A reactive transport model for calcite-rich caprocks in the context of geological carbon storage

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Increased concentrations of greenhouse gases in the atmosphere are known to be the primary cause of the increase in global surface temperature and, consequently, climate change [6]. In order to limit global warming, several decarbonisation strategies have been proposed: among them, geological CO_2 storage represents very likely the only short- to medium-term option for substantially improving CO_2 sinks and reducing net carbon emissions into the atmosphere.

To achieve secure and lasting storage of CO_2 in underground spaces, it is necessary to have both a reservoir and a low-permeability caprock (seal), that maintains its integrity. Deep saline aquifers, depleted oil and gas fields and unminable coal seams are thus the primary targets for the underground storage of supercritical CO_2 [2]. The occurrence of natural reservoirs implies that certain lithotypes have a certain sealing capacity, which can prevent leakage of gas to the atmosphere over long geological time periods (i.e. million of years); however, in order to assess the risk of CO_2 leakage through caprock above storage sites, the potential caprock alterations due to the contact with CO_2 must be considered. In fact, although certain caprocks can be suitable for hydrocarbons, CO_2 in contact with the seal may pose additional risks. As for natural hydrocarbon accumulation, shales and evaporites are potential seals also for carbon storage. With particular reference to shales, their mechanical and transport properties are controlled by the behaviour of clay minerals. The sealing efficiency of intact shale caprocks is in fact dominated by the high specific surface clays, which are characterized by high capillary entry pressures, but are also susceptible to electro-chemical interaction. From the engineering perspective, capillary and electrical phenomena also have relevant effects at the Representative Elementary Volume scale, causing mechanical couplings which could affect porosity, clay fabric, hydraulic conductivity, compressibility, and shear strength [3]. Besides these electro-chemical effects, CO_2 dissolution and diffusion in water also result in acidification of the in situ brine, causing chemical reactions with some caprock minerals and potentially affecting the mechanical and transport properties [4].

This work presents a reactive transport model to assess the effects of pore water acidification on caprock materials. The model includes the water mass balance equation for the saturated porous medium and the mass balance equation for all the primary species dissolved in water, according to the theoretical approach presented in [7]. The modelling approach proposed accounts for both the aqueous (homogeneous) reactions of the CO_2 dissolved in water (assumed to be in equilibrium) and the dissolution kinetics of calcite in the acidic environment induced by CO_2 injection (see [1] for details). Calcite dissolution is finally linked to porosity changes via the reactive surface area of the mineral and the reaction rate. Chemo-hydraulic coupling is addressed by considering porosity changes in the storage term of the balance equations and by introducing a suitable link between hydraulic conductivity and current porosity. The model requires the solution of an initial chemical speciation problem, which has been performed with the software PHREEQC, and then the integration of a set of partial differential equations (the mass balance equations of water and of the master primary species dissolved in water) and non-linear algebraic equations (to obtain the concentration of all the chemical species involved), which in this study has been performed via the Finite Element software Comsol Multiphysics ®, according to the approach presented in [8].

The numerical model has been validated according to the numerical benchmark proposed in [5], developed to reproduce a geochemical scenario where mineral dissolution causes permanent alterations in the transport properties of a porous medium. In particular, the benchmark reproduces a flow-through columns experiment, with the porosity and permeability of a calcite-rich interlayer changing under sulfuric acid attack. Figure 1 shows a comparison between the predictions of the current model and the model proposed in [5] in terms of the spatial evolution of porosity, permeability and dissolved calcite, after 400 hours since the injection of sulfuric acid. The model is able to reproduce that, as the acidic front proceeds into the sample from left to right, calcite is progressively dissolved causing porosity changes and the consequent permeability increase. The agreement between the two models is satisfactory, despite some slight differences that may be attributed to the different numerical mesh and the different numerical solver scheme.
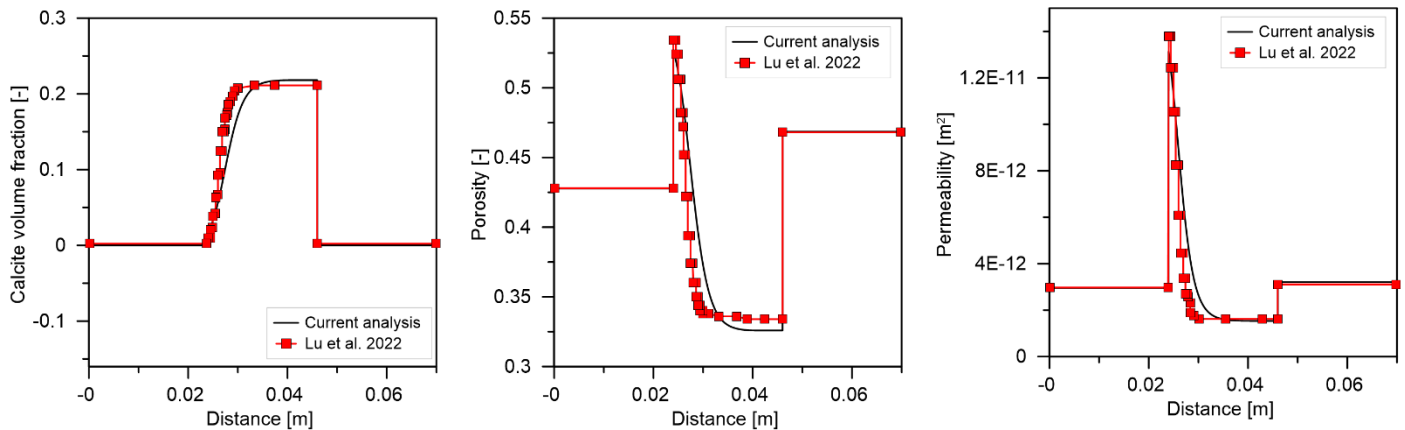

Figure 1: Comparison between [7] and the proposed model in terms of the spatial distribution of calcite volume fraction, permeability and porosity. All the curves are evaluated at t=400 h.

Contributor statement

Liliana Gramegna: Conceptualization, Methodology, Software, Validation, Formal analysis, Data Curation; Guido Musso: Supervision, Writing – Review & Editing; Alessandro Messori: Funding acquisition; Gabriele Della Vecchia: Conceptualization, Methodology, Formal analysis, Supervision, Writing – Original Draft.

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