SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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APPROVED for Release for Unlimited (Release to Public)

To: Bruce Martin, 766-H

From: Jim Cook, 773-43A

Technical Review: _____ Management Concurrence: _____
K. H. Rosenberger W. E. Stevens

Estimation of the Potential Contamination on Corrosion Products in Tank 19

Introduction and Summary

SRNL has been asked by High Level Waste to estimate the amount of radioactive contamination that might be found on the interior walls of Tank 19. Data was requested from HLW on the composition of the liquid in Tank 19 when it was in service. B. J. Weirsma, of SRNL-MTS provided an estimate of the mass of corrosion products in the tank. This revision incorporates a pH dependent K_d for selenium into the calculation and the includes the latest estimates of the residuals in Tank 19.

Methodology

When a solution is in contact with a solid phase, the constituents partition between the solid and liquid. The factor used to quantify this is called the partition coefficient, or K_d. It is defined as the concentration in the solid phase divided by the concentration in the liquid phase and has the units volume/mass:

$$K_d = (Ci/Kg)/Ci/L = L/Kg \qquad \text{Eq. 1}$$

In the High Level Waste Tanks system, liquid tank contents are in contact with corrosion products in the tank walls. The question to be answered is how much radioactive contamination could be held on the corrosion products. K_d values for many chemical species have been measured for hydrous iron oxides (FeOOH, goethite, rust). Given information on the liquid concentrations, K_ds and the mass of corrosion products, the K_d definition equation can be used to answer this question.

$$Ci_{solid} = K_d * (Ci/L)_{liquid} * Kg_{solid} \qquad \text{Eq. 2}$$

High Level Waste recommended using the analytical data for 1975 to represent the solution that was in contact with the tank walls when the tank was in service (See Attachment A). Results were given for four species, ^{90}Sr, ^{134}Cs, ^{137}Cs and Pu. According to Ann Gibbs (Personal Communication, 2002) the analysis for ^{90}Sr requires a chemical separation step, so the Pu result is most likely the result of another chemical separation step and represents total alpha from plutonium. This alpha activity would have been almost exclusively due to ^{238}Pu and ^{239}Pu. Assuming the Pu was in the same ratio as found in Tank 18 (see below), the activity split would have been 69.1% ^{238}Pu and 30.9% ^{239}Pu. The results are given in Table 1.

In order to include a greater number of radionuclides, HLW suggested using recent data from Tank 18 to represent the solution in Tank 19 when it was in active use. These data are given in Table 2.

The partition coefficients for the elements in question on iron oxide (goethite) for an alkaline environment are given in Table 3.

The Materials Technology Section of SRNL gave an estimate of 497 lb (226 Kg) of rust for the tank (Wiersma 2002).

Table 1. 1975 Analytical Results for Tank 19

Radionuclide	Concentration, d/m/mL	Concentration, Ci/L
^{90}Sr	2.9×10^{3}	1.3×10^{-6}
^{134}Cs	5.0×10^{6}	2.2×10^{-3}
^{137}Cs	7.4×10^{8}	3.3×10^{-1}
Pu	1.5×10^{4}	6.8×10^{-6}
^{238}Pu		4.7×10^{-6}
^{239}Pu		2.1×10^{-6}

Table 2. 2001 Dip Sample Analytical Results for Tank 18

Radionuclide	Concentration, Ci/L
^{3}H	6.83E-06
^{79}Se	4.95E-06[a]
^{99}Tc	2.4E-03[a]
^{233}U	4.66E-08
^{234}U	3.01E-08
^{235}U	7.82E-11
^{236}U	3.11E-10
^{238}U	2.19E-09
^{237}Np	3.39E-09
^{238}Pu	9.63E-07
^{239}Pu	4.30E-07
^{240}Pu	<1.10E-06
^{241}Pu	1.32E-06
^{242}Pu	<1.84E-08
^{241}Am	<1.54E-07

[a] Estimate from J. R. Hester e-mail 12/6/02 - attached

Table 3. Partition Coefficients for Goethite (FeOOH) in an Alkaline Environment

Element	K_d, L/Kg
H	0 (Table E.4-1, WSRC, 2000)
Se	2 (Attachment B)
Sr	3 (Table E.4-1, WSRC, 2000)
Tc	0 (Table E.4-1, WSRC, 2000)
Cs	5 (Ohnuki, 1991)
U	6000 (Table E.4-1, WSRC, 2000)
Np	750 (Table E.4-1, WSRC, 2000)
Pu	2000 (Table E.4-1, WSRC, 2000)
Am	3700 (Table E.4-1, WSRC, 2000)

Combining the results in Tables 1, 2 and 3 and the mass of rust from MTS, according to Equation 2 gives an estimate of the radioactive contamination that might be on the walls of Tank 19. These results are shown in Table 4, with the results from 1975 corrected for radioactive decay.

