

Mechanical stress due to the capillary bridging in unsaturated zone

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Crystallization pressure is known to take place in micrometric pores and to cause stone damage. Actually, growing salts in pores can exert a stress on the pore walls such as to cause the failure of the material [e.g. 1,2]. The present contribution argues that another mechanism may act to influence stress development and cracking in pores. It is connected to the traction generated by the capillary bridges taking place in unsaturated porous domains. We performed a series of observations in diversely-sized porous membranes submitted to a continuous moderate evaporation from saturated conditions down to controlled humidity conditions. The SEM observation of the resulting situation inside the materials shows that the inner surface of the membrane pores has undergone a stress when the growing salt is able to anchor them through capillary bridges (Fig. 1).

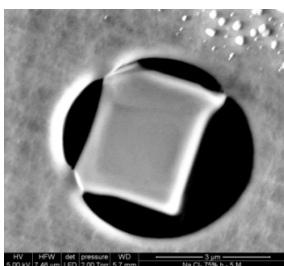


Figure 1: NaCl growing crystal in 5 µm membrane.

These observations are totally consistent with other already collected results [3], demonstrating the capability of capillary bridges to deform confining materials, potentially inducing the matrix cracking. Application to identify the possible effect on the permeability of compacted argillaceous media close to the (Unsaturated) Excavation Damaged Zone in nuclear waste deep disposals is developed.

[1] Scherer (1999) *Cement Concrete Res.* **29**, 1347-1358.

[2] Scherer (2004) *Cement Concrete Res.* **34**, 1613-1624.

[3] Tas *et al.* (2003) *Nano Lett.* **3**, 1537-1540.

XPS study of calcite interaction with gases

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Calcite (CaCO_3) is one of the most abundant salts in the Earth's crust. Its surface behaviour in the presence of liquids and gases controls its behaviour during dissolution, precipitation, adsorption and desorption. To help understand these complicated phenomena, a fundamental understanding of surface/gas interaction is useful.

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique that allows quantitative and qualitative investigation of solid surfaces. A series of clean calcite {10.4} surfaces, prepared by cleavage in vacuum, have been examined with XPS under a range of conditions, including exposure to various concentrations of CO_2 , ethane, ethanol and H_2O vapour under a spectrum of temperatures. Adsorption and desorption behaviour is different for each gas and is consistent with the nature and the strength of the bond it forms with calcite. For example, ethanol is adsorbing on freshly cleaved calcite at 120 K and desorbs at 370 K, see figure below.

We are using this information to interpret interaction of more complex organic molecules that adsorb from solution and inhibit calcite growth and recrystallisation.

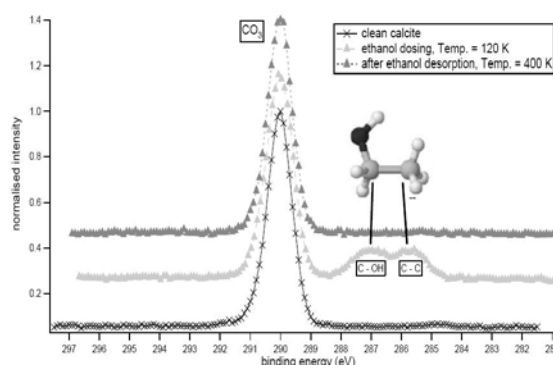


Figure 1: XPS spectra of the carbon region during ethanol dosing on a calcite surface freshly cleaved in vacuum. The ethanol is present at low temperature and it desorbs at $T = 370$ K, returning the surface to its initial clean state.