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Creep of saturated materials as a chemically enhanced rate-dependent damage process

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SUMMARY

Material behaviour that exhibits characteristics of creep induced by a spontaneous mineral dissolution enhanced by material damage is studied. It is believed that the characteristic rates of the chemical processes involved determine the time-rate dependence of the resulting strain. A basic model of a combined chemo-plastic softening and chemically enhanced deviatoric strain hardening for saturated geomaterials is presented. Chemical softening is postulated to occur as a consequence of the net mass removal resulting from dissolution and precipitation of specific minerals occurring at the damage-generated inter-phase interfaces. Closed and open systems are discussed. In the former case, deformation at constant stress results entirely from a local compensation mechanism between the chemical softening and strain hardening. The classical three stages of creep are interpreted in terms of mechanisms of dissolution and precipitation, as well as the variation in the reaction surface areas involved in the mass exchange. In an open system, the above local mechanism is enhanced by the removal of mass *via* diffusion of species affecting the mass balance. Such a system is addressed *via* a boundary value problem as shown in an example. Copyright © 2007 John Wiley & Sons, Ltd.

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1. INTRODUCTION

Creep strain can develop at a constant stress of a sufficient intensity in almost all solids. The idea that it arises exclusively as a result of time elapse goes back to Kelvin [1] and Bingham and Durham [2] and has now as many supporters as foes. This is a very practical idea, but it has repeatedly been blamed for lacking a physical mechanism behind it, and for not fitting in a larger

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scheme of inelastic stress–strain laws. Hence, numerous attempts in various contexts and for various materials were undertaken, first, to frame creep within visco-plasticity, rate-dependent plasticity or endochronic theory, and second, to attribute particular mechanisms to creep (e.g. dislocation motion, inter-grain diffusion (Nabarro [3]), or intra-grain diffusion (Coble [4]) resulting in macroscopically observed strains at constant stress). Intrinsic time or similar variables were introduced to link the phenomenology to the actual progress of the involved processes, see e.g. Valanis [5]. For soils, early efforts in this direction were undertaken by Murayama and Shibata [6], Christensen and Wu [7], Mitchell [8] and Singh and Mitchell [9] or Kuhn and Mitchell [10].

In this paper, we advance a hypothesis that one of the mechanisms of creep in earthen materials is a chemical process triggered by a prior mechanical damage. The general idea comes from the observation that what is perceived as creep occurs only when yielding, and hence some damage involving formation of new water/mineral interfaces is inflicted to the material. The slow pace of the deformation triggered by that damage suggests a coincidence with a simultaneous chemical process. In this specific case, a time-dependent chemical enhancement occurs through dissolution of minerals from a zone of dilatant damage and subsequent mass removal *via* diffusion. The damage is associated with microcracking (see e.g. Brace *et al.* [11]), which generates a new free surface area at the crack walls. When in contact with interstitial fluid, these walls constitute new solid/fluid interface and hence new dissolution sites. Consequently, the removal of the mineral mass *via* dissolution leads to an ulterior material softening and further deformation at constant stress.

Similar scenarios have been repeatedly suggested as possible mechanisms of pressure solution in compacting rocks, such as halite and sandstone. Experiments and field evidence corroborating such a hypothetical mechanism were reported by Tada and Siever [12], Milliken [13] and others. Microcracks are widely observed (He *et al.* [14]) near the intergranular contact zone and have been suggested (den Brok [15]) to be the precursors of the well-known structure of channels and islands etched in the contact surfaces (see e.g. Schutjens and Spiers [16]). On the other hand, the effect of chemistry of the aqueous environment on the stress-enhanced chemical reaction at the crack tip has been intensely investigated in mid 1980s as a possible cause of crack propagation at constant load in silicate rocks (see e.g. Atkinson [17], Freiman [18] and Scholz [19]).

This paper addresses a combined chemically enhanced strain hardening and damage-enhanced chemical softening at a macroscopic level. A simplest possible form of the rigid plasticity theory is used to put the emphasis on the formulation of a two-way chemo-mechanical coupling. A new, chemo-mechanical softening variable is introduced in the form of the mass removal. As based on dissolution theory, the mass removal is proportional to the inter-phase surface and it becomes substantially enhanced by formation of the new surface area generated by the mechanical damage.

Two basic cases are considered: a closed system with a local precipitation controlling the mass removal, when dissolution is partially counterbalanced by a local precipitation, and an open system (a boundary value problem, in fact) when the mass removal is affected by a local dissolution and diffusion away from the dissolution site. For the closed system the classical three stages of primary, secondary and failure creep are interpreted in terms of mechanisms of dissolution and precipitation, as well as the variation in the reaction surface areas involved in the mass exchange.

Clearly, other sources of creep may exist at the microscale. Processes that are rate dependent, such as microscale seepage, electric charge difference-dependent osmotic water transport or timedependent intergranular friction may all constitute alternative or simultaneous sources of creep (see e.g. Navarro and Alonso [20], Kuhn and Mitchell [10]).

2. DAMAGE-ENHANCED REACTIVE PLASTICITY

We shall build on the previously developed idea (Hueckel [21, 22] and Loret *et al.* [23]) that a mass removed from a solid adiabatically (without heat exchange) and isochorically (without the volume change of the representative elementary volume (REV) of the porous medium) affects both the medium compliance and strength. These two effects will be addressed in the framework of what is called reactive chemo-plasticity. The term reactive chemo-plasticity (Hueckel [22]) is used as opposed to non-reactive chemo-plasticity (Hueckel *et al.* [24]) when an instantaneous change in concentration (of selected species) in pore fluid may produce a mechanical change in the response of the soil skeleton. This is distinguished in analogy to reactive and non-reactive transport, and is important because of a difference in time scales.

The scenario of the chemo-mechanical loading process we intend to simulate comprises the following hypotheses:

- (i) the material is isotropic; strains are small;
- (ii) the material is rigid plastic (this assumption is made exclusively for convenience of the simulation to focus on chemo-plastic effects, and may easily be removed);
- (iii) the material is saturated with water; the pore system is interconnected; the material is perfectly drained, which implies that the pore fluid flow is fast enough for pore pressure to play no role;
- (iv) a sufficient load is applied to induce initial yielding;
- (v) yielding induces dilatancy damage, which is linked to microcracking;
- (vi) microcracking results in generation of a new solid-fluid interface, at which dissolution of mineral species can take place resulting in the solid mass removal;
- (vii) dissolution is assumed to occur as a kinetic process;
- (viii) dissolution rate is proportional to the specific surface area of the newly generated interfaces;
- (ix) two mechanisms contribute to the response of the material in terms of plastic hardening: deviatoric strain hardening and mass removal softening;
- (x) as the mass removal is linked to the specific surface area of the newly generated interfaces, and this in turn is dependent on the dilatancy damage, the two mechanisms are coupled;
- (xi) during creep the two hardening mechanisms become compensatory, and hence, the chemical dissolution induces further damage enhancement: this results in a two-way coupling;
- (xii) flux of the dissolved species diffuses across the solid driven by the concentration boundary condition;

In what follows we formulate a mathematical model to simulate the above-described scenario. To maintain the focus on damage we assume at this stage that the considered medium is rigid plastic, which is to say that there is no strain (ε_{ij}) for a stress σ_{ij} within the yield locus, f = 0 (stress and strain are positive when compressive)

for
$$f < 0$$
, $\varepsilon_{ij} = 0$ (1)

whereas at yielding, the strain rate is entirely irreversible

$$f(\sigma_{ij}, p_c(\kappa, \xi_k)) = 0 \quad \text{and} \quad \dot{f}(\dot{\sigma}_{ij}, \dot{p}_c) = 0, \quad \dot{\varepsilon}_{kl} = \dot{\varepsilon}_{kl}^{\text{irr}} \neq 0 \tag{2}$$

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where p_c is an isotropic hardening functional. The rate of the latter is prescribed *via* an evolution function which depends on rates of scalar hardening parameters, that are mechanical or chemical in nature (Hueckel [21, 22]). p_c is an isotropic stress characteristics of the yield locus. A superimposed dot over a symbol denotes its time rate.

