A conceptual model for the chemo-mechanical degradation of granular geomaterials

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A conceptual model is presented, the main aim of which is to elucidate the microscopic origins of the chemo-mechanical coupling in granular geomaterials. The study focuses on the interplay between the inelastic response under high compressive stresses and the chemical reactions leading to mineral dissolution. Chemical and mechanical processes are incorporated within a thermodynamic framework in which energy storage mechanisms depend on microstructural properties. Coupling between the two processes is reproduced through a simplified microscopic idealisation that establishes a link between the evolving microstructure (i.e., particle size geometry) and a chemical state variable. The mechanical implications at the continuum scale are finally derived through statistical homogenisation. The results disclose a relation between the evolution of the elastic properties of a chemically weathered geomaterial and the yielding threshold under high compressive stresses. Such dependency is obtained as an emergent property by advocating that the main contribution to the mechanical dissipation derives from the brittle breakage of the mineral compounds. This result stresses the importance of identifying the key physical processes that regulate macroscopic inelastic phenomena and can constitute a conceptual springboard for the development of chemo-mechanical models.

KEYWORDS: chemical properties; constitutive relations; elasticity; particle crushing/crushability; theoretical analysis

INTRODUCTION
Societal interest in technologies such as carbon dioxide sequestration (Wawersik et al., 2001) and underground storage of hazardous waste (Gens, 2010) has promoted renewed attention in the chemo-mechanics of porous media exposed to aggressive environments. The response of rock formations to the introduction of external substances is indeed coupled with physico-chemical processes that have potential mechanical implications. Prior studies have explored the role of chemical degradation on the evolution of earth pressure coefficients, in situ stresses, porosity and shearing resistance (Lumb, 1962; Taylor, 1988; Hueckel, 1997; Shin and Santamarina, 2009). Laboratory studies focused on the inelastic nature of these mechanical processes (Castellanza & Nova, 2004) have suggested that they could be reproduced by incorporating convenient chemical state variables into strain-hardening plasticity models (Nova et al., 2003). More recently, similar concepts have been used to explain creep in saturated geomaterials (Hu & Hueckel, 2007a) or to investigate the chemo-mechanics of intergranular contacts through multi-scale techniques (Hu & Hueckel, 2007b).

This note shares the latter ideas and aims at developing a continuum approach that incorporates mechanical and chemical variables in a unified framework. At variance with prior formulations, however, chemo-mechanical state variables are defined in the light of a micromechanically based thermodynamic framework. This choice is motivated by the goal of reconciling the phenomenological response predicted by continuum chemo-mechanical models with the evolution of the microstructure and the physical mechanisms of energy storage/dissipation.

THERMODYNAMICS OF CHEMICAL DEGRADATION PROCESSES
Chemo-mechanical processes have been addressed in the context of continuum thermodynamics by several authors (e.g. de Groot & Mazur, 1962; Kestin, 1968; Hueckel, 2005). Hereafter, the mathematical formalism adopted by Coussy (2004) is followed. Guidance for selecting an appropriate set of chemo-mechanical state variables is given by the second principle of thermodynamics, which, for an isothermal process, can be expressed as

$$\delta \Phi = \sigma' \delta \varepsilon + \mu_{sol} \delta m_M - d\Psi \geq 0$$

(1)

where $\delta \Phi$ is the energy dissipation increment (with the symbol $\delta$ indicating that $\delta \Phi$ is not a proper differential form) and $d\Psi$ is the differential of the Helmholtz free energy of the skeleton $\Psi$. The above expression includes

(a) the incremental work done for deforming a porous saturated skeleton, $\sigma' \delta \varepsilon$ ($\sigma' = \sigma - \mu_{sol} \delta \varepsilon$ being the effective stress tensor, $\sigma$ the total stress tensor, $\mu_{sol}$ the pressure of the pore solution and $\delta \varepsilon$ the Kronecker’s delta)

(b) the energy supply for the introduction of minerals in solution, $\mu_{sol} \delta m_M$ ($\mu_{sol}$ being the chemical potential of the dissolved mineral and $m_M$ the mass of solid mineral per total unit volume).

