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Numerical Treatment of Oxide Particle Dissolution in Multicomponent Slags with Local Gibbs Energy Minimization

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Herein, a diffusion model for the dissolution of oxide particles in multicomponent slag systems is developed. It is assumed in this model that a sharp-interface separates the solid particle from the liquid slag. Minimization of the Gibbs energy provides the conditions at the interface. The differential equations for multicomponent diffusion in the liquid slag are solved numerically via a finite-difference scheme. It is indicated via parameter studies that the diffusion controlled dissolution kinetics may result in strongly different dissolution profiles depending on the initial conditions. It is demonstrated that the rate-controlling dissipative process is the diffusion of components for cases where earlier investigations claimed that a coupled diffusion-reaction process is in charge of the dissolution kinetics. Eventually, the numerical results are compared to data obtained from high-temperature laser scanning confocal microscopy (HT-LSCM) experiments.

1. Introduction

The dissolution of oxide particles in metallurgical slags are decisive processes during basic oxygen steelmaking (BOS). Especially the dissolution of lime (CaO) is a determining step in the formation of suitable slags used in BOS.

Preconditions for optimized processes are on the one hand slags with appropriate physical properties, for example, suitable viscosities, and melting occurring in the optimal temperature and composition range. In contrast, slags are expected to promote certain chemical reactions, for example, removal of

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phosphor from the melt. A fast dissolution of lime contributes significantly to the productivity of the BOS process. Thus, the properties of the molten steel are enhanced by metallurgically active CaO required in the liquid slag.^[1]

In addition, an effective and efficient inclusion removal routine in secondary metallurgy is essential in the context of high steel cleanliness, see for example, Holappa and Helle.^[2] Dissolution of unwanted oxide inclusions is possible by slags specially designed for this purpose. A thorough understanding of the underlying thermodynamic and kinetic foundations of these processes is paramount for this aim. An old adage restated by Mills et al.^[3] stresses the importance of under-

standing the reactions in metallurgical slags in terms of process control: "Look after the slag and the metal will look after itself."

Different modeling approaches for the dissolution of oxide particles in liquid slag are discussed in the open literature and the rate determining steps for the dissolution of oxides in molten slags are still a topic of ongoing research. Verhaeghe et al.^[4–6] proposed a lattice Boltzmann dissolution model for the simulation of the dissolution of arbitrarily shaped solid particles in fluid flows. In a later work, this model was applied to the dissolution of spherical alumina particles in ternary slags.^[7] It is worth mentioning that the lattice Boltzmann method is very demanding in terms of computing power. Thus, its applicability to comprehensive process models is limited.

The well-known shrinking-core model^[8,9] is applied to the dissolution of lime in various works, see for example, refs. [10-17]. Generally, the spherical system representing the dissolving particle is divided into four subunits, namely the solid core, surrounded by a product layer, which is covered by a liquid boundary layer and enclosed by the liquid bulk slag. The diffusion/reaction processes occurring during the dissolution of solid particles in liquid slags are classified into several steps within this model, details can be found in ref. [8]. The individual steps during particle dissolution occur simultaneously on different time scales, with the slowest steps being rate controlling for the overall dissolution process. In this sense, the shrinking core model has been used to discuss the rate-limiting steps for dissolution kinetics.^[18] Sarkar et al.^[11] apply an extended shrinking core model with the possibility to use a spherical, cylindrical, or plate geometry of the system. They use a mixed control approach for calculating the dissolution of lime in steelmaking IDVANCED

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Guo et al.^[19] divide the dissolution of lime into different stages that correlate with the formation and dissolution of an interfacial reaction layer. They argue for a shift in the rate controlling step from diffusion in the boundary layer to a mixed control stage, where both, the chemical reaction at the interface and diffusion in the boundary layer, determine the kinetics of the process.

dissolution of spherical oxide particles The in CaO-Al₂O₃-SiO₂ slags is investigated by Feichtinger et al. and Michelic et al.^[12,13] both experimentally and by computer simulations. These authors assume that the solid/liquid interface is fixed to circumvent mathematical difficulties when calculating the concentration profile, details can be found in ref. [20]. Strictly speaking, however, the theoretical concept of this quasi-static dissolution can only be applied to growing particles. In this sense, it is worth mentioning that growth and melting are different situations in principle^[21] as the particle serves as a solute source or sink, respectively. In the case of oxide particle dissolution, this quasi-stationary "invariant interface approximation" is, thus, an unrealistic assumption (for a deeper discussion on approximate solutions for dissolution problems see, for example, ref. [22]); hence, an additional correction factor had to be introduced that allows for describing the experimental results in the works by Feichtinger et al. and Michelic et al.^[12,13] As discussed by Xuan and Mu,^[23] this correction factor implies a mixed control mode for the kinetics, which, however, only corrects the oversimplifications in the quasi-stationary diffusion model. Xuan and Mu^[23] also started from the quasi-stationary approximation and developed an analytical diffusion-distancecontrolled dissolution model. Within this model, the shape of the dissolution profile is explained via the diffusion distance of the dissolving component. A profile coefficient is required in Xuan and Mu's quasi-static model^[23] that controls the diffusion distance to obtain dissolution profiles that agree with experimental results.

