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Modelling of mass transfer coupling with crystallization kinetics in microscale

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ABSTRACT

Microstructure technologies have attracted interests in chemistry, chemical engineering, and biotechnology. To investigate the mass transfer of ions and crystallization of crystals in microscale and then to explain the formation mechanism of the porous structure materials, a microscale mathematical model for mass transfer processes coupling with local reactions is proposed in which the chemical potential gradient $\Delta\mu$ is used as the driving force to avoid the discontinuity of the kinetics equations in the micro-channels. Meanwhile, the dissolution kinetics of KCl at 298.15 K is measured to determine the dissolution rate constant k_d and the average area of crystals A_c . The investigation for the fractional crystallization process of carnallite shows that the calculated mixing time versus channel width agree with the Einstein diffusion equation, which validates that the model can be used to describe the ion diffusion very well. Meanwhile, to have an accurate $\Delta\mu$ of KCl, in the channel width of or narrower than 2.0×10^{-6} m, it is enough to consider the diffusion only, while in the channel width of or wider than 2.0×10^{-5} m, diffusion should be coupled with reaction. The investigation also shows the vital of the consideration of the ionic activity coefficient for the investigated systems in micron scales. Moreover, the new formation mechanism of the porous structures in the inorganic material fabrication will be proposed from the process simulation for the synthesis of porous KCl, which will provide a reference for the porous structure formation in the advanced inorganic material synthesis.

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1. Introduction

The development of microreaction technology is attractive for the multidisciplinary research and applications due to its advantages, such as increased yields, selectivity and product quality, improved heat transport and mass transport, offering the potential for process intensification, increased safety, decreased inputs and wastes, on-line reaction monitoring, etc. (Jensen, 1999; Hsing et al., 2000; Jensen, 2001; Chow, 2002; Kobayashi et al., 2004; Abdallah et al., 2006; Tagawa et al., 2007). Microchemical systems have been used in inorganic and organic material synthesis, nanoparticles synthesis, catalytic reactions, and photochemical and electrochemical reactions (Jensen, 1999; Stone and Kim, 2001; Jähnisch et al., 2004; Lin et al., 2004; Delamarche et al., 2005; Zhao et al., 2006; Mason et al., 2007; Tagawa et al., 2007).

The development of microchannel reaction technology offers tremendous multidisciplinary research opportunities across chemistry, materials, biology and electronics, as well as in the traditional chemical engineering subdisciplines of catalysis, transport phenomena, and reaction engineering (Jensen, 1999;

Stone and Kim, 2001; Chow, 2002). Meanwhile, it also brings a lot of scientific and engineering challenges (Jensen, 1999; Stone and Kim, 2001). Whether the classical transport and reaction fundamentals are adequate to describe the transport and reaction behaviors in micro-channels and how the reaction affects the diffusion are two of these challenges.

Recently, computational fluid dynamics (CFD) has been used to describe the fluidic flow behaviors in microchannels (Schönfeld and Hardt, 2004; Yamaguchi et al., 2004) and to quantitatively estimate the mass transfer of microdevices (Abdallah et al., 2006; Schönfeld and Hardt, 2004; Yamaguchi et al., 2004; Salman et al., 2007). Abdallah et al. (2006) simulated the mass transfer of a catalytic multiphase microstructure film contactor with a fast hydrogenation of α -methylstyrene and a Pd/ γ -alumina catalyst. However, the simulation results were inconsistent with the experimental results. This might be because that the concentration gradient is considered as the mass transfer driving force. Kashid et al. (2007) developed a CFD model to simulate the mass transfer with or without chemical reactions for the liquid–liquid slug flow capillary microreactor, and the diffusion driving force was also simplified to be the concentration gradient, which causes some errors in simulation.

