Simulation of Dissolution in Porous Media in 3D with Lattice Boltzmann, Finite Volume and Surface Rescaling Methods

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Abstract

We present a coupled transport and dissolution model for use in pore-scale modelling of reactive transport in complex media such as carbon-storage injection operations. We couple a lattice Boltzmann model for flow calculation with a finite volume method for solving chemical transport equations. The computational grid is allowed to change as mineral surfaces are dissolved according to first order reaction kinetics. We show how the popular first-order convection scheme is affected by severe numerical diffusion when grid Peclet numbers exceed unity, and confirm that this can be overcome relatively easily by using a second order method in conjunction with a flux limiter function. A novel rescaling method is used to counteract errors in surface area exposed by the Cartesian grid and avoid the use of more complex embedded surface methods when surface reaction kinetics are incorporated. Finally, we compute dissolution in an image of a real porous limestone rock sample injected with HCl for different Peclet numbers and obtain dissolution patterns in concordance with theory and experimental observation. A low injection flow rate was shown to lead to erosion of the pore-space concentrated at the face of the rock, whereas a high flow rate leads to wormhole formation.

Keywords: Dissolution; Reactive; Transport; Porous Media; Lattice Boltzmann; Finite Volume

1. Introduction

Convection-diffusion of solutes coupled with reactive surface dissolution are commonly encountered phenomena in science and engineering problems, such as drug delivery [1], wet etching [2], acidizing operations for enhanced oil recovery [3] and carbon dioxide (CO₂) storage in subsurface rock formations [4]. The injection of supercritical CO₂ into geological formations, including saline aquifers and depleted oil and gas reservoirs, is being actively considered as a climate change mitigation measure. However, uncertainty regarding effectiveness and economic feasibility is a significant barrier to actual implementation. Injected CO₂ reacts with water already present in the pore-space of these reservoirs to form carbonic acid (dissociated H₂CO₃) which flows through the rock structure dissolving the mineral according to a complex series of reactions [5]. Furthermore, the particular conditions of the injection process strongly influence the resulting dissolution pattern [3], which in turn can have a pronounced effect on the flow behaviour and long term storage integrity. This can be particularly important near the injection well where wormhole-type dissolution at high flow rates can lead to structural degradation and well collapse.

The simulation of the reactive transport processes in complex porous media when applied to real subsurface problems presents a considerable challenge in computational physics because of the coupled nature of the problem, involving flow, transport and changes in geometry which all change over time. To construct a robust and versatile 3-dimensional reactive flow model which can accurately compute the complex chemical kinetics of a CO₂-brine system in highly complex geometries, whilst handling hydrodynamic Peclet numbers which can be in excess of $O(10^3)$ [6], is a major task, requiring the use of high-order convection schemes, grid-refinement methods and high performance computing. In this work, we address some of these issues and construct a dissolution model which can efficiently compute the dissolution behaviour of a realistic limestone sample injected with HCl acid. The chemical system is far simpler than that of the real carbonic acid system, but we aim here to emphasise the computational methods which will form the basis of a more complete model in future work.

A number of different approaches have been formulated in the literature [7, 8]. The Lattice Boltzmann (LB) method is shown to be efficient and accurate in capturing the fluid dynamics at the pore-scale in complex geometries and has been extended to reactive systems [9-11], but is currently limited to low Peclet numbers in the absence of upwind differencing [12]. Kang *et al.* [13] used this approach for flow and chemical transport to study different dissolution regimes in 2-dimensional systems. Szymczak and Ladd [14, 15] approached the dissolution problem using a stochastic particle method to compute transport and reactions at boundaries. This is useful in 2-dimensional simulations and is freed from limitations in Peclet number, but it may not be practical to extend to this to realistic 3-dimensional systems, as the number of particles to accurately estimate the local surface concentrations for non-linear kinetics becomes too demanding. Tartakovsky *et al.* used smooth particle

hydrodynamics (SPH) to study mixing and precipitation in microfluidic systems of circular grains and fractures at different Peclet and Damkohler numbers [16] and upscaled this to continuum models [17]. They also extended this model into a 3-dimensional fracture system [18]. The SPH method is again freed from the numerical diffusion effects associated with grid methods at high Peclet numbers, but incurs greater computational cost. Flukiger and Bernard [19] computed the carbonic acid chemical system to equilibrium using a first order upwinding finite volume method (FVM) in realistic 3D pore geometries, whereas Molins *et al.* also computed the CO₂-brine system flowing through a bead-pack geometry [20] and experimental calcite system [21] but using a higher-order flux-limiter FVM model. These studies [19-21] did not allow mineral geometries to change in time according to surface reactions. Jiang [22] used an LB flow solver in conjunction with a high order FVM and flux limiter model to compute calcite precipitation in a 3D image of a carbonate pore-structure. Yoon *et al.* [23] also combined an LB flow solver with a second order FVM method to compute precipitation and dissolution of calcite through a microfluidic chamber in 2 dimensions. Yu and Ladd [24] also used an LB flow solver combined a finite-difference scheme with upwind differencing and convection interpolated directly along velocity characteristics with a sub-grid resolution surface algorithm which allowed the use of coarse grids.

