An Experimental Study of Matrix Dissolution and Wormhole Formation Using Gypsum Core Flood Tests: 2. Dissolution Kinetics and Modeling

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Abstract In the parallel paper by Li et al. (2019; https://doi.org/10.1029/2018JB017238), an effluent chemistry monitoring system was designed and used in core flood experiments to continuously measure the effluent concentration and study the evolution of the rock-fluid system. In this study, the results from the parallel paper were used for interpretation and modeling of the dissolution and wormhole formation. Based on the behavior of the effluent concentration, two transient states and two quasi-steady states were defined to describe the dissolution in the rock-fluid system. Dimensional analysis was used to identify the controlling mechanisms of the dissolution and transport in the matrix and the wormholes. The dimensional analysis showed that the dissolution in the matrix was reaction controlled, while the dissolution in the wormholes was diffusion controlled. It also showed that the rock-fluid system evolved from reaction-controlled dissolution to diffusion-controlled dissolution during the core flood tests. A continuum model and the extended Graetz solution were used to model the dissolution in the matrix and in the wormholes, respectively. In the continuum model, this study estimates the effective surface area as a function of the flow rate (injection flux), to account for the effect of flow conditions on dissolution. Finally, a semiempirical model combining the continuum model and the extended Graetz solution was developed to simulate the formation of wormholes and the evolution of the dissolution kinetics during core flood tests.

1. Introduction

Dissolution of the rock matrix and formation of wormholes occur in various conditions and timescales. Natural rock dissolution such as limestone and gypsum karst formations are usually induced by slow groundwater flow. The evolution of the dissolution in natural rock-fluid system lasts for years (Dreybrodt, 1996; Groves & Howard, 1994; Johnson, 2008; Kaufmann & Romanov, 2008). In industrial applications such as oil reservoir acid stimulation, several days of rock dissolution will significantly increase the permeability of the reservoir (Daccord, 1987; Gomaa & Nasr-El-Din, 2010; Hoefner & Fogler, 1988; Taylor & Nasr-El-Din, 2002). During the evolution of the rock-fluid system, wormholes form due to the flow and dissolution heterogeneity in the rock matrix (Budek & Szymczak, 2012; Hoefner & Fogler, 1988). The formation of wormholes increases the rock permeability and the flow heterogeneity, which in turn change the dissolution kinetics of the rock-fluid system (Daccord et al., 1993). The parallel paper (Li et al., 2019) presented the advances in the experimental setup and the X-ray CT data analysis algorithms so that new insights were gained into the evolution of dissolution kinetics and the effect of the flow rate on wormhole geometries. This paper focuses on answering the question of how the formation of wormholes under different flow rates influences the dissolution kinetics of the rock-fluid system and how the dissolution in the matrix-wormhole system can be modeled.

Core flood testing is a useful experimental method to investigate the coupled flow and reaction processes in the rock matrix. During such tests, the reactions in the rock-fluid system were usually studied by sampling and analyzing the effluent. Inductively coupled plasma-mass spectroscopy, ion chromatography analysis, ion-specific electrode analysis, and pH probe were often used to measure the concentrations of the chemical species of interest in the effluent samples (Al-Khulaifi et al., 2018; Mohamed et al., 2013; Noiriel et al., 2005, 2009; Smith et al., 2013, 2014, 2017). The overall reaction rate, the reaction kinetics, and the evolution of the
rock-fluid system were also estimated from the effluent chemistry analysis. In addition, the measured effluent concentrations were used to validate the models that were developed to simulate the reactive transport processes in the rock-fluid system (Noiriel et al., 2009).

Continuum reactive transport models are common models to simulate the flow and dissolution in the porous rock matrix. One of the key parameters used in the continuum models is the effective surface area (Carroll et al., 2013; Cheng et al., 2016; Fu et al., 2015; Noiriel et al., 2009; Panga et al., 2005; Qiao et al., 2016; Wen & Li, 2017), which is defined as the total surface area in a unit volume of rock matrix that is reactive with the fluid in the pore space. The effective surface area was estimated based on the experimental measurement of specific surface area using mercury intrusion porosimetry (MIP), gas absorption surface area measurement, high-resolution X-ray CT scanning, and 2-D scanning electron microscope image processing and numerically by fitting the continuum models to the effluent concentration data (Beckingham et al., 2017; Hao et al., 2013; Noiriel et al., 2009, 2016; Smith et al., 2013). Models estimating the effective surface area based on the pore size distribution, the thermodynamic state of the system, and the presence of flow have also been proposed (Noiriel & Daval, 2017; Wen & Li, 2017). These methods have gained partial success in simulating the effluent concentration of the core flood tests with certain flow rates.

However, these past studies have the following limitations: First, the effluent chemistry analysis so far relied on the limited discrete effluent concentration data, which may not capture the sudden changes of the effluent concentration during the core flood tests. As discussed in the parallel paper by Li et al. (2019), possible errors could be induced by effluent depressurizing during the chemical analysis. Second, the dimensional analysis based on the initial geometry might not capture the geometrical evolution of the system due to flow and reaction (Daccord et al., 1993). The formation of wormholes induced flow heterogeneity, which needed to be accounted for in the dimensional analysis and continuum models. In addition, the continuum reactive transport models usually assumed a constant effective surface area for different flow conditions. The flow conditions, for example, flow rate, should be accounted for when estimating effective surface area, since the flow affects the thermodynamic equilibrium between the pore fluid and the soluble minerals.

