Hydro-chemo-mechanical coupling in sediments: Localized mineral dissolution

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Abstract: Mineral dissolution is inherently a chemo-hydro-mechanical coupled process. Field evidence and laboratory results show that dissolution may localize and form open conduits in cohesive media such as carbonate rocks. This study focuses on the evolution of localized dissolution in soils (i.e., frictional and non-cohesive granular materials) under effective confining stresses. Experimental results show the development of localized dissolution (“pipe”) when a carbonate-quartz sand is subjected to reactive fluid flow: only loosely packed quartz grains remain within pipes, and the number of pipes decreases away from the inlet port. Concurrent shear wave velocity measurements show a decrease in stiffness during dissolution due to stress and fabric changes, and more complex signal codas anticipate the development of internal heterogeneity. The discrete element method is used to simulate localized vertical dissolution features in granular materials, under constant vertical stress and zero lateral strain far-field boundaries. As porosity increases along dissolution pipes, vertical load is transferred to the surrounding soils and marked force chains develop. In terms of equivalent stress, principal stress rotation takes place within pipes and the sediment reaches the Coulomb failure condition inside pipes and in the surrounding medium. Dissolution pipes alter the geo-plumbing of the subsurface, enhance fluid transport but limit the long term performance of storage systems, alter the fluid pressure and effective stress fields, soften the sediment and may trigger shear failures.

19 List of Symbols and Abbreviations

20

21	D	Chemical diffusion coefficient [m^2/s]
22	D_{10}	Grain diameter (in mm) corresponding to the 10% percentile by weight
23	D_{50}	Grain diameter (in mm) corresponding to the 50% percentile by weight
24	Da	Damköhler number
25	g	Gravitational acceleration
26	h	Representative vertical length scale
27	HR	percentage of rotationally hindered particles in a specimen
28	i	hydraulic gradient
29	ID	Inner diameter
30	k_0	Coefficient of at-rest lateral earth pressure
31	k_a	Coefficient of active and passive lateral earth pressure
32	l	Characteristic length scale of the problem [m]
33	n	Porosity
34	Pe	Péclet number
35	Ri	Richardson number
36	SF	Fraction of soluble particles
37	v	Flow velocity [m/s]
38	V_s	Shear wave velocity
39	α	shear wave velocity at $\sigma' = 1 \text{ kPa}$
40	β	stress sensitivity of the shear wave velocity
41	ϵ_h	Lateral strain conditions
42	ϕ	Sediment angle of internal shear strength
43	θ	Reaction rate constant [$1/\text{s}$]
44	σ	Effective stress ($\sigma_{\parallel}$ σ_{+} direction of propagation and particle motion; σ_1 σ_3 minor and
45		major principal stress)

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Introduction

Mineral dissolution and re-precipitation are common processes in the chemical weathering of soils and rocks, and typically involve changes in mineralogy towards more stable compositions within a given geologic environment. Layering and discontinuities, state of stress, changes in fluid chemistry and gravity-dominated fluid flow contribute to the development of preferential flow paths in sediments and rocks (Boggus and Crawfis, 2009, Criss et al., 2008, Gillieson, 1996). Vertical tubes are initiated by infiltration, while horizontal tubular cavities result from strata bound water flow (Ford and Williams, 2007). Dissolution is relatively slow in nature, yet, geological strata that contain carbonates or evaporites are particularly prone to dissolution in high fluid advection systems. Localized dissolution is the cause of sinkholes and settlements in karst regions and calcareous terrains (Waltham, 2009).

Human activity can move natural systems far from equilibrium, such as the injection fluids that change the natural pH and pumping-driven advective transport (Hunt, 2007, Veni et al., 2001). Accelerated dissolution rates caused by high hydraulic gradients undermine the performance of dams by increasing uplift pressure and accelerating seepage and piping (Gutiérrez et al., 2003, Payton and Hansen, 2003, Dreybrodt et al., 2002). The dissociation of load-bearing gas hydrate leads to instability in sediments and has been considered the cause of marine landslides (Rothwell et al., 1998, Sultan et al., 2004, Vogt and Jung, 2002, Freij-Ayoub et al., 2007). The geological storage of CO₂ acidifies pore water and causes mineral dissolution that may lead to porosity and mineralogy changes, settlement, and tensile fracturing of the seal rock (Watson et al., 2004, Espinoza et al., 2011, Renard et al., 2005, He et al., 2003, Le Guen et al., 2007, Kvamme and Liu, 2009). Dissolution and precipitation affects permeability changes over time in enhanced geothermal systems (Taron and Elsworth, 2009, Ledesert et al., 2010). Finally,