The treatment of reactive surface area in structured cubic grids needs to be given particular consideration when mineral surface reaction kinetics are incorporated as the 'staircase' effect of the discrete boundary represents more area than an equivalent smooth representation. Level-set methods represent the surface as a contour of a continuous function which evolves according to its own advection equation at the fluid solid interface, and was used by Li *et al.* to simulate precipitation in fractures in 3 dimensions [25]. However the method has inherent problems such as mass loss which stems from the discrete nature of the grid. This needs to be counteracted with additional mass-conserving constraints, adding considerable complexity [26]. The similar phase-field approach evolves a smooth order parameter representing the solid/fluid state but results in a finite transition region [27]. In our model, we compute reaction kinetics directly on the discrete staircase grid, but we calculate a scaling factor at each reactive face, representing the projection of the interface onto a piecewise parabolic surface (Figure 1). This guarantees that the surface is always continuous, but ensures that dissolution kinetics are computed according to a smooth surface area. Additionally, the surface rescaling method ensures that the surface always follows the edge of the solid nodes, so that the depletion of solid mass of boundary nodes can be tracked without ambiguity. Marching Cubes has been used for surface-area characterisation in complex porous media [28] but, as Figure 1 shows, it does not guarantee that a reconstructed surface can be coupled directly to a solid volume, and the mass evolution of surrounding boundary solid nodes would become ambiguous. The parabolic rescaling scheme can also change smoothly with the gradual depletion of a node's mass

fraction, like level-set and phase-field methods, but is as simple as marching cubes while maintaining a direct coupling to the Cartesian grid.

In our model, we compute the flow field using the lattice Boltzmann (LB) method in preference to a finite volume method because of its large time-step and parallel efficiency, but use a finite volume method (FVM) to compute reactant transport to access high Peclet numbers. These are described in sections 2 and 3 respectively. Then we show in section 4 how the use of a high order convection scheme is imperative to obtain accurate steady-state concentration fields, in contrast to first order upwind schemes which become very inaccurate for grid Peclet numbers $Pe_{\text{Grid}} > 1$. In section 5, we develop the surface rescaling method which can estimate local surface area accurately and efficiently. Finally in section 6, we simulate the dissolution of a 3-dimensional image of Ketton limestone injected with HCl, which is efficiently computed using the GPU architecture.

2. Flow Calculation

Flow is computed using the lattice Boltzmann (LB) method. The central variable in this scheme is the velocity-space distribution function $\mathbf{f}(\mathbf{x}, t)$ from which the local hydrodynamic variables density ρ and velocity $\mathbf{u}$ are obtained

$$\rho = \sum_i f_i \quad \rho \mathbf{u} = \sum_i \mathbf{e}_i f_i + \frac{\rho \mathbf{g}}{2} \quad (1)$$

where $\mathbf{g}$ is a body-force acting on the fluid. The distribution function evolves according to a discrete form of the Boltzmann equation

$$f_i(\mathbf{x} + \mathbf{e}_i dt, t + dt) = f_i(\mathbf{x}, t) + \Omega_i[\mathbf{f}(\mathbf{x}, t)]. \quad (2)$$

Each component of the distribution function streams to its neighbouring node at $\mathbf{x} + \mathbf{e}_i dt$, where $\mathbf{e}_i$ is the discrete velocity associated with each component f_i . We use the D3Q19 scheme in which $\mathbf{f}(\mathbf{x}, t)$ has 19 components [29]. Ω_i is an operator which modifies the distribution function according to collisions in the fluid and is described in the LB framework as a relaxation towards the Maxwell-Boltzmann distribution. Here, we use the multiple-relaxation-time (MRT) model in conjunction with a body-force term $\mathbf{F}$ [30]

$$\Omega_i[\mathbf{f}(\mathbf{x}, t)] = \mathbf{M}_i^{-1} \left[\mathbf{S} \mathbf{M} (\mathbf{f}^{Eq} - \mathbf{f}) + \left(\mathbf{I} - \frac{1}{2} \mathbf{S} \right) \mathbf{M} \mathbf{F} \right]. \quad (3)$$

