Reactive transport under stress: Permeability evolution in deformable porous media

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Abstract

We study reactive transport in a stressed porous media, where dissolution of the solid matrix causes two simultaneous, competing effects: pore enlargement due to chemical deformation, and pore compaction due to mechanical weakening. We use a novel, mechanistic pore-scale model to simulate flooding of a sample under fixed confining stress. Our simulations show that increasing the stress inhibits the permeability enhancement, increasing the injected volume required to reach a certain permeability, in agreement with recent experiments. We explain this behavior by stress concentration downstream, in the less dissolved (hence stiffer) outlet region. As this region is also less conductive, even its small compaction has a strong bottleneck effect that curbs the permeability.

Our results also elucidate that the impact of stress depends on the dissolution regime. Under wormholing conditions (slow injection, i.e. high Damkohler number, \(Da\)), the development of a sharp dissolution front and high porosity contrast accentuates the bottleneck effect. This reduces transport heterogeneity, promoting wormhole competition. Once the outlet starts eroding, the extreme focusing of transport and hence dissolution—characteristic of wormholing—becomes dominant, diminishing the bottleneck effect and hence the impact of stress at breakthrough. In contrast, at high flow rates (low \(Da\)), incomplete reaction upstream allows some of the reagent to traverse the sample, causing a more uniform dissolution. The continuous dissolution and its partial counteraction by compaction at the outlet provides a steady, gradual increase in the effect of stress. Consequently, the impact of stress is more pronounced at high \(Da\) during early stages (low permeability), and at low \(Da\) close to breakthrough. Our work promotes understanding of the interplay between dissolution and compaction and its effect on the hydromechanical property evolution, with important implications for processes ranging from diagenesis and weathering of rocks, to well stimulation and carbon geosequestration.

1. Introduction

The transport of reactive fluids in porous media is a fundamental process in many earth systems, including weathering and diagenesis of rocks, contaminant transport, subsurface remediation, energy recovery, and CO\textsubscript{2} sequestration. Reactive transport is a complex, nonlinear process: the transport and reactive properties and hence the rate and spatial distribution of fluid flow and reaction strongly depend on the microstructure, which in turn keeps evolving in time with the reaction [36, 13, 30].

Much interest has been given to the dissolution of the solid matrix and the consequent evolution of the porosity and permeability. Experiments and numerical simulations pointed out a rich range of behavior, or regimes, depending on the hydrochemical conditions. It has been shown that for reactions which are slow relative to the rate of fluid flow (the ratio being the Damkohler number, \(Da\)), ample reagent is provided throughout the sample, leading to relatively spatially-uniform dissolution, and steady enhancement of permeability. In contrast, at higher \(Da\) (the so-called transport-limited regime), most of the reagent is consumed by preferential dissolution of the most conductive flow paths ("wormholes").

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This further enhances their conductivity relative to other, less conductive regions, leading eventually to runaway permeability increase [12, 4, 18, 39].

In many cases, for instance in the subsurface, the medium is under appreciable stress, such that dissolution (“chemical deformation”) also induces mechanical deformation. Chemomechanical deformation and the coupled changes in the transport and mechanical properties is key in many applications, such as enhanced energy recovery and carbon geosequestration [35, 26, 11, 32, 14, 7]. A large body of literature exists on rough fractures, due to their importance, e.g. dominance of fracture flow, and their quasi two-dimensional (2-D) nature, which simplifies experimental setup and imaging as well as numerical simulations [e.g. 22, 14, 16, 19, 2]. Relatively fewer works addressed porous media such as soils [8] and rocks [e.g. 46, 11, 47, 16, 6, 29, 22, 29], mostly focusing on the evolution of the mechanical properties.

The evolution of transport properties in a porous rock sample has been addressed by recent experiments, in which rock cores subjected to external stress were flushed by a reactive fluid [43, 41, 17, 42, 40, 9]. These experiments show considerable reduction in mechanical stiffness, and inhibition of permeability enhancement, in spite of net removal of solid mass. A model providing fundamental quantitative understanding of mechanisms governing the permeability evolution in these experiments—the objective of this paper—is lacking. Existing models of stressed rock dissolution are either at much larger scales (reservoir) [29], much smaller scales (describing changes in microstructure and porosity but not in permeability) [16], or consider other mechanisms such as pressure solution and re-precipitation [46].

