Numerical Models in Geomechanics-NUMOG IX-Pande & Pietruszczak (eds)

Chemo-mechanical coupling and damage enhanced dissolution at intergranular contact

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ABSTRACT: Many processes in geomechanics, such as structuration and aging of natural soils, compaction and pressure solution of oil bearing sediments involve mineral dissolution at grain contacts. Dissolution and subsequent precipitation lead to a redistribution of mass within the pore space, affecting soil porosity and stiffness. We simulate dissolution at a micro scale using chemo-plasticity for penetration of asperity. We assume that dilatancy resulting from material damage generates new free surface around the asperity, in turn accelerating dissolution and material weakening.

1 INTRODUCTION

Several basic processes in geomechanics depend on the microscopic level dissolution of mineral at stressed intergranular contact. They include: structuration, soil aging in laboratory tests and pressure solution in oil bearing sediments. The mechanisms of the removal include: dissolution of mineral at the interface between grains, plastic deformation and free-face pressure solution. While time scale and contribution of different mechanisms constituting the process may be different in each of the phenomena mentioned, one common feature of these phenomena is removal of mass from the contact area. The specific mechanisms of this removal are subject of a more or less intense debate in the respective communities and subject of both theoretical and experimental research. The removal is often linked to subsequent processes such as formation of gel in pores, precipitation of the mass on exposed free surfaces with possible changes in mechanical properties of material at a macro-scale.

A proper understanding and identification of variables responsible for these interface processes is crucial for exploration and production in petroleum engineering, geotechnics in natural structured materials, and interpretation of laboratory testing. In this paper, we postulate asperity indentation as a dominant intergranular mechanism that involves a coupled dilatant damage and dissolution. Experiments show massive micro-cracking and micro-granulation near stressed contact (Tada et al., 1987).

2 MODEL

We model damage enhanced dissolution of minerals at an elasto-plastic contact between soil grains at a micro scale. To start with we assume a rigid-plastic grain, with chemically sensitive yielding induced by an indentation of an infinitely rigid asperity. We will make use of Johnson's (Johnson, 1985) approximation, widely accepted in contact mechanics, extending it to include a chemo-mechanical coupling. Our purpose is to examine chemo-mechanical couplings necessary to see meaningful values of the principal variables involved. For simplicity we adopt plane strain state.

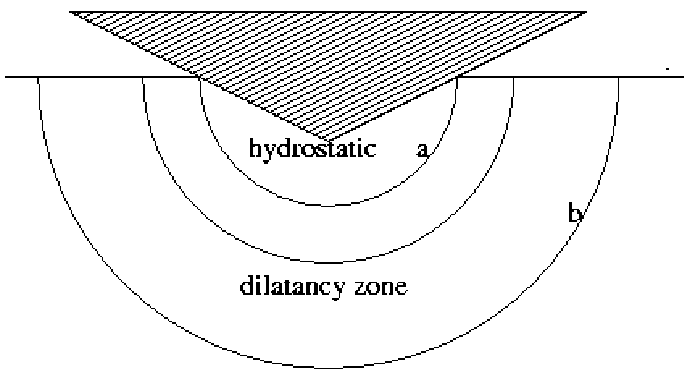

Figure 1. Indentation model

Following Johnson's approximation, the contact surface of the indenter is assumed to be encased in a hemi-spherical 'core' of radius a, within which the stress state is represented by purely hydrostatic stress. Outside this core it is assumed that stress, strain and displacement are axisymmetric and the same as in an internally loaded rigid-plastic tube with *a, b* as the inner and outer radius, respectively. This approximation, with no stress applied at the external boundary corresponds to a central part of a grain indented by a much stiffer mineral and away from other contact points.

The postulated chemo-mechanical mechanism includes: a field of mechanical damage induced during dilatant plastic strain around the indenter; generation of new free surface by the micro-cracking associated with the plastic dilatancy; an enhancement of dissolution of silica from the newly generated surfaces; and in turn chemo-mechanical weakening of quartz as a result the silica mass removal, followed by transfer of the dissolved silica mass into the pore solution.

