REVIEW OF BRITISH NUCLEAR FUELS LIMITED, INC. DESIGN SAFETY FEATURES DELIVERABLE: HYDROGEN CONTROL IN HIGH-LEVEL WASTE STORAGE TANKS

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: CNWRA-generated original data contained in this report meets quality assurance requirements described in the CNWRA Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data.

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1 INTRODUCTION

This report provides the Center for Nuclear Waste Regulatory Analyses (CNWRA) staff assessment of the British Nuclear Fuels Limited (BNFL, Inc.) proposed design safety features for hydrogen control in the high-level waste (HLW) storage vessels (Edwards, 1999). The HLW storage vessels represent a potential explosive hazard because hydrogen is evolved by radiolysis in the aqueous radioactive wastes. The mixture of hydrogen and air can explode violently if an ignition source is present. National Fire Protection Association (NFPA) 69 limits the accumulation of hydrogen in air to less than 1/4 of the lower flammability limit (LFL) of 4 percent hydrogen by volume. BNFL, Inc. plans to transfer the contents of Tanks AZ–101 and AZ–102 into at least four different vessels, each containing approximately 1/4 concentration of the insoluble radionuclides. These solids will be stored for 1–2 yr before the HLW vitrification facility will be ready to accept solids for vitrification. In their calculations, BNFL, Inc. assumed the Best-Basis inventory for estimating hydrogen generation rates. While the Best-Basis inventory is an acceptable estimate for performing process calculations, the 90th percentile inventory should be used for designing the safety features to bound reasonable accident scenarios. To evaluate whether the BNFL, Inc. results are sufficiently conservative, the CNWRA staff reviewed the BNFL, Inc. calculations and proposed design safety features as well as a source document that provides radionuclide inventory and uncertainty estimates for Tanks AZ–101 and AZ–102. The staff independently reviewed the hydrogen generation calculations and assumptions in estimating hydrogen generation rates. In addition, staff reviewed the conservativeness associated with G-factors and the influence of organics on the hydrogen generation rate. Results, as discussed in the following chapters, indicate that hydrogen generation rates calculated using the Best-Basis inventory are nonconservative.

2 HYDROGEN GENERATION CALCULATIONS

BNFL, Inc. plans to transfer the contents of the Tanks AZ-101 and AZ-102 into four different vessels located in-cell in the BNFL, Inc. facility. Prior to storage, the waste in the tanks will be washed to remove soluble radionuclides. BNFL, Inc. assumes that radionuclides from the four tanks will be homogeneously distributed and equally partitioned, and has estimated a hydrogen generation rate of 68 L/hr (2.4 ft^3/hr) using the Best-Basis inventory. The assumption that the radionuclides are evenly distributed within the waste does not have a reasonable basis. BNFL, Inc. provided the rationale for this assumption in section 2.1.3 of Edwards (1999) based on the distribution of Sr in solids and the fact that the waste will be mixed before transfer; however, perfect mixing is not necessarily possible. Consequently, BNFL, Inc. should investigate the affect on their calculations of a higher percentage of the radionuclide inventory (30–35 percent) residing in a single tank.

In fiscal years (Fys) FY97 and FY98, the Pacific Northwest National Laboratory (PNNL) developed and tabulated estimates of the empirical probability distributions of the Hanford Tank Waste inventories to allow investigators to make uncertainty statements regarding the Standard Inventory Estimates (Ferryman et al., 1998). These files are also located in the TWINS database and can be downloaded to perform calculations (http://twins.pnl.gov.8001/). The radionuclide inventory was calculated using the Best-Basis Inventory Method and Uncertainty Method. The mean, median, standard deviation, and 1–99th percentile inventories were calculated using an Uncertainty Method. Because the Best-Basis Inventory Method and Uncertainty Method are different, the mean and median inventory values calculated from the Uncertainty Method may or may not match the Best-Basis Inventory Method. For some radionuclides, the inventory is one to two orders of magnitude different for the Uncertainty Method. For example, the Best-Basis Inventory Method estimate for ^{241}Am is 22,600 Ci, while the mean is 22,516 Ci and the median is 216 Ci, based on uncertainty analysis. The inventory table is reproduced here (table 2-1) as an example to show the Tank AZ-101 inventory based on the Best-Basis Inventory Method and the Uncertainty Method. Similar differences are observed in the Tank AZ-102 inventory. According to Ferryman et al. (1998), "Uncertainty estimates for which the Best-Basis inventory estimate falls between the 10^{th} and 90^{th} percentiles are confirmatory and probably reliable. When the Best-Basis inventory estimate lies in the tails of the distribution, there remains substantial concern regarding the information associated with both estimates. The Best-Basis Inventory and Uncertainty Methods are similar in approach but differ in implementation details and some of the specific data values. These differences may be due to different phase volumes, waste types, concentrations or density estimates." Review of these methods is beyond the scope of work of this report.

