

Oxidation of Chemically-Reduced Aquifer Sediments as Characterized by Abiotic Reactivity and Induced Polarization

Jim E. Szecsody (jim.szecsody@pnnl.gov), Tim C Johnson, Paul Tratnyek*,
Edmundo Placencia-Gomez, Miranda Bradley*, Mike J. Truex, C. Tom Resch, and
Brandy N. Gartman
(Pacific Northwest National Laboratory, Richland, WA, USA)
*(Oregon Health and Science University, Portland, OR, USA)

Background/Objectives. This project is focused on predicting abiotic transformation of contaminants over time in groundwater aquifers modified by reducing technologies using geophysical methods (electrical resistivity and induced polarization tomography, ERT/IP). Although abiotic/biotic technologies have shown good success in initially degrading/mineralizing energetics, in many cases degradation rates are not sustained over time. Prediction of long-term reactivity requires characterization of the spatial distribution (and temporal changes) of reduced phases, which is challenging at field scale because of the limited number of wells to address spatial variability. If ERT/IP could identify partially oxidized zones in a reduced permeable reactive barrier, targeted re-reduction could be used to efficiently maintain long-term reactivity. In this project, the fundamental relationships between the iron mineral phases, contaminant reactivity, and complex conductivity (ERT/IP) are quantified at multiple laboratory scales for four in situ reduction technologies.

Approach/Activities. The fundamental relationships between sediment iron mineral phases, the resulting abiotic reactivity (i.e., contaminant degradation rates) and time-lapse ERT/IP responses are initially established in 1-D and 2-D laboratory experiments, which will then be tested at field scale. The in situ reduction technologies that are tested include reduction by nanoscale zero-valent iron (nZVI), Ca-polysulfide, Na-dithionite, and bioreduction. Abiotic reactivity is measured by the chromate, nitrate, and RDX reduction rate. Sequential iron extractions, surface area, chemical oxygen demand, benchtop impedance spectroscopy, and ERT/IP measurements were used to characterize sediment iron phase changes. These geochemical-geophysical comparisons were done with idealized porous media (i.e., silica with additions of ferrous iron or FeS or reductive treatments) and with real aquifer sediments that received different reductive treatment.

Results/Lessons Learned. Laboratory results show that strong correlations between redox reactivity and the out-of-phase complex conductivity measured by spectral induced polarization (SIP) for sediments that were abiotically reduced with Na-dithionite or Ca-polysulfide or bioreduced. During sediment reduction, the higher frequency (10 to 1000 Hz) conductivity and phase response is the greatest, which may reflect formation of small precipitates. Specifically, FeS (mackinawite) precipitation acts as a capacitor. A significant change in capacitance (or chargeability) during sediment reduction by Na-dithionite may reflect initial precipitation of an amorphous phase, which later becomes more crystalline. Redox reactivity in sediments that received different treatments have one or more reduced iron phases (e.g., adsorbed ferrous iron and FeS precipitate), and there is some ability to quantify adsorbed ferrous iron from iron precipitate phases due to a diagnostic IP-effect caused by each phase. During subsequent sediment oxidation, there is a shift in conductivity and phase to lower frequency, which correlated well with a decreasing contaminant degradation rate. At field scale, frequencies that can be used are in the 0.01 to 100 Hz range, and phase changes greater than 0.2 mrad can be quantified. Therefore, these laboratory-derived correlations between ferrous iron phases, contaminant reduction rate, and ERT/IP response may provide the basis to predict reduction reactivity over time using ERT/IP monitoring in the field.