Uranium Sequestration with pH Manipulation by Ammonia Gas

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Injection of reactive gases such as NH_3 represents a novel method to decrease U mobility in the vadose zone via creation of alkaline pore water conditions. The injection of this highly soluble, weak base can significantly alter the pore water chemistry due to release of cations from mineral phases followed by co-precipitation of new U and non-U mineral phases as NH_3 gas dissipates. However, there is a lack of understanding of the potential phases forming and controlling U behavior in this system. Batch experiments were utilized to examine the effect of aqueous Ca^{2+}, Al^{3+}, Si, and HCO_3^- on removal of U in synthetic pore water solutions as well as the impact of sediments and mineral phases.

Our results with synthetic pore waters show that precipitation is always correlated with aqueous removal of U(VI), Si, Al with little effect from variable HCO_3^- concentrations (Katsenovich *et al.*, 2018). At elevated U (aq) concentration, SEM-EDS correlated U with Si in solids and speciation modeling predicts the formation of uranyl silicate phases like boltwoodite. However, at lower concentrations of U, co-precipitation processes are expected to play a role in U removal especially as porewaters will be saturated with respect to carbonate minerals like calcite at elevated pH. XRD also confirms formation of uranyl carbonate phases.

For experiments in the presence of aluminosilicate minerals, dissolution following gas injection is incongruent and secondary precipitate formation was identified by SEM prior to dissipation of NH_3 gas (Emerson, *et al*., 2017). U was immobilized in the solid phase with a significant reduced fraction as shown by XANES. Moreover, U partitioning coefficients increase by more than two orders of magnitude at elevated pH with minimal release following aeration. These results highlight that NH_3 gas injection may effectively immobilize U through complex co-precipitation with aluminosilicate and carbonate minerals as well as reduction.

[1] Katsenovich, et al. (2018) *Appl Geochem* 92, 94-103.
[2] Emerson et al. (2017) *J Environ Rad* 167, 150-159.