Besides, in our previous work, porous structured KCl with a pore size of 10–50 μm was produced from the fractional crystallization

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of carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) (Liu et al., 2007). Moreover, Fick's second law was used to investigate the diffusion of the K^+ , Mg^{2+} and Cl^- , and the ionic product of carnallite and KCl was analyzed to explain the formation mechanism of the porous KCl (Liu et al., 2007). However, in the fractional crystallization of carnallite, during the diffusion of ions, the dissolution or crystallization may take place at a certain position inside the carnallite crystal. In order to analyze the formation mechanism of the porous structure further and then to provide a reference for the porous structure formation, it is important to modify the theoretical model previously used.

In this work, a diffusion–reaction model will be proposed to analyze mass transfer and crystallization or dissolution in microscale systematically, in which the driving force of the diffusion and reaction will be represented with the potential gradient. The dissolution kinetics of KCl at 298.15 K will be investigated experimentally to determine the dissolution rate constant k_d and the average area of crystals A_c . The diffusion of K^+ , Mg^{2+} , Cl^- and the crystallization kinetics of KCl in aqueous solutions will be studied in detail with the channel width in a range from 2.0×10^{-7} to 0.2 m, which covers the width of a microreactor (Chow, 2002; Jähnisch et al., 2004; Ehrfeld et al., 2000).

2. Experimental section

The dissolution kinetics of KCl at 298.15 K is investigated online using a chloride solid-state ion selective electrode (ISE) (Model pCl-1, China) and a calomel reference electrode. By sieving, the sizes of KCl crystals are in a range from 1.54×10^{-4} to 3.00×10^{-4} m. The initial weight of KCl crystals is 3.950 g. The concentrations of Cl^- are measured by detecting the cell potential with a SCHOTT-GERÄTE pH-meter (Model CG0841, Germany) with a resolution of ± 0.1 mV.

The dissolution experiments are carried out in a double-walled crystallizer. The apparatus are described in Fig. 1. The pH-meter has a connecting interface to a personal computer and the potential data at a time interval of 1 s are automatically recorded. The constant stirring speed is 300 r min^{-1} .

3. Diffusion–reaction model

The physical diffusion–reaction model can be schematically represented as shown in Fig. 2. In this model, ion diffusion and crystal crystallization/dissolution are considered while the fluid flow is neglected. The ion diffusion starts from the left boundary, and dissolution or crystallization may take place at a certain position inside the channel. The positive $\Delta\mu$ (chemical potential

Fig. 2. Schematic representation of the diffusion–reaction model.

gradient) means that the aqueous solution is supersaturated and the crystallization may take place, the negative $\Delta\mu$ means that the aqueous solution is unsaturated or crystal dissolves, and the zero value of $\Delta\mu$ means that the aqueous solution is saturated and neither crystallization nor dissolution will happen.

The ion diffusion is governed by the convection–diffusion equation:

$$\frac{\partial m}{\partial t} + u \cdot \nabla m = D \Delta m \pm r \quad (1)$$

where m is the molality of ions in aqueous solutions, mol kg^{-1} ; t is time, s; u is the flow velocity, m s^{-1} ; D is the diffusivity, $\text{m}^2 \text{s}^{-1}$; and r represents the source or consumption rate term depending on the kinetics of the reaction, $\text{mol kg}^{-1} \text{s}^{-1}$. In this work, the term r is the coupling of the crystallization rate with the dissolution rate in the crystallization or dissolution process. That is

$$r = A_c(J - G) \quad (2)$$

where J and G are the dissolution and crystallization rates ($\text{mol kg}^{-1} \text{m}^{-2} \text{s}^{-1}$), respectively. The magnitude of J and G is dependent on chemical potential gradient. And A_c is the average area of the crystals, m^2 .

The dissolution rate is expressed as

$$J = k_d(K_{sp} - A_{sp}) \quad (3)$$

where k_d is the dissolution rate constant, $\text{mol kg}^{-1} \text{m}^{-2} \text{s}^{-1}$. K_{sp} is the dimensionless solubility product constant, A_{sp} is the dimensionless ionic product.