A major challenge in our understanding of chemomechanical deformation is the dependency on pore-scale mechanisms and heterogeneity inherent to geologic media [37]. While the importance of pore-scale processes has long been recognized, rigorous studies are only recently made possible, owing to advancements in experimental and computational capabilities, as highlighted in a recent special volume of review papers [37]. The natural complexity of pore-scale processes associated with heterogeneity makes characterization [e.g. 8, 30] as well as modeling and interpretation [e.g. 21, 38, 28, 17, 34] extremely challenging. This is especially true for cases where the coupling with mechanical deformation occurs [e.g. 16, 18, 23]. Despite of the advancements in experimental techniques [31, 30], numerical simulations remain highly attractive [e.g. 21, 23, 25, 28, 19, 27, 14, 34].

In this paper, we present a novel pore-scale model, which, to the best of our knowledge, is the first to describe the permeability evolution caused by coupling between dissolution and compaction in a porous medium. Our simulations show that increasing stress inhibits the permeability evolution, requiring longer time or larger volumes injected to reach a certain permeability, in agreement with experiments [41, 17, 9]. We also expose the impact of the dissolution regimes (Da), that is how stress effect changes between wormholing and a more uniform dissolution. We find that at high Da, stress acts to reduce the transport and dissolution heterogeneity, promoting wormhole competition.

2. Pore-scale model

We simulate the injection of a reactive fluid into a porous medium held under a fixed confining stress. We consider the gradual, continuous dissolution of the solid matrix and the consequent compaction, excluding mechanisms such as fracturing [e.g. 23, 9], detachment of mineral grains [e.g. 24, 9], and pressure solution and welding of microporous zoness [e.g. 19, 15, 9].

Seeking fundamental understanding rather than quantitative predictions for a specific type of medium, we use here an analog model with simplified geometry: a 2-D network of cylindrical channels between soluble solid blocks. The coupling between dissolution and compaction at the pore-scale is captured by combining two discrete, overlapping representations: (i) pore network modeling of reactive transport and (ii) a network of interacting linear elastic porous solid blocks. Each discrete model unit (termed “cell” hereafter) includes one solid block, bounded by four “half-channels”—the respective void space associated with that cell (Fig. 1). Our model can be considered as a realization of a granular sediment or a fractured rock, where each pore represents an interparticle void or a fracture, respectively.

Numerically, coupling is provided through staggering, executing sequentially at each time step the following steps: (1) evaluate the liquid pressures and fluxes, from mass conservation of liquid; (2) compute liquid composition, reaction rate and amount of dissolved mass, from conservation of solute mass; (3) compute stress distribution and pore deformation from force balance; and (4) update transport and mechanical properties (to be used in the subsequent time step) due to the combined effects of chemical pore enlargement by dissolution and mechanical compaction. Our use of a quasi-static model via staggering
Figure 1: Schematics of our pore-scale model of reactive transport in a stressed, deformable porous medium. We capture the coupling between chemical and mechanical deformation through a discrete representation, combining: (i) pore network modeling of reactive transport, with (ii) interacting network of linear elastic blocks. (a) We simulate the injection of a reactive fluid into a sample held under fixed isotropic stress, $\sigma$. The sample is square, with two open faces (inlet and outlet, in the $y$ direction) and two impermeable ones (in $x$). (b) The pore space is discretized into a 2-D regular network of cylindrical pores connected by volumeless nodes (or junctions), squeezed in between solid blocks. Heterogeneity is provided by variations in pore sizes. (c) The basic model unit (“cell”) includes a solid block, with four parts of pores engraved in the solid. The network properties, parametrized via the pore radius (assuming pores retain their cylindrical shape), are updated at each time step considering both the chemical and mechanical effects of dissolution.

is justified by the disparate time scales of the different processes: the time required to reach equilibrium of ion concentration is much longer than that for fluid pressures to equilibrate, which in turn is much slower than mechanical deformation and stress equilibration. Therefore, the process hindering the rate of changes in the hydromechanical properties of the solid matrix is the dissolution, allowing us to treat the other processes as occurring instantaneously at every time step [2]. That is, we approximate the continuous evolution of the sample properties by a discrete sequence of geochemical and mechanical equilibrium configurations. The different model components describing these processes are outlined below.

2.1. Reactive transport

We model the reactive transport and dissolution using a pore network model that closely follows the one in Budek and Szymczak [5]; therefore, we only briefly describe it here, elaborating further on the coupling with mechanical compaction.