the consequences of dissolution extend beyond geosystems; for example, dissolution is one of the main causes of natural deterioration of Portland cement concrete by acid rain (Okochi et al., 2000, Xie et al., 2004), and demineralization makes bones porous and vulnerable to brittle fractures (Marcus et al., 2009).

Chemical reaction, advective mass transport, and diffusive transport rates control the evolving topology of dissolution. These can be captured in two dimensionless numbers in terms of flow velocity v [m/s], the characteristic length scale of the problem l [m], the chemical diffusion coefficient D [m²/s], and the reaction rate constant θ [1/s]:

$$\text{Péclet number} \quad \text{Pe} = \frac{vl}{D} = \frac{\text{Advective transport rate}}{\text{Diffusive transport rate}} \quad (1)$$

$$\text{Damköhler number} \quad \text{Da} = \frac{\theta l}{v} = \frac{\text{Reaction rate}}{\text{Advective transport rate}} \quad (2)$$

Experimental and numerical studies show dissolution topology in terms of Pe and Da numbers (Fredd and Fogler, 1998, Golfier et al., 2002, Hoefner and Fogler, 1988): (a) compact dissolution when $\text{Pe} < 10^{-3}$, (b) uniform dissolution when $\text{Da} < 10^{-3}$, (c) dissolution localization at high $\text{Da} > 10^{-2}$ and $\text{Pe} > 10^{-2}$ numbers. In addition, density variation in the fluid affects dissolution morphologies due to gravity (Luo et al., 2012); buoyancy prevails over advection when the Richardson number $\text{Ri} = gh/v^2 \geq 1$, where g is the gravitational acceleration and h is a representative vertical length scale (Oltéan et al., 2013).

Previous studies reveal that homogeneously distributed particle-scale dissolution affects both the small and large-strain properties of sediments (Cha and Santamarina, 2014, Tran et al., 2012, Truong et al., 2010, Muir Wood et al., 2010): a distinct “honeycomb fabric” emerges (Shin et al., 2008), vertical displacement and void ratio increase (Fam et al., 2002, Truong et al., 2010, Shin and Santamarina, 2009, Lee et al., 2012, McDougall et al., 2013), the stress ratio between

horizontal to vertical effective stress k_0 decreases often to Rankine- k_a failure condition (Shin and Santamarina, 2009), shear wave velocity decreases and attenuation increases (Truong et al., 2010, Fam et al., 2002), and the peak friction angle decreases (Fam et al., 2002). Furthermore, fluid permeability changes (Zheng and Elsworth, 2012), and strain localization may emerge (Shin et al., 2008). Hu and Hueckel (2007) and Pietruszczak et al. (2006) introduced important concepts and models of chemo-mechanical couplings for granular contact dissolution and deformation.

This study centers on coupled chemo-hydro-mechanical processes during dissolution in uncemented granular materials under effective confining stress. First, experimental evidence is presented for the emergence of localized dissolution in sediments. Then, discrete element numerical simulations are conducted to gain particle-level insight on the mechanical consequences of localized dissolution in soils.

Experimental study

Device and materials. The experimental study is conducted using a quartzitic-carbonate sandy sediment from the Atlantic coastal plains in Georgia, USA ($D_{10}=0.25\text{mm}$; $D_{50}=0.8\text{mm}$; 100% passes sieve #10 and is retained on sieve #100. Composition: 52% calcite, 47% quartz, and trace of clay minerals). The chamber is a zero-lateral strain cell (stainless steel cell, ID=100mm - Figure 1); the lower and upper loading plates have a dense groove pattern beneath porous stones to ensure even 1D flow. A linear variable differential transducer LVDT attached to the loading plates tracks the sediment vertical displacement. Piezo-ceramic bender elements installed at the bottom and top plates are used to monitor the evolution of shear wave velocity in the sediment throughout the experiment. Fluid flow is imposed through the bottom plate.

