Arsenic Chronospeciation in a Biostimulated Aquifer

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The Deparment of Energy (DOE) monitors numerous former mill sites where bioremediation represents a potential approach for addressing groundwater contamination by uranium (U) and other aqueous metals. Bioremediation studies at DOE's Rifle, CO (USA) site have explored conversion of soluble U(VI) to insoluble U(IV) through organic carbon (acetate) addition, with work repeatedly demonstrating the ability to lower groundwater U concentrations through stimulation of iron and sulfate reducing bacteria. Ores milled at Rifle were enriched in numerous redox sensitive metals including arsenic (As), with ferric oxides present in sediments acting as strong sorbents for arsenate (As(V)). Pathways accompanying bioreduction of U can result in reductive dissolution of oxide sorbents and hence release of As(V) to groundwater.

Such As releases have been repeatedly observed at Rifle during acetate injection, with the increases most pronounced when sulfate reduction is the primary form of metabolism. Although dissolution of sorbents is expected to account for some fraction of the increases, the close correspondence between elevated As and sulfidic conditions warranted analyis to assess the contribution of thiolated forms. To assess this possibility, speciation studies are being used to characterize As species present during various stages of the bioremediation process ('chronospeciation').

Using ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS), As species are determined by comparison with retention times of prepared standards including arsenite, arsenate, mono-, di-, tri-, and tetra-thioarsenate. Groundwater samples obtained during sulfidic conditions when As concentration exhibited a 5-fold increase above pre-acetate injection values showed predominance of thioarsenic species, with di- and tri-thioarsenates the most abundant. The change in the coordination environment of the thiolated forms relative to those of arsenate or arsenite may explain the abrupt increase in groundwater As, as desorption from oxide surfaces is enhanced following exchange of As-O for As-S bonds occurs. Evaluation of U bioremediation success must therefore take into consideration the possibility of creating redox conditions favorable for the release of secondary contaminants.