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Deformation and stress from in-pore drying-induced crystallization of salt

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Abstract

The deformation and the fracture of porous solids from internal crystallization of salt is explored in the framework of the thermodynamics of unsaturated brittle poroelasticity. In the first place the usual theory of crystal growth in confined conditions is further developed in order to include both the deformation and the drying of the porous solid. The thermodynamics reveals the existence of a dilation coefficient associated with the crystallization process, and provides a solute–crystal equilibrium condition which involves the relative humidity, the supersaturation, and the salt characteristics. This thermodynamic condition and the mechanical equilibrium of the solution–crystal interface combine to give the current crystallization pore radius. Upscaling this information at the macroscopic scale, and taking into account the salt mass supplied by the invading solution, the approach leads to a quantitative analysis of the role of the pore size distribution on the crystal growth under repeated imbibition–drying cycles. The deformation and the fracture of the porous solid from drying-induced crystallization are then considered in the context of brittle poroelasticity. The current unsaturated macroscopic poroelastic properties are upscaled from the microscopic elastic properties of the solid matrix and from the current liquid, crystal and gas saturations. The adoption of a fracture criterion based on the elastic energy that the solid matrix can ultimately store finally leads to the determination of how long a stone can resist repeated cycles of drying-induced crystallization of salt.

Keywords: Crystal growth; Drying; Unsaturated brittle poroelasticity; Pore radius distribution; Weathering

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1. Introduction

Soluble salts are recognized as being important weathering agents in dry environments close to the sea (Evans, 1969). The crystallization of sea-salts can generate stresses, and lead to serious deterioration in porous sedimentary rocks used for building in coastal areas (Fassina, 2000). As pointed out in Scherer (1999), it is generally not possible to prevent the penetration of the crystallizing solution, nor the formation of salt crystals, so that it becomes essential to understand the mechanisms of deterioration at work. Actually, the quantification of the factors governing the stone weathering will be of great help when looking for the recourse to allow the porous material to accommodate the crystallization without harm.

After the deposition of saline solutions in the form of salt-spray, and their further penetration by capillary action, the supersaturation increases and the induced crystal growth in small pores are originated by two main causes: (i) the drying of the porous material resulting in the increase of the salt concentration of the residual solution; (ii) the decrease of the current salt solubility induced by the lowering of the temperature. Because of the need to obtain results in a short time, and to reduce the number of factors that produce weathering, drying temperatures between 40 and 60°C are often used in standard procedures for artificial weathering tests. Although these testing routines are very useful for establishing the relative resistance of different types of rocks, and for assessing the efficiency of conservation treatments, they do not reproduce the field conditions, and they even may produce effects which are not seen in natural environments. More realistic procedures have been developed, aiming at experimentally establishing the intrinsic parameters involved in natural weathering. In these ageing tests (Cardell et al., 2003), the samples are subjected to cycles of saline spray, followed by drying by forced air at 35–39 °C and 50% of relative humidity obtained by using a controlled atmosphere chamber. These experiments identified the total porosity, the solid grain size and the pore system as the main recurrent factors determining the susceptibility to weathering.

Although these realistic experiments, especially when combined with NMR measurements (Pel et al., 2002), provide precious information on the combined evolution of the moisture content and of the crystallization within the stone, the physical mechanisms governing the damage process caused by the growth of salt crystals are still the object of interrogations. A survey of the theories and models aiming at explaining the process of confined crystallization of salts and the related build up of the crystallization pressure can be found in Rodriguez-Navarro and Doehne (1999). Following the pioneering works of Correns (1949) and Weyl (1959), confined crystallization has been recently reconsidered at the pore scale in Scherer (1993, 1999, 2004). Two significant conclusions were reached: (i) crystal growth is expected to occur in large pores by the invasion from the connecting capillary channels, whose radius governs the percolation process; (ii) owing to intermolecular forces and to the associated disjoining pressure (Israelachvili, 1991), a thin layer of aqueous solution always remains between the crystal and the internal solid walls of the porous network. This thin layer facilitates the further in-pore crystallization by allowing the solute to diffuse to the previously crystallized sites. The solute–solid thermodynamic equilibrium has been explored in Flatt (2002), in order to account for the combined effects of the stoichiometry of the crystallization reaction, and of the water activity upon the generation of supersaturation. Along the same guidelines, yet in the absence of any drying, the combined role of the main factors affecting the crystallization,