2.1.1. Fluid flow

We consider a dilute liquid solution (e.g. CO$_2$-rich water), neglecting the effect of its pressure and solute concentration on its density. For a given configuration (network geometry), we solve for the fluid fluxes by enforcing steady-state fluid mass conservation, namely the continuity equation, at each pore junction (node) $i$,

$$\sum_j q_{ij} = 0,$$

where $q_{ij}$ is the volumetric flow rate through pore $ij$ ($q_{ij} > 0$ indicates flow from node $i$ to $j$), and the summation is over all neighboring nodes, $j$ (Fig. 1b). Assuming Stokes flow, the interpore fluxes, $q_{ij}$, are

$$q_{ij} = C_{ij} \Delta p_{ij}.$$

Here $C_{ij} = a_{ij} R_{ij}^2 / (8 \mu l_{ij})$ is the pore conductivity, $R_{ij}$ and $a_{ij} = \pi R_{ij}^2$ are the pore radius and cross-sectional area, and $\mu$ is the fluid viscosity. The term $\Delta p_{ij} = (p_i - p_j)$ is the pressure drop between the two nodes, which are $l_{ij}$ apart. The linear system in Eq. 1 provides the fluid pressure at the nodes. Note that this formulation assumes that flow is driven by fluid pressure alone, i.e. a horizontal system; to generalize the formulation to include gravity effects, node pressures $p_i$ should be replaced by the total energy, e.g. in terms of hydraulic head.

2.1.2. Reagent transport and reaction rate

The computation of dissolution rates is based on the following assumptions [5]: (1) steady-state liquid and solute transport; (2) solute transport in each pore is dominated by convection in the longitudinal
(axial) direction, and by diffusion in the radial (transverse) direction; (3) reaction kinetics can be approximated via a linear law, \( J_r = \lambda c_w \), where \( \lambda \) is the surface reaction rate coefficient \([\text{LT}^{-1}]\) and \( c_w \) is the concentration at the pore surface; and (4) for 1-D radial diffusion, the diffusive flux can be evaluated from the difference between the surface concentration \( c_w \) and cross-sectional averaged concentration (“mixing cup concentration”) \( c \), by \( J_{\text{diff}} = D \text{Sh} (c - c_w)/2R \). Here \( D \) is the molecular diffusion coefficient, and \( \text{Sh} \) is the Sherwood number.

The reaction rate, \( J_r \), is expressed in terms of the pore-averaged concentration \( c_{ij} \),

\[
J_r = \lambda_{ij}^{\text{eff}} c_{ij},
\]

where the effective reaction rate coefficient, \( \lambda_{ij}^{\text{eff}} \), is computed assuming that it is set by radial diffusion between the pore center and the solid wall, \( J_{\text{diff}} = J_r \), providing

\[
\lambda_{ij}^{\text{eff}} = \frac{\lambda}{1 + 2\lambda R_{ij}/\text{Sh}}.
\]

The pore-averaged concentration, \( c_{ij} \), is resolved from the 1-D steady-state analytical solution for solute mass conservation in each pore, providing an exponential concentration profile along the pore,

\[
c_{ij} = c_{ij}^0 e^{-A_{ij} \lambda_{ij}^{\text{eff}} q_{ij} / q_{ij}^0},
\]

where \( A_{ij} = 2\pi R_{ij} l_{ij} \) is the reactive surface area, and \( c_{ij}^0 \) is the concentration at node \( j \) evaluated at the previous time step (denoted by the superscript \( 0 \)). The node concentration is evaluated from the conservation of solute in each node,

\[
c_{ij} = -\sum_{j(q_{ij} < 0)} q_{ij} c_{ij} / \sum_{j(q_{ij} > 0)} q_{ij}.
\]

2.2. Updating network properties due to chemomechanical deformation

We consider cylindrical pores which erode uniformly such that they retain their shape and length (here uniform, \( l_{ij} = l \)). This simplifies our computations, allowing us to parametrize the network properties such as the conductivity and reactive surface area by a single parameter, \( R_{ij} \). With staggering, the properties are updated at each time step considering the combined effects of (i) dissolution (increasing the radius by \( \Delta R_{ij}^{\text{chem}} \) relative to the previous time step) and (ii) compaction (decreasing it by \( \Delta R_{ij}^{\text{mech}} \)), \( R_{ij} = R_{ij}^0 + \Delta R_{ij} \), where \( \Delta R_{ij} = \Delta R_{ij}^{\text{chem}} + \Delta R_{ij}^{\text{mech}} \).

