



In-pore tensile stress by drying-induced capillary bridges inside porous materials

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ABSTRACT

We present here some evidences that capillary liquid bridges are able to deform micrometric cylindrical pores by tensile stress. Brine-soaked filter membranes are submitted to drying conditions leading to NaCl precipitation inside the 5–10 μm pores. A close examination demonstrated that two forms of NaCl crystallites are successively generated. First, primary cubic crystals grow, driven by the permanent evaporation. When this angular primary solid gets near the pore wall, while the evaporation makes the pore volume to be partly invaded by air, capillary liquid can bridge the now-small gap between the halite angles and the pore wall. In a second step, these small capillary bridges are frozen by a secondary precipitation event of concave-shaped NaCl. The proposed interpretation is that the liquid capillary bridges deform the host matrix of the membrane, and the situation is fossilized by the growth of solid capillary bridges. A quantitative interpretation is proposed and the consequences towards the natural media outlined.

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1. Introduction

The porous or finely fractured unsaturated systems are widely present in natural systems, like the non-saturated soils or the three-phases oil-depleted aquifers, as well as in anthropogenized media like the excavation damaged zone around deep geological nuclear waste disposals. Another common such systems are the building stones when extracted from natural quarries, and exposed to drying–wetting cycles along an hydrological year. They typically contain water suspended over air against gravity, by bridging the solid-to-solid pore space owing to the capillary forces. The capillary state of the soil solutions has direct consequences on the mechanical equilibrium and the chemical weathering at the pore scale. The first effect is related to the time of the solid–aqueous solution interaction due to the immobilization of the capillary solutions (e.g., [1,2]). Another effect depends on the thermodynamic properties of a capillary liquid (and therefore its solvent properties) which differ from those of the free liquid [3–10]. On the mechanical side, capillary bridges pull on the solid(s) to which they are anchored, and so play a role in the compaction and the strength of soils (e.g., [11–13]), and in general of any granular wetted stacks (e.g., [14,15]). Furthermore, Scherer [16] and Smith et al. [17] for gels, Tas et al. [18,19] for massive solids (silicon chips),

gave grounds that the capillary bridges are able to mechanically deform solid matrix, even at moderate capillary pressure.

In parallel, many field observations in the arid zones report the erosive role of the salts precipitating in the micro-porous regions of rocks, due to the drying of the network. Salt weathering is able to provoke the *in situ* breakdown of massive rocks like granite (e.g., [20–24]). That corresponds to coupled processes, interlinking chemistry and mechanics taking into account the capillary state of the media. The Wellman and Wilson's model [20] highlighted the role of the smaller pores and the salt precipitation inside them to provoke the most efficient rock breakdown in coastal and arid environments. Scherer [16] highlighted the role of the small pores by replacing the discussion in the context of the drying of any heterometric pore network: as the large pores empty first, then the tension in the neighbouring small pores may deform the pore wall and causes cracking (see especially Fig. 7 in [16]). Meanwhile, a lot of parameters are acting in these processes, as the host microstructural properties, the environmental conditions, the interfacial tensions, or still the composition of the soaking solution, and so the causal connections are very complex to decompose.

The present paper reports simple experiments targeting to illustrate how the capillarity may take place in the salt weathering process. To do that, we decided to work with hand-made saline solutions (initially) saturating homogeneous simple pores under soft drying conditions. After detailing the protocol and the main results, we will present a thermodynamic interpretation of the successive events which includes the capillarity arising during the drying. Clues of the occurrence of this capillary weathering in the

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fields are collected to outline the potential importance of this effect in non-saturated media, submitted to drying–wetting cycles, typically natural soils or the area around any excavated tunnels. However, the complexity of such media makes this endeavour very exploratory, and worth to be deepened in the future by field geochemists.

2. Back to capillarity

The conditions of occurrence of capillarity have been treated for long with the respective roles of the pore radius (Young–Laplace law) and of the relative humidity (RH hereafter) of air (Kelvin law) inside the system.

2.1. Young–Laplace law

The first capillarity “Young–Laplace” law correlates the curvature of an interface with the pressure difference across it. For a liquid–air interface:

$$\Delta P = \gamma_{LV} \times \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1a)$$

with $\Delta P = P_L - P_V$ is the pressure difference (in Pa) between the liquid phase (at P_L) and the air phase (at P_V). As capillary menisci are concave towards the atmosphere, the liquid pressure is lower than that of the atmosphere, possibly reaching negative values (commonly called tensile or stretched liquid water) while vapour pressure is obviously always positive. r_1 and r_2 (in meters), are the main radii of curvature of the meniscus, and for spherical meniscus: $r_1 = r_2$. The radius is counted negative for concave meniscus (positive for a droplet), which maintains the correct sign balance between the two members of Eq. (1). γ_{lv} is the surface tension between the liquid water and the vapour in air, and its high value for H₂O at room temperature is one of the reasons allowing the liquid water to undergo high curvatures.

