AN ALTERNATIVE TO PERFORMING REMOTE-HANDLED TRANSURANIC WASTE CONTAINER HEADSPACE GAS SAMPLING AND ANALYSIS

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ABSTRACT

The Waste Isolation Pilot Plant (WIPP) is operating under a Resource Conservation and Recovery Act (RCRA) Hazardous Waste Facility Permit (HWFP) for contact-handled (CH) transuranic (TRU) waste. The HWFP contains limitations on allowable emissions from waste disposed in the underground. This environmental performance standard imposed on the WIPP consists of limiting volatile organic compound (VOC) emissions from emplaced waste to ensure protection of human health and the environment. The standard is currently met by tracking individual waste container headspace gas concentrations, which are determined by headspace gas sampling and analysis of CH TRU waste containers.

The WIPP is seeking a HWFP modification to allow the disposal of remote-handled (RH) TRU waste. Because RH TRU waste is limited to approximately 5% of the waste volume and is emplaced in the disposal room walls, it is possible to bound the potential RH TRU waste contribution to VOC emissions using conservative upper bounds. These conservative upper bounds were developed as an alternative to RH TRU waste canister headspace gas sampling and analysis.

The methodology used to perform the calculations used to evaluate VOC emissions from emplaced RH TRU waste canisters applied the same equations as those used to evaluate VOC emissions in the original HWFP application. This approach was taken because the processes that will contribute to VOC emissions from the RH TRU waste canisters are the same as those originally evaluated for CH TRU waste containers. However, because RH TRU waste canisters are located in the walls of the disposal rooms behind shield plugs (as opposed to being stacked on the disposal room floor), the actual methodology applied was the same as that used for waste in a closed room.

Based upon the conservative assumptions used to bound the potential for VOC emissions from RH TRU waste, the calculations show that the RH TRU waste could contribute a maximum of 0.09% to 8.23% of the emissions limit for any of the VOCs of concern. Because these contributions from the RH TRU waste are so small, the existing allowable maximum VOC emissions rates in the HWFP can be reduced to account for the RH TRU waste emissions indirectly. This accomplished by conservatively incorporating the maximum potential VOC contribution from RH TRU waste in the maximum allowable VOC emission limits established by the HWFP. This approach eliminates the need for any direct measurements of the headspace gases in RH TRU waste canisters.
INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is operating under a Resource Conservation and Recovery Act (RCRA) Hazardous Waste Facility Permit (HWFP) that contains limitations on allowable emissions from contact-handled (CH) transuranic (TRU) waste. The environmental performance standard imposed on the WIPP consists of controlling volatile organic compound (VOC) emissions to ensure the public and facility worker safety. The environmental performance standard for VOC emissions is based on the container headspace gas concentration, filter type, number of containers emitting, and the mine ventilation rate. All of these factors were considered in the requirements specified in the Permit.

The waste disposal area within WIPP consists of eight panels, each containing seven rooms between access drifts. The RH TRU wastes will be emplaced in a manner different from that for the CH TRU wastes because of packaging, shielding, and loading requirements; operational equipment; and structural considerations. The current disposal configuration of the CH TRU inventory includes emplacement of the waste packages in disposal rooms that measure 33 ft wide, 13 ft high, and 300 ft long (1). The current configuration for RH TRU disposal includes emplacement into the walls in horizontal boreholes. These boreholes will be drilled 4 feet from the floor on 8-foot centers (1). There will be approximately 7,955 RH TRU waste boreholes. A shield plug capping each borehole after emplacement of the RH TRU canister in the room wall will provide the necessary shielding required for worker safety. Appendix A of the Remote-Handled Transuranic Waste Study (2) includes a description of the RH TRU shield plug currently planned for implementation.

METHODOLOGY

The processes that will contribute to VOC emissions from the RH TRU waste canisters are the same as those evaluated for CH TRU waste. Therefore, the calculations used to evaluate VOC emissions from emplaced RH TRU waste canisters will use the same equations as those used to evaluate VOC emissions in the original permit application. However, because RH TRU waste canisters are located in the walls of the rooms behind shield plugs, the actual methodology is the same as that used for waste in a closed room.