116
117 *Procedure.* The dry sediment is prepared in a zero-lateral strain cell (stainless steel cell,
118 ID=100mm; 60mm sediment height - Figure 1), and then loaded in several steps to 200kPa
119 vertical stress. While subjecting the sediment to a constant 200kPa vertical stress: (1) 9 liters
120 (~20 pore volumes) of tap water are passed through the sediment to saturate it; (2) a slight
121 settlement observed during and after the water flow due to soil wetting is fully stabilized and the
122 sediment is allowed to chemically equilibrate with the introduced pore water for 72 hours; (3) 12
123 liters (~25 pore volumes) of 1 molar solution of acetic acid CH_3COOH are injected through the
124 bottom porous stone at a constant hydraulic gradient ($i=35$) while effluent is collected from the
125 top cap; then, (4) fresh water is flushed through the sediment to stop chemical reactions. Finally,
126 the sediment is further loaded 900kPa vertical effective stress to compare the pre and post
127 dissolution compressibilities. After unloading, the specimen is carefully extruded from the cell,
128 and subjected to tomographic imaging, followed by slicing for visual inspection and mineral
129 analysis.

130
131 *Results.* Load-dissolution tests were repeated with various specimens subjected to different
132 vertical effective stress levels ($\sigma_z=200$ and 400 kPa), flow rates, and molar concentrations of
133 acetic acid.

134 Specimens settle almost linearly with time during reactive fluid flow until fresh water is
135 flushed through the sediment to remove acid (Figure 2). Void ratio is calculated using recorded
136 vertical deformation (thus volume) and measuring dry soil weight before and after dissolution
137 tests. Specimens also settle almost linearly with the log of the applied vertical stress during
138 loading (Figure 3). The volume-average global void ratio increases during dissolution (from

e=0.64 to e=0.75 for the case reported in Figure 3). The sediment compressibility $\Delta e / \log[(\sigma + \Delta\sigma)/\sigma]$ is higher after dissolution than before dissolution (almost doubled in Figure 3), and the post-dissolution sediment has an increased tendency to volumetric contraction upon loading.

The shear wave velocity experienced a pronounced drop during dissolution even though the effective stress remained constant (Figure 3). Signature codas gained marked complexity during dissolution (not shown), anticipating the increased spatial variability evolving inside the specimen.

Tomographic images reveal the presence of distinct low-density vertical columns; the localized dissolution structure is confirmed by gradually shaving sediment layers from the top, as shown in Figure 4 where dark brown regions show the volume affected by dissolution surrounded by the light colored natural sediment. We will call this low-density regions resulted from localized dissolution as “pipe” to highlight its function as a high-permeability path. In the similar context, “wormholes” are used for dissolution cavities created in carbonate rocks (Fredd and Fogler, 1998, Golfier et al., 2002). Unlike complete voids in wormholes, pipes in our study are filled with insoluble or less soluble grains such as quartz.. XRD results show that the mineralogy of the background medium consists of both quartz and calcite, but that only quartz remains in pipes i.e., there has been a ~52% mass loss in pipes (Figure 4). Calcite has been completely dissolved at the inlet surface due to its direct contact with acid solution; some pipes are fully formed from inlet to outlet, while others appear as abandoned pathways. From volumetric analyses and X-ray intensity, the internal porosity in pipes is estimated to be $n=0.47$.

Discrete Element Simulation

Discrete element simulations represent the sediment as an arrangement of individual particles in a Newtonian mechanics framework (Cundall and Strack, 1979). The discrete element code PFC (ITASCA Consulting Group, Inc.) is used to study the geo-mechanical implications of localized dissolution both in 2D and 3D conditions in order to gain particle-scale insight during localized dissolution. The simulation environment is summarized in Table 1. The interparticle friction coefficient is 0.5, and there is no friction between grain and the rigid lateral boundaries (i.e., zero-lateral strain conditions $\epsilon_h=0$). In both 2D and 3D cases, the granular packing is formed by randomly placing small grains with uniform size distribution in a container and gradually expanding them under zero gravity and zero interparticle friction to attain the target porosity (similar approach to (Bagi, 2005, O'Sullivan, 2011)). The gradual expansion process involves a re-equilibrium stage before attempting the next expansion step; more than 5000 expansion-equilibration cycles are conducted to form the granular packing.

