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 NaHCO₃ 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 U₃O₈/U₄O₉/UO₂. 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 used U(VI) initial concentration of 168.0 µM or 40 mg/L 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 (UO₃·2H₂O) 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 (U₃O₈, U₄O₉, UO₂) corroborate the fact that U(VI) reduction was not quantitative. Quantitative U(VI) reduction would have yielded UO₂.

Second, using a 25 mM NaHCO₃ solution for uranium speciation is not acceptable. In fact the used 0.18 g/L FeS suspension contents more than 2,000 µM of Fe (for 168.0 µM U(VI)) which can potentially oxidize to Fe(III) and precipitate primarily as amorphous Fe(OH)₃. In the course their precipitation, Fe(OH)₃ moieties will certainly sequestrated some U(VI) (co-precipitation). A comparison of reported Fe(II) concentration with solubility data from Rickard (5) showed that reported solution were also over-saturated with regard to Fe(II), suggesting that even FeS will inevitably precipitate in the system. For co-precipitated U(VI) to be released, iron hydroxides (and or iron sulphides) must be dissolved. NaHCO₃ can not dissolved 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 (UO₃·2H₂O) has precipitated, its undergoes recrystallisation (ageing) yielding for example more stable U₃O₈ that will not readily dissolve in NaHCO₃. Non-dissolved U₃O₈ 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 no be conclusive. In fact, in the ideal case of dynamic equilibrium, when one atom Fe(II) reacts with one atom U(VI), one atom Fe(II) is released from FeS. In a series of complementary experiments, Hua and Deng (1) could be find a direct proportionality between released Fe(II) and total amount of U(VI) removed from the solution ([U(VI)]/[[Fe(II)]= 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 steadily decrease of extractable U with time can be attributed to several processes (including ageing/recrystallisation of both schoepite and iron hydroxides) regardless whether U is reduced or not. In this regard, re-oxidizing U(IV) which is co-precipitated will not remove it from the matrix of iron hydroxides for instance.

**Literature Cited**


Figure S1: Comparison of FeS solubility data from Rickard (2006) with experimental from Hua and Deng (2008). It is evident that Hua and Deng’s studies were performed under conditions where solubility limits of FeS have been exceeded.