RH TRU waste canisters will not release VOCs into the underground ventilation the same way as CH waste containers in an active room. The RH waste is placed in a dead-end borehole that is capped by a low-permeability shield plug. Because the RH TRU waste canister is in a dead-end borehole with a shield plug, mine ventilation will not pass over the canister as it does for containers on the floor of an active room. This lack of ventilation causes an emplaced RH TRU waste canister with a shield plug to release VOCs similarly to a closed room.

A closed room uses ventilation barriers to restrict the flow of mine ventilation through a filled room. The shield plugs on each borehole containing an RH TRU waste canister will function similarly to the ventilation barriers. The shield plugs will restrict the movement of mine ventilation and diffusion of VOCs from the borehole just as the ventilation barriers will restrict the movement of mine ventilation and diffusion from a filled room.

The RCRA Part B permit application demonstrated that gas pressurization is the primary mechanism that might cause VOCs to migrate out of a closed room. Based on this analysis, the WIPP’s Hazardous Waste Facility Permit establishes VOC limits for operations. Therefore, the analysis of the emissions from an emplaced canister in a shield plug capped dead-end borehole results in the maximum credible gas pressurization rate per borehole and the per room potential maximum VOC emission rates from the RH TRU waste following the existing closed room methodology.

As a bounding conservative assumption, all canister headspaces are assumed to have saturated VOC concentrations at the temperature of WIPP. Pressurization within a borehole will be caused by a combination of
gas generation and reduction of the borehole due to creep closure of the salt (3), which might result in VOC emissions from the canister into the room.

**VOC CONCENTRATIONS IN THE RH TRU WASTE CANISTER HEADSPACE**

The VOC concentrations in the canister headspace are assumed to be equal to the saturated vapor pressure concentrations. This is the maximum concentration in the gas phase that can occur at the temperature in the underground at the WIPP. In addition, physical interactions of the VOCs within the liquid phase are ignored because these would reduce the concentrations in the gas phase. The saturated vapor concentrations of the VOCs are calculated from the vapor pressures at the temperature of WIPP (i.e., at 303 K) (4).

The vapor pressures of the VOCs at 303 K were calculated using Equation 1 from Appendix A of Reid et al. (5) as:

\[
\ln \left( \frac{P_{vp}}{P_c} \right) = (1 - x)^{-1} \left[ (VP_A)x + (VP_B)x^{1.5} + (VP_C)x^3 + (VP_D)x^6 \right]
\]  

where,

- \( x = 1 - T/T_c \)
- \( P_{vp} = \) VOC vapor pressure at 303 K, (bars)
- \( P_c = \) VOC critical pressure, (bars)
- \( T_c = \) VOC critical temperature, (K)
- \( T = \) Temperature of WIPP disposal room (303 K)

The critical pressures and temperatures of the VOCs as well as the coefficients VP A, VP B, VP C, VP D required for Eq. 1 are listed in Table I.

There are no vapor pressure coefficients available for 1,1-dichloroethene. The vapor pressure of this VOC was interpolated from a vapor pressure table for this compound from the *Handbook of Chemistry and Physics* (6). The relevant values are listed in Table II. In interpolating the vapor pressure at 303 K, the relationship that the logarithm of the vapor pressure is inversely proportional to the temperature (7) was used as shown in the following equation.

\[
\frac{1/287.8 - 1/303}{1/287.8 - 1/304.7} = \frac{\log 400 - \log P_{vp}(303)}{\log 400 - \log 760}
\]  

Solving for the vapor pressure of 1,1-dichloroethene at 303 K, \( \log P_{vp}(303) \) gives

\[
\log P_{vp}(303) = 6.572 \quad (E q. 3)
\]

\[
P_{vp}(303) = 715 \text{ mm Hg} = 715 \text{ mmHg} / (760 \text{ mmHg/atm}) = 0.9408 \text{ atm} \quad (E q. 4)
\]