The deviatoric strain-hardening parameter κ is defined as

$$\dot{\kappa} = \left(\frac{2}{3}\dot{e}_{ij}^{\rm irr}\dot{e}_{ij}^{\rm irr}\right)^{1/2} \quad \text{where } \dot{e}_{ij}^{\rm irr} = \dot{e}_{ij}^{\rm irr} - \frac{1}{3}\dot{e}_{kk}^{\rm irr}\delta_{ij} \tag{3}$$

variables ξ_k , k = 1, 2, 3, ..., where k is the number of a reaction, represent accumulated relative mass removals of particular mineral species, the partial strength of which is deemed to contribute to the overall material strength or yield limit. It is calculated with respect to the original total mass of that particular species. Its rate can be determined from the rate of the reaction. In principle, more than one reaction or process, may affect the strength of a geomaterial. These processes may be simultaneous or sequential, and each with a possibly different rate with which they progress. There is currently no widely accepted approach to the question how to identify and quantify mineral component contributions to the overall geomaterial strength. However, for many materials, a phenomenological relationship between strength and reaction progress variable may be established empirically. In what follows we will address a single reaction effect only, with a single rate.

When the material is at yielding, i.e. when criteria (2) are satisfied, the strain rate is determined by the flow rule. A common associativity hypothesis is made for simplicity, while any non-associativity hypothesis could easily be incorporated. According to the former assumption the strain rate mode is co-linear with the yield locus gradient, while the amount of strain rate is controlled by the rate of change of plastic multiplier, $\dot{\lambda}$, which in turn depends on the rates of stress, temperature and reaction progress, as follows:

$$\dot{\varepsilon}_{ij}^{\rm irr} = \dot{\lambda} \frac{\partial f}{\partial \sigma_{ij}} \tag{4}$$

Multiplier $\dot{\lambda}$ is determined from the Prager consistency condition, $\dot{f}(\sigma_{ij}, \kappa, \xi) = 0$, which constrains all hardening component rates and the stress rate

$$\frac{\partial f}{\partial \sigma_{ij}} \dot{\sigma}_{ij} + \frac{\partial f}{\partial \kappa} \dot{\kappa} + \frac{\partial f}{\partial \xi} \dot{\xi} = 0$$
(5)

Substituting Equations (3) and (4) into the above equation yields

$$\frac{\partial f}{\partial \sigma_{ij}} \dot{\sigma}_{ij} + \frac{\partial f}{\partial \kappa} \dot{\lambda} \left[\frac{2}{3} \frac{\partial f}{\partial s_{ij}} \frac{\partial f}{\partial s_{ij}} \right]^{1/2} + \frac{\partial f}{\partial \xi} \dot{\xi} = 0$$
(6)

Thus,

$$\dot{\lambda} = -\frac{\frac{\partial f}{\partial \sigma_{mn}} \dot{\sigma}_{mn} + \frac{\partial f}{\partial \xi} \dot{\xi}}{\frac{\partial f}{\partial \kappa} \left[\frac{2}{3} \frac{\partial f}{\partial s_{ij}} \frac{\partial f}{\partial s_{ij}}\right]^{1/2}}$$
(7)

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whereas $s_{ij} = \sigma_{ij} - \frac{1}{3} \sigma_{kk} \delta_{ij}$. For creep, hence at $\dot{\sigma}_{ij} = 0$, the creep strain rate becomes proportional to the rate of the relative mass removal, as follows:

$$\dot{\varepsilon}_{ij}^{\rm irr} = -\frac{\frac{\partial f}{\partial \sigma_{ij}} \frac{\partial f}{\partial \xi} \dot{\xi}}{\frac{\partial f}{\partial \kappa} \left[\frac{2}{3} \frac{\partial f}{\partial s_{kl}} \frac{\partial f}{\partial s_{kl}}\right]^{1/2}}$$
(8)

It needs to be noted that when at yielding one of the three variable rates in Equation (5), stress rate is zero, while the other two hardening rates have to compensate one another. This is known as 'compensatory mode'. Such a mode is common whenever an environmental softening is present, such as one due to a change in temperature (Hueckel and Borsetto [25]), contaminant concentration (Hueckel [26]), mass transfer (Hueckel [22]), weathering (Nova [27], Nova et al. [28]) or suction (Alonso et al. [29], Laloui and Nuth [30], Liu et al. [31]). In other words, when the chemical (or thermal, etc.) softening occurs, the material must develop a sufficient amount of strain hardening to compensate for the softening, in order to maintain the imposed constant stress state. On the same token, when both strain and chemical hardening are negative, this condition cannot support a constant stress condition, and as the second and third term in Equation (5) are of the same sign, any further increment of ξ becomes statically inadmissible. This indeed may be the case for the volumetric strain-softening case. This is also why the choice of the deviatoric strain for the mechanical strain-hardening parameter rather than the volumetric strain hardening, the latter often considered typical for geomaterials, is critical here. Indeed, deviatoric hardening allows for modelling creep in the dilatant range of behaviour, which would not be possible (as compensatory mode is impossible) with the volumetric softening hypothesis for that range.

3. MASS REMOVAL AS A RESULT OF CHEMICAL REACTION IN GEOLOGICAL SYSTEM

To use a specific process as an example, we focus on the rate of reaction of pure silica in contact with water in a geological system

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

The rate of this reaction is directly proportional to the area of the interface between the two phases. For a system, which contains mass of water $M_w = M^0 = 1 \text{ kg}$, the fluid/solid interface surface area, A, is normalized with respect $A^0 = 1 \text{ m}^2$ to yield a non-dimensional quantity $\tilde{A} = A/A^0$. The mass loss of silica from the solid phase is expressed *via* activity (molar fraction) of silicic acid, H₄SiO₄, dissolved in water that can be directly measured in an experiment in a closed environment. Following Rimstidt and Barnes [32], under the assumption that the interfacial area between the phases is the same in the case of dissolution and precipitation, the rate equation for silica interaction with water represented through the activity change reads

$$\frac{da_{H_4SiO_4}}{dt} = \tilde{A}\gamma_{H_4SiO_4} \left(k_+ a_{SiO_2} a_{H_2O}^2 - k_- a_{H_4SiO_4}\right)$$
(9)

where a_i are activities and γ_i are activity coefficients of *i*th species, while k_+ and k_- are rate constants of, respectively, forward and backward reactions. \tilde{A} is a dimensionless-specific interfacial

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surface area per unit area, as above, per unit mass of pore fluid, M_f^0 at which the reaction occurs. The applicability of the above reaction rate expression to *in situ* conditions is a separate, widely debated issue (see e.g. Steefel and MacQuarrie [33]), which will be addressed later on.

Activity of an individual species as expressed in Equation (9) is defined *via* molar fraction x_{kF} of that species, *k* in the fluid phase *F*, assumed as a dilute solution, and linked to the species mass content, $m_{kF} = M_{kF}/V_0$, *via* a molar fraction or relative number of moles, x_{kL} . V_0 is the reference volume of the entire porous medium. Hence,

$$a_{kF} = \gamma_{kF} x_{kF}, \quad x_{kK} = \frac{N_{kK}}{\sum_{l \in K} N_{lK}} = \frac{m_{kK}/m_k^{(M)}}{\sum_{l \in K} m_{lK}/m_l^{(M)}}$$
 (10)

where N_{kL} is the number of moles of the species in the phase, $m_k^{(M)}$ is its molar mass. Note that the latter relationship is a nonlinear one.