The orthogonal matrix $\mathbf{M}$ transforms the velocity-space distribution function into a moment-space whose components can be relaxed individually by the diagonal matrix $\mathbf{S}$. The components of this matrix are determined by the fluid viscosity, before the inverse matrix $\mathbf{M}^{-1}$ returns the distribution to velocity space [31, 32]. $\mathbf{I}$ is the identity matrix and the equilibrium function $\mathbf{f}^{Eq}$ is the discrete Maxwell-Boltzmann distribution approximated to second order in velocity

$$f_i^{Eq}(\rho, \mathbf{v}) = \rho w_i \left[1 + 3\mathbf{e}_i \cdot \mathbf{u} + \frac{9}{2}(\mathbf{e}_i \cdot \mathbf{u})^2 - \frac{3}{2}\mathbf{u}^2 \right] \quad (4)$$

141 where the weights are given in D3Q19 by $w_0 = 1/3, w_{1-7} = 1/18, w_{8-18} = 1/36$. The
142 force term used is expanded to second order and given in component form by [33]

$$F_i = 3w_i[\mathbf{e}_i \cdot \mathbf{g} + \mathbf{u} \mathbf{g} : (3\mathbf{e}_i \mathbf{e}_i - \mathbf{I})]. \quad (5)$$

143 3. Convection Diffusion Model

144 The transport of chemical species $C(x, t)$ through the pore-space is described by the
145 convection-diffusion equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C - \mathbf{u} \cdot \nabla C \quad (6)$$

146 where $\mathbf{u}(x, t)$ is the velocity field, assumed to have zero divergence everywhere
147 (incompressible flow), and D is the molecular diffusion coefficient for the chemical species.
148 We solve this equation using a Finite Volume Method (FVM) on the same grid used for the
149 flow calculation, using face velocity vectors obtained by linear interpolation.

150 The diffusion term is discretised to second order approximation directly by summing
151 diffusion fluxes from the 6 Cartesian neighbours with grid spacing dx .

$$D \nabla^2 C_i = D \sum_{d=\{x,y,z\}} \frac{C_{i-1}^d - 2C_i + C_{i+1}^d}{dx^2} \quad (7)$$

152 The convection term is computed by obtaining expressions for the concentration flux at
153 each of the cell faces, as shown for 1 dimension in Figure 2, and explicitly time-stepping the
154 solution. In one dimensional form, the convection term is given by

$$C_i^{t+1} = C_i^t + \frac{dt}{dx} [f_{i-1/2} - f_{i+1/2}] \quad (8)$$

155 where $f_{i+1/2}$ denotes the flux at the right face for each Cartesian direction, and the left face
156 $f_{i-1/2}$ is obtained by direct translation of indices. For second order accurate expressions for
157 the fluxes at each face, we use the central difference approximations

$$f_{i+1/2} = f_{i+1/2}^H = u^+ \frac{C_i + C_{i+1}}{2} \quad (9)$$

158 However, this expression fails to satisfy the stability criterion that it should be total-
159 variation-diminishing (TVD) [34], and above a critical grid Peclet number Pe_{Grid} , spurious
160 oscillations appear in even a smooth solution and grow unbounded. One way of overcoming

161 this problem is to revert to a low-order flux approximation above a certain grid Peclet
 162 number such as the first-order upstream approximation

$$f_{i+1/2} = f_{i+1/2}^L = \begin{cases} u^+ C_i & \text{if } u^+ \geq 0 \\ u^+ C_{i+1} & \text{if } u^+ < 0 \end{cases} \quad (10)$$

163 As we will demonstrate in the next section, this method becomes very inaccurate when
 164 Pe_{Grid} exceeds unity as artificial numerical diffusion comes to dominate over physical
 165 diffusion. Alternatively, the face fluxes can be expressed as a combination of high and low
 166 order approximations of the form

$$f_{i+1/2} = f_{i+1/2}^L + \Psi(r_i)[f_{i+1/2}^H - f_{i+1/2}^L] \quad (11)$$

167 The function $\Psi(r_i)$ is called the flux-limiter function which dynamically adds a high-order
 168 correction, or anti-diffusional flux, depending on the local smoothness of the solution which
 169 is quantified as the ratio of consecutive gradients r_i

$$r_i = \frac{C_i - C_{i-1}}{C_{i+1} - C_i} \quad (12)$$

170 Multiple forms of the function $\Psi(r_i)$ satisfy the TVD criteria [35], and we have elected to
 171 use the superbee limiter in this work, defined as

$$\Psi(r_i) = \max\{0, \min(2r_i, 1), \min(r_i, 2)\} \quad (13)$$

172 The value of this limiter function ranges from 0 to 2, and is shown in Figure 3. A value of 0
 173 reverts to the first-order upstream approximation, 1 to the second-order central difference,
 174 and 2 to a first-order downstream approximation.

