

The Importance of pH, Oxygen, and Bitumen on the Oxidation and Precipitation of Fe(III)-(oxy)hydroxides during Hydraulic Fracturing of Oil/Gas Shales

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Abstract:

Hydraulic fracturing of unconventional hydrocarbon reservoirs is important to the United States energy portfolio. Hydrocarbon production from new wells generally declines rapidly over the initial months of production. One possible reason for the decrease is the mineralization and clogging of microfracture networks proximal to propped fractures. One important but relatively unexplored class of reactions is oxidation of Fe(II) derived from Fe(II)-bearing phases (primarily pyrite, siderite, and Fe bound directly to carbon) and subsequent precipitation of Fe(III)-(oxy)hydroxides. To explore this topic, we reacted synthesized fracture fluid, at 80°C with shale from four different geological localities (Marcellus Fm., Barnett Fm., Eagle Ford Fm., and Green River Fm.). Reaction times for various reactors were set at 3 weeks, 3 months, and 6 months. A variety of wet chemical and synchrotron-based spectroscopic techniques were used to monitor Fe in solution as well as changes to Fe speciation in the solid samples. In all of the above systems, solution pH was the greatest factor for releasing Fe into solution. Solutions in the sand-sized shale reactors containing either Barnett or Marcellus shale showed an initial release of Fe into solution during the first 96 hours of reaction followed by a plateau or significant drop in Fe indicating that mineral precipitation occurred. In reactors with high carbonates, Eagle Ford and Green River, no Fe was detected in solution indicating fast Fe oxidation and precipitation. Bulk EXAFS spectroscopy shows that a significant amount of Fe in the shales is bound directly to organic carbon. Throughout the experimental time inorganic Fe(II)-bearing phases reacted while Fe bound to C showed no indication of reaction. Synchrotron-based x-ray fluorescence mapping coupled with micro x-ray absorption near edge structure spectroscopy showed that when solution is pH < 4.0, Fe(III) bearing phases precipitated as diffuse surface precipitates initially as ferrihydrite, and magnetite, which converts to goethite as experimental time increases. In systems with near circum-neutral pH, the Fe(III)-bearing phases form as large particles 10's of μm 's in diameter near Fe(II) hot spots.

Unlike the low pH systems, as solution pH increases the Fe(III)-bearing precipitates initially as a mixture of ferrihydrite and magnetite converts to highly crystalline hematite as reaction time increases. Idealized systems containing synthesized fracturing fluid and dissolved ferrous chloride showed that bitumen released during reaction with fracturing fluids is able to oxidize Fe(II) to Fe(III) at pH 2.0 and 7.0. The phases of Fe(III) precipitates in these idealized reactors mirrors that of the shale reactors indicating that bitumen can play a large role in Fe oxidation and speciation in the subsurface. This work shows that shale mineralogy has a significant impact on morphology and phase of Fe(III) precipitates in the subsurface.