## Electro-chemo-mechanical coupling phenomena in geomechanics and biomechanics

Some chemically sensitive clays undergo *swelling*: this is a well-known fact to soil mechanicians. There has been interest in modeling parts of this phenomenon in the sixties and seventies, but failure to embed engineering observations in a continuum mechanics framework has hampered the developments. Renewed interest is just emerging, capitalising upon the progresses of the theory of mixtures, the thermodynamics of irreversible processes and computational methods.

On practical grounds, we have seized the opportunity of recent publications of systematic experimental investigations where both the chemical and mechanical aspects were taken care of.

Details in the development of clay modeling have attracted my interest to adjacent fields, namely cartilage and heart muscle. Just a few hints:

• **Cartilage and clays both swell**.
Cartilage is a porous medium where the fluid is an electrolyte transporting sodium chloride and nutrients. Due to the presence of negatively charged proteins, cartilage swells to resist mechanical loads. Therefore, cartilage presents many similarities with chemically sensitive clays, both in its constitution and in its chemo-mechanical behaviour. But cartilage is not a soil: it is highly interesting to develop models that are able to seize the similarities and differences.

• **The membranes of cardiac cells and clay clusters exchange numerous ionic species**.
Physiologically, the cardiac muscle is very far from cartilage. Articular cartilage is avascular, its cells in adults occupy a small percentage of the medium and are practically inactive, and the chemo-mechanical activity is extracellular. The cardiac muscle on the other hand is a syncitium, that is cells communicate quickly and they occupy a large portion of the space. In addition, there are numerous exchanges of ionic species through the cell membranes. These exchanges are dictated by electro-chemo-mechanical effects. This is this aspect of the heart muscle, which is actively studied by biochemists and physiologists, that has driven me to cardiomechanics. In fact, we had to devise models of membranes for our clay cells (clay clusters for soil mechanicians) that also exchange ionic species with the electrolyte. Of course, membranes of clay cells and biological cells display key differences: in particular, clay membranes do not show active transfers, like those originated by ATP-channels in living tissues.

We animate this multidisciplinary field on electro-chemo-mechanical phenomena by organising, see p.11,
- a workshop on clay behaviour, Maratea, June 27-29, 2001;
- a special issue of Mechanics of Materials devoted to geomechanical and biomechanical aspects;
- a graduate school, currently under review, proposed to an international institute.

## Swelling of elastoplastic clays

Swelling of clayey soils is an important factor in their engineering, but the accurate prediction of its amount and its consequences have been eluding engineers for several decades. The main reason for this is usually seen in a non-mechanical character of the phenomena involved and difficulties in linking them to soil mechanical analyses. Swelling is critically involved in such problems as borehole stability in petroleum extraction, liner and buffer stability in containment of nuclear or hazardous contaminants in environmental geotechnology.

In [16], we focus on chemically induced swelling and collapse of heteroionic clays, which constitute the majority of natural clays and a great part of engineered clays. In a preliminary paper [15], we address swelling of homoionic clays: these clays rarely occur in natural conditions, but they can be manufactured for specific industrial applications. Homoionic clays serve also as a good material model for preliminary studies.

The microstructure, and especially the organization of water in different pore spaces, is very much the same in both homoionic and heteroionic clays. In both cases, swelling arises as a result of chemical or electrochemical disequilibrium of a structural unit comprising:

- an amorphous substructure of quasi-crystals (clusters) of the parallel clay mineral platelets,
- absorbed water within the quasi-crystals and adsorbed water enveloping the substructure,
- the free pore water, and critically
- ions in the interplatelet space and in the free water.

*Chemical swelling* will cover both *crystalline swelling* due to absorption of water into interlamellar space and *osmotic swelling* due to adsorption of water to the external surface, and no distinction will be made between adsorbed and absorbed water. The amorphous structure is conceptualized as being wrapped in a semi-permeable membrane. This membrane serves as a gate-keeper for ion and water transfer between the free pore water and the clusters including the absorbed water. Unlike in biological tissues, such a membrane is not a physical object, rather it is a separation across which the two types of water fractions exchange cations at a certain rate.

The two-phase multi-species approach

Saturated clay is considered as a porous deformable continuum consisting of two overlapping phases, each phase containing several species. A kinematic criterion is used for phase identification and the absorbed water is attributed to the solid phase based on the affinity of their velocities. Capital in the modeling of deformable porous media is the coupling of the deformation of pore space in soil and the concomitant in- or out-flow of pore liquid. In chemically sensitive soils, this coupling is additionally affected by the presence of charged species in both phases. Thus, mechanics of the medium, e.g. balance of momentum, is considered at the phase level, whereas chemical processes, i.e. balances of masses, concern the species. The link between the two levels is obtained through energetic considerations.

