of the anode particles during gasification are revealed and their effect on the gasification process are discussed. The simulation results demonstrated that the anode structure (specific surface area and porosity) has a significant effect on both the intrinsic reaction rate and the intra-particle mass transport. The relative importance of intrinsic reaction and diffusion on the overall gasification process are quantified by calculating the Thiele modulus and effectiveness factor. Analyzing these factors reveals that their contribution on gasification rate may evolve at different stages of reaction, i.e., diffusion is more important at the beginning and chemical reaction becomes dominant towards the end of gasification. The L−H type reaction, integrated in the model, allowed revealing the inhibition effect CO on the gasification reaction. Although the inhibition effect of CO on carbon gasification is a well-known feature, our model allows quantifying this effect along the whole gasification process. The effect of three different concentrations of CO in the inlet gas were given as examples. In summary, the model predicts well the gasification rate of anode particles, considering structural and diffusion parameters, thus offering a useful tool for optimization of gasification of anode particles.

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**NOMENCLATURE**

**Latin symbols**

\(a\) stoichiometric coefficient, (−)

\(b\) stoichiometric coefficient, (−)

\(C_C\) concentration of anode reactant, (mol·m\(^{-3}\))

\(C\) concentration of gaseous species, (mol·m\(^{-3}\))

\(C(O)\) surface concentration of carbon−oxygen complex, (mol·m\(^{-2}\))

\(D\) diffusion coefficient, (m\(^3\)·s\(^{-1}\))

\(D_e\) effective diffusion coefficient, (m\(^3\)·s\(^{-1}\))

\(k\) reaction rate constant, (mol·m\(^{-3}\)·(1−α)·s\(^{-1}\))

\(k_0\) pre-exponential factor, (bar\(^n\)·s\(^{-1}\))

\(L_0\) pore length, (m·kg\(^{-1}\))

\(H\) number of experimental data, (−)

\(M\) molecular weights, (kg·mol\(^{-1}\))

\(m\) mass of anode particle, (kg)

\(n\) partial reaction order, (−)

\(P\) pressure, (kg·m\(^{-2}\)·s\(^{-2}\))

\(r\) particle radius, (m)

\(R\) chemical reaction rate, (mol·s\(^{-1}\)·m\(^{-3}\))

\(R_m\) gas constant (kJ·mol\(^{-1}\)·K\(^{-1}\))

\(S\) specific surface area, (m\(^{-1}\))

\(t\) reaction time, (s)

\(T\) temperature, (K)

\(V\) pore volume (m\(^3\)·kg\(^{-1}\))

\(X\) gasification conversion of anode particle, (−)

**Greek symbols**

\(α\) modified random pore model constant, (s\(^{-1}\))

\(ε\) void fraction, (−)

\(ϕ\) Thiele module, (−)

\(η\) effectiveness factor, (−)

\(λ\) modified Thiele module, (−)

\(ρ\) density, (kg·m\(^{-3}\))
\( \sigma \) Lennard-Jones collision diameter, (m)

\( \Omega_b \) collision integral for molecular diffusion, (–)

\( \tau \) tortuosity, (–)

\( \omega \) power-law constant, (–)

\( \psi \) structural parameter, (–)

**Subscripts**

abs absolute

ap apparent

ave average

C carbon

CO carbon monoxide

\( \text{CO}_2 \) carbon dioxide

diss dissolved

f active carbon site

g gas phase

I gas species

J gas species

m molten

s solid phase

sh shrinkage start point

t instantaneous

0 initial

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