Metal cycling in acid geosystems

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CO_2 is injected into geologic formations for long-term storage, to improve production of fossil fuels (enhanced oil and gas recovery as well as shale oil and gas production), and to enhance energy production in geothermal systems. CO_2 injection leads to carbonation and acidification of formation fluids, changing rock-dominated systems to systems dominated by mixed fluid (CO_2 + formation water +/- hydrocarbons) equilibria. The new geochemical regime induces a cycle of mineral dissolution and metal release followed by secondary mineral precipitation and metal scavenging.

Hydrothermal experiments elucidate the dynamics of these cycles within both CO_2-charged reservoirs (sandstones and carbonates) and shale caprocks as well as at the geologic contact between reservoir and caprock. Experiments yield geochemical data (both aqueous and mineralogic) that define real-time reaction pathways and constrain mixed-phase fluid-rock interactions that take place at reservoir conditions. The lithology of the caprock and reservoir and the chemistry of the formation fluid determine the specifics of a particular cycle. Carbonate and silicate minerals in carbonate and sandstone reservoirs as well as shale caprocks are sources for metals; precipitation of secondary clays, oxides, and sulfides provide sinks for these metals. Redox state and pH of the formation water control mechanisms of release and subsequent scavenging. Ba, Co, Cr, Fe, Ni, Pb, V, and Zn are among the metals cycled with reservoirs, caprocks, or both. These soluble metals potentially serve as *in-situ* tracers to identify fluid sources and document fluid mobility within a reservoir and along potential leakage pathways such as faults in caprocks and well bores. More importantly, the longevity of soluble metals within formation waters constrains the timing of mineral dissolution and precipitation relative to injection of CO_2. Coupled with reaction paths that are defined by the evolution of the major ion chemistry of formation waters, the evolutionary trends of these metals serve as indicators of in-situ geochemical processes that influence efficient and secure geological storage of CO_2.