We shall now establish a link between the rate of silica dissolution and the accumulated relative mass removal of silica from the solid. The latter is defined in terms of mass change of silica per its initial mass, or in terms of number of moles, as

$$\xi = \frac{\Delta M_{\rm SiO_2}}{M_{\rm SiO_2}^0} = \frac{\Delta N_{\rm SiO_2}}{N_{\rm SiO_2}^0} \tag{11}$$

where $M_{SiO_2}^0$ and $N_{SiO_2}^0$ are the initial mass and number of moles of silica, respectively. The change of the number of moles of silicic acid H₄SiO₄ during the quartz–water reaction, initially assumed to be zero, is equal to the change in the number of moles of SiO₂ during the process. Hence, the rate of mass removal of silica can be derived based on the activity of silicic acid defined by Equation (10)

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\Delta N_{\mathrm{SiO}_2}}{N_{\mathrm{H}_2\mathrm{O}}^0} \right) = \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{N_{\mathrm{H}_4\mathrm{SiO}_4}}{N_{\mathrm{H}_2\mathrm{O}}^0} \right) = \frac{\mathrm{d}a_{\mathrm{H}_4\mathrm{SiO}_4}}{\mathrm{d}t} \tag{12}$$

where $N_{\text{H}_2\text{O}}^0$ is the initial number of moles of water in a REV. The activity coefficient has been assumed to be equal to unity. Henceforth, the activity becomes directly equal to molar fraction $a_{\text{H}_4\text{SiO}_4} = x_{\text{H}_4\text{SiO}_4}$.

Therefore, the rate of relative silica mass removal

$$\dot{\xi} = \frac{d}{dt} \left(\frac{\Delta N_{\text{SiO}_2}}{N_{\text{SiO}_2}^0} \right) = \frac{d}{dt} \left(\frac{\Delta N_{\text{SiO}_2}}{N_{\text{H}_2\text{O}}^0} \frac{N_{\text{H}_2\text{O}}^0}{N_{\text{SiO}_2}^0} \right) = \frac{d}{dt} \left(\frac{\Delta N_{\text{SiO}_2}}{N_{\text{H}_2\text{O}}^0} \right) \frac{N_{\text{H}_2\text{O}}^0}{N_{\text{SiO}_2}^0} = \frac{da_{\text{H}_4\text{SiO}_4}}{dt} s$$
(13)

where s denotes a molar ratio between water and silica in the initial volume of the material,

$$s = \frac{N_{\rm H_2O}^0}{N_{\rm SiO_2}^0}$$
(14)

Note that the molar ratio *s* is a scale change factor, as it is introduced to refer the removed mass of silica to the total available silica mass per REV, while the silicic acid activity in expression (9) is referred to the unit volume of pore water. By normalizing the mass of removed silica in Equation (13) *via* coefficient *s* with respect to the original mass of silica, ξ is constrained by the following inequality: $0 \leq \xi \leq 1$, and hence can be treated as a reaction progress variable

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(De Groot [34]). When $\xi = 1$, the reaction is completed, that is, all silica is removed from the material. Two examples of a closed and an open system of dissolving quartz are shown in Figures 2 and 10.

A significant novelty in the proposed approach is the fact that it takes into account an increased dissolution occurring at the sites at the newly generated internal surface area of the solid/fluid interface formed by the walls of the microcracks. Let us introduce a hidden (in thermodynamics sense, see e.g. Lubliner [35]) scalar variable representing the amount of the added surface area, \tilde{a} , per unit volume of the porous medium.

The total surface area of microcracks can be measured directly in experiments. Moreover, it has been known for sometime that it is proportional to the total acoustic energy released during cracking and measured by acoustic emission method (Sagaidak and Elizarov [36]). As the interest here in the surface area for the purpose of evaluating the dissolved mass release, no directional properties are needed, and a scalar representation is sufficient. On the other hand, variable \tilde{a} needs to be linked to the relative reaction area, \tilde{A} , and hence related to the volume of water with which the solid is reacting. Therefore, an appropriate conversion is required

$$\tilde{A} = \tilde{a} \frac{m^0}{n\rho_{\rm w}} \tag{15}$$

where $m^0 = 1 \text{ kg/m}^3$, ρ_w is the density of water, and *n* is the porosity.

Following Brace *et al.* [11], Scholz [37] has demonstrated that the cumulative frequency of acoustic emission events is proportional to the inelastic volumetric strain (dilatancy). To devise a simple formula linking the dilative inelastic volumetric strain to the newly generated free open surface area, a simple, regular, hexagonal 2-D crystal assembly is considered in Appendix. It is assumed in this model that the volumetric straining is equivalent to an increase in the number of the inter-crystal crack segments, and not to the change in their width or segment length; which implies that a macro-crack propagation consists of opening of a sequence of microcracks (intergrain cracks) of the same width. This includes the sub-critical crack propagation into a chemically weakened crack tip environment when flooded with water (see e.g. Wiederhorn *et al.* [38], Oldecop and Alonso [39]).

Combining the above two premises we propose that the rate of increase of the new surface area of the internal fluid/solid interface generated in quartz by cracking per unit volume of the medium is related linearly to the rate of inelastic volumetric strain (dilatancy)

$$\tilde{a} = \psi_{a}(\chi' | \varepsilon_{v}^{\text{irr}} | + \tilde{a}_{0}'), \quad \varepsilon_{v}^{\text{irr}} < 0$$

$$\tag{16}$$

where χ' is the coefficient of proportionality between the dilative volumetric strain and the total relative free surface area increase in quartz (see Appendix for details) and ψ_q is the mineral volume fraction for quartz. This is valid under the assumption that the new crack surface area in silica is a fraction (equal to quartz mineral volume fraction) of the total new free surface area proportional to volumetric strain. In addition, we impose that $\chi' = 0$, if $\varepsilon_v^{irr} > 0$, which means that the compactive irreversible volumetric strain cannot be linked to any microcracking. \tilde{a}'_0 is the initial pre-existing pore interface area per unit volume of the medium, which produces a basal dissolution.

This theory addresses an extensive range of pre-failure behaviour when microcracking is diffusive and can be represented by a continuum type of variable. When localization occurs after microcracks coalesce, a different relationship between dissolution surface area and damage measures needs to be sought.

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The rate equation (9) has been established in laboratory conditions (Rimistid and Barnes [32]) where quartz grains were exposed to water for a period of time. In the context of microfracturing rocks, several modifications of Equation (9) need to be introduced. First, the surface areas considered in Equation (9) must be re-scaled to be related to the REV of the porous medium, as in Equation (10).

Second, it needs to be realized that within a REV, the dissolution sites and precipitation sites are not necessarily coincident and not even have to occur within the same microcrack. A short-range diffusive transport on the scale of the characteristic dimension of the REV may be involved, but with dissolution being a controlling step, in most cases, as suggested by Berner [40]. However, applying Equation (9) to the REV scale allows us to include this transport in the kinetic rate.

Third, the reaction area is considered as a factor of notorious complexity (Lichtner [41]), especially when the volume fraction of quartz is variable due to dissolution. Lichtner suggests that the current reaction area is proportional to the current mineral volume fraction to the power $\frac{2}{3}$. In the proposed model, the variation of the dissolution site area is connected to microfracturation occurring during the damage process, as in Equation (16). Precipitation may occur either locally, at remote sites, or may not be occurring at all (Steefel and MacQuarrie [33]). Walderhaug [42, 43] suggests that the reaction area of precipitation of quartz during cementation of sandstone is substantially reduced due to several processes, including progressive grain and/or pore-wall coating, and other forms of contributions to porosity reduction. In what follows, we differentiate the dissolution reaction area \tilde{a}_d from that of precipitation \tilde{a}_p , so that

$$\dot{\xi} = s \frac{\mathrm{d}a_{\mathrm{H_4SiO_4}}}{\mathrm{d}t} = s \gamma_{\mathrm{H_4SiO_4}} (\tilde{A}_d k_+ a_{\mathrm{SiO_2}} a_{\mathrm{H_2O}}^2 - \tilde{A}_p k_- a_{\mathrm{H_4SiO_4}}), \quad \tilde{A}_i = \tilde{a}_i \frac{m^0}{n\rho_{\mathrm{w}}}, \quad i = p, d$$
(17)

and link directly the dissolution reaction area to dilatancy as in Equation (16).