The methodology used to calculate the vapor pressure concentration for each of the VOCs in the gas phase ignores the effects of the other VOCs present. This is another conservative assumption because, in reality, interference from other VOCs will cause the actual concentrations to be less than the saturated vapor pressure concentrations in air. In addition, no credit is taken for the diffusion of the filters or any source reduction resulting in a steady state concentration being assumed behind the shield plug. Therefore, the gas being emitted into the room is conservatively assumed to constantly be at the saturated vapor pressure concentrations.
### Table I. VOC Properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>Properties of Gases &amp; Liquids App. A No.</th>
<th>MW (g/mol)</th>
<th>Tc (K)</th>
<th>Pc (bar)</th>
<th>VP A</th>
<th>VP B</th>
<th>VP C</th>
<th>VP D</th>
<th>x from Eq. 1 for VP</th>
<th>ln(Pvp/Pc) from Eq. 1 for VP</th>
<th>Pvp (bar)</th>
<th>Pvp (atm)</th>
<th>VOC Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carcinogens</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>94</td>
<td>153.84</td>
<td>556.4</td>
<td>45.6</td>
<td>-7.07139</td>
<td>1.71497</td>
<td>-2.8993</td>
<td>-2.49466</td>
<td>0.4554277</td>
<td>-5.4897228</td>
<td>0.1883</td>
<td>0.1858</td>
<td>0.1858</td>
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<tr>
<td>Chloroform</td>
<td>103</td>
<td>119.39</td>
<td>536.4</td>
<td>53.7</td>
<td>-6.95546</td>
<td>1.16625</td>
<td>-2.1397</td>
<td>-3.44421</td>
<td>0.435123</td>
<td>-5.1186177</td>
<td>0.3214</td>
<td>0.3172</td>
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<tr>
<td>1,1-Dichloroethene</td>
<td>None</td>
<td>96.95</td>
<td>513</td>
<td>48.1</td>
<td>-7.35739</td>
<td>2.17546</td>
<td>-4.07038</td>
<td>3.50701</td>
<td>0.4058824</td>
<td>-4.511202</td>
<td>0.6921</td>
<td>0.6830</td>
<td>0.6830</td>
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<td>1,2-Dichloroethane</td>
<td>158</td>
<td>98.97</td>
<td>566</td>
<td>53.7</td>
<td>-7.36864</td>
<td>1.76727</td>
<td>-3.34295</td>
<td>-1.4353</td>
<td>0.4646643</td>
<td>-6.0037215</td>
<td>0.1326</td>
<td>0.1309</td>
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<td>Methylene Chloride</td>
<td>107</td>
<td>84.94</td>
<td>510</td>
<td>63</td>
<td>-7.35739</td>
<td>2.17546</td>
<td>-4.07038</td>
<td>3.50701</td>
<td>0.4058824</td>
<td>-4.511202</td>
<td>0.6921</td>
<td>0.6830</td>
<td>0.6830</td>
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<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>143</td>
<td>167.86</td>
<td>661.2</td>
<td>58.4</td>
<td>-7.98542</td>
<td>2.49931</td>
<td>-4.07076</td>
<td>-0.6918</td>
<td>0.5417423</td>
<td>-8.7160059</td>
<td>0.0096</td>
<td>0.0094</td>
<td>0.0094</td>
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<tr>
<td>1,1,1-Trichloroethane</td>
<td>149</td>
<td>133.42</td>
<td>545</td>
<td>43</td>
<td>-7.31317</td>
<td>2.04642</td>
<td>-3.77747</td>
<td>-0.45475</td>
<td>0.4440367</td>
<td>-5.3528837</td>
<td>0.2036</td>
<td>0.2009</td>
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<td><strong>Noncarcinogens</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Chlorobenzene</td>
<td>340</td>
<td>112.56</td>
<td>632.4</td>
<td>45.2</td>
<td>-7.587</td>
<td>2.26551</td>
<td>-4.09418</td>
<td>0.17038</td>
<td>0.5208729</td>
<td>-7.6709981</td>
<td>0.0211</td>
<td>0.0208</td>
<td>0.0208</td>
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<tr>
<td>Toluene</td>
<td>400</td>
<td>92.13</td>
<td>591.8</td>
<td>41</td>
<td>-7.28607</td>
<td>1.38091</td>
<td>-2.83433</td>
<td>-2.79168</td>
<td>0.4880027</td>
<td>-6.7421505</td>
<td>0.0484</td>
<td>0.0478</td>
<td>0.0478</td>
</tr>
</tbody>
</table>

### Table II. 1,1-Dichloroethene Vapor Pressures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (K)</th>
<th>Vapor Pressure (Pvp) (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.8</td>
<td>287.8</td>
<td>400</td>
</tr>
<tr>
<td>31.7</td>
<td>304.7</td>
<td>760</td>
</tr>
</tbody>
</table>
NUMBER OF RH TRU WASTE CANISTERS IN A ROOM

The first step in establishing the total rate of gas pressurization from RH TRU waste canisters is to establish the number of RH TRU waste canisters per room. Based on Figure 4.2-7 of the WIPP RH PTSR (8), a typical panel will have 730 RH boreholes. Room 1 of a panel will have the most boreholes i.e. 120 RH. As a conservative assumption, the calculations will use this maximum number.

