Experimental and numerical modeling of CO_2-water-rock interactions aimed for geological storage in the Denver Basin

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Geological storage of carbon dioxide is one of the most promising solutions for climate change mitigation. CO_2 captured from large stationary sources such as coal fired power plants and refineries can be safely injected and stored in appropriate geological formations, which include mature and depleted oil fields and saline aquifers.

The Hygiene Formation, an Upper Cretaceous member of the Pierre Shales Group (located in the Denver Basin - Colorado, USA), is a potential candidate reservoir for carbon dioxide storage. The Hygiene Formation consists of paralic, medium sized quartzarenitic sandstones with average-low porosity.

Batch experiments were carried out in autoclaves using four samples collected from outcrops of both formations, with time ranging from 7 to 12 days. A synthetic saline solution (14 g/L) was used, based in a representative water sample analysis (data from the NETL National Brine Database). A temperature of 60°C was assumed. Injected CO_2 pressure was set at 100 bar. (Both conditions ensuring a supercritical state for carbon dioxide.)

Geochemical modeling was carried out using the Geochemist's Workbench suite (v.7.0). Mineralogical composition was obtained from petrographic analysis of the samples. Simulations of the kinetics of dissolution and precipitations of the mineral phases (including secondary minerals determined by an equilibrium state calculation) in presence of the saline solution and supercritical CO_2 was carried out for each sample, reproducing the experimental reaction stages: pressurization of the autoclave, reaction period (7-12 days), depressurization and equilibration with room conditions.

Overall, the simulations reproduce the usually observed phenomena in batch experiments - carbonate dissolution and re-precipitation following depressurization of the autoclaves. A good match between experimental and modeled values of initial and final pH values and water species concentrations was also found.

As(III) oxidation in the presence of reduced and oxidized nontronite NAu^{-1} under O_2 and N_2 atmosphere

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The oxidation state of arsenic (As) is a major factor affecting its mobility in soil and aquatic systems. Metal-oxide and clay minerals are effective sorbents for As. Some of these substrates may also facilitate redox reactions on their surfaces through catalysis or direct electron transfer. Iron, which substitutes for Al in the octahedral lattice sites in clays, has the potential to be in variable oxidation states. In soil clays cycling between Fe^{2+}/Fe^{3+} is a common process [1]. The goal for this project was to determine whether structural Fe can affect the oxidation state of As sorbed by clays.

The experimental systems included batch reactors with: (1)As^{3+}aq and nontronite suspension under O_2 atm, (2)As^{3+}aq and reduced nontronite suspension under O_2 and (3)N_2 atm. The equilibration times were 0.5-720 hours at pH 5.5. The oxidation state of arsenic was determined by Liquid Chromatography coupled to an Inductively Coupled Plasma Mass Spectrometer (LC ICP MS).

Contrary to the expected results, reduced nontronite was the most effective oxidant for As^{3+} under O_2 atmosphere (Figure 1); also confirmed by X-Ray Absorption Near Edge Structure (XANES) analysis. The Fenton cycle is the proposed reaction mechanism based on the mass and charge balance. The structural Fe^{2+} acts as a catalyst while dissolved O_2 is the oxidant. The simultaneous adsorption/desorption and oxidation reactions result in the same As^{3+}/As^{5+} aqueous dynamics in all 3 systems: initial fast oxidation of As^{3+} followed by a slow increase of aqueous As^{3+}, likely due to the surface exchange of strongly sorbing As^{5+} for As^{3+} (Figure 1).

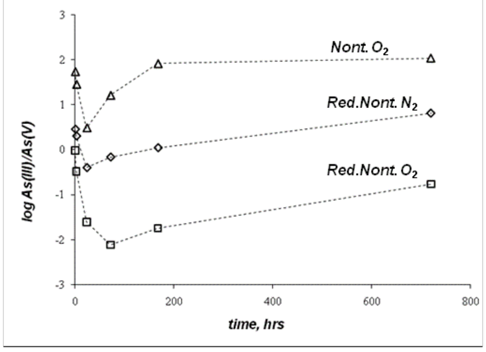

Figure 1.

[1] Stucki (2006) Chapter 8 in *Handbook of Clay Science* (eds Bergaya F., Theng B.K.G. & Lagaly, G.), pp.429–482.