Table 2-2 shows the calculated total heat generation rates for selected radionuclides from Tanks AZ-101 and AZ-102 using the data available in the TWINS database. Also, included in the table are the heat generation rates calculated by BNFL, Inc. The radionuclides listed in the table are the radionuclides that were assigned by BNFL, Inc. as insoluble radionuclides present in the tanks. The total inventory is assumed to be homogeneously distributed in four vessels. Therefore, heat generation per tank will be 1.70E+04 W for $\beta\gamma$ radiation and 3.28E+02 W for α radiation. The hydrogen generation rate is given by the expression

Hydrogen generation rate (molecules/sec) = $G(H_2)_{\beta\gamma} \times (\text{total heat generation})_{\beta\gamma} + G(H_2)_{\alpha} \times (\text{Total heat generation})_{\alpha}$

Table 2-1. Tank AZ–101 inventory from Ferryman et al. (1998)

Analyte	Best-Basis Value	Standard Units of Measure	Basis	Uncertainty Analyte	Mean	Median	Standard Deviation	90th Percentile
Al	4.90E+04	kg	E	Al	3.34E+04	3.26E+04	1.44E+04	5.13E+04
Bi	—	kg	E	Bi	2.84E+02	1.55E+02	3.33E+02	7.70E+02
Ca	5.70E+02	kg	S	Ca	4.76E+03	1.81E+03	8.16E+03	1.30E+04
Cl^-	6.40E+02	kg	S	Cl^-	2.40E+03	7.11E+02	3.04E+03	6.97E+03
TIC as CO_3	1.07E+05	kg	S	CO_3	1.07E+05	1.07E+05	2.18E+04	1.35E+05
Cr	2.64E+03	kg	S	Cr	3.88E+03	1.78E+03	4.82E+03	1.10E+04
F	6.06E+03	kg	S	F	5.00E+03	5.01E+03	2.43E+03	8.17E+03
Fe	2.34E+04	kg	S	Fe	6.43E+03	4.82E+03	8.11E+03	1.33E+04
Hg	—	kg	E	Hg	1.00E+00	0.00E+00	1.00E+00	2.00E+00
K	1.57E+04	kg	S	K	2.94E+04	1.99E+04	3.25E+04	7.74E+04
La	8.90E+02	kg	S	La	4.20E+01	3.70E+01	3.50E+01	9.10E+01
Mn	5.22E+03	kg	S	Mn	4.28E+02	2.32E+02	4.96E+02	1.15E+03
Na	3.52E+05	kg	S	Na	3.25E+05	3.25E+05	7.35E+04	4.20E+05
Ni	1.36E+03	kg	S	Ni	1.20E+03	7.90E+02	1.40E+03	2.86E+03
NO_2^-	2.09E+05	kg	S	NO_2^-	1.73E+05	1.74E+05	7.54E+04	2.70E+05
NO_3^-	2.42E+05	kg	S	NO_3^-	1.90E+05	1.89E+05	1.11E+05	3.36E+05

Table 2-1. Tank AZ–101 inventory from Ferryman et al. (1998) (cont'd)

