Vapor Sampling of the Headspaces of Radioactive Waste Storage Tanks

D. A. Reynolds
Nicholas W. Kirch
Westinghouse Hanford Company

J. L. Huckaby
Pacific Northwest National Laboratory

Date Published
May 1966

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse Hanford Company
Management and Operations Contractor for the U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release; distribution is unlimited
LEGAL DISCLAIMER
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced from the best available copy.

Printed in the United States of America

DISCLM-2.CHP (1-91)
Vapor Sampling of the Headspaces of Radioactive Waste Storage Tanks
10. LEGENDS/NOTICES/MARKINGS (Required by WMC-CM-3-4 or Reviewer). Reviewer indicates applicable markings to be affixed or removed.

<table>
<thead>
<tr>
<th>AFFIX</th>
<th>REMOVE</th>
<th>INITIALS</th>
<th>AFFIX</th>
<th>REMOVE</th>
<th>INITIALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Technology</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Availability - OSTI</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Availability - ESTSC</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Availability - NTIS</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Business-Sensitive Information</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Computer Software Notice</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Copyright License Notice</td>
<td>☒</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Export Controlled Information</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Legal Disclaimer</td>
<td>☒</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td>Limited Disclosure</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
<td>☐</td>
</tr>
</tbody>
</table>

11. MANDATORY COMMENTS (List only mandatory comments here. All other comments shall be made on the document and returned to the author.)

<table>
<thead>
<tr>
<th>REVIEWER (PRINT &amp; SIGN)</th>
<th>DATE</th>
<th>RESOLVED BY AUTHOR/REQUESTOR (PRINT &amp; SIGN)</th>
<th>DATE</th>
</tr>
</thead>
</table>

12. ADDITIONAL INFORMATION/COMMENTS:

______________________________
______________________________
______________________________
______________________________
______________________________
______________________________

A-0001-401R (07/94)
VAPOR SAMPLING OF THE HEADSPACES OF RADIOACTIVE WASTE STORAGE TANKS

Daniel A. Reynolds
Westinghouse Hanford Company
P. O. Box 1970
Richland, Washington 99352
(509) 373-3115

James L. Huckaby
Pacific Northwest National Laboratory
P. O. Box 999
Richland, Washington 99352
(509) 376-5524

Nicholas W. Kirch
Westinghouse Hanford Company
P. O. Box 1970
Richland, Washington 99352
(509) 373-2380

ABSTRACT

At the Hanford Site in southeast Washington State, 177 underground storage tanks have been built since 1943 to store radioactive waste. During the