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Reactive plasticity for clays during dehydration and rehydration. Part 1: concepts and options

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Abstract

A mixture theory framework is adapted to analyze the effects of changes in clay chemistry during dehydration and rehydration on clay mechanical properties. Macroscopic and microscopic evidence points to a possibility of modeling the mineralogical processes of illitization of smectites and re-smectitization of illite as kinetic reactions in closed systems. A version of thermo-chemo-plasticity for rehydrating illite is presented in which a hidden variable of hardening depends on temperature and the reaction progress variable in addition to plastic strain. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Dehydration and rehydration are common phenomena affecting geological materials of engineering interest, especially clays, such as illite or smectite. These clays are commonly used in barriers against chemical, or nuclear contamination, including exposure to nuclear waste heat. However, during a prolonged contamination and/or heating the original clay minerals may be transformed, respectively releasing or acquiring substantial amounts of water. Consequently, mechanical and seepage properties of the end product and the original clay materials may substantially differ. Monitoring and control of the evolution of clay properties during the above processes is crucial for the industry of clay barrier technology. The monitoring of the evolving material properties requires a prediction tool that includes a link between chemical, physico-chemical, or mineralogical reactions and constitutive description of mechanical properties of the material. Theories of reactive multiphase mixtures of deformable materials offer such a possible framework for clays.

The objective of this paper is to examine options open in the formulation of governing and constitutive equations to include changes in mechanical properties of

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clay materials occurring as a result of chemical processes to which these materials are subjected. It appears that there is no a priori structure for such a formulation, other than through a set of postulates of physical correlation between mass changes in some clay components and observed facts of hardening or softening of clay. The issue of idealization of clay as a closed or open system exchanging mass internally, i.e. between components, or externally, is examined from the phenomenological and thermodynamics points of view. Basic clay property changes observed in the laboratory as well as in the field are hypothesized to be related to specific elements of their thermal and mineralogical history. Formulation of the chemo- plastic softening due to reactions is given, which allows to describe the reversible and irreversible effects of chemical changes.

A companion paper (Hueckel and Pellegrini, 2001) presents detailed analysis of the site at Orciatico from the point of view of mineralogical and mechanical changes induced by heating. A procedure to identify constants for thermal and chemical softening described in this paper from the field and laboratory data is presented in the companion paper as well.

2. General framework

To account for changes in mechanical material properties in mathematical simulations one needs to formulate a set of constitutive hypotheses on how to couple the mechanics of the soil solids or that of interstitial liquid to their chemistry, and in particular to the evolution and possibly transport of chemical species. The focus of our considerations are changes in such mechanical properties of clay as the yield limit and elasticity moduli, caused by mineralogical changes, or in general by chemical reaction progress. This includes chemically induced swelling/shrinkage strain.

To frame such constitutive hypotheses into a workable theory we will adopt the principles of theories of reactive, two-phase (porous-solid and liquid) mixtures following the path of earlier developments by Eringen and Ingram (1965), Bowen (1969), Aifantis (1980a,b, 1981), Prevost (1980), Hassanizadeh (1986), Truesdell (1984), Lai et al. (1991), Hueckel (1992), Ma and Hueckel (1992) and Murad and Cushman (1997). This paper concentrates on the effects of specific mineralogical transformations of dehydration and rehydration of clay, involving mass exchanges between its components, which are postulated to be responsible for the observed changes in mechanical properties of materials.

One of the important aspects of coupled theories is the sheer number of possible couplings between the phenomena involved. To reduce that number to make the idealization numerically tractable and meaningful from the engineering standpoint we postulate certain limitations. First, we postulate that the considered mixture of the solid and fluid is a strongly interacting one [in Bataille and Kestin's (1977) sense]. In general, each phase may contain some chemical species, which move independently and which may take part in chemical reactions or physico-chemical processes within a phase or between the phases. Strongly interacting mixture postulate implies the balance of linear momentum only for phases, but not for single species. Species are constrained only by the mass balance and flux (if any) constitutive laws. Second, the solid is represented as an elasto-plastic porous continuum interacting with the saturating pore fluid. Third, both solid and fluid are subjected to temperature changes and chemical reactions (or physico-chemical processes) occurring between the species either of the same or different phases. Fourth, temperature is considered as the same in both phases. Fifth, the chemical reactions produce and/or destroy mass of some species, whereas the physico-chemical processes produce changes that may be viewed as mass transfer between the phases (e.g. release of adsorbed water in clays). Finally, sixth, the mechanical (including flow) material properties will be attributed to phases, but not to species. The main interest in this paper is on the choice of variables describing the species and the reactions between them, and how they need to be included in mechanical constitutive relationships. Restrictions on such choice and their significance will also be discussed as will be the resulting restrictions on such relationships.

3. Experimental evidence

3.1. Macroscopic evidence of variation in mechanical properties of clays due to dehydration/rehydration

Dehydration and rehydration of clays may occur in principally three types of settings. They may be caused by, respectively, heating or cooling at temperatures and pressure below boiling point (Pusch, 1987; Tessier et al., 1998). They may also be induced by a change in pore water ionic content, at constant temperature, leading to so called "osmotic" swelling or shrinkage (El Swaify and Henderson, 1967; Sridharan and Jayadeva, 1982; Fu et al., 1990; Hetzel et al., 1994). Finally, dehydration may be caused by replacement of water as interstitial fluid when clay is inundated with concentrated organic liquids of low permittivity, (e.g. Sridharan and Venkatappa Rao, 1973; Acar et al., 1985a,b; Fernandez and Quigley, 1988, 1991). In all these circumstances, significant changes in mechanical or seepage properties of clays, as well as non-mechanical strain (at constant stress) may occur, as described below.

3.1.1. Strength

A visible, even if not dramatic, decrease in peak strength with temperature is seen in Spanish clay, IC-1, at overconsolidation ratio (OCR) = 6, during heating at a constant confining stress of 0.75 MPa (Fig. 1; Hueckel et al., 1998). Strength of clay is also affected by changes in ionic concentration (see e.g. Anson and Hawkins, 1998), by change in ion type (valency), Olson (1974), or by changes in permittivity (or dielectric constant) of the pore fluid, as shown in Fig. 2 (Sridharan and Venkatappa Rao, 1973) for kaolinite. Strength increases particularly visibly when permittivity drops below 10.

3.1.2. Overconsolidation ratio

Changes in OCR, or in the apparent maximum preconsolidation axial stress occur during heating or uncontrolled chemical reactions at constant stress in one dimension strain conditions, as shown for Boom clay (Robinet et al., 1996) or North Adriatic Dalia sand (Hueckel et al., 1999) in Fig. 3a and b. After a cycle of drained heating and cooling at constant stress, clay that is originally in a normally consolidated state (meaning at yield), upon further loading shows a typically elastic stiffness. It requires a substantial stress increment to reach again the yielding mode. This suggests that during the heating/cooling cycle the yield domain has significantly increased. Similar response has been seen (Perret, 1995; Leroueil et al., 1996; Hueckel et al., 1999) to occur during periods of "aging" when strain developed at constant stress at normally consolidated conditions due to stress assisted dissolution of silica in sand (as suggested by Denisov and Reltov, 1961) or possibly due to a stress assisted increase in ionic concentration in pore liquid in clay (Mitchell and Solymar, 1984).

3.1.3. Thermal and chemical expansion

The amount of volumetric strain generated at constant stress during heating or exchange of pore fluid appears to depend on the value of the effective stress. During heating volumetric strain results to be reversible and expansive at low stress, and compressive and irreversible at high stress as shown in Fig. 4a (De Olmo et al., 1996). During chemical contamination, specifically during inundation with ethanol at different concentration seeping at constant rate into the specimen, Fernandez and Quigley (1991) have seen that strain in clay was expansive at low stress, and compressive at high stress (Fig. 4b; Hueckel, 1997). Similarly Hueckel et al. (1996) have shown (Fig. 4c) that in a high clay content soil with a slow transient seepage of

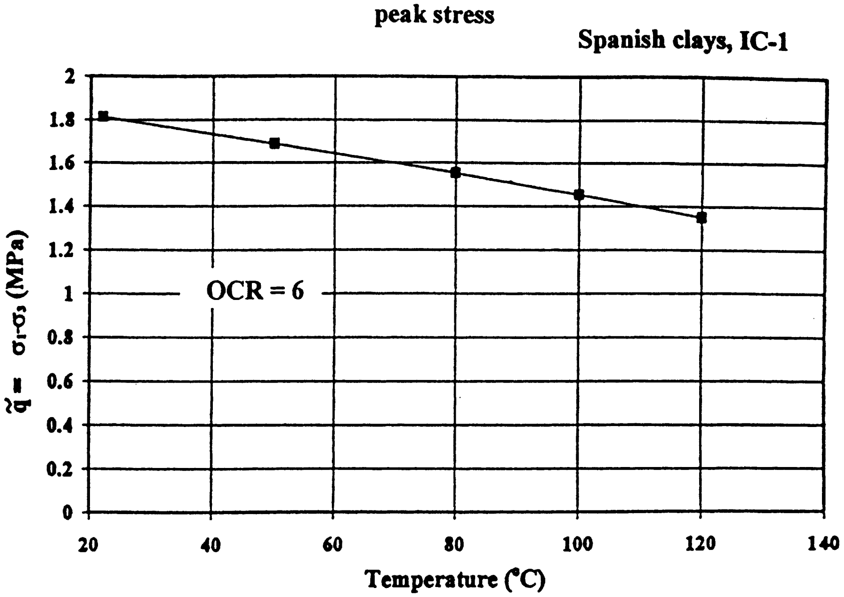

Fig. 1. Decrease in peak strength with temperature in Spanish clay, IC-1, at OCR = 6, during heating at a constant confining stress of 0.75 MPa (after Hueckel et al., 1998).

ethanol there is a clay expansion at low and compression of the specimen at high effective stress.

