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Ms. Trais Kliphuis, Staff Manager
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, New Mexico 87505-6303

Subject: Transmittal of Requested Information

Dear Ms. Kliphuis:

Enclosed is the information you recently verbally requested pertaining to an estimation of the gas generation rate of some remote-handled TRU mixed waste streams. The enclosed describes the waste streams and the method used to estimate gas generation.

If you have any questions regarding this information, please contact me at (575) 234-7488.

Sincerely,

George T. Basabilvazo

George T. Basabilvazo, Director
Office of Environment, Safety & Health

Enclosure

cc: w/ enclosure
C. Smith, NMED *ED
CBFO M&RC
*ED denotes electronic distribution

Estimation of a Worst Case Hydrogen Generation Rate from Potential RH TRU Waste in Future WIPP Panels

February 4, 2014

Prepared by

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1 Purpose and Scope

The purpose of this paper is to provide a worst case estimate of the hydrogen gas generation from radiolysis of the potential future remote-handled transuranic (RH TRU) waste inventory to be disposed of in a Waste Isolation Pilot Plant (WIPP) panel. The potential RH TRU waste forms, listed in the 2013 Annual Transuranic Waste Inventory Report (ATWIR-2013) (Reference 1), are used in defining a worst case RH TRU waste inventory in a future panel. Potential waste streams are waste streams that currently cannot be disposed of at the WIPP facility; however, with further action, such as additional characterization, decision-making and/or regulatory changes, they may become eligible for disposal at the WIPP facility. The purpose of this paper is to estimate the worst case effect on radiolytic hydrogen generation in a future waste panel if these potential waste streams were eventually disposed in the WIPP facility.

A multi-year monitoring program in Panels 3 and 4 has recorded concentrations of hydrogen and methane in these panels. A statistical analysis of the monitoring data in Panels 3 and 4 is presented in Reference 2. The panel monitoring results from Panel 4 (which is the only one of the two panels that includes RH TRU waste) are used, along with the potential RH TRU waste inventory, to estimate the relative contributions of RH TRU and contact-handled transuranic (CH TRU) wastes to the total hydrogen concentration in a future panel.

2 Estimation of Potential Future RH TRU Waste Inventory

In terms of overall inventory, a future panel can hold a maximum of 650 m^3 (or 730 RH TRU canisters) of RH TRU waste and a maximum of 19,750[1] m^3 of contact-handled (CH) TRU waste (Reference 3). Therefore, RH TRU waste is approximately 3.2% of the volume capacity of a future panel. The potential future RH TRU waste inventory is defined by Table 4-1 of the ATWIR-2013 (Reference 1), which summarizes the potential RH TRU waste streams that may be destined for disposal at the WIPP and their associated final form anticipated volumes. All but one of the RH TRU waste streams are solid organic waste forms (e.g., heterogeneous debris). Waste Stream IN-SBW-01A, Sodium-Bearing Waste Treatment Steam Reforming Carbonate Waste Form, is a solidified inorganic waste in its final form. The final waste form is a carbonate waste form dried to 1% moisture. Waste Stream IN-SBW-01A composes 54.5% of the potential RH TRU waste inventory. The remaining 45.5% of the potential RH TRU waste inventory is composed of solid organic waste forms.

One debris (solid organic and inorganic) waste stream (identified as RL300-11) in the potential RH TRU inventory contains radioactivity contamination about three orders of magnitude above the others and represents the worst case waste stream in the potential RH TRU inventory with respect to wattage and the potential for having a high flammable gas generation rate (FGGR). The RL300-11 waste stream is included in the potential RH TRU inventory because of a regulatory restriction. Specifically, the RL300-11 exceeds the Land Withdrawal Act limit of 23 curies/liter for RH TRU waste allowed to be disposed of at the WIPP facility. According to the

[1] Maximum CH TRU waste is derived from the maximum values identified in Permit Part 4 Table 4.1.1 plus an additional 1,000 m^3 allowable from Permit Part 4, Section 4.1.1.2.i.