Equation (1) derives from the balance equations for the porous medium. In particular, the mass balance for solid and dissolved minerals allows eliminating the mass transfer term between these two species (Coussy, 2004), thus using only $m_M$ as chemical state variable.
A convenient expression for the Helmholtz free energy of the skeleton is

\[ \Psi = \Psi^M(e_{ij}, m_M, \xi) + \Psi^C(m_M) \] (2)

which includes a mechanical term associated with the elastically stored energy (\(\Psi^M\)) and a term related to the chemical potential of the mineral in the skeleton (\(\Psi^C\)). The chemical contribution to the free energy can be expressed as \(\Psi^C(m_M) = \mu_M m_M\), with \(\mu_M\) being the chemical potential of the solid in the non-deformed configuration. For the sake of generality, the state variables of \(\Psi^M\) include the elastic strains \(e_{ij}\), the mineral mass \(m_M\) and a vector of internal variables \(\xi\) associated with irreversible mechanical processes.

Energy dissipation involves terms deriving from both mechanical processes (\(\delta \Phi^M\)) and chemical dissolution of mineral species (\(\delta \Phi^C\)), and can be expressed as

\[ \delta \Phi = \delta \Phi^M + \delta \Phi^C \geq 0 \] (3)

If both terms \(\delta \Phi^M\) and \(\delta \Phi^C\) are restricted to be positive, the combination of equations (1) and (2) implies

\[ \delta \Phi^M = \sigma_{ij} d_{ij} - \frac{\partial \Psi^M}{\partial e_{ij}} d_{ij} - \frac{\partial \Psi^M}{\partial \xi} \Rightarrow 0 \] (4a)

\[ \delta \Phi^C = (\mu_{sol} - \mu_M) dm_M \geq 0 \] (4b)

where

\[ \mu_M = \mu_{M0} + \frac{\partial \Psi^M}{\partial m_M} \]

indicates the chemical potential of the mineral bound in the solid skeleton. Equations (4a) and (4b) impose a stronger thermodynamic constraint than equation (3) and allow chemical and mechanical processes to be restricted in a separate manner. For instance, equation (4b) restricts the direction of the chemical process, identifying \(E_{\text{CHEM}} = \mu_{sol} - \mu_M\) as the driving thermodynamic force of the reaction.

When the chemical potential of the solid mineral exceeds that of the mineral in solution (\(\mu_{sol} < \mu_M\)), equation (4b) is associated with a dissolution process (\(dm_M < 0\)), while if \(\mu_{sol} > \mu_M\), mineral precipitation is predicted (\(dm_M > 0\)). It is interesting to note that non-negligible values of \(\partial \Psi^M/\partial m_M\) imply coupling between the deformation of the skeleton and the chemical process (a relevant example being pressure solution phenomena (Ghoussoub & Leroy, 2001; Hu & Hucckel, 2007b)). Similarly, \(\delta \Phi^M\) in equation (4a) depends on the assumptions on the irreversible mechanical processes, and in the simple case of an elastic skeleton (i.e. \(d_{ij} = d_{ij}\)), mechanical dissipative contributions are reflected by the variation of the internal variables \(\xi\) only (i.e. \(\delta \Phi^M = -\mathbf{E}_c \delta \xi \geq 0\), with \(\mathbf{E}_c = -\partial \Psi^M/\partial \xi\) representing a set of inelastic thermodynamic forces). The description of irreversible processes requires complementary evolution laws linking the thermodynamic forces to their associated state variables. Such laws allow addressing reaction kinetics and mechanical dissipative processes through a similar mathematical formalism and are often defined in a phenomenological manner, being inspired by considerations on how stiffness (Carde & Francois, 1997), damage patterns (Gerard et al., 1998) and plastic yielding properties (Castellanza & Nova, 2004) evolve with changes in chemical composition. Micromechanical arguments, however, can elucidate how chemo-mechanical properties (e.g. reaction rate constants or chemically driven inelasticity) depend on the microstructure, therefore enriching the usual continuum formulations.