It is reasonable to assume that fluid flow due to natural convection occurs during experimental investigations of oxide particle dissolution. Convection may be caused by temperature gradients in the experimental setup, differences in molar densities, or capillary effects due to the interfacial energy at the interface of the particle with the surrounding melt.^[23] The influence of convection on the dissolution is out of the scope of the modelling by means of the sharp-interface diffusion model as presented in this work. However, this phenomenon is expected to be of minor importance in small scale high-temperature laser scanning confocal microscopy (HT-LSCM) experiments and will be one point of discussion in the results section.

It is the aim of this paper to demonstrate that the dissolution of oxide particles in melts can be described properly by considering multicomponent diffusion in the liquid phase and simultaneous interface motion (i.e., shrinkage of the solid particle), where the influence of the interface motion on the concentration profile is automatically considered without the need for empirical fitting parameters. In this sense, a sharp-interface model, see, for example, refs. [24–27], is developed, where local equilibrium is assumed at the solid/liquid interface.

2. Theory

2.1. Geometry of the System, Phase Transformation, and Diffusion

The system is considered to be 1D, that is, one spatial parameter r describes the position in the system. In this sense, the boundary of the system can be a plate, a cylinder or a sphere, see **Figure 1** for the case of a spherical system. The two phases present in the system are the solid particle and the liquid slag, which are separated by a sharp (i.e., infinitely thin) interface.

All chemical potentials $\mu_{k,1}^{\text{solid}}$ of the components k in the dissolving solid phase are assumed to be equal to the chemical potentials $\mu_{k,1}^{\text{liquid}}$ of the components k in the liquid phase at the interface, that is, local equilibrium prevails at the interface

$$\mu_{k,\mathrm{I}}^{\mathrm{solid}} = \mu_{k,\mathrm{I}}^{\mathrm{liquid}} \tag{1}$$

The mole fractions $x_{k,1}^{\text{solid}}$ and $x_{k,1}^{\text{liquid}}$ at the solid and the liquid side of the interface I are calculated based on this local equilibrium assumption. Furthermore, $x_{k,S}^{\text{liquid}}$ is the mole fraction of component *k* at the system boundary and $\Delta x_{k,S}$ is the maximum mole fraction in the melt. The evolution of the mole fraction profiles with time are obtained by simultaneously solving the



Figure 1. Graphical representation of the sharp-interface model in the case of the dissolution of a spherical particle. Mole fraction x_k of component k versus spatial coordinate r is depicted in the upper schematic sketch. In the lower sketch, the spherical particle is shown, dissolving with a velocity v, where fluxes j_k of the components in the liquid slag occur.

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diffusion equation and the mass balance in the liquid phase. The diffusion equation for spherical geometry follows as

$$\frac{\partial x_k}{\partial t} = D\left(\frac{\partial^2 x_k}{\partial r^2} + \frac{2}{r}\frac{\partial x_k}{\partial r}\right), \quad t \ge 0, \quad R \le r \le R + S$$
(2)

where *D* is the diffusion coefficient, x_k the mole fraction of the diffusing component, and *t* the time. Since diffusion in this model takes only place in the liquid phase, the spatial coordinate *r* ranges from *R*, the radius of the solid particle to (*R*+*S*), the outer boundary of the system. The relevant range for the calculations lies in the liquid zone of thickness *S*. The boundary conditions at *r* = *R* and *r* = *R* + *S* are

$$x_k(r = R, t) = x_{k,1}^{\text{liquid}}$$
(3a)

$$\frac{\partial x_k(r=R+S,t)}{\partial r} = 0 \tag{3b}$$

and the initial conditions at t = 0 are

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$$x_k(r = R, t = 0) = x_{k,1}^{\text{liquid}}$$
(4a)

$$x_k(r > R, t = 0) = x_{k,0}$$
 (4b)

where $x_{k,0}$ are the initial mole fractions of components k in the liquid. A discretization is applied which transforms Fick's second law to the following form by means of finite difference approximation

$$\frac{\Delta x_{k,i}}{\Delta t} = D\left(\frac{x_{k,i-1} + x_{k,i+1} - 2x_{k,i}}{\Delta r^2} + \frac{2}{r_i} \frac{x_{k,i+1} - x_{k,i-1}}{2\Delta r}\right)$$
(5)

with the node points *i* ranging from n + 2 to p - 1. The position of the interface is marked by the index *n*, see **Figure 2**. The mole fractions are updated iteratively for each time step

$$x_{k,i}^{t+\Delta t} = x_{k,i}^t + \Delta x_{k,i} \tag{6}$$

The position- and time-dependent mole fractions $x_k(r, t)$ are evaluated at all node points in the liquid except at the node point corresponding to the interface position n and the position n + 1. The mole fractions at the liquid side of the interface follow from the local equilibrium conditions (see boundary condition 3a); details with respect to the required thermochemical equilibrium calculations are provided in the next section. The mole fractions at node n + 1 are approximated by a parabola of the form