In this study, the continuous effluent concentration data measured by the effluent chemistry monitoring system (ECMS) in the parallel paper (Li et al., 2019) are analyzed in detail. Each core flood test can be divided into two transient states and two quasi-steady states based on the behavior of the effluent concentration (section 2). Dimensional analysis is then used to study the mechanisms controlling dissolution in the rock matrix and wormholes. The evolution of dissolution kinetics during the core flood tests is discussed with the help of the dimensional analysis (section 3). A continuum model is developed to simulate the dissolution in the rock matrix. A new relation between the effective surface area and the flow rate is proposed, based on the wormhole geometry analysis and parallel tube modeling. For the dissolution in the wormholes, the extended Graetz solution (Li & Einstein, 2017) is used to simulate the dissolution process in the evolving wormholes. Combining the continuum model and the extended Graetz solution, a semiempirical reactive transport model is developed. The semiempirical model is then used to simulate the development of wormholes, wormhole breakthrough, and the evolution of dissolution kinetics induced by wormhole formation (section 4). This is followed by a comparison of the model results to those of the experiments.

### 2. Effluent Concentration Analysis

#### 2.1. Four States During a Core Flood Test

The effluent concentrations monitored by the ECMS in seven core flood tests are presented in the parallel paper (Li et al., 2019) and section 4.3. Since the behavior of the effluent concentrations in the seven tests is similar, this paper uses the effluent concentration data of the core flood test with $Q = 20 \mu L/s$ as an example for detailed analysis (Figure 1). The measured effluent is plotted as a function of the injected pore volume ($V_p$), which is defined as the injected volume ($V_{\text{inj}}=Q \cdot t$) normalized by the initial pore volume of the specimen $V_{\text{pore}}$. $V_p=Q \cdot t/V_{\text{pore}}$. In a core flood test where the initial pore volume $V_{\text{pore}}$ and flow rate $Q$ were constant, the injected pore volume ($V_p$) can also represent a dimensionless linear time coordinate. The effluent concentration in the beginning part of the curve is out of range due to the dissolved air during the overnight saturation as discussed by Li et al. (2019). Since the ECMS was only calibrated for the concentrations ranging from 0.01 to 2.6 g/L, the beginning part of the curve greater than 3 g/L is plotted as 3 g/L.
The effluent concentration can be used to study the overall dissolution rate $R_{\text{overall}}$ and the dissolution kinetics in the rock-fluid system. As discussed by Noiriel et al. (2009), the overall dissolution rate can be calculated as

$$R_{\text{overall}} = Q (C_{\text{eff}} - C_{\text{in}}),$$

(1)

where $Q$ is the flow rate and $C_{\text{in}}$ is the inlet concentration ($C_{\text{in}}=0$). Since the flow rate is constant during each core flood test, the evolution of the effluent concentration reflects the evolution of the dissolution kinetics of the rock-fluid system.

Based on the effluent concentration, the core flood tests can be divided in two transient states and two quasi-steady states, as shown in Figure 1:

- A. 0.0–1.5 $V_p$, initial transient state;
- B. 1.5–4.0 $V_p$, mixed dissolution quasi-steady state (MDSS);
- C. 4.0–4.5 $V_p$, breakthrough transient state; and
- D. 4.5–end $V_p$, wormhole dissolution quasi-steady state (WDSS).

In the initial transient state (Section A in Figure 1), the newly injected distilled water pushed out the initial pore fluid, which had a relatively high concentration due to the overnight saturation (Li et al., 2019). Both dissolved gypsum and dissolved air contributed to the concentration, making it higher than the equilibrium concentration of the gypsum (2.6 g/L). As the newly injected distilled water replaced the initial pore fluid, the dissolution starts to approach the first quasi-steady state.

In the MDSS (Section B in Figure 1), the effluent concentration reaches its first steady state value. A steady state value of the effluent concentration indicates the dissolution is in a “quasi-steady state.” Quasi-steady state is used to describe the slowly evolving state of the dissolution (Detwiler & Rajaram, 2007; Hanna & Rajaram, 1998), where the geometric evolution of the pore space or the wormholes is much slower than the evolution of the flow and mass transport. In this state, the wormholes had already developed from the inlet, but not yet reached the outlet. Flow and dissolution occur both in the wormholes and in the porous rock matrix as shown with the schematic in Figure 1.

In the breakthrough transient state (Section C in Figure 1), the wormhole breakthrough transformed the flow state from mixed flow to wormhole flow. The dissolution state was also transformed from dissolution in the pores to dissolution in the wormholes.

In the WDSS (Section D in Figure 1), since the flow was localized in the wormholes, the gypsum dissolution mostly occurs in the wormholes, as shown with the schematic in Figure 1. The rock-fluid system is in quasi-steady state, because the geometry of the wormholes are evolving slowly while the flow and mass transport are in steady state. The effluent concentration in this state was lower than the effluent concentration in the MDSS because of the smaller contact area.
The four states discussed above were based on the test with $Q = 20 \mu l/s$ as an example. The other tests all had these four states, except that the range of pore volume $V_p$ for each state differed with the flow rates. With the help of the ECMS, the evolution of the dissolution kinetics in the rock-fluid system was monitored directly, and the four states during a core flood test were identified.

### 2.2. Summary of the Quasi-Steady State Effluent Concentrations

The effluent concentrations of the two quasi-steady states are normalized to the equilibrium concentration ($C_{eq} = 2.6$ g/L, according to Jeschke et al., 2001) and plotted against the injection flux $q$ in Figure 2. The normalized effluent concentrations for the two states are each fitted with a power law curve. The coefficient of determination ($R^2$) for each fit is also calculated in Figure 2.

The effluent concentrations in the MDSS (MDSS-$C_{eff}$) are higher than in the WDSS (WDSS-$C_{eff}$), as shown in Figure 2. Both quasi-steady state effluent concentrations decrease with the increasing injection flux. In comparison with WDSS-$C_{eff}$, MDSS-$C_{eff}$ has a smaller power dependence on the flux with the power being $-0.036$.

Given that $Q = q \cdot A_s$ ($A_s$ is the specimen cross-section area), the overall dissolution rate $R_{overall}$ has a power dependence on the flow rate. For the MDSS, $R_{overall} \propto Q^{0.964}$, while for the WDSS, $R_{overall} \propto Q^{0.665}$. The differences in the two quasi-steady states are likely to be the result of different dissolution mechanisms as will be confirmed with the dimensional analysis in the next section.