Analyte	Best-Basis Value	Standard Units of Measure	Basis	Uncertainty Analyte	Mean	Median	Standard Deviation	90th Percentile
Pb	4.55E+02	kg	E	Pb	6.98E+02	2.44E+02	9.09E+02	2.06E+03
PO_4^{3-}	4.72E+03	kg	S	PO_4^{3-}	3.94E+03	3.85E+03	2.51E+03	7.33E+03
Si	1.38E+03	kg	S	Si	2.50E+03	1.68E+03	4.92E+03	4.65E+03
SO_4^{2-}	5.75E+04	kg	S	SO_4^{2-}	5.84E+04	5.78E+04	5.50E+03	6.41E+04
Sr	1.17E+02	kg	S	Sr	6.83E+01	4.32E+01	7.52E+01	1.77E+02
TOC	6.06E+03	kg	S	TOC	4.76E+03	4.53E+03	3.46E+03	9.46E+03
U (Total)	2.46E+03	kg	S	U (Total)	1.17E+04	5.54E+03	1.60E+04	7.33E+05
Zr	8.24E+03	kg	S	Zr	2.60E+02	1.20E+02	3.15E+02	7.42E+02
^{3}H	4.00E+00	Ci	S	^{3}H	4.14E+00	4.00E+00	1.76E+00	6.67E+00
^{14}C	4.30E-01	Ci	S	^{14}C	4.46E-01	4.30E-01	2.76E-01	8.13E-01
^{59}Ni	1.99E+01	Ci	E	^{59}Ni	3.14E+01	1.99E+01	3.92E+01	7.82E+01
^{60}Co	4.61E+03	Ci	E	^{60}Co	3.42E+04	4.62E+03	1.44E+05	4.13E+04
^{63}Ni	2.30E+03	Ci	E	^{63}Ni	3.63E+03	2.30E+03	4.53E+03	9.04E+03
^{79}Se	4.13E+01	Ci	E	^{79}Se	4.33E+01	4.13E+01	1.74E+01	6.12E+01
^{90}Sr	6.36E+06	Ci	E	^{90}Sr	2.74E+06	6.24E+05	1.00E+07	6.10E+06
^{90}Y	6.36E+06	Ci	E	^{90}Y	2.80E+07	6.36E+06	1.02E+08	6.23E+07
^{93}Zr	1.99E+02	Ci	E	^{93}Zr	4.71E+02	1.99E+02	5.85E+02	1.37E+03

Table 2-1. Tank AZ–101 inventory from Ferryman et al. (1998) (cont'd)

Analyte	Best-Basis Value	Standard Units of Measure	Basis	Uncertainty Analyte	Mean	Median	Standard Deviation	90th Percentile
^{93m}Nb	8.74E+01	Ci	E	^{93m}Nb	2.07E+02	8.74E+01	2.57E+02	6.02E+02
^{99}Tc	1.10E+03	Ci	E	^{99}Tc	2.10E+03	1.10E+03	2.49E+03	5.71E+03
^{106}Ru	4.85E+04	Ci	S/E	^{106}Ru	1.44E+05	1.06E+05	1.90E+05	3.05E+05
^{113m}Cd	2.12E+03	Ci	E	^{113m}Cd	6.17E+03	2.12E+03	8.07E+03	1.82E+04
^{125}Sb	1.31E+05	Ci	E	^{125}Sb	2.53E+05	1.31E+05	3.04E+05	6.98E+05
^{126}Sn	6.57E+01	Ci	E	^{126}Sn	1.91E+02	6.57E+01	2.50E+02	5.65E+02
^{129}I	7.10E+00	Ci	S	^{129}I	2.40E+01	7.10E+00	3.05E+01	6.99E+01
^{134}Cs	4.34E+04	Ci	E	^{134}Cs	4.66E+04	4.34E+04	1.83E+04	6.47E+04
^{137}Cs	7.43E+06	Ci	E	^{137}Cs	6.09E+06	5.89E+06	1.11E+06	7.19E+06
^{137m}Ba	7.03E+06	Ci	E	^{137m}Ba	7.45E+06	6.93E+06	2.92E+06	1.03E+07
^{151}Sm	1.42E+05	Ci	E	^{151}Sm	2.19E+05	1.42E+05	2.48E+05	5.80E+05
^{152}Eu	2.73E+02	Ci	E	^{152}Eu	4.21E+02	2.73E+02	4.78E+02	1.12E+03
^{154}Eu	5.76E+04	Ci	E	^{154}Eu	8.87E+04	5.76E+04	1.01E+05	2.35E+05
^{155}Eu	7.15E+04	Ci	E	^{155}Eu	1.10E+05	7.15E+04	1.25E+05	2.92E+05
^{226}Ra	1.80E-04	Ci	E	^{226}Ra	3.02E-04	1.80E-04	3.46E-04	8.06E-04
^{227}Ac	1.00E-03	Ci	E	^{227}Ac	1.54E-03	1.00E-03	1.75E-03	4.09E-03
^{228}Ra	1.10E-08	Ci	E	^{228}Ra	2.18E-08	1.30E-08	2.50E-08	5.82E-08

