

## Rates of uranium(VI) reduction by hydrogen sulfide in aqueous media: Effects of carbonate and pH

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Uranium is a redox-sensitive metal radionuclide under ambient environment conditions. Since its mobility depends largely on its redox speciation, elucidating the factors that control its redox transformation has significant environmental significance. This study examined the effects of carbonate and pH on U(VI) reduction by hydrogen sulfide in aqueous media, with some result shown in Fig. 1

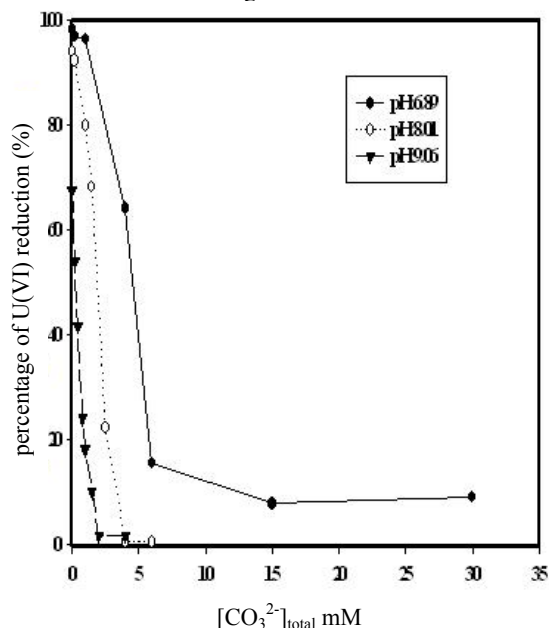


Figure 1. Experimental results

### Discussion of the results

The reduction was almost completely inhibited when  $[\text{CO}_3^{2-}]_{\text{total}} \geq 15.0$  mM at pH 6.89,  $\geq 4.0$  mM at pH 8.01, and  $\geq 4.0$  mM at pH 9.06. Comparing the calculated carbonate-U(VI) and hydroxo-U(VI) speciation with the reaction rates suggested that carbonate-U(VI) complexes were not the major species reduced, instead, it were the hydroxo-U(VI) complexes that were reduced under the experimental conditions.

### Reference

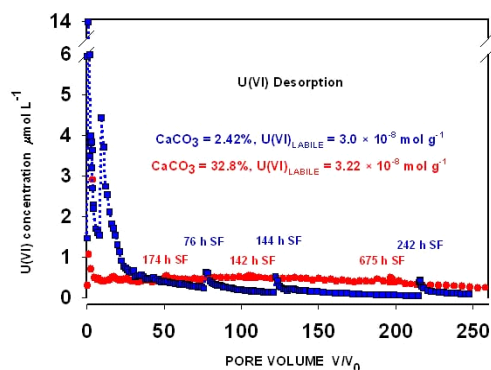
Kochenov A.V.; Korolev K.G.; Dubinchuk V.T.; Medvedev Y.L. (1978), *Geochemistry International*, 14, 82-87.

## Uranium(VI) desorption from long-term contaminated sediments

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Uranium-contaminated sediments were obtained at the U.S.DOE Hanford site from a deep vadose zone plume ( $\approx 35$  m below ground surface) whose mobility has decreased since its release 30 y ago. Two U-containing sediments were studied from the plume that spanned the pleistocene-pleistocene contact in supra-basalt sediments, and that contained 7.7 and 15 ppm of sorbed U(VI). The sediment from above the contact was calcite-poor (e.g.,  $\approx 2.4$  %) while that from below the contact was paleosol with high calcite (e.g.,  $\approx 32.8$  %). Saturated column experiments were conducted at pH 8 in a Na/Ca-HCO<sub>3</sub> electrolyte to investigate the desorption rate of sorbed U(VI) as a basis for assessing future plume mobility. The stop-flow technique to assess nonequilibrium effects was periodically applied.



The desorption behavior of the calcite-poor and calcite-rich sediments were markedly different. Both of the advective desorption profiles could be described with a two site (equilibrium and kinetic) model. Sorbed U(VI) was released rapidly from the calcite-poor sediment. The leaching profile was described with an equilibrium site fraction of 80% and a half-life of 33 h for the kinetic sites (20%). The calcite-rich sediment, in contrast, exhibited slow, sustained U(VI) release for extended leaching volumes. Modeling of the effluent data indicated that 97% of the sites in the calcite-rich sediment were kinetically controlled with a desorption half-life of 85 h. These results are discussed in terms of sediment mineralogy and the reaction chemistry of U(VI) with fine-grained pedogenic calcite. This calcite-rich paleosol has effectively arrested the downward migration of the U(VI) vadose zone plume.