### 3. Dimensional Analysis

#### 3.1. Definition of $G$ and $D_{ae}$

The overall dissolution rates in the MDSS and WDSS have different power dependence on the flow rates, which reflects the different dissolution kinetics during these two states. Dimensional analysis is often used to identify the controlling process during dissolution. As discussed by many researchers (Jeschke et al., 2001; Li & Einstein, 2017), the dissolution of a solid in an aqueous solution without further chemical reaction of the dissolved ions is controlled by two processes: the chemical reaction at the surface and the mass transport of the ions away from the surface. The mass transport, in this case, includes ion diffusion from the surface and advection with the flowing fluid. Therefore, there are three processes in total that influence the dissolution, namely, reaction, diffusion, and advection.

The reaction in the gypsum-water system is the dissociation of gypsum into calcium ions and sulfate ions:

$$\text{CaSO}_4 \cdot \text{H}_2\text{O}(s) = \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) + 2\text{H}_2\text{O}. \quad (2)$$

Since the pore space can be represented by connected tubes (Budek & Szymczak, 2012; Fredd & Fogler, 1998; Wang et al., 2016), the dimensional analysis can be conducted based on tubular geometries for both the pore space and the tubular-shaped wormholes. For laminar flow in tubular geometries, the sequence of the three processes for the solid to dissolve in the flowing fluid is reaction, diffusion, and advection. The slowest process controls the overall dissolution of the solid. Dimensionless quantities, which are the fraction of one rate to the other rate, can be used to describe the relative magnitude of two rates. A group of two dimensionless quantities is enough to provide a complete description of the dissolution phenomenon (Budek & Szymczak, 2012; Daccord et al., 1993; Detwiler & Rajaram, 2007; Fredd & Fogler, 1998). Similar to the dimensional analysis by Budek and Szymczak (2012), the kinetic parameter $G$ and the effective Damköhler number $D_{ae}$ are used:

$$G = \frac{\text{Reaction rate}}{\text{Diffusion rate}}, \quad (3)$$

$$D_{ae} = \frac{\text{Effective dissolution rate}}{\text{Advection rate}}. \quad (4)$$
The kinetic parameter \((G)\) compares the first two processes: reaction and diffusion. \(G \gg 1\) indicates that the reaction is faster than diffusion and that the dissolution is diffusion controlled. In this case, the reaction supplies enough ions to the solid-liquid interface, maintaining its chemical equilibrium state. \(G \ll 1\) indicates that the reaction rate is lower than the diffusion rate and that the dissolution is reaction controlled. The overall rate of the first two processes can be calculated as the effective dissolution rate \((k_{\text{eff}}; \text{Budek & Szymczak, 2012; Detwiler & Rajaram, 2007; Fredd & Fogler, 1998})\). For a derivation of the effective dissolution rate, refer to Appendix A. The effective dissolution rate is compared with the rate of the third process, advection, using the effective Damköhler number \((D_{\text{ae}})\). \(D_{\text{ae}} \gg 1\) indicates that the effective dissolution rate is higher than the advection rate and that the dissolution is advection controlled. \(D_{\text{ae}} \ll 1\) indicates that the dissolution is controlled by the first two processes, for which the controlling process can be determined using the kinetic parameter \((G)\).

The detailed derivation for the two dimensionless quantities can be expressed as

\[
G = \frac{2Rk_r}{DS_h}, \quad \text{(5)}
\]

\[
D_{\text{ae}} = \frac{k_{\text{eff}}}{U}, \quad \text{(6)}
\]

where \(R\) is the tube radius, \(k_r\) is the reaction-controlled dissolution rate coefficient, \(D\) is the diffusivity, \(S_h\) is the Sherwood number, \(k_{\text{eff}}\) is the effective dissolution rate coefficient, and \(U\) is the average flow velocity. From the definition (equation (5)), the kinetic parameter \((G)\) does not seem to have a direct relation to the flow rate. However, as discussed by Li and Einstein (2017), the flow rate affects the value of the Sherwood number, which in turn affects \((G)\).

### 3.2. \(G\) and \(D_{\text{ae}}\) for Dissolution in the Pore Space

In order to calculate the kinetic parameter \((G_M)\) and the effective Damköhler number \((D_{\text{aeM}})\) for the matrix flow (subscription \(M\) indicates the porous matrix), the pore radius and pore flow velocity need to be calculated. The pore radius \(R_p\) according to the MIP result in the parallel paper is in the order of 1 micron. The average pore flow velocity can be estimated as \(U = q/n\), where \(q\) is the injection flux and \(n\) is the porosity. According to Jeschke et al. (2001), the reaction-controlled dissolution rate coefficient \(k_r\) is \(7.1 \times 10^{-3} \text{ (cm/s)}\); and the diffusivity \(D\) is \(9.0 \times 10^{-6} \text{ (cm}^2\text{/s)}\) for calcium ions in water. As discussed in Appendix A, the Sherwood number in a high near the entrance and asymptotically approaches 3.66 along the tube. Hence, the value \(S_h=4\) is used for the Sherwood number in a porous medium as also used by Budek and Szymczak (2012). This results in the dimensionless quantities for the matrix flow:

\[
G_M = 0.04, \quad \text{(7)}
\]

\[
D_{\text{aeM}} = 0.76\text{−}6.09. \quad \text{(8)}
\]

In the pore space, the diffusion distance is short across the pore diameter, so the diffusion process is relatively fast, as indicated by \(G_M\) being less than one. Therefore, dissolution in the porous medium is reaction controlled. The effective Damköhler number is related to the flow rate and ranges from 0.76 to 6.09 in the core flood tests. Since the flow is not uniformly distributed due to the initial heterogeneity of the matrix, the average flow velocity usually underestimates the velocity of the major pore flow. With higher velocity in the major pore flow, the effective Damköhler number should be less than one according to the definition (equation (6)). Therefore, the effective dissolution rate is lower than the advection rate. Given that the reaction in the pores is slower than both diffusion and advection, the dissolution in the pore space is reaction controlled.

