

**KEY WORDS:**  
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**High Level Waste Tank, Uranium,**  
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**RETENTION:**  
**Permanent**

**SUGGESTED SORPTION PARAMETERS FOR URANIUM ONTO THE  
WALLS OF HIGH-LEVEL WASTE TANKS.**

**Daniel I. Kaplan**

**DECEMBER 4, 2006**

Savannah River National Laboratory  
Washington Savannah River Company  
Savannah River Site  
Aiken, SC 29808

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**Prepared for the U.S. Department of Energy Under  
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12/7/2007

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12/7/2007

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## 1.0 EXECUTIVE SUMMARY

The SRS is conducting a performance assessment to evaluate the long-term impacts of closing waste tanks by filling them with grout. Some radioactivity will remain in the “heel” of the tanks, as well as adsorbed to the rust associated to the tank walls. The amount associated with the rust is not directly measured, instead it is calculated through the use of a distribution coefficient,  $K_d$  value. Greater the  $K_d$  value, the greater concentration of radionuclide is estimated to be associated with the rust.

The objective of this task was to evaluate whether the uranium  $K_d$  value used in these calculations, 6000 L/kg, was appropriate for Type IV tank conditions. This  $K_d$  value was calculated for use in the radiological performance assessment for the E-Area LAW facility. No measurements of U  $K_d$  values have been measured under tank waste conditions. The 6000 L/kg  $K_d$  value was evaluated by making inferences from experimental work reported in the literature.

This  $K_d$  value appears to be appreciably higher than it ought to be. The high pH of the rust/supernate systems (pH 12 to 14) is likely the most important factor limiting U(VI) sorption to rust. At such high pH levels, U(VI) has an anionic character and the rust (Fe-oxides) surfaces are extremely negatively charged, resulting in the rust surfaces repelling the like-charged uranium anions, not adsorbing them. Consequently, essentially no U(VI) sorption has been reported at pH levels greater than about pH 10. Uranium adsorption is further hampered by the high ionic strength, which introduces competing anions for the adsorption sites on the rust.<sup>1</sup> The presence of moderately high carbonate concentrations in the supernate may further limit U(VI) adsorption. The findings from this literature review do not support the use of a supernate U  $K_d$  value of 6000 L/kg. A value two, possibly three, orders-of-magnitude smaller is more in line with the literature.

## 2.0 INTRODUCTION

Savannah River National Laboratory has been asked by Site Regulatory Integration and Planning to reevaluate the uranium distribution coefficient,  $K_d$  value, used in a previous calculation conducted by Cook (2005). Cook provided an estimate of the potential mass of U (and 22 other isotopes) left on corrosion products in Tank 18 after the tank had been emptied of liquids and most of the solids sludge had been removed. He used Eq. 1 for these calculations:

$$C_{i\text{solid}} = K_d * (C_{i/L})_{\text{liquid}} * \text{kg}_{\text{solid}} \quad (1)$$

---

<sup>1</sup> The ionic strength also has an impact on surface charge, namely, generally collapsing the double layer around the particles, thereby promoting solution ion contact with the pH-dependent charge surface.

where  $C_{i_{solid}}$  is the U activity on the solid phase (units = Ci),  $K_d$  is the distribution coefficient (units = L/kg), and  $(Ci/L)_{liquid}$  is the supernatant U concentration. Equation (1) can be derived directly from the definition of a  $K_d$  value,

$$K_d = \frac{Ci / kg_{solid}}{Ci / L_{liquid}} \quad (2)$$

Analytical data from a dip sample taken from Tank 18 was used to represent the solution  $[(Ci/L)_{liquid}]$  that was in contact with the tank walls when the tank was in service. This data is presented in Table 1. The amount of rust present in the tank walls ( $kg_{solid}$ ) was calculated by Wiersma (2003) to be  $329 \text{ kg}^2$ . The  $K_d$  value used in the calculation was set to 6000 L/kg and was based on sorption of U to iron oxides (goethite) in a cementitious grout environment (Table E.4-1; WSRC, 2000). The rust in vault environment came from waste containers (B25 boxes) and rebar. Using Eq. 1 and these sets of input values, the amount of U attached to the walls were directly calculated (Table 1).