GAS GENERATION MECHANISMS

Based on existing studies, potential gas generation mechanisms include: 1) Microbial degradation of plastics, 2) Anoxic corrosion of metal, 3) Radiolysis of waste materials, and 4) Gas displacement due to creep closure of the salt borehole.

The potential for and magnitude of each mechanism on VOC emissions from the RH TRU waste canisters are discussed below.

Microbial Gas Generation

Microbial gas generation due to degradation of plastics produces 0 to 0.04 mole/kg cellulosics/yr. under humid conditions. (4). The total mass of equivalent cellulosics is given by Equation 6 of Gas Generation Information (8) as:

\[
Total\ cellulosics (kg) = actual\ cellulosics (kg) + 1.7\ plastics (kg) + rubbers (kg)
\]

(Eq. 5)

The materials in the RH inventory are obtained from the Transuranic Waste Baseline Inventory Report, Revision 3 (9) and are summarized in Table III.

Table III. Mass of Cellulose, Rubber, Plastic and Cellulosics Equivalents in RH Inventory

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass in RH Inventory (kg)</th>
<th>Equivalent Cellulosics (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>(1.2036 \times 10^5)</td>
<td>(1.2036 \times 10^5)</td>
</tr>
<tr>
<td>Rubber</td>
<td>(0.2336 \times 10^5)</td>
<td>(0.2336 \times 10^5)</td>
</tr>
<tr>
<td>Plastic</td>
<td>(1.2815 \times 10^5)</td>
<td>(2.1786 \times 10^5)</td>
</tr>
<tr>
<td>Total</td>
<td>(2.7187 \times 10^5)</td>
<td>(3.6158 \times 10^5)</td>
</tr>
</tbody>
</table>

The number of RH TRU waste canisters to be disposed at WIPP is assumed to be 7,955 (2). Therefore the average mass of cellulosics per RH TRU waste canister is \(3.6158 \times 10^5\) kg cellulosics / 7,955 canisters or 45.4 kg cellulosics / RH TRU waste canister. Assuming a microbial gas generation rate of 0.01 mole/kg cellulosics/year, which is the same rate used for CH TRU waste under humid conditions in Appendix D9 of the WIPP RCRA Part B Permit Application (3), the microbial gas generation rate (MGGR) of a single RH TRU waste canister is:

\[
MGGR = \left(0.01 \text{ mole} / \text{kg cellulosics} / \text{yr}\right)45.4 \text{ kg cellulosics} / \text{RH canister}
\]

(Eq. 6)

\[
MGGR = 0.45 \text{ mole} / \text{yr} / \text{RH canister}
\]

Anoxic Corrosion

Anoxic corrosion of iron and aluminum alloys in TRU waste has the potential to consume water and produce hydrogen, assuming several repository conditions are present (4). The primary conditions that must be satisfied
for anoxic corrosion to occur are (1) sufficient quantities of brine from the surrounding Salado Formation enter the WIPP disposal rooms after closure and/or (2) initial water in the waste is available. Gas generation rates from anoxic corrosion for CH TRU and RH TRU wastes are similar because there are no significant differences between these waste forms that would directly influence corrosion.