Grain angularity implies rotational resistance and it is simulated by hindering the rotation of a fraction of randomly selected grains (Percentage of particles with hindered rotation in a specimen HR=0% for “round particles” and 80% for “angular particles”). The vertical stress is kept constant during dissolution using a numerical servo-control function. The positions and sizes of vertical columnar regions that will undergo dissolution, and insoluble regions (“host”) are predefined in the sediment, and soluble particles (in red) are chosen at random (Table 1). The fraction of soluble particles within the columns are SF=25% and 50% in 2D, and SF=50% and 100% in 3D simulations. Dissolution is simulated by gradually decreasing the size of all the soluble particles over time at the same rate. The gradual size reduction involves numerous steps of minute size reduction (radius reduction of 1/50000 times initial radius in each step), each step followed by a full equilibrium stage. In particular, the ratio of the mean unbalanced force to the

mean contact force is always smaller than 0.001 to ensure stable conditions throughout the dissolution processes. The results subset presented next adequately represents all trends observed in this study (complete results in Cha (2012)).

Normalized vertical displacement (Figure 5a). While dissolution takes place in soluble columns only, sediments settle almost linearly with the mass loss of soluble grains SF during early stages of dissolution (the mass loss is captured using the normalized size reduction $\Delta R/R_0$ – similar response was experimentally observed). Angular sediments HR=80% experience lower vertical displacement particularly in 3D simulations due to higher interlocking and rotational frustration that hinders particle rearrangement.

Porosity (Figure 5b). Porosity increases within dissolved regions (pipes) and to a lesser extent in the surrounding medium. Interlocked sediments with hindered rotation (HR=80%) experience a higher increase in porosity. Sudden collapse events in angular interlocked sediments are accompanied by changes in porosity.

Equivalent global stress ratio $k_0 = \sigma_h/\sigma_v$ (Figure 5c). Equivalent stresses can be readily computed from inter-particle forces and affected areas. The equivalent horizontal stress σ_h acting against the boundaries in both 2D and 3D systems increases in sediments with no interlocking (HR=0%) during early stages of dissolution, but it decreases in interlocked sediments (HR=80%). Similar trends have been numerically and experimentally observed when dissolving grains are homogeneously distributed throughout the sediment (Cha and Santamarina, 2014, Shin and Santamarina, 2009).

Contact force chains. Force chains are strong in the vertical direction before dissolution, in agreement with principal stress directions. After dissolution, marked force chains remain preferentially vertical away from pipes, yet, they are preferentially horizontal within pipes (Figure 6). In fact, horizontal contact forces inside pipes prevent the buckling of granular columns in the surrounding sediment. As dissolution continues, surrounding soils slide towards the looser pipes, and structural differences between the two zones become less prominent (Figure 6c).

Discussion and implications

Experiments and simulations were designed to gather complementary information. General trends clearly show strong parallelisms between experimental and numerical results, in particular, linear settlement with the progression of dissolution and increased porosity in pipes and global (experiment: $n=0.39$ to 0.43 ; 3D numerical: $n=0.40$ to 0.43 for $HR=0\%$ and $n=0.40$ to 0.48 for $HR=80\%$). Innate differences between numerical and experimental conditions hinder further quantitative comparisons, due to bottom-up vs. simultaneous dissolution, random vs. predetermined pipe location, natural grains vs. spherical particles with hindered rotation).

The analysis of particle-scale forces in terms of equivalent stresses can be extended to explore the interaction between grains in pipes and in the surrounding host medium. The equivalent vertical stress increases rapidly in the host medium when dissolution starts in pipes, as vertical load is shed to the host medium (Figure 7 – Note: global vertical equilibrium with boundary loads is verified in all cases). In the horizontal direction, horizontal stresses σ_h in pipes and host are almost identical $\sigma_{h|pipe} \approx \sigma_{h|host}$, in agreement with equilibrium requirements.

