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Geochemistry of subsurface sequestration of bio-oil: Reactions between pyrolysis bio-oil, rocks, and brine

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The efficiency of photosynthetic carbon capture by biomass, the low energy cost and high carbon content of bio-oil derived from its pyrolysis, and the large inventory of potential reservoirs accessible by abandoned oil and gas wells make subsurface bio-oil sequestration a promising option for durable carbon-dioxide removal and storage. At the same time, increasing anthropogenic impacts in the subsurface, as well as distinctive characteristics of bio-oil — including low pH (2-3), high density (~1.2 g/cm3), and complex and diverse organic molecular composition — motivate understanding the mineralogical reactions, phase changes, and elemental partitioning associated with reaction with rocks and resident fluids (e.g., brines) in potential reservoirs.

To address some of these questions we performed mixing experiments between several types of bio-oil, natural brines and lithologies including sandstones, limestone, basalt, granite, as well as less common feedstocks including clays, regolith, tailings, and coal and clinker ash. Results include the following. Bio-oil effectively dissolves calcite in proportions of ~10:1 (bio-oil:calcite), increasing porosity in carbonates and calcite-cemented sandstones. Reaction with rocks and brine results in precipitation of Na, and dissolution of nearly all other elements from the rock. However, dissolution of Si, Al, HFSE, and alkali metals is extremely low. In contrast, in sandstones, Mn losses are 35-80%, and Ca, Sr, REE, and some transition metal (V, Ni) losses are typically 5-25% depending on mineralogy. In all cases observed so far, bio-oil dissociates into a less dense aqueous phase (~60%) miscible with brine, and a denser and high-viscosity, gel-like organic phase (~40%). Both phases are enriched in elements dissolved from the rock, but Ca, Mn, Sr, and in some cases REE, are strongly partitioned into the aqueous phase, while all other elements strongly partition into the organic phase.

Although temperature, pressure, oxidation potential, and microbial conditions will differ and vary in actual subsurface sequestration settings, our preliminary results point to several first-order observations informing considerations for durable and low-risk bio-oil injection. These include the importance of calcite dissolution for porosity/permeability, leaching of Mn and other transition metals, and disassociation of bio-oil into two phases with contrasting compositions, physical properties, and migration potential.