Table 4. Estimate of Contamination on Tanks 19 Walls

Radionuclide	Activity, Ci
^{3}H	0
^{79}Se	2.2E-03
^{90}Sr[a]	4.6E-04[b]
^{99}Tc	0
^{134}Cs[a]	1.1E-04[b]
^{137}Cs[a]	200[b]
^{233}U	6.3E-02
^{234}U	4.1E-02
^{235}U	1.1E-04
^{236}U	4.2E-04
^{238}U	3.0E-03
^{237}Np	5.7E-04
Pu[a]	
^{238}Pu	1.7[b]
^{239}Pu	0.94[b]
^{238}Pu	0.44
^{239}Pu	0.19
^{240}Pu	<0.50
^{241}Pu	0.60
^{242}Pu	<8.3E-03
^{241}Am	<0.13

[a] from 1975 analysis of Tank 19 contents
[b] decay corrected from 1975

Conclusions

The radionuclide inventories shown in Table 4 are compared to the estimates of the residual heel (sludge plus supernate) in Tank 19 in Table 5. Table 5 also presents the results for the tank walls in terms of a percentage of the residual on the tank bottom. In the Tank Farm Closure Plan (WSRC 2002) an allotment of 20% of the bottom residual is given for ancillary equipment. One radionuclide exceeds this percentage, ^{234}U (4.1E-2 Ci). This small inventory will produce no measurable effect at the point of assessment. .

Using intermediate results provided by TTNUS, estimates were made of the seepline dose resulting from the activity estimated to be on the tank walls. Estimates were made assuming that the wall contamination was released the same way as assumed for ancillary equipment (no reducing grout, no basemat) and for the tank heel (reducing grout and basemat) and correcting for the difference in corrosion product K_d and tank residual K_d by multiplying by the ratio of the corrosion product K_d to the tank residual K_d. These results are presented and compared to the peak seepline doses for Tank 19 in Table 6. The peak seepline doses from the tank residual were modified from the TTNUS data to account for the inventory estimates by multiplying by the ratio of the new inventory to the old inventory. This shows that only one radionuclide (^{237}Np) believed to be in the tank wall corrosion products will reach the seepline in the 10,000 year period of interest with a concentration high enough to produce a discernable fraction of the performance objective. The estimated doses from the wall corrosion products are one to three orders of magnitude lower than reported in the Tank 19 Closure Module (modified to account for the new inventory estimates) and therefore should impact neither the conclusions of the closure plan nor any decisions based upon the Closure Module.

It should be noted that the K_d for Tc on goethite under alkaline conditions is 0 L/Kg, meaning that this radionuclide would not be expected to be associated with corrosion products in a high level waste tank. This is the radionuclide with the greatest dose contribution at the point of assessment. The new estimate

for Tc in the residual material (6.7 Ci) is a factor of 3.35 higher than the previous estimate (2.0 Ci), so the seepline dose is higher by the same amount, 0.12 mrem/year versus 0.034 mrem/year.

Table 5. Comparison of Estimated Wall Residual and Bottom Residual in Tank 19

Radionuclide	Wall Residual, Ci	Residual Sludge and Supernate, Ci[a]	Wall Residual as Percentage of Heel
^{3}H	0	3.8E-01	0%
^{79}Se	2.2E-03	5.7E-02	4%
^{90}Sr	4.6E-04[b,c]	4.0E+01	0%
^{99}Tc	0	6.8E+00	0%
^{134}Cs	1.1E-04[b,c]	7.5E-03	1%
^{137}Cs	200[b,c]	4.9E+04	0%
^{233}U	6.3E-02	9.2E-01	7%
^{234}U	4.1E-02	4.9E-02	84%
^{235}U	1.1E-04	1.3E-03	8%
^{236}U	4.2E-04	2.9E-03	15%
^{238}U	3.0E-03	4.2E-02	7%
^{237}Np	5.7E-04	1.1E-02	5%
Pu			
^{238}Pu	1.7[b,c]	2.3E+01	7%
^{239}Pu	0.94[b,c]	3.0E+01	3%
^{238}Pu	0.44	2.3E+01	2%
^{239}Pu	0.19	3.0E+01	1%
^{240}Pu	<0.50	1.1E+01	<5%
^{241}Pu	0.60	5.4E+01	1%
^{242}Pu	<8.3E-03	3.6E-01	<2%
^{241}Am	<0.13	1.2E+01	<1%

