The fate and transport of heavy metals and radionuclides in subsurface environments is closely tied to the biogeochemical cycling of the major elements, particularly the redox cycling of C, Fe, and S. By definition, redox transformations entail the transfer of electrons between chemical species, and the inherent complexity of natural systems creates a network of pathways for electron transfer that intimately couple the C, Fe, and S cycles. Understanding these complex systems requires a fundamental understanding of the highly coupled biotic and abiotic processes that drive the biogeochemical cycling of C, Fe, and S in subsurface environments.
Fe-S-C-U coupling in reducing environments

DIR Bacteria
Oxidized products
Fe\(^{2+}\)

e\(^-\) donor
organic C, H\(_2\)

Oxidized products
FeS, FeS\(_2\)
insoluble

Fe\(^{3+}\)
insoluble or complexed

Fe\(^{2+}\), magnetite, green rust, reduced clays, siderite, vivianite

DIR Bacteria

Oxidized
Fe\(^{2+}\)

U\(^{6+}\) (soluble)

U\(^{4+}\) (less soluble)

Reduced

U\(^{6+}\)

U\(^{4+}\)

DSR Bacteria

e\(^-\) donor
organic C, H\(_2\)

Oxidized products

SO\(_4^{2-}\) (S\(^{6+}\))
soluble

HS\(^-\) (S\(^{2-}\))
aqueous

Warthmann et al., *Extremophiles* 9 (2005), 255

Image courtesy of Ken Bart at Hamilton College
From an engineering perspective, various treatment/control strategies are considered for managing subsurface contamination, including intrinsic bioremediation and biostimulation implemented as in situ permeable reactive barriers (PRBs). Intrinsic bioremediation (a key component of natural attenuation) relies on the biological processes of indigenous microbial populations to control the fate and transport of contaminants of concern. However, when the background activity of indigenous microorganisms is insufficient to provide the desired level of attenuation, biostimulation may improve results. In the biostimulation treatment approach, amendments (typically limiting nutrients such as C, N, and phosphate) are introduced into the subsurface to stimulate the activity of specific populations within the native microbial community and create conditions conducive to desired contaminant transformations. For many contaminants (e.g. Cr, U, Hg, or chlorinated solvents), this means creating or maintaining Fe- or sulfate-reducing conditions by stimulating the activity of indigenous Dissimilatory Iron Reducing (DIR) or Dissimilatory Sulfate Reducing (DSR) microbes. Abiotic methods for reductive remediation are also considered and implemented, such as zero-valent iron (ZVI) permeable reactive barriers.

Regardless of whether the goal is the development of efficient remediation technology or the refinement of models describing the transport of contaminant plumes,
limited information is available on the mechanisms of contaminant-mineral and contaminant-bacteria interactions. The availability of molecular-scale mechanistic information can provide direction for remediation technology development, as well as improve the reaction networks in reactive transport models, thus increasing their predictive value. To this end, the Laboratory of Transfer Processes in Multiphase Media is conducting laboratory- and synchrotron-based experiments to investigate coupled transformations of biotic and abiotic contaminants, with a focus on biologically driven Fe- and sulfate-reducing conditions, over a range of spatial scales. Research involves laboratory-based experimention with mixed-batch reactors and columns with single-crystalline-phase Fe oxides (including oxides, oxyhydroxides, and hydroxides), fabricated Fe-rich mineral assemblies mimicking field mineralogical conditions, and geomaterial collected from field sites. Microbial species used as inocula for promoting Fe-reducing and sulfate-reducing conditions include monocultures of DIRB (e.g., Geobacter spp., Anaeromyxobacter spp.) and DSRB (e.g., Desulfovibrio spp.). Characterization methods include standard laboratory methods, as well as taking samples to synchrotron x-ray sources for characterization of the solids by X-ray Absorption Spectroscopy (XAS).

Synchrotron-based XAS is a nondestructive, noninvasive method that can probe the interactions between metal or radionuclide contaminants and geo- and biomaterials. XAS can provide molecular-level, element-specific, chemical and structural information on a given element. The two XAS techniques — x ray absorption near-edge structure (XANES) and extended x ray absorption fine structure (EXAFS) spectroscopy are particularly valuable for studying dilute (with contaminant concentrations as low as 100 ppm), multielement, and disordered systems. Because every element has its own absorption edges corresponding to the unique binding energies of its electrons, individual elements in a multielement system can be studied. The XANES technique provides an in situ probe of an element’s oxidation state and can contribute significantly to understanding the fate of an element in the environment, in both solid and aqueous phases. The EXAFS technique provides information on the local chemical environment of the element of interest. The Fourier transform of EXAFS data separates the signals from the shells of atoms around the atom whose absorption edge is being measured on the basis of distance from that atom (similar to a radial distribution function). The amplitude of the signal is related to the neighboring atom type and the number of neighboring atoms. Analysis of EXAFS spectra can be used to differentiate between aqueous, surface-absorbed, co-precipitated, and precipitated species.
**XAFS = XANES + EXAFS**

**Fourier transform**

**X-ray Absorption Fine Structure spectroscopy**

**Publications:**

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