For the crystallization process, three kinds of crystal growth mechanisms have been proposed, i.e. spiral growth mechanism, two-dimensional nucleation growth mechanism, and adhesive-type mechanism (Sunagawa, 2005). In this work, the adhesive-type mechanism is adopted because the process investigated in this work is very fast and it is reasonable to assume that the nucleation and crystal growth occur simultaneously. Therefore, the crystallization rate is expressed as (Sunagawa, 2005)

$$G = A \left(\frac{\Delta\mu}{RT} \right) = A \ln \left(\frac{A_{sp}}{K_{sp}} \right) \quad (4)$$

where A is a constant, $\text{mol kg}^{-1} \text{m}^{-2} \text{s}^{-1}$; $\Delta\mu$ is the chemical potential difference at the solid–liquid interface (Cheng et al., 2006), J mol^{-1} ; R is the universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$ and T is the temperature, K.

Therefore, for the static aqueous solution ($u=0$), the diffusion–reaction equation can be written as

$$\frac{\partial m}{\partial t} = D \Delta m + A_c \cdot k_d(K_{sp} - A_{sp}) - A_c \cdot A \ln \left(\frac{A_{sp}}{K_{sp}} \right) \quad (5)$$

Fig. 1. Apparatus for measuring the dissolution of potassium chloride: 1 PC; 2 pH-meter; 3 Cl^- ISE; 4 calomel reference electrode; 5 rubber stopper; 6 double-walled crystallizer; 7 magnetic stir bar; 8 mercury thermometer; 9 thermostatic bath; 10 magnetic stirrer.

3.1. Fractional crystallization process of carnallite

The fractional crystallization process of carnallite is selected as our study case since the carnallite produced is a material with micron to millimeter scales. In the fractional crystallization process of carnallite, the carnallite is dissolved, and K^+ , Mg^{2+} and Cl^- begin to diffuse from the solid–liquid interface. Since the solubility of magnesium chloride is very large and the crystal magnesium chloride will never appear under the investigated conditions, the following equations can be obtained:

$$\frac{\partial m_{K^+}}{\partial t} = D_{KCl} \frac{\partial^2 m_{K^+}}{\partial x^2} + \underbrace{Ack_d (Ksp_{KCl} - Asp_{KCl}) - A c A \ln \left(\frac{Asp_{KCl}}{Ksp_{KCl}} \right)}_{\text{reaction term } r} \quad (6)$$

$$\frac{\partial m_{Mg^{2+}}}{\partial t} = D_{MgCl_2} \frac{\partial^2 m_{Mg^{2+}}}{\partial x^2} \quad (7)$$

$$\frac{\partial m_{Cl^-}}{\partial t} = \frac{\partial m_{K^+}}{\partial t} + 2 \cdot \frac{\partial m_{Mg^{2+}}}{\partial t} \quad (8)$$

In Eq. (6)

$$Asp_{KCl} = \frac{m_{K^+}}{m^0} \cdot \frac{m_{Cl^-}}{m^0} \cdot \gamma_{\pm KCl}^2 \quad (9)$$

$$Ksp_{KCl} = \frac{m_{s,K^+}}{m^0} \cdot \frac{m_{Cl^-}}{m^0} \cdot \gamma_{\pm s,KCl}^2 \quad (10)$$

where $\gamma_{\pm KCl}$ is the mean ionic activity coefficient of KCl in the aqueous solution, and it is calculated with Lu–Maurer (1993) model. m_{s,K^+} is calculated on the basis of solid–liquid equilibrium in the aqueous $K^+ - Mg^{2+} - Cl^-$ solution at a certain concentration of Mg^{2+} . x is the position inside a channel with a certain width w .