Figure 2. Representation of the 1D mesh of the numerical model.

$$x_k = ar^2 + br + c \tag{7}$$

where the mole fractions x_k at positions n and n + 2 are the endpoints of the parabola. The coefficients of the parabola follow from the following relations

$$a = \frac{x_{k,n}\Delta r + x_{k,n+2}\Delta r_n - x_{k,n+1}(\Delta r + \Delta r_n)}{\Delta r_n\Delta r(\Delta r_n + \Delta r)}$$
(8)

$$b = \frac{x_{k,n+2}\Delta r_n^2 - x_{k,n}\Delta r^2 + x_{k,n+1}(\Delta r^2 - \Delta r_n^2)}{\Delta r_n \Delta r(\Delta r_n + \Delta r)}$$
(9)

$$c = x_{k,n+1} \tag{10}$$

The coefficients *a*, *b*, and *c* are position dependent and time dependent as the mole fractions $x_{k,n+1}$, $x_{k,n+2}$, and Δr_n depend on both position and time.

The time derivative of the mole fraction $\dot{x}_{k,n+1}$ is obtained by inserting *a* and *b* from Equations (8) and (9) into Equation (2)

$$\dot{x}_{k,n+1} = 2aD\left(3 + \frac{b}{ar_{n+1}}\right) \tag{11}$$

The mole fraction profile is mirrored at the system boundary, which is defined by the position of the system boundary vertex p. This effectively accounts for the constraint that no mass is allowed to cross the system boundaries as required by boundary condition 3b and thus the fluxes $j_{k,p}$ at nodal point p are all zero, $j_{k,p} = 0$. The diffusive flux of components k in the melt at the spherical interface are computed by using the mass balance

$$j_{k,n} = \frac{\frac{\Delta r + \Delta r_n}{2} r_{n+1}^2 \dot{x}_{k,n+1} + \sum_{i=n+2}^{p} \Delta r r_i^2 \dot{x}_{k,i}}{V_m (r_n + \frac{\Delta r_n}{2})^2}$$
(12)

The partial molar volumes V_k are assumed to be equal for all components k in the liquid phase. They are, thus, equal to the molar volume V_m . Finally, the interface velocity v_g follows in general from

$$\nu_{\rm g} = \frac{(j_k^{\rm solid} - J_k^{\rm liquid})V_{\rm m}}{(x_k^{\rm solid} - x_{k,n})}$$
(13)

It is assumed that the fluxes j_k^{solid} of the components k in the solid phase are small compared to those in the liquid phase and are neglected. The interface velocity ν , which is defined to be positive for shrinking particles, that is, the sign is changed, is provided by

$$\nu = \frac{J_k^{\text{liquid}} V_{\text{m}}}{(x_k^{\text{solid}} - x_{k,n})}$$
(14)

The interface mobility is infinitely high and does not hinder the interface movement, which is a consequence of the assumed local equilibrium at the interface. For a pure condensed phase that solely consists of a single diffusing component, $x_k^{\text{solid}} = 1$ holds. The extension to multicomponent diffusion for an *M*-component system is done in a straightforward way extending Equation (2) to

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$$\frac{\partial x_k}{\partial t} = \sum_{j=1}^{M-1} D_{kj} \left(\frac{\partial^2 x_k}{\partial r^2} + \frac{2}{r} \frac{\partial x_k}{\partial r} \right), \quad k = 1, 2 \dots, M-1$$
(15)

with the elements $D_{k,j}$ of the diffusivity matrix being defined as (see $also^{[28]}$)

$$D_{k,j} = \frac{D_k n_k}{a_k} \cdot \frac{\partial a_k}{\partial n_j}$$
(16)

where a_k is the activity of component k, D_k is its mobility, and n_k is its molar amount.

2.2. Thermochemical Calculations

The mole fractions $x_{k,l}^{\text{solid}}$ and $x_{k,l}^{\text{liquid}}$ of component k at the solid and the liquid side of the interface (see Figure 1) are calculated by means of Gibbs energy minimization. The difference of the mole fractions $x_{k,l}^{\text{liquid}}$ and $x_{k,p}^{\text{liquid}}$ between the interface and the right boundary (p) of the system is denoted by $\Delta x_{k,s}$. The length Sis the time-dependent distance from the interface to the right boundary of the system, see Figure 1. In this context, it is worth mentioning that the mole fraction of component k decreases monotonically from the interface to the right boundary of the system. The mole fraction difference $\Delta x_{k,s}$ is a parameter that is proportional to the distance of the system from equilibrium, that is, the dissolution process is promoted by positive values of $\Delta x_{k,s}$.