The big picture: mechanical, transfer and diffusive constitutive equations

Whether or not the electro-chemical potentials are in equilibrium, water absorbed between the clay platelets can transfer into free pore water, or conversely, depending on the chemical composition of the clay and pore water phases, and on the mechanical conditions in terms of volume and pressure.

The electro-chemo-mechanical elastic-plastic constitutive equations involve the species of the solid phase (the clay platelets) but treat the fluid phase as a whole. The species of the latter only diffuse through the porous medium, obeying generalized Darcy's diffusion equations. The transfer of absorbed water and species between the solid and fluid phases involves a fictitious membrane surrounding the clay platelets, which may be permeable to the chemical species at various degrees. For the sake of simplicity, all chemical species that appear in the present analysis, except clay particles, can cross the membrane. Electroneutrality is required in each of the two phases, giving rise to an electrical field.

Chemical consolidation and swelling

The theoretical framework is illustrated by simulations of typical phenomena observed during laboratory experiments: the change of chemical composition of pore water has, due to the electro-chemo-mechanical couplings, consequences on the mechanical state of the porous medium. Parameters involved in the model are calibrated. Increase of the salinity of pore water at constant confinement leads to a volume decrease, so-called *chemical consolidation*. Subsequent exposure to a distilled water solution displays *swelling*. For pure Na-Montmorillonite clays, however, the latter is smaller than the chemical consolidation so that the chemical loading cycle results in a net contractancy whose amounts increases with the confinement. The situation is quite different for heteroionic clays as the influence of ionic species on mechanical properties vary greatly from one species to the other. Replacement of a Na-dominated pore solution by distilled pore water produces a quite different swelling strain than if the replacement were made using a K-dominated pore solution.

With respect to previous publications, the key feature of the present analysis is that the constitutive approach developed is more than qualitative. It embodies not only elasticity but also elasto-plasticity which is a necessary requirement to simulate the key features of the chemo-mechanical behaviour of swelling clays, as highlighted by experimental data which have been recently published. On the other hand, as a first attempt only two cations are assumed to be present in the clay clusters. While natural clays contain certainly more cations, their relative influence on the mechanical response of the clays certainly depends on the electrolyte filling the pore space. Therefore, extension of the model to clays with many ionic species requires experimental data to be available.

Boundary value problems

The elastic-plastic constitutive equations are embedded in a general formulation where both transfer and diffusion processes can be considered in initial and boundary value problems to be treated through the finite element method [17] [18].

Future developments: the effect of pH

Future developments will introduce the effect of pH. Indeed, electrokinetic remediation processes have been used with success to remove heavy metals (cadmium, chromium, copper, strontium, ...) from several clays, including kaolinites and montmorillonites, as well as organic pollutants dissolved in contaminated soils (acid acetic, phenol, ...). A key issue that characterizes the effect of pH consists in an accurate description of the change of the fixed negative charge of platelets. In variably charged clays like kaolinites, platelets become positively charged below the isoelectric point.

The modeling of electrokinetic remediation processes has so far mainly assumed a rigid solid skeleton. Advection of ions by water flow is accounted for but simplifications in the coupling flows were assumed by the first models, e.g. ionic mobility was neglected. Electrochemical reactions, other than electro-osmosis and ionic migration, were not included either.

A significant step forward is due to the contribution of Acar et al. [1994]. They show that the most prominent of these reactions is the development of an acid front starting close to the anode and moving towards the cathode, where negative pore pressures develop.

Quite satisfactory preliminary simulations of these processes have been performed, using the finite element method with our coupled electro-chemo-mechanical model, with elementary effects of pH included. Experimental data that would allow to quantify the mechanical couplings are in progress.

This work on clays has been performed with A. Gajo, Università di Trento, Italia, and T. Hueckel, Duke University, USA.

## Swelling of articular cartilage. Mechanobiology of engineered cartilage

Articular cartilage is the dense connective tissue, 2-4 mm thick, that covers the extremities of bones and provides load bearing capacities and frictionless movement along the synovial joints. It is a porous medium circulated by an electrolyte. The presence of negative fixed charges gives rise to hydration and swelling, that is viewed as a tool to sustain mechanical loads.

Histological data

Cartilage from adult animals and humans is avascular, aneural and alymphatic. Transport of nutrients towards young cells is performed through the synovial fluid. The cells in foetus and young subjects, called chondroblasts, are very active and they produce the extracellular matrix (ECM) composed essentially of fibrillar proteins (elastin, fibronectin and mainly collagen) and highly negatively charged proteoglycans. In adults, the cells become almost inactive; they are then called chondrocytes. Mature chondrocytes occupy only 2% of the volume. In that respect, cartilage is the opposite extreme of a syncitium, like the heart muscle, where cells occupy most of the volume and are linked together by gap junctions.