**Table 1.** Uranium isotope supernate concentrations and estimated concentration on Tank 18 walls (Cook 2005).

Isotope	Concentration (Ci/L) <sup>(a)</sup>	Estimated Concentration on Tank 18 Walls (Ci) <sup>(a)</sup>
U-233	1.84E-6	3.6E0
U-234	1.19E-6	2.3E0
U-235	1.06E-9	2.1E-3
U236	1.23E-8	2.4E-2
U-238	2.69E-8	5.3E-2

The U  $K_d$  value used in Cook (2005) is inappropriate for tank conditions. It is based on conditions expected in the vault after it has aged. The U  $K_d$  value of 6000 L/kg (or 6000 mL/g) was estimated using Eq. 3:

$$K_d = \frac{S \times X}{r \times S_{exp} \times (1 - X)} \quad (3)$$

where

- $S$  is the specific surface area of the waste ( $32,000 \text{ cm}^2/\text{cm}^3$ )
- $X$  is the fraction sorbed
- $r$  is the bulk density of the waste ( $1.6 \text{ g}/\text{cm}^3$ )
- $S_{exp}$  is the concentration of solids in the literature adsorption experiment ( $\text{cm}^2/\text{mL}$ )

<sup>2</sup> Mr. Wiersma has refined this estimate of rust mass in the tanks. The value of 329 kg used by Cook (2005) is provided for information.

Importantly, the “waste” referred to in the definition of  $S$  is the total surface area of the Low Activity Waste (LAW). This term and therefore the derived  $K_d$  value are not the same for the tanks and the LAW vault.

The objective of this task is to identify an alternative U  $K_d$  value that can be used in Eq. 1 to determine the amount of U remaining on the sides of the tank wall after removing the tank supernatant and subsequent washes. The approach will be to evaluate relevant literature and then provide another U  $K_d$  estimate.

### 3.0 LITERATURE

There have been several adsorption studies of the uranyl ion on Fe oxides and Fe oxyhydroxides (Tripathi 1983; Ho and Doern 1984, Hsi and Langmuir 1985, Ho and Miller 1986, Payne and Waite 1991, Waite et al. 1994, Duff and Amrhein 1996). However, none of them have been conducted in precisely the conditions expected in the SRS tanks. However, together these studies indicate some consistent trends that shed light on the likely geochemical behavior of U and Fe-oxyhydroxides.

#### 3.1 URANIUM SPECIATION

Uranium is expected to exist in the tanks in the uranyl ( $\text{UO}_2^{2+}$  or U(VI)) form. The speciation of the uranyl is expected to be  $\text{UO}_2(\text{OH})_4^{2-}$  and  $\text{UO}_2(\text{OH})_5^{3-}$  and no polymeric in the supernate (Clark 1999). The  $\text{UO}_2(\text{CO}_3)_3^{4-}$  species is expected to dominate between pH 8 and 10 (Allen 1995). The important point to make from this discussion is that all the U(VI) is likely to exist as an anion. Uranium does not exist primarily as a cation until the pH drops below ~6.

#### 3.2 Fe-OXIDE SURFACE CHARGE

The rust of the tank walls is composed primarily of Fe oxides: including goethite ( $\alpha$ -FeOOH), ferrihydrite (amorphous  $\text{Fe}(\text{OH})_3$ ), and hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ). All of these minerals have a pH-dependent surface charge. Above a critical pH, referred to as the zero point of charge (ZPC), the Fe oxides will have a net negative charge. Below the ZPC, the net surface charge is positive. Furthermore, the greater the pH is above or below the ZPC, the greater the negative and positive charge, respectively. The ZPC for iron oxides is between pH 6.5 to 8.5<sup>3</sup>. Since the pH of the supernate is between 12 and 14, this means that these minerals have very strong negative charges, i.e., a charge that would electrostatically repel anions (and absorb cations) from their surfaces. Given that the U(VI) exists as anions and the rust is very negatively charge, there is little reason to expect that adsorption is responsible for much removal of U from the supernate.