At constant pressure and temperature the total Gibbs energy *G* of the system is given by

$$G = \sum_{\varphi=1}^{\Phi} \sum_{l=1}^{L} n_{l}^{\varphi} \mu_{l}^{\varphi}$$
(17)

Phases are denoted by φ , where Φ is their total number. Various constituents l of total number L may be present in the phases φ ; n_l^{φ} and μ_l^{φ} represent the molar amount and the chemical potential of constituent l in solution phase φ , respectively. The mathematical expressions of the chemical potentials μ_l^{φ} are functions of temperature T and composition, where the latter is defined by the mole fractions x_l^{φ} of the constituents lof phase φ .

As discussed, for example, in ref. [29] or [30], the equilibrium conditions for a closed system at constant temperature and pressure are: 1) The chemical potential of every component in the system must be equal in all phases and must be spatially constant constrained by mass balances. 2) The Gibbs phase rule must be satisfied.

The mass balance constraints for M-independent components k are defined as

$$b_k - \sum_{\varphi=1}^{\Phi} \sum_{l=1}^{L} a_{l,k}^{\varphi} n_l^{\varphi} = 0; \quad k = 1, 2, \dots, M$$
 (18)

where b_k is the total amount of the component k in the system. The elements of the stoichiometric matrix are denoted as $a_{l,k}^{\varphi}$. The Lagrangian $\mathscr{L}(\underline{n}, \underline{\lambda})$ of the optimization problem follows as

$$\mathscr{L}(\underline{n},\underline{\lambda}) = \sum_{\varphi=1}^{\Phi} \sum_{l=1}^{L} n_l^{\varphi} \mu_l^{\varphi} + \sum_{k=1}^{M} \lambda_k \left(b_k - \sum_{\varphi=1}^{\Phi} \sum_{l=1}^{L} a_{l,k}^{\varphi} n_l^{\varphi} \right)$$
(19)

where λ_k are the Lagrange multipliers for the mass balance constraints and $\underline{\lambda}$ denotes the vector containing all Lagrange multipliers λ_k . The entries of the vector \underline{n} are the molar amounts n_l^{φ} of the constituents l. The Lagrange multipliers λ_k have a physical meaning as they represent the chemical potentials of the components of the system.

According to the first equilibrium condition provided earlier, these chemical potentials λ_k have to be equal for each component in all stable phases at equilibrium. This becomes very clear when looking at the partial derivatives of the Lagrangian with respect to n_l^{φ} , see Equation (20). In addition, also charge neutrality and other constraints can be taken into account; however, this is not within the scope of this work. It can be easily seen that the solution for the minimum of the Lagrangian, Equation (19), also corresponds to the minimum of the Gibbs energy function, Equation (17). To find the minimum of the Lagrangian, the derivatives of the Lagrangian with respect to all variables (in this case n_l^{φ} and λ_k) must be performed and set to zero

$$\left(\frac{\partial \mathscr{L}(\underline{n},\underline{\lambda})}{\partial n_{l}^{\varphi}}\right)_{n_{j\neq l}^{\varphi},\underline{\lambda}} = \mu_{l}^{\varphi} - \sum_{k=1}^{M} \lambda_{k} a_{l,k}^{\varphi} = 0$$
(20)

$$\left(\frac{\partial \mathscr{L}(\underline{n},\underline{\lambda})}{\partial \lambda_k}\right)_{\lambda_{j\neq k},\underline{n}} = b_k - \sum_{\varphi=1}^{\Phi} \sum_{l=1}^{L} a_{l,k}^{\varphi} n_l^{\varphi} = 0$$
(21)

This results in a set of equations which can be solved iteratively, for example, via a Newton–Raphson procedure. The root of the system of equations corresponds to the phase compositions with minimum Gibbs energy. Furthermore, only solutions with positive values for the molar amounts of all stable substances have a physical meaning ($n_l^{\varphi} > 0$). On the one hand, it is possible that the molar amount of a phase becomes negative during an iteration step. In this case, the phase is removed from the set of stable phases by the Gibbs energy minimization algorithm. On the other hand, a phase that has not been considered as stable in previous iteration steps becomes stable at the current iteration in case that $\mu_l^{\varphi} < \sum_{k=1}^M \lambda_k a_{l,k}^{\varphi}$ holds. Consequently, this phase φ is added to the set of stable phases for the next iteration step. A flowchart representing the algorithm with the crucial calculation steps is shown in **Figure 3**.

