



Project Title: “Monitoring Oxidation-Reduction Processes in Subsurface Systems”

Investigator: Richard Wilkin (U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory, GWERD, Ada, OK 74820; 580-436-8874)

Collaborators: Robert Ford, Chunming Su, John Wilson (U.S. EPA)

Background: The oxidation state of metal contaminants often determines chemical and biological behavior, such as toxicity, reactivity, and mobility in the environment. Thus, accurate field monitoring of oxidation-reduction processes, both in the aqueous phase and the solid phase, is fundamental to characterizing the geochemistry, microbiology, and fate of inorganic and organic contaminants in ground water systems. Redox characterization is virtually always a key aspect of remedial investigations, including the selection and performance assessment of applied remedial technologies, such as Monitored Natural Attenuation, Permeable Reactive Barriers, In-situ Reactive Zones, and Enhanced Anaerobic Bioremediation.

Objectives: The overall goal of this project is to develop recommendations and guidelines for evaluating redox processes in contaminated ground water, sediment, and soil systems. One objective is to evaluate existing methodologies (iodometric, colorimetric, electrode) for determining dissolved oxygen concentrations, and document appropriate field practices for carrying out accurate and repeatable dissolved oxygen (DO) measurements. A second goal is to evaluate, by using a platinum electrode, the extent of equilibration between reduced sulfur species (H_2S , HS^-) and partially oxidized (S^0 , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-}) forms of dissolved sulfur. These aqueous species are common products of anaerobic bioremediation in contaminated ground water systems; however, their distributions are governed by a mixture of incompletely understood inorganic and organic geochemical processes. Studies are also on-going that evaluate methods for determining the speciation of sulfur and carbon in aquifer materials and soils. This work is being carried out to provide characterization tools to identify and quantify the quantities of reactive minerals in aquifers systems that may contribute to the natural attenuation of organic and inorganic contaminants.

Approach: The research approach involves laboratory experimentation and detailed analysis using a variety of wet-chemical and solid-phase characterization techniques.

Accomplishments:

Wilkin, R.T., McNeil, M.S., Adair, C.J., and Wilson, J.T. (2001). Field measurement of dissolved oxygen: A comparison of methods. *Ground Water Monitoring and Remediation*, Fall, v. 21, 124-132.

Wilkin, R.T., Ludwig, R. D., and Ford, R. G., eds. (2002). Monitoring Oxidation-Reduction Processes for Ground Water Restoration: A Workshop Summary, EPA Report, EPA/600/R-02/002.

Smieja, J. and Wilkin, R.T. (2003). Preservation of As(III) in sulfidic waters. *Journal of Environmental Monitoring*, v. 5, 913-916.

Wilkin, R.T. (2003). Reactive minerals in aquifers: Formation processes and quantitative analysis, In *Air Force Center for Environmental Excellence Technology Transfer Workshop* (San Antonio, TX).