The driving force $\Delta\mu$ (difference of chemical potential or chemical potential gradient) of the crystallization or dissolution of KCl is calculated by the following equation:

$$\Delta\mu_{KCl} = RT \ln \left(\frac{Asp_{KCl}}{Ksp_{KCl}} \right) \quad (11)$$

3.2. Parameter determination

k_d , D_{KCl} , D_{MgCl_2} , Ac and A are parameters in the proposed model for the investigated process. The areas of crystals at different time At are calculated by the method in Ji et al. (2001) according to the dissolution kinetics data. In the calculation of At , the initial diameters of crystals are assumed to satisfy the normal distribution. Ac is obtained as an average area value. k_d is determined with the modified statistical rate theory (SRT) (Dejmek and Ward, 1998; Ji et al., 2001) from the dissolution kinetics data that are measured in this work, which will be described in detail in the later part of this paper. The modified SRT (Dejmek and Ward, 1998; Ji et al., 2001) can be used to describe the instantaneous rate of molecular transport across the interface between the solid and liquid phases. The rate expression is in terms of (a) the chemical potential of the molecules in the solid; (b) the chemical potential of the molecules in the liquid solution at the interface with the solid phase and (c) the equilibrium exchange rate between the phases that would exist if the isolated system is allowed to evolve into equilibrium and both phases are present. For the modelling of the fractional crystallization process of carnallite, D_{KCl} and D_{MgCl_2} are assumed to be constants, and they are equal to the values in dilute solutions (Zaytsev and Aseyev, 1992).

$$D_{KCl} = 1.856 \times 10^{-9} \text{ (m}^2 \text{ s}^{-1}\text{)} \quad (12)$$

$$D_{MgCl_2} = 1.25 \times 10^{-9} \text{ (m}^2 \text{ s}^{-1}\text{)} \quad (13)$$

The parameter A represents the Arrhenius relationship of the crystal growth rate coefficient related with the temperature and hydrodynamic state in solutions (Cheng et al., 2006). The value of A for crystallization of KCl is considered to be similar to that of K_2SO_4 which is $0.4371 \text{ mol kg}^{-1} \text{ m}^{-2} \text{ s}^{-1}$ at 298.15 K.

3.3. Discretization, initial and boundary conditions

Galerkin method is used for spatial discretization of the governing equations. The details of the discretization method have been described by Skeel and Berzins (1990).

The ion diffusion in three aqueous solutions is investigated under the initial conditions listed in Table 1.

For the modelling of the fractional crystallization process of carnallite, at left boundary, $m_{K^+} = 3.1406 \text{ mol kg}^{-1}$, $m_{Mg^{2+}} = 3.1406 \text{ mol kg}^{-1}$, and the molality of Cl^- is determined according to the neutrality of charges, and the right boundary conditions are the same as the initial conditions in the bulk phase.

4. Results and discussions

4.1. Experimental results

To determine the dissolution rate constant for the diffusion–reaction model, the dissolution kinetics of KCl at 298.15 K is investigated experimentally. The experimental results are shown in Fig. 3. As shown in Fig. 3, the molality of chloride ion increases sharply with time at the beginning of the dissolution process, and then increases slowly and becomes a constant value, which means the dissolution has finished.

Table 1
Initial conditions for the diffusion–reaction model.

Solutions	K^+ concentration (mol kg ⁻¹)	Mg^{2+} concentration (mol kg ⁻¹)	Cl^- concentration (mol kg ⁻¹)
KCl aqueous solution	3.930	0	3.930
MgCl ₂ aqueous solution	0	3.151	6.302
Distilled water	0	0	0

Fig. 3. Molality of chloride ions with time during the dissolution process of KCl crystals at 298.15 K.

The changing of areas of crystals with time is considered in this work. According to the dissolution kinetics data, the areas of crystals at different time t are calculated by the method in Ji et al. (2001) in which the initial diameters of crystals are assumed to satisfy the normal distribution. A_c is obtained as an average value for the areas of the crystals at different time, with the value of $3.639 \times 10^{-4} \text{ m}^2$. k_d is obtained with the statistical rate theory (SRT) (Dejmek and Ward, 1998; Ji et al., 2001) with the value of $6.000 \times 10^{-4} \text{ m s}^{-1}$.