The experimental evidence presented indicates clearly that short term heating and/or relatively fast chemical reactions affect the apparent maximum pre-consolidation stress, compressive strength, in addition to producing strain in various instances of environmental loading. Dehydration/rehydration processes in clays may be either fast processes or develop over an extended period of time, depending on the driving mechanisms, as discussed further on. In the case of long term mineralogical changes of interest to nuclear waste technology of clay barriers, the processes escape direct laboratory scrutiny because it seems practically impossible to perform meaningful

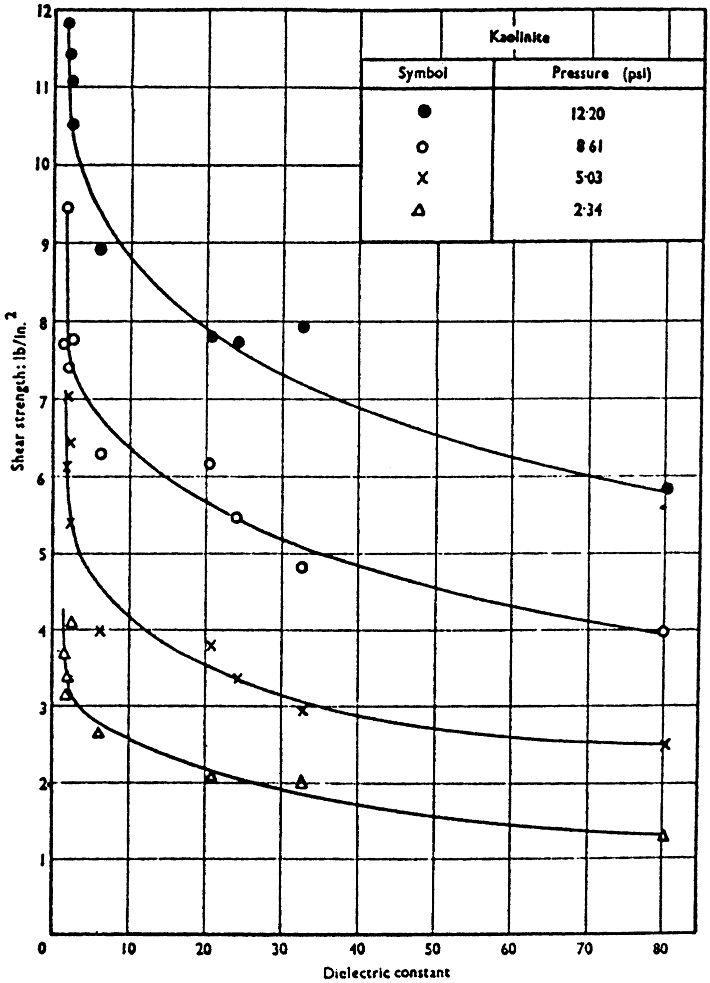

Fig. 2. Effect of dielectric constant (permittivity) of pore fluid on shear box strength of kaolinite (after Sridharan and Venkatappa Rao, 1973).

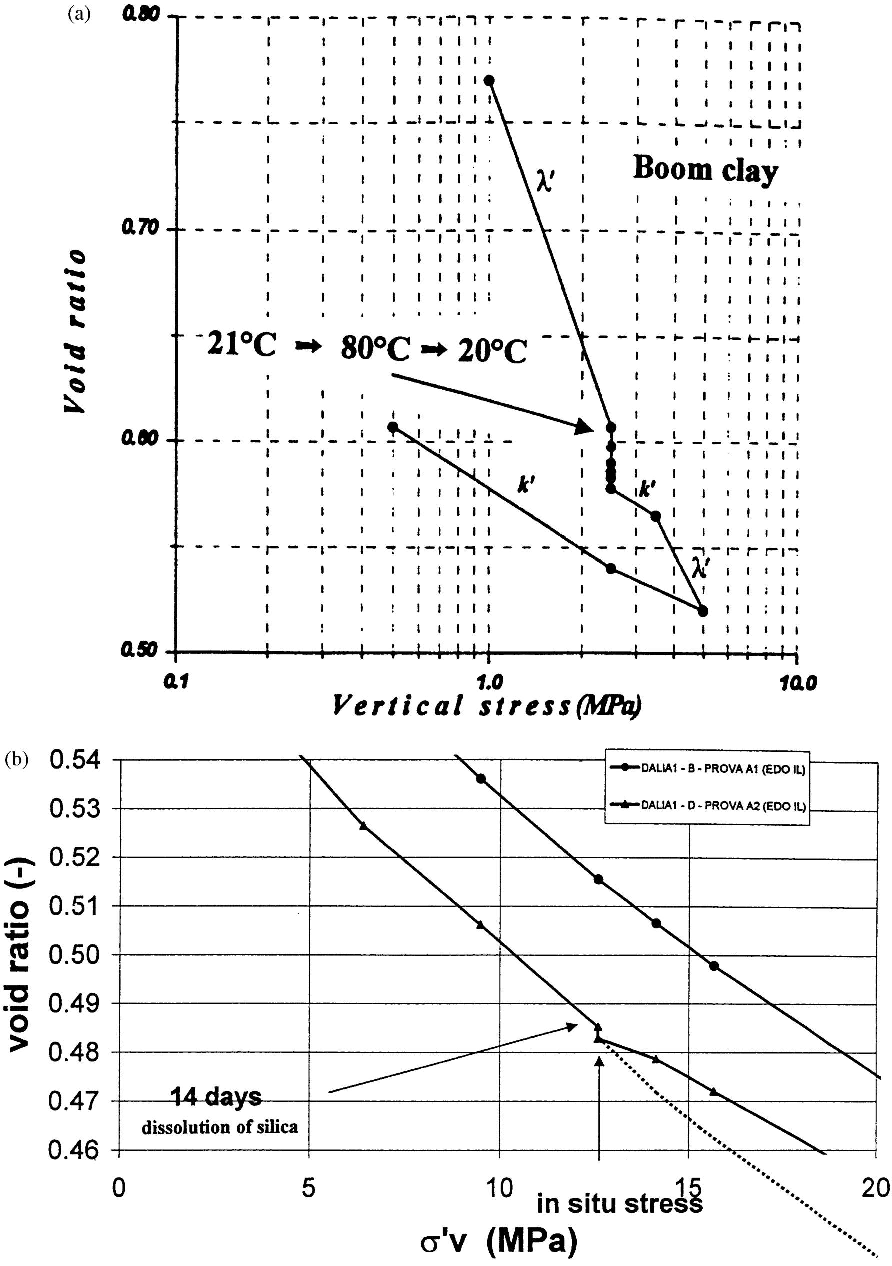

Fig. 3. Changes in overconsolidation ratio (apparent maximum preconsolidation axial stress) occurring (a) during heating for Boom clay (after Belanteur's thesis, 1993; see Robinet et al., 1996), or (b) uncontrolled chemical reactions of North Adriatic Dalia Sand, at constant stress in one-dimension strain conditions (from Hueckel et al., 1999).

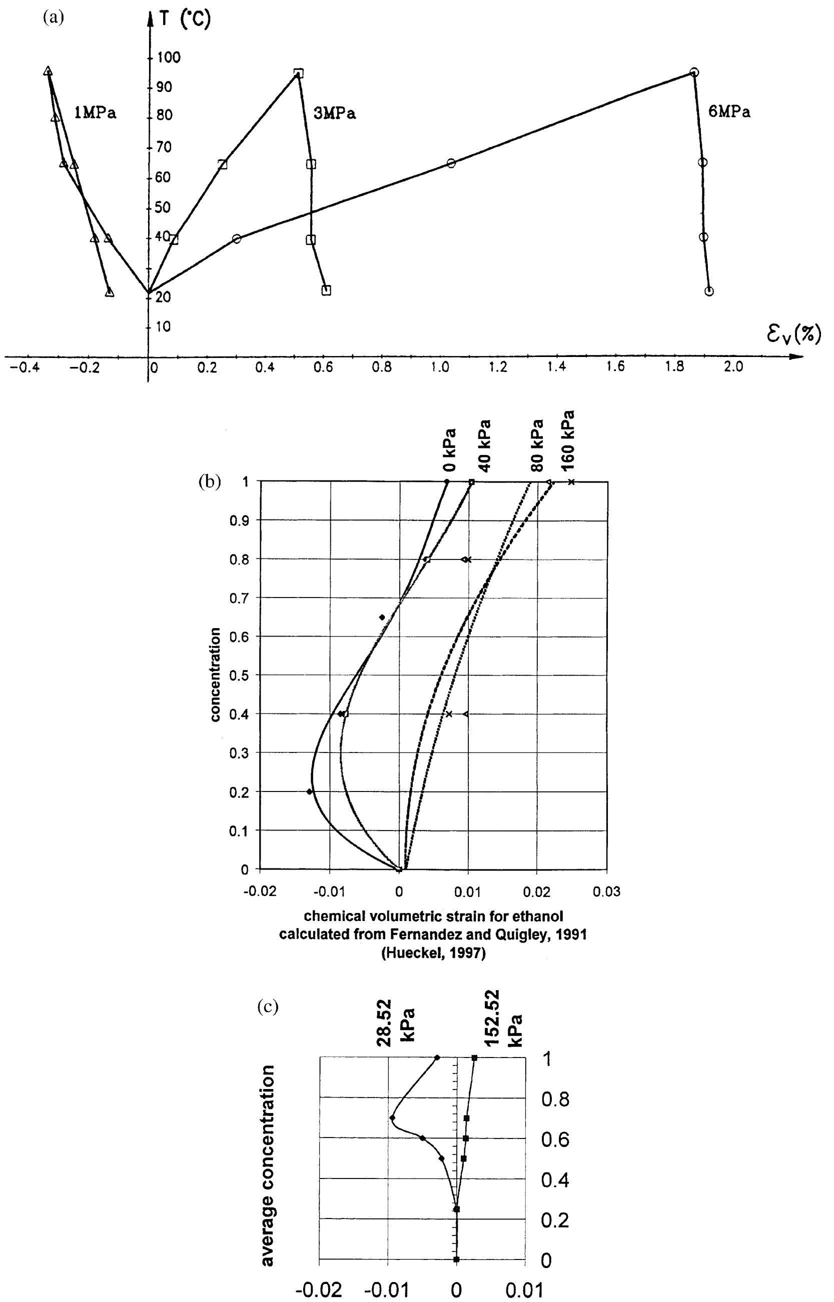

Fig. 4. (a) Thermal strain during heating at different constant stress values for Boom clay (after Del Olmo et al., 1996); (b) chemical strain due to seepage of 100% ethanol at constant rate at different constant confining stress [calculated from Fernandez and Quigley (1991) by Hueckel (1997)]; (c) chemical strain due to seepage of 100% ethanol at constant pressure at different constant confining stress (after Hueckel et al., 1996).

mechanical experiments over the timeframe required for the mineralogical reactions to occur. For that reason, studies of natural analogs are undertaken, in which clay masses that have been thermally affected by natural long term phenomena, such as at a clay contact with hot magma during a volcanic event, are examined in the field and in laboratory (Hueckel and Pellegrini, 2001).

