Full Length Article

Population balance model and experimental validation for reactive dissolution of particle agglomerates

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ABSTRACT

We propose a population balance model coupled with a mass transfer model to simulate the simultaneous shrinkage and breakage of particles during the reactive dissolution of particle agglomerates in stirred tank. The high-order moment-conserving method of classes is adopted to solve the population balance model. In the mass transfer model, the driving force is estimated by considering the physical constraints including electroneutrality, water dissociation and dissolution equilibrium. The simulation results, including the concentration and the particle size distribution of the final products, were validated by experiments carried out in a laboratory scale stirred tank. The unknown physical parameters in the particle breakage model were fitted against the experimental data. The results underline the importance of particle breakage in the reactive dissolution modeling under the investigated operating conditions. Several daughter size distributions functions found in literature were tested. Among them, the beta distribution provides the most flexible way to describe breakage of the particle agglomerates.

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1. Introduction

Several efforts have been devoted to the experimental and numerical studies on solid-liquid reactive dissolution in various industrial applications such as reduction of metallic oxides, hydrometallurgy, kraft pulping, chemical leaching and aqueous mineral carbonation (Aydogan et al., 2005; Bandi, 1990; Grénman et al., 2010; Hövelmann et al., 2012; Kolodziej and Adamski, 1990). Three steps are involved in the reactive dissolution: the first step is mass transfer of the reactants from the bulk solution to the solid-liquid interface; the second step is surface reaction between the liquid reactant and solid reactant; the last step is mass transport of the product from the solid-liquid interface to the bulk solution. The slowest step exerts a dominating influence on the overall dissolution rate.

Shrinking particle model is usually employed to describe the solid-liquid mass transfer during the dissolution of non-porous powder particles. It is commonly based on the assumption that particles are monodispersed, i.e., all the particles have the same diameter (Levenspiel et al., 1999). Several analytical expressions of dissolution rates in the special cases where a single mechanism is rate limiting step, namely mass transfer control or surface reaction control, have been reported in the literature (Dickinson and Heal, 1999; Grénman et al., 2011). In reality, the polydispersity of the raw materials has a strong influence on the dissolution behavior: models formulated in terms of the average particle size can lead to large errors in the prediction of the realistic dissolution rate (LeBlanc and Fogler, 1987, 1989LeBlanc and Fogler, 1989). Therefore, Leblanc and Fogler (1987) first developed the analytical expression for the dissolution rate of solids with polydispersity, which is limited by the assumption of constant liquid concentration and single rate limiting regime. Then a more general form of expression for the dissolution rate, which combined the models of mass transfer and surface reaction controlling regime, was proposed by Bhaskarwar (1989). On one hand, the actual particle size significantly affects the solid-liquid mass transfer coefficient. On the other hand, the particle size distribution (PSD) itself is essential to determine the interfacial area, especially in case of complex surface reactions. In the multiphase precipitation of $Mg(OH)_2(s)$-$CO_2(g)$-$H_2O(l)$ system, for instance, the total solid surface area calculated from PSD of the dissolving particles could provide the crystal growth area for the simultaneous crystallization process (Hövelmann et al., 2012; Zhao et al., 2016). Another example is the solid-liquid catalytic reaction, where the variation of the PSD of solid catalyst due to the chemical or mechanical process plays an important role in the mechanisms of catalyst deactivation (Bartholomew, 2001).

The solid-liquid mass transfer of uncharged molecules can be described by the typical Noyes-Whitney equation (Noyes and Whitney, 1897). For the reactive dissolution, the mass transfer rate is instead determined by the transport of charged ions. Therefore,

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Nomenclature

a	Dimensionless shape factor of beta distribution, $[-]$
A_{tot}	Total mass transfer area, m^2
B	Breakage table
c	Concentration of component, mol/m^3
D	Diffusion coefficient of component p, m^2/s
g	Breakage frequency, $1/s$
G	Growth rate, m/s
k	Mass transfer coefficient, m/s
K_{sp}	Solubility product, mol^3/m^9
k_v	Volume shape factor, $[-]$
K_w	Water auto-ionization constant, mol^2/m^6
L	Particle size, m
m	Amount of component, mol
n	Number density, $\#/m^4$
N	Mass transfer flux, $mol/(m^2 s)$
Re_ε	Reynolds number, $[-]$
Sc	Schmidt number, $[-]$
Sh	Sherwood number, $[-]$
V	Volume, m^3
v_m	Molar volume, m^3/mol
Y	Paricle number density, $\#/m^3$
z	Charge of the cationic and anionic, $[-]$