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Table 2-1. Tank AZ–101 inventory from Ferryman et al. (1998) (cont'd)

Analyte	Best-Basis Value	Standard Units of Measure	Basis	Uncertainty Analyte	Mean	Median	Standard Deviation	90th Percentile
^{229}Th	1.20E-06	Ci	E	^{229}Th	2.60E-06	1.20E-06	3.67E-06	7.40E-06
^{231}Pa	3.10E-03	Ci	E	^{231}Pa	6.73E-03	3.10E-03	9.48E-03	1.91E-02
^{232}Th	1.61E-08	Ci	E	^{232}Th	3.47E-08	1.60E-08	4.89E-08	9.87E-08
^{232}U	4.46E-02	Ci	S/M	^{232}U	9.98E-04	4.60E-04	1.41E-03	2.84E-03
^{233}U	1.70E-01	Ci	S/M	^{233}U	5.86E-04	2.70E-04	8.25E-04	1.67E-03
^{234}U	1.18E+00	Ci	S/M	^{234}U	2.60E+00	1.20E+00	3.67E+00	7.40E+00
^{235}U	4.51E-02	Ci	S/M	^{235}U	9.55E-02	4.40E-02	1.35E-01	2.71E-01
^{236}U	9.59E-02	Ci	S/M	^{236}U	2.15E-01	9.90E-02	3.03E-01	6.11E-01
^{237}Np	1.96E+01	Ci	E	^{237}Np	1.48E+02	1.96E+01	7.45E+02	2.43E+02
^{238}Pu	1.65E+02	Ci	S	^{238}Pu	1.25E+03	1.65E+02	6.27E+03	2.05E+03
^{238}U	8.19E-01	Ci	S/M	^{238}U	1.78E+00	8.20E-01	2.51E+00	5.06E+00
^{239}Pu	9.58E+02	Ci	S	^{239}Pu	7.24E+03	9.58E+02	3.64E+04	1.19E+04
^{240}Pu	2.72E+02	Ci	S	^{240}Pu	2.06E+03	2.72E+02	1.03E+04	3.37E+03
^{241}Am	2.26E+04	Ci	E	^{241}Am	2.25E+04	2.17E+02	1.60E+05	1.99E+04
^{241}Pu	9.99E+03	Ci	S	^{241}Pu	7.55E+04	9.99E+03	3.80E+05	1.24E+05
^{242}Cm	2.54E+01	Ci	E	^{242}Cm	1.92E+02	2.54E+01	9.66E+02	3.15E+02
^{242}Pu	7.40E-02	Ci	E	^{242}Pu	5.59E-01	7.40E-02	2.81E+00	9.18E-01
^{243}Am	9.98E+00	Ci	E	^{243}Am	7.54E+01	9.98E+00	3.79E+02	1.24E+02

Table 2-1. Tanks AZ–101 inventory from Ferryman et al. (1998) (cont'd)

Analyte	Best-Basis Value	Standard Units of Measure	Basis	Uncertainty Analyte	Mean	Median	Standard Deviation	90th Percentile
^{243}Cm	4.36E+00	Ci	E	^{243}Cm	3.29E+01	4.36E+00	1.66E+02	5.41E+01
^{244}Cm	1.09E+02	Ci	E	^{244}Cm	7.77E+03	1.02E+02	3.88E+03	1.26E+03

E = Engineering assessment based
S = Sample based
M = Model based (Hanford defined waste)

Table 2-2. Calculated heat generation rate from Tanks AZ–101 and AZ–102 using Best-Basis inventory