Principal stresses rotate inside pipes during dissolution as the vertical stress decreases and the horizontal stress increases to become the major principal stress. The peak equivalent global stress ratio $\sigma_1/\sigma_3|_{\max}$ reaches the Coulomb failure condition $\sigma_1/\sigma_3 = \tan^2(45-\phi/2)$ both in the pipes and in the host medium.

The shear wave velocity V_s followed a Hertzian power-type trend during loading, both before and after dissolution (Figure 3). In uncemented granular materials, the shear wave velocity is determined by the mean stress in the polarization, i.e., the average between the stress in the direction of propagation σ_1 and in the direction of particle motion σ_+

$$V_s = \alpha \left(\frac{\sigma_1 + \sigma_+}{2 \text{ kPa}} \right)^\beta \quad (3)$$

Fitted parameters before ($\alpha = 74 \text{ m/s}$, $\beta = 0.226$) and after dissolution ($\alpha = 28 \text{ m/s}$, $\beta = 0.394$) show higher stiffness sensitivity to stress after dissolution. This is in agreement with the higher sediment compressibility after dissolution observed in experimental results (Figure 3), i.e., there is a rapid increase in coordination number when loosely packed grains are subjected to loading. These results fall in with data compiled for loose and densely packed natural soils worldwide (Cha et al., 2014). The shear wave velocity dropped from 274 m/s to 199 m/s during dissolution at constant vertical effective stress σ_1 (Figure 3). Given that the horizontal stress cannot be smaller than the condition at Coulomb failure, $\sigma_+ \geq \sigma_1 \tan^2(45-\phi/2)$, this marked decrease in velocity cannot be justified by a decrease in transverse stress σ_+ alone (Equation 3). Hence, shear-wave velocity tracks changes in stiffness due to the applied stress and due to fabric changes associated with dissolution.

The highly porous flow paths created by localized dissolution alters the “geo-plumbing” of the subsurface by creating highly permeable conduits underground that facilitate flow. These

hydraulic short-circuit paths can be engineered to enhance fluid transport (e.g., acid treatment for enhanced oil recovery); however, their emergence often diminishes system efficiency (e.g., enhanced geothermal systems), or limit the long term performance of storage systems (e.g., dams and CO₂ geological storage). Furthermore, localized dissolution pipes bring high fluid pressure fronts towards the outlet, increase the hydraulic uplift pressure, heighten the vulnerability to retrogressive piping erosion, lower the effective stress in the medium, and systems subjected to shear may experience failure (e.g., slopes).

The nucleation of localized dissolution in rocks is often associated to the presence of high conductivity natural fractures or interlayers with hydraulic conductivity contrast. Dissolution evolves as a consequence of gravity, convection and advection and creates open cavities and conduits. Karst topology is a salient example.

In contrast, dissolution pipes in soils emerges as a consequence of the spatially-correlated pore size variability in natural sediments whereby most of the flow takes place through a small fraction of the pore space (Jang et al., 2011). Under these conditions, reactive fluid transport creates the positive feedback conditions to favor dissolution along the already more pervious paths. However, open cavities cannot form in uncemented sediments, and neighboring sediments continue yielding into dissolving channels until they are filled with loosely packed insoluble grains. Therefore, the formation of dissolution pipes in soils is inherently a coupled hydro-chemo-mechanical phenomenon.

The modified pressure and flow fields around a pipe hinder the formation of other pipes nearby. The exclusion distance decreases and the pipe density increases with increasing flow rate (Cohen et al., 2008, Golfier et al., 2002). Longer pipes reach closer to the outlet, have higher exit gradients, transport more fluid, grow faster than smaller ones, and there is a lower pipe density

towards the outlet (Buijse, 2000) as observed in Figure 4.

Conclusions

Hydro-chemo-mechanical coupling can lead to dissolution localization in single- and multi-mineral sediments. The number of dissolution pipes decreases away from the inlet port. While porosity increases within pipes, empty cavities cannot form in cohesionless sediments. The sediments that have undergone localized dissolution are more compressible than pre-dissolution sediments.