For precipitation, the availability of the precipitation surface area is reduced progressively as a direct function of time, shown in Figure 1, as it appears from the observation of Walderhaug [43]. Such a relationship can be represented by the following function:

$$\tilde{a}_p = \tilde{a}'_{p0} \exp\left[-\left(\frac{t}{t_c}\right)^2\right]$$
(18)

where t_c is the constant defining the time of disappearance of about 64% the surface area available for precipitation and \tilde{a}'_{p0} is the initial specific area available for precipitation. Hence, the reaction rate (Equation (9)) applied to the considered situation yields the following rate of relative mass removal:

$$\dot{\xi} = s \frac{da_{H_4SiO_4}}{dt} = s \gamma_{H_4SiO_4} \{ (\chi | \varepsilon_v^{irr} | + \tilde{a}_0) k_+ a_{SiO_2} a_{H_2O}^2 - \tilde{a}_{p0} k_- a_{H_4SiO_4} \exp[-(t/t_c)^2] \}$$

$$\chi = \psi_q \chi' \frac{m^0}{n\rho_w}, \quad \tilde{a}_0 = \psi_q \tilde{a}'_0 \frac{m^0}{n\rho_w}, \quad \tilde{a}_{p0} = \tilde{a}'_{p0} \frac{m^0}{n\rho_w}$$
(19)

As a result it appears that the chemical-softening variable is explicitly a function of time, the accumulated irreversible strain and of the activity of silicic acid. Integration of Equation (19) must be coupled to that of Equations (4) and (7).

In what follows, two approaches are considered, in which the medium is represented by a closed system (REV) within which dissolution is partially counterbalanced by a local precipitation, and



Figure 1. Normalized precipitation surface area $\tilde{a}_p/\tilde{a}'_{p0}$.

the mineral mass does not leave the REV, as well as an open system, a boundary value problem in fact, which is affected by the local dissolution and a long-range diffusion away from a dissolution site, while the local precipitation is considered negligible.

4. CREEP IN A CLOSED SYSTEM AFFECTED BY A LOCAL DISSOLUTION AND PRECIPITATION

In this section, we discuss an example in which chemical weakening is affected by dissolution and precipitation processes, which are both local. It means that the product of dissolution is subsequently precipitated within the same REV on the interfacial surface area available. The net amount of the species that is removed from the solid is a result of different rates with which dissolution and precipitation take place. It does not imply that the precipitation occurs at the wall surface of the same microcrack that dissolution takes place. It however, entails that transport of dissolved species, if any, is limited to the interior of the REV. The restriction of the closed system refers only to the dissolved mineral species. It does not refer to the water, as this is dragged into a newly formed pore space by the very process of dilatancy damage that creates a pore pressure deficit. It is assumed that the water transport is instantaneous. Such a selectively closed system idealization is quite common in groundwater systems (see e.g. Appelo and Potsma [44]). Figure 2 presents a cartoon illustrating such a selectively closed REV within which distinct dissolution and precipitation sites exist. However, the dissolved mass of silica does not leave the REV and hence only short-range diffusion is considered and incorporated into precipitation rate effect.

Our goal in this section is to identify a correspondence between the well-known creep phases and different elements of the processes involved in the proposed mechanism of chemical softening. The classical representation of creep comprises three phases of the strain development with time, at constant stress, which are referred to as primary, secondary and tertiary phase (Figure 3), all

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Figure 2. A cartoon showing a REV which forms a selectively closed system (open for water, closed for minerals). The removal of the mineral mass from dissolution sites (marked symbolically with ○) at the microcrack walls induces weakening of the solid. The precipitation sites (marked with ▲) occur within the same REV, but because of a short-range diffusion not necessarily at the same site. Short-range diffusion effect contributes to the precipitation rate.



Figure 3. A three-phase creep curve.

preceded by a phase of elastic (often seen as instantaneous) strain. This phase is not present in our analysis as the material is considered rigid plastic. Still, some strain due to a stress increase in the plastic domain may be present prior to the creep stage. Primary creep is characterized by an initial period with a strain rate which is relatively high, but in a well-marked transition period deccelerates to a constant rate. Secondary creep is characterized by a constant rate of strain. Tertiary creep indicates a phase of a rapidly accelerating strain, ending likely with a very high, possibly infinite, strain rate and hence failure.

The mechanisms in this model which activate the above described creep phases are: dissolution and precipitation, that together with the corresponding (variable) reaction surface areas affect the variable of mass change of silica, and finally two hardening function: strain hardening and chemical softening, which control the change in the material strength. We will now discuss those mechanisms in detail.



Figure 4. Yield surface in Equation (20).

The material strength is determined by a yield condition defined in terms of stress. A specific yield condition adopted here is similar to the parabolic function developed by Dragon and Mróz [45] (see Figure 4)

$$f(\sigma_{ij}, \kappa, \xi) = s_{ij} s_{ij} - 2p_{\rm h} (I_1^0 - \sigma_{kk})$$
⁽²⁰⁾

where s_{ij} is the deviatoric stress, while hardening parameter, p_h , defining the size of the yield locus is a resultant of a mechanical and chemical hardening

$$p_{\rm h}(\kappa,\xi) = p_0[1 + \alpha(\kappa) - \beta(\xi)], \quad p_{\rm h} > 0 \tag{21}$$

 α and β are two independent hardening functions. I_1^0 is a constant isotropic stress value, at which the yield limit intersects the isotropic stress axis. Parameter $p_h = p_0$ at no hardening is related to the pre-peak yielding stress value, kf_c (f_c is the uniaxial strength), during uniaxial compression of the material, with $0.4 \le k \le 0.6$, via (Dragon and Mróz [45])

$$p_0 = \frac{1}{3} \frac{k^2 f_c^2}{I_1^0 - k f_c} \tag{22}$$

Substituting the chosen constitutive functions into Equation (8) one arrives at a creep strain rate expressed by the relative mass loss rate as follows:

$$\dot{\varepsilon}_{ij} = \frac{\partial \beta / \partial \xi}{\partial \alpha / \partial \kappa} \frac{s_{ij} + p \delta_{ij}}{(\frac{2}{3} s_{kl} s_{kl})^{1/2}} \dot{\xi}$$
(23)

As an example, consider a biaxial compression of a homogeneous isotropic material element loaded symmetrically with the stress components $\sigma_2 = \sigma_3$, $\sigma_1 = 0$. Such a loading path is of interest as it renders deviatoric loading depending on one stress value only.

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Figure 5. Logarithmic chemical-softening function.

First, let us specify the hardening function in Equation (21) as a linear deviatoric strain hardening and a logarithmic chemical softening, that is

$$p_{\rm h}(\kappa,\,\xi) = p_0 \left[1 + \alpha_0 \kappa - \beta_0 \ln \frac{\beta_1 - \xi_0}{\beta_1 - \xi} \right] \tag{24}$$

in which the reaction progress ξ is expressed through its rate in terms of aqueous silica activity rate, via Equation (19). α_0 , β_0 are material constants. β_1 is a constant defining the chemical-softening curve as in Figure 5, in particular, the entity of the strength loss at the complete mass removal of the mineral being dissolved, i.e. at $\xi = 1$. ξ_0 is the reference pre-creep mass loss. With the function chosen in (24) the material remains in nearly full strength when no chemical softening occurs, while it may lose even all its strength when completely depleted of silica ($\beta_1 = 0.252$). In reality, a complete depletion of silica is an unlikely occurrence, and a complete loss of strength is also only a theoretical case. The loss of strength is moderate at the beginning of mass depletion and at 75% of depletion it is still less than 30% of the initial strength. However, beyond that range the loss of strength is far more dramatic.