3.2. Microscopic mechanisms of dehydration and rehydration

Dehydration and rehydration of clays may by triggered by different factors, and despite apparently the same effect: loss or gain of interlamellar water, may involve different microscopic mechanisms. It appears that dehydration–rehydration may also be treated differently from physico-chemical point of view depending on types of "loading" or stimulus. However, one observation, that the water removal from, or addition to the interlayer nano-space occurs in a discrete manner by entire molecular liquid sheets, seems to be universally valid. The following review of the micro-mechanisms of dehydration should allow us to examine options of idealizing clay as an open or closed thermodynamic system in the above cases.

3.2.1. Osmotic swelling

This type of swelling is induced by a difference in ionic concentration between the pore and interlayer water. Osmotic pressure and surface hydration theories seem to capture principal features of such behavior by considering the capability of surface of clay mineral to adsorb certain amount of water molecules (El Swaify and Henderson, 1967; Low, 1987; Sherwood, 1994). Sposito and Prost (1982) suggest that counter-ion solvation is the dominant mechanism in swelling, while Low (1987) links swelling to hydration of clay platelet surfaces. Recent Monte Carlo simulations of the behavior of water and cations in the nano-space between clay platelet surfaces indicate that at lower temperatures the Mg^{2+} and Na^{+} cations are fairly immobile, whereas above 350 °K the cations may diffuse. Water molecules in the interlayer (at 300 °K) exhibit diffusion constants of the order of 1/3 of that of pure water (Refson et al., 1993). Boek et al. (1995a) simulated hydration of sodium montmorillonite by increasing water content up to 300 mg/g and its dehydration. Some hysteresis of hydration/dehydration behavior indicates irreversibility of the process at certain stages (Fu et al., 1990; see also Huang et al. 1994 discussed below). Fu et al. (1990) and Boek et al. (1995a) attribute the hysteresis to an effect of deformability of solid clay structure. Recent experiments show also, that the arrangement of the multilayer particles and the size of inter-particle pores play a major role in swelling strain development (Hetzel et al., 1994). In particular upon adsorption of more than three water layers, particles have shown a tendency to break into smaller ones, with larger pores between them. It remains unknown however, to what extent this process is reversible. Systems of cracks observed in clays by Murray and Quirk (1990) attributed to swelling–drying cycles suggest at least some irreversibility.

Prost et al. (1998) identified two mechanisms of swelling: adsorption on hydrophilic sites and free surfaces, and capillary condensation in inter-granular pores. They also found that last one or two layers of molecular water can only be removed by applying elevated temperatures. In fact, most of dehydration/rehydration experiments to accelerate the process are performed at the elevated temperature and pressure conditions (see e.g. Koster van Groos and Guggenheim, 1984).

3.2.2. Thermal swelling/shrinkage

Huang et al. (1994) observed that dehydration of montmorillonite with initially three H_2O layers occurred around a specific temperature of 350°C by an abrupt loss of one one-molecule thick layer of water. This was followed by a loss of another layer at 490°C. During rehydration, clay exhibited a large hysteresis. In fact, rehydration did not occur in a two interlayer dehydrated montmorillonite until it cooled to 88°C (with a jump from 15.33 to 16.55 Å), and again at 40°C (from 16.55 to 17.75 Å which is slightly less than ordinary three layers of water) (Fig. 5). Thus, almost perfect reversibility was established for that system. Rate of dehydration is very high, indeed dehydration occurs in minutes, after the application of pressure or temperature step. Rehydration also occurs in minutes, even if it is slower than dehydration.

However, in a separate case of a mineral with two initial H_2O interlayers, rehydration seemed irreversible both for one interlayer configuration and for completely dehydrated material. A possible cause of the irreversibility may be a locked-in reconfiguration of the clay particle system. Wu et al. (1997) suggest two stages of rehydration: first, a swelling stage, as interlayer H_2O molecules re-arrange themselves, and a second stage, with water molecules diffusing into the enlarged space between the solids.

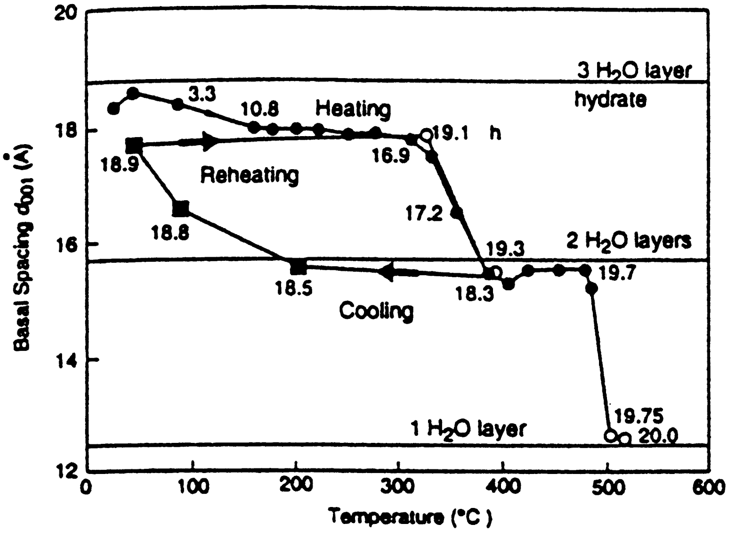

Fig. 5. Change in interplatelet distance d_{001} during dehydration and rehydration of montmorillonite with originally three molecular layers of water. Solid circles, heating; solid squares, cooling; open circles, reheating (from Huang et al., 1994).

3.2.3. Diagenetic processes

A particular form of dehydration/rehydration reaction: illitization of smectite and its reverse, resmectitization of illite are common elements of diagenetic process of clays. Their importance is paramount for geological process of diagenesis of clays. Huang et al. (1994) make a substantial distinction between illitization and smectite dehydration. They consider the latter one as being a rapid process, requiring much higher temperature, and controlled by the equilibrium rate of import of external potassium and export of interlayer water. In illitization of smectite the amount of time is much higher, and possible structural changes including dissolution and precipitation are present as well (Nadeau et al., 1985). Studies of illitization are often performed on field cases and on natural analogs, where contact with magmatic heat source and clay occurred for a prolonged period of time.

Based on a study of natural analog in the upper Pierre Shale at Walsenburg, CO, (Pytte and Reynolds, 1989), and on laboratory data, Huang et al. (1994) present an argument that dehydration in smectite-to-illite transition is kinetics controlled. They suggested that in the presence of an unlimited supply of potassium, the process lasts until the whole material becomes pure illite. They confirmed previous findings about a K-feldspar consumption proportional to the illite fraction in the final product, and about a transition from a random to ordered inter-stratification in I/S occurring at 60% of illite in the product. Notably, the involvement of potassium is important. The above study concludes that the presence of potassium contributes significantly to the process by adding to the activation energy. Numerical confirmation was obtained by Boek et al. (1995b). Also previous findings were confirmed, that termination of the process took place whenever exhaustion of K-feldspar occurred. Formation of illite needs potassium, which is required to replace interlayer water present in smectite. This link is often invoked, and since indigenous bentonites (smectite) usually contain little potassium, or none, it must be transported into bentonite site from external sources. That suggests that while none of the other principal reactants and products is changing mass through transport, potassium, which seems to play a critical role, does.

As for the physical mechanism of dehydration, the universally accepted one is that of thermal ejection of an entire mono-molecular layer of water from the inter-platelet space, followed by inter-platelet space collapse (Pusch, 1987). The discrete mechanism of layer-by- layer ejection of water is confirmed by numerical simulations (Schoen et al., 1993). On the other hand, Whitney and Velde (1993) identify a dissolution/precipitation mechanism instead of interlayer space collapse as a principal mechanism in dehydration. This mechanism composes of the following four stages of the process: dissolution of original smectite, possible transport, epitaxial nucleation of illite on smectite substrate, growth of illite crystals. Pusch and Madsen (1995) found that, for Kinnekulle clay, precipitation of newly created illite is a dominant mechanism of dehydration.

Resmectitization is rarely addressed alone. Some laboratory experiments indicate that rehydration of illite could be seen, at least phenomenologically, as a reverse of dehydration of smectite. However, it is clear, that the process does not need potassium, which in illitization is required to replace interlayer water in smectites. During resmectitization K-ions are released into the solution, since no potassium is found in the rehydrated smectite. It possibly contributes to the formation of K-feldspar. However, at natural analog site of Orciatico intrusion, neo-formed smectite is found on the wall of micro-cracks, suggesting a precipitation in relation to the water influx upon cooling (Leoni et al., 1986). There is no suggestion of a long distance mineral migration. Thus, it seems that the only imported species during rehydration is that of water.

It is worth noting, that the previously discussed changes observed during de- and re-hydration occurred within hours or even minutes, after an increment of temperature, pressure and potassium supply, was applied. This is obviously in contrast with diagenetic or even contact metamorphosis time scale, where clays are believed to have been exposed to the millenia of elevated temperature and pressure, at roughly constant values.

3.2.4. Contamination related swelling

Finally dehydration of smectite may occur as a result of replacement of interlayer water with contaminants. Clearly, deformational, strength and permeability aspects of the process are somehow, but not entirely, different from the case of ionic strength induced changes (Brown and Thomas, 1976; Gnanapragasam et al., 1995). Reduced repulsion between particles leads to formation of crystalline ordering of silicate layers and alcohol layers (Annabi-Bergaya et al., 1981; Permien and Lagaly, 1994a,b). However as before, a larger picture, with consequent changes in macro-fabric, such as flocculation of macro-particles or clusters needs to be considered (Sridharan and Venkatapa Rao, 1973; Fernandez and Quigley, 1985; Hueckel, 1997).

4. Modeling

The goal in this section is to link mechanical clay properties, such as elastic moduli, and yield limit to the reactions or mineralogical transformations described above. A mechanical property may be evaluated before the start of a reaction and after its completion, as well as during its progress. The link between chemical processes and mechanical changes in materials may be formulated through thermodynamics, since it is used both in chemistry and mechanics for basic considerations on constitutive laws. A constitutive relationship characterizing a change in a property may be formulated through a free energy dependence on state parameters. To establish a framework for the constitutive laws we shall employ the concept of the positiveness of the local rate of entropy production of the whole system. To determine the entropy rate we shall express it through the rates of internal energy and the total density of work.