Radionuclide	AZ–101 Inventory (Ci)	AZ–102 Inventory (Ci)	Total Inventory (Ci)	Total Inventory (Bq)	Heat Generation Rate (W/Bq)	Heat Generation (W)	BNFL, Inc. Estimated Heat Generation (W)
^{60}Co	4.61E+3	3.42E+3	8.03E-3	2.97E+14	4.16E-13 (βγ)	1.24E+2	1.24E+2
^{90}Sr	6.36E+06	3.70E+6	1.01E+7	3.72E+17	3.14E-14 (βγ)	1.17E+4	6.73E+4 (^{90}Sr and ^{90}Y)
^{90}Y	6.36E+06	3.70E+6	1.01E+7	3.72E+17	1.49E-13 (βγ)	5.55E+4	
^{152}Eu	2.73E+2	1.42E+02	4.15E+2	1.54E+13	1.22E-13 (βγ)	1.87E+0	1.53E+1
^{154}Eu	5.76E+4	2.31E+4	8.07E+4	2.99E+15	2.43E-13 (βγ)	7.26E2	1.45E+3
^{155}Eu	7.15E+4	2.66E+4	9.81E+4	3.63E+15	1.95E-14 (βγ)	7.08E+1	7.10E+1
^{233}U	1.70E-1	6.71E-2	2.37E-1	8.77E+9	7.68E-13 (α)	6.74E-3	6.73E-3
^{235}U	4.51E-2	1.77E-1	2.22E-1	8.22E+9	7.32E-13 (α)	6.02E-3	3.01E-2
^{237}Np	1.96E+1	1.17E+1	3.13E+1	1.16E+12	7.78E-13 (α)	9.01E-1	2.70E+0
^{238}Pu	1.65E+2	1.81E+2	3.46E+2	1.28E+13	8.81E-13 (α)	1.13E+1	1.13E+1
^{239}Pu	9.58E+2	1.25E+3	2.21E+3	8.17E+13	8.24E-13 (α)	1.23E+3	1.35E+2
^{241}Pu	9.99E+3	1.71E+4	2.71E+4	1.00E+15	8.38E-16 (α)	8.40E-1	8.4E-1
^{241}Am	2.26E+4	1.48E+4	3.74E+4	1.38E+15	8.86E-13 (βγ)	1.23E+3	1.23E+3
^{244}Cm	1.09E+2	4.21E+1	1.51E+2	5.59E+12	9.30E-13 (α)	5.20E+0	2.75E+1
					Total (βγ)	**6.81E+4**	**6.89E+4**
					Total (α)	**1.31E+3**	**1.40E+3**

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where

$G(H_2)_{\beta\gamma}$ = molecules of H_2 per 100 eV $\beta\gamma$ radiation absorbed
= 0.45 molecules/100 eV
= 2.81E + 16 molecules/joule

$(\text{total heat generation})_{\beta\gamma}$ = 6.81E + 4 W for 4 tanks
= 1.70E + 4 W per tank

$G(H_2)_{\alpha}$ = molecules of H_2 per 100 eV α radiation absorbed
= 1.57 molecules/100 eV
= 9.81E + 16 molecules/eV

$(\text{total heat generation})_{\alpha}$ = 1.31E + 3 W for 4 tanks
= 3.28E + 2 W per tank

Using these values, the hydrogen generation rate is given by

Hydrogen generation rate (molecules/s) = 2.81E+16 × 1.7E+4 + 9.81E + 16 × 3.28E + 2
= 5.11E+20 molecules/s

Assuming the hydrogen generation rate at standard pressure and temperature, the volume of hydrogen generated is given by

$$\text{Hydrogen generation rate (L / hr)} = \frac{5.11\text{E}+20\,\text{molecules / s} \times 22.4\,\text{L / mole} \times 60\,\text{s / hr}}{6.023\text{E}+23\,\text{molecules / mole}} = 68.4\,\text{L / hr}$$

Assuming a well mixed tank, the time required to reach 1 percent hydrogen in free space of 85,000 L in the tank is given by

$$\text{Time to reach 1 percent LFL} = \frac{85{,}000\ \text{L}}{68.4\ \text{L/hr} \times 100} = 12.4\ \text{hrs}$$

In this report, the hydrogen generation rate was also calculated for mean, median, and 90th percentile inventories. Also included is a scenario that represents 25 percent extra radionuclides in one tank. Table 2-3 shows the hydrogen generation rates and time required to reach 25 percent LFL (1 percent hydrogen in the tank). The hydrogen generation rates vary from 55 to 620 L/hr, with time required to reach 25 percent LFL from 1.4 to 15.4 hr. The analysis assumed the same set of radionuclides and G-factors for hydrogen generation as were used by the BNFL, Inc.

Given the uncertainty in radionuclide inventory, as observed in the standard deviation, the BNFL, Inc. estimate for hydrogen generation to reach 25 percent LFL is nonconservative. In addition, the calculations provided assume that standard temperature and pressure conditions are present in all materials in the tanks. The generated hydrogen may be released at elevated temperatures where the dilution air is injected, causing the hydrogen to occupy a larger volume fraction than the mole fractions would indicate. However, it is mentioned on page 4 of 7 of the calculation package that for operating systems, standard temperatures and pressures will be corrected for flow sheet conditions. That statement probably satisfies this concern as long as it is implemented in practice.