[a] from Tran, 2005
[b] from 1975 analysis of Tank 19 contents
[c] decay corrected from 1975

Table 6. Estimated Dose or Concentration from Wall Residual

Radionuclide	Wall Residual, Ci	Wall Dose as Heel, mrem/yr	Wall Dose as Equipment, mrem/yr	Peak Seepline Dose from Tank 19, mrem/yr
^{3}H	0	0	0	0
^{79}Se	2.2E-03	3.2E-06	3.1E-06	1.8E-03
^{90}Sr	4.6E-04	0	0	0
^{99}Tc	0	0	0	1.2E-01
^{134}Cs	1.1E-04	0	0	0
^{137}Cs	200	0	0	0
^{233}U	6.3E-02	0	0	0
^{234}U	4.1E-02	0	0	0
^{235}U	1.1E-04	0	0	0
^{236}U	4.2E-04	0	0	0
^{238}U	3.0E-03	0	0	0
		pCi/L	pCi/L	pCi/L
^{237}Np	5.7E-04	9.3E-03	1.3E-02	1.6E-01
Pu				
^{238}Pu	1.7	0	0	0
^{239}Pu	0.47	0	0	0
^{238}Pu	0.44	0	0	0
^{239}Pu	0.19	0	0	0
^{240}Pu	<0.50	0	0	0
^{241}Pu	0.60	0	0	0
^{242}Pu	<8.3E-03	0	0	0
^{241}Am	<0.13	0	0	0

References

Tran, H. Q. 2005. *Tank 19F Residual Material Radionuclide Inventories.* CBU-PIT-2005-00068, Revision 3, March 31, 2005.

Ohnuki, Toshihiko. 1991. *Characteristics of Migration of ^{85}Sr and ^{137}Cs in Alkaline Solution Through Sandy Soil.* Material Research Society Symposium Proceedings, Vol. 212.

Wiersma, B. J. 2002. *Calculation of Amount of Corrosion Product in HLW Tank 19,* SRT-MTS-2002-20004, Rev 1, Feb. 8, 2002.

WSRC. 2000. *Radiological Performance Assessment for the E-Area Low-Level Waste Facility*. Westinghouse Savannah River Company, Aiken, SC.

WSRC. 2002. Industrial Wastewater Closure Module for High Level Waste Tank 19 System, WSRC-TR-2002-00474.

ATTACHMENT A

E-mails

Jonathan02 Thomas

To: Jim Cook/WSRC/Srs@srs
cc:
Subject: Tank 19 wall fixed contamination issue

01/17/02 04:27 PM

Jim, here is the Tank 19 data from the historical Tank Levels Database (look at worksheet "Tk19"). Important notes from this data: the highest tank levels occurred in the 1970's before the bulk salt waste removal campaign in 1980-1981.


Tank levels database.x

Next, I've attached the sample database (mainly supernate samples) for Tank 19 (Location: \Wg08\waste8\SAMPLES\HLWTankChemistryFolderpler). Note that the only sample taken before the 1980 salt removal campaign that contains radionuclide concentration data is the one from 1975. In trying to estimate the Curie content of the salt historically present in Tank 19 pre-1980, Bob Hester told me that the salt contained almost no radionuclides and that the supernate in the tank contained all the dissolved radionuclides from the salt. Therefore, the 1975 supernate sample should theoretically give you data about the type of solution that was historically in contact w/ the walls (before 1980).


NTank19.xls

I will be out of the area this weekend, but if you have any questions tomorrow (Friday), you might try to reach Bruce Martin at 8-0498. I will be back in on Monday the 21st.

