

The spatial distribution of reactivity as acidic fluid imbibes into shales

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Hydraulic stimulation initiated with HCl solutions, commonly used to extract hydrocarbons from unconventional shale reservoirs, results in a strong disequilibrium between acidic injectate fluids and shales. This disequilibrium leads to rapid mineral dissolution, followed by secondary mineral precipitation and migration of fines. Such chemical reactivity significantly alters the formation's pore structure, impacting the transport of fluids. To better understanding the impact of acidic fluid imbibition into shale, we investigated the temporal and spatial changes in mineralogy and pore structure within a carbonate-poor shale. μ CT and SEM-FIB images of reacted shale revealed important and rapid increases in porosity that were largely driven by short timescale dissolution of carbonates, such as calcite. Such dissolution opened new porosity in the existing pore network. Because the calcite dissolution quickly neutralizes the acidity of fluids penetrating the reservoir, it could control the spatial distribution of physicochemical reactivity.

Upon this basis we designed a set of experiments to evaluate the impact of rapid calcite solubilization on matrix geochemical reactivity and pore space alteration concomitant with imbibition. We tracked acidic fluid transport in shales by monitoring the rate and spatial extent of bromide tracer transport using synchrotron X-ray fluorescence, while simultaneously imaging the spatial profiles of calcium as a proxy of calcite. We showed that although the reaction of the acidic fluids with carbonate minerals in shales enhances calcite dissolution and increases porosity, the spatial extent of calcite dissolution in the shale matrix is limited due to a rapid neutralization of pH. Consequently, increased calcite content in the shale matrix inhibits the spatial extent of the pore-volume increase and, by extension, the spatial extent and rate of imbibition.

Of the various controls on reactivity, calcite content most significantly and rapidly contributes to the evolution of fluid chemistry. Rapid neutralization of acidic fluids as a function of the abundance of calcite governs the spatial extent and volume of chemically reacted regions, the potential erodability of the fracture surface, and the location and overall amounts of secondary minerals, moderating porosity and permeability of the shale matrix.