4.1. Phases, species, reaction, mass balance and transfer, and transport of species

The material (mixture) enclosed in a representative elementary volume (REV) is postulated to be composed of two superimposed phases, each characterized by its mass, stress and velocity. The species present in each phase are treated as separate components, and are described by their density, velocity, and therefore constrained by the mass balance, reaction and mass flux (if any) constitutive laws only. Some species may occur in solid and fluid phase, and distinguishing it may be important. The assumption of the strongly interacting character of the mixture in Bataille and Kestin's (1977) sense allows us to consider the balance of linear momentum only for the phases, but not for single species. There are no deformation, stresses or forces associated with species, or their transport. Therefore the mechanical properties of the material will be associated with phases only. What constitutes the phases and species in hydrating/dehydrating clays will be discussed in the forthcoming sections. Consequently, we will develop phenomenological relationships between the phase properties and specific reactions, but we will not exploit a link between the velocities of species and that of phases, nor will we link explicitly changes in mass of all species and that of phases in terms of phase mass balance.

It is postulated that the removal or addition to the solid phase of an amount of mass of selected species (ions, minerals, or moles of water in the interlamellar space alone) may result in changes in the mechanical properties of soil. This may occur either through a generation of a new mass of a species, or through transport of mass from or to the outside of the REV. To link in a general case the mass fraction changes to any type of delivery of mass, the mass balance law of species is invoked. In principle, such mass balance is written for each single species, *k,* in each phase, solid or fluid. In practice however it may limited to a few species of "structural" importance. The mass of a species transported outside the representative volume is represented by the species mass flux J_i^k (positive for an outflow), whereas the mass increments resulting from chemical reactions $\alpha = 1, 2 \ldots n$, or physico-chemical processes are represented by reaction rates J_c^a per unit volume (positive for the product growth), and thus

$$\rho \frac{\mathrm{d}c^k}{\mathrm{d}t} = -J^k_{i,i} + \sum_{\alpha=1}^{r} v^{k\alpha} \mathbf{J}_c^{\alpha}, (k = 1, 2, 3 \ldots n) \tag{1}$$

where concentration of a species in a given phase, c^k, is defined by its mass fraction as

$$c^k = \frac{\rho^k}{\rho}; \sum_k c^k = 1 \tag{2}$$

and ρ is a total specific mass of the solid or fluid phases per unit element volume of soil. Coefficients $v^{k\alpha}$ are proportional to the stoichiometric coefficients for the *k*th species participating in the αth chemical reaction. Such coefficients are positive when they relate to the reaction product, and negative for reactants. On the same token, ρ^k is a mass of the species per unit element volume of soil.

Consequently, we have several options regarding the choice of the variable describing the mechanical property dependence on species mass, or their changes. The dependent variable may be: (i) current value of the relative content of a given species in the phase, (ii) species mass fraction change with respect to a reference value of the given species, (iii) progress of, or mass changed in a specific reaction or, finally, (iv) the mass changed as a result of diffusion or flow of species from, or toward, the outside of the REV. On the top of the above, a purely phenomenological choice must be made which specific species change, or which specific reactions are to be considered as causing the property changes.

It should be noted that current mass fraction of a single mineral, or a species may not be sufficient to determine mechanical properties of a soil, as other factors, such as porosity, if not the entire mineralogical composition, have often strong effect. Comparion of a selected species content is used to scale mechanical properties in highly inhomogeneous soils (see e.g. Del Olmo et al., 1996). Also both time and space variations of a species content alone may in some cases be not a sufficient descriptor of the change in a mechanical property. For instance, the dependence of the maximum pre-compression stress in clays on carbonate content is known to be highly non-linear (Hueckel et al., 1998), and probably requires a more sophisticated description. McKown and Ladd (1982) suggest the existence of an upper threshold value of carbonate content, above which an increase of carbonate content does not seemingly affect the strength of interparticle cement bridges essential for the overall strength, but rather results in the filling of not necessarily contributing interparticle voids.

Time variations in mechanical properties in soils linked to mineralogical changes are classically described through a measure of advancement of mineralogical reactions (Lasaga, 1981; Lichtner, 1996). It must be pointed out that there is a different relationship between reaction rate and reaction progress depending on whether the system is closed or open to transport (see e.g. De Groot, 1966). Whenever diffusion occurs, an elementary volume cannot be considered as closed, as transport leads to exchange of material points between the neighboring elementary volumes (Kestin, 1979, Vol. 2, p. 24.4). In addition, different species diffuse with different local velocities, and each such velocity needs to be related to the velocity of the phase, at the same point. Therefore, it is impossible to define a system around such point that would contain all the same material points all the time. Thus, a diffusing system must be open.

In closed systems, the flux of species J_i^k is not allowed, $J_i^k = 0$. All mass changes must therefore result from reactions within the system. In turn, we can define the reaction progress for each reaction in terms of their differential being the mass produced with a given chemical reaction rate over the increment of time

$$\rho \mathrm{d}\xi^{\alpha} = \mathbf{J}_c^{\alpha}(t)\mathrm{d}t \tag{3}$$

As a result, mass of any component may be obtained by integrating (3) from the beginning of the reaction and does not depend explicitly on time, but on the reaction progress ξ^{α} which is a variable of state. Analogously for densities

$$\rho^k = \rho_0^k + \rho \sum \nu^{k\alpha} \xi^{\alpha} \tag{4}$$

In contrast to closed systems, in open systems a relationship such as (3) cannot be established (De Groot, 1966). Indeed, even with one reaction only, its rate, $\mathbf{J}_c = (\rho/v_k)d^{(i)}M_k/M$ involves only the part of the change ($d^{(i)}$) of masses which are transformed within the boundaries of the system. The other part, as seen from Eq. (1) is the external mass supply, that is the mass flux $d^{(\varepsilon)}(M_k/M) = -J^k_{j,j}$. Since this part depends on the solution of a boundary value problem, and not the local properties of the material, and need not to be any explicit function of time, Eq. (1) solved for $\mathbf{J}_c$ may not be integrable, or in other terms, the reaction rate $\mathbf{J}_c$ is unlikely to be a total differential, as $\rho\mathbf{dc}^k + J^k_{j,j}\mathrm{d}t$ is unlikely to be one. In other words, the same change in the system can be achieved either by a reaction or by external transport. As a result, $J^a_c \neq (1/\rho)\mathrm{d}\xi^\alpha/\mathrm{d}t$ and the state variable ξ^a cannot be defined for open systems.

Yet, all masses involved in the internal exchange or reactions must be conserved, so that,

$$\sum_k d^{(i)}c^k = 0 \tag{1a}$$

For the sake of completeness, mass balance for the phases needs to be satisfied. The corresponding equations, as well as the equations for phase momentum balance will not be discussed in detail. Their form is analogous to that presented by Hassanizadeh (1986). The inter-phase exchange of mass will be defined through appropriate masses of species moving between phases as a result of dissolution or precipitation reactions described by Eq. (1).

4.2. Effects of reactions and mass fluxes in thermodynamic considerations and restrictions

In order to investigate restrictions on constitutive functions for clays resulting from chemo-mechanical coupling described above we shall examine the basic thermodynamic relationships. One particular question with important implications from the thermodynamics point of view is whether we should consider the reacting clay as an open or closed system. In general, since soil does exchange fluid mass with its surroundings, it should be considered as an open system. However, there are reasons, both theoretical and practical, to consider clay in some conditions as a closed system.

In the first law for an open system representing the dependence of the entropy change of the entire system on internal energy change and on the incremental work

$$T\mathrm{d}s = \mathrm{d}q = \mathrm{d}u + \mathrm{d}w \tag{5}$$

(where q, s and u are heat, entropy and internal energy, respectively, per representative volume, V) work, w, is the entire work that is exchanged by the bi-phase system with the surroundings. This work of an open system, incrementally exchanging mass and momentum with the surroundings, includes also a chemical work density component, in addition to the usual mechanical work component (Katchalsky and Curran, 1965), so that

$$\mathrm{d}w = -\frac{1}{V}\sum_{\mathrm{Ph}}\sigma_{ij}^{\mathrm{Ph}}\mathrm{d}\varepsilon_{ij}^{\mathrm{Ph}} - \sum_{k=1}^{\gamma}\mu^{*k}\mathrm{d}c^{k} \tag{6}$$

where $\sigma_{ij}^{\mathrm{Ph}}$, $\varepsilon_{ij}^{\mathrm{Ph}}$ and μ^k are respectively stress and strain in the phases, Ph = s and f, and chemical potential of a kth species. Note that the second summation symbol in (6) refers only to species ($*k$) transported between the system and its surroundings. Note also that the last term does not appear for closed systems which by definition does not exchange mass with the surroundings. We will omit from now on the Ph superscript for species, and stresses and strains will refer to the solid phase, while pressure and volume to fluid phases, which in principle may be more than one.

The internal energy term in (5) can be expressed through a number of thermodynamic potentials such as Helmholtz free energy h, or its Legendre transform counterpart, with respect to strain, i.e. Gibbs free energy, g, expressed as follows

$$\begin{aligned} &h\left(\varepsilon_{ij}^{e}, V^{wi}, T, r^{\beta}, \xi^{\alpha}, \Delta c^{m}\right) = u - sT \\ &\text{and } g = \left(\sigma_{ij}, V^{wi}, T, r^{\beta}, \xi^{\alpha}, \Delta c^{m}\right) = \frac{\partial h}{\partial \varepsilon_{kl}^{e}}\varepsilon_{kl} - \frac{\partial h}{\partial V^{wi}}V^{wi} - h \end{aligned} \tag{7}$$

The list of the variables on which free energies h or g depend, includes all state variables, internal state variables such as r^{β}, to describe irreversible changes of internal material arrangement that are not specified on microscopic level. Since in general, chemical reactions or physico-chemical transformations may either result from, or in, an exchange of mass between the species of the system, or from or in, a transfer of mass from the system to the surroundings, or both, free energy (7) will be postulated to depend either on variable of change in concentration, Δc^{m}, or on reaction progress variable, ξ^{α} considering the changes caused by the former as reversible, and by the latter as irreversible. While this is most probably the actual situation for illitization reaction, given the dependence of the process on availability (and thus often the external supply) of potassium, mineral species are rarely subjected to transport outside the neighborhood of the reaction site (Lichtner, 1996). Such dependence leads to partial local equilibrium, for which we are not able to define ξ^{α}, as pointed by Prigogine (see De Groot, 1966), and discussed earlier. It is unlikely, however, that both types of changes will be considered simultaneously, as discussed later.