ATWIR-2013, the final form volume for waste stream RL300-11 is 7.5 cubic meters; however, to comply with the 23 curie/liter limit, this 7.5 cubic meters would have to be packaged in more canisters than the physical volume requires. The radioactivity content in the RL300-11 waste stream is also subject to other packaging limitations for transport in the RH TRU 72-B shipping package as follows:

- A 50 watt limit per canister
- Radiation dose curie limits associated with the shielding capability of the RH-TRU 72-B Cask

Of these restrictions, the most limiting for this waste stream is from the curie limits associated with the RH-TRU 72-B Cask shielding. Specifically, the requirements for shipment of RH TRU waste in RH-TRU 72-B shipping package limits the amount of cesium-137 (Cs-137) in a canister to a maximum value of 1.268×10^{3} (Reference 4). Using the Cs-137 activity concentration presented in the ATWIR-2013 for the RL300-11 waste stream, the Cs-137 curie limitation would require more than the 730 canister maximum allowed in a panel.

Therefore, the worst case composition of a future WIPP panel will be assumed to consist of 730 canisters of waste stream RL300-11. This is considered a worst case evaluation for the following reasons:

- The future panel is assumed to contain the maximum amount of the highest activity and wattage waste stream (i.e., contains 730 canisters of RL300-11)
- While the high wattage RH300-11 waste stream appears to be predominantly inorganic (lower gas generation potential), the gas generation potential for typical debris waste is conservatively used in this evaluation.

3 Estimation of Hydrogen Gas Generation Rate from Potential RH TRU Waste Inventory in a Future Panel

The flammable (hydrogen) gas generation rate (FGGR), in units of g-mole H_2 per second, from the RH TRU waste in a panel can be determined as follows (Reference 5):

$$FGGR = W * G * C \qquad \text{(Equation 1)}$$

where,

W = Total RH TRU decay heat per panel (watts)

G = Number of molecules of H_2 gas produced per 100 eV of energy absorbed

C = Conversion constant [1.04×10^{-7} (g-mole) (100 eV) / (molecule) (watt-sec)]

For the inventory established in the previous section, an estimate of the G value and wattage can be made as discussed in the following sections.

3.1. *IN-SBW-01A Waste Stream*

Waste Stream IN-SBW-01A is an inorganic carbonate waste form with maximum moisture content of 1%. A bounding G value for water has been established as 1.6 (Reference 6). Therefore, a bounding G value for this waste form (with 1% water) is estimated as 1% of the bounding G value for water, or:

$$G = 0.01 * 1.6 = 0.016.$$

The wattage of a canister containing IN-SBW-01A waste has been determined from the typical isotopic composition for this waste stream (Reference 1). For this waste stream, a typical canister decay heat is 0.71 watts and a typical FGGR for a canister is calculated to be 1.18×10^{-9} g-mole H_2 per second.

3.2. *Typical Solid Organic Waste Streams*

The typical solid organic waste streams contain organic debris and are the primary RH TRU waste form that has been disposed of at the WIPP facility to date. Individual drum headspace hydrogen sampling data are available for a portion of this inventory (215 drums) and have been used to calculate an average G value for the population using the hydrogen concentrations and decay heat values (Reference 7). G values were calculated for individual drums (solving for G using Equation 1) with the following assumptions:

- If the hydrogen and/or methane were reported only at the method detection limit (MDL), one-half the MDL value was used.
- Half of the reported decay heat error was added to the decay heat value for each drum in calculating the G value.

These assumptions represent the probable or average values and are valid over the relatively large population of canisters per future panel (for example, when a measurement is below the MDL, it could vary between zero and the MDL with the midpoint or one half the MDL representing a probable value).

The average G value calculated for the RH TRU solid organic waste population from this methodology is 0.044.

From the RH TRU solid organic waste drums disposed of at the WIPP facility to date, the average decay heat per canister is 0.52 watts (Reference 7) and the average FGGR per canister is calculated as 2.38×10^{-9} g-mole H_2 per second.

3.3. RL300-11 Waste Stream

This waste stream contains predominantly inorganic debris (lower gas generation potential) with some organic debris, but conservatively the gas generation potential for this waste stream is assumed to be that of the typical solid organic waste streams discussed in Section 3.2. The average G value for the RL300-11 waste stream is therefore estimated to be 0.044.