3 DEFORMATION ENHANCED DISSOLUTION DURING INDENTATION

Several scenarios of contact dissolution may be envisioned. We shall focus on the one involving two stages: a purely mechanically induced indenter penetration (increase of the indenter penetration inducing yielding up an unstable phase, as described by Hueckel & Mroz, 1971); followed by a phase at a constant indentation pressure with a progress occurring due to chemical softening and strain hardening. The equilibrium equation and kinematic relationships for the plane strain axisymmetric problem are as follows

$$\frac{d\sigma_r}{dr}+\frac{\sigma_r-\sigma_\theta}{r}=0,\ \dot{\varepsilon}_r=-\frac{d\dot{u}}{dr},\dot{\varepsilon}_\theta=-\frac{\dot{u}}{r} \quad (1)$$

where r,θ are outward radial and circumferential coordinates, respectively, u is the radial displacement. The mechanical boundary conditions are: at $r=a$, $\sigma_r=p$ and at $r=b$, $\sigma_r=0$. The yield surface is as simple as possible, expressed via single principal stress components, Fig. 2.

$$\sigma_r=\sigma_{1i}(\varepsilon,\zeta)\ for\begin{cases}-\tan\varphi<\sigma_\theta/\sigma_r<1,\sigma_r\geq 0\\ -\text{ctan}\,\varphi<\sigma_\theta/\sigma_r<1,\sigma_r<0\end{cases}$$

$$\text{and}\ \sigma_\theta=\sigma_{2i}(\varepsilon,\zeta),\ \text{elsewhere} \quad (2)$$

The yield limit undergoes strain hardening and chemical softening, as ζ represents the chemically induced mass loss. The flow rule is associative. We consider a linear deviatoric strain hardening and chemical softening rules, as follows *(for $\sigma_r > 0$):*

$$\frac{\sigma_r}{\sigma_{01}}=1+\gamma\varepsilon_q-\beta\zeta\geq 0,\frac{\sigma_\theta}{\sigma_{02}}=1+\gamma\varepsilon_q-\beta\zeta\geq 0;\ \sigma_{01}\geq 0;\sigma_{02}\leq 0 \quad (3)$$

where γ and β respectively strain hardening and chemical weakening material constants, taken here for simplicity as the same for σ_r and σ_θ; ε_q is deviatoric strain: $\varepsilon_q=\sqrt{2/3}|\varepsilon_\theta-\varepsilon_r|$. It is essential in establishing the hardening functions (3) that the two mechanisms may compensate one another, in order to simulate process of chemically induced strain at constant stress. Clearly, there is also a limitation on the amount of softening and hardening, as the principal stresses are not intended to change their sign.

We consider a quartz-water system undergoing the reaction of dissolution

$$SiO_2(s)+2H_2O(l)\longleftrightarrow H_4SiO_4(aq)$$

To quantify the loss of mass of silica from the mineral, we will adopt the rate equation for activity change in dissolution reaction after Rimstidt and Barnes (1980):

$$\frac{da_{H_4SiO_4}}{dt}=A\gamma_{H_4SiO_4}\left(k_+a_{SiO_2}a^2{}_{H_2O}-k_-a_{H_4SiO_4}\right)\equiv\dot{\zeta} \quad (4)$$

where a is activity, γ is activity coefficient, k_+ and k_- are the rate constants for the forward and backward reaction respectively.

A is a dimensionless quantity representing the specific interfacial surface per unit volume of fluid phase at which dissolution occurs.