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<sup>3</sup>  $\alpha$ -FeOOH has a zero point of charge (ZPC) of pH 7.8, amorphous  $\text{Fe}(\text{OH})_3$  has a ZPC of pH 8.5 and  $\text{Fe}_2\text{O}_3$  has a ZPC of 6.7 (Stumm and Morgan 1981)

### 3.3 AQUEOUS PARAMETERS THAT INFLUENCE URANIUM SORPTION TO FE OXIDES

As mentioned above, pH has an important role in U(VI) speciation and Fe-oxide surface charge. An example of the pH dependence of U(VI) adsorption to an Fe-oxide (in this case, ferrihydrite) is presented in Figure 1 (Waite et al. 1994). This figure shows that essentially no U(VI) is adsorbed above a pH of 8.9. This figure also shows that sorption decreases as the concentration of U(VI) increases. Uranium concentrations in Tanks 18F and 19F were moderately low ( $<10^{-6}$  M; **Table 2**) with respect to the U(VI) concentrations tested by Waite et al. (1994). Therefore the U(VI) concentration present in the supernate likely did not hinder U(VI) adsorption. Waite et al. (1994) also reported that ionic strength had a slight impact on U(VI) adsorption. This consistent trend was observed for environmentally relevant groundwater ionic strengths of 0.004 to 0.5 M. The authors attributed this trend to competition for surface sorption sites. The solution ionic strength of the Tank 18F and 19F supernates are appreciably higher than those studied; they were  $>5$  M (as implied by **Table 2**). Therefore the high ionic strength of the supernate would decrease the tendency of these Fe-oxide surfaces to adsorb U(VI).

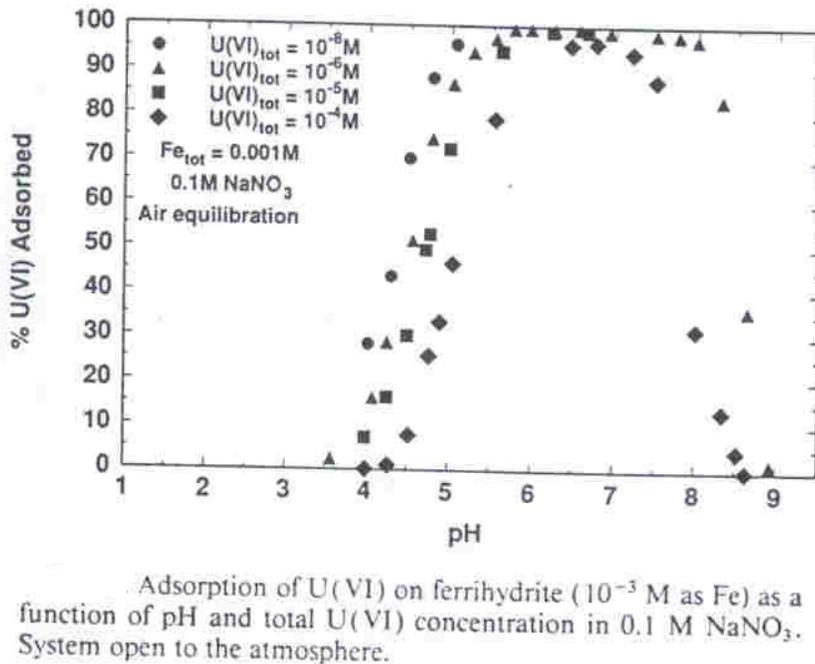
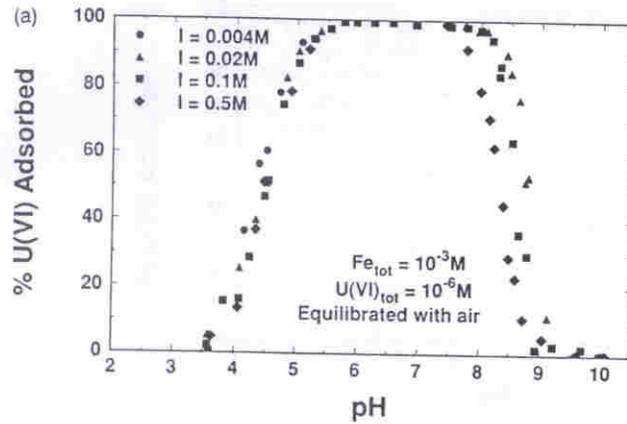


Figure 1. Influence of U(VI) concentration and pH on U(VI) sorption to ferrihydrite (Waite et al. 1994).

Table 2. Supernate chemistry of Tank 18F and 19F (Ondrejcin 1976).