2.2.1. Pore opening due to dissolution (chemical deformation)

The computation of the direct effect of dissolution on pore geometry is based on conservation of solid mass. The incremental change in radius at every time step \( \Delta t \) is

\[
\Delta R_{ij}^{\text{chem}} = \frac{q_{ij} \Delta t c_{ij}^0}{A_{ij} c_{\text{sol}} \nu} \left( 1 - e^{-A_{ij} \lambda_{ij}^{\text{eff}} q_{ij} / q_{ij}^0} \right)
\]

where \( c_{\text{sol}} \) is the concentration of soluble material at the surface, and \( \nu \) accounts for the stoichiometry of the reaction. Our model accounts for two important aspects: the merger of adjacent pores following extensive dissolution, and that the amount of soluble solid is finite. The effect of merging is demonstrated in Budek and Szymczak by comparing models with and without merging. However, these models do not limit the dissolution, considering an infinite amount of soluble solid. For simplicity, we use here the same threshold for merging and complete local dissolution. Thus, once all soluble solid associated with a cell has been consumed, (i) the dissolution reaction cease and the transport and mechanical properties of that cell remain fixed throughout the simulation; and (ii) each of the two pairs of pores associated with that cell (a pair in each direction, \( x \) and \( y \)) are merged.

Computationally, we model pore merger by an abrupt increase in the conductivity of the associated pores, while retaining the same discretization of nodes and pores. That is, the pair of merged pores are each assigned a conductivity \( C_{ij} = C_{ij}^* \), which depends on the spatial extent of dissolution. When a cell experiences complete dissolution, while its adjacent neighbors did not, the conductivity of the pores in between them is set to \( C_{ij}^* = a_{ij}^* R_{ij}^2 / (8\mu l_{ij}) \), where \( R_{ij}^* = d_{ij} / 2 \), \( d_{ij} = 4a_{ij}^* / P_{ij} \) is the pore’s hydraulic
diameter, and \( P_{ij} \) is its perimeter. In evaluating \( a_{ij}^\prime \) and \( P_{ij} \) we associate the following regions to each pore: (1) half of a cylinder with radius \( R_{ij} \), plus (2) half of the (completely dissolved) unit cell, common to both pores of that pair. To allow consideration of merging due to focused dissolution in a single pore (only from one side of the cell), we set the cell height (out-of-plane size) to be twice the lateral (in-plane) size, such that the cell dimensions are \( l \times l \times 2l \); with this, the radius of a single pore can approach \( l \), and undergo merging (Fig. 1c). Once two adjacent cells completely dissolve, the pore separating them is assigned with the conductivity of two parallel plates, \( C_{ij}^* = 2l^3/(3\mu) \).

2.2.2. Pore compaction (mechanical deformation)

Pore compaction is evaluated by enforcing mechanical equilibrium (here, balance of forces). As before (for modeling reactive transport), we exploit the separation of time scales of compaction and dissolution to describe the continuous deformation as a sequence of static equilibrium configurations, each attained instantaneously. We assume that each cell is a linear elastic, homogeneous and isotropic solid, such that the stress and strain in each cell \( \sigma_{ij} \) and \( \epsilon_{ij} \) are related via Hooke’s law, \( \sigma_{ij} = \kappa_{ij} \epsilon_{ij} \), where \( \sigma_{ij}^\prime \) and \( \epsilon_{ij}^\prime \) are the stress and strain in the \( \beta \) direction (\( x \) or \( y \)). The cell effective stiffness, \( \kappa_I \), is evaluated using effective medium theory [25],

\[
\kappa_I = \left[ \frac{1}{\kappa_s} + \frac{\phi_I}{\kappa_\phi} \right]^{-1},
\]

where \( \phi_I \) is the cell’s porosity—the ratio of pore to total volume—which changes with dissolution and compaction, \( \kappa_s \) is the bulk modulus of the solid (a fixed material property), and \( \kappa_\phi \) is the pore stiffness, which can be determined experimentally [42] [10]. Our model considers compaction induced solely by changes in the local porosity, \( \phi_I \), without accounting for the secondary effect of pore stiffness degradation [42] [10]; thus, we use a fixed \( \kappa_\phi \) value.