The matrix is circulated by an electrolyte, namely water containing dissolved ionic species, essentially NaCl. The presence of electrical charges induces the existence of absorbed water within the intrafibrillar space of collagen, which can be as high as 20 to 30% of the mass of the cartilage. Absorbed and free water represent together 70 to 80 of this mass in articular cartilage and a little bit less in meniscus.

The negative charges of proteoglycans are hydrated, neither $Na^+$ nor $Cl^-$ bind to the charged groups but they induce a shielding effect that decreases the repulsion force between proteoglycans.

Absorption of water results in *swelling* of the collagen fibrils. The amount of swelling depends on the concentration of proteoglycans and on the stiffness of collagen.

Modeling the couplings

Articular cartilage undergoes repetitive high stresses reaching 3-18 MPa as many as 1 million times a year. Collagen fibers endow cartilage with high *tensile* properties in the fiber directions. The collagen content become higher and the fibers become more and more aligned with the articular surface as one moves from the cancellous bone to the articular surface.

Therefore, the mechanical properties of articular cartilage both vary from point to point and display anisotropy. In addition, the fibrous collagen structure induces much higher elastic moduli in tension than

in compression. On the other hand, the *compressive* properties are provided by the proteoglycans who resist compression because glyco-amino-glycans (GAG) repulse each other due to their negative charges. Tensile stiffness may be 5-10 times higher than compressive stiffness.

Coupled physico-chemical phenomena are observed on articular cartilage. For example, articular cartilage changes dimensions when immersed in an ionic solution with variable salt concentration.

Several models of the electro-chemo-mechanical couplings have been published in the last ten years. In fact, the diffusional part that describes the transport of ionic species through the porous medium is very much similar to what we have for clays [18]. On the other hand, Maroudas has shown in several studies that the existence of two water compartments, intrafibrillar and extrafibrillar, could not be disregarded, as all models have done so far. Therefore the situation is quite similar to that of clays where we have absorbed water and free water. These aspects are being looked at now.

Future developments: mechanobiology for osteo-arthritis and tissue-engineering

Future developments will be concerned with two problems.

*Osteo-arthritis* (OA) is due to the disruption of collagen fibers. Therefore, collagen is less able to oppose the swelling potential due to proteoglycans. No coupled model so far has been able to furnish a satisfactory explanation of this pathology and its evolution.

As already mentioned, adult cells are inactive and cartilage is avascular. Therefore, repair of damaged cartilage is practically nil, unless failure extends down to the subchondral bone, in which case bone cells might migrate to replace the damaged cartilage. However, the mechanical quality of such a replacement is much lower than that of natural cartilage. One way explored these days is to use engineered cartilage. It has been observed that mechanical excitation enhances chondrocyte activity in cell-seeded polysaccharide gels. The experimental procedures are still in infancy, and there is no agreement yet on how to proceed to optimise the resulting product. Needless to say that a modeling of the mechanical activation of chondrocytes is an exciting challenge.

This study on soft tissues, cartilage, cornea and polyelectrolyte gels of biological interest, is performed in collaboration with F. Simões, Instituto Superior Tecnico, Lisboa, Portugal.

## Cardiac muscle: the mechano-chemical and mechano-electric feedbacks

Cardiomechanics intends to provide a global understanding of the various aspects of the heart. As an organ, the heart receives various types of information (electrical, chemical, mechanical) from the body to which it re-acts. As such its is an object of study for automaticians. Now clearly, this interaction depends on the behaviour of the heart itself. This is by what we are interested here. In a quite classical way, the first step is to provide an electro-chemo-mechanical model of its "normal" behaviour. The next step is to endow this model with sufficient details so as to be able to explain, through actual quantitative simulations, various pathologies, like arrythmia, modifications of the blood circulation, Fontaine disease, etc...

Current finite element simulations, whether really 3D or axisymmetric, consider the isolated heart under steady periodical sollicitations, induced by the sino-atrial node and vascular pressure, that is the body is not yet invited to react, see http://cmrg.ucsd.edu. I have been surprised by the fact that these finite element simulations of the heart behaviour are *decoupled*:
- first the electric field is computed independently;
- next the chemo-mechanical response is deduced.

Clearly, in our simulations of consolidation and swelling of clays, this decoupling is not possible. But, the models of heart muscle that are used these days allow for such a decoupling. It turns out that, to be able to reproduce some specific experiment on muscle fibers, mechano-chemical and mechano-electrical feedbacks should exist that *ruin* the decoupling possibility: this is our starting point.

This model is currently being developed. Let me just give a brief overview. There are several length-scales involved in the model: cell, muscle fibers, heart.