The key assumption of this theory is that, as the dilatant irreversible deformation of the mineral is linked to generation of microfractures, such microfractures form new interface surface area, at which dissolution takes place at contact with pore fluid. Hence, $A = A\ (\varepsilon_v)$ where ε_v is volumetric strain. Furthermore, the local precipitation term in the reaction equation is ignored, as we consider the remote mass precipitation in the up-scaling framework, elsewhere. Thus, the rate of reaction in equation (4) becomes:

$$\dot{\zeta}=k_+\phi\varepsilon_v+c \quad (5)$$

where ϕ is a proportionality constant between the specific interfacial area and volumetric strain, while c = const. represents the kinetic rate associated with pre-existing interfacial surface in pores, assumed constant.

We will focus on the second phase of the process, which is dissolution at a constant indentation pressure, *p,* with a progress occurring due to chemical softening and strain hardening is controlled by the dissolution time scale, while the results for the precedent phase of the time independent mechanical loading from *0* to *p* is included for completeness.

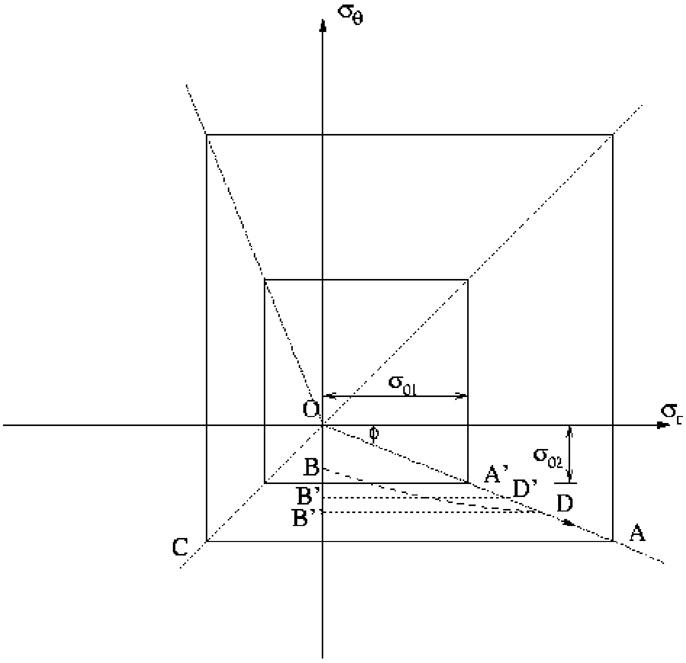

Figure 2: Linear yield condition and stress profiles

We consider a constant inner boundary pressure *p* shown at point A in the stress profile, Fig.2. The solution requires existence of two zones. An inner zone forms with the stress on the critical line DA, of which D represents the boundary at $r=\xi$, between the inner and outer zone. Initially, under the increasing inner pressure, it pushes the outer zone, which is originally rigid. The latter starts yielding with the stress state at $B''D$. As the pressure is stopped at *p=const,* the material undergoes simultaneous strain hardening and simultaneous chemical softening. With time progressing, the stress at boundary ξ grows along $D'D$, while physically the boundary moves inward. Hence, the inner zone gets smaller and the outer zone of dilatancy increases. With the choice of extremely simple yield function, the following constraints are imposed on eqs. (1): for the inner zone $a \le r \le \xi$, $\dot{\varepsilon}_r = 0$, and $u = u_0 = const$, for the outer zone $\xi \le r \le b$, $-\sigma_\theta/\sigma_r = \tan\varphi$. The two zones are required to be continuous, as far as stress is concerned, hence $\sigma_{r\xi}^{inner} = \sigma_{r\xi}^{outer}$, $\sigma_{\theta\xi}^{inner} = \sigma_{\theta\xi}^{outer}$. With these conditions and equations (1) through (5), we could calculate the internal pressure-displacement relationship under different intensity of the chemical process, as a solution of the following system of differential equations:

$$\frac{p}{\sigma_{01}\tan\varphi}\left(\frac{a}{\xi}\right)^{1+\tan\varphi} = (1-K_c t)\left(\frac{b}{\xi}-1\right) - \left(\frac{\int_0^t \beta\phi k_+ u_0 dt}{r} - \frac{\sqrt{2}\gamma u_0}{3r}\right)\ln\frac{b}{\xi}$$

$$\frac{p}{\sigma_{01}}\left(\frac{a}{\xi}\right)^{1+\tan\varphi} = (1-K_c t) - \left(\frac{\int_0^t \beta\phi k_+ u_0 dt}{r} - \frac{\sqrt{2}\gamma u_0}{3r}\right)$$

$$\frac{u_a}{a} - \frac{u_0}{\xi} = \frac{3}{\sqrt{2}\gamma}\left\{\frac{p/\sigma_{01}}{1+\tan\varphi}\left[\left(\frac{a}{r}\right)^{1+\tan\varphi} - \left(\frac{a}{\xi}\right)^{1+\tan\varphi}\right] + \text{In}\frac{r}{\xi}\right\}$$

The results of calculations performed using *Matlab* 6.5 are shown in Fig. 3. The values used in this simulation are $b/a=10$, $\gamma=2.36$, $\tan\varphi=0.2$. K represents the coefficient of chemical softening dissolution associated with dilatancy related dissolution, $K=\beta\phi k_+$, while the chemical softening effect due to pre-existing fractures and pores $K_c = 1.0e-6\,\text{s}^{-1}$ is assumed as a constant. The evolution of the zones of different kinematic response is shown in Fig. 4. Notably, the case of a one way coupling, with β=0, and hence K=0, represents the situation in which there is no effect of dissolution on hardening, but there is still an effect of straining (dilatancy) on dissolution.

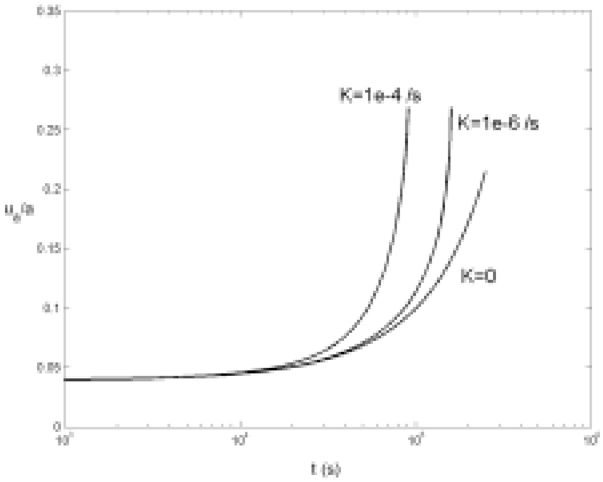

Figure 3. Penetration vs. time

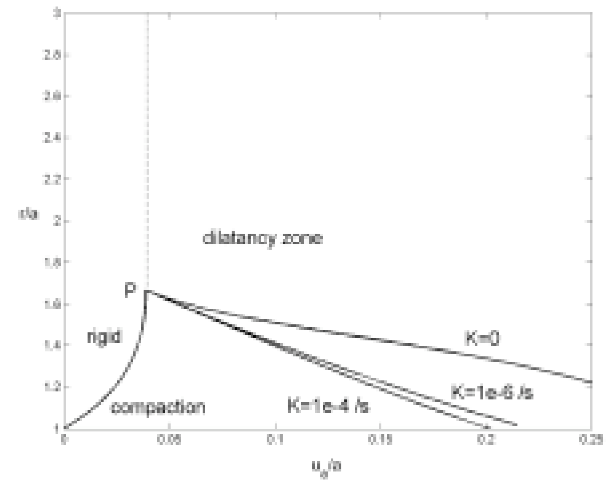

Figure 4. Propagation of zones

As can be seen, chemical softening due to dissolution of the material can significantly accelerate the penetration of the indenter. At larger chemical softening parameter values, the dissolution effect prevails over the strain hardening and the penetration becomes uncontained, until small strain hypothesis ceases to hold. As a result of dissolution-dilation coupling, dissolution accelerates the advancement of the dilatancy zone into the body of the grain. Notably, the compaction zone withdraws, and eventually, vanishes.