In what follows the initial dissolution-specific surface \tilde{a}_0 in Equation (19) is assumed to be zero, all the interface surface being created by dilatancy. The volumetric strain (dilatancy) at a constant stress and hence at $p_h = \text{const}$, $s_{kl} = \text{const}$, can then be determined by solving the following couple of differential equations determining ε_v and ξ , as a function of time t, assuming that at t = 0, $\xi = 0$:

$$\dot{\varepsilon}_{\rm v} = \frac{\beta_0}{(\beta_1 - \xi)\alpha_0} \frac{3p_{\rm h}}{(\frac{2}{3}s_{kl}s_{kl})^{1/2}} \dot{\xi}$$
(25)

$$\dot{\xi} = s\chi |\varepsilon_{\rm v}| \gamma_{\rm H_4SiO_4} k_+ a_{\rm SiO_2} a_{\rm H_2O}^2 - \tilde{a}_{p0} k_- \xi \exp[-(t/t_c)^2]$$
(26)

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Figure 6. Deviatoric creep strain (a) and creep strain rate (b) at different stress levels.

Equations (25) and (26) define the creep behaviour of the material in question. Once the equation system is solved, the creep strain rate components can be obtained as

$$\dot{\varepsilon}_1 = \frac{\beta_0}{(\beta_1 - \xi)\alpha_0} \frac{s_{11} + p_{\rm h}}{(\frac{2}{3} s_{kl} s_{kl})^{1/2}} \dot{\xi}$$
(27)

$$\dot{\varepsilon}_2 = \dot{\varepsilon}_3 = \frac{\beta_0}{(\beta_1 - \xi)\alpha_0} \frac{s_{22} + p_{\rm h}}{(\frac{2}{3} s_{kl} s_{kl})^{1/2}} \dot{\xi}$$
(28)

The integration of the system (25, 26) has been performed numerically using *Matlab* 7.0. The activity coefficients of silica and water are assumed to be unity. The parameters are chosen as follows: $I_1^0 = -63.036 \text{ MPa}$, $p_0 = -0.095 \text{ MPa}$, s = 3.33, $\chi = 1 \times 10^6$, $\tilde{a}_{p0} = 0.12 \times 10^6$, $t_c = 2.16 \times 10^5$ s, $\alpha_0 = 1$, $\beta_0 = 0.252$, $\beta_1 = 1.02$, $\xi_0 = 0$. The rate constants are taken as $k_+ = 6.091 \times 10^{-11} \text{ s}^{-1}$, $k_- = 3.758 \times 10^{-10} \text{ s}^{-1}$, hence $K_e = 0.000 \text{ m}^2$.

The rate constants are taken as $k_+ = 6.091 \times 10^{-11} \text{ s}^{-1}$, $k_- = 3.758 \times 10^{-10} \text{ s}^{-1}$, hence $K_e = k_+/k_- = 0.16$. The precipitation rate constant has been taken directly as that of Rimistid and Barnes [32]. The choice of the rate constant for dissolution is the subject of the parametric study which follows. First, creep is analysed at different stress level with the rate constants provided above. Creep strain is simulated for three particular stress levels: (i) $\sigma_1 = 0$, $\sigma_2 = \sigma_3 = 4.832$ MPa; (ii) $\sigma_1 = 0$, $\sigma_2 = \sigma_3 = 6.569$ MPa; and (iii) $\sigma_1 = 0$, $\sigma_2 = \sigma_3 = 7.691$ MPa. The corresponding initial strain components at the onset of creep are calculated for the instantaneous rigid-plastic behaviour: (i) $\varepsilon_1^0 = -0.022$, $\varepsilon_2^0 = \varepsilon_3^0 = 0.010$; (ii) $\varepsilon_1^0 = -0.116$, $\varepsilon_2^0 = \varepsilon_3^0 = 0.051$; and (iii) $\varepsilon_1^0 = -0.190$, $\varepsilon_2^0 = \varepsilon_3^0 = 0.082$.

The resulting deviatoric creep strain and its strain rate are shown in Figure 6(a) and (b) as a function of time for the three stress levels. Significantly larger strain develops at higher stress levels. The transitions between the primary stage, secondary stage and tertiary stage also occur quicker at a higher stress because of a larger dilatancy and hence, an accelerated dissolution. The character of creep curves is well reproduced by the mechanisms postulated.

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Figure 7. Deviatoric creep strain at different strain-hardening coefficients (a) and creep strain at different equilibrium constants (b).

In what follows we present results of a parametric study of the material time response to a constant loading at stress level (ii).

First, we investigate the creep strain under different equilibrium constant $K_e = k_+/k_-$ by fixing the value of $k_- = 3.758 \times 10^{-10} \text{ s}^{-1}$ while varying the value of k_+ (Figure 7(b)). Clearly, the higher dissolution rate constant accelerates the mass removal. This triggers a higher deviatoric strain *via* the corresponding hardening effects. Similarly, as a result of this compensatory mechanism, the smaller the material hardening coefficient α_0 , the greater the creep strain developed (Figure 7(a)).

In general, it is possible to attribute each of the three phases of creep to a different contribution of the mechanisms involved: the mechanism of strain hardening, controlled by deviatoric strain ε_q and the chemical mechanism of mass change controlled by the relative mass removal ξ . By virtue of the compensatory mechanism triggered by the creep conditions, $\dot{\sigma}_{ij} = 0$, as mentioned earlier, the two hardening variables become inter-dependent *via* Equations (25)–(26). Due to the logarithmic form of the chemical-softening function, the deviatoric strain is visibly augmented near the mass removal completion. However, it has to be reminded that the theory becomes less accurate when we leave the small strain range. It is easy to see that integrating and subtracting Equations (27) and (28) yield a stress-independent deviatoric strain function, depicted in Figure 8. This is not the case of the volumetric (dilative) strain, which generally increases with the value of the imposed stress, Figure 9. The relative mass removal, ξ , is clearly enhanced by the acting compressive stress, Figure 10(a).

The resultant relative mass removal, ξ , is affected by four factors: dissolution rate constant, the specific surface area available for this reaction, the constant of the rate of precipitation (which is subtracted) and the corresponding specific surface area available for this reaction (Equations (17) and (19)). The first stage of the relative mass removal, ξ , for less than 10 first hours shows the prevailing effect of dissolution part of the reaction progress, Figure 10(a) and (b). This is despite the fact that dissolution rate constant is about seven times smaller than the precipitation. However, the initial surface area which is also an important factor in the resultant specific reaction rate (Equation (17)) is much higher for dissolution than that for precipitation. In fact, the initial surface area of dissolution depends directly on the dilatant volumetric strain accumulated during

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Figure 8. Deviatoric creep strain $vs \xi$.



Figure 9. Volumetric creep strain vs ξ .

pre-creep loading stage, which increases with the level of stress, see Figure 9. Additionally, for the physical reasons, the surface area for dissolution area increases as a result of damage/dilatancy, while that for precipitation decreases due to accumulative grain and/or pore-wall coating. The above evolution yields the partial and total rates presented in Figure 10(c).

Consequently, the *primary* creep is initially dominated by dissolution. As a result of an increasing precipitation that reduces the net mass removal rate, the strain rate has a decelerating trend. Both the initial reaction rate (initial slope at Figure 10(a)) and deviatoric strain rate (Figure 6(b)), as well as the threshold deviatoric strain opening the secondary creep phase (Figure 6(a)), are all

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Figure 10. Evolution of (a) ξ ; (b) the components of ξ at 4.832 MPa; and (c) the components of the rate of relative mass removal at 4.832 MPa.

directly related to the stress level dependent, pre-creep dilatancy. Pre-creep dilatancy corresponds to the surface area of microcracks generated during the initial loading phase. The latter feature represents the transition to the *secondary* phase in which while the creep strain increases, the strain rate diminishes. This phase includes the mechanism of the reduction of the surface area of precipitation (Equation (18), Figure 1), as well as a monotonic increase of the activity of silicic acid $a_{H_4SiO_4}$. As the former one gradually starts to dominate over the latter effect, the overall mass removal rate and deviatoric strain rate begin to increase again relatively slowly. Notably, the minimum strain rate depends on the pre-creep damage, and through it on the stress level, Figure 5. Eventually, the *tertiary* phase is induced by the terminal phase of the chemical-softening effect, for approximately $\xi > 0.75$, in this case. At this point the process is significantly accelerated towards the completion of the depletion of the mass, as described by the logarithmic chemical-softening function $\beta(\xi)$, Equation (24). Hence, it is consistent with the concept of failure nature of tertiary creep, which in this formulation is linked to the terminal phase of the chemical softening. It has to

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Figure 11. A cartoon showing two REVs, each forming an open system (both for water and minerals). The removal of the mineral mass occurs at dissolution sites (marked symbolically with ○) at the microcrack walls within one REV, while long-range diffusion lowers the concentration of dissolved silica near the source. Precipitation may occur at remote locations at another REV sites (marked with ▲).

be realized that the shape of the chemical-softening function may be such as to produce a critical softening earlier, i.e. before mass removal is near completion. Finally, it needs to be realized that even at the low stress value the tertiary creep does develop. In reality, it may take a substantial amount of time to take place, especially at low stress. In this model, the physical argument is that the tertiary creep sets off depending on when the mass removal ξ reaches a particular level (in our particular example a value about $\xi = 0.75$) which is at an extremely long time for a truly low stress level.