175 To avoid divide-by-zero errors in the numerical realisation of (12), we follow the approach of
 176 Jameson [36, 37] who expressed the flux limiter as a two-parameter averaging function
 177 $\Psi(r_i) = \xi(1, r_i)$ which obeys the following relations: (P1) $\xi(a, b) = \xi(b, a)$; (P2)
 178 $\xi(cb, ca) = c\xi(a, b)$; (P3) $\xi(a, a) = a$ and (P4) $\xi(a, b) = 0$ if $ab \leq 0$. The superbee limiter
 179 is then written as

$$\xi(a, b) = \beta(a, b) \cdot \max\{\min(2|a|, |b|), \min(|a|, 2|b|)\} \quad (14)$$

180 where $\beta(a, b)$ is the synchronised sign function

$$\beta(a, b) = \frac{\text{sign}(a) + \text{sign}(b)}{2} = \begin{cases} 1 & \text{if } a > 0 \text{ and } b > 0 \\ -1 & \text{if } a < 0 \text{ and } b < 0 \\ 0 & \text{otherwise} \end{cases} \quad (15)$$

Equation (11) written in these terms and using the property (P2) leads to the simple expression for the flux at the right face when $u^+ > 0$

$$f_{i+1/2} = u^+ C_i + \frac{u^+}{2} \xi(C_{i+1} - C_i, C_i - C_{i-1}) \quad (16)$$

Likewise, when $u^+ < 0$, the expression for the right face becomes

$$f_{i+1/2} = u^+ C_{i+1} + \frac{u^+}{2} \xi(C_i - C_{i+1}, C_{i+1} - C_{i+2}) \quad (17)$$

Expressions for the left face are obtained by direct translation of the indices.

4. Validation and Numerical Diffusion

We validate the transport model by comparing our numerical solutions to a reference calculation performed with COMSOL Multiphysics 5.1. In COMSOL we coupled the physics of Laminar Flow and Transport of Diluted Species, and ran the reference calculation on an extremely fine physics-controlled mesh. The geometry used is shown in Figure 4a and consists of a sphere placed in a rectangular channel. First, flow is computed in the low Reynolds number creeping flow regime ($Re < 1$) until it reaches steady-state (Figure 4b). Then the transport of a single chemical component is computed. A constant concentration is imposed at the inlet, a zero concentration is imposed on the central sphere and a zero gradient is imposed at the outlet. The calculation is run until the concentration field reaches steady-state. Finally, the concentration is plotted along characteristic lines at intervals along a central plane of the solution (Figure 4c) and compared to the corresponding calculation using COMSOL. All parameters matched between the calculations were dimensional to add further rigour to the validation, and represented a rectangular channel of 5cm width and height, with a flow rate of 3.92 mLmin^{-1} and a diffusion coefficient of $1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The results are shown in Figure 5. Good agreement is observed, although we note small deviations of a few percent in regions of high curvature in the solution. This could be due to numerical diffusion effects in either the second order TVD model, or in COMSOL.

We elucidate this important computational effect in the same geometry by comparing solutions at different hydrodynamic Peclet numbers $Pe = u_{av} L / D$ (for which the length scale L is the sphere diameter) of $Pe = 73, 730$ and 7300 using a) the first order upstream method and b) the second order TVD scheme described in the previous section. Each calculation is performed in the domain using two different resolutions: the first of dimension $L = 200$ lattice units (Lu), and the second with $L = 100$ Lu. Aside from very small differences in the geometries caused by the discrete nature of the grid, we expect that any inconsistencies in the solutions for each will be due to numerical diffusion effects.

The central plane of solutions computed in the $L = 200$ Lu size geometry are shown in Figure 6 for the three different Peclet numbers. Although qualitative agreement is apparent

for $Pe = 73$, differences between the first and second order methods are becoming clear above $Pe = 730$. Namely, the solution computed from the first order method is clearly more diffuse than by the second order solution. By $Pe = 7300$, the solutions barely correspond.

These observations are quantified by plotting the concentration across the back of the central plane and are shown in Figure 7 for each transport model in each geometry resolution for the three Peclet numbers. It is clear that numerical diffusion causes a sizable error in the solution when the first order approximation is used, even at a relatively low Peclet number of $Pe = 73$. Note that this corresponds to a grid Peclet number of $Pe_{Grid} = 1.46$ in the geometry of dimension $L = 100$ Lu, and $Pe_{Grid} = 0.73$ when $L = 200$ Lu. The second order TVD method in conjunction with the superbee limiter maintains a consistent solution across the range of Peclet numbers tested, though we note that the solution is seen to be slightly sharper in the $L = 100$ Lu geometry when $Pe = 7300$ and $Pe_{Grid} = 146$. We might therefore be inclined to choose another flux limiter function which applies anti-diffusional flux slightly less stringently in sharp regions of the solution. Nonetheless, we remain with the highly effective superbee limiter in this work.