### 3.3. \(G\) and \(D_{\text{ae}}\) for Dissolution in the Wormholes

The kinetic parameter \((G_T)\) and the effective Damköhler number \((D_{\text{aeT}})\) for the tube flow in the wormholes (subscription \(T\) indicates the wormholes) can be calculated with the data from the CT scan. According to the CT reconstruction in the parallel paper, the radius of the major wormhole \(R_t\) is in the order of 0.5 mm. Since the injected flow is localized in the one wormhole connecting the inlet and outlet, the average flow velocity
can be estimated as \( \bar{U} = Q/(\pi R_f^2) \), where \( Q \) is the injection flow rate. Similar to the calculation of dimensionless quantities for the dissolution in the pore space, the dimensionless quantities for the dissolution in the wormholes can be calculated:

\[
G_T = 19.72, \\
D_{\text{eff}} = 6.73 \times 10^{-5} \sim 53.82 \times 10^{-5}.
\]

The wormhole diameter is 3 orders of magnitude larger than the pores, which results in a longer diffusion distance and relatively slow diffusion. The dissolution in the wormholes is diffusion controlled, as indicated by \( G_T \) being greater than one. The range of the effective Damköhler number indicates that the effective dissolution rate is much lower than the advection rate. Given that the diffusion in the wormholes is slower than both reaction and advection, the dissolution in the wormholes is diffusion controlled.

### 3.4. Summary of the Dimensional Analysis

The dimensional analysis shows that the dissolution mechanisms in the pore space and the wormhole are different. In both cases, the injection results in a fast advection process, so advection is not a controlling mechanism for dissolution. In the pore space, the diffusion distance is short across the pore diameter, so the diffusion process is relatively fast. The dissolution in the pore space is reaction controlled. On the contrary, wormhole diameter is 3 orders of magnitude larger, which results in a longer diffusion distance and relatively slow diffusion. Thus, the dissolution in the wormholes is diffusion controlled.

The study of dissolution mechanisms in the pore space and the wormholes also shed light on the evolution of the overall dissolution kinetics of the rock-fluid systems. During the core flood tests, the enlarging of the wormholes and redistribution of flow in the wormholes cause the evolution of the overall dissolution kinetics. More specifically, in the initial state of the system, the rock-fluid system only contains matrix flow and reaction-controlled dissolution. In the MDSS, part of the specimen has tube flow because of the wormholes, while part of the specimen still has matrix flow. Reaction-controlled dissolution and diffusion-controlled dissolution coexist in the rock-fluid system before the breakthrough of the wormholes. In the WDSS, the flow is localized in the wormholes, so the dissolution in the rock-fluid system is diffusion controlled.

### 4. Modeling of the Effluent Concentration

As discussed in section 2.1, the effluent concentration reflects the overall dissolution rate and the evolution of the rock-fluid system. The continuously measured effluent concentration can also be used to validate the model for dissolution in porous media. In this section, the models for dissolution in the rock matrix and wormholes are discussed separately, and then a semiempirical model combining the two is developed to simulate the formation of wormholes and the evolution of the dissolution kinetics during core flood tests.

#### 4.1. Dissolution in the Rock Matrix

Flow and dissolution in the porous rock matrix are usually simulated using continuum models (Carroll et al., 2013; Fu et al., 2015). In the continuum models, a representative elementary volume (REV) is defined for the rock matrix and pore fluid, so that averaged parameters such as Darcy velocity and concentration can be used for the REV. In the first two states of core flood tests, the flow and dissolution in the porous matrix can be modeled using a continuum model.

#### 4.1.1. Governing Equation

A REV is used to analyze the flow and dissolution in the gypsum matrix, as shown in Figure 3. Assuming the flow is unidirectional in the \( z \) direction as in the core flood tests, the injection flux \( q_{in} \) is the injection rate \( Q \) normalized by the cross-sectional area of the specimen, which is also known as the Darcy velocity. The REV has the dimensions of \( \Delta X, \Delta Y, \) and \( \Delta Z \). The fluid enters the REV with a gypsum concentration of \( C_{in} \) and exits the REV with a concentration of \( C_{out} \) due to dissolution in the REV.

As discussed in Appendix A, the dissolution mass flux of gypsum \( R_{eff}[M/(L^2 \cdot T)] \) can be expressed as

\[
R_{eff} = k_{eff}(C_e = C_b),
\]

where \( C_e \) is the equilibrium concentration (solubility) and \( C_b \) is the bulk concentration. As discussed in section 3, the diffusion in the pores is relatively fast, so the concentration in each pore is relatively...
uniform and can be used as the bulk concentration. In the REV, the mass conservation of the solute gypsum can be expressed as
\[ q_{in} \Delta X \Delta Y (C_{out} - C_{in}) = A_{REV} \cdot k_{eff} (C_{eq} - C_{b}) , \] (12)

where \( A_{REV} \) is the total area in the REV that is reactive with the pore fluid and contributing to the dissolution flux. Equation (12) can be normalized by the volume of the REV \( (\Delta X \Delta Y \Delta Z) \), which yields
\[ q_{in} \cdot \frac{\partial C_{b}}{\partial z} = A_{e} \cdot k_{eff} (C_{eq} - C_{b}) . \] (13)

\( A_{e}[L^{-1}] \) is the effective surface area, which is the normalized \( A_{REV} \):
\[ A_{e} = \frac{A_{REV}}{\Delta X \Delta Y \Delta Z} . \] (14)

Equation (13) is the governing equation for simulating the dissolution in the rock matrix using a continuum model. This formulation has been used in many analytical and numerical studies.