Finally, it is interesting to note that the aforementioned compensatory mechanism regarding the hardening variables of Equation (5) can be used to address the dual phenomenon of creep, which is relaxation. For simplicity, one may consider relaxation under a constrained deviatoric strain invariant, i.e. for $\dot{\kappa} = 0$. The condition for the progress of the process of the chemo-plastic softening, Equation (5), under those conditions implies that $(\partial f/\partial \sigma_{ij})\dot{\sigma}_{ij} < 0$, for the relative mass removal $\dot{\xi} > 0$, given the fact that for chemical softening $\partial f/\partial \xi > 0$. Hence, the stress rate is required to be oriented to the interior of the current yield locus, which in a 1-D case means that the stress is decreasing. However, to model properly the evolution of the reactive surface area *via* dilatancy may require to consider elastic strains or a strain or displacement component-based relaxation condition.

5. CREEP IN AN OPEN SYSTEM AFFECTED BY A LOCAL DISSOLUTION AND LONG-RANGE DIFFUSION

In an open system, masses of all species move in and out of the REV. Material properties, and in particular the chemical softening is therefore, in addition to the local dissolution and precipitation, affected by a long-range mineral diffusion. Thus, as presented in the cartoon (Figure 11) silicic acid diffuses out of REV and may undergo precipitation away from the local dissolution site in a remote REV. However, as the local precipitation depends on the activity (hence concentration) of

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silicic acid, and therefore a mass diffused away, the latter one impacts the mechanical properties of the material. Clearly, to include a long-range diffusion a boundary value problem needs to be analysed.

In this way, two independent rates are now controlling the material chemical weakening process, that is dissolution and diffusion. The former one is an intrinsic property of a mineral, the latter one is a transport property and its result depends also on the gradient of concentration. Therefore, the problem to be considered is a coupled field problem, governed by a chemo-mechanical deformation equation on the one hand, and on the other hand a reactive transport equation.

We consider here a special case when the local precipitation is ignored. Parameter ξ as defined earlier, is the relative mass removal, as its rate is described by the kinetic equation (17). Hence, the mass removal is exclusively controlled by dissolution

$$\dot{\xi} = A_d s k_+ a_{\rm SiO_2} a_{\rm H_2O}^2 \tag{29}$$

As before (Equation (19)), the surface area of dissolution A_d is assumed as linearly related to the volumetric irreversible strain. The activities of solid and pure liquids are assumed to be unities. As a result, $\dot{\xi}$ becomes

$$\dot{\xi} = k_+ (\Xi |\varepsilon_{\rm v}| + \Xi_0), \quad \Xi = s\chi = \text{const}$$
(30)

 Ξ_0 is a constant related to the surface area of the initial void space.

As variance to the previous local case, the presence of diffusion requires the mass rate of quartz to be controlled by the reactive diffusive transport law

$$\frac{\partial x_{\rm H_4SiO_4}}{\partial t} = D\nabla^2 x_{\rm H_4SiO_4} + F(\xi(\varepsilon_{\rm v}))$$
(31)

where $x_{H_4SiO_4}$ is the molar fraction concentration of the solute H_4SiO_4 , *D* is the diffusion coefficient, *F* is the rate of mass production. *F* is enhanced by a volumetric strain resulting from the dilatancy damage. The process is approximated by assuming \tilde{A} as a linear function of dilatant volumetric strain ε_v in Equation (19) and by ignoring the local precipitation. So, the last term of Equation (31) is fully coupled to the mechanical part of the solution, as follows.

As an example, consider an infinitely long thick cylinder with internal and external radii a and b, permeated by water. From the point of view of plasticity, it is an extension to reactive chemo-plasticity of a classical problem of a thick tube as formulated by Hill [46] and adapted to Cam-clay type of granular materials by Mróz and Kwaszczynska [47] and Hueckel and Mróz [48]. Our interest is in its long-term response to a constant state of loading. An initial, pre-loading phase is assumed to consist of a proportional increase of an inner and external pressures at a and b until the values p_a and p_b are reached, respectively. The value of p_a is assumed significantly larger than p_b . In the subsequent creep phase the cylinder is subject to constant external pressures at values $p_a > p_b$. Therefore, this phase can be considered as an axisymmetric cylindrical expansion (creep) under a constant mechanical boundary load, hence occurring exclusively as a result of a chemically driven damage process.

The process is constrained by equilibrium equation and kinematic relationships, and the assumption of plane strain, which for the axisymmetric problem are as follows:

$$\frac{\mathrm{d}\sigma_r}{\mathrm{d}r} + \frac{\sigma_r - \sigma_\theta}{r} = 0, \quad \dot{\varepsilon}_r = -\frac{\mathrm{d}\dot{u}}{\mathrm{d}r}, \quad \dot{\varepsilon}_\theta = -\frac{\dot{u}}{r}, \quad \dot{\varepsilon}_z = \mathrm{const}$$
(32)

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Figure 12. Yield condition and stress profiles.

where r, θ and z are outward radial, circumferential and axial co-ordinates, respectively, u is the radial displacement. The mechanical boundary conditions are: at r = a, $\sigma_r = p_a$ and at r = b, $\sigma_r = p_b$. The material is assumed as rigid plastic. The yield surface is taken as simple as possible, expressed *via* single principal stress components, as shown in Figure 12.

$$\sigma_r = \sigma_{0i} f_r(\varepsilon_q, \xi) \quad \text{for} \begin{cases} -\tan \varphi < \sigma_\theta / \sigma_r < 1, & \sigma_r \ge 0, \quad i = 1 \\ -\cot \varphi < \sigma_\theta / \sigma_r < 1, & \sigma_r < 0, \quad i = 2 \end{cases}$$
(33)

and

$$\sigma_{\theta} = \sigma_{0i} f_{\theta}(\varepsilon_{q}, \xi) \quad \text{for} \begin{cases} -\tan \varphi < \sigma_{r} / \sigma_{\theta} < 1, & \sigma_{\theta} \ge 0, \quad i = 1 \\ -\cot \varphi < \sigma_{r} / \sigma_{\theta} < 1, & \sigma_{\theta} < 0, \quad i = 2 \end{cases}$$

 σ_{01} and σ_{02} are constant values of initial yield stresses, and f_r and f_{θ} are hardening rule functions.

It is further assumed that the yield limit undergoes strain hardening and chemical softening, as ξ represents the chemically induced relative mass loss. The flow rule is associative. We consider deviatoric strain hardening and chemical-softening rules, expressed *via* linear functions $f_r = f_{\theta}$ as follows (for $\sigma_r > 0$):

$$\frac{\sigma_r}{\sigma_{01}} = 1 + \gamma' \varepsilon_q - \beta' \xi \ge 0, \quad \frac{\sigma_\theta}{\sigma_{02}} = 1 + \gamma' \varepsilon_q - \beta' \xi \ge 0, \quad \sigma_{01} \ge 0, \quad \sigma_{02} \le 0$$
(34)

where γ' and β' are, respectively, strain hardening and chemical weakening material constants, taken here for simplicity the same for σ_r and σ_θ ; ε_q is the deviatoric strain and is defined as $\varepsilon_q = |\varepsilon_\theta - \varepsilon_r|$.

