

Microscopic Evidence of U Association with Fe-Minerals (Pyrite and Magnetite-Like Phases) in Naturally Bioreduced Sediment Cores Obtained from a U-Contaminated Aquifer

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The shallow, unconfined aquifer of a U.S. Department of Energy's (DOE) Uranium Mill Tailings Remedial Action (UMTRA) site at Rifle, Colorado (a former U ore processing site) has residual U concentration above the EPA's drinking water maximum contaminant level (0.13 mM or 0.03 ppm). Field-scale research is funded by DOE's Environmental Remediation Science Program (ERSP) program to address microbiological, geochemical, and hydrological process controlling U mobility at this Integrated Field-Scale Subsurface Research Challenge Site (IFRC). As part of initial geochemical task of the project several sediment cores were obtained during a drilling campaign (June 2007) at various depths (down to 20-feet below the ground surface), preserved anoxically, and analyzed by various spectroscopic and microscopic techniques to gain insights into determine the role of redox-sensitive Fe-bearing minerals on soluble U(VI) attenuation (sorption and reduction). U(VI) is highly soluble and readily transports in groundwater or is sorbed to surfaces of minerals depending up on groundwater conditions, unlike U(IV) which exists as solid UO_2 or sorbed U on surfaces of minerals.

^{57}Fe -Mössbauer spectroscopy (technique unique to ^{57}Fe -nuclide) and microscopic techniques were undertaken on a selected sample (<53-micron fraction from a naturally bioreduced zone) since powder XRD didn't detect Fe-oxide(s) nor Fe-sulfides, or U-containing phases because of detection limits. Mössbauer study showed the presence of Fe-oxides (goethite, hematite, and magnetite) and Fe-containing clays unambiguously unlike Fe-sulfides (e.g., pyrite [FeS_2], and mackinawite [FeS]) since their peaks were not resolved from Fe-clay features. U contents were around 5×10^{-8} mol/g, based on a chemical extraction method.

Spatial analysis of the sediment samples by microscopic techniques proved valuable. Pyrite, which was not evident from both XRD or Mössbauer techniques and a known U sorbent, was "abundant" (~ 1 wt.%) and existed mostly as framboidal (spherical clusters of equimorphic and equidimensional microcrystals of varying packing densities) aggregates. U presence on the surfaces of framboidal pyrite (that existed up to 30-micron with microcrystals of up to 1 micron) was detectable by EMPA-WDS technique, up to 120 ppm. The extent of U sorption on the pyrites appears to be related to weathered state of the mineral and nature of aggregation. TEM of FIBed thin-sections indicated pyrite microcrystals to be single-crystal in nature and a variation in chemical composition between rim and bulk of the crystal. Further studies, e.g., micro-XAS and high resolution TEM analysis with spot-sizes of 100-nm are being planned to analyze the surface state of pyrites. U association with magnetite-like phase was also evident from EMPA analysis (up to 200 ppm). Further more, polycrystalline nature of the magnetite-like particle was evident

from selected area electron diffraction (SAED) of a thin section excavated from a “large” (~20-micron) particle by FIB technique.

The use of microscopic techniques to identify various Fe-minerals and their association was a significant contribution to the project. We believe this is the first time U was found to be associated with framboidal pyrite and magnetite-like phases at a DOE contaminated site. However, the role of framboidal pyrite and magnetite-like phases in attenuation of U in natural aquifers is not yet well understood. In addition, some questions remain, for example origin of the Fe-minerals and U association (abiotic or biotic?) and their role in U(VI) sorption and reduction. Further characterization, for example, cryo-SEM and -TEM, may be necessary to characterize microbe-mineral interactions.

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