Date Sampled	Tank 18F 10/14/75	Tank 19F 10/14/75
Na <sup>+</sup>	8.9	11.0
K <sup>+</sup>	0.076	0.20
NO <sub>3</sub> <sup>-</sup>	2.6	2.4
NO <sub>2</sub> <sup>-</sup>	1.6	0.74
OH <sup>-</sup>	4.8	6.9
Al(OH) <sub>4</sub> <sup>-</sup>	0.70	0.66
CO <sub>4</sub> <sup>2-</sup>	0.009	0.020
SO <sub>4</sub> <sup>2-</sup>	0.08	0.07
PO <sub>4</sub> <sup>3-</sup>	0.05	<0.02
Cl <sup>-</sup>	0.013	0.015
F <sup>-</sup>	0.009	0.005
CrO <sub>4</sub> <sup>-</sup>	5.6x10 <sup>-3</sup>	<3.4x10 <sup>-4</sup>
Ca <sup>2+</sup>	<6x10 <sup>-5</sup>	<6x10 <sup>-5</sup>
Fe	7.3x10 <sup>-5</sup>	7.3x10 <sup>-5</sup>
U	<1.3x10 <sup>-6</sup>	<3.8x10 <sup>-6</sup>
Density, g/mL	1.364	1.430



(a) Adsorption of  $10^{-6} M$  U(VI) on ferrihydrite ( $10^{-3} M$  as Fe) as a function of pH and ionic strength. System open to the atmosphere.

Figure 2. Influence of pH and ionic strength on U(VI) sorption to ferrihydrite (Waite et al. 1994).

Carbonate has a significant influence on U(VI) speciation (Waite et al. 1994, Duff and Amrhein 1996, His and Langmuir 1985). Carbonate concentrations in the supernates of Tank 18F and 19F were moderately high, between 0.009 to 0.02 M (Table 2). As the carbonate concentrations increase, the tendency for U(VI) to adsorb to all surfaces quickly decreases (

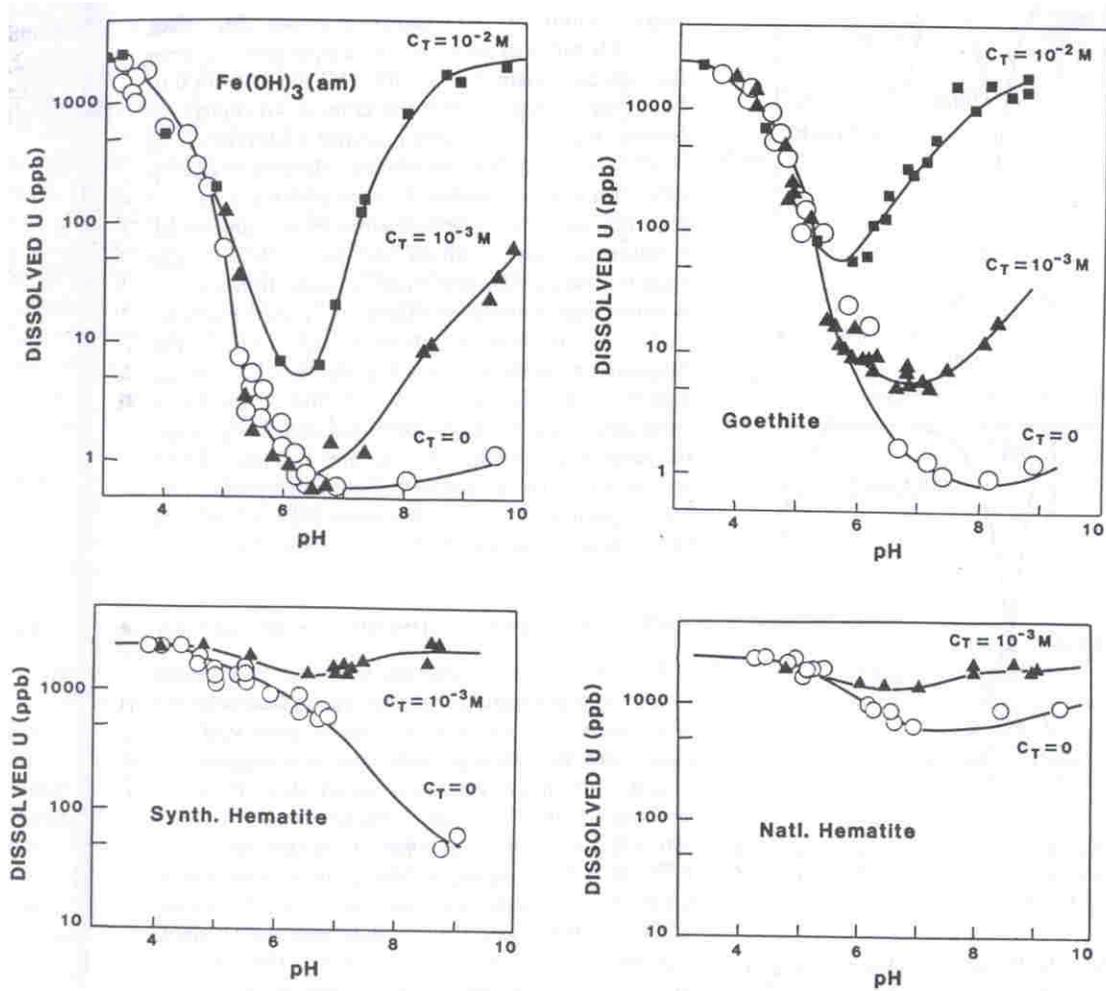
Figure 3; not that unlike the other figures, this one presents “Dissolved U” concentrations, which is the inverse of “% U(VI) Adsorbed”). This occurs because carbonate forms very strong bonds with U(VI), stronger bonds than oxalate, sulfate, fluoride or nitrate. When carbonate concentrations are elevated, they tend to complex with the  $UO_2^{2+}$  ion to form zero charge species (at pH ~7 to 9) or negatively charged when the carbonate concentrations are elevated further (and the pH is maintained constant). The experimental results presented in