It should be noted that mass of water removed or added externally to REV is not explicitly a variable included in (7), at variance to total stress theories, such as Biot's (1978). It is, however, included through volumetric change of liquid phases.

4.3. Thermodynamic systems for illitization — resmectitization reaction

A question needs now to be addressed, whether dehydration and rehydration should be considered as a process far from equilibrium in a closed system, in local equilibrium in an open system, or in equilibrium in open systems. In the case of equilibrium in an open system the net total reaction rate is zero, and the process is reversible. For an open system in local equilibrium it is assumed that reaction rate does not vanishes and is controlled by the flux and properties of the transported species into the system. Far from equilibrium, the reaction rate is controlled by the kinetics of reaction, independent of concentration rate but dependent on concentration and temperature. This type of the process is understood to be dependent on the material of REV itself, as a closed system, and not its surrounding. The process is also deemed to be irreversible. The above attributes will be our criteria to establish the nature of the type of reaction to be considered.

The first task is to identify the nature, the extent and a set of properties of a representative elementary volume for clay–water system. In general, the considered REV includes solid platelets of clay mineral, containing few layers of adsorbed water between them forming particles surrounded by external adsorbed water, stagnant or trapped free water, and flowing free water. Given the geological scale of the phenomenon, the regional flow of free water will be considered only, and assumed as steady flow or none. As far as species are considered, it is not a priori specified what they may be. They may be molecules of water, cations, oxides solved in water, or right away entire minerals. The latter option is often used in geochemistry for its simplicity and lack of knowledge about specific reaction mechanisms. Overall reactions between minerals and aqueous solutions are then considered based on transition state theory (Lichtner, 1996).

There are two general clear-cut tendencies in considering geochemical systems affected by chemical processes resting on physically based assumptions. In the first one, open, purely transport based systems are considered. No kinetic reactions are considered and chemical equilibrium with instantaneous mass transfer is assumed to control the simulated processes. As an example are models in which effects of highly concentrated organic contaminants on yield surface and critical state are reproduced (Fernandez and Quigley, 1985, 1991; Hueckel et al., 1997, 1998) with contaminant concentration as a state variable. On the other end of the spectrum, soils are idealized as closed system, kinetic reactions being the only processes (by definition with no transport of external mass) as is the case with most mineralogical processes (Lichtner, 1996). Even if in reality, rarely the phenomena involved correspond to these two idealized situations, the conceptual and numerical simplifications are very appealing.

A third, hybrid approach to reactive–diffusive open systems was developed by Biot (1977, 1978), with petroleum applications in mind. An open system is proposed, called a *hypersystem,* consisting of three components: primary cell made of a solid at uniform temperature,which may exchange mass in the form of pure species in solution, a set of "large", rigid supply cells, each with a different pure species, at the same pressure and temperature, and a "large" isothermal reservoir at the same temperature, called "thermal well'. Heat and mass are exchanged between the cells, but not the exterior. The behavior of the system is described in terms of a "collective potential" of all the cells, including the variables of masses exchanged with the supply cells. With this contrivance the open system is turned into an effective closed system.

From the phenomenological point of view, based on the background of the mineralogical processes described in the previous sections, it appears that four options can be envisaged in treating clay as an open or closed system.

i. We may consider clay as a closed system (Fig. 6a) composed of two phases: solid (mineral and adsorbed liquid) and liquid (free) phase containing ions. The exchange of mass of flowing free water in steady state is conservative. The process of adsorption/desorption of water may be thus treated as an interphase interaction and mass transfer (Ma and Hueckel, 1992). An anticipated advantage is to have all mass transfers as internal of the system, a disadvantage, two phases to be dealt with, and possible water flow to be modeled separately.
ii. Adsorbed water and free water may be considered as two separate liquid phases (Murad and Cushman, 1997), in addition to the solid mineral phase together forming a closed system (Fig. 6b). A disadvantage is to have now three phases to be dealt with. Another disadvantage is seen in difficulty in obtaining experimentally macroscopic properties of separate solid and adsorbed water phases.
iii. One may consider an open thermodynamic system (Fig. 6c) composed only of the solid (mineral) phase, and the species, being, becoming part of, or removed from it, including adsorbed water. Therefore, free water will be considered as a part of the surroundings of the system. The qualification of the system as open implies that there is a chemically driven exchange of mass and energy between the system and its surroundings (Katchalsky and Curran, 1965). The advantage in this approach is in ignoring the influence of the flowing water phase, which in the geological time scale of the problem on hand will be limited to the adsorption/desorption transfer. This can be dealt with as with an exchange of mass with surroundings.
iv. Finally, one may consider a two-phase, in principle open, system (Fig. 6d), consisting of the solid skeleton, adsorbed water, as one phase and a fraction of free water defined as stagnant (not adsorbed, but with zero velocity, trapped) water (van Genuchten and Wierenga, 1976), as a second phase. The remaining, freely flowing water is outside the system. The exchange of mass is limited to the two former water components or cations contained within them. Thus, the exchange is internal to the system. Therefore, in effect the system can be considered as closed. This presents a number of advantages, and is defendable on the physical basis. In essence, such formulation corresponds to Biot's (1977) hypersystem.

It should be stressed that the above-presented options may have different advantages and disadvantages for different engineering situations. The choice of the system should be made in correlation to the goals of the simulations to be performed.

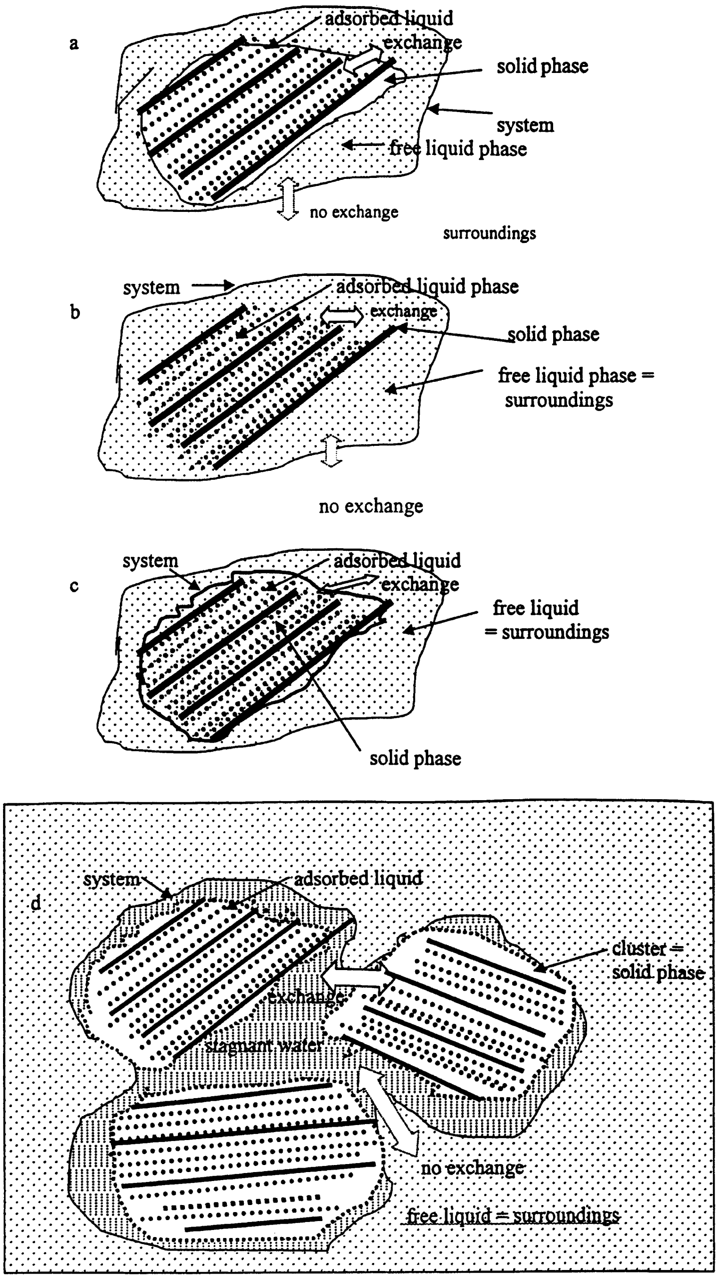

Fig. 6. a. Clay material as a closed system of two phases: adsorbed water is a part of the solid. b. Clay material as a closed system of three phases: adsorbed water is a separate phase. c. Clay material as an open system of one phase: adsorbed water is a part of the solid. Free water is a part of surroundings. d. Clay material as a system closed for selected constituents. The two-phase system includes adsorbed water as a part of the solid and stagnant water of zero velocity as fluid phase. Free water is a part of surroundings.

These options certainly require a different approach from the thermodynamic point of view, depending whether the system is open or closed. In open systems, the internal energy rate expressed in terms of rates of all the extensive variables changing in the material, includes the mass exchange rate. By solving the resulting equation for $T\mathrm{d}s$, using Eqs. (5)–(7), Gibbs equation is obtained which is valid both for open and closed systems:

$$T\mathrm{d}s = \mathrm{d}u - \frac{1}{V}\sigma_{ij}\mathrm{d}\varepsilon_{ij} + p^i\mathrm{d}V^{wi} - \sum_{\alpha=1}^{\gamma}\mu^{*k}\mathrm{d}c^k \tag{5.1}$$

where p^i is pressure in ith liquid phase.