4.2. Model results

To investigate the effects of reaction term r in Eq. (6) and activity coefficient in Eqs. (9)–(11) on diffusion, the model in three cases is performed, i.e.

- case 1: considering diffusion but neglecting reaction, i.e. $r=0$ in Eq. (6);
- case 2: considering diffusion coupling with reaction; and
- case 3: considering diffusion coupling with reaction but activity coefficient is assumed to be unity in the calculation of Asp and Ksp .

4.2.1. Mixing time in different aqueous solutions

Mixing time can be obtained from the value of $\Delta\mu$ with time. When $\Delta\mu$ keeps a constant throughout the whole channel, the mixing process is completed. The calculated mixing time versus channel width is shown in Fig. 4 where the double logarithmic coordinate axes are used to describe the large range of time and channel width.

In Stokes flow characteristic in microchannels, mixing time (t) is dictated by thermal diffusion described approximately by the Einstein diffusion equation (Chow, 2002):

$$t = w^2 / (2D) \quad (14)$$

where w is the channel width and D is the molecular diffusion coefficient.

As shown in Fig. 4(a), the logarithm of the mixing time calculated with the model in case 1 is proportional to the logarithm of the channel width in the solutions of aqueous KCl, aqueous MgCl_2 and distilled water, which follows the Einstein diffusion equation (Eq. (14)). This observation validates that the model can be used to describe the diffusion of ions very well. The calculated results also reveal that the mixing time can be highly reduced by shortening the channel width.

With the model in case 2, as shown in Fig. 4(b), in aqueous KCl solutions, an almost linear relationship between the logarithms of the mixing time and the logarithms of channel width is obtained. However, in the solution of aqueous MgCl_2 and distilled water, the dual logarithm relationship of the mixing time versus channel width is nonlinear, especially for the wide channel, and the mixing time in these two solutions is obvious different for the channel width of $2.0 \times 10^{-3} \text{ m}$.

As shown in Fig. 4(c), with the model in case 3, the dual logarithm relationship of the mixing time versus channel width is linear for the channel width of and narrower than $2.0 \times 10^{-4} \text{ m}$. Fig. 4(c) also shows nearly the same mixing time in aqueous MgCl_2 solutions and distilled water. These observations validate that ion diffusion can be described with the model in the cases from 1 to 3. These observations agree with those from the view of Jensen (1999) that the mixing occurs primarily by diffusion for the small widths in microreactor channels.

Fig. 4. Mixing time at different channel widths calculated with the model in different cases: (a) in case 1, diffusion neglecting reaction; (b) in case 2, diffusion coupling with reaction; and (c) in case 3, diffusion coupling with reaction but the value of activity coefficient is unity.

4.2.2. Diffusion and reaction behaviors inside the channel

The value of $\Delta\mu$ of KCl in distilled water calculated by assuming the activity coefficient to be unity is always less than zero, which disagrees with the experimental observations (Liu et al., 2007).

Therefore, in the following investigation, the activity coefficient is always calculated with Lu–Maurer (1993) model.

$\Delta\mu$ of KCl inside a channel under the initial condition of distilled water is investigated in detail. In calculation, the channel widths are set to be 2×10^{-6} , 2×10^{-5} , 2×10^{-4} , 2×10^{-3} , 0.02 and 0.2 m, respectively, which covers the width of a microreactor (Chow, 2002; Jähnisch et al., 2004; Ehrfeld et al., 2000). $\Delta\mu$ of KCl at different position inside the channel is calculated. Fig. 5 (A1, A2) shows the results at 0.001, 0.1 and 10 s calculated with the model in case 1 and Fig. 6 (B1, B2, B3) shows those at 0.001, 1 and 1200 s calculated with the model in case 2.