Table 2-3. Hydrogen generation rates

Inventory	Hydrogen generation rate L/hr (ft^3/hr)	Time to reach 25% LFL (hr)
Best-Basis inventory	68.4 (2.42)	12.4
Mean (Uncertainty Method)	224 (7.90)	3.80
Median (Uncertainty Method)	55.2 (1.95)	15.4
90^{th} percentile (Uncertainty Method)	495 (17.5)	1.72
90^{th} percentile with 25% extra radionuclide in one of the four storage tanks	619 (21.9)	1.37

Table 2-4 shows percent differences between the radionuclide inventories calculated using the Best-Basis Inventory Method, and the mean and median calculated using Uncertainty Methods. The Best-Basis inventory is closer to the median inventory than to the mean inventory. The mean values for several actinides are 400–500 percent higher compared to the Best-Basis inventory. ^{90}Y, which is a major contributor to the heat generation rate, has a 300 percent higher mean radionuclide inventory compared to Best-Basis inventory. The higher hydrogen generation rate of 224 L/hr calculated from the mean inventory estimates compared to 68.4 L/hr calculated from Best-Basis inventory estimate is attributed to the higher inventory of ^{90}Y.

Table 2-4. Percent difference between the Best-Basis, mean and median inventories for the combined Tanks AZ-101 and AZ-102

Radionuclide	Percent Difference between Best-Basis and Mean Inventory	Percent Difference between Best-Basis and Median Inventory
^{60}Co	-548%	12%
^{90}Sr	41%	84%
^{90}Y	-302%	0%
^{152}Eu	-55%	0%
^{154}Eu	-55%	0%
^{155}Eu	-119%	-41%
^{233}U	99%	100%
^{235}U	-14%	-40%
^{237}Np	-543%	0%
^{238}Pu	-498%	0%
^{239}Pu	-485%	0%
^{241}Pu	-465%	0%
^{241}Am	5%	97%
^{244}Cm	-528%	6%

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3 G-FACTOR ANALYSIS

There have been various sources for selecting $G(H_2)_{\beta\gamma}$ and $G(H_2)_{\alpha}$ values. Henrie et al. (1986) gives a $G(H_2)_{\beta\gamma}$ for pure water of 0.45. Kasten (1991) compiled $G(H_2)_{\beta\gamma}$ values from the literature—the values range from 0.41 to 0.70, with a median of 0.45. The standard textbook by Spinks and Woods (1990) cites two values of $G(H_2)_{\beta\gamma}$, 0.40 and 0.45, taken from two sources. Kasten (1991) compiled literature on $G(H_2)_{\alpha}$ values—the values range from 1.3 to 4.6, with a median of 1.9. The higher values are from the older literature. Spinks and Woods (1990) cites a $G(H_2)_{\alpha}$ value of 1.57 from experiments using ^{210}Po α-particles (5.3 MeV) as the radiation source.

None of these references provided a critical evaluation of uncertainties in $G(H_2)_{\beta\gamma}$ and $G(H_z)_{\alpha}$ data, hence, it is not possible to make a determination whether the use of a $G(H_2)_{\beta\gamma}$ of 0.45 and a $G(H_2)_{\alpha}$ of 1.57 by BNFL, Inc. is or is not conservative. However, those values are reasonable, given the spread in the data and the stochastic nature of radiolysis reactions.

4 HYDROGEN GENERATION FROM ORGANICS IN THE TANK

There are two key generation mechanisms for H_2 production in Hanford tank wastes: radiolysis of water and organic compounds and thermal degradation of organics. The BNFL, Inc. analysis accounts for H_2 generation from radiolysis of water only. However, the tank inventory data taken from the TWINS2 database indicate that Tanks AZ-101 and AZ-102 each contain about 6,000 kg of total organic carbon (TOC). The contribution of thermal and radiolytic degradation of organic compounds needs to be accounted for in the safety analysis pertaining to H_2 gas.