Let us now consider the interface in a system, where a solid particle consisting of a single constituent is dissolving in a multicomponent liquid. The equilibrium at this interface can be calculated by minimizing the Gibbs energy subjected to the constraint

$$\mu^{\text{solid}} - \sum_{k=1}^{M} \lambda_k a_k^{\text{solid}} = 0$$
(22)

where μ^{solid} denotes the chemical potential of the solid phase. Additionally, the amount of solid n^{solid} is kept zero

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Figure 3. A flowchart representing the Gibbs energy minimization algorithm that is used to calculate the boundary conditions at the interface.

$$n^{\text{solid}} = 0 \tag{23}$$

to find the liquidus composition.

These thermochemical calculations are performed using a newly developed Gibbs energy minimization algorithm in combination with an in-house thermochemical database built on the modified quasi-chemical model for the description of the liquid phase.^[31–43] For a deeper discussion on the Gibbs energy minimization method, see, for example, refs. [29,30,44–49]. There also exist a number of commercial implementations of Gibbs energy minimization algorithms, including refs. [26,50,51].

3. Results and Discussion

3.1. Parameter Studies

In a first step, a simulated mole fraction profile around a spherical particle of constant size is compared to the analytical solution, which can be found in Glicksman.^[28]

$$x(r,t) = \frac{R}{r} \operatorname{erfc}\left(\frac{r-R}{2\sqrt{Dt}}\right)$$
(24)

The results obtained from the numerical model and the analytical solution, Equation (24), for different diffusion times are





Figure 4. Numerical and analytical solution of Equation (24) for a spherical particle with an immobile interface at $R = 10 \,\mu\text{m}$ at different times $t = 50 \,\text{s}$, $t = 100 \,\text{s}$, $t = 150 \,\text{s}$. The diffusion coefficient is set to $D = 1 \,\times \,10^{-12} \,\text{m}^2 \,\text{s}^{-1}$.

shown in **Figure 4**. The analytical solution, however, is only valid for an immobile interface, that is, the position *R* is constant. In this case, *R* set to the arbitrary value of 10 µm for the following calculations. Furthermore, Equation (24) holds only for infinitely large systems. To approximate Equation (24) by using the earlierdescribed finite-difference scheme, the system size *p* is set to a sufficiently high value, here $p = 10 \cdot R = 100 \,\mu\text{m}$. As can be seen in Figure 4, the numerically obtained profiles approximate the analytical solution calculated for different times *t*. The numerical model seems to work well for an immobile interface and is applied to a moving interface in the following section.

The maximum mole fraction difference in the melt $\Delta x_{k,S}$, the system size p, and the diffusion coefficient D influences the dissolution profile of spherical particles. The effect of these parameters on the dissolution kinetics is investigated via the following case studies. In each case, the time-dependent evolution of the particle radius R is calculated where R_0 is the initial radius, that is, the radius at the beginning of the dissolution process.

In the following, the influence of the diffusion coefficient *D* on the total dissolution time is investigated numerically. It should be noted that within the context of this case study, the dissolution process is simplified by assuming that the kinetics is controlled only by the diffusion of one component in the liquid. The starting radius R_0 is equal for each case and the time is normalized using the total dissolution time of a reference case t_0^{ref} with the diffusion coefficient $D = D_0$ resulting in a normalized time $\tilde{t} = t/t_0^{\text{ref}}$. As expected, higher diffusion coefficients result in a faster dissolution of the spherical particle, see **Figure 5**. In addition, another time normalization is introduced, where time is normalized with the total dissolution time t_0 of the individual process, resulting in a normalized time $\bar{t} = t/t_0$. Then, each dissolution ends at $\bar{t} = 1$.

The influence of the diffusion coefficient on the dissolution profile is presented in **Figure 6**. It is evident that all dissolution profiles are self-similar in the case that only the diffusion coefficient is changed.





Figure 5. Influence of the diffusion coefficient on the dissolution kinetics. The radius, maximum mole fraction difference in the melt and system size are set to the same values for each case.



Figure 6. Self-similar dissolution profiles in the case that only the diffusion coefficient is changed. The radius, maximum mole fraction difference in the melt and system size are set to the same values for each case.

The influence of the maximum mole fraction difference $\Delta x_{k,S}$ in the melt on the dissolution kinetics is presented in **Figure 7**. The system size is assumed to be $p = 10 \cdot R_0$ and the diffusion coefficient is set to the constant value $D = 1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The initial particle radius R_0 is the same for all cases investigated. The normalization of the radius is performed by dividing the current radius R by the initial radius R_0 . Time is normalized by dividing the actual time t by the total dissolution time t_0^{ref} of a reference case with $\Delta x_{k,S} = 0.13$. The relative particle size R/R_0 is plotted versus normalized time \tilde{t} in Figure 7. The kinetics of the dissolution of the particle is enhanced with increasing $\Delta x_{k,S}$ values.

