Modeling of water-rock reactions driven by the injection of supercritical CO_2 – H_2S mixtures in a natural gas layer.

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The underground injection of CO_2-H_2S mixtures is of interest for the storage of (i) GHG mixtures containing H_2S as a contaminant of CO_2 captured in a coal gasification process, and (ii) acid gases produced during the exploitation of sour hydrocarbon reservoirs. The reactive processes driven by the injection may induce changes of mineralogical composition and petrophysical properties of reservoir formation with possible relevant consequences on injection performances and the safe containment of injected gas mixture. Simulations of the injection of gas mixtures containing different mass ratios of CO_2-H_2S were performed to study the short-to-medium term physical processes and chemical alterations occurring when GHG sequestration takes place in an exploited natural gas layer.

The petrophysical properties and mineralogical composition of the reservoir rock, and the initial composition of the formation water reproduce the field conditions of a sand layer containing natural gas mainly composed by methane. A uniform initial temperature of 45˚C is considered all through the system which is at an initial pressure of 140 bar. The porosity, permeability and liquid saturation are assumed uniformly distributed into the domain with initial mean values of 0.32 (volume fraction), 400 mD and 0.15, respectively. The system is described by means of an horizontal 1D-radial grid having an external radius of 1E4 m (to minimize boundary effects) and the injection well lying along the symmetry axis. The constant rate injection of a dry supercritical gaseous

mixture is simulated for a period of 100 years.

Our simulations employed the nonisothermal, multicomponent reactive geochemical transport simulator TOUGHREACT (Xu et al., 2004) coupled to the equation of state (EOS) module TMGAS (Snamprogetti, 2006) developed in the framework of the TOUGH2 V.2 reservoir simulator (Pruess et al., 1999). TMGAS provides an accurate description of two-phase thermodynamic equilibrium of mixtures of organic and inorganic gases with NaCl-dominated brines. TMGAS calculates the phase equilibria and the properties of the phases up to a pressure of 1000 bar and a temperature of 200 °C, such to include the conditions typically encountered in saline aquifers and geological structures of interest for CO_2 disposal.

Two scenarios are presented differing for the composition of the injected GHG mixture: a reference case (A) where only supercritical CO_2 is injected, and a case (B) where a mixture of CO_2 and H_2S as contaminant (in the order of few percent in mass) is injected. The effects due to the presence of H_2S may be hence estimated from a direct comparison of the two cases. In our calculations the reactivity of the minerals is kinetically controlled. Because of the lacking of reliable data about elemental sulfur kinetics, a sensitivity analysis on relevant parameters, i.e. kinetic rate constants and specific reactive areas, was therefore performed.

In both cases the simulations predict a methane displacement with an advancing front reaching after 100 years a radius of about 1000 m. The displacement of methane by a dry gaseous mixture moreover induces an evaporation front which at the end of the injection is located at about 50 m from the injection well. In the portion of the domain delimited by these two fronts the aqueous phase is characterized by an high content of dissolved acid gases and a fairly low pH (just below 5). In the short term however the geochemical evolution of the system is constrained by the kinetic inertia of the solid phases. Also the low water-rock ratio limits the geochemical reactivity of the system, and only negligible amounts of mineral are involved in the precipitation/dissolution processes. Porosity by consequence roughly maintains its initial value even in the vicinity of injection well. In case B the model predicts a slight precipitation of elemental sulphur due to the partial oxidation of the dissolved H_2S into S^0. Pyrite precipitation is bound to chlorite dissolution and occurs in very negligible amounts as the kinetics of these processes are low in respect to the simulation times. Anhydrite, in this redox contest, remains undersaturated and does not precipitate at all.

Preliminary calculations suggest that the increase of the activity of dissolved H_2S in the reservoir enhances the competition between the deposition of elemental sulphur and anhydrite. This effect is likely due to the very high kinetics of anhydrite precipitation which may result in a deviation from thermodynamic equilibrium predictions.

The competition between the precipitation of elemental sulphur and anhydrite is now under further investigation, as it may govern the whole system evolution by common ion effects, constraining the reactivity of the Ca-bearing minerals present in the formation, including carbonates.

References

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