4 TRANSPORT OF MASS AWAY FROM THE DAMAGE/DISSOLUTION ZONE

The accelerated dissolution as a result of generation of free surface area around the asperity due to the material damage is expected to have a considerable effect on the mass transfer during the indentation process. The effect of the dissolution in the total transfer of mass outside of the grain is simulated using the reactive transport equation as follows:

$$\frac{\partial C}{\partial t} = D\nabla^2 C + F \qquad (6)$$

where C is the molar fraction concentration of the solute H_4SiO_4, D is the diffusion coefficient, F is the rate of mass production. As discussed above, F is enhanced by the mechanical deformation during the process. The process is approximated as the linear function of dilatant volumetric strain, ζ in Eq. (5) and by ignoring the local precipitation.

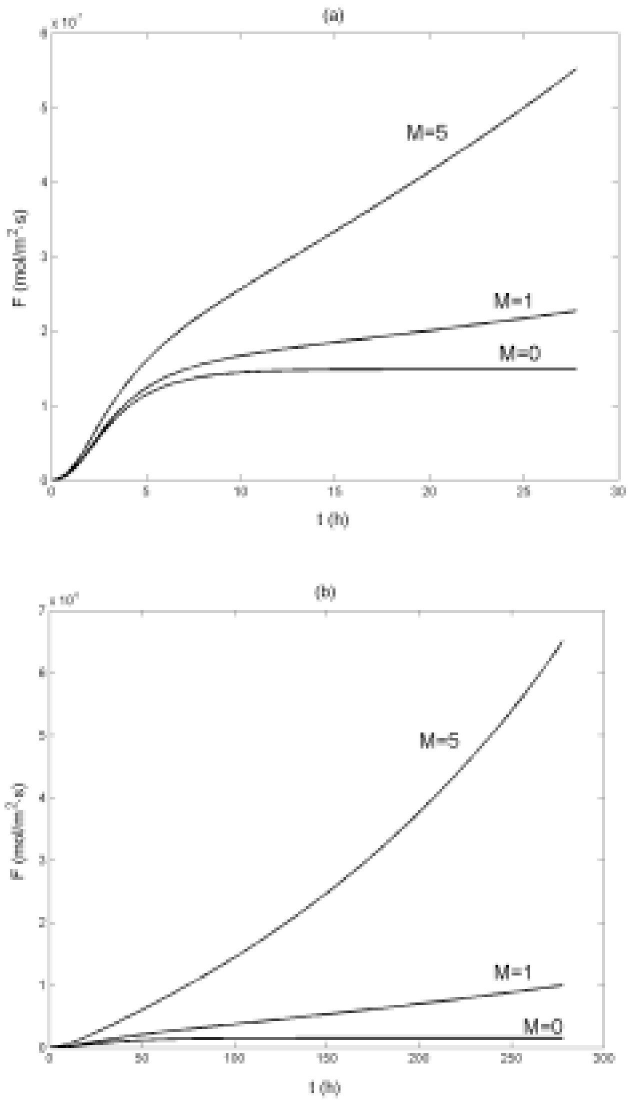

Figure 5. Flux across the external grain surface: (a) short term; (b) long term

Assuming that the transport is uniquely driven by the concentration gradient created by the dissolved mass, that is imposing at the inner boundary a constant concentration, $C = C_a$ at $r = a$, $C = 0$ at $r = b$, eq. (5) and (6) were numerically integrated using *Matlab* 6.5 to yield the flux generated at $r = a$. Coefficient M represents the deformation effect associated with dilatant volumetric strain on the mass transfer, $M = \phi k_+ a^2 / DC_a$. The results are presented in Fig. 5a and b in terms of the actual mass flux simulated for the following data: $a = 10^{-5} m$, $b = 10^{-4} m$, $k_+ = 1\times 10^{-12} s^{-1}$, $D = 1\times 10^{-13} m^2/s$ (Rimstidt & Barnes, 1980; Shimizu, 1995), still, $b/a = 10$, $\tan\varphi = 0.2$, and $\gamma = 2.36$.