Following the classical procedure, we identify the external, $\mathrm{d_e}s$, and internal, $\mathrm{d_i}s$, parts of the entropy change $\mathrm{d}s$, with the former one identified as related to externally induced heat and mass exchanges

$$T\mathrm{d_e}s = \mathrm{d}u - \frac{1}{V}\sigma_{ij}\mathrm{d}\varepsilon_{ij} + p^i\mathrm{d}V^{wi} - \sum_{\alpha=1}^{\gamma}\mu^{*k}\mathrm{d_e}c^k \tag{8}$$

where μ^{*k} is specific enthalpy of the supplied matter. Therefore, the entropy production becomes

$$Td_is = T_ds - T\mathrm{d}_es = T\mathrm{d}s - \mathrm{d}u + \frac{1}{V}\sigma_{ij}\mathrm{d}\varepsilon_{ij} - p^i\mathrm{d}V^{wi} + \sum_{a=1}^{\gamma}\mu^{*k}\mathrm{d_e}c^k \tag{9}$$

On the other hand, substituting for u the free energies resulting from (7), we obtain what is defined as the dissipation function, D,

$$D = \mathrm{d_i}sT = \frac{1}{V}\mathrm{d}\varepsilon_{kl}\sigma_{kl} - p^i\mathrm{d}V^{wi} - \mathrm{d}Ts - \mathrm{d}h - \sum_{\alpha=1}^{\gamma}\mu^{*k}\mathrm{d}c^k \geqslant 0 \tag{10.1}$$

or

$$D = \mathrm{d_i}sT = -\varepsilon_{kl}\mathrm{d}\sigma_{kl} + V^{wi}\mathrm{d}p^i - \mathrm{d}g - \sum_{\alpha=1}^{\gamma}\mu^{*k}\mathrm{d}c^k \geqslant 0 \tag{10.2}$$

Substituting for $\mathrm{d}h$ the total differential of the Helmholtz free energy, we obtain finally,

$$\begin{aligned} D = {} & \left(\sigma_{kl} - \frac{\partial h}{\partial\varepsilon_{kl}}\right)\mathrm{d}\varepsilon^e_{kl} - \left(p^i - \frac{\partial h}{\partial V^{wi}}\right)\mathrm{d}V^{wi} - \left(s + \frac{\partial h}{\partial T}\right)\mathrm{d}T \\ & - \sum_k\left(\frac{\partial h}{\partial c^{*k}} + \mu^{*k}\right)d_e c^{*k} - \sum_\alpha\frac{\partial h}{\partial\xi^\alpha}\mathrm{d}\xi^\alpha + \sigma_{kl}\mathrm{d}\varepsilon^{pl}_{kl} - \sum_\beta\frac{\partial h}{\partial r^\beta}\mathrm{d}r^\beta \geqslant 0 \end{aligned} \tag{11}$$

or alternatively, for the Gibbs free energy

$$D = \left(\frac{\partial g}{\partial \sigma_{kl}} - \varepsilon_{kl}\right)\mathrm{d}\sigma_{kl} - \left(\frac{\partial g}{\partial p^i} - V^{wi}\right)\mathrm{d}p^i + \left(\frac{\partial g}{\partial T} - s\right)\mathrm{d}T$$
$$- \sum_k \left(\frac{\partial g}{\partial c^{*k}} + \mu^{*k}\right) d_{\mathrm{e}} c^{*k} - \sum_\alpha \frac{\partial g}{\partial \xi^\alpha}\mathrm{d}\xi^\alpha - \mathrm{d}\sigma_{kl}\varepsilon_{kl}^{pl} + \sum_\beta \frac{\partial g}{\partial r^\beta}\mathrm{d}r^\beta \geqslant 0 \qquad (12)$$

The last two terms in Eqs. (11) and (12) represent dissipative components linked to plastic processes, in particular related to plastic strain and plastic hardening (see e.g. Casey, 1998). The preceding terms are the reaction components of the dissipation inequalities. The term before those correspond to the reversible exchanges of species of mass with the exterior. Note that the internal variables r^β describing hardening due to plastic strain, temperature or chemical changes may be functions or functionals of ΔT, ξ^α or Δc^m representing irreversible effects these variables may have on material strength and plastic straining, as described in Section 4.5.

4.4. Constitutive assumptions for dehydration and rehydration

In this section we will analyze options in formulating constitutive assumptions for clay subjected to dehydration and rehydration, with the objective to apply them to simulate the natural analogs of the processes induced by heat of nuclear waste in clays. Thus, we will not consider the case of dehydration due to contamination of clays by concentrated chemicals.

At most of the investigated sites of natural analogs for the nuclear waste heat effect on clays the reported phenomena were that of illitization of smectite with a presence or supply of sufficient amounts of potassium (see e.g. Ferry et al., 1987; Pytte and Reynolds, 1989; Kamei et al., 1990; Pusch and Madsen, 1995).

At Orciatico, Italy site, the peculiarity consists in the fact that a 14% smectite fraction developed from 0% at a location where the heat source was presumably located, with a simultaneous drop from 37 to 14% in the illite content. Leoni et al. (1986) who originally analyzed the site, proposed that the reaction that occurred at the Orciatico site was that of re-smectitization of illite instead of illitization of smectite.

We will now attempt to identify dominant effects from the point of view of the influence of the mineralogical changes on clay mechanical properties. Two ways of measuring this influence can be conceived. One, by considering the mass concentration changes of species involved in all possible reactions, and another one, by considering advancement of changes in specific reactions.

Without specifying individual species taking part in dehydration the reaction equation identifies the principal species as mineral species (see e.g. Pytte, 1982; Ransom and Helgeson, 1994; Pusch and Karnland, 1996).

$$\text{smectite} + \text{potassium} \rightarrow \text{illite} + \text{Si} + \text{H}_2\text{O} \qquad (13)$$

A number of other possible reactions may be associated with reaction (13) as listed by Pusch and Karnland (1996).

During rehydration the principal reaction as observed at Orciatico is believed to consist in transformation of quartz + (original clays = illite + vermiculite + chlorite intergrades + I/S mixed layers) into smectite and K-feldspar + plagioclase (Leoni et al., 1986). Transformation of quartz without any doubt may contribute to a weakening of soil. However, now we will confine our interest to the clay mineral components only. Thus, we will consider the following reaction:

$$\begin{aligned}&(\text{illite} + \text{vermiculite} + \text{chlorite intergrades}) + \text{ I/S mixed layer} + \text{water}\\&\quad \rightarrow \text{ smectite (including adsorbed water)} + \text{potassium}\end{aligned} \tag{14}$$

To represent the above postulate we will identify six species contributing to the total change in specific mass of the system: the original clay minerals enclosed in the parenthesis in (14) and called for brevity *illite* for its dominant component, stagnant water, free water, adsorbed water, smectite and potassium (the superscripts “aw”,“fw” and “sw” stand for adsorbed, free and stagnant water, respectively):

$$\mathrm{d}c = \mathrm{d}c^{\mathrm{ill}} + \mathrm{d}c^{\mathrm{sw}} + \mathrm{d}c^{\mathrm{fw}} + \mathrm{d}c^{\mathrm{sm}} + \mathrm{d}c^{\mathrm{aw}} + \mathrm{d}c^{K} \tag{15}$$

The above mass change can be split into its internal and external part, with the same applied to free water, as follows:

$$\mathrm{d}_{\mathrm{i}}c = \mathrm{d}c^{\mathrm{ill}} + \mathrm{d}c^{\mathrm{sw}} + \mathrm{d}c^{\mathrm{aw}} + \mathrm{d}c^{\mathrm{fw1}} + \mathrm{d}c^{K} \tag{15a}$$

$$\mathrm{d}_{\mathrm{e}}c = \mathrm{d}c^{\mathrm{fw2}} = J^{\mathrm{fw}}_{i,i} \tag{15b}$$

Eqs. (15a) and (15b) apply to any of the four options of open and closed water-clay systems described in Section 4.3.

However, if the stagnant water mass is large enough to constitute a “large supply cell” of the Biot’s (1977) hypersystem we will argue on the physical basis that none of the species is transferred from, or to the system surroundings, at least on long term, and therefore that the system is actually closed for all species of importance to the considered process, as in system (iv) (Fig. 6c, Section 4.3). Thus, $\mathrm{d}c^{\mathrm{fw1}}$ may be dropped from (15a) and $\mathrm{d}_{\mathrm{i}}c = 0$, while c^{fw2} is not a part of the system. Therefore, by definition of closed system $J^{\mathrm{sw}}_{i,i} = 0$. This process can produce a volume increase of the skeleton, i.e. solid phase, but no change in global mass of water in the entire system. Thus, there is a conversion of the state of water at a point (except for a possible water density change inducing its shrinkage), rather than an in-flow (Morgenstern and Balasubramonian, 1980). On the other hand, the assumption and the physical argument that there are separated species of adsorbed, stagnant and free water, implies a necessity of imposing a mass balance of water species, which would involved the above three physical states of water. This is equivalent to assuming, that as far as water is concerned, the mass exchange is limited to that between adsorbed water and stagnant water only, if $\rho^{\mathrm{aw}} = \rho^{\mathrm{sw}}$ and

$$\mathrm{d}c^{\mathrm{aw}} = -\mathrm{d}c^{\mathrm{sw}} \text{ and } J^{\mathrm{sw}}_{i,i} = 0 \tag{16}$$

In the case in which we would like to include possibly significant changes in density of water while it converts from the stagnant to adsorbed state, the situation is different. The density of adsorbed water is a contentious issue. It is considered to be 1.05 g/cm^3 following the measurements of Hawkins and Egelstaff (1980). This number may be somewhat higher, namely, $\rho^{\mathrm{aw}} = 1.14$ g/cm^3 as suggested by Skipper et al., 1991 on the basis of the Monte Carlo simulations. In the case of saturation of water in stagnant pore space, the mass balance of water in adsorbed and stagnant state would imply a flux of free water becoming stagnant water in the quantity

$$J^{\mathrm{sw}}_{i,i} = -\rho \mathrm{d}_{\mathrm{e}} c^{\mathrm{sw}} = -\left(1 - \frac{\rho^{\mathrm{sw}}}{\rho^{\mathrm{aw}}}\right)\rho \mathrm{d}c^{\mathrm{aw}} \tag{17}$$

This would imply that the system is not closed any more. In practical terms it is however convenient to assume that either the saturation condition is not maintained, or that water density remains constant during the adsorption/desorption processes. Note, that the choice of the water-system denoted as (iv) in Section 4.3 implies no flow of water within the system. Such a choice is viewed as suitable for the long-term conditions of the natural analog of nuclear waste disposal as at Orciatico. It must be emphasized that this is not necessarily the case in many other situations of dehydration or rehydration, as discussed earlier.

The choice of the above mass change of adsorbing or desorbing water as a variable determining the mechanical properties of clay has been widely used in swelling or swelling pressure analysis (see e.g. Low, 1980; Wong, 1998) and in the present context of the effects of nuclear waste heat (Hueckel, 1992; Ma and Hueckel, 1992).