The following part of this article will attempt to illustrate these dependencies on the basis of simple mechanical and geometrical considerations at particle scale. Since the aim of this work is to focus on the mechanical aspects of the problem, however, the following section will not concentrate on the detailed description of the kinetics of the reaction. On the contrary, only dissolution effects will be incorporated at the particle scale through a simplified procedure, with the goal of describing their mechanical implications across the microscopic and continuum scales of granular assemblies.

**CHEMO-MECHANICS OF BRITTLE YIELDING: LINKING MICROSCOPIC AND CONTINUUM SCALES**

Aggressive agents are usually hosted into pore fluids. As a result, porous natural media such as granular sedimentary rocks are particularly prone to chemical degradation. Under high compressive stresses, the inelastic response of such geomaterials is controlled by both the cement matrix and the particle skeleton (Fig. 1(a)) (Leroueil & Vaughan, 1990; Wong et al., 2003). In this work, however, it will be assumed that the granular structure plays a dominant role in the mechanisms of force transmission and energy storage (Fig. 1(b)). This simplification is convenient for describing energy dissipation in compressed heterogeneous media in which the stress-bearing microstructures are characterised by an evolving geometry. The following developments are therefore obtained with reference to an idealised weakly bonded granular material (Fig. 1(c)), bearing in mind that, to a certain extent, they can also be applied to other geomaterials in which the granular skeleton is the main component involved in the process of stress transmission (Das et al., 2011).

Given the above assumptions, the initiation of yielding can be studied through the breakage mechanics theory (Einav, 2007a, 2007b), which assumes that an evolving particle size distribution (PSD) can be represented through a scalar variable \(B\), called breakage, which spans from \(B = 0\) (unbroken material) to \(B = 1\) (complete breakage). In order to incorporate the microscopic effects of chemical degradation within the theory, mineral dissolution processes are described as a chemically driven change in particle geometry. An idealisation of this notion is represented in Fig. 2, in which a portion of the mass constituting the initially non-weathered particles is dissolved by a chemical reaction. Although mineral degradation processes are likely to induce a complex change in particle geometry (Fig. 2(b)), the ideal scheme of spherical particles is here maintained (Fig. 2(c)), with the goal of devising a straightforward strategy for expressing the change in particle size as a function of the dissolved mass. In addition to the above assumptions, in the following it will be assumed that energy redistribution primarily involves the granular skeleton. It is worth noting, however, that the presence of a weak cementation is maintained at a notional level, with the conceptual role of inhibiting significant changes of the granular topology.

To represent the contraction in size of the chemically weathered particles, it is convenient to introduce a degradation index \(X_d\)

\[ X_d = 1 - \frac{m_{M0}}{m_{M1}} \] (5)

where \(m_{M0}\) is the initial mass content of the fresh rock. The index given by equation (5) spans from \(X_d = 0\) (fresh...
Fig. 1. Microscopic idealisation of the microstructure of sedimentary porous rocks. (a) Assembly of particles in a cement matrix. (b) Idealised microstructure consisting of spherical particles connected by cement bonds. (c) Skeleton of spherical particles (here assumed as the main stress-bearing microstructure).

Fig. 2. (a) Sketch of non-weathered spherical particles (cement is included for illustration purposes only). (b) Geometrical effects of microscopic chemical degradation processes (e.g., mineral dissolution). (c) Idealised scheme for chemically weathered microstructure consisting of spherical particles. (d) Homothetic contraction of the particle distribution in a chemically weathered material (PSDs are assumed to be initially uniform until breakage is initiated).
material) to \( X_d = 1 \) (complete degradation). By further assuming that the mass is proportional to the volume of the particles \((m_M \sim x^3, x \text{ being the particle size})\), it is possible to relate \( X_d \) to the average particle size of a weathered material, \( x_D \), as follows.

\[
X_d = 1 - \left( \frac{x_D}{x_0} \right)^3
\]  

(6)

Equation (6) leads to a simple relation between current particle size and degradation index

\[
x_D = x_0 (1 - X_d)^{1/m}
\]  

(7)

where \( m \) is a positive scaling parameter that, according to equation (6), can be assumed to be \( m = 3 \). However, given the complex microscopic geometries that can be originated (Figs 2(b) and 2(c)), in the following \( m \) will be considered as a free parameter to be assessed from more detailed information on the degradation process.

