

1 **Comments on “Reductive Immobilization of Uranium(VI) by Amorphous Iron Sulfide”**

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6 In a recent article, Hua and Deng (1) reported on the reductive immobilization of uranium
7 (VI) by synthetic amorphous iron sulfide (FeS) under anoxic conditions. The tests mostly
8 used 168.0 μM U(VI) and 0.18 g/L FeS suspensions at pH values varying from 6.0 to 10.0.
9 The extent of U(VI) removal was determined by monitoring the changes of aqueous U(VI)
10 concentration, and the extent of U(VI) reduction was determined by the difference between
11 initial amount of U(VI) and the amount extracted by 25 mM NaHCO_3 solution. Results
12 showed a rapid U(VI) removal from the aqueous phase coupled with Fe(II) release in the
13 solution. Reduction of adsorbed U(VI) at the surface of FeS was completed after hours or a
14 week. X-ray photoelectron spectroscopy analysis of reaction products evidenced
15 $\text{U}_3\text{O}_8/\text{U}_4\text{O}_9/\text{UO}_2$. The given interpretation of possibly good experimental data is very doubtful
16 as shown in the following paragraphs.

17 First, the experimental conditions are not adequate for the investigation of U(VI) reductive
18 immobilization. In fact the used U(VI) initial concentration of 168.0 μM or 40 mg/L is
19 necessarily too high at near neutral pH values (2). Therefore, the experiments of Hua and
20 Deng (1) were (at least) partly performed under conditions where solubility limits of
21 schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) have been exceeded. Schoepite is the most soluble U(VI) solid phase
22 (2,3). Even though no spontaneous U(VI) precipitation in a FeS-free solution was documented
23 by Hua and Deng (1), surface precipitation has been reported for several materials (4).
24 Therefore, the "rapid removal of U(VI) from the aqueous phase" is merely due to surface
25 precipitation. Surface precipitation is a fast process. The results of X-ray photoelectron

26 spectroscopy analysis (U_3O_8 , U_4O_9 , UO_2) corroborate the fact that U(VI) reduction was not
27 quantitative. Quantitative U(VI) reduction would have yielded UO_2 .

28 Second, using a 25 mM $NaHCO_3$ solution for uranium speciation is not acceptable. In fact the
29 used 0.18 g/L FeS suspension contents more than 2,000 μM of Fe (for 168.0 μM U(VI))
30 which can potentially oxidize to Fe(III) and precipitate primarily as amorphous $Fe(OH)_3$. In
31 the course their precipitation, $Fe(OH)_3$ moieties will certainly sequestered some U(VI) (co-
32 precipitation). A comparison of reported Fe(II) concentration with solubility data from
33 Rickard (5) showed that reported solution were also over-saturated with regard to Fe(II),
34 suggesting that even FeS will inevitably precipitate in the system. For co-precipitated U(VI)
35 to be released, iron hydroxides (and or iron sulphides) must be dissolved. $NaHCO_3$ can not
36 dissolved iron hydroxides because iron (Fe(II) and Fe(III)) is not soluble in carbonate
37 solutions. Sequestered U(VI) is regarded by Hua and Deng (1) as reductively immobilized.
38 On the other hand, both U(IV) and U(VI) are soluble in carbonate solutions. Moreover, once
39 schoepite ($UO_3 \cdot 2H_2O$) has precipitated, its undergoes recrystallisation (ageing) yielding for
40 example more stable U_3O_8 that will not readily dissolve in $NaHCO_3$. Non-dissolved U_3O_8 is
41 equally regarded as reductively immobilized by Hua and Deng (1).

42 Third, the proposed mechanism of U(VI) reduction is questionable. How should U(VI) be
43 reduced to U(IV) by Fe(II) when Fe(II) (and not Fe(III)) is released in the solution as U(VI) is
44 accumulated at the FeS surface? As iron dissolution and precipitation is necessarily a dynamic
45 process, the comparison of soluble Fe(II) to the amount of U(VI) associated with FeS can no
46 be conclusive. In fact, in the ideal case of dynamic equilibrium, when one atom Fe(II) reacts
47 with one atom U(VI), one atom Fe(II) is released from FeS. In a series of complementary
48 experiments, Hua and Deng (1) could be find a direct proportionality between released Fe(II)
49 and total amount of U(VI) removed from the solution ($[U^{VI}]_0/[Fe^{II}]_{aq} = 0.85$). The interested
50 reader is left alone with the significance of this correlation because U(VI) reduction is
51 reported to occur with a time delay of up to one week. The reader is equally left alone with

52 the rationale of randomly interchanging reduced U (e.g. U(IV)) and non extractable U. The
53 reported steadily decrease of extractable U with time can be attributed to several processes
54 (including ageing/recrystallisation of both schoepite and iron hydroxides) regardless whether
55 U is reduced or not. In this regard, re-oxidizing U(IV) which is co-precipitated will not
56 remove it from the matrix of iron hydroxides for instance.

57 **Literature Cited**

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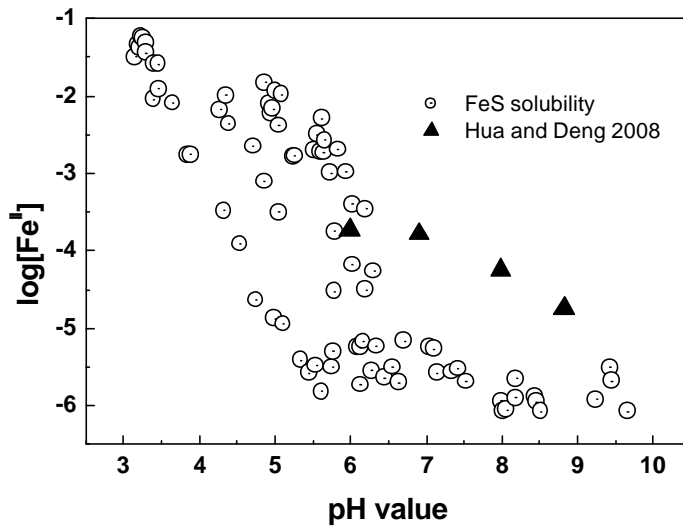
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69 **Supporting Material (only for review)**



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