During the initial (non-chemical) phase, the external loading at the inner boundary r = a increases to $\sigma_r = p_a(p_a > \sigma_{01})$ and to a much smaller value $\sigma_r = p_b$ at the outer boundary r = b (see Figure 13). The stress values at the two boundaries are imposed to change proportionally, so that $\sigma_{ra} = m\sigma_{rb}$, m = const. As p_b is much smaller than p_a , the initial yielding is expected at r = a. In what follows we address one particular type of solution for a 'thick' cylinder with the

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Figure 13. Radial stress and concentration BC.

ratio of the external to internal radius $b/a > (b/a)_{crit}$. This type of solution results from the fact that the yield condition is piece-wise linear, and load bracket between the interior and exterior load corresponds to more than one segment of the yield surface (see Hueckel and Mróz [48] for a complete discussion). The value of the critical proportions $(b/a)_{crit}$ is derived from a limiting condition of existence of a single segment yielding (along *EA* in Figure 12)

$$\sigma_{02}\left(\frac{b}{a}-1\right) + \frac{b}{a}m\sigma_{01} < \sigma_{01} \quad \text{hence } \left(\frac{b}{a}\right)_{\text{crit}} = \frac{\sigma_{01} + \sigma_{02}}{m\sigma_{01} + \sigma_{02}} \tag{35}$$

For the 'thick' cylinder, before the inner load reaches the initial yield stress σ_{01} , the material remains rigid and the stress state in the whole cylinder remains within the initial yield limit ADFE as shown in Figure 12. The only solution for the purely mechanical phase of the pre-creep loading with the particular boundary conditions as above, a piecewise yield condition and a particular thickness of the cylinder, requires existence of two distinct zones: an inner plastic zone and a outer initially rigid zone. The inner plastic zone between a and a certain radius c develops, once σ_r exceeds σ_{01} at r = a. As the radial stress at r = a moves along the critical line OA', from A ($\sigma_{ra} = \sigma_{01}$) dragging the yield surface to a position at C until it reaches its destination value $\sigma_{ra} = p_a$ at A'. The critical state line represents the only stress states that are kinematically admissible, but to satisfy the stress boundary conditions, the presence of the outer rigid ring (stress profile BA segment in Figure 12) is necessary in this phase of the process. The strain rate is determined by a 'corner rule' along AA'. The radial stress at the growing outer radius of this zone, r = c, remains at stress point A, i.e. $\sigma_{rc} = \sigma_{01}$. By the same token, the shrinking of the size of the outer zone between $c \leq r \leq b$, with stress profile segment B^0A inside the yield surface, continues until the circumferential stress component at r = b and at all other points reach the yielding point of σ_{02} . Continuity of radial stress and displacement across the internal boundary r = c is imposed. The entire outer zone then starts to yield at the same instant along the line BA and undergoes a uniform radial displacement $u = u_0$ as a result of the peculiar yield locus and normality rule. This particular moment is chosen as a starting point (t = 0) for the subsequent creep phase, driven by the chemical softening due to mass removal. The values of p_a and p_b , determined by the

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deformed configuration at this particular moment when the outer zone undergoes yielding, are taken as the constant stress boundary conditions that are applied to the cylinder during the creep process discussed as follows.

In the creep phase, the radial stresses at the internal and external radii remain constant at $\sigma_{ra} = p_a$, $\sigma_{rb} = p_b$. This obviously does not imply that locally stress remains constant, but the process becomes driven by the chemical reaction of dissolution of silica. while all three variables in Equation (5) are potentially active. The material develops a strain as a combination of strain hardening *via* the compensatory mechanism mentioned already in the previous case, and a stress adjustment. Dissolution within the outer zone starts to take place due to dilatancy caused by yielding and producing new interface surface area in addition to an original interfacial dissolution surface present within the material.

The ensuing strain hardening drives the displacement at the inner boundary. With time progressing, the stress at boundary c grows along AA', while physically the boundary between the zones moves inward, $\dot{c} < 0$. Hence, the inner zone becomes smaller and the outer zone of dilatancy expands. With the choice of extremely simple yield function, the following constraints are imposed: for the inner zone, $a \le r \le c$, stresses stay at the corners (between A' and C) of the subsequent yielding curves (see Figure 12). The flow rule at the corner points is non-unique, but on the other hand, σ_r and σ_{θ} are in constant relation: $-\sigma_{\theta}/\sigma_r = \tan \varphi$. The latter condition, together with the strain-hardening function, imposes a contractile kinematics in the inner zone; for the outer zone, $c \le r \le b$, the yield is determined by its circumferential stress component, hence $\dot{\varepsilon}_r = 0$ and $u = u_0 = \text{const.}$ The stress is required to be continuous at the boundary, hence $\sigma_{rc}^{\text{inner}} = \sigma_{\rho c}^{\text{outer}}$, $\sigma_{\theta c}^{\text{inner}} = \sigma_{\theta c}^{\text{outer}}$. With these conditions and Equations (32)–(34), the uniform displacement u_0 and boundary radius c, both time dependent, can be calculated as a solution of the following system of differential equations for the coupled chemo-mechanics in the outer zone, $c \le r \le b$, constrained by the continuity conditions with the inner zone

$$\frac{p_a}{\sigma_{01}\tan\varphi} \left(\frac{a}{c}\right)^{1+\tan\varphi} - \frac{p_b}{\sigma_{01}\tan\varphi} \frac{b}{c} = (1-K_c t) \left(\frac{b}{c}-1\right) - \left(\frac{\int_0^t K u_0 \, \mathrm{d}t}{r} - \frac{\alpha' u_0}{r}\right) \ln\frac{b}{c} \tag{36}$$

$$\frac{p_a}{\sigma_{01}} \left(\frac{a}{c}\right)^{1+\tan\varphi} = (1 - K_c t) - \left(\frac{\int_0^t K u_0 \,\mathrm{d}t}{r} - \frac{\alpha' u_0}{r}\right) \tag{37}$$

In Equations (36)–(37), the chemical coefficients $K = \beta' \Xi k_+$ and $K_c = \beta' \Xi_0 k_+$ represent the chemical softening associated with dilatancy and initial microcracking, respectively. The deformation of the inner zone, $a \leqslant r \leqslant c$ can be determined by its equilibrium equation. The inner zone is very small (Figure 15), hence the chemical-softening effect can be neglected for this zone, and its displacements can be calculated as

$$\frac{u}{r} - \frac{u_0}{c} = \frac{1}{\alpha'} \left\{ \frac{p_a/\sigma_{01}}{1 + \tan\varphi} \left[\left(\frac{a}{r}\right)^{1 + \tan\varphi} - \left(\frac{a}{c}\right)^{1 + \tan\varphi} \right] + \ln\frac{r}{c} \right\}$$
(38)

At the same time, the above equation system (36)–(38) is coupled with the diffusion equation (32) which reads

$$\frac{\partial x_{\mathrm{H_4SiO_4}}}{\partial t} = D\left(\frac{\partial^2 x_{\mathrm{H_4SiO_4}}}{\partial r^2} + \frac{1}{r}\frac{\partial x_{\mathrm{H_4SiO_4}}}{\partial r}\right) + \frac{k_+(\Xi\varepsilon_v + \Xi_0)}{s}$$
(39)

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Figure 14. Evolution of displacement of the internal radius.

Note that Equation (39) contains $\varepsilon_v = -u_0/r$ for the outer zone (it is replaced with zero for the inner zone), which produces coupling of that equation to the three other (35)–(37). The other way of coupling of Equations (36)–(38) to (39), coming originally from the presence of $a_{H_4SiO_4} = x_{H_4SiO_4}$ in Equation (9), is not considered here, as we have chosen to ignore the local precipitation in this formulation.