The wattage of a canister containing RL300-11 waste has been determined from the typical isotopic composition for this waste stream (Reference 1). For this waste stream, a typical canister decay heat is 2.47 watts and a typical FGGR for a canister is calculated to be 1.13×10^{-8} g-mole H_2 per second.

4 Results and Discussion

Using Equation 1 and the variable values established above, the FGGR for RH TRU waste in a future panel is 8.25×10^{-6} g-mole H_2 per second (see footnote to Table 1 for numerical calculation). For comparison, the FGGR from CH TRU waste in a panel was previously estimated as 4.50×10^{-5} g-mole H_2 per second (Reference 8). The estimated percent contribution from RH TRU waste to the total FGGR in a future panel can, therefore, be estimated as ≈15.5%.

The concentration of hydrogen and methane accumulating in Panels 3 and 4 have been monitored for more than four years, with the results of this monitoring analyzed statistically in Reference 2. As shown in Reference 2, both Panels 3 and 4 showed very low concentrations of hydrogen and no measurable methane. A maximum measured mean concentration in Panel 4, which includes RH TRU waste, is 531 ppm (Reference 2). This is a conservative estimate given the more recent decreasing trend in hydrogen concentration in the panel over time. Panel 3 is not considered here because it does not have RH TRU waste.

Panel 4 contains 198 canisters of RH TRU waste. The waste in these canisters is composed of solid organic waste with an estimated G value of 0.044 (see Section 3.2). The total decay heat in these canisters is 8.11 watts (Reference 7) and the calculated FGGR[2] for the RH TRU waste in Panel 4 is 3.71×10^{-8} g-mole H_2 per second. The estimated percent contribution from RH TRU waste in Panel 4 is 0.082% (i.e., $3.71\times10^{-8}\times100/(3.71\times10^{-8}+4.50\times10^{-5})$). Therefore, the estimated RH contribution to the 531 ppm maximum mean H_2 concentration obtained from Panel 4 is 0.4 ppm and the calculated CH TRU contribution is 530.6 ppm.

The worst case contribution of RH TRU waste in a future panel can be estimated from the Panel 4 monitoring data and the RH TRU hydrogen generation rate estimate for a future panel. A future WIPP panel will contain the RH TRU waste inventory described in Section 3 in a maximum of 730 canisters. The hydrogen monitoring results from Panel 4 can be scaled up to reflect the larger RH TRU waste inventory of a future panel.

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[2] (8.11 watts)(0.044 molecules H_2/100 eV)(1.04×10-7 (g-mole) (100 eV)/(molecule) (watt-sec)) = 3.71×10^{-8} g-mole H_2 per second in Panel 4.

In case the RL300-11 waste stream is not disposed of at the WIPP facility, a more typical case was also evaluated. This typical case does not include the emplacement of any canisters containing waste stream RL300-11. Instead, the typical case consists of 730 canisters filling a single future panel where 54.5% of the 730 canisters contain waste stream IN-SBW-01A and 45.5% of the 730 canisters contain typical solid organic waste forms rounded to the nearest whole number. The specific composition of the 730 canisters is as follows:

- 398 canisters of Waste Stream IN-SBW-01A
- 332 canisters of solid organic waste forms

The estimates of the contribution of RH TRU waste for both the worst case and typical case scenarios of the future waste inventory are shown in Table 1.

Table 1. Estimates of Worst Case and Typical Case RH TRU Waste Contributions to Hydrogen Concentration in Future Panels

Future Panel RH TRU Inventory Composition	RH FGGR (g-moles/s)	RH $[H_2]$ Contribution to Future Panel	% of Total Panel H_2
WORST CASE 730 Canisters RL300-11	8.25×10^{-6} [a]	97.3 ppm H_2 [c]	15.5%
TYPICAL CASE 398 canisters ID-SWB-01A 332 canisters of Solid Organic Waste	1.25×10^{-6} [b]	14.8 ppm H_2	2.7%