Equation (7) allows definition of the probability density functions for initial and ultimate PSDs of weathered assemblies

\[
g_0(x, X_d) = \delta(x - x_D)
\]  

(8a)

\[
g_d(x, X_d) = (3 - x) \left( \frac{x}{x_0} \right)^{3/2 - x} \left( \frac{x_D}{x_0} \right)^{1/2 - x}
\]  

(8b)

where \( \delta(\cdot) \) is the Dirac delta function and \( x_D(Y_d) \) introduces the dependence of the particle size on the chemical process. For ease of mathematical manipulation, the initial PSD represented by \( g_0(x, X_d) \) is assumed to be uniform, while a fractal power law is used for the ultimate grading (here represented by \( g_d(x, X_d) \)), \( x \) being the fractal dimension (here, \( x = 2.7 \) (Sammis et al., 1986)). It is worth noting that the mathematical expressions given by equations (6)–(8) derive from assuming a uniform particle size for the fresh rock and a homothetic contraction of the weathered particles (Fig. 2(d)). Removal of these assumptions would require a detailed description of the reaction kinetics and a study of how particle dissolution is influenced by the initial geometrical properties of the assembly (which are both beyond the objectives of this letter).

The above assumptions on initial and ultimate PSDs allow one to write the current particle grading as a function of the breakage index \( B \) (Einav, 2007a)

\[
g(x, X_d, B) = g_0(x, X_d)(1 - B) + g_d(x, X_d)B
\]  

(9)

Since the evolution of the PSD depends on both chemical processes and particle breakage, a homogenisation procedure can suggest the appropriate analytical expression for \( \Psi^M \). Following Einav (2007a), the Helmholtz free energy stored in particles of size \( x \) can be expressed as a function of elastic strains and particle size

\[
\Psi^M(e^{e_x}, x) = \Psi^M(e^{e_x}) f(x)
\]  

(10)

where \( \Psi^M \) indicates the strain energy stored in a reference particle size \( x_R \), while \( f(x) \) is a scaling function given by

\[
f(x) = \left( \frac{x}{x_R} \right)^n
\]  

(11)

in which \( n \) is a scaling parameter. In order to maintain a unique reference dimension for equation (11) during the weathering process, the reference particle size is assumed to coincide with the initial size of the fresh particles \( (x_R = x_0) \).

The homogenised Helmholtz free energy, \( \Psi^M \), is finally obtained through statistical homogenisation, where the current PSD in equation (9) is used to weigh the grain-size-dependent contributions given by equation (10)

\[
\Psi^M(e^{e_x}, X_d, B) = \int_{x_a}^{x_d} \Psi^M(e^{e_x}) g(x, X_d, B) \, dx
\]  

(12)

\[
d_m \psi_0(X_d) \int_{x_a}^{x_d} g(x, X_d, B) f(x) \, dx
\]  

where \( d_m \) and \( d_M \) are the minimum and maximum particle sizes respectively (here \( d_m = 0 \) and \( d_M = x_0 \)). By combining equations (9) to (12), it follows that

\[
\Psi^M(e^{e_x}, X_d, B) = [J_0(X_d)(1 - B) + J_d(X_d)B] \psi(e^{e_x})
\]  

(13)

in which \( J_0(X_d) \) and \( J_d(X_d) \) are two grading indices, given by

\[
J_0(X_d) = (x_D)^{\gamma}(x_0)^{-\gamma} = (1 - X_d)^{n/m}
\]  