Whereas the accelerating effect of higher $\Delta x_{k,S}$ with normalized time \tilde{t} is demonstrated by using the first normalization (see Figure 7), the differences in the dissolution profile are emphasized by using the second normalization with $t = \bar{t}$. The influence of the maximum mole fraction difference $\Delta x_{k,S}$ in the melt on the shape of the dissolution profile is shown in **Figure 8**. It is evident that $\Delta x_{k,S}$ does not only influence www.steel-research.de



Figure 7. Influence of the maximum mole fraction difference in the melt on the dissolution. The radius at the beginning of the dissolution, diffusion coefficient, and system size are set to the same values for each case. Time is normalized by the total dissolution time of a reference case, here $\Delta x_{k,S} = 0.05$.



Figure 8. Influence of the maximum mole fraction difference in the melt on the dissolution profile. Time is normalized by the total dissolution time of each individual case.

the total dissolution time of the particle (Figure 7), but has also a strong impact on the curvature of the dissolution profile, see Figure 8. Complementary to the results mentioned earlier, the mole fraction profiles at $\bar{t} = 0.5$ for the different $\Delta x_{k,S}$ – values are presented in **Figure 9**. Increasing $\Delta x_{k,S}$ – values lead to a faster dissolution and the mole fraction profiles in the melt become more pronounced.

The impact of the system size, defined by p, on the dissolution is shown in **Figure 10**. The case with a system size $p = 10 \cdot R_0$ is chosen as the reference case for calculating \tilde{t} . The dissolution kinetics is increasingly suppressed with decreasing system size as the bulk concentration of the diffusing component in the slag rises more rapidly; effectively resulting in a smaller gradient of the mole fraction of the dissolving component in the melt. The total dissolution time is more than twice as high for a system that is 2.75 times the particle radius compared to the total dissolution





Figure 9. The mole fraction profile of a dissolving particle with starting radius of 35 μ m at $\bar{t} = 0.5$ for different maximum mole fraction differences in the melt.



Figure 10. Influence of the system size p on the dissolution profile. The starting radius at the beginning of the simulation, diffusion coefficient, and maximum mole fraction difference in the melt are set to the same values for each case.

time for a system size that is 10 times the starting particle radius. The system size has also an effect on the curvature of the dissolution profile. The normalized radius R/R_0 with respect to normalized time \bar{t} shrinks strongly at the beginning of the dissolution process for small systems. In the later stages, the shrinkage of the radius is less pronounced in smaller systems compared to larger systems (see **Figure 11**).

It is illustrated via the previously discussed case studies that the dissolution profile of spherical particles is heavily influenced by the boundary conditions imposed on the system. Hence, the curvature of the dissolution profile should not solely be discussed in terms of the mathematical approximations of the dissolution problem as seems to be common practice for oxide particle dissolution in metallurgical slags. Moreover, the presented case studies emphasize the flexibility that comes with the finite-difference multicomponent diffusion scheme in combination with the previously discussed Gibbs energy minimization method. In the



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Figure 11. Influence of the system size on the dissolution profile.

following section, data from experimental oxide particle dissolution studies are used to validate the presented dissolution model.

3.2. Dissolution of Lime and Silica Inclusions in Metallurgical Slags

Dissolution mechanisms of lime and CaO-containing additives in molten oxides were investigated experimentally in the past in various works, for example, refs. [10,19,52–61]. In addition, the formation of a boundary layer around the lime particle during dissolution is reported in several works, for example, refs. [19,53,60]. The dominant boundary phase has been identified as dicalcium silicate $2CaO\cdot SiO_2(C2S)$ with a melting point of around $2130 \,^{\circ}C$. The formation of C2S around the lime particle slows down the dissolution. Generally, two dissolution mechanisms of lime can be identified: 1) Direct dissolution, where CaO reacts directly with liquid slag. 2) Indirect dissolution, which is characterized by the reaction of lime with the liquid slag through an intermediate phase (C2S).

Direct dissolution of CaO is preferred during steelmaking compared to the relatively slow kinetics of the indirect dissolution process. Thus, it is important to identify those composition and temperature ranges, where indirect dissolution is of minor importance for the overall dissolution process. Guo et al.^[19,62] investigated the dissolution of lime particles in various slag systems via HT-LSCM under static conditions. They observed the formation of an intermediate solid phase at the interface of the lime particle in CaO-Al₂O₃-SiO₂ slag systems at a certain transformation stage. The observed intermediate solid phase has been identified as the C2S phase. The C2S phase is reported to grow up rapidly to a maximum thickness. After reaching the point of maximum thickness, the C2S phase dissolves into the molten slag until it disappears. Further experimental findings are presented in Sun et al.^[63] for the dissolution of a lime particle in liquid slag at 1480 °C. These experimentally observed dissolution kinetics are compared to the numerical results for the dissolution of a spherical particle in this work. The composition at the interface is calculated by means of Gibbs energy minimization as described earlier. The chemical diffusion coefficients $D_{k,i}$ for multicomponent

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Table 1. Chemical compositions of two different slags (SM04 and 1.1) where experimental investigations are reported in literature. The slag composition 7 was used to determine the chemical diffusion coefficients.