Figure 3 indicate that at the higher pH test, pH ~10, that two orders of magnitude increase in dissolved U(VI) occurred in the ferrihydrite and goethite when the total carbonate concentrations were increased from  $10^{-3}$  to  $10^{-2}$ , the approximate concentrations of carbonate in Tanks 18F and 19F (Table 2).

Not surprisingly, the type of Fe oxide present also influences U(VI) sorption. Figure 3 also shows the relative tendency of various Fe-oxides to adsorb U(VI). Ranking these minerals for their tendency to adsorb U(VI) is:

$$\text{ferrihydrite} > \text{goethite} > \text{hematite} \tag{4}$$

The relative amounts of these minerals in the rust would vary with the conditions they were formed. Ferrihydrite and goethite are commonly assumed to be present.



The effect of changes in total carbonate ( $C_T$ ) on the adsorption of uranyl vs. pH at  $\Sigma U = 10^{-5}$  M onto 1 g/l suspensions of ferric oxyhydroxides in 0.1 M  $\text{NaNO}_3$  solutions at 25°C.

Figure 3. Influence of form of Fe-oxide, pH and total carbonate concentrations ( $C_T$ ) on dissolved U(VI) concentrations. ( $\text{Fe}(\text{OH})_3(\text{am})$  is amorphous ferrihydrite,  $\text{FeOOH}$  is goethite, an synthetic hematite is amorphous  $\text{Fe}_2\text{O}_3(\text{am})$  and natural hematite is a more crystalline form of hematite) (Hsi and Langmuir 1985).

## 4.0 CONCLUSIONS

The objective of this task was to evaluate whether the U  $K_d$  value of 6000 L/kg was appropriate for calculating the sorption of supernate U onto LAW tank wall rust. This  $K_d$  value was calculated for use in the radiological performance assessment for the E-Area LAW facility. No measurements of U  $K_d$  values have been measured under tank waste conditions. The 6000 L/kg  $K_d$  value was evaluated by making inferences from experimental work reported in the literature.

This  $K_d$  value appears to be appreciably higher than it ought to be. The high pH of the rust/supernate systems (pH 12 to 14) is likely the most important factor limiting U(VI) sorption to rust. At such high pH levels, U(VI) has an anionic character and the rust (Fe-oxides) surfaces are extremely negatively charged, resulting in the rust surfaces repelling the like-charged uranium anions. Consequently, essentially no U(VI) sorption has been reported at pH levels greater than about pH 10. Uranium adsorption is further hampered by the high ionic strength, which introduces competing anions for the adsorption sites on the rust.<sup>4</sup> The presence of moderately high carbonate concentrations in the supernate may further limit U(VI) adsorption. The findings from this literature review do not support the use of a supernate U  $K_d$  value of 6000 L/kg. A value two, possibly three, orders-of-magnitude smaller is more in line with the literature.

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<sup>4</sup> The ionic strength also has an impact on surface charge, namely, generally collapsing the double layer around the particles, thereby promoting solution ion contact with the pH-dependent charge surface.

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