The uncertainties about the actual course of many mineralogical transformations led to an alternative practice in reactive transport modeling of developing empirical reaction rate formulas (Oelkers, 1996). In particular, considering changes in masses of a single reactant and single product expressed through molar fraction of neosmectite in the mixed layer illite/smectite mass, with $\tilde{c}^{\mathrm{sm}} = c^{\mathrm{sm}} + c^{\mathrm{aw}}$ including mass of adsorbed water in the count of mass of smectite, and denoting by M^{sm} and M^{ill} molar masses of so understood smectite and of illite, the reaction advancement may be measured by

$$S = \frac{\tilde{c}^{\mathrm{sm}}/M^{\mathrm{sm}}}{\tilde{c}^{\mathrm{sm}}/M^{\mathrm{sm}} + c^{\mathrm{ill}}/M^{ill}} \tag{18}$$

as proposed by Pytte and Reynolds (1989). With this definition we shall employ a kinetic reaction equation adapting the original formulation for dehydration by Pytte and Reynolds (1989) in the presence of unlimited supply of potassium.

$$\frac{\mathrm{d}\xi^{\mathrm{ill}}}{\mathrm{d}t} = -\frac{\mathrm{d}S}{\mathrm{d}t} = k(K/Na)^b S^a \tag{19}$$

For rehydration we postulate

$$\frac{\mathrm{d}\xi^{\mathrm{rs}}}{\mathrm{d}t} = \frac{\mathrm{d}S}{\mathrm{d}t} = k(1 - S)^{a} \tag{20}$$

where S is the mole fraction of smectite in the entire clay fraction which is believed to contribute to resmectization, including smectite itself, illite, I/S, vermiculite and chlorite intergrade. The exponent a is degree of the reaction, while k is the rate constant defined through the Arrhenius equation

$$k = A\exp\left(-\frac{U}{RT_{\mathrm{K}}}\right) \tag{20a}$$

and U is the activation energy for the reaction, R is the gas constant and T_{K} is absolute temperature. A is the frequency factor. Note that in difference to the original Pytte–Reynolds equation the component relative to potassium has been dropped from Eq. (19). In fact, the amount of potassium available does not play in rehydration a discriminant role that it does for dehydration. Pytte and Reynolds determined experimentally that the order of dehydration reaction is $a=5$. Alternative formulation could be based on the illite content, or illite crystallinity. The actual meaning of Illite Crystallinity Index (Weaver, 1960; Weber, 1972), used by evaluating the diminishing breath of the 10 Å peak to measure a growing crystallinity of illite, has been recently reevaluated. It is believed now (Srodon and Eberl, 1984; Weaver and Broekstra, 1984) that it rather reflects simply an amount of I/S component of the material. It should be emphasized also that by assuming the same kinetics for the reverse reaction as used for the direct one implies the same temperature dependence, and theoretically no hysteresis, except for the effect of the lack of potassium in (20). Due to lack of direct data for the rehydration branch of the hysteresis, the data for dehydration are used, following Pytte and Reynolds (1989): $A = 5.2 \times 10^{7}$ 1/s, $U = 33$ kcal/mol.

An earlier theory (Whitney and Northop, 1988) of illitization of smectites postulated a transformation mechanism of collapse of smectite layer about selectively adsorbed ions of potassium. Recent experiments indicate that illitization of smectite may involve some dissolution of smectite which then dehydrates and precipitates as illite on the remaining smectite substrate, coating the interior of pores (Nadeau et al., 1985; Whitney and Velde, 1993; Hetzel et al., 1994; Pusch and Madsen, 1995). This hypothesis was earlier limited to illitization in sandstone. Current understanding includes both mechanisms as concomitant (Meunier et al., 1998). Finally, let us note that potassium that seems to have been transported from the magmatic body, has been released at early stage of thermal phase. At the time of interest potassium is believed to be uniformly distributed and abundant to eliminate any potassium flux between stagnant and free water. More, we will assume that potassium is not contributing in terms of mass to creation of the product, and thus that $\mathrm{d}c^{\mathrm{K}} = 0$.

Clearly the above cited work refers to dehydration reaction mostly, for simple lack of sources. However, the experiments that did include a rehydration of partially dehydrated (one layer of hydrates) smectite (Huang at al., 1994; Wu et al., 1997) indicate similar stages in both processes. Even with the dissolution/precipitation hypothesis we will assume that these occur locally, and there is no mineral in- /outflow of mass for a representative elementary volume, and therefore that $\mathrm{d}c^{\mathrm{ill}} = -\mathrm{d}c^{\mathrm{sm}}$

4.5. Thermo-chemo-plastic constitutive equations

The dependence of mechanical properties on chemical reactions will be limited to the following phenomena described by their appropriate constitutive functions: strain-, thermal- and chemical- plastic softening/hardening and thermal and chemical reversible strain. In view of the application described in Hueckel and Pellegrini (2001), we shall focus from now on resmectitization. The dependent variable will be that resmectitization reaction rate, ξ^{rs} defined in (20). Numerous macroscopic experiments show that clays exhibit thermal softening due to heating below water boiling point (e.g. Hueckel et al., 1998), chemical softening or chemical hardening, depending on chemical reactions or chemo-physical processes involved (Hueckel, et al. 1998). To include into the description of hardening the appropriate environmental variables we will extend Cam-clay model with the elliptic yield surface (Roscoe and Burland, 1968)

$$f = p'^2 - p'p_c + (q/M)^2 = 0 \tag{21}$$

where p', q, M and p_c are effective stress first invariant, deviatoric stress second invariant, critical state coefficient, and apparent maximum preconsolidation isotropic stress.

To start with, we will postulate that there is only one hidden hardening variable, $r = p_c$. However, its rate is a function of the rates of the plastic strain rate, temperature rates and the rate of chemical reactions (see e.g. Lubliner, 1972; Marquis and Costa Mattos, 1991):

$$\mathrm{d}r = \left\langle \varepsilon_{kl}^{\mathrm{pl}}, \mathrm{d}\varepsilon_{kl}^{\mathrm{pl}}, T, \mathrm{d}T, \xi^{\alpha}, \mathrm{d}\xi^{\alpha} \right\rangle \tag{22}$$

where $<x> = x$, if $\mathrm{d}\lambda > 0$ or $<\mathrm{x}> = 0$, if $\mathrm{d}\lambda = 0$, corresponding to the cases of loading (including the softening range) and unloading. $d\lambda$ is a plastic multiplier to be retrieved from consistency condition. As described above we consider clay as a closed system, and the reversible equilibrium reactions are ignored.

An alternative formulation to the above is to assign various portions of the (22) to separate hidden variables of strain, thermal and chemical softening

$$\begin{aligned} \mathrm{d}r^{s} &= \mathrm{d}r^{s}\left(\varepsilon_{kl}^{\mathrm{pl}}, \mathrm{d}\varepsilon_{kl}^{\mathrm{pl}}, T, \xi^{\alpha}\right) \\ \mathrm{d}r^{t} &= \mathrm{d}r^{t}\left(\varepsilon_{kl}^{\mathrm{pl}}, T, \mathrm{d}T, \xi^{\alpha}\right) \\ \mathrm{d}r^{c} &= \mathrm{d}r^{c}\left(\varepsilon_{kl}^{\mathrm{pl}}, T, \xi^{\alpha}, \mathrm{d}\xi^{\alpha}\right) \end{aligned} \tag{23}$$

In this formulation, each environmental variable and plastic strain activates a different hidden variable. However, whenever the rates of hidden variables depend on the rates of the other state variables, the Coleman method (see e.g. Truesdell, 1984) for determining constitutive laws cannot directly be applied.

More than one hidden variable may be needed for clays subjected to some environmental loads (Hueckel, 1992). For smectitic or rehydrating illitic clays, internal friction angle (or the related coefficient M) was identified as another variable visibly dependent on mineralogical changes (see in addition to the apparent pre-consolidation isotropic stress. Knowing about a relative insensitivity of the former toward strain history and temperature (Hueckel, 1992), the evolution equations read

$$\begin{aligned} \mathrm{d}r^1 &= \mathrm{d}p_c\left(\varepsilon_{kl}^{\mathrm{pl}}, \mathrm{d}\varepsilon_{kl}^{\mathrm{pl}}, T, \mathrm{d}T, \xi^{\alpha}, \mathrm{d}\xi\alpha\right) \\ \mathrm{d}r^2 &= \mathrm{d}M(\xi^{a}, \mathrm{d}\xi^{\alpha}) \end{aligned} \tag{24}$$

where M is a critical state coefficient, related to the internal friction angle.

To pursue further the first avenue, with a single hidden variable r [Eq. (22)], let us expand the original idea of Lubliner (1972), and apply to clays, by assuming that (Hueckel, 1992),

$$\mathrm{d}r = \mathrm{d}p_c = \left\langle \phi_{ij}^{\varepsilon}\mathrm{d}\varepsilon_{kl}^{\mathrm{pl}} + \phi^{T}\mathrm{d}T + \phi^{a}\mathrm{d}\xi^{\alpha} \right\rangle, \text{where}\, \phi_{ij}^{\varepsilon}, \phi^{T} \text{and}\, \phi^{\alpha} = \phi\left(\varepsilon_{kl}^{\mathrm{pl}}, T, \xi^{\alpha}\right) \tag{25}$$

The chemical and thermal plastic hardening/softening function is formulated in a slightly different way than by Hueckel (1992), by separating coupled thermal and chemical hardening effects and uncoupled ones. This later option allows for elimination of the coupling, in the case when data are not sufficient for the constant identification. In addition, this formulation provides a simple expansion of the previous thermo-plasticity model (Hueckel and Borsetto, 1990).

$$p_c' = p_{c0}'\left[(\lambda - \kappa)^{-1}(1 - \alpha_0 \xi^{\mathrm{rs}} \mathit{\Delta} T)(1 + e_0)\left(\varepsilon_v^{\mathrm{pl}}\right)\right] + 2A(\Delta T) + 2B(\xi^{\mathrm{rs}})$$

where

$$\begin{aligned} A &= \alpha_1(\Delta T) + \alpha_2(\Delta T)^2 \\ B &= b_1(\xi^{\mathrm{rs}}) + b_2(\xi^{\mathrm{rs}})^2 \end{aligned} \tag{26}$$