Slag	WCaO	W _{SiO2}	WAI2O3	Reference
SM04	0.267	0.533	0.200	[63]
1.1	0.341	0.546	0.106	[13]
7	0.25	0.60	0.15	[64]

diffusion (see Equation (16)) are estimated from Liang and Davis^[64] with Al_2O_3 as the dependent diffusing component. It has to be remarked that the chemical diffusion coefficients where measured for slightly different slag constitutions and temperatures compared to the slag compositions used in the HT-LSCM experiments (see **Table 1**). The temperature dependence of the chemical diffusion coefficients is considered via the well-known Arrhenius ansatz

$$D_{k,j}(T) = D_{k,j}^{0} \exp\left(-\frac{\Delta E_{k,j}}{N_{\rm A}k_{\rm B}T}\right)$$
(25)

where $D_{k,i}^{0}$ is a temperature-independent pre-exponential factor and $\Delta E_{k,i}$ denotes the activation energy of diffusion. The Avogadro constant and the Boltzmann constant are denoted by $N_{\rm A}$ and $k_{\rm B}$, respectively. The composition of the liquid phase is provided in Table 1. The chemical diffusion coefficients $D_{CaO-CaO}$, $D_{CaO-SiO_2}$, D_{SiO_2-CaO} , and $D_{SiO_2-SiO_2}$ used for the simulation of the lime particle dissolution are given in Table 2, see ref.[64] as mentioned earlier. The maximum mole fracion differences in the melt $\Delta x_{CaO,S}$, $\Delta x_{SiO_2,S}$, and $\Delta x_{Al_2O_2,S}$ are calculated by means of the Gibbs energy minimization routine described in Section 2 and are provided in Table 2. The system size parameter *p* is given a sufficiently high value to account for the experimental conditions where the particle size is small compared to the system size. With respect to the experimental observations of Sun et al.,^[63] the dissolution process is divided into the following three stages: 1) The first stage corresponds to the direct dissolution of lime into liquid slag where diffusion of the components in the liquid melt control the dissolution rate. 2) The second stage is associated with the assumed immediate formation and subsequent dissolution of the boundary layer at the interface of the particle with the surrounding oxide melt. The dissolution kinetics is strongly retarded during this stage. Again the diffusion of the components in the liquid slag are assumed to be the rate determining processes. To this aim, the diffusion coefficient matrix is altered by multiplication with a retardation factor $\alpha = 0.3$ in the numerical model. In this sense, α is a fitting parameter in this model. 3) In the third and final stages, the remaining C2S-free CaO particle dissolves



Figure 12. Dissolution of CaO in CaO–SiO₂–Al₂O₃ slag at 1480 °C. The global composition of the the system is given in Table 1. The numerical result is calculated by means of the model parameters provided in Table 2.

in a diffusion-controlled manner, which is simulated by using the same diffusion coefficients as in the first stage.

The compositions of the slags used in the experimental studies^[13,63,64] are provided in mass fractions w_k in Table 1. As mentioned earlier, the diffusion coefficients relevant for these slag compositions were estimated based on the work of Liang and Davis.^[64] As Sun et al.^[63] did their work on slightly different slag compositions, a systematic error in the numerical results is to be expected. Nonetheless, these slag compositions seem to be close enough as the numerical results compare well with the experimental data. The solid line in **Figure 12** represents the calculated time-dependent radius of the lime particle during dissolution. The previously discussed three stages of lime dissolution can be distinguished clearly by the kinks in the dissolution rate in Figure 12.

In terms of steel cleanliness, the dissolution of oxides that are unwanted in the final product is a fundamental process.^[65] In this context, Michelic et al.^[13] investigated the dissolution of oxide inclusions in secondary steelmaking slags via in situ HT-LSCM experiments. In contrast to the dissolution of CaOcontaining additives, no intermediate boundary phase is formed during the dissolution of silica particles. Consequently, the dissolution of silica particles proceeds via direct dissolution only. The experimentally observed shrinking behaviour of SiO₂ particles at 1450 °C, taken from Michelic et al.,^[13] is simulated by the sharp-interface multicomponent diffusion model developed in this work. The composition of the slag used in ref.[13] is given in Table 1. The chemical diffusion coefficients $D_{CaO-CaO}$, $D_{\text{CaO-SiO}_2}$ $D_{\text{SiO}_2-\text{CaO}}$, and $D_{\text{SiO}_2-\text{SiO}_2}$ are estimated from^[64] and are provided together with the maximum mole fraction differences in the melt $\Delta x_{CaO,S}$, $\Delta x_{SiO_2,S}$, and $\Delta x_{Al_2O_3,S}$ in **Table 3**. The

 Table 2.
 The chemical diffusion coefficients, maximum mole fraction differences in the melt, and system size for the simulation of lime dissolution in slag

 SM04 shown in Figure 12.