Marked force chains form within pipes and in the surrounding medium as a result of internal unloading and pronounced force redistribution during dissolution. In terms of equivalent stresses, principal stress may rotate inside pipes, and the stress ratio may reach the Coulomb failure condition both in pipes and in the host medium.

Concurrent geophysical monitoring using shear-wave propagation reflects undergoing changes in stiffness due to both changes in effective stress (Hertzian effect) and fabric evolution during dissolution. More complex signal codas reveal the development of internal heterogeneity.

Dissolution pipes alter the geo-plumbing of the subsurface, enhance fluid transport but limit the long term performance of storage systems, alter the fluid pressure and effective stress fields, soften the sediment and may cause shear failure.

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Table 1. DEM simulation environment

	Properties	2D	3D
Particle properties	Configurations - insoluble (“host”) and soluble regions	vertical cross section	horizontal cross section
	Particle size distribution	Uniform size distribution ($R_{\min}=0.3\text{mm}$, $R_{\max}=0.45\text{mm}$)	Uniform size distribution ($R_{\min}=1\text{ mm}$, $R_{\max}=1.5\text{ mm}$)
	Number of particles	11272 disks	9167 spheres
	Particle density	2650 kg/m^3	2650 kg/m^3
	Contact model	Linear contact model -Normal stiffness $k_n = 10^8\text{ N/m}$ -Shear stiffness $k_s = 10^8\text{ N/m}$	Hertzian contact model -Shear modulus $= 2.9 \times 10^9\text{ Pa}$ -Poisson's ratio $= 0.3$
	Inter-particle friction	0.5	0.5
	Hindered rotation HR	0% and 80%	0% and 80%
	Fraction of soluble particles in predefined soluble regions SF	25% and 50% (red particles in the configuration above)	50% and 100% (red particles in the configuration above)
Boundary conditions	Initial cell size	(Height $\times$ Width) $6\text{ cm} \times 10\text{ cm}$	(Height $\times$ Width $\times$ Length) $5\text{cm} \times 5\text{cm} \times 5\text{cm}$
	Vertical load	100 kPa (during dissolution)	100 kPa (during dissolution)
	Lateral boundaries	Zero strain	Zero strain
	Particle-to-wall friction	0	0

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Figure 1. Experimental study of dissolution in a zero-lateral strain cell. 1D flow is enforced at constant inlet fluid pressure. Note: piezocrystal bender elements BE are used for shear wave generation and detection.

Figure 2. Vertical strain versus time during the reactive flow.

Figure 3. Void ratio and shear wave velocity changes during ① loading, ② reactive fluid transport and dissolution, and ③ additional loading. Device shown in Figure 1.

Figure 4. Specimen dissection by successive layer removal. Slices at various depths show localized carbonate dissolution. The light-color sand has both carbonate and quartz; the dark-color sand patches are the carbonate-free pipes after dissolution. Mineral composition: XRD spectra correspond to the carbonate-quartz around pipes, and the non-soluble quartz grains that remain in pipes.

Figure 5. Sediment response during localized dissolution under zero lateral strain. 2D and 3D numerical simulations (a) Normalized vertical displacement. (b) Porosity. (c) Equivalent global stress ratio $k = \sigma_h / \sigma_v$. Note: grains in the “host” medium experience no dissolution while SF=50% of grains in pipes dissolve. Simulation details in Table 1.

	Hindered rotation HR=0%	Hindered rotation HR=80%
(a) After k_0 loading
(b) During dissolution at min. k
(c) After dissolution

Figure 6. Evolution of contact force chains during localized dissolution along pipes (2D and SF=50% within the pipes). (a) After zero lateral strain loading and before dissolution. (b) During dissolution at minimum stress ratio $k=\sigma_h/\sigma_v$. (c) After complete dissolution. Note: The network of contact lines is drawn with thickness proportional to normal contact forces. Simulation details in Table 1.

Figure 7. Evolution of the equivalent horizontal σ_h and vertical σ_v stresses normalized by the constant vertical stress applied during dissolution. Trends shown for sediments in pipes and in the host medium (Note: 2D simulation; SF=50% within the pipes; hindered rotation HR=80%). Simulation details in Table 1.