5. Surface Rescaling

Mineral dissolution kinetics are incorporated by a simple first order rate law, assuming the system is far from chemical equilibrium

$$R = -AkC_s \quad (18)$$

C_s is the concentration of a reactant species at the surface, k is a reaction rate constant and R is the dissolution rate occurring over a surface area A . The surface concentration is computed by balancing diffusion and reaction with the $\beta \geq 1$ neighbouring fluid nodes

$$\sum_i \frac{D(C_i - C_s)}{dl} = AkC_s \quad (19)$$

where C_i are the neighbour concentrations and $dl = dx/2$ is half the lattice spacing. Solving for C_s leads to

$$C_s = \frac{D \sum_i C_i}{Akd + \beta D} \quad (20)$$

As noted by Yu [24], more general reaction terms than (18) require numerical solutions for C_s . In the surface rescaling model, the staircase effect of the Cartesian grid is counteracted by estimating the area of a boundary grid cell as $A = \psi A_{Grid}$ where ψ is a scaling coefficient associated with the node (Figure 1) and A_{Grid} is the amount of area the boundary node exposes to the fluid. The normalised mass σ of a boundary solid node is then depleted from 1 to 0 according to

$$d\sigma = -\psi A_{Grid} k \frac{C_s}{C_M} dt \quad (21)$$

where C_M is the mineral molar concentration and dt is the time-step. This expression assumes all quantities are expressed in lattice units.

The scaling coefficient ψ is obtained by interpolating a parabola at the grid cell face and computing the projection of the grid area onto this curve. The algorithm is fast and can be reapplied regularly as the mineral geometry changes. Additionally, the surface interpolation scheme uses the fractional fill of solid nodes so that the estimate changes smoothly as mass is depleted. In the present model, flow and transport solvers use discrete boundary methods so that a boundary solid node is considered completely solid until its mass σ is depleted to 0, at which point it is turned into a fluid node. This is a reasonable approximation for well-resolved grids necessary for high Pe number flows.

Calculating ψ proceeds as follows. For a boundary node located at the position $\mathbf{r}_0$, with a solid fraction $\sigma(\mathbf{r}_0)$, the normalisation scheme is applied to each of the $\beta > 0$ faces exposed to the fluid. For each of the β faces in turn, we take a unit normal vector $\mathbf{n}_0$ pointing out from the face. We then obtain a set of 8 immediate neighbour nodes at vector displacements $d\mathbf{r}_i$ from the node at $\mathbf{r}_0$, perpendicular to the face vector $\mathbf{n}_0$, that is satisfying $d\mathbf{r}_i \cdot \mathbf{n}_0 = 0$ (Figure 8). We then define a Cartesian coordinate system (x, y, z) where x and y lie on the plane of the face, and z is in the normal direction. Then, a parabolic function σ^s of the solid fraction is interpolated over the face (Figure 9) of the form

$$\begin{aligned} \sigma^s(x, y) &= \sigma_x^s(x) \sigma_y^s(y) + c \\ \sigma_x^s(x) &= (a_x x^2 + b_x x + 1) \\ \sigma_y^s(y) &= (a_y y^2 + b_y y + 1) \end{aligned} \quad (22)$$

where $c = \sigma(\mathbf{r}_0) - 1$ is obtained by imposing $\sigma^s(0, 0) = \sigma(\mathbf{r}_0)$ and the coefficients a_x, b_x are to be determined in terms of the neighbour solid fractions in the x direction, and similarly for a_y, b_y in y . The following boundary conditions are used to compute the coefficients in x where $\hat{\mathbf{x}}$ is a unit vector in the x direction

$$\sigma^s(1, 0) = \sum_{i: d\mathbf{r}_i \cdot \hat{\mathbf{x}} > 0} [\sigma(\mathbf{r}_0 + d\mathbf{r}_i - \mathbf{n}_0) + \sigma(\mathbf{r}_0 + d\mathbf{r}_i) + \sigma(\mathbf{r}_0 + d\mathbf{r}_i + \mathbf{n}_0) - 1] \lambda(|d\mathbf{r}_i|) \quad (23)$$

$$\sigma^s(-1, 0) = \sum_{i: d\mathbf{r}_i \cdot \hat{\mathbf{x}} < 0} [\sigma(\mathbf{r}_0 + d\mathbf{r}_i - \mathbf{n}_0) + \sigma(\mathbf{r}_0 + d\mathbf{r}_i) + \sigma(\mathbf{r}_0 + d\mathbf{r}_i + \mathbf{n}_0) - 1] \lambda(|d\mathbf{r}_i|) \quad (24)$$

so that $\sigma^s(1, 0)$ is specified by summing over neighbours in the $+x$ direction, and $\sigma^s(-1, 0)$ in $-x$. The weight function $\lambda(|d\mathbf{r}_i|)$ is defined as

$$\lambda(|d\mathbf{r}_i|) = \begin{cases} 1/2 & \text{if } |d\mathbf{r}_i| = 1 \\ 1/4 & \text{if } |d\mathbf{r}_i| = \sqrt{2} \end{cases} \quad (25)$$

