Diagnosing Reduction Capacity at ISCR Sites and Pre-Screening of Reductant Demand

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Background/Objectives. In situ chemical reduction (ISCR) involves adjustment of aquifer redox conditions to favor abiotic degradation pathways, usually by adding chemical reductants. In addition to creating conditions with sufficiently reducing *potential* to make contaminant reduction thermodynamically favorable, the quantity of reductant must be sufficient to degrade the total mass of contaminants to target end points (i.e., the reductant *capacity* criteria must be met). Meeting these potential and capacity criteria for contaminants is not enough for field applications because site materials contain other oxidizing agents (e.g., organic matter, minerals, co-contaminants) that contribute additional *demand* for the reductant. This makes it necessary to consider the overall reductant demand when determining the reductant dose (Reductant Demand + Reductant Capacity) at a site. The goal of this work is to develop a framework for characterizing the reductant capacity of ISCR site materials, including development of a technique for estimating reductant demand prior to in situ emplacement of reductant.

Approach/Activities. ZVI soil mixing was selected to evaluate our approach, in part because most soil mixing is operated in a similar mode. The reductant capacity ~5 years after mixing was estimated by determining the remaining zero-valent iron content using hydrogen gas evolution at pH 0. Similarly, the remaining reactivity was estimated by hydrogen evolution at pH 7. Knowing that the geochemical conditions within the mixing zones are similar, a set of column experiments were designed to determine the reductant demand of the natural subsurface materials. This was accomplished by adding a reduced dye (dihydroindigodisulfonate, DI2S) to the soil and tracking the oxidation of the DI2S using a spectrophotometric determination. When oxidation of the dye ceases, the electron equivalents for the oxidizing materials in the soil can be determined based on the amount of dye oxidized. This provides an operational estimate of the natural reductant demand for the media that can then be applied for any chemical reductant. (This process is analogous to determination of oxidant demand using a chemical like permanganate.)

Results/Lessons Learned. Two ZVI soil mixing sites are discussed here. Both received 1 to 2% wt ZVI material and intended to treat source zone concentrations of chlorinated solvents. However, due to site specific conditions prior to emplacement (most importantly oxidizing mineral phases, DO), the reductant capacity remaining at the sites suggests that at one site ZVI remains, and at the other the natural reductant demand has exceeded the ZVI dose. The protocol used in this study to assess both sites, can be utilized to diagnose natural reductant demand a priori of ISCR installation at future soil mixing sites providing a valuable tool for practitioners.