The cellular membrane

The cell is geometrically bounded by its membrane.

- The myocardium is a *syncitium*, that is cells are (electrically) linked by *gap junctions* which ensure the fast transmission of electric signals;
- The membrane is constituted of two layers of phospholipids. Membranar proteins ensure different functions, in particular controlled transport of matter, reception and transduction of signals, enzymatic reactions, contact with other cells through gap junctions.
- The membrane behaves as capacitor of fixed capacitance. There are three types of channels through the membrane, namely ligand-gated, voltage-gated and stretch-gated channels. For the myocardiac cells, the ligand is ATP and the channels are then called *ionic pumps*, in as far as ATP allows the transport of ions across these channels against a concentration gradient.

Over the last fifteen years, several electrophysiological models of cells have been published. The more advanced one, from the Johns Hopkins Cardiomechanics Group, uses seventeen electrical currents. The whole point of this machinery is to deliver, at the appropriate time, the appropriate concentration of low-affinity $Ca^{2+}$ that will allow the fiber muscle to function (*this is the electro-chemical coupling*).

The behaviour of the fibers of cardiac muscle

Models describing muscle behaviour can be classified in two main groups. So-called *cross-bridge models* address mechanical aspects that occur at a *microscopic scale*, typically of the order of the nanometer, where a Myosin head and the associated bonding site on the Actin filament are the key objects. A subsequent upscaling is performed by a simple statistical averaging, so that the tension of the muscle fiber is obtained at a *macroscopic scale*, typically of the order of the micrometer or even millimeter, where the fine physical details of the thin and thick filaments are not visible any longer. Their effects are nevertheless not wiped out by the upscaling.

Other models address the behaviour of muscle fibers directly at a *macroscopic scale*, although they try to incorporate typical physiological details of the tension development during both diastole (passive tension) and systole (active tension). Indeed, it is commonly accepted that the tension at the muscle fiber scale is contributed by active tension and passive tension, The *active* tension is due to the relative sliding of the thick filament (myosin) with respect to the thin filament (actin): mysosin heads can fix to actin sites, and their change of conformation leads to shortening.

The *passive* tension due in part to the giant protein titin that endows the diastolic muscle properties with linear elasticity and moderate rate effects. Collagen is responsible for tension at larger stretches, it practically limits the latter and it is usually described by non-linear hyperelasticity.

A key point: tension deficit during instantaneous muscle shortening

The above remarks were up-to-date, but otherwise, not original observations. Our own work starts from here. Experiments show that, after rapid shortening of skinned cardiac fibers, the tension falls and there is no complete *tension recovery* even after a long rest period. Note that this tension deficit is too large to be due only to an elastic parallel contribution. We attribute this *tension deficit* phenomenon to an increased Ca-detachment from the binding sites. It seems that the phenomenon is much less marked for skeletal muscles.

The point is to be able to simulate the force deficit observed during rapid shortening of skinned fibers by an appropriate kinetics of the binding of $Ca^{2+}$ to Troponin sites with low affinity to calcium. The idea is to make this kinetics tension-dependent, more exactly to increase the detachment rate of $Ca^{2+}$ when the (active) tension is low. Therefore we have *mechano-chemical* and *mechano-electrical feedbacks*. Notice that these feedbacks are not identical to the ones advocated by the Oxford Group to explain commotio cordis: these are due to stretch-gated channels.

Challenging developments: cardiac metabolism

In the current version of this model, the electrophysiological cell model I use does not make reference to energetics, that is ATP necessary to crossbridges is assumed to be available. Improvement on that aspect is possible as partial ATP-metabolism has been recently introduced in cell electrophysiology by A. Michailova. However, much work remains to be done to obtain a realistic control of the metabolic activities of the cardiac cells by the ATP demand of crossbridges. Indeed, the various parts of the cardiac metabolism (glycolysis, TCA cycle, $\beta$-oxidation, oxidative phosphorylation) are themselves described by complex models that involve many parameters which vary over species, more often than expected, in an unknown way. Chemical reactions at the various steps are usually viewed as enzymatic reactions defined

by various (and uncertain) kinetics [14]. Metabolic aspects and $\beta$-adrenergic factors are certainly required in the modeling of the cardiac function, and especially for the simulations of ischemia and hypoxia. Drastic simplifications are necessary if they are to be introduced in cell electrophysiology models used in a chemo-mechanical approach. This simplification however requires a deep understanding of the key features of the metabolic activities.

For these preliminary analyses on the cardiac muscle, I have benefited from the advices of the Cardiac Mechanics Research Group at the University of California San Diego, USA, led by Prof. A. McCulloch. I learned cardiac metabolism from Prof. J. Bassingthwaighte, University of Washington, Seattle.