

# Plutonium (VI) and Uranium (VI) Reduction by Iron (II) at High pH under Subsurface Conditions

Jean Francois Lucchini, Hnin Khaing, Michael K. Richmann, Marian Borkowski, Donald T. Reed

Los Alamos National Laboratory, Earth and Environmental Sciences Division, Carlsbad, NM 88220, USA

## ABSTRACT

Reduced iron species, that are present in and/or generated from the steel canisters used in waste disposal, are expected to help generate and maintain a reducing environment in an underground nuclear waste repository. Radionuclides, in this context, are maintained in less soluble and therefore less mobile forms [1]. The reduction of higher-valent plutonium to less soluble Pu(IV) in simulated WIPP brine was previously established in our laboratory [2,3]. We are in the process to extend this work to a broader range of experimental conditions. Different iron phases and oxidation states (coupons, powder,  $Fe^{2+}$ ,  $Fe^{3+}$ , ferric oxide, iron (II,III) oxide) have been investigated in WIPP brines at various pH values from 7 to 10. The reduction of Pu(VI) was always observed when iron (II) was present in solution. It was found that Pu(IV) was preferentially associated with the iron phases formed. In WIPP brine at high pH, an Fe(II, III) oxide ("green rust") was formed with bromide ion as the interstitial anion in the oxide structure based on XANES analyses performed.

The role of iron as a reducing agent in our systems was also established for uranium (VI), which is typically known to be very stable under subsurface conditions. Preliminary studies published in the literature reported the reduction, at least partially, of uranium (VI) by iron corrosion products under reducing saline conditions [1]. Our study focused on the Fe(II)/U(VI) interactions at pH 6 to 10 and the presence or absence of complexants. A spectrophotometric method based on ferrozine that was adapted and extensively tested for our iron systems [4] was used to detect the concentration of iron in both oxidation states. The total concentration of iron and uranium was measured by ICP-MS. Unlike plutonium, where reduction was almost always noted, the reduction of U(VI) was strongly affected by the experimental conditions and speciation. The presence of magnetite in solution enhanced the removal of uranium from the solution which is consistent with observations made by others [5].

## CONCLUSIONS

- Higher-valent plutonium was reduced to Pu(IV) under all conditions investigated when reduced iron solids were investigated
- Reduction of U(VI) by aqueous  $Fe^{2+}$  and Fe(II) solids was also observed. This was clearcut in non-complexing media where U(IV) precipitated, but further work is needed to confirm the trends observed when soluble U(IV) phases were formed.
- These results support the current WIPP PA assumptions that higher valent Pu will not prevail in the WIPP and argue for a predominance of the U(IV) oxidation state although a 50/50 U(VI) to U(IV) species distribution is currently assumed.

## REFERENCES

- [1] B. Grambow et al., Radiochim. Acta, **74**, 149, 1996
- [2] D.T. Reed et al., Plutonium Futures - The Science Conference Transactions, 2003
- [3] D.T. Reed et al., Radiochim. Acta, **94**, 591, 2006
- [4] S.E. Pepper et al., submitted to Environ. Sci. Technol., 2008
- [5] J.K. Fredrickson et al., Geochem. Cosmochim. Acta, **64**, 3085, 2000
- [6] C.F. Baes, J. Physical Chem., **60**, 805, 1956

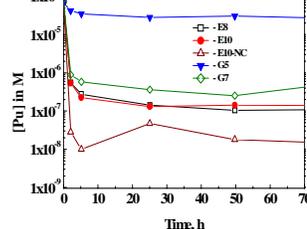
## Pu(VI) Reduction By $Fe^{2+}$ and Fe(II) Oxides

Pu(VI) can be stable in brine under anoxic conditions when no reductants are present. The addition of reduced iron, Fe(0) phases, Fe(II) phases or  $Fe^{2+}$ (aq), lead to the reduction of Pu(VI) to form Pu(IV) sorbed and precipitated phases. These were often strongly associated with the Fe phases present. Iron (II/III) phases, e.g. magnetite, reduced Pu(VI) more rapidly than Fe(0). Final dissolved plutonium concentrations were in the  $10^{-7}$  to  $10^{-8}$  M range consistent with our current estimates for the solubility of Pu(IV) in WIPP Brine.

At  $pC_{H^+} = -5$ , and when only Fe(III) phases were present, Pu(VI) was reduced to Pu(V) and some sorption of Pu(V) was noted.

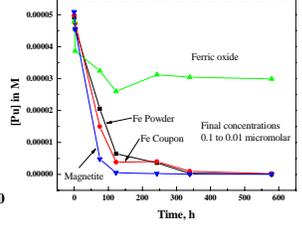
Under WIPP-relevant conditions, where anoxic conditions and large amounts of reduced iron is present, these results support the current assumptions by the WIPP that lower-valent Pu(III) and Pu(IV) will predominate.

