

On the constitutive equations for coupled chemical reaction and deformation of porous rocks

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Deformation, chemical reactions, fluid flow in geological formations, and many engineering materials, such as cement, are coupled processes. Most existing models of chemical reactions coupled with fluid transport assume the dissolution-precipitation process or mineral growth in rocks. However, dissolution-precipitation models predict a very limited extent of reaction hampered by pore clogging and blocking reactive surfaces, which will stop reaction progress due to limited fluid supply to reactive surfaces. Yet, field observations report that natural rocks can undergo 100% hydration/carbonation. Mineral growth models, on the other hand, preserve solid volume but do not consider its feedback on porosity evolution. In addition, they predict an unrealistically high force of crystallization on the order of several GPa that must be developed in minerals during the reaction. Yet, experiments designed to measure the force of crystallization consistently report values on the order of hundreds of MPa, which is close to the failure limits for most rock types. Recent experimental and observational studies suggest that mineral replacement is a coupled dissolution-precipitation process that preserves porosity and increases the solid volume. Here, we propose a new model for reaction-driven mineral expansion, which preserves porosity and limits the unrealistically high build-up of the force of crystallization by allowing inelastic failure processes at the pore scale. First, we look at fluid-rock interaction at the pore scale and derive effective rheology of a reacting porous media. We use a two-phase continuum medium approach and local equilibrium thermodynamic models to investigate the coupling between reaction, deformation, and fluid flow on a larger scale. We assume that rock or cement consists of an assembly of solid reactive grains, initially composed of a single, pure phase. The reaction occurs at the fluid-solid contact and progresses into the grain. We approximate the pores and surrounding solid material as cylindrical shells. We derive macroscopic constitutive laws that account for chemical alteration and viscoelastoplastic deformation of porous rocks. Our model explains experimental observations on natural and engineering geomaterials, such as the possibility of achieving a complete reaction, preservation of porosity, moderate values of the crystallization force, and dependence of mechanical rock properties on fluid chemistry.

