Geologic storage of carbon dioxide: Potential environmental impacts of CO₂-organic interactions

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Sedimentary basins in general and deep saline aquifers in particular are being investigated as possible long-term repositories for large volumes of anthropogenic CO₂ to mitigate global warming and related climate changes. Results obtained from detailed chemical analyses of brine and gas samples from the Frio Brine pilot (Dayton, TX), SEACARB phase III (Cranfield, MS) and other US DOE-funded multilaboratory field tests, show mobilization of DOC, including benzene and other BTEX compounds, phenols, polycyclic aromatic hydrocarbons (PAHs) and other toxic compounds, following CO₂ injection. The DOC values obtained in Frio samples before CO₂ injection were expectedly low (1-5 mg/L), increasing during the CO₂ injection to 5-8 mg/L. A slug of high dissolved organics (DOC values >700 mg/L), however, was observed in samples collected several weeks after injection stopped. The concentrations of organic acid anions, BTEX and PAHs in Frio samples were low (<1 mg/L), but values of formate, acetate, and toluene were higher in high DOC samples. Results obtained to date in brine samples from Tuscaloosa Formation (Cranfield), indicate mobilization and solubility enhancement of organic compounds, in particular the alkylated PAHs, following CO₂ injection for EOR operations. The concern about potential contamination of overlying groundwater by leakage of CO₂ and/or displaced brine is warranted as high concentrations of organic acid anions (<10, 000 mg/L as acetate) and toxic organic compounds, including BTEX (up to 60 mg/L, phenols (<20 mg/L), and PAHs (up to 10 mg/L), have been reported in oilfield waters, and injected supercritical CO₂ is both buoyant and a good solvent for organics.

Citric acid promoted dissolution of phosphated Fe-, Al-, Ca-based binary and ternary mineral mixtures as affected by P solid state speciation: Implications for Phosphate bioavailability

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Phosphorus is an essential plant macronutrient and also a potential water pollutant. Most soils are P deficient because phosphate minerals are sparingly soluble. Citric acid is released by plant roots and microbes in response to P deficiency and is hypothesized to be the main mechanism for solubilising P and ameliorating Al toxicity. Our goal is to investigate citric acid promoted P dissolution in ferrihydriteboehmite, ferrihydrite-calcite, and ferrihydrite-boehmiteapatite mixtures using an integrated wet chemical, spectroscopic (P-K x-ray absorption near edge structure-XANES), and microscopic (transmission electron microscopy) approach. P dissolution and release in acid and alkaline soils is mainly controlled by P sorption to Fe and Al-oxyhydroxide minerals and Fe-oxide and calcite minerals respectively. Ferrihydrite and boehmite are poorly crystalline analogs of Feand Al-oxyhydroxides respectively in soils. The current understanding of organic acid mediated phosphate dissolution is limited by the lack of a molecular scale characterization of its solid state speciation. We hypothesize that citric acid promoted phosphate dissolution in binary and ternary mixtures is controlled by its quantitative distribution between minerals. Previously, we showed using P K-XANES spectroscopy that phosphate distributed itself between ferrihydrite and boehmite essentially in proportion to its maximum sorption capacity on each mineral and more phosphate dissolved from Fe-oxide minerals. We will present results from experiments characterizing citric acid promoted phosphate dissolution in single minerals and mineral-mixtures as a function of pH (4, 6, and 8) and time to understand the role of mineral interactive effects on P dissolution in soils.