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

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Deformation, chemical reactions, and fluid flow in the geological materials are coupled processes. While some reactions are thought to be a consequence of fluid assisted dissolution on the stressed mineral surfaces and precipitation on the free surface, other reactions are caused by mineral replacement wherein a less stable mineral phase is replaced by a more stable phase, involving a change in solid volume and build-up of stresses on grain contacts, also known as a force of crystallization. Most of the existing models of chemical reactions coupled with fluid transport either assume dissolution-precipitation process or mineral growth in rocks. However, dissolution-precipitation models used together with fluid flow modelling predict a very limited extent of reaction hampered by pore clogging and blocking of reactive surfaces, which will stop reaction progress due to the limited supply of fluid 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 the unrealistically high force of crystallization on the order of several GPa that must be developed in minerals during the reaction. Here, using a combination of effective media theory and irreversible thermodynamics approaches, we propose a new model for reaction-driven mineral expansion, which preserves porosity and limits unrealistically high build-up of the force of crystallization by allowing inelastic failure processes at the pore scale. To fully account for the coupling between reaction, deformation, and fluid flow we derive macroscopic poroviscoelastic stress-strain constitutive laws, that account for chemical alteration and viscoelastic deformation of porous rocks. These constitutive equations are then used to simulate the reactive transport in porous rocks.