In Situ Chemical Reduction (ISCR): The Role of Reactive Mineral Intermediate Phases and Sulfidation

Paul G. Tratnyek (tratnyek@ohsu.edu), Richard L. Johnson, Chris Kocur, and Ying Lan
(Oregon Health & Science University, Portland, OR, USA)

Background/Objectives. Contaminant degradation by reduction reactions that are—more or less—abiotic has been well documented in the academic literature since at least the 1980s, but evidence that in situ abiotic reduction contributes significantly to natural attenuation was lacking. Recent studies, however, have demonstrated that there can be an abiotic component to natural attenuation, even for relatively recalcitrant contaminants like trichloroethylene. Interest in abiotic natural attenuation (ANA), together with the proliferation of remediation technologies based on strong chemical reductants like zerovalent iron (ZVI), has led to the emergence of a general class of groundwater treatment processes known as in situ chemical reduction (ISCR).

Approach/Activities. As the field of ISCR matures, it is developing "core concepts" that link fundamental understanding of the controlling processes to technology performance in the field. We have been working to identify and develop these core concepts, in recent presentations and publications. Perhaps the best example of this is "reductant demand", which is easily understood as the ISCR analog to the "oxidant demand" that is a key concept for in situ chemical oxidation (ISCO). However, reductant demand often is not explicitly addressed in ISCR applications, in part because there is not yet any standard method for its determination.

More recently, we have focused mainly on another emerging concept: sulfidation. In general, sulfidation is the modification or transformation of any metal-based material by exposure to sulfur, but in the context of ISCR it refers mainly to the formation of iron sulfide on iron metal or oxides. Sulfidation has been shown to increase rates of some contaminant reduction reactions, but the most important effect may be the decrease in reduction of water to hydrogen. We have developed a model for the formation of hydrogen from ZVI, which explains almost all of the available data, and postulates a reactive mineral intermediate (RMI) phase with properties similar to ferrous hydroxide. Additional evidence for the importance of RMI phases in abiotic reduction processes will be presented from on-going laboratory column studies.

Results/Lessons Learned. Multiple lines of evidence suggest that RMI phases play a greater role in ISCR than previously recognized. In so far as they are transient species, they are analogous to the reactive species that mediate ISCO processes. This analogy may help explain some of the challenging aspects of ISCR, such as the usually poor correlations between abiotic reduction rates and measured redox potentials.