The key parameter in equation (13) is the effective surface area \( A_{e} \). \( A_{e} \) represents the total area in a unit volume of REV that is reactive with the pore fluid and contributes to the dissolution flux. It should be differentiated from the specific area, which is the total pore area in a unit volume (or mass) of rock. The effective surface area is not only determined by the pore structure but also by the chemical reactions and flow conditions (Guo et al., 2015, 2016; Soulaine et al., 2017). The effective surface area has been estimated using core flood tests, in which the chosen flow rates are relatively high and usually kept constant for a set of tests (Noiriel et al., 2009). These studies assume that the effective surface area \( A_{e} \) is constant under different flow conditions. However, this assumption is not necessarily correct, as discussed by Soulaine et al. (2017) and Wen and Li (2017). The following two sections provide two methods to estimate \( A_{e} \): wormhole geometry and parallel tube modeling.

4.1.2. \( A_{e} \) Estimation Based on the Wormhole Geometry

Since the wormholes are the result of flow and dissolution heterogeneities in the porous matrix, the wormhole geometries resulting from different flow rates can be used to evaluate the effect of flow rate on the dissolution in the porous matrix. According to the experimental observations in the parallel paper (Li et al., 2019), higher flow rates result in more wormholes and branches in the rock matrix, which indicates that higher flow rates force the fluid to react in more pores in the matrix. The greater number of wormholes and branches developed near the inlet of the specimen in turn distribute flow more uniformly into the porous matrix. This also implies that higher flow rates result in a larger effective surface area \( A_{e} \).

The 3-D quantitative wormhole geometry analysis in the parallel paper can be used to further explore this concept. This analysis showed that the number of wormholes \( N_{wh} \) is proportional to the 0.42 power of the flux \( q \); the number of branches is proportional to the 0.25 power of the flux \( q \); and the tortuosity is proportional to the 0.05 power of the flux \( q \). Since the wormholes reflect flow and dissolution occurring in the matrix, it is reasonable to propose that the reactive surface area \( A_{e} \) is proportional to the \((0.42 + 0.25 + 0.05 = 0.72)\) power of the injection flux \( q \):
\[ A_{e} \propto q^{0.72} . \] (15)

Equation (15) proposes a relation between the effective surface area \( A_{e} \) and the injection flux \( q \) based on the wormhole geometries. This relation indicates that higher flux in the matrix activates more pore surfaces to react with the pore fluid. It should be noted that equation (15) is based on limited experimental data and is likely to be valid only in the range of injection flux used in the core flood tests. However, as shown in the next section and the semiempirical model, equation (15) more accurately predicts the dissolution in the porous matrix.
4.1.3. \( A_e \) Estimation Based On Parallel Tube Modeling

As a simple numerical method to investigate the relation between effective surface area and injection flow rate, parallel tube modeling is used. This model has been used to study the flow and dissolution in porous rock-fluid systems such as in limestone-acid and limestone-CO\textsubscript{2}-water systems (Wang et al., 2016; Zhang et al., 2016). The parallel tube model uses a large number of parallel tubes connecting the inlet and outlet, to mimic a porous medium, as shown in Figure 4. The flow and dissolution in each tube can be explicitly calculated using the Poiseuille equation and the extended Graetz solution (Li & Einstein, 2017), respectively.

In this validation, a 2,000-tube parallel tube model is used. The tube diameters are stochastically generated based on the distribution measured using MIP (Li et al., 2019). The flow rates used in the core flood tests are applied to the parallel tube model. To calculate the effective surface area, the definition proposed by Wen and Li (2017) is used: The effective surface area is the area of pores, in which the pore fluid is far from equilibrium. This definition is consistent with the definition introduced in section 4.1.1, given that the pore area is contributing to the dissolution flux when the pore fluid is far from equilibrium and reacting with the rock. According to Wen and Li (2017), to determine if the pore fluid is far from equilibrium, the threshold value of \( C \) can be between 0.50 and 0.99. The threshold value of 0.60 is used in the parallel tube modeling. Therefore, when the concentration of the pore fluid satisfies the criterion (equation (16)), the pore surface contributes to the effective surface area.

\[
\frac{C}{C_{eq}} < 0.6, 
\]

where \( C \) is the concentration of the pore fluid and \( C_{eq} \) is the equilibrium concentration of the solid.

In the parallel tube model, the effective surface area is the sum of the areas of the tube sections, in which the pore fluid satisfies the criterion in equation (16). Since the tube diameters are stochastically generated, a Monte Carlo scheme is used in which 100 simulations are conducted for each of the seven flow rates used in the core flood tests. In each simulation, the effective surface is normalized to the total tube area as the effective surface ratio (\( A_{SR} \)) for comparison between simulations. The results are plotted in Figure 5.

In Figure 5, the small values of the effective surface ratio show that the surface area that is reactive with the pore fluid is only a small part of the total surface area, as discussed by Beckingham et al. (2016). The effective surface ratio is higher when the flow rate is higher. A power law fit shows that the effective surface ratio is proportional to the 0.79 power of the flow rate. This relation is similar to equation (15), which was based on the wormhole geometry.

It should be noted that the parallel tube model is a simplified representation of the flow and dissolution in the porous matrix, which can mimic the behavior of the rock-fluid system. The parallel tube model is used here only to validate the concept that the effective surface area is larger when the flow rate is higher.
Both of the two methods discussed above led to the conclusion that the effective surface area is larger when the flow rate is higher. Similar power law relations between the effective surface area and the injection flux are produced by these two methods. Hence, equation (15) for $A_e$ is applied in the continuum model to simulate the dissolution in the porous matrix.