It should be pointed out that the deviatoric strain hardening in the constitutive functions plays an important role to compensate the weakening effect induced by dilatancy which causes more material to dissolve and transfer. The following Figure 6(a) and (b) demonstrate the mass flux simulated with the same data used in Fig.5(a) and (b) and $M = 5$, but under different deviatoric strain hardening coefficient γ.

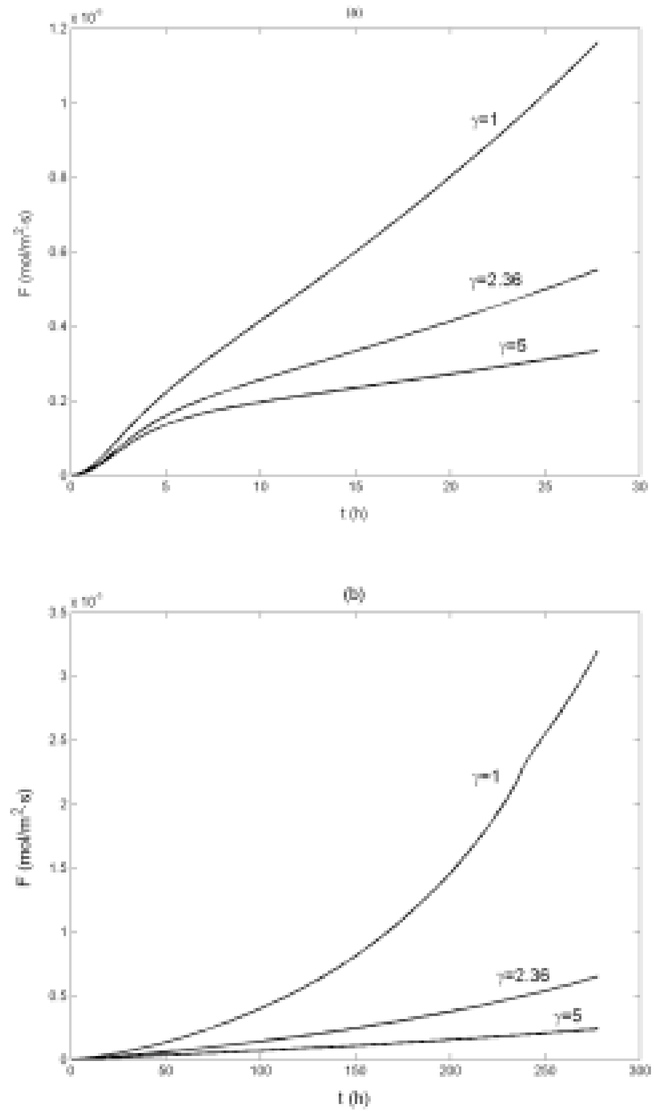

Figure 6. Flux across the external grain surface with different deviatoric strain hardening coefficient: (a) short term; (b) long term

5 CONCLUSIONS

It is seen that the deformation enhances the mass transport significantly. Clearly, the solutions presented are based on very simple constitutive functions. Indenter penetration is dramatically enhanced by mineral dissolution, even at constant pressure. When $M = 0$, transport is purely diffusive, and flux reaches steady state after a period. However, under the increasing mechanical damage (deformation), substantially more material is dissolved and transferred through the free surface to pore solution.

ACKNOWLEDGMENT

Portion of this work was supported by a grant from the National Science Foundation, Geomechanics and Geotechnical Systems Program, Division of Civil & Mechanical Systems.

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