Impact of Carbonate Dissolution on Arsenic Release during Shale Gas Extraction

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Shale gas flowback and produced waters are often highly saline and may contain elevated levels of trace toxic metals and naturally occuring radionuclides. Treatment and proper management of these waste fluids will benefit from improved understanding of how hydrualic fracturing fluid components may promote contaminant leaching from the shale reservoirs. Hydraulic fracturing fluids commonly contain strong acids in addition to other chemical additives that help enhance reservoir production. Previous sequential extraction studies have demonstrated that most of the trace elements including radionuclides and ~90% of total arsenic are present in reduced mineral phases. The addition of acids and oxidizers to fracturing fluids can thereby contribute to the release of these trace metals and radionuclides.

Two core flooding experiments of synthetic hydraulic fracturing fluids through proppant-packed fractured shale cores were conducted under reservoir temperature and pressure conditions. Substantial carbonate mineral dissolution occurred along the fracture pathway and the rate of arsenic release increased over time. The role of non-uniform carbonate mineral dissolution in altering flow along the fractures and in controlling dissolution of more recalcitrant phases (*e.g.*, arsenopyrite) was investigated by a combination of X-ray computed tomography and scanning electron microscopy (SEM). Post-reaction SEM analysis demonstrated the co-occurance of calcite-depleted regions and exposed pyrite at the fracture face. These observations indicate that erosion of calcite by the acidic fracturing fluids increased the surface area of other less soluble minerals exposed to the oxic influent fluids. This combination of acid-driven and oxidative dissolution processes enhanced the rate of arsenic leaching from the fractured shale. Future work will seek to quantify the expected increase in surface area of pyrite framboids in carbonate-rich shales exposed to acidic fracturing fluids and estimate effective pyrite dissoltuion rates, and subsequent arsenic release, during hydraulic fracturing completions.