$D_{CaO-CaO} \ [m^2 s^{-1}]$	$D_{CaO-SiO_2} \ [m^2 s^{-1}]$	$D_{SiO_2-CaO} \ [m^2 s^{-1}]$	$D_{SiO_2-SiO_2} \ [m^2 \ s^{-1}]$	$\Delta x_{CaO,S}$	$\Delta x_{SiO_2,S}$	$\Delta x_{Al_2O_3,S}$	р
$3.9 imes 10^{-11}$	0.36×10^{-11}	-1.9×10^{-11}	$\textbf{0.8}\times \textbf{10}^{-11}$	0.21	-0.07	-0.14	20∙ <i>R</i> ₀

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 Table 3.
 The chemical diffusion coefficients, maximum mole fraction differences in the melt and system size for the simulation of silica dissolution in slag

 1.1
 shown in Figure 13.

$D_{CaO-CaO} \ [m^2 s^{-1}]$	$D_{CaO-SiO_2} \ [m^2 \ s^{-1}]$	$D_{SiO_2-CaO} \ [m^2 \ s^{-1}]$	$D_{SiO_2-SiO_2} \ [m^2 s^{-1}]$	$\Delta x_{CaO,S}$	$\Delta x_{SiO_2,S}$	$\Delta x_{Al_2O_3,S}$	р
5.2×10^{-11}	$-0.14 imes 10^{-11}$	-0.21×10^{-11}	$-0.18 imes 10^{-11}$	0.11	0.13	-0.018	20· <i>R</i> ₀



Figure 13. Dissolution of silica (SiO₂) in CaO–SiO₂–Al₂O₃ slag at 1450 °C. The global composition of the the system is given in Table 1. The numerical result is calculated by means of the model parameters provided in Table 3.



Figure 14. The evolving mole fraction profiles of SiO_2 at different times during the dissolution of silica (SiO_2) in CaO-SiO₂-Al₂O₃ slag at 1450 °C.

system size parameter *p* is provided in Table 3. The numerical results are compared with the experimental data in **Figure 13**. The corresponding mole fraction profiles x_{CaO} and x_{SiO_2} during the dissolution of silica (SiO₂) are shown at times *t* = 10, 50, 100, 150, and 200 s in **Figures 14** and **15**, respectively.

The resulting dissolution curves for both lime and silica mimic the experimental points, see Figures 12 and 13. In the case of lime dissolution (see Figure 12), there is no need for introducing another reaction-controlling mechanism in addition to diffusion in the case of indirect dissolution where a boundary phase forms at the interface. The solid line in Figure 13 representing the calculated time-dependent radius of the silica particle



Figure 15. The evolving mole fraction profiles of CaO at different times during the dissolution of silica (SiO₂) in CaO–SiO₂–Al₂O₃ slag at 1450 °C.

during dissolution shows the same characteristic curvature as the experimental results and agrees in terms of total dissolution time without the need to introduce the numerical correction factor used in ref. [13]. Thus, it is concluded that the diffusion of components in liquid slags is the rate-determining process during dissolution in multicomponent systems. As the calculated dissolution curves mimic the experimentally deduced dissolution kinetics without the use of any additional fitting parameters, it can be concluded that for HT-LSCM experiments with small sample size the effect of convection on the dissolution process is of minor importance. This most likely holds as long as the experimental studies using HT-LSCM or other methods do not include external stirring.

4. Conclusion and Outlook

A flexible sharp-interface multicomponent diffusion model is applied together with a Gibbs energy minimization algorithm to numerically describe oxide particle dissolution in oxide melts. The following conclusions are drawn: 1) Although a purely diffusion controlled process is assumed, the kinetics strongly depends on the initial and boundary conditions (diffusion coefficient, maximum mole fraction difference in the melt, and system size). It is demonstrated that the shape of the dissolution curve (normalized particle radius versus normalized time) is highly flexible. 2) The time-dependent radii of shrinking oxide particles are simulated by means of the sharp-interface multicomponent diffusion model for both direct and indirect dissolutions and compare well with experimental data from HT-LSCM investigations. 3) Further precisely defined dissolution experiments and corresponding simulations are planned in the future. Thereby, the understanding of the kinetics of oxide particle

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dissolution in metallurgical slags is expected to be expanded to various slag compositions and temperature ranges that are relevant to steelmaking processes.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

diffusion, dissolution of oxide particles, Gibbs energy minimization, phase transformation, slags, steelmaking

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