### 4.2. Dissolution in the Wormholes

The effluent concentration and dimensional analyses have shown that the dissolution in the wormholes is diffusion controlled. In the WDSS of a core flood test, the flow was pipe flow localized in the major wormholes, which is in the validity domain of the extended Graetz solution (Li & Einstein, 2017). The extended Graetz solution is used to model the effluent concentration in the WDSS.

The extended Graetz solution is an analytical solution that extends the validity domain of the Graetz solution (Graetz, 1882) from an ideal cylindrical tube to an enlarging tapered tube. The extended Graetz solution assumes that the rock-fluid interface (tube wall) is in thermodynamic equilibrium and the dissolution is diffusion controlled. It explicitly solves the 2-D advection-diffusion equation for the concentration profile in the tube ($C=C(r,z)$). The extended Graetz solution yields the Sherwood number (defined in Appendix A) accounting for the entrance region and the tapered geometry. The governing equation for the extended Graetz solution is

$$0 = -v_z \frac{\partial C}{\partial z} - v_r \frac{\partial C}{\partial r} + D \frac{\partial^2 C}{\partial z^2} + D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right),$$

with the boundary conditions being

$$\frac{\partial C}{\partial r}\big|_{r=R_0} = 0 \quad \text{(axisymmetric boundary condition)},$$
$$C|_{r=R_0} = C_{eq} \quad \text{(thermodynamic equilibrium boundary condition)},$$
$$C|_{z=0} = 0 \quad \text{(concentration of dissolved gypsum at inflow)}.$$

In equation (17), $z$ and $r$ are axial and radial coordinates with $z$ along the tube and $r$ in the radial direction. $v_z$ and $v_r$ are the axial and radial flow velocities. $D$ is the diffusivity, and $R_0$ is the radius profile long the tube.

When the flow rate in the tube is constant, the extended Graetz solution predicts that the effluent concentration will be constant despite the evolution of the wormhole geometry from a cylindrical tube to a tapered tube (Li & Einstein, 2017). This prediction is consistent with the experimental observation that in each core flood test, the effluent concentration in the WDSS (WDSS-$C_{eq}$) is constant, as shown in Figure 1.

Since several tests with different flow rates were conducted, the WDSS-$C_{eq}$ as a function of flow rate can also be compared with the prediction of the extended Graetz solution. The extended Graetz solution is expressed using dimensionless parameters: the normalized effluent concentration ($C_{eff}/C_{eq}$) and the dimensionless length of the tube ($L_{diel}$). The experimental results are converted to the dimensionless parameters using the definition in the extended Graetz solution:

$$L_{diel} = \frac{\pi D}{2Q} \frac{1}{L_{wormhole}},$$

where $D$ is the diffusivity, $Q$ is the flow rate in the wormhole, and $L_{wormhole}$ is the length of the wormhole, which is calculated using the CT scan data, as discussed by Li et al. (2019). As shown in equation (19), apart from the constants, the dimensionless length is determined by the length of the wormhole and the flow rate $Q$ in the wormhole. The dissolution-induced enlargement of the wormhole does not affect the dimensionless length of the wormholes. Therefore, the effluent concentration is constant, despite the evolution of wormhole geometry.

In Figure 6, the normalized effluent concentration is plotted as a function of the dimensionless length and compared with the extended Graetz solution. The comparison shows that the effluent concentration predicted by the extended Graetz solution matches the WDSS-$C_{eff}$ from the core flood tests.
The above analysis shows that despite the complex evolving geometry of the wormholes, the dissolution kinetics is relatively simple and can be modeled using the extended Graetz solution. The extended Graetz solution can predict not only the behavior of the effluent concentration but also its quantitative relation with the flow rate.

### 4.3. Semiempirical Model

Sections 4.1 and 4.2 show that the flow and dissolution in the porous matrix can be modeled using the continuum model (equation (13)), while the flow and dissolution in the wormholes can be modeled using the extended Graetz solution. An additional model is needed to determine the formation of the wormholes. This can be done using a conceptual model proposed by Daccord et al. (1993). The three models are combined as a semiempirical model to simulate the formation of wormholes and the evolution of the dissolution kinetics in the rock-fluid system during core flood tests.

The conceptual model proposed by Daccord et al. (1993) divided the specimen into the wormhole section with length $L_w$ and the matrix section with length $L_m$, as shown in Figure 7. This model assumes that the wormhole section has infinite permeability, while the matrix section has the permeability of the intact porous matrix. With these assumptions, the lengths of the two sections ($L_w$ and $L_m$) can be predicted based on the pressure data measured during core flood tests. The dissolution in the wormhole section with length $L_w$ and the matrix section with length $L_m$ is simulated using the extended Graetz solution and the continuum model, respectively. The dissolution and wormhole formation during the core flood tests can then be simulated by combining the extended Graetz solution for the wormhole section with length $L_w$ and the continuum model for the matrix section with length $L_m$.

Based on the pressure data, the length of the wormhole section increases linearly with the injected pore volume ($V_p$) before the wormhole breakthrough ($V_p < V_{pbt}$; Li et al., 2019). The rate of increase is a function of the injection flux ($q$) as discussed by Li et al. (2019). After the wormhole breakthrough ($V_p \geq V_{pbt}$), the wormhole section has the same length as the specimen. The length of the wormhole section is predicted as

$$L_w = \begin{cases} L_s V_p (0.996q^{-0.419}), & \text{for } V_p < V_{pbt} \\ L_s, & \text{for } V_p \geq V_{pbt}, \end{cases}$$

where $L_s$ is the specimen length, $V_p$ is the injected pore volume, and $V_{pbt}$ is the breakthrough pore volume. In the wormhole section, there are several wormholes developed from the inlet. The number of wormholes $N_{wh}$ can be predicted using the empirical relation based on the 3-D quantitative wormhole geometry analysis in the parallel paper:

$$N_{wh} = A_s \cdot N_{whN} = A_s \cdot 0.42 \cdot q^{0.42},$$

where $A_s$ [cm$^2$] is the inlet area, $N_{whN}$ is the number of wormholes per unit inlet area, and $q$ is the injection flux. Given the tortuous nature of the wormholes, the lengths of the wormholes are slightly longer than the wormhole section. Therefore, when using the extended Graetz solution to simulate the dissolution in the wormhole section, the wormhole length $L_{wh}$ is calculated:

$$L_{wh} = L_w \cdot \tau,$$

where $\tau$ is the tortuosity of the wormholes. Similar to $N_{wh}$, $\tau$ can be predicted using the empirical relation summarized in the parallel paper (Li et al., 2019):

$$\tau = 1.14q^{0.05}.$$

Therefore, the dissolution in the wormhole section can be modeled as dissolution in $N_{wh}$ wormholes with lengths of $L_{wh}$. The flow in the wormhole section is assumed to be distributed evenly in the $N_{wh}$ wormholes.
before the wormhole breakthrough. The concentration at the end of the wormhole section $C_{wh}$ is explicitly calculated using the extended Graetz solution in each wormhole. After the wormhole breakthrough, the flow concentrated in the major wormhole, in which the effluent concentration is modeled as discussed in section 4.2.

The dissolution in the porous matrix section is modeled using the continuum model (equation (13)). The concentration $C_{wh}$ from the wormhole section is the boundary condition for the dissolution in the matrix section. Thus, the governing equation for the matrix section is

$$ q_{in} \frac{\partial C_b}{\partial z} = A_e \cdot k_{eff} (C_{eq} - C_b) \quad (L_m < z < L_s) \tag{24a} $$

$$ C_b = C_{wh} \quad (z = L_m). \tag{24b} $$

In sum, this combination of the empirical model (equations (20), (21), and (23)) and the dissolution models (sections 4.1 and 4.2) result in the semiempirical model for dissolution and wormhole formation during core flood tests.

The effluent concentrations predicted by the semiempirical model are compared with the results of the core flood tests. In the semiempirical model, the assumption of an effective surface area as a function of injection flux is applied to the continuum model for the flow and dissolution in the matrix section. The function $A_e=0.4q^{0.72} \text{cm}^{-1}$ is used as discussed in section 4.1.2. The factor 0.4 is used to fit the effluent concentration. In comparison, the assumption of a constant effective surface area is also applied to the continuum model. The value $A_e=4.0 \times 10^{-2} \text{cm}^{-1}$ is used so that the simulation results can fit the experimental results. The parameters listed in Table 1 are used in the semiempirical model. The predicted effluent concentrations are compared with the core flood test results as shown in Figure 8.

The semiempirical model predicts the effluent concentrations that have a similar trend to the effluent concentration data measured in the tests. The effluent concentration was high before the wormhole breakthrough and low after. The sudden drops in the effluent concentration were caused by the wormhole breakthrough, which concentrated almost all the flow in the one major wormhole. This sudden drop is predicted reasonably well based on the empirical relations (equation (20)). The small difference in the predicted breakthrough pore volumes and the test results are the results of the difference between the power law fitting and the test data in the parallel paper.

Before the wormhole breakthrough, the effluent concentration is modeled by combining the extended Graetz solution and the continuum model (Figure 7). With the assumption of constant effective surface area ($A_e=4.0 \times 10^{-2} \text{cm}^{-1}$), the model overestimates the effluent concentration when flow rates are low and underestimates the effluent concentration when the flow rates are high. In comparison, with the proposed relation ($A_e \propto q^{0.72}$), the model produced a more accurate effluent concentration. The residual sum of squares (RSS; $RSS = \sum (C_{eff}(test) - C_{eff}(model))^2$) between the experimental and modeling results are calculated to evaluate the performance of the two assumptions. Since the semiempirical model does not account for the initial transient state, the RSS for the results where $V_p > 1$ were calculated for all seven tests, as indicated with corresponding colors in Figure 8. Except for the cases where $Q=7.07$ and $14.14 \mu l/s$, the proposed relation $A_e \propto q^{0.72}$ provides more accurate prediction than the assumption of constant effective surface area according to RSS. However, the differences between the two modeling results are small, because of the high

| Table 1: Parameters Used in the Semiempirical Model |
|-----------------------------------------------|
| Symbol | Value | Unit | Variable |
|--------|-------|------|----------|
| $A_e$  | 9.10  | cm$^2$ | Specimen inlet area |
| $C_{eq}$ | 2.6 | g/L | Solubility of gypsum in distilled water |
| $D$    | $9.0 \times 10^{-6}$ | cm$^2$/s | Diffusion coefficient |
| $k_t$  | $7.1 \times 10^{-3}$ | cm/s | Reaction-controlled dissolution rate coefficient |
| $L_s$  | 8.50 | cm | Specimen length |
| $n$    | 0.46–0.48 | | Porosity |
| $q$    | 5.5–44 | $\mu m/s$ | Injection flux |
thermodynamic driving force near the inlet of the specimen \( \Delta C_{eq} - C_b \) in equation (24a). After the wormhole breakthrough, the effluent concentration is predicted by the extended Graetz solution only (section 4.2); therefore, the two modeling results converge.

The semiempirical model does not represent the exact physical processes of flow and dissolution in the pores and wormholes; however, it provides a simple and fast simulation of the evolution of the rock-fluid system regarding the wormhole formation, wormhole breakthrough, and dissolution kinetics. By dividing the specimen into the wormhole section and the matrix section, the semiempirical model accommodates the application of dissolution kinetic models such as the extended Graetz solution and the continuum model.

5. Summary and Conclusions

The continuous effluent concentration data provided useful insights into the evolution of dissolution kinetics in the gypsum-water system during the core flood tests. Based on the effluent concentration, the gypsum-water system in the core flood tests went through four states: initial transient state, MDSS, breakthrough transient state, and WDSS. A sudden effluent concentration drop was observed at wormhole breakthrough, which indicated that the wormhole breakthrough concentrates almost all of the flow in the major wormhole and in turn changed the dissolution kinetics.