In the absence of H_2 gas generation rates from organic degradation (radiolytic and thermal) specific to AZ-101 and AZ-102 tank wastes, preliminary calculations can use the data from Meisel (1991) for radiolytic H_2 generation derived from synthetic Hanford wastes (using γ-radiation). To a good approximation, Meisel (1991) found $G(H_2)$ to vary linearly with the molar concentration of the organic compound:

$$\mathbf{G(H_2) = G(H_2)_{[RH=0]} + R_2 \times [RH]} \qquad (4\text{-}1)$$

where R_x (units of G values per mole) is the conversion efficiency for organic X, values of which are given in Meisel (table B3-1, 1993), and [RH] is the molar concentration (M, moles/L) of organic X. In the absence of information on the identities of the organic compounds in Tanks AZ-101 and AZ-102 wastes, the R_x value of 0.167 for EDTA is used in the calculations shown next. The same assumption was used by Graves (1994) in evaluating the flammable gas hazard in Hanford waste tanks. Graves (1994) also noted that $G(H_2)$ predicted from Eq. (4-1) for tank SY-101 is low compared to the value calculated from the measured rate of hydrogen generation in Tank SY-101 and the tank heat load. Graves (1994) used a factor of 1.55 to account for the underprediction.

The value of 0.031 molecules/100 eV for $G(H_2)_{[RH=0]}$ (no organic present) was measured by Meisel (1993) for a Hanford synthetic waste containing 2.79 M nitrate and 2.2 M nitrite. This value is low compared to the G value for pure water because of the high nitrate and nitrite concentrations. For the purposes of this analysis, nitrate and nitrite concentrations are assumed to be zero and $G(H_2)_{[RH=0]}$ is set equal to $G(H_2)$ for pure water (0.45 molecules/100 eV of ionizing radiation). Thus, for this analysis, the following equation is used to calculate $G(H_2)$ from radiolysis of water and organics:

$$\mathbf{G(H_2)_{(\beta\gamma)}(molecules/100\ eV) = 0.45 + 0.167 \times 1.55 \times [RH]} \qquad (4\text{-}2)$$

Tanks AZ-101 and AZ-102 have approximately 6,000 kg TOC each—a total of 12,000 kg TOC that will be transferred into four holding tanks (4101C) after washing. Using the BNFL, Inc. assumption that each 4101C holding tank is filled to its operating volume of 197,000 L and assuming that all the organics are EDTA ($C_{10}H_{16}N_2O_8$), the molar concentration of EDTA is given by

$$\mathbf{[RH]\ (moles/L) = \frac{12{,}000\ kg\ TOC}{4\ tanks} \times \frac{1{,}000\ g}{1\ kg} \times \frac{1\ mole\ C}{12\ g\ C} \times \frac{1\ mole\ EDTA}{10\ mole\ C} \times \frac{1}{197{,}000\ L}} \qquad (4\text{-}3)$$

$$\mathbf{[RH]\ (moles/L) = 0.127\ moles/L\ EDTA}$$

thus,

$G(H_2)_{(\beta\gamma)}$ = 0.48 molecules/100 eV

No data is available to calculate the effect of alpha-radiation on H_2 generation by organic degradation.

For the current analysis, the contribution of thermal degradation of organics to the generation of H_2 gas can be neglected because of the relatively low concentration (0.127 M) of organics in the 197,000 L of waste feed. For example, the analysis by Graves (1994) for Tank AZ-101, which had a mean TOC concentration of 0.12 g/L, indicated that H_2 generation by thermal degradation of organics is less than 1 percent of the H_2 generation by radiolysis of organic compounds. On the other hand, the results of Graves (1994) indicate that for tank AZ-102, with a mean TOC of 1.59 g/L, the thermal generation of H_2 gas is about 11 percent of the H_2 generation by radiolysis. Thus, thermal degradation of organics could be important if the concentration of organic compounds is higher than the value assumed in this analysis, or if the temperature is much higher than that considered for this analysis (25 °C).

5 INSOLUBILITY OF RADIONUCLIDES

Radionuclides present in the Best-Basis inventories for Tanks AZ-101 and AZ-102 were reviewed for their insolubility under anticipated tanks conditions. CNWRA agrees with the inclusion of Co, Sr, Y, U, Eu, Np, Pu, Am, and Cm as insoluble species in the calculations. It is not evident why some isotopes of U, Pu, Am, and Cm are not included in the calculations—BNFL, Inc. should provide a basis for these exclusions. These isotopes may have been excluded because of their low heat production, but this is uncertain absent a thorough review. Note that an estimate of solubility depends strongly on solution chemistry, kinetics, and the particular solids present. Thus, only an educated guess can be made because the final chemistry of the washed solids is not known at this time. Other elements that could conservatively be considered insoluble and should have been included in the calculations are Zr, Nb, Cd, Sn, Sm, Ra, Ac, Th, and Pa. The radionuclide ^{106}Ru and ^{125}Sb could probably be neglected due to the short half-life of 1 yr for ^{106}Ru and 2.8 yr for ^{125}Sb. Based on the radionuclide solubility data, the radionuclides H, C, Ni, Se, Tc, I, and Cs are expected to be removed from the sludge during sludge wash. The most questionable inclusion in this list is Ni. BNFL, Inc. should provide the basis for its inclusion as a soluble radionuclide.