RH TRU corroible metals (i.e., RH TRU iron, aluminum, and waste packaging) will contribute 6 percent by mass and 31 percent by weight assuming a corroible shield plug to the total corroible metal content (i.e., all TRU iron, aluminum, and waste packaging) of the repository. However, if sufficient brine is available, microbial degradation will produce carbon dioxide and/or hydrogen sulfide (in addition to other gases) that could potentially passivate steels and other iron-base alloys and thus prevent additional hydrogen production and water consumption from anoxic corrosion of these waste metals. Further, small amounts of brine could initiate anoxic corrosion, which will produce hydrogen, consume water, increase the pressure, and perhaps slow or prevent additional brine inflow or even cause brine outflow, thus impeding additional anoxic corrosion and hydrogen generation. Thus, the availability of water in the WIPP repository will limit anoxic corrosion and therefore hydrogen generation, regardless of the quantity of CH TRU and RH TRU steels and other iron-base alloys and packaging materials included in the WIPP inventory. Therefore, the anoxic humid steel corrosion rate during the operational period of the WIPP for the cases with microbial gas generation is 0.0 mm/yr. or 0.0 mole/yr.

Radiolysis of Waste Materials

Gas generation from alpha radiolysis is not as important as anoxic corrosion and anaerobic microbial degradation because results from radiolysis studies indicate that gas generation rates from alpha radiolysis are substantially lower than rates from anoxic corrosion and anaerobic microbial degradation. Given the high energies of the gamma rays and the fairly low density of the waste matrix, only a small fraction of the gamma energy will actually be deposited within the waste. The majority of radiolytic gas production is attributable to alpha and beta radiation, similar to that for CH TRU wastes. Because the RH TRU waste contains lower percentages of cellulosics, rubber, and plastic materials than in CH TRU wastes, the potential for radiolysis in RH wastes is actually somewhat lower than that for CH wastes. Preliminary data on gas generation measurements of RH TRU waste canisters at the Los Alamos National Laboratory indicate very low rates of gas generation and in fact the consumption rate of oxygen in the canisters may be higher than the net rate of gas generation. Because radiolysis of CH TRU waste materials has been shown to be insignificant relative to anoxic corrosion and microbial gas generation, radiolysis of RH TRU waste materials will also be insignificant relative to these mechanisms.

Gas Displacement

The rate of gas displacement within the RH TRU waste canister borehole excavation is based on the data from the WIPP Part B Permit Application, Appendix D9 Exposure Assessment for Protection of the Atmosphere. Specifically, the percentage volume reduction rate of the borehole is conservatively assumed to be the same percentage as the reduction in panel volume. Because the borehole geometry is cylindrical and the dimensions are much smaller than the panel, the actual borehole volume reduction rate will actually be smaller than that based on the panel value.

According to Appendix D9, the reduction of the panel void volume is 812 m$^3$/yr/panel. The initial panel volume is calculated from the following equation:

$$V(0)_{panel} = 7hlw + 12hw + 14hw^2$$

(Eq. 8)
where,
- \( h \) = height of room (13 ft)
- \( w \) = width of room (33 ft)
- \( l \) = length of room (300 ft)
- \( d \) = width of pillar (100 ft)

and the initial panel volume is:

\[
V(0)_{\text{panel}} = 1,613,898 \text{ ft}^3 / \text{panel} = 45,700 \text{ m}^3 / \text{panel} \tag{Eq. 9}
\]

The percentage volume reduction, PVR is calculated as:

\[
PVR = \frac{812 \text{ m}^3 / \text{panel} / \text{yr}}{45,700 \text{ m}^3} \times 100\% = 1.778\% / \text{year} \tag{Eq. 10}
\]

This percentage volume reduction will be applied to the borehole to calculate the molar (gas) displacement rate.

**VOLUME OF BOREHOLE**

The diameter of a borehole excavation will be 30 in or 76.2 cm. Thus the radius of the excavation, \( r_{\text{borehole}} \), will be 38.1 cm. The length of a borehole, \( l_{\text{borehole}} \), is 16 ft or 487.68 cm (2). Thus, the initial volume of the borehole excavation will be:

\[
V(0)_{\text{borehole}} = \pi r_{\text{borehole}}^2 l_{\text{borehole}} = \pi (38.1 \text{ cm})^2 (487.68 \text{ cm}) (\text{fm}^3 / 10^6 \text{ cm}^3) = 2.2240 \text{ m}^3 \tag{Eq. 11}
\]

**EXTERNAL VOLUME OF CANISTER**

The dimensions of the canister and pintle are shown in Figure 1 (2).