The constants α_i and b_i are respectively thermal and chemical hardening coefficients, where α_0 is a coupling coefficient. The coefficient is responsible for diverse chemo-plasticity effects at elevated constant temperatures, or plastic deformability dependence on temperature or reaction progress. Plastic strain is defined through the co-linearity to the plastic gradient vector

$$\mathrm{d}\varepsilon_{ij}^{\mathrm{pl}} = \mathrm{d}\lambda \frac{\partial f}{\partial \sigma_{ij}} \tag{27}$$

Plastic multiplier $\mathrm{d}\lambda$ is obtained analogously as in Prager's (1958) thermo-plasticity theory from the consistency equation, assuming that during plastic strain in chemically active conditions, i.e. for $\dot{\xi}^{\mathrm{rs}} \neq 0$, the rates of effective stress, mass concentration and plastic strain are such, that the yield function and its rate is always equal to zero

$$\mathrm{d}_f = \frac{\partial f}{\partial \sigma_{ij}} \mathrm{d}\sigma_{ij} + \frac{\partial f}{\partial \varepsilon_v^{pl}} \mathrm{d}\varepsilon_v^{pl} + \frac{\partial f}{\partial T} \mathrm{d}T - \frac{\partial f}{\partial \xi^{rs}} d\xi^{rs} = 0 \tag{28}$$

Thus, plastic multiplier $d\lambda$ becomes

$$\mathrm{d}\lambda = \frac{1}{H}\left(\frac{\partial f}{\partial \sigma_{ij}} \mathrm{d}\sigma_{ij} + \frac{\partial f}{\partial T} \mathrm{d}T + \frac{\partial f}{\partial \xi^{\mathrm{rs}}} \mathrm{d}\xi^{\mathrm{rs}}\right) \tag{29}$$

whereas the plastic strain hardening modulus H retains its classical form, but may be affected by the coupling effects through the constant a_0

$$H = -\frac{\partial f}{\partial \varepsilon_v^{\mathrm{pl}}} \frac{\partial g}{\partial p'} \tag{30}$$

From (27 and 29) it is clear that there are plastic strain components that may be induced by pure heating or by a chemical change, at constant stress. Thus, the constitutive law for total strain increment can be re-written by separating deviatoric and volumetric strain as a function of mechanical, thermal and chemical solicitation rates

$$\mathrm{d}\varepsilon = \mathbf{D}\mathrm{d}\sigma + \mathbf{E}\mathrm{d}T + \mathbf{C}\mathrm{d}\xi^{rs}$$

or

$$\begin{Bmatrix} \mathrm{d}\varepsilon_v \\ \mathrm{d}\varepsilon_q \end{Bmatrix} = \begin{bmatrix} D_{vp}^{\mathrm{el}} + D_{vp}^{\mathrm{pl}} & D_{vq}^{\mathrm{pl}} \\ D_{vq}^{\mathrm{pl}} & D_{qq}^{\mathrm{el}} + D_{qq}^{\mathrm{pl}} \end{bmatrix} \begin{Bmatrix} \mathrm{d}p \\ \mathrm{d}q \end{Bmatrix} + \begin{Bmatrix} E_v^{\mathrm{el}} + E_v^{\mathrm{pl}} \\ E_q \end{Bmatrix} \mathrm{d}T + \begin{Bmatrix} C_v^{\mathrm{el}} + C_v^{\mathrm{pl}} \\ C_q \end{Bmatrix} \mathrm{d}\xi^{rs} \tag{31}$$

where the elements of the constitutive matrix **D** and constitutive vectors ***E*** and ***C*** are as follows

$$\begin{aligned} &D_{vp}^{\mathrm{el}} = \frac{\kappa}{1+e_0} \frac{1}{p'};\ D_{vp}^{\mathrm{el}} = \frac{1}{H} \frac{\partial f}{\partial p'} \frac{\partial f}{\partial p'} \\ &D_{vq}^{\mathrm{pl}} = \frac{1}{H} \frac{\partial f}{\partial q} \frac{\partial f}{\partial p'};\ D_{qq}^{\mathrm{el}} = \frac{1}{3G};\ D_{qq}^{\mathrm{pl}} = \frac{1}{H} \frac{\partial f}{\partial q} \frac{\partial f}{\partial q}; \\ &E_v^{\mathrm{el}} = -\alpha;\ E_v^{\mathrm{pl}} = \frac{1}{H} \frac{\partial f}{\partial T} \frac{\partial f}{\partial p'};\ E_q = \frac{1}{H} \frac{\partial f}{\partial T} \frac{\partial f}{\partial q} \\ &C_v^{\mathrm{el}} = -\beta;\ C_v^{\mathrm{pl}} = \frac{1}{H} \frac{\partial f}{\partial \xi^{\mathrm{rs}}} \frac{\partial f}{\partial p'};\ C_q = \frac{1}{H} \frac{\partial f}{\partial \xi^{\mathrm{rs}}} \frac{\partial f}{\partial q} \end{aligned} \tag{32}$$

where α and β are coefficients of thermal and chemical expansion, κ and G are elasticity bulk and shear moduli. The chemo-thermo-plastic loading and chemo-thermo-elastic unloading incremental criteria result from Eq. (29) as follows. For thermo-chemo-elastic unloading:

$$f < 0\,\mathrm{or}\,f = 0\,\mathrm{and}\ \frac{\partial f}{\partial \sigma_{ij}}\mathrm{d}\sigma_{ij} + \frac{\partial f}{\partial T}\mathrm{d}T + \frac{\partial f}{\partial \xi^{\mathrm{rs}}}\mathrm{d}\xi^{\mathrm{rs}} < 0 \tag{33}$$

For thermo-chemo-plastic loading, for the positive hardening modulus:

$$H > 0,\, f = 0\,\mathrm{and}\ \frac{\partial f}{\partial \sigma_{ij}}\mathrm{d}\sigma_{ij} + \frac{\partial f}{\partial T}\mathrm{d}T + \frac{\partial f}{\partial \xi^{rs}}\mathrm{d}\xi^{rs} > 0 \tag{34}$$

The inequality is inverse in the softening range, $H < 0$.

As a consequence of the assumption of considering clay rehydration in a closed system and assumptions (22) and (26), the constitutive inequality (11) becomes

$$\begin{aligned} D = \left(\sigma_{kl} - \frac{\partial h}{\partial \varepsilon_{kl}}\right)\mathrm{d}\varepsilon^{\mathrm{e}}_{kl} - \left(s + \left.\frac{\partial h}{\partial T}\right|_{r=\mathrm{const}} + \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial T}\right)\mathrm{d}T \\ - \left(\left.\frac{\partial h}{\partial \xi^{\mathrm{rs}}}\right|_{r=\mathrm{const}} + \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial \xi^{\mathrm{rs}}}\right)\mathrm{d}\xi^{\mathrm{rs}} + \left(\sigma_{kl} - \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial \varepsilon^{\mathrm{pl}}_{v}}\delta_{kl}\right)\mathrm{d}\varepsilon^{\mathrm{pl}}_{kl} \geqslant 0 \end{aligned} \tag{35}$$

Clearly, the Coleman's method does not apply in this case. However, we will claim that since for an unloading (elastic) state the method still yields classical definitions of stress, entropy and hidden variable, these definitions remain valid in the plasticity range as well,

$$\sigma_{kl} = \frac{\partial h}{\partial \varepsilon_{kl}};\ s = -\frac{\partial h}{\partial T} \tag{36}$$

By that, the dissipation requirement reads

$$\left(\sigma_{kl} - \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial \varepsilon^{\mathrm{pl}}_{v}}\delta_{kl}\right)\mathrm{d}\varepsilon^{\mathrm{pl}}_{kl} - \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial T}\mathrm{d}T - \left(\left.\frac{\partial h}{\partial \xi^{\mathrm{rs}}}\right|_{r=\mathrm{const}} + \frac{\partial h}{\partial p_c}\frac{\partial p_c}{\partial \xi_{rs}}\right)\mathrm{d}\xi^{rs} \geqslant 0 \tag{37}$$

This inequality imposes restrictions on the hardening function p'_c and on the irreversible changes of the elasticity moduli caused by the reaction.

5. Conclusions

Open options in the formulation of a thermo-chemo-plasticity model for illitization of smectite and resmectitization of illite have been examined. The goal of such a formulation is to include the effects caused by purely chemical changes in strain as well as changes in strength and hardening of clay. A number of hypotheses have been identified which lead to simplification of constitutive modeling of the system. A strongly interacting mixture of solid and multiple liquid phases with multiple species was postulated to avoid variables related to momentum of individual species. To identify a proper thermodynamic system to represent clay–water interaction, four options of open and closed systems were proposed. Four types of chemical variables were examined for parametrization of changes in mechanical properties during the chemical processes: current value of the relative content of a given species in the phase, species mass fraction change with respect to a reference value of the given species, progress of, or mass changed in a specific reaction, and the mass changed as a result of diffusion or flow of species from, or toward, the outside of the REV. On the top of the above, a purely phenomenological choice has been discussed which specific species changes, or which specific reactions are to be considered as causing the property changes. Following similar developments by Biot (1978) a closed system has been identified as a more suitable for the simulation of dehydration for the intended application in the analysis of natural analog of nuclear waste heat effect on clays. Such a system contains solid phase that includes adsorbed water, and liquid phase that is limited to stagnant (non-flowing water), leaving the actual flowing water in the surroundings of the system. This confines all the chemical changes to those within the system, and allows one to use reaction progress variable as a measure of chemical changes affecting mechanical properties of clay.

An extension of the Cam-clay model, following the previous template of the thermo-plasticity model (Hueckel and Borsetto, 1990), is proposed based on the hidden hardening variable approach, linked through evolution equation to temperature and reaction progress variable.

The study is aimed at showing a possibility for geo-chemo-mechanical simulations of the behavior of clay barriers against nuclear contamination subjected to long term thermo-chemical loading. Such goal is achieved, if only in an approximate and focused way. However, the process also helped to identify a large number of issues requiring further studies both in laboratory and in the field. In a parallel paper (Hueckel and Pellegrini, 2001), an application of this model to simulate thermo-mineralogical changes that presumably have occurred at the site of natural analog at Orciatico, Italy is described. Special emphasis is placed on the identification of the constants for thermal and chemical softening on the basis of tests on thermally affected and unaffected specimens from the site.

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