### Reduction of Pu(VI) by $Fe^{2+}$



Effect of added  $Fe^{2+}$  on the stability of Pu(VI) in brine. Total plutonium concentrations were reduced by four orders of magnitude with the exception of experiment G5 which was conducted at  $pC_{H^+} = -5$  in G-Seep Brine where aqueous Pu(V) species persisted [3]

### Reduction of Pu (VI) in Brine by Iron and Iron Oxide Solids



Reduction of Pu(VI) in ERDA-6 brine. Both Fe(0) and Fe(II) phases lead to the reduction of Pu(VI) to Pu(IV) - confirmed by XANES analysis. When Fe(III) was present, reduction to Pu(V) and sorption occurred.

## Reduction of U(VI) by Iron (II)

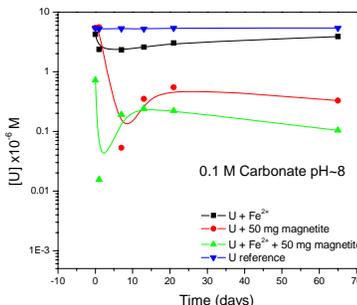
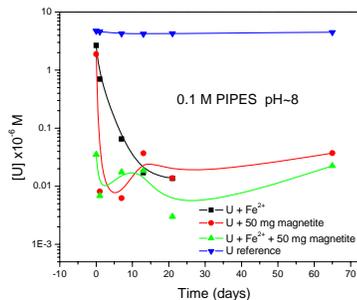
The effect of Fe(II) on the redox stability of U(VI), in the presence or absence of magnetite, was investigated in the following anoxic systems: 0.1M PIPES at pH-8, 0.1M carbonate at pH-8, and 0.1M carbonate at pH-10. We also confirmed the reduction of U(VI) by  $Fe^{2+}$  under acidic conditions in phosphoric acid [6].

The systems at higher pH are relevant to the expected environment in the WIPP. Iron, as 1 mM  $Fe^{2+}$ , was stable when no carbonate was present - this was confirmed by both total Fe analysis by ICP-MS and the ferrozine colorimetric technique that is specific to the detection of aqueous  $Fe^{2+}$ . The concentration of iron was not affected by the presence of magnetite solid and both oversaturation and undersaturation approaches gave the same concentration of aqueous  $Fe^{2+}$ . In the presence of 0.1 M carbonate, some precipitation occurred, presumably siderite, leading to a decrease to ~90% in the iron concentration although what was in solution remained as  $Fe^{2+}$ .

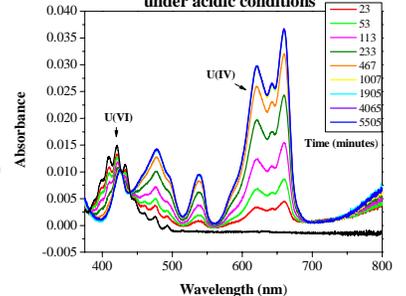
Five micromolar U(VI) was stable in these systems in the absence of reduced iron and no evidence of reduction was noted. In the presence of 1 mM  $Fe^{2+}$ , the concentration of uranium, initially present as U(VI), was reduced to ~0.1 micromolar in the non-complexing PIPES medium in < 10 days. This was interpreted as the result of the reduction of U(VI) to U(IV) followed by the precipitation of U(IV) phases. Reduction was also noted when only magnetite was initially present and was much faster (typically < 2 days). At pH 8, in the presence of 0.1 M carbonate, U(VI) reduction was also noted but this did lead to a combination of U(IV) carbonate phases and U(IV) precipitates. The presence of magnetite accelerated the reduction and enabled the removal of U(IV) from solution presumably by sorption [5].

At pH-10, the precipitation of uranium from solution only occurred in the presence of both magnetite and  $Fe^{2+}$ . It is possible at this pH that reduction by magnetite was slowed and its reduction by  $Fe^{2+}$  only lead to the removal of uranium from solution when magnetite was present. This would mean that  $Fe^{2+}$  reacted with U(VI)-carbonate species to form soluble U(IV)-carbonate species. Further analyses are however needed to convincingly establish the redox trends at this pH.

This set of experiments are being extended to simulated WIPP brine. Ongoing experiments in carbonate free GWB brine also show a decrease in uranium concentration in solution at  $pC_{H^+} = 8.5$  in the presence of an excess of  $Fe^{2+}$ . The ferrous ion concentration was also decreasing, and precipitate was observed - so similar trends are being observed.



## Reduction of U(VI) by $Fe^{2+}$ in phosphate media under acidic conditions



## ACKNOWLEDGEMENTS

The authors would like to thank Dr. Sarah Pepper for the developmental experiments performed in this area in our lab. This research was sponsored by the US Department of Energy, Carlsbad Field Office.