The external volume of the canister is calculated as:

\[
V_{\text{canister}} = \pi r_{\text{canister}}^2 l_{\text{canister}} = \pi (26 \text{ in} / 2)^2 (12 \text{ in} - 6.2 \text{ in}) = 60,951 \text{ in}^3 \tag{Eq. 12}
\]

The volume occupied by the pintle is:

\[
V_{\text{pintle}} = \pi [(6.6 \text{ in} / 2)^2 (5.1 \text{ in}) + (9.1 \text{ in} / 2)^2 (1.1 \text{ in})] = 246 \text{ in}^3 \tag{Eq. 13}
\]

Thus, the total volume occupied by the canister and pintle is 61,197 in\(^3\) or 1.0028 m\(^3\).

**EXTERNAL VOLUME OF SHIELD PLUG**

The dimensions of the shield plug and pintle are shown in Figure 2 (2).

The external volume of the shield plug is calculated as:

\[
V_{\text{shieldplug}} = \pi r_{\text{shieldplug}}^2 l_{\text{shieldplug}} = \pi (29 \text{ in} / 2)^2 (70 \text{ in}) = 46,236 \text{ in}^3 = 0.7577 \text{ m}^3 \tag{Eq. 14}
\]
Canister

Fig. 1. Dimensions of Canister and Pintle

Note:
Drawing Not to Scale
* These are nominal estimates which support the inventory assessment for corrodible metals.
Fig. 2. Dimensions of Shield Plug and Pintle

Note:
Drawing Not to Scale
* These are nominal estimates which support the inventory assessment for corrodiible metals.
The volume occupied by the pintle is 246 in$^3$. Thus, the total volume occupied by the shield plug and pintle is 46,482 in$^3$ or 0.7617 m$^3$.

**Void Volume Inside Borehole**

The void volume within the excavation at time, $t$, is calculated as:

$$V_v(t) = V_{borehole}(t) - (V_{canister} + V_{pintle}) - (V_{shield plug} + V_{pintle})$$

(Eq. 15)

The initial void volume is calculated as:

$$V_v(0) = 2.2240 m^3 - 1.0028 m^3 = 0.4595 m^3$$

(Eq. 16)

The borehole void volume at 1 year is calculated as:

$$V_v(1 \ yr) = 2.1844 m^3 - 1.0028 m^3 = 0.4199 m^3$$

(Eq. 17)

The reduction of the borehole excavation void volume in one year is therefore 0.4595 m$^3$ – 0.4199 m$^3$ or 0.0396 m$^3$/yr.

The volumetric reduction rate is converted into a molar (gas) displacement rate (GDR) using the ideal gas law as:

$$GDR = 0.0396 m^3 / yr \times \frac{P}{RT}$$

(Eq. 18)

$$GDR = (0.0396 m^3 / yr)\times(10^3 L / m^3) \times \frac{1 \ atm}{0.08206 \ atm L (mol K)}(303 K)$$

(Eq. 19)

$$GDR = 1.59 \ mol / yr$$

(Eq. 20)

**Total Gas Pressurization Rate**

The total gas pressurization rate or effective gas generation rate (microbial gas generation rate plus gas displacement rate) per RH TRU waste canister borehole is calculated as follows, which is analogous to Equation D9-3 from Appendix D9, *Exposure Assessment for Protection of the Atmosphere* (3):

$$GR = MGGR + GDR$$

(Eq. 21)

or

$$GR = 0.45 \ mol / yr + 1.59 \ mol / yr = 2.04 \ mol / yr$$

(Eq. 22)

**Maximum RH TRU waste canister VOC Emission Rates**

The individual canister VOC emission rate is calculated as:

$$ICER_{VOC} = GR \times MF_{VOC}$$

(Eq. 23)
where,
\[
\text{ICER}_{\text{VOC}} = \text{Individual canister VOC emission rate (mole/canister/year)}
\]
\[
\text{GR} = \text{Effective canister total gas generation (i.e., pressurization) rate (2.04 mole/canister/year)}
\]
\[
\text{MF}_{\text{VOC}} = \text{VOC mole fraction in canister headspace (dimensionless)}
\]

The total emission rate of a VOC into a room from all canisters is calculated as:
\[
\text{TCER}_{\text{VOC}} = N_c \cdot \text{ICER}_{\text{VOC}}
\]  
(Eq. 24)

where,
\[
N_c = \text{Number of RH TRU waste canisters per room (120 canisters)}.
\]

