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Comment on "Reductive Immobilization of Uranium(VI) by Amorphous Iron Sulfide"

In a recent article, Hua and Deng (1) reported on the reductive immobilization of uranium (VI) by synthetic amorphous iron sulfide (FeS) under anoxic conditions. The tests mostly used 168.0 μM U(VI) and 0.18 g/L FeS suspensions at pH values varying from 6.0 to 10.0. The extent of U(VI) removal was determined by monitoring the changes of aqueous U(VI) concentration, and the extent of U(VI) reduction was determined by the difference between initial amount of U(VI) and the amount extracted by 25 mM NaHCO_3 solution. Results showed a rapid U(VI) removal from the aqueous phase coupled with Fe(II) release in the solution. Reduction of adsorbed U(VI) at the surface of FeS was completed after hours or a week. X-ray photoelectron spectroscopy analysis of reaction products evidenced U_3O_8 / U_4O_9 / UO_2 . The given interpretation of possibly good experimental data is very doubtful as shown in the following paragraphs.

First, the experimental conditions are not adequate for the investigation of U(VI) reductive immobilization. In fact the U(VI) initial concentration of 168.0 μM or 40 mg/L used is necessarily too high at near neutral pH values (2). Therefore, the experiments of Hua and Deng (1) were (at least) partly performed under conditions where solubility limits of schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) have been exceeded. Schoepite is the most soluble U(VI) solid phase (2, 3). Even though no spontaneous U(VI) precipitation in a FeS-free solution was documented by Hua and Deng (1), surface precipitation has been reported for several materials (4). Therefore, the "rapid removal of U(VI) from the aqueous phase" is merely due to surface precipitation. Surface precipitation is a fast process. The results of X-ray photoelectron spectroscopy analysis (U_3O_8 , U_4O_9 , UO_2) corroborate the fact that U(VI) reduction was not quantitative. Quantitative U(VI) reduction would have yielded UO_2 .

Second, using a 25 mM NaHCO_3 solution for uranium speciation is not acceptable. In fact the 0.18 g/L FeS suspension used contained more than 2000 μM Fe (for 168.0 μM U(VI)) which can potentially oxidize to Fe(III) and precipitate primarily as amorphous $\text{Fe}(\text{OH})_3$. In the course their precipitation, $\text{Fe}(\text{OH})_3$ moieties will certainly sequester some U(VI) (coprecipitation). A comparison of reported Fe(II) concentration with solubility data from Rickard (5) showed that the reported solution were also oversaturated with regard to Fe(II), suggesting that even FeS will inevitably precipitate in the system. For coprecipitated U(VI) to be released, iron hydroxides (and or iron sulfides) must be dissolved. NaHCO_3 can not dissolve iron hydroxides because iron (Fe(II) and Fe(III)) is not soluble in carbonate solutions. Sequestered U(VI) is regarded by Hua and Deng (1) as reductively

immobilized. On the other hand, both U(IV) and U(VI) are soluble in carbonate solutions. Moreover, once schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) has precipitated, it undergoes recrystallization (aging) yielding for example more stable U_3O_8 that will not readily dissolve in NaHCO_3 . Non dissolved U_3O_8 is equally regarded as reductively immobilized by Hua and Deng (1).

Third, the proposed mechanism of U(VI) reduction is questionable. How should U(VI) be reduced to U(IV) by Fe(II) when Fe(II) (and not Fe(III)) is released in the solution as U(VI) is accumulated at the FeS surface? As iron dissolution and precipitation is necessarily a dynamic process, the comparison of soluble Fe(II) to the amount of U(VI) associated with FeS can not be conclusive. In fact, in the ideal case of dynamic equilibrium, when one atom of Fe(II) reacts with one atom of U(VI), one atom of Fe(II) is released from FeS. In a series of complementary experiments, Hua and Deng (1) could find a direct proportionality between released Fe(II) and total amount of U(VI) removed from the solution ($[\text{U}^{\text{VI}}]_0 / [\text{Fe}^{\text{II}}]_{\text{aq}} = 0.85$). The interested reader is left alone with the significance of this correlation because U(VI) reduction is reported to occur with a time delay of up to one week. The reader is equally left alone with the rationale of randomly interchanging reduced U (e.g., U(IV)) and non-extractable U. The reported steady decrease of extractable U with time can be attributed to several processes (including aging/ recrystallization of both schoepite and iron hydroxides) regardless of whether U is reduced or not. In this regard, reoxidizing U(IV) which is coprecipitated will not remove it from the matrix of iron hydroxides for instance.

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