Isotopic signature of calcium and sulfur partitioning during biostimulation: experiments and simulations

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Stable isotope fractionations of key species in the bioreduction process provide information complementary but distinct from traditional concentration measurements. Detection and modeling of such enrichments therefore provide novel constraints on the rates, progress and secondary mineralization processes associated with *in situ* biostimulation. At the field scale, as with variations in major and trace ion concentrations, stable isotope fractionations are typically subject to reactive path lengths less than the distance between the injection and first row of monitoring wells. Incorporation of stable isotope fractionations into biogeochemical reactive transport models has thus required development of intermediate or meso-scale column studies designed to operate as direct analogs to field conditions with the added benefit of sub-20 cm fluid sampling resolution. This combination of field and laboratory datasets has supported adaptation of the CrunchFlow reactive transport model to accommodate both sulfur and calcium isotope fractionations.

At the Rifle field site, sulfur isotope fractionation has been used to constrain the onset of sulfate reducing conditions. This technique has been applied to multiple years of electron donor amendment in a single well gallery resulting in a previously undocumented trend towards earlier onset of sulfate reduction in subsequent years. In clogged injection wells at the Rifle site, a large enrichment in the stable isotope ratio of aqueous calcium has been documented in association with carbonate precipitation providing a potentially new means of quantifying secondary mineral precipitation rates. In the laboratory, datasets generated from meso-scale column studies indicate sulfur isotope fractionation is only adequately modeled when the dual Monod equation is used to accommodate the rare isotope through the transition from a zero to first order reduction rate. With sulfur isotope fractionation implemented in the CrunchFlow code, a field scale model is developed which reproduces the observed temporal shifts in $\delta^{34}S$ and sulfide as a function of the population density and distribution of sulfate reducing bacteria. Calcium isotopes show a complex relationship between calcite precipitation (enrichment) and ion exchange (mixing) leading to a ~50 cm zone down-gradient of the electron donor source in which the fractionation serves as a novel constraint on both rate and exchange coefficients.

Based on the field and laboratory datasets generated thus far, we are now adequately prepared to develop a reactive transport model at the field scale that fully incorporates the fractionations of sulfur and calcium as independent parameters. This development will yield new constraints on the timing, rates, and pathways of contaminant remediation.