Jonathan L. Thomas
HLWE/Waste Removal Closure
(803) 208-0500

Jrbob Hester

02/06/02 10:10 AM

To: Jonathan02 Thomas/WSRC/Srs@Srs
cc: Bruce Martin/WSRC/Srs@Srs, Ed Stevens/WSRC/Srs@Srs, Jim Cook/WSRC/Srs@Srs, Neil Davis/WSRC/Srs@Srs, Noel Chapman/WSRC/Srs@Srs, Paul Dentremont/WSRC/Srs@Srs
Subject: Re: Tank 19F Se79 Estimate

After talking it over with Paul, I recommend that we use the following for Jim's Tank 19F rust calculations:

1. Actinide and tritium concentrations from the 2001 sample per his original calculation

2. Cs-137 concentration of 0.33 Ci/L (7.4E08 d/m/ml) from the 1975 dip sample

3. Se-79 concentration of 4.95E-06 Ci/L (1.1E04 d/m/ml), derived from the 1975 sample as shown below

4. Tc-99 concentration of 2.4E-03 Ci/L (5.4E06 d/m/ml), using a Tc-99/Cs-137 ratio of 7.2E-03 derived from the 1975 sample in the same way as Se-79

Bob Hester
Phone 80511
Pager 14214

Jonathan02 Thomas

02/05/2002 04:33 PM

To: Jrbob Hester/WSRC/Srs@Srs
cc: Bruce Martin/WSRC/Srs@Srs, Ed Stevens/WSRC/Srs@Srs, Jim Cook/WSRC/Srs@Srs, Paul Dentremont/WSRC/Srs@Srs, Noel Chapman/WSRC/Srs@Srs, Neil Davis/WSRC/Srs@Srs
Subject: Re: Tank 19F Se79 Estimate

When you convert Bob Hester's historical Tank 19 Se-79 concentration estimate of 1.1E04 d/m/ml, it equals a concentration of 4.95E-06 Ci/L. This is about 30% lower than the Se-79 concentration used in the last version of Jim Cook's report (7.00E-06 Ci/L).

Jrbob Hester

02/04/02 05:17 PM

To: Jim Cook/WSRC/Srs@srs, Paul Dentremont/WSRC/Srs@srs, Ed Stevens/WSRC/Srs@Srs, Bruce Martin/WSRC/Srs@Srs, Jonathan02 Thomas/WSRC/Srs@Srs
cc:
Subject: Tank 19F Se79 Estimate

I recommend using 1.1E04 d/m/ml Se79 in the Tank 19F PA. Here's why:

WSRC-TR-94-0564, Characterization of Radionuclides in HLW Sludge Based on Isotopic Distribution in Irradiated Assemblies, G. K. Georgeton and J. R. Hester, January 1995, Table III and IV indicates that Se79:Cs-137 in fresh waste is the same in PUREX versus HM waste, in high heat versus low heat waste, and in supernate versus sludge.

DPST-83-932, Demonstration of In-Tank Sludge Processing Part II: Effect of Processing on Radionuclides, R. E. Eibling and B. A. Hamm, October 1983, Table II.A.2, indicates that Se79:Cs-137 in aged mixed waste fromTanks 18F, 15H, and 21H supernate was 1.5E-05. DPST-83-695, Sample Analyses from the Full Scale In-Tank Demonstration of the Precipitation Process, D. D. Walker and B. A. Hamm, July 1983, Table I.D, indicates that Se79:Cs137 in aged salt solution in Tank 48H was between 1E-05 and 2E-05.

The foregoing results all agree, so using a ratio of 1.5E-05 and the 1975 Cs137 result for Tank 19F of 7.4E08 d/m/ml, yields 1.1E04 d/m/ml Se79.

This estimate is consistent with Tc99 results in the reports above and in WSRC-RP-93-1009, Composition of Tank Farm Supernate Samples, D. D. Walker, C. J. Coleman, and D. D. Walker, July 1993, Table II, which indicate that Tc-99 concentrations should be an order of magnitude or so higher than Se79.

Bob

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ATTACHMENT B

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Calculation of Selenium K_d on Goethite at pH 10

The K_d for Se on goethite in the E Area PA (WSRC 2000) of 170 L/Kg is based on a pH of 8. There is sufficient information in the PA to calculate a Kd at higher pH, up to 10. The actual pH when the tank was in active operation was even higher.

The curve of Se sorption vs. pH on page E-18 gives about 30% sorbed at pH 10.

Equation 1 on page E-4 is:

$K_d = SA\ X / r\ SA_{exp}(1-X)$, where

SA = specific surface area of the waste (32,000 cm^2/cm^3 for LAW vaults,

X = fraction sorbed,

r = bulk density of the waste (1.6 g/cm^3), and

SA_{exp} = concentration of solid in the adsorption experiment (cm^2/mL).

The curve on page E-18 give a percent sorbed of 0.3. The paragraph on Se on page E-10 says the SA_{exp} is 3806 cm^2/mL..

Using these values in the equation gives a K_d of 2.

As a check, using X = 0.97, as stated in the PA, gives the K_d of 170 in the PA.

Distribution

J. E. Marra, 773-A
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