We consider external confining stress on the sample applied via rigid walls that remain planar. While this imposes uniform displacement of all outermost (boundary) cells, the stress distribution on them becomes nonuniform due to the nonuniform stiffness resulting from the heterogeneous dissolution. Finally, to compute the compaction, we invoke the following additional simplifying assumptions: (i) perfectly-drained conditions, without consideration of poroelastic effects, i.e. changes in pore pressure due to mechanical deformation; and (ii) deformations remain sufficiently small such that they can be decoupled in \( x \) and \( y \). The above assumptions, together with superposition provided by linearity of the stress-strain relations, makes evaluation of compaction highly computationally efficient.

The computational procedure used to establish mechanical equilibrium and associated compaction is as follows. At each time step we compute: (1) the stiffness of each cell, \( \kappa_I \), using Eq. (8) (2) the effective sample stiffness in each direction, \( \kappa_{\text{eff}}^\beta \); (3) the boundary displacements (macroscopic strains), \( \epsilon_{\text{eff}}^\beta = \sigma/\kappa_{\text{eff}}^\beta \) given the macroscopic external stress applied on the boundary, \( \sigma \); (4) the stress on cell \( I \), \( \sigma_{ij}^\prime \), noting that due to the decoupling in \( x \) and \( y \), force balance reduces to the equality of the stress on all cells in a given row \( s \), \( \sigma_{ij}^\prime = \sigma_s \). The stress in row \( s \) is computed from \( \sigma_s = \kappa_s \epsilon_s \), using the effective stiffness of each row, \( \kappa_s \), where the planarity of the boundaries implies uniform strain of all rows in a specific direction, \( \epsilon_s = \epsilon_{\text{eff}}^\beta \); (5) the radial strain of each pore, \( \epsilon_{ij} = \sigma_{ij}/\kappa_\phi \), assuming the radial stress on a pore is equal to the one acting on the cell, \( \sigma_{ij} = \sigma_{ij}^\beta \); and (6) the decrement in pore radius from geometrical arguments,

\[
\Delta R_{ij}^\text{mech} = R_{ij}' \sqrt{1 - \epsilon_{ij}} - R_{ij}^0
\]

where \( R_{ij}' \) is the radius considering dissolution alone (excluding compaction) since the beginning of the simulation, and \( R_{ij}^0 \) is the radius considering both dissolution and compaction; both \( R_{ij}' \) and \( R_{ij}^0 \) are the known values from the previous time step. Note that the radius of a pore can experience a decompaction within a time step, \( \Delta R_{ij}^\text{mech} < 0 \), if stress redistribution leads to local release of stress in that area.

2.3. Initial and boundary conditions

Simulations begin at geochemical and mechanical equilibrium, with zero reagent concentration, \( c(t = 0) = 0 \). We inject a liquid at fixed concentration \( c = c_{in} \) and flow rate \( Q \). We fix the rate throughout the dissolution—as permeability changes—by adjusting the pressure at the inlet nodes at every time step (keeping zero pressure at the outlet nodes). Injection occurs from the inlet face towards the outlet
face, as the two perpendicular faces are impermeable (see Fig. 1b). At the outlet pores, we enforce free-flow boundary conditions, computing their concentration from solute mass conservation (Eqs. 5–6). Mechanically, we apply a constant confining stress on the boundaries, \( \sigma \), keeping the boundaries planar; that is, we enforce uniform displacement of the boundary cells, which therefore experience non-uniform forces (depending on the stiffness).

2.4. Parameter values used in the simulations

In all simulations, we used a domain of \( 100 \times 100 \) nodes. We chose a square sample with an aspect ratio of one to minimize the interference of the lateral boundaries with wormhole development [10]. We enforce an initial heterogeneity by assigning the pores with volumes drawn from a uniform distribution, \( V_i \in [1 - \alpha, 1 + \alpha \bar{V}] \), where \( \bar{V} \) is the average volume and \( \alpha \) is a measure of the heterogeneity, here \( \alpha = 0.8 \). The initial overall sample porosity is \( \phi = 0.1 \). The amount of insoluble solid is a fixed, spatially-uniform fraction of the total cell volume, \( \rho = 0.2 \). Due to the initial heterogeneity in pore sizes, solid volume and porosity vary among cells.

