Doctoral Defense

“Investigating the Role of Iron Sulfide on the Long-Term Stability of Reduced Uranium under Oxic Groundwater Conditions”

Yuqiang Bi

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Chair: Kim F. Hayes
Professor, Civil & Environmental Engineering

The historical accumulation and improper disposal of radioactive waste from extensive extraction and processing activities have caused widespread uranium contamination of groundwater and soils in the United States. Because uranium is a toxic heavy metal and radiological hazard, its migration poses serious human health and ecological risk. While successful remediation has been practiced at selected uranium contaminated sites, recent concerns have been raised over maintaining the long-term immobilization of reduced uranium solids in the subsurface when oxidants re-enter the reducing zone. Previous studies reported that iron sulfide minerals formed during bioreduction may retard UO$_2$ reoxidation by consuming dissolved oxygen, yet limited mechanistic information is available detailing the thermodynamic and kinetic constraints that control UO$_2$ oxidative dissolution in the presence of iron sulfide in groundwater.

This research aims at understanding the role of iron sulfide in affecting the stability of uraninite (UO$_2$(s)) under oxic groundwater conditions. Synthetic nano-particulate mackinawite (FeS) and uraninite solids were prepared to simulate the reduced precipitates in groundwater systems dominated by sulfate reducing conditions. Completely mixed batch and flow-through reactor experiments were conducted to investigate UO$_2$ oxidative dissolution rate in artificial groundwater as a function of pH, FeS content, and carbonate and oxygen concentrations. FeS and UO$_2$ oxidation products were characterized by various analytical techniques to examine reaction pathways and rate-controlling mechanisms during oxidation.

This research demonstrates that FeS serves as an effective oxygen scavenger and inhibits UO$_2$ oxidative dissolution. The dissolution rate of UO$_2$ in the presence of FeS is over one order of magnitude lower than those in the absence of FeS. The preferential reaction of FeS with oxygen leads to surface-oxidation limited dissolution of UO$_2$, which is facilitated by a fast detachment of ternary Ca-U(VI)-CO$_3$ complexes. When FeS content significantly diminishes, increasing oxygen concentration may passivate UO$_2$ surface by forming a less reactive U(VI) layer. However, dissolved calcium and carbonate can reduce the formation of passivation layer by promoting soluble U(VI) release rate from UO$_2$ surface. The results contribute to the understanding of uranium fate and transport in the presence of iron sulfide during periods of persistent oxygen intrusion in heterogeneous groundwater systems.