266 The coefficients in x are therefore obtained as

$$a_x = \frac{\sigma^s(1, 0) + \sigma^s(-1, 0)}{2} - \sigma(\mathbf{r}_0) \quad (26)$$

$$b_x = \frac{\sigma^s(1, 0) - \sigma^s(-1, 0)}{2} \quad (27)$$

267

268 From the parabolic estimate of the surface (22), we compute a unit vector $(\delta x, \delta y, \delta z)$
 269 normal to the curve. It can be shown that the expression for the z component $\delta z(x, y)$ over
 270 the face surface, which lies parallel to the face normal vector $\mathbf{n}_0$, is (appendix 1)

$$\delta z(x, y) = \left[1 + \left(\frac{d\sigma^s}{dx} \right)^2 + \left(\frac{d\sigma^s}{dy} \right)^2 \right]^{-1/2} \quad (28)$$

271 From (22), the z component function $\delta z(x, y)$ can be written explicitly using the differential
 272 results

$$\frac{d\sigma^s}{dx} = [2a_x x + b_x] \sigma_y^s(y) \quad (29)$$

$$\frac{d\sigma^s}{dy} = [2a_y y + b_y] \sigma_x^s(x) \quad (30)$$

273 We define a face normalisation factor ψ_f which measures the projection of the lattice cell
 274 face onto the smooth surface, so that we integrate the inner product $(\delta x, \delta y, \delta z) \cdot \mathbf{n}_0 = \delta z$
 275 over the face surface area

$$\psi_f = \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \delta z(x, y) dx dy \quad (31)$$

276 We have been unable to solve this integral analytically, and even a power series
 277 representation of the result converges too slowly to be of practical use. Instead, we
 278 approximate the result as a 2-dimensional Riemann sum

$$\psi_f = \frac{1}{n^2} \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} \delta z(x_i, y_j) \quad (32)$$

where $x_i = \frac{1}{n} \left(i + \frac{1}{2} \right) - \frac{1}{2}$ and $y_j = \frac{1}{n} \left(j + \frac{1}{2} \right) - \frac{1}{2}$ define discrete positions on the cell surface; effectively an $n \times n$ grid of values, where n may be chosen to balance accuracy with computational performance. Finally, for simplicity, we take an average scaling coefficient for the whole cell so that boundary nodes with $\beta > 1$ use the same factor for all faces

$$\psi = \frac{1}{\beta} \sum_{f=0}^{\beta} \psi_f \quad (33)$$

This algorithm is tested on a set of simple geometries for which an analytical surface area can be prescribed. Two discrete planes, one aligned diagonally in 2 dimensions and the other in 3 dimensions demonstrate how the method counteracts the staircase effect in binarised solid/fluid interfaces, which often represents initial data; and a smooth cylinder in which surface nodes are partially filled according to the cell fraction lying inside the shape, which better represents the state of a geometry which has been partly dissolved during the simulation. These are shown in Figure 10.

Geometry	Grid Area	Scaled Area
Discrete Plane 2D	1.41	1.00
Discrete Plane 3D	1.50	1.00
Smooth Cylinder	1.27	1.07

Table 1 – The surface area computed for 3 geometries using a) the grid surface area and b) the scaled grid surface area, relative to the analytical surface area.

Table 1 gives the surface area of each geometry relative to the analytical area. We used $n = 8$ in computing the overlap integral (32) and found this to be consistent to within 1% of using $n = 80$. The rescaling method completely counteracts the staircase effect in the discrete planes, and reduces the error by a factor of 4 in the case of the smooth cylinder.

It is worth noting that the boundary conditions (23) and (24) are not the only way of specifying the parabolic surface, and even better estimates of a smooth surface might be obtained by constraining the integral of the curve σ^s according to neighbour solid fractions instead.

6. Dissolution in Porous Media

We compute the dissolution of the pore-space of a real carbonate rock sample according to the following first order reaction of limestone with HCl acid, characterised by a reaction rate constant $k = 1.5 \times 10^{-4} \text{ ms}^{-1}$ [38].

In this work, we assume far-from-equilibrium conditions, so that the products of the reaction can be neglected. This is justifiable in practice if the rock core is short, and the acid

is dilute enough so that the concentration of products does not build up near reactive surfaces. In future work, we will incorporate the effects of the product solubility on the reaction rate.

The geometry used is a Ketton limestone, obtained by micro-CT scanning with a resolution of $15.8\mu\text{m}$ [39]. The domain size is 200^3 lattice units which represents a 3.2mm cubic sample and is shown in Figure 11 along with the initial flow-field. We simulate the dissolution of this geometry at two different Peclet numbers: $Pe = 0.8$ and $Pe = 80$ which correspond to dimensional flow rates of $1.5\mu\text{Lmin}^{-1}$ and $150\mu\text{Lmin}^{-1}$, and the HCl concentration is $5\times 10^{-3}\text{mol dm}^{-3}$ (pH 2.3). The diffusion coefficient is that of H^+ in ambient conditions: $D = 9.3\times 10^{-9}\text{m}^2\text{s}^{-1}$. The length scale used in the definition of Peclet number is $475\mu\text{m}$ as an estimate of the mean grain diameter.