The reactive transport conditions can be described by two dimensionless groups [5]: (i) \( Da \), the ratio between the reaction rate and the mean flow rate in pores; and (ii) \( G \), the extent to which the dissolution rate is hindered by diffusive transport of reactant from the pore to the wall,

\[
Da = \frac{2\pi \bar{R}\lambda / \bar{q}_m}{1 + \lambda 2\bar{R}/DSh}
\]

and

\[
G = \frac{\lambda 2\bar{R}/DSh}{10}
\]

where \( \bar{q}_m \) and \( \bar{R} \) are the average flow rate at the inlet and the initial average radius, respectively. We use a fixed value of \( Sh = 4 \) [5]. We focus on two regimes: (a) heterogeneous dissolution or wormholing with \( Da = 1 \), and (b) a more uniform dissolution, \( Da = 0.01 \). We control \( Da \) via the total flow rate, \( \bar{Q}_m \), while fixing \( G = 1 \). We note that compaction due to the application of stress changes slightly the values of \( Da \) and \( G \) (by up to \( \sim 5\% \) and \( \sim 20\% \), respectively).

To simulate carbonate dissolution we set \( c_{in} = 0.001 \) M; this corresponds to pH=3, for which the system is sufficiently far from geochemical equilibrium to justify the approximation of first order reaction kinetics. We use a molecular diffusion coefficient of \( D = 3 \times 10^{-9} \) m\(^2\)/s and a rate coefficient of \( \lambda = 5 \times 10^{-4} \) m/s [51, 4]. Mechanically, we apply a fixed stress, \( \sigma \), ranging between 0 and 60 MPa. We set stiffness of \( \kappa_0 = 22 \) GPa and \( \kappa_a = 0.01 \kappa_0 \), characteristic of soft sediments [42, 40].

We keep the numerical error associated with staggering and time discretization small by using a sufficiently small time step \( \Delta t \), 20 and 0.5 s for \( Da = 1 \) and 0.01, respectively. This value was chosen by trial and error, running a set of simulations with decreasing time step until the pore volume to breakthrough \( (PV_{BT}) \) stabilized. Breakthrough is defined here as a ten-fold increase in the permeability, \( K/K_0 = 10 \), where \( K \) and \( K_0 \) are the current and initial permeability.

3. Results

3.1. Permeability evolution

Our simulations demonstrate the intricate interplay between chemical and mechanical deformation, capturing the inhibition of permeability enhancement associated with stress-induced compaction, observed experimentally [17, 42, 40, 9]. Increasing the external stress results in longer time, or equivalently larger amounts of injected fluid, \( PV \), required to reach a certain permeability (Fig. 2).

Permeability and its inhibition by compaction strongly depends on the spatial extent of the dissolution, e.g. on the regime \( (Da) \), and changes with time. We quantify this through the increase in \( PV \) required to reach a certain \( K/K_0 \) under high stress of \( \sigma = 60 \) MPa relative to \( \sigma = 0 \), \( \Delta PV = [PV_{\sigma=60} - PV_{\sigma=0}]/PV_{\sigma=0} \). At early times (low \( K/K_0 \)), the impact of stress is more noticeable for wormholing (\( Da = 1 \)); for instance, at \( K/K_0 = 2 \) the increment \( \Delta PV \) is \( \sim 45\% \) for \( Da = 1 \) vs. only \( \sim 10\% \) for \( Da = 0.01 \). This trend however flips later on: at breakthrough, \( \Delta PV \) is five times larger for \( Da = 0.01 \), with \( \Delta PV \approx 50\% \) (Fig. 2). For both regimes, the reduction in dissolution efficiency (increase in \( PV \)) associated with stress causes the dissolution front to progress further downstream (e.g. compare insets in Fig. 2 at a given \( K/K_0 \)). Regardless of stress,
Our simulations demonstrate the inhibition of permeability enhancement by stress. Increasing stress, $\sigma$, lowers the dissolution efficiency, such that a larger volume of fluid, $PV$, (or, equivalently, longer time), is required to reach a given permeability, $K/K_0$. Consequently, the dissolution front progresses further downstream at a given $K/K_0$ value (see insets). At early times (low $K/K_0$), stress effect is more noticeable at $Da=1$, delaying the sharp rise in permeability. For example, the difference in $PV$ required to double the permeability ($K/K_0=2$) under $\sigma=60$ MPa vs. $\sigma=0$, is about five times larger for $Da=1$ ($\sim 45\%$, panel a) than for $Da=0.01$ ($\sim 10\%$, b). This trend is reversed later on: at breakthrough ($K/K_0=10$), the increase in $PV_{BT}$ is about five times larger at $Da=0.01$ than at $Da=1$. The curves represent ensemble averages from multiple realizations (see text).

permeability enhancement remains much more efficient at high $Da$, consuming about a third of the reagent volume at breakthrough.