As shown in Fig. 5 (A1, A2, (a–c)), fluctuations may appear. At 0.001 s, the fluctuations appear in the channel widths of 2.0×10^{-5} and 2.0×10^{-4} m. At 0.1 s, the fluctuations appear in the channel widths of 2.0×10^{-4} and 2.0×10^{-3} m. At 10 s, the fluctuations occur in the channel widths of 2.0×10^{-3} and 2.0×10^{-2} m. For the channel width of 2.0×10^{-6} m, no fluctuation appears at any time.

As shown in Fig. 6 (B1), at 0.001 s, fluctuation appears only in the channel widths of 2.0×10^{-5} and 2.0×10^{-4} m. At 1 and 1200 s, no obvious fluctuation appears in the channel widths of 2.0×10^{-6} , 2.0×10^{-5} , 2.0×10^{-4} and 2.0×10^{-3} m. From Fig. 6 (B2, B3), we can observe obvious fluctuations appear at different time in the

Fig. 5. $\Delta\mu$ of KCl in distilled water calculated with the model considering diffusion but neglecting reaction (model in case 1).

Fig. 6. $\Delta\mu$ of KCl in distilled water calculated with the model considering diffusion coupling with reaction (model in case 2).

channel widths of 0.02 and 0.2 m. The fluctuations of the $\Delta\mu$ of KCl around $\Delta\mu=0$ in Fig. 6 (B2, B3) give an explanation on how the porous structures form after the carnallite dissolving in distilled water, i.e. when $\Delta\mu$ is positive, the aqueous solution is super-saturated and the crystallization may occur; when $\Delta\mu$ is negative, the aqueous solution is unsaturated or the crystals which have been formed may dissolve again. As shown in Fig. 6 (B3(d)), the magnitude of $\Delta\mu$ for the dissolution of KCl is larger than that for the nucleation and the differences between these two driving forces near the carnallite boundary lead to the porous crystal structures.

From the results shown in Figs. 5 and 6, we can observe that in the channel width of 2.0×10^{-6} m the $\Delta\mu$ of KCl obtained in the cases of diffusion with and without reactions is the same, and the same for the channel width of 2.0×10^{-7} m. While in the channel width of or wider than 2.0×10^{-5} m, the $\Delta\mu$ of KCl obtained in the case of diffusion neglecting reaction (case 1) is different from that obtained in the case of diffusion coupling with reaction (case 2). Therefore, we may conclude that in the channel width of or narrower than 2.0×10^{-6} m, the contribution of reaction to the $\Delta\mu$ of KCl can be neglected, while in the channel widths of or wider than 2.0×10^{-5} m, both diffusion and reaction have to be considered in order to obtain a reliable of KCl.

5. Conclusions

In this work, a microscale mathematical model for local reactions and mass transfer processes is proposed to investigate the mass transfer of ions and nucleation of crystals in microscale,

and the chemical potential gradient instead of concentration gradient is used as the driving force to avoid the discontinuity of the kinetics equations in the micro-channels. Porous structured KCl with a pore size of 10–50 μm is produced and the dissolution kinetics of KCl at 298.15 K is investigated experimentally to determine the dissolution rate constant k_d and the average area of crystals A_c . For the aqueous K–Mg–Cl systems, the dual logarithm relationship of the calculated mixing time versus channel width is linear, which agrees with the Einstein diffusion equation. This validates that the model can be used to describe the diffusion of ions very well. Meanwhile, in the channel width of or narrower than 2.0×10^{-6} m, the contribution of reaction to the $\Delta\mu$ of KCl can be neglected, while in the channel width of or wider than 2.0×10^{-5} m, both diffusion and reaction have to be considered. It is also shown the vital of the mean ionic activity coefficient for the investigated systems in micron scales. Moreover, the calculated results of the proposed model reveal the formation mechanism of the porous structures in the inorganic material fabrication. This will provide a reference for the regular and ordered porous structure formation and microphase separation mechanisms in the advanced inorganic material synthesis.

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