A constant concentration is imposed at the inlet and zero gradient at the outlet in the flow direction. Boundaries in the perpendicular directions are impermeable and non-reactive. The flow field is computed to steady-state, and the transport model and mineral dissolution kinetics are fully coupled. Flow is recomputed after a change of 0.2% in the porosity of the geometry to ensure that the physics is strongly coupled during unstable wormhole formation.

In the interest of computational efficiency, we impose an inlet concentration of $1\text{mol dm}^{-3} H^+$ instead of $5\times 10^{-3}\text{mol dm}^{-3}$ and scale the physical time of the simulation to correspond to the latter. This is acceptable in this case because of the linearity of the reaction term (18) and the fact that the flow and transport models reach a steady-state on a much shorter time-scale than the change in mineral boundaries. When more complex forms of the reaction term are used, such as when product solubility is taken into account, we will allow the concentration field to reach a steady state and interpolate the boundaries backwards over a larger time-step. In this way, arbitrary experimental time-scales can be accessed. Calculations are performed on a GTX Titan Black GPU and each simulation requires approximately 10 hours. A steady-state flow field is obtained in between 16 and 60 seconds depending on the porosity of the geometry.

Concentration fields of the H^+ acid species are shown for the two different Peclet numbers in Figure 12 and Figure 13. As expected, the $Pe = 0.8$ leads to a dissolution behaviour concentrated almost entirely at the rock face as convection barely transports the reactive species into the pore structure before it is depleted by the fast surface reaction rate. At $Pe = 80$, convection plays a stronger role and transports the acid species through the pore-structure (Figure 13a). The highest permeability flow paths draw the largest quantity of reactant and widen at the highest rate (Figure 13b). Finally, a single high permeability path comes to dominate, forming a dominant wormhole (Figure 13c). The rock structures after dissolution are shown in Figure 14 for the two Peclet numbers at the same porosity, and videos of the dissolution of the geometry at each Peclet number may be found in supplemental materials. The time-dependant porosity is also plotted in Figure 15. It is

important to note that unstable dissolution processes like wormhole formation can cause grains inside the rock to move, and although the simulation can be continued to any extent of dissolution, the result may become unphysical unless the mechanical movement of grains is incorporated into the model. Finally, the permeability of the two different dissolution patterns is compared in Figure 16 against the same porosity. It is clear that the wormhole formation leads to orders of magnitude greater increase in permeability than the face dissolution case for the same amount of mineral dissolved.

7. Conclusion

We constructed a model for simulating dissolution in porous media including dynamically evolving mineral boundaries according to reaction kinetics at the surface. Flow was computed to steady-state using the lattice Boltzmann method and transport of a reactive species was performed with a second order TVD FVM scheme incorporating a flux limiter function which was confirmed to effectively counteract numerical diffusion effects at high Peclet numbers. Surface area was approximated using parabolic interpolation, and used to calculate local rescaling coefficients for dissolving boundary nodes so that a direct coupling to the Cartesian grid could be maintained.

We showed how the model is able to compute the dissolution of a Ketton limestone sample injected with HCl in far-from-equilibrium conditions. By varying the Peclet number (flow rate), different dissolution patterns were predicted in concordance with experimental observation. The simulation thereby enables the collection of all manner of data useful for subsurface operations including porosity, permeability, overall dissolution rate, surface area and outlet pH.

The model was found to be computationally efficient when run on GPU and a rescaling of the acid concentration and physical time was used here to reduce the number of time-steps required. A more sound approach which will be incorporated in the future is to decouple the transport and surface dissolution methods so that the concentration field is allowed to reach steady-state in the same way as the flow field, and use a much larger time-step in eroding the mineral boundaries. This will then make practicable the incorporation of the more complicated chemical system relevant to CO₂ storage operations.

375 Figures

376

377 Figure 1 – A discrete surface (blue is solid; white is fluid) on which a smooth surface is
 378 interpolated by parabolic sections (dashed orange lines). Scaling factors $\psi^i \leq 1$ associated
 379 with the nodes' exposed faces are computed from projections of the lattice area onto the
 380 parabolic curves. The method is applied to all boundary faces; three examples are shown.
 381 The finely dashed black line shows a case where marching cubes would decouple the
 382 surface from the solid volumes.

383

384

385 Figure 2 – Adjoining cells in one dimension indexed relative to cell i , with concentration
 386 values C_i . The central cell is shown with velocities at the left and right faces of u^- and u^+ ,
 387 and scalar fluxes $f_{i-1/2}$ and $f_{i+1/2}$.

