

Comparison of the ligand-promoted dissolution of kaolinite and goethite with different organic chelators at pH 6

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The cycling and environmental fate of many elements often involve the bioactivity of the microenvironment. The ability of organic acids to solubilize and complex key elements confer them a major role in the bioavailability of otherwise insoluble nutrients and toxins. The ligand-promoted dissolution of two major soil constituents, goethite and kaolinite, has been investigated in the presence of different organic ligands.

The polysaccharide alginate dissolves only little goethite until a second ligand enters the solution. The addition of oxalate and the siderophore DFO-B, respectively significantly enhances goethite dissolution. This synergistic effect on goethite dissolution in the 2-ligand systems alginate/oxalate and alginate/DFO-B can be explained by a considerable increase in the chemical affinity of the dissolution reaction in the presence of the second ligand (Wolff-Boenisch and Traina, 2007a). For oxalate, the ligand-promoted effect on goethite becomes only noticeable when the amount of goethite and/or oxalate in solution overcomes certain concentration thresholds. As to the siderophores, on an equimolar basis, far-from-equilibrium goethite dissolution rates in the presence of enterobactin are 5 times higher than analogous DFO-B-promoted rates although both chelators show low fractional adsorption <6%. Increased iron solubility and the related shift away from solution equilibrium is a more compelling explanation of the driving force behind goethite dissolution than surface complexation of these siderophores.

In separate systems, DFO-B and oxalate each caused a ligand-promoted dissolution of kaolinite and this rate increase is consistent with a mechanism involving ligand adsorption rather than chemical affinity or aluminum inhibitory effects (Wolff-Boenisch and Traina, 2007b). The concept of ligands competing for the same adsorption sites is corroborated by experiments where DFO-B and oxalate were employed to assess a potential synergistic effect on kaolinite dissolution. However, no such effect was observed. Species calculations as well as experiments indicate that DFO-B was preferentially adsorbed on the kaolinite surface. Further support for this hypothesis comes from the finding that siderophore-promoted dissolution of kaolinite showed the same relationship with aqueous ligand concentration as does the surface coverage: At low aqueous DFO-B concentrations <100 μM , increases in surface coverage and dissolution rates are more pronounced than at aqueous DFO-B concentrations >100 μM , where increase in these parameters is only marginal.

References

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Experimental investigation of the CO₂ sealing efficiency of cap rocks

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Using a combination of experimental, petrophysical and mineralogical methods, transport processes of CO₂ in shales and marls, and its interactions with the mineral phase have been studied. The investigations comprised permeability, gas breakthrough and diffusion experiments under in-situ P/T conditions on cylindrical plugs of 10 - 20 mm thickness and 28.5 mm diameter.

Single phase flow tests with water were conducted to assess permeability coefficients and ensure complete water saturation of sample plugs before each gas breakthrough and diffusion experiment.

Capillary gas breakthrough tests were performed as described by Hildenbrand *et al.* (2002). To test for reproducibility and petrophysical changes due to the interaction of the samples with CO₂, repetitive runs were carried out on the same sample. Series of experiments with Helium and CO₂ under the same conditions have been conducted to compare the transport properties of inert and reactive gases.

CO₂ diffusion experiments were carried out according to the procedure described by Schloemer and Krooss (2004). These tests yielded unexpectedly high CO₂ storage capacities. Significant increases in (water) permeability coefficients were observed after CO₂ diffusion experiments.

Repetitive CO₂ gas breakthrough tests revealed irreversible changes of the petrophysical properties, possibly due to the interaction between the CO₂ and the sample. An increase in (water) permeability was noted after the first CO₂ gas-breakthrough test while permeability remained constant after the follow-up tests.

Mass balance calculations indicated significant CO₂ loss from the gas phase during the first breakthrough tests, whereas subsequent runs did not show any CO₂ loss. This loss of CO₂ from the gas phase is attributed to dissolution, sorption and mineral reactions.

High CO₂ storage capacities were also evidenced by manometric sorption experiments on powdered samples. In order to further clarify this issue, XRD analyses, BET tests, and Hg porosimetry measurements are presently being performed on the original and CO₂-exposed samples.

References

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