RESULTS

The allowable room emission rates for the VOCs from a disposal room are summarized in Table IV. VOC concentrations in the canister headspace based on saturated vapor pressure values are listed in the third column of Table 4. The individual RH TRU waste canister VOC emission rates, ICER, and the maximum potential VOC emission rates for all RH TRU waste canisters in a room, TCER, are listed in Columns 4 and 5 of the table. The individual TCER values were divided by the allowable VOC room emission rates to establish the magnitude of the RH TRU waste canister emissions contributions. The percentages contributions range from 0.09% for chlorobenzene to 8.23% for 1,1-dichloroethene.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Current Maximum Allowable VOC Emission Rate (mole/room/year)</th>
<th>Vapor Pressure VOC Concentration (ppmv)</th>
<th>Canister Emission Rate (ICER) (mole/canister/year)</th>
<th>Room Emission Rate (TCER) (mole/room/year)</th>
<th>Percentage of Current Maximum Allowable Room Emission Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>4,250</td>
<td>185,800</td>
<td>0.379</td>
<td>45.5</td>
<td>1.07%</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4,860</td>
<td>317,200</td>
<td>0.650</td>
<td>77.6</td>
<td>1.60%</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2,800</td>
<td>940,800</td>
<td>1.930</td>
<td>230</td>
<td>8.23%</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1,160</td>
<td>130,900</td>
<td>0.268</td>
<td>32.0</td>
<td>2.76%</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>53,650</td>
<td>683,000</td>
<td>1.40</td>
<td>167</td>
<td>0.31%</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>1,300</td>
<td>9,400</td>
<td>0.0194</td>
<td>2.3</td>
<td>0.18%</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>14,880</td>
<td>200,900</td>
<td>0.412</td>
<td>49.2</td>
<td>0.33%</td>
</tr>
<tr>
<td>Noncarcinogens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5,500</td>
<td>20,800</td>
<td>0.0426</td>
<td>5.10</td>
<td>0.09%</td>
</tr>
<tr>
<td>Toluene</td>
<td>4,780</td>
<td>47,800</td>
<td>0.0979</td>
<td>11.7</td>
<td>0.24%</td>
</tr>
</tbody>
</table>

IMPLEMENTATION

To conservatively account for potential VOC emissions from RH TRU waste, the current maximum allowable VOC emission rate values must be reduced by subtracting the maximum potential room emission rate from RH TRU waste (TECR from Table IV) from the current maximum allowable VOC emission rate for a room. Therefore, the maximum allowable VOC emission rates currently in the permit should be adjusted to reflect the potential contributions from RH TRU waste as shown in Table V.
Table V. Maximum VOC Emission Rates Accounting for Potential RH TRU Waste Emissions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Current Maximum Allowable VOC Emission Rate (mole/room/year)</th>
<th>Adjusted Maximum Allowable VOC Emission Rate (mole/room/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carcinogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>4,250</td>
<td>4,204</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4,860</td>
<td>4,782</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>2,800</td>
<td>2,569</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1,160</td>
<td>1,127</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>53,650</td>
<td>53,482</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>1,300</td>
<td>1,297</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>14,880</td>
<td>14,830</td>
</tr>
<tr>
<td>Noncarcinogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5,500</td>
<td>5,494</td>
</tr>
<tr>
<td>Toluene</td>
<td>4,780</td>
<td>4,768</td>
</tr>
</tbody>
</table>

CONCLUSION

A conservative approach to calculating the potential VOC emissions from RH TRU waste in a room was developed to bound the effects of RH TRU waste on total room emissions. Based upon the conservative assumptions used to bound the RH TRU waste VOC emissions, the RH TRU waste could contribute a maximum of 0.09% (for chlorobenzene) to 8.23% (for 1,1-Dichloroethene) for any of the VOCs of concern. Because the contributions from the RH TRU waste are so small, the existing maximum VOC emissions rates were reduced to account for the RH-emissions indirectly. This approach eliminates the need for any direct measurements of the headspace gases in RH TRU waste canisters by conservatively incorporating the maximum possible VOC contribution from RH TRU waste in the maximum allowable VOC emission limit in the Permit.

REFERENCES