Hydrogen and the heat generation rates were recalculated based on the additional insoluble radionuclides determined based on their solubility. The additional power that would be generated, if the additional insoluble radionuclides present in the Tanks AZ-101 and AZ-102 were considered in the waste, would have minimal affect on the hydrogen generation rate (less than a 1 percent increase). Primarily, the heat from insoluble elements in the tanks comes from the decay of ^{90}Sr and its daughter ^{90}Y (^{137}Cs/^{137}Ba is the other major heat producer, but Cs is soluble and Ba decays quickly after the Cs is removed). The only element that BNFL, Inc. has not considered that contributes more than 100 W (compared to 69,400 W total) is ^{125}Sb (870 W).

6 NONCONFORMITY IN SELECTION OF RADIONUCLIDES FOR ANALYSIS

Review of the data indicates that the radionuclides selected for calculating the hydrogen generation rate (Excel spreadsheet, Edwards, 1999) are different compared to the radionuclides used for calculating dose rates to the workers, colocated workers, and the public (table 2, Calc–W375–NS00001, Edwards, 1999). The two tables should be consistent.

7 DOSE CONVERSION FACTORS

The inhalation dose conversion factor used by the licensee to calculate the impacts of the accident does not use the most conservative lung clearance class. The BNFL, Inc. uses a lung clearance class of D, which yields a dose conversion factor of 6.47E-8 Sv/Bq, whereas a lung clearance class of Y for the radionuclide yields a dose conversion factor of 3.51E-7 Sv/Bq. Industry practice is to use the most conservative lung clearance class unless evidence is available indicating the chemical forms present at the site will correspond to a less conservative lung clearance class.

8 HYDROGEN IN VESSEL VENTILATION SYSTEM

The hydrogen control strategy selected by BNFL, Inc. employs an active vessel vent system (AVVS) designed to maintain the hydrogen concentration in the vessel vapor space at <1 vol. % (4 vol. % is the LFL). In addition, a passive vessel vent system (PVVS) will be employed in case of failure of the AVVS and will be used to maintain the hydrogen concentration in the vessel vapor space at <4 vol. %. The PVVS will use the buoyancy of hydrogen to draw in dilution air from the process cell. The AVVS will be designed for a probability of failure of $<10^{-2}$/yr, and the PVVS will have a failure rate of $<10^{-4}$/yr. During a failure of the AVVS, the residual hydrogen in the vessel vent system will separate from the offgas due to buoyancy. This separation can form hydrogen rich pockets in the offgas piping, scrubber, filters, fans, and the like. These pockets will need to be cleared safely during restart of the AVVS. The BNFL, Inc. design and operating procedures should therefore be examined to verify that there is adequate provision to safely clear the hydrogen rich pockets during restart of the AVVS. In addition, the slope of the offgas lines, as shown in figure 3 (Edwards, 1999), indicates that a hydrogen rich pocket will tend to form in the AVVS fan (i.e., the fan appears to be at the high point). If this fan is of a positive displacement design (e.g., dual lobe blower), it will seal in the offgas, trapping the hydrogen; whereas, a centrifugal fan design will allow passage of the offgas onward toward the stack. The design of the proposed fan will therefore play a part in the hydrogen control strategy with regard to restart of the AVVS.

According to the BNFL, Inc. proposed conceptual design, the AVVS will be a common vessel ventilation system servicing the headspace in all the Tank Waste Remediation System-P process vessels. Multiple vessels will discharge through a common header. This implies that hydrogen-bearing offgas from the HLW storage vessels will mix with vapors generated in other process vessels. Further, during a failure of the common vessel ventilation system, a potential exists for hydrogen rich pockets to contact exhaust gases from the other process vessels on line. The BNFL, Inc. processes, when details become available, should be examined to ensure that either of these scenarios does not constitute a safety hazard.

9 REFERENCES

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