The inner zone is contractile in the pre-creep phase and it remains contractile over most of its thickness, during the creep phase. There is a narrow dilatant ring induced by the kinematic continuity condition across r = c, as seen in Figure 16. However, the dissolution from this zone has been neglected in the simulation.

Concentration boundary conditions are: r = a, $x_{H_4SiO_4} = 0$; r = b, $x_{H_4SiO_4} = x_0$ for $t > t_0$. Hence, there is an initial background transport from the exterior to the interior of the cylinder driven by the difference in the imposed external values of concentration. Subsequently, the point-wise production of silicic acid coupled to the mechanical damage affects the concentration distribution and consequently the flux of the solute mass at the inner boundary. Such a diffusive flux, defined as $J = -D\nabla x_{H_4SiO_4}$ is of significant interest, as it allows one to determine the influence of the mechanical damage on the net mass production of the solute.

Dimensionless variables τ and j are defined as, $\tau = tD/a^2$ and $j = Ja/Dx_0$. Coefficient M represents the effect of deformation associated with the dilatant volumetric strain on the mass transfer, $M = \Xi k_+ a^2/Dx_0$.

The system of Equations (36)–(39) is solved numerically. First, Equations (36)–(38) are numerically solved at each time step to obtain the deformation and strain, the volumetric strain is then calculated at each node and substituted into Equation (39), which is subsequently solved with a finite difference scheme. The results of the numerical solution are shown in Figures 14–19. The values of the input parameters used are: $p_a/\sigma_{01} = 2.0133$, $p_b/p_a = 0.015$, $-\sigma_{02}/\sigma_{01} = \tan \varphi = 0.2$, $\alpha' = 5$, b/a = 10. Figure 14 represents the kinematics of the cylinder during creep, and shows the displacement u_a of the internal circumference, r = a, induced purely by the chemical process. It



Figure 15. Propagation of zones.



Figure 16. Development of volumetric strain.

can be seen that the chemical softening due to dissolution of the material can significantly accelerate the displacement of the inner surface of the cylinder. Figure 15 illustrates the development of the different zones across the cylinder, at a given time, t. In particular, one may observe here the chemical coupling at the field level. In fact, for larger chemical coefficient values K, the critical state zone (r < c) and compaction zone become smaller and disappear all together earlier showing clearly that the dilatant damage zone is markedly increased due to the chemical reaction damage (softening).

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Figure 17. Dimensionless flux at the inner boundary.



Figure 18. Inner boundary flux vs total displacement of the internal radius.

Volumetric strain within the whole cylinder at different moments is shown in Figure 16, showing again the distribution of dilatancy and contractancy along the radius as it changes in time. It may also be inferred that the dissolution surface area which is proportional to ε_v in the dilatant zone is the largest and increases most near the boundary r = c between the inner and outer zones. So, the most of dissolution comes from the interface area between the two zones.

A notable finding is the evolution of the solute mass flux at the stressed boundary r = a. It can be seen that the damage-related increase in dissolution rate can significantly accelerate the mass flux,

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Figure 19. Reactive flux vs penetration (creep).

as in Figure 17. The case, when M = 0, represents a pure transient diffusion solution in response exclusively to the concentration gradient imposed between the inner and outer external boundaries. It is interesting to see from Figure 18 that the boundary flux vs creep caused displacement, the mass flux generation develops clearly in a different way in the early stage from the later evolution. Initially, it is mainly contributed to the diffusive flux due to the initial prescribed concentration gradient. The flux is higher for lower coefficient $M(M = \Xi k_+ a^2/Dx_0)$. Contrarily, in the later phase, the dissolution effect becomes dominant. It can be seen from Figure 19 that the reactive flux, calculated by subtracting the pure diffusion flux from the total flux, is intensified by the dissolution during the entire process, as represented by higher coefficients M.

6. CONCLUSIONS

A damage-enhanced reactive chemo-plasticity model is developed to reproduce the creep behaviour of saturated geomaterials. Two types of geo-environmental systems are examined: a closed system in which the chemical softening is affected by both local dissolution and precipitation, and an open system in which a mass removal due to dissolution and long-range diffusion is considered, while local precipitation is neglected. The deformation at a constant load in the closed system exhibits most of the characteristics of the classical creep. The strain and strain rate are visibly higher under higher constant loads. Primary, secondary and tertiary creep can be interpreted in terms of dominant mechanisms in each creep phase, emphasizing the role of the rates of dissolution and precipitation, variable reaction areas, as well as chemical-softening intensity, as shown schematically in Figure 20. The results show the central role of the compensatory mechanism between strain hardening and chemical softening. In the diffusion-affected boundary value problem, it is interesting to see how the chemical processes affect the evolution of the zones of different regimes of the coupled

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Figure 20. Dominant mechanisms in different phases of chemically induced creep.

deformation and dissolution. This boundary value problem is a generalization to coupled chemoplastic processes of the classical thick tube problem in plasticity, originally solved by Hill [46].

The problems considered are deliberately rather abstract and not related to any specific geomaterial except for the requirement that it contains a meaningful amount of quartz. Constitutive functions adopted for the BVP solution are all linear. However, they demonstrate a validity of the hypothesis that chemo-mechanical damage process, enhanced spontaneously in time by a basic reactive rate process, produces creep deformation. The outline of the presented model should be helpful in organizing experiments targeting well-defined measurements. An application of the theory as originally proposed by Hueckel and Hu [49] to specific micro-scale processes of intergranular contact penetration is discussed elsewhere (Hu and Hueckel [50]).

It is concluded that coupling the constitutive equation of plasticity (Equation (2)) to chemical reaction and/or transport phenomena (Equations (9), (19), (26), (30) and (31)) renders the plasticity laws (Equations (5), (8) and (34)), explicitly rate dependent. The advantage of that dependency is its direct link to more fundamental concepts, laws and data of basic geochemistry. In addition, the evolution of the material behaviour through the individual phases of creep can be attributed to specific chemical and deformational mechanisms developing during the process. The above demonstration obviously does not free the potential user of the verification of the applicability of the specific constitutive assumptions and formulae to the geomaterial under consideration, as other sources of microscale rate dependence are clearly possible.

APPENDIX

In this Appendix, a relationship is sought between a surface area opened during irreversible soil microcrack damage and the corresponding volumetric (dilatant) irreversible strain. A simple form of such a relationship can be obtained considering a regular, hexagonal, 2D crystal assembly with two inter-crystalline cracks producing a vertex split with the width δ at the apex, Figure A1. Assume for simplicity that microcracks have equal depth everywhere. The ratio of the new internal interface surface area generated by cracking per unit volume of the medium to the volumetric strain, ε_v^{irr} , reads $\tilde{a}/|\varepsilon_v^{irr}| = 8/(\sqrt{3}\delta) \cdot 1m$ and is independent of the number of cracks per grain, and of the number of grains in the assembly (Hu [51]); \tilde{a} is defined in Equation (15), δ is the crack

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Figure A1. Interfacial free surface within crystalline assembly.

opening at the apex. It is furthermore assumed that the increase in volumetric strain is attributed to the increase in the number of the crack segments only, and not to the change in their width, δ , or segment length, d. This implies that a macro-crack propagation consists of opening of a sequence of microcracks (inter-grain cracks) of the same δ , then the ratio remains constant. Thus,

$$\tilde{a} = \chi' |\varepsilon_{\rm v}^{\rm irr}| + \tilde{a}'_0, \quad \varepsilon_{\rm v}^{\rm irr} < 0 \quad \text{where } \chi' = \frac{8}{\sqrt{3}\delta} \cdot 1m$$
 (40)

Note that these conditions are valid for a mono-mineral medium. For a poly-mineral medium, the surface area \tilde{a} needs to be multiplied by a volume fraction of the dissolving mineral as shown in Equation (16).

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