388

389 Figure 3 – The value of the superbee limiter $\Psi(r_i)$ as a function of the curvature sensor r_i .
 390 The limiter takes on values of 0 for $r_i \leq 0$ and 2 when $r_i \geq 2$.

391

392 Figure 4 – a) Geometry used for validation and numerical diffusion tests. The diameter of
 393 the sphere is half the dimension of the channel; b) the velocity field – orange (light) zones
 394 are fast flow and blue (dark) zones are slow; and c) steady-state concentration field (scale
 395 normalised to inlet concentration) at $Pe = 73$, injected from rear.

396

Figure 5 – Concentration of a tracer plotted along characteristic lines of the geometry. Solid lines: second order flux-limiter transport model; dashed lines: COMSOL calculation. (N.B. for greyscale versions of this figure: the order of the curves from top to bottom corresponds to that of the legend read from left to right and downwards)

Figure 6 – Concentration fields computed in the geometry of dimension $L = 200$ and shown in the central slice for different hydrodynamic Peclet numbers. The convection schemes used were a) first order and b) second order with superbee limiter. The scale is normalised to the inlet concentration.

407

408

409

Figure 7 - Concentration profiles across the central part of the outlet of the geometry for a) $Pe = 73$, b) $Pe = 730$ and c) $Pe = 7300$. (N.B. for greyscale versions of this figure: the order of

410 the curves corresponds to that of the legend except in c. where *second order 100 cubed* lies
 411 below *second order 200 cubed*)

412

413 Figure 8 – A grid cell at position $\mathbf{r}_0$ with solid fraction $\sigma(\mathbf{r}_0)$. An exposed cell face is shown
 414 with the unit normal vector $\mathbf{n}_0$, and 8 perpendicular neighbours at displacements $d\mathbf{r}_i$. A
 415 Cartesian coordinate system is defined on the face so that $\hat{\mathbf{z}} = \mathbf{n}_0$.

416

417 Figure 9 - Construction of parabolic surface and the projection of its normal vector
 418 $(\delta x, \delta y, \delta z)$ onto the grid surface face vector $\mathbf{n}_0$.

419

420 Figure 10 – Textured surfaces: a) a discrete plane in 2 dimensions, b) a discrete plane in 3
 421 dimensions and c) a smooth cylinder in which boundary nodes are partially filled according
 422 to their overlap with the circular radius.

423

424 Figure 11 – Ketton carbonate geometry and flow-field. The image resolution is $15.8\mu\text{m}$ and
 425 the grid size is 200 lattice units cubed.

426

427 Figure 12 - The concentration of H^+ in the dissolution of Ketton carbonate at $Pe = 0.8$,
428 injected from left/rear at different times: a) $t = 2.3$ hr, b) $t = 150$ hr.

429

430 Figure 13 – The concentration of H^+ in the dissolution of Ketton carbonate at $Pe = 80$ at
 431 different times: a) $t = 19\text{min}$, b) $t = 2.7\text{hr}$, c) $t = 5.4\text{hr}$. HCl was injected from left/rear.
 432 The wormhole is apparent in c) as the large flow path at the centre of the domain.

Figure 14 – Cutaways of the Ketton limestone geometry after dissolution at a) $Pe = 0.8$ at $t = 56.4\text{hr}$ and b) $Pe = 80$ at $t = 5.4\text{hr}$ showing a wormhole through the sample. Injection was from left/front. The porosity is 38.5% in both cases.

Figure 15 – The porosity of the Ketton limestone sample against time undergoing dissolution at two different Peclet numbers. The dashed region of the $Pe = 80$ curve indicates where the mechanical movement of the rock grains likely needs to be taken into account.

Figure 16 – The permeability of the Ketton carbonate sample as the porosity changes during dissolution at Pe = 80 (top line) and Pe = 0.8.

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542 Appendix 1

543 A unit vector $(\delta x, \delta y, \delta z)$ normal to a parabolic surface $\sigma^s(x, y)$ is described by the
544 following equations.

545 A unit vector requires that

$$\delta x^2 + \delta y^2 + \delta z^2 = 1 \quad (\text{A.1})$$

546 The gradient of a line normal to a curve is the negative inverse of the gradient of the curve,
547 so that

$$\delta x = -\frac{d\sigma^s}{dx} \delta z \quad (\text{A.2})$$

$$\delta y = -\frac{d\sigma^s}{dy} \delta z \quad (\text{A.3})$$

548 Substitution of A.2 and A.3 into A.1 leads to an expression for the z component

$$\delta z(x, y) = \left[1 + \left(\frac{d\sigma^s}{dx} \right)^2 + \left(\frac{d\sigma^s}{dy} \right)^2 \right]^{-1/2} \quad (\text{A.4})$$

549