Abstract of the dissertation

The Immobilization of Molybdenum in the Presence of zero valent iron:

The Role of Reductive Precipitation versus Adsorption

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Anthropogenic release of molybdenum (Mo) into the environment poses a potential health and ecological risk. Major sources of anthropogenic Mo releases are from mining and milling sites where other elements of concern such as uranium (U) may also be released. Mo may be removed concurrently with U from contaminated groundwater by zero valent (elemental) iron (Fe0) permeable reactive barriers (PRB). Knowledge of the sequestered form of Mo in Fe0 PRBs is critical if this *in situ* technology is to be a viable passive solution for remediation of Mo-contaminated groundwater. Sequestered Mo must be in a non-labile form in order for it to no longer be a threat to the environment. The form of Mo was investigated in solids recovered from a Fe0 PRB designed to remove Mo and U from contaminated groundwater that leached from unlined U mill tailings ponds. Historic groundwater trends indicated effective Mo sequestration under both oxidizing and reducing conditions within the Fe0 zone. Geochemical models predicted sequestration mechanisms to be reductive precipitation as molybdenite and weak adsorption of molybdate (MoO42-) to Fe oxyhydroxides. To identify the form of Mo, the recovered barrier solids (RBS) were analyzed by X-ray fluorescence, X-ray diffraction and a scanning electron microscope equipped with energy dispersive X-ray spectroscopy. Crystalline formations were observed in thin section polished slides with optical light microscopy. A sequential leaching procedure was performed on the RBS, extracting loosely held Mo with alkaline solution and extracting Mo-bearing minerals with acid-oxidizing reagents. The majority of the sequestered Mo in RBS was in a reduced valence mineral form, molybdenite and/or molybdenum dioxide. Some Mo was loosely held to Fe oxyhydroxides. Geochemical models suggested the loosely held Mo was adsorbed to goethite, which was the XRD identified Fe oxyhydroxide in the RBS. Reductive precipitation of MoO42- to Mo(IV)-bearing minerals is the preferred sequestration mechanism since adsorbed Mo may desorb should groundwater conditions change. Fe0 PRBs need to be designed to sustain strong reducing conditions and permeability over many years in order to insure long-term sequestration of Mo and thereby effectively treat Mo-contaminated groundwater.