(14a)

\[
J_d(X_d) = \left( \frac{3 - x}{3 + n - x} \right) (x_D)^{\gamma}(x_0)^{-\gamma} = \left( \frac{3 - x}{3 + n - x} \right) (1 - X_d)^{n/m}
\]  

(14b)

By introducing the index \( \psi_0 = 1 - \left( \frac{3 - x}{3 + n - x} \right) \), it is finally possible to simplify equation (13) as follows

\[
\Psi^M(e^{e_x}, X_d, B) = (1 - X_d)^{\gamma/m}(1 - \psi_0 B) \psi_0^M(e^{e_x})
\]  

(15)

The statistical homogenisation introduces a dependence of the Helmholtz free energy on both the breakage index \( B \) and the degradation index \( X_d \), having that \( \Psi^M \) is expressed as a function of two variables with a clear physical meaning.

The state of stress and the yielding threshold for a given state of degradation are obtained by combining equation (15) with a mathematical representation of \( \psi_0^M \). Hereafter, for the sake of simplicity, a quadratic expression is assumed, corresponding to a linear elastic skeleton

\[
\psi_0^M(e^{e_x}) = \frac{1}{2} K_{0e} e^{e_x}^2 + G_{0e} e^{e_y} e^{e_y}
\]  

(16)

where \( K_{0e} \) and \( G_{0e} \) are the bulk and shear modulus of the fresh and unbroken material, respectively, and \( e^{e_y} = e^{e_y} - \frac{1}{3} \varepsilon_{kk} \delta_{kk} \) represents the deviatoric elastic strains. It is then possible to evaluate the isotropic stress prior to the initiation of particle breakage

\[
p' = \frac{\sigma_{kk}}{3} = \frac{2}{3} \frac{\Psi^M}{\varepsilon_{kk}} = (1 - X_d)^{\gamma/m}(1 - \psi_0 B) K_{0e} e^{e_x}
\]  

(17)

which shows that the index \( X_d \) is associated with the chemical degradation of the stiffness, thus reproducing a chemical damage effect that is conceptually similar to that observed in chemically weathered cement-based materials (Gerard et al., 1998; Le Bellégo et al., 2003; Ulm et al., 2003).

By using the breakage mechanics formalism (see the Appendix for more details on this procedure), it is finally possible to incorporate equation (17) in the breakage yield criterion (equation (23)) and evaluate the yield stress for the current value of \( X_d \).
where $p_{B0}'$ indicates the yield threshold of the fresh and unbroken material and $E_{c0}$ is a constant of integration associated with the specific energy supply that is necessary for initiating particle breakage.

The use of a constant reference grain size for any state of chemical degradation allows evaluation of the yielding threshold on the basis of the constitutive parameters of the fresh material. This is valid under the assumption that $E_{c0}$ is not altered by the chemical process. Since such a constant is an indicator of the energy dissipated for breaking the particles and redistributing the stored energy (Nguyen & Einav, 2009), a constant magnitude for $E_{c0}$ is valid as long as the chemical process does not modify the fracture properties of the particles or impair the original topology of the skeleton. This assumption may not hold for all states of degradation (e.g. when the degradation of inter-particle contacts is enhanced by pressure solution phenomena) and its range of validity needs to be assessed in separate investigations.

As illustrated by Einav (2007b) and Buscarnera & Einav (2012), the breakage dissipation in equation (22) can be linked to other forms of dissipation (e.g. friction), to obtain yield surfaces in the stress space. This procedure allows estimation of the yield domain in the $(q, p')$ plane (Fig. 3), with the breakage threshold (equation (18)) acting as a scaling parameter for non-isotropic yield conditions. An important consequence of incorporating chemical degradation in $\Psi^M$ is therefore the overall contraction of the elastic domain under increasing values of $X_d$. This effect is similar to the so-called ‘chemical softening’ that is at the core of several chemo-plastic models for geomaterials (Hueckel, 1997; Nova et al., 2003; Hu & Hueckel, 2007a). At variance with prior formulations, however, this property has here been derived from the link between the chemically weathered microstructure and continuum mechanical properties.

