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Laboratory investigations of geochemical evolution in unconventional reservoirs during hydraulic stimulation

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Hydraulic fracturing fluids (HFF's) have been used for several decades to control mechanical, hydraulic, and geochemical behavior in unconventional reservoirs during stimulation. The interactions that occur in these environments during stimulation (hydrofracturing) are designed to prevent scaling, improve production, and prevent damage to formations. However, there is still uncertainty with regards to near fracture geochemical reactions and the evolution of the fluids temporally as they interact with the reservoir rock¹.

Rock cores taken from the Marcellus shale, both in outcrop and from a production well, were exposed to simulated HFF's and simulated formation brines (SFB). The fluids were designed based on regional averages obtained from operators. The tests were conducted at pressures and temperatures representative of regional reservoir conditions, 19.3 MPa and 71°C respectively, and with all fluids under a nitrogen atmosphere to limit free oxygen. Core samples were fractured and loaded with 40/70 US Silica White™ quartz proppant. Tests lasted approximately 96 hours with low flow rates to represent a shut-in period. Geochemical samples were taken daily and analyzed using Inductively Coupled Plasma Mass Spectrometry and Ion-Chromatography. Imaging of the cores was done before exposure using Computed Tomography (CT) scanning and after exposure using CT, Scanning Electron Microscopy (SEM), and Raman Spectrometry.

Control samples, using deionized water as the flow medium, exhibited little to no change in the rock core or in the effluent of the system, dominated by Ca and SO₄. Experiments using only SFB showed minor increases in major elemental chemistry in the effluent, consistent with minor dissolution or entrainment of free particles, and minor precipitation of barite/calcite on the fracture surface observed with SEM. HFF chemicals, without SFB, resulted in increases in most elemental constituents in the effluent, with few exceptions including barium which showed an increase followed by a major decrease in concentration. The rock core exhibited significant reaction in CT images and only minor traces of barite/calcite precipitation. The combination of HFF and SFB resulted in large increases in most metal constituents in the effluent during the reaction with the core and significant alteration of the rock matrix adjacent to the fracture. However, this mixture resulted a continual decrease in Ba and SO₄ during the experiment, signaling potential deposition of these constituents.

In general, experiments indicated minor pyrite oxidation/dissolution, dissolution of carbonates, and minor precipitation of barite. The degree of precipitation was not of the magnitude observed in Paukert et al. (2017), but there is evidence that carrier fluid composition (>90% of the total volume) is an important consideration in precipitation within unconventional systems and may provide the nucleation surfaces for precipitation. Work continues analyzing precipitates, fracture surfaces, and base-fluid importance in precipitation.

References

A. N. Paukert Vankeuren, J. A. Hakala, K. Jarvis, and J. E. Moore, "Mineral Reactions in Shale Gas Reservoirs: Barite Scale Formation from Reusing Produced Water As Hydraulic Fracturing Fluid," *Environ. Sci. Technol.*, vol. 51, no. 16, pp. 9391–9402, (2017).

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