[a] $(1.13\times10^{-8})(730) = 8.25\times10^{-6}$ moles H_2 per second per panel

[b] $(1.18\times10^{-9})(398)+(2.36\times10^{-9})(332) = 1.25\times10^{-6}$ moles H_2 per second per panel

[c] The estimated contribution of the potential RH TRU waste streams to the total FGGR in a future panel is 15.5%, and the H_2 contribution from CH TRU waste is 530.6 ppm, based on data from Panel 4. Then (RH contrib.)(RH contrib. + CH contrib.) = 0.155, and solving for the RH contribution, RH contrib. = (0.155/(1 – 0.155)*CH contrib.= (0.155)/(1 – 0.155)*(530.6 ppm) = 97.3 ppm.

The results show that the worst case hydrogen concentration contribution of RH TRU waste to flammable gas generation in a future panel will be less than the CH TRU waste contribution. The contribution will be approximately 2.4% of the action level of 4,000-ppm hydrogen, and approximately 0.24% of the lower explosive limit of 40,000-ppm hydrogen.

The results in Table 1 show that the typical case hydrogen concentration contribution of RH TRU waste to flammable gas generation in a future panel will be insignificant. The contribution will be approximately 0.37% of the action level of 4,000-ppm hydrogen and approximately 0.037% of the lower explosive limit of 40,000-ppm hydrogen.

It should be noted that the higher dose rate for RH TRU waste (compared to CH TRU waste) does not correlate to a higher gas generation potential. As an example, a high dose (gamma-emitting) radionuclide, packaged directly in a metal container like a drum, can have a high surface dose rate with no hydrogen generation if there are no materials present, such as plastics or water, that are a source of hydrogen generation from radiolysis.

5 Summary and Conclusions

The estimated worst case contribution of the potential RH TRU waste inventory to the total hydrogen gas generation rate in a given future WIPP panel is expected to be less than the currently set action levels in the Permit. This is due to the following reasons:

- The RH TRU waste volume allowed in a panel is a very small percentage of the total waste inventory in a panel.
- The gas generation potential (G value) of the future RH TRU waste forms is low. For example, the potential Waste Stream IN-SBW-01A from INL, regardless of expected high surface dose rate, contains no organic materials, and less than 1% moisture, thereby, minimizing the potential for hydrogen gas generation.
- Hydrogen monitoring data from Panel 4, which includes RH TRU waste, indicates that the contribution of RH TRU waste to the hydrogen in a panel will be below conservatively established action levels.
- Hydrogen generation rates estimated in Table 1 are assumed to remain constant over time. In reality, as the waste matrix is depleted of hydrogen content, the G values and hydrogen generation rates are expected to decrease asymptotically to very low values – i.e., gas generation decreases with increasing dose (in units of watt-years).

6 References

1. U.S. Department of Energy, "Annual Transuranic Waste Inventory Report – 2013," DOE/TRU-13-3425, Revision 0, October 2013, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico.
2. URS Professional Solutions, LLC, "Statistical Analysis to Evaluate Methane and Hydrogen Concentrations in Filled Panels at the Waste Isolation Pilot Plant," Revision 2, August 2013, URS Professional Solutions, LLC, Aiken, South Carolina.
3. Waste Isolation Pilot Plant Hazardous Waste Facility Permit, NM 4890139088-TSDF, issued by the New Mexico Environment Department
4. U.S. Department of Energy, Table 3.2-2 of "Remote-Handled Transuranic Waste Authorized Methods for Payload Control," Revision 2, November 2013, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico
5. U.S. Department of Energy, Appendix 2.1 of "RH-TRU Payload Appendices," Revision 2, September 2013, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico.
6. U.S. Department of Energy, Appendix 2.2 of "RH-TRU Payload Appendices," Revision 2, September 2013, U.S. Department of Energy, Carlsbad Field Office, Carlsbad, New Mexico.
7. WIPP Waste Data System (WDS)

8. Letter from M. Devarakonda to D. Mercer (DOE-CBFO), dated July 26, 2006, subject: Estimation of Hydrogen Generation Rates from Radiolysis in WIPP Panels