CONCLUSIONS

This letter has outlined a conceptual approach for understanding the microscopic origin of chemical degradation in geomaterials. The study was motivated by the notion that simple microscopic arguments can disclose the interplay between chemical and mechanical processes in a natural manner. In order to guarantee mathematical simplicity, important assumptions have been introduced, mainly concerning the microstructural features of the idealised geomaterial. Such simplifications, however, have not precluded the drawing of useful conclusions and the establishment a conceptual connection between the microscopic effects of chemical reactions and the mechanical response of the material.

In particular, a relation between the stress threshold at the elastic–inelastic transition and the chemical state variables has been recovered through statistical homogenisation. While this result is consistent with prior chemo-mechanical models, it does not derive from phenomenological assumptions and was obtained as an emergent property. In addition, an explicit relation between the degradation of the stiffness and the contraction of the elastic domain has been obtained. This relation is also derived naturally from assumptions on the chemical degradation of the stress-bearing microstructures and the breakage dissipation, thus capturing an interesting physical connection between yielding and elastic energy storage.

Given the simplicity of the underlying assumptions, this theory does not address some important chemo-mechanical phenomena such as pressure solution at interparticle contacts or changes in geometry driven by mineral precipitation. However, the enrichment of the microscopic description by incorporating other microstructural elements (e.g. interparticle cement, additional mass from solid precipitants, etc.) represents a strategy that can be pursued for enhancing the theory and coping with more realistic processes. As a consequence, the conceptual results presented in this letter can be considered to be a springboard for the future development of micromechanically based models and contribute to the enhancement of current chemo-mechanical formulations.

**APPENDIX**

This appendix details some of the thermo-mechanical relations necessary to define yielding conditions for particle breakage (Einav, 2007a, 2007b). If particle breakage is assumed to be the only dissipative source of an otherwise elastic assembly of particles, equation (4a) can be rewritten as

$$\delta \Phi^M = \delta \Phi_B = \sigma_{ij}^e \varepsilon_{ij}^e - \frac{\partial \Psi^M}{\partial B} \varepsilon_{ij}^e - \frac{\partial \Psi^M}{\partial B} dB \geq 0$$

Fig. 3. (a) Evolution of the yielding threshold for breakage under isotropic stress conditions (equation (18) is used with $n = 2$ and $m = 3$). (b) Contraction of the elastic domain induced by chemical degradation.
where $\delta \Phi_B$ indicates the rate of energy dissipation associated with particle breakage, with $B$ the only inelastic internal variable of the system. This term can be expressed as

$$\delta \Phi_B = E_B B \geq 0$$  \hspace{1cm} (20)

where $E_B$ is the breakage energy (i.e. the thermodynamic force associated with $B$). By differentiating the Helmholtz free energy in equation (15) and using Ziegler’s orthogonality postulate (Ziegler, 1983) it follows that

$$\sigma'_{ij} = \frac{\partial \Phi}{\partial e'_{ij}}$$  \hspace{1cm} (21a)

$$E_B = -\frac{\partial \Phi}{\partial \mathcal{B}}$$  \hspace{1cm} (21b)

It is finally possible to predict the occurrence of yielding by specifying the expression for $\delta \Phi_B$. As suggested by Einav (2007a), it can be assumed that for particle breakage

$$\delta \Phi_B = \frac{E_B^2}{E_0^2} \geq 0$$  \hspace{1cm} (22)

$$E_B^2 = E_B (1 - B)$$  \hspace{1cm} (23)

The isotropic breakage threshold is finally obtained when equation (23) is satisfied as an equality. This can be derived by combining equations (20) and (22), having

$$E_B^2 (1 - B) \geq 1$$  \hspace{1cm} (24)

$$\delta \Phi = \sqrt{(\delta \Phi_B)^2 + (\delta \Phi')^2} \geq 0$$  \hspace{1cm} (25)

therefore obtaining yield envelopes such as those given in Fig. 3.

REFERENCES


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