2.2. Capillary-elastic pressure for solids

The Young–Laplace law also applies to the solid–air interface and writes for a spherical interface:

$$\Delta P = \gamma_{SV} \times \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1b)$$

with $\Delta P = P_S - P_V$ is the pressure difference (in Pa) between the solid phase (at P_S) and the air (at P_V); γ_{sv} is the surface tension between the air and the solid having a concave spherical curvature toward the air defined by r_1 and r_2 .

One possible ambiguity comes from the twofold origin of the “solid pressure” parameter. Actually, it can be related to both an energy concept (chemical free energy of the solid) and a mechanical concept (surface stress). Cahn [25] outlined that the solid surfaces can change either by creating or destroying surface at constant surface structure and properties, or by an elastic strain along the surface at constant number of surface lattice sites. The first case requires a chemical driving force correlated to the surface free energy (work of creating a unit area of surface), the second requires a mechanical driving force correlated to the surface stress (work of elastic deformation of the surface). When one applies principles of capillarity to solids, the pressure jump across the interface and the corresponding shape of the interface obviously refer to a Gibbs free energy effect. It is why the capillary pressure jump is sometimes called the capillary-elastic pressure (e.g., [26]).

The chemical potentials of the naturally-shaped solids are tabulated so that to meet the known solubility (in aqueous solutions) at normal conditions. In this sense, these chemical potentials are

the 10⁵ Pa reference. Any perturbation of the system pressure makes the chemical potential to vary by the $V_s dP$ term, V_s being the (assumed) constant solid volume. It follows that the Young–Laplace law applied to a solid–air equilibrium can be rewritten as:

$$\Delta P = \frac{\Delta \mu_s}{V_s} = \gamma_{SV} \times \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1c)$$

where $\Delta \mu_s = \mu_{solid,1bar} - \mu_{capillary\ solid}$ is the difference in the chemical potentials between the two forms of the given mineral. Eq. (1c) correlates the shape change of a solid as a function of the capillary state inside the studied system to a solid pressure variation through the usual surface tension parameter.

2.3. Kelvin law

The second capillarity “Kelvin” law makes clear that the driving force to “capillarize” is the difference between the chemical potentials of the two partners separated by the curved interface. Again, for one liquid–air interface, that writes:

$$\log \frac{p}{p^\circ} = \frac{\Delta P \cdot V_L}{RT \ln 10} \quad (2)$$

where p and p° , in Pa, are the pressure in equilibrium with, respectively, the curved and the plane interface; V_L , in m³/mol, is the molar volume of the liquid, stated constant as a function of P_L ; ΔP is the Young–Laplace pressure difference across the interface (Eq. (1a)).

3. Protocol and experimental techniques

Polycarbonates membranes (filters) having homogeneous pores, in size (10 and 5 μm) and shape (cylindrical), are soaked with brines in a Petri cell filled with the suitable solution (see below). After, they are put in a drying chamber under fixed relative humidity (RH hereafter) of air, set to favor the water evaporation which should lead to the precipitation of solid salts inside the initially large and cylindrical pores. After 15–20 days, the remaining brine is removed and the filters are directly observed by scanning electron microscopy (SEM).

3.1. Filters

The basic materials are polycarbonate membranes (Nuclepore, Whatman), whose pores are drilled by laser resulting in a perfect round shape (Fig. 1).

The reproducibility of the drilled shape is very good as exemplified by the white circles, all of the expected scaled size. The pores are scattered on the whole surface (membrane diameter: 47 mm), and the depth of each pore equals the thickness of the membrane, around 10 μm. The membranes are made of polyaliphatic carbonates and so are totally non-hygroscopic, especially toward the atmospheric moisture. To test the stability of the pore geometry throughout the drying process, irrespective of other geochemical event, we compared the before–after states with one membrane soaked in pure water (Fig. 1b). It becomes obvious that the pristine membrane (Fig. 1a) and the water-treated one (Fig. 1b) are identical, establishing that the protocol, especially the drying stage (see below), is not able to modify the pore geometry. That is consistent with the hydrophobic behaviour of the polycarbonate itself.

3.2. Salt solution and solid salt

The sodium chloride (NaCl) is commonly encountered in salt crystallisation decay and is frequently used for salt crystallisation laboratory tests (e.g., [27,28]). A vast literature deals with what happens when saline solutions evaporate in pores, and the

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