Greek letters

β	Daughter size distribution function, $[-]$
γ	Exponent of the particle size in power-law breakage kernel, $[-]$
ρ	Density, kg/m^3
η	Kolmogorov length scale, m
η_T	Kolmogorov time scale, s
ξ	growth table, m^{-1}
μ	Dynamic viscosity of the liquid, $P_a s$
ψ	Breakage rate constant, $[-]$
ε_T	Overall energy dissipation, m^2/s^3
ν	Kinematic viscosity of liquid, m^2/s

Subscripts

br	Breakage
disp	Dispersion
i, j	Index of the particle size classes
L	Liquid phase
p	Index of the components
s	Solid phase

the electroneutrality of the mass transfer fluxes must be satisfied during the dissolution of particles in electrolyte solutions. This aspect can be addressed by introducing the Nernst-Planck equation, which is capable of calculating the flux of ions under the influence of both ionic concentration gradient and electric field (Newman, 1991). Thus, the transports of cations and anions of all the components are taken into account in the mass transfer model. In addition, the solid-liquid interface concentrations are commonly calculated from the solubility of the component. However, Ji et al. proposed that the interface concentration could be lower than the saturated concentration, and this concentration difference could affect the prediction of dissolution rate (Ji et al., 2001). Therefore, it is interesting to see whether the interface concentration can be estimated by rigorous physical constraints rather than a simple saturated concentration.

Another important but often neglected phenomenon, is the breakage of the particles due to high shear rates occurring in the reactors (most commonly stirred tanks) where the dissolution process takes place. The raw materials are not always perfect spheres or cubes, but rather agglomerates with various morphology, and the breakage of such large agglomerates may alter the total solid-liquid contact area, influencing the dissolution rate in both mass transfer and surface reaction regimes. For this reason, a detailed population balance equation (PBE), accounting for both particle shrinking due to chemical dissolution and particle breakage due to intensive turbulence, is needed to properly describe the behavior of the dissolution process (Hänchen et al., 2007).

As the most important character of the dispersed phase in the multiphase processes, the variation of PSD caused by physical mechanisms including nucleation, growth, agglomeration and breakage can be described by solving population balance equation (PBE) (Randolph and Larson, 1988). However, for the reactive dissolution process under investigation, only the growth and breakage terms are relevant. Although the analytical solution of the PBE exists under limited and well defined simplified cases, for the realistic physical process, efficient numerical techniques are required to solve the PBM. Among many different approaches, the method of classes emerged as a valuable tool to predict the PSD in particle-based processes (Vanni, 2000). The most popular numerical scheme belonging to the method of classes family is the so-called fixed-pivot technique. It predicts the exact PSD of raw material by conserving two distribution moments (Kumar and Ramkrishna, 1996a, 1996b). The accurate solution of such low order approach, however, is only conserved by using a large number of classes, which may be unacceptable when PBM is coupled with Computational Fluid Dynamics (CFD) simulations or when the PBM is used to formulate and test new sub-models. Therefore, the low order fixed-pivot approach was extended by conserving defined number of moments of the distribution, leading to the high-order moment method of classes (HMMC)(Alopaeus et al., 2006, 2007). Comparing to the traditional numerical methods, HMMC offers accurate solution with considerably lower number of classes, as well as tracks the actual shape of PSD directly. Moreover this method is very flexible, since it allows to preserve an arbitrary set of moments, as well as a different number of internal variables of the population balance equation (Buffo and Alopaeus, 2016).

In this work, we propose a population balance model coupled with a mass transfer model to simulate the reactive dissolution of $Mg(OH)_2(s)$ in aqueous HCl solution. The surface reaction between H^+ and OH^- is a typical diffusion controlled reaction, in which the external mass transfer is the rate-controlling step (Tinoco et al., 1995). The growth term described by the mass transfer model is calculated by the Nernst-Planck equation. For the particle breakage term, a semi-theoretical power-law function is adopted to predict breakage rate while beta distribution is introduced as the daughter size distributions (DSD) function to describe particle size changes. In parallel with the modeling work, reactive dissolution experiments were carried out in a laboratory scale stirred tank reactor with different initial and operating conditions and the obtained experimental data were used to verify and validate the model. Eventually, the empirical parameters including the breakage rate constant and the parameter of beta distribution were fitted against the experimental data.

2. Mathematical modelling

The reactive dissolution of $Mg(OH)_2$ solids in aqueous HCl solution can be expressed as:

$$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O \tag{1}$$
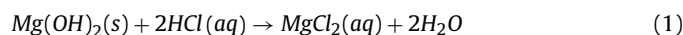
The shrinking particle model can be adopted to calculate the solid-liquid mass transfer during the reactive dissolution as shown in Fig. 1(a) (Levenspiel et al., 1999). Meanwhile, breakage of particle