Figure 8. Comparison of the effluent concentrations. The effluent concentrations predicted by the semiempirical model with constant effective surface area assumption, and the semiempirical model with proposed relation \( A_e = 0.4q^{0.72} \)(cm\(^{-1}\)) are compared with the measurement in the core flood tests. RSS = residual sum of squares.
Dimensional analysis was used to study the controlling mechanisms of dissolution in the matrix and the wormholes. According to the dimensional analysis, the dissolution in the matrix was reaction controlled, while the dissolution in the wormholes was diffusion controlled. This provided an explanation for the evolution of the effluent concentration during the core flood tests. Initially, the flow in the specimen was in the matrix, and the dissolution was reaction controlled. Then, wormholes dominated part of the specimen, making the dissolution in the wormhole-dominated part diffusion controlled and the dissolution in the other part reaction controlled. After the wormhole breakthrough, the flow was only in the wormholes, so the dissolution was diffusion controlled. Hence, the effluent concentration and dimensional analysis led to the conclusion that during the core flood test the dissolution evolved from reaction controlled to diffusion controlled.

The effluent concentration measurements and dimensional analysis also provided directions for modeling the dissolution in the gypsum-water system during the core flood tests. The dissolution in the matrix was modeled using a continuum model. To account for the flow conditions when estimating the effective surface area in the continuum model, a relation between the effective surface area and the injection flow was proposed based on the 3-D wormhole geometry analysis and parallel tube modeling. Since the dissolution in the wormholes was diffusion controlled according to the dimensional analysis, it was modeled using the extended Graetz solution. The conceptual model proposed by Daccord et al. (1993) was then used as a simplified representation for the porous rock specimen with developing wormholes. The specimen was divided into the wormhole section, in which the dissolution was modeled using the extended Graetz solution, and the matrix section, in which the dissolution was modeled using the continuum model. The length of each section was predicted using the empirical equation for wormhole growth rate, as discussed in the parallel paper (Li et al., 2019). This combination of the empirical model and the dissolution models resulted in the semiempirical model that was able to accurately simulate the wormhole formation, wormhole breakthrough, and the evolution of dissolution kinetics in the rock-fluid system during the core flood tests. This methodology can be adapted for modeling the evolution of dissolution kinetics and wormhole geometry in other rock-fluid systems with proper calibration from experiments.

In addition, this study proposed a relation between the effective surface area and the flow rate (injection flux), to account for the effect of flow conditions on reactions in the porous rock matrix. The relation is based on the 3-D wormhole geometry analysis in the parallel paper (Li et al., 2019) and parallel tube modeling. Even with the somewhat limited number of tests and effluent concentration data, the relation between the effective surface area and flow rate predicted the dissolution kinetics for the gypsum-water system reasonably well. Future studies are needed to further investigate the effect of flow conditions on effective surface area for a wider range of flow rates and other rock-fluid systems.

Appendix A: Derivation of the Dimensionless Quantities

The following derivation is similar to the discussion by Budek and Szymbczak (2012). To provide a consistent notation and definition, the equations are rewritten, and some parameters are redefined. To simplify the formulation, the first-order reaction model can be used to calculate the reaction-controlled dissolution mass flux $R_r [M/(L^2 \cdot T)]$:

$$R_r = k_r (C_{eq} - C_s), \quad (A1)$$

where $k_r[L/T]$ is the reaction-controlled dissolution rate coefficient, $C_r[M/L^3]$ is the concentration on the surface, and $C_{eq}$ is the equilibrium concentration (solubility).

If the dissolution is reaction controlled, the diffusion is relatively fast, and the concentration on the surface can be approximated by the bulk concentration $C_b$. The diffusion rate for a tubular geometry with laminar flow can be calculated using the Graetz solution (Li & Einstein, 2017):

$$R_t = k_t (C_{eq} - C_b), \quad (A2)$$

where $k_t$ is the diffusion-controlled dissolution rate coefficient and $C_b$ is the bulk concentration in the tube. According to the Graetz solution, $k_t$ can be estimated as

$$k_t = \frac{S_h \cdot D}{2R^2}, \quad (A3)$$
where $S_h$ is the Sherwood number, $D$ is the diffusivity, and $R$ is the radius of the tube. The Sherwood number is the dimensionless mass transfer coefficient, which is determined by the hydrodynamic condition (Bird et al., 2007; Graetz, 1882; Levich, 1962; Li & Einstein, 2017). For transport-controlled dissolution in a tube, the Sherwood number is high near the entrance then asymptotically approaches 3.66 along the tube (Bird et al., 2007). According to equations (A1), (A2), and (A3), the kinetic parameter $G$ can be expressed as

$$G = \frac{2Rk_r}{DS_h}.$$  \hfill (A4)

Similar to mixed controlled dissolution model proposed by Budek and Szymczak (2012), the effective dissolution rate coefficient is defined as

$$k_{\text{eff}} = \frac{k_r k_f}{k_r + k_f}.$$  \hfill (A5)

Thus, the effective dissolution rate considering both the reaction-controlled and diffusion-controlled cases can be expressed as

$$R_{\text{eff}} = k_{\text{eff}}(C_{\text{eq}} - C_h).$$  \hfill (A6)

The rate of advection can be expressed as the average flow velocity $\bar{U}$. For matrix flow and tube flow, $\bar{U}$ can be expressed as

$$\bar{U} = \frac{q}{n} \quad \text{(matrix flow)},$$  \hfill (A7)

$$\bar{U} = \frac{Q}{(\pi R_d^2)} \quad \text{(tube flow)}. $$  \hfill (A8)

Then the effective Damköhler number can be expressed as

$$D_{\text{ae}} = \frac{k_{\text{eff}}}{\bar{U}}.$$  \hfill (A9)

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