The curves in Fig. 2 are obtained by ensemble averaging over multiple realizations, namely different sample geometry with similar statistical properties. As wormholing instability is more sensitive to the initial conditions than uniform dissolution—showing greater variability between realizations, more realizations were required to obtain a statistically-representative result: 200 for $Da=1$, vs. only 15 for $Da=0.01$. This provided a standard error in $PV_{BT}$ smaller than 1% (relative to the mean), and a standard deviation of $\sim10\%$ and $\sim1\%$ for $Da=1$ and $Da=0.01$, respectively.

### 3.2. Stress distribution

We explain the complex interplay between dissolution and compaction through the dynamic evolution of stiffness and stress distribution. While matrix dissolution in a region increases its compliance, the very same process has another, opposite effect: it decreases the load that region bears, since stiffer regions carry more of the load. The competition between these two mechanisms controls the compaction, affecting permeability. In particular, the permeability is governed by the least conductive region; here, this is the downstream region, which—being furthest away from the inlet—experiences the least dissolution. In both regimes, intensive dissolution upstream significantly increases the load downstream (Fig. 3). Even minute compaction of the less conductive downstream region (see flow resistance in insets of Fig. 3) intensifies the bottleneck effect, limiting the permeability. Insets in Fig. 3 show longitudinal resistance, $1/C_y$, normalized by the initial ($t=0$) average resistance.

The effect of stress depends on its spatial distribution, which in turn depends on the evolving dissolution pattern. For $Da=1$, dissolution is focused within the wormholes, creating a distinct dissolution front. Ahead of this front remains a wide undissolved and hence stiffer zone (extending from the most advanced wormhole tip to the outlet), upon which most of the load is distributed (Fig. 3). The elevated stress on this region, which hardly experiences dissolution until breakthrough, significantly retards the permeability enhancement (insets of Fig. 3). This decreases the transport heterogeneity, promoting wormhole competition (cf. Section 3.3). As the wormholes propagate, the stress is progressively relieved from the newly dissolved region, and increases downstream. Once the outlet starts eroding, the focused dissolution characteristic of wormholing becomes dominant, diminishing the bottleneck effect and providing a sharp permeability increase.

The behavior changes at $Da=0.01$: the rapid injection and incomplete reaction allows some reagent to propagate further downstream, resulting in a much more uniform dissolution and mechanical weakening throughout the sample. The continuous dissolution at the outlet region, experiencing both pore enlargement as well as its partial counteraction by compaction, leads to a steady, relatively-linear increase in the effect of stress on permeability (increasing the divergence among the curves in Fig. 2). The effect of stress, which is initially larger at $Da=1$, becomes more noticeable at $Da=0.01$ as breakthrough is approached.
Figure 3: We explain the permeability evolution through the spatiotemporal distribution of stress. Intense dissolution upstream increases its compliance, hence the load carried by the stiffer downstream region. Since the latter is also less conductive (insets), its compaction provides a strong bottleneck effect that constrains permeability. (a) For $Da=1$, the sharp dissolution contrast between the upstream and downstream regions amplifies the bottleneck effect at early times (low $K/K_0$). Once the dissolution (i.e. main wormhole) reaches the outlet, the effect of this mechanism becomes less noticeable. (b) In contrast, for $Da=0.01$, the incomplete reaction allows the dissolution to propagate throughout the sample, leading to a much smaller conductivity contrast. Dissolution at the outlet induces both pore enlargement and its partial counteraction by compaction, with a steady, continuous increase in the effect of stress on permeability. Near breakthrough, the impact of stress at $Da=0.01$ overtakes that at $Da=1$ (Fig. 2). Panels a–b show the local stress (normalized by the macroscopic stress, $\sigma = 60$ MPa) in the transverse direction, $\sigma^*_x$, responsible for compacting pores along the main flow direction. (c) Stress in the longitudinal direction, $\sigma^*_y$ (shown at $t=0$ and breakthrough), despite its high heterogeneity (attaining a maximum at the stiffer regions between the wormholes [8]) (Fig. 3c), has only a minor effect on permeability. Each curve represents an ensemble average at a given $K/K_0$ values; the corresponding volumes (normalized by $PV_{BT}$), $PV$, are also provided in the legend.

In our 1-D flow settings, pores parallel to the flow direction ($y$) mostly control the permeability. Therefore, we plot in Fig. 3a–b the local stress in the transverse direction, $\sigma^*_x$. The highly heterogeneous distribution of stress in the longitudinal direction, $\sigma^*_y$, where the stress is concentrated at the stiffer regions between the wormholes [8] (Fig. 3c), has only a minor effect on permeability.

3.3. Wormhole competition

A further quantitative insight into the impact of stress on the complex dynamics at high $Da$ can be provided from analyzing the pattern evolution. Stress increases the competition among wormholes, hence the number and length of secondary wormholes on the expense of the dominant wormhole (e.g. insets in Fig. 2a). Fig. 4a shows the relative increment in the number of wormholes at different confining stresses (compared to $\sigma = 0$), $\eta$, measured in three regions of width of 0.2$L$ (centred at $y=0.3$, 0.5 and 0.7$L$). A wormhole is defined here as a contiguous region which has been completely dissolved.

Heterogeneous dissolution due to heterogeneous transport, where the most advanced wormhole increasingly draws more fluid and thus propagates at the expense of less developed neighbors, is the mechanism responsible for the sharp increase in permeability (Fig. 2a). Application of stress reduces the transport heterogeneity, slowing down the propagation of the main wormhole, thus breakthrough. We demonstrate this quantitatively via a simple system consisting of two straight wormholes (Fig. 4b, inset), measuring the ratio of flow rates through the long and short wormholes, $\chi$. Increasing stress is shown to divert less of the flow into the main wormhole (lowering $\chi$), indicating a reduction in the degree of preferential fluid flow—and hence reagent transport (Fig. 4b).

Interestingly, stress was found to have an opposite effect—increasing transport heterogeneity—in a different system: non-reactive transport in a rough fracture [20]. The authors show that stress increases the number of solid-solid contacts, forcing the solute to pass through fewer, hence more preferential pathways. In our system, stress reduces the conductivity contrast among the wormholes, hence the dominance of the main wormhole. That is, stress promotes dissolution of smaller wormholes, reducing transport heterogeneity and dissolution efficiency.
4. Summary and conclusions

We study the permeability evolution in a stressed, deformable porous sample undergoing dissolution. We present a novel pore-scale model describing the coupling between (a) pore opening (chemical deformation) and (b) mechanical weakening and pore compaction. Our simulations point to a complex, unintuitive effect of stress. As the upstream region undergoes substantial dissolution, higher load is being carried by the stiffer downstream region. Since this region is also less conductive, even its small compaction has a significant bottleneck effect, such that larger injected volume (or equivalently, longer time) is required to reach a certain permeability.

The manner by which the permeability enhancement is curbed by stress depends on the dissolution regime ($Da$). At high injection rates (low $Da$), the relatively uniform dissolution (including downstream) leads to a steady increase in the effect of stress, caused by continuous dissolution at the outlet and its partial counteraction by compaction. In the wormholing regime (high $Da$), the undissolved region ahead of the dissolution front has an acute bottleneck effect. This acts to reduce transport heterogeneity, by decreasing the contrast between wormhole conductivity which promotes wormhole competition. At early times (low permeability), this mechanism strongly suppresses the permeability enhancement, much more than at low $Da$. Once the main wormhole approaches the outlet, this mechanism diminishes and focused reagent transport and dissolution leads to a sharp permeability rise. Consequently, close to breakthrough the impact of stress becomes larger at low $Da$. Our work improves the understanding of how the hydromechanical properties change with reactive transport, a process with important implications in natural engineered systems ranging from diagenesis and weathering of rocks, to well stimulation and carbon geosequestration.

Acknowledgments

We gratefully acknowledge financial support by the United States-Israel Binational Science Foundation (BSF-2012140), Israeli Science Foundation (ISF-867/13), and Israel Ministry of Agriculture and Rural Development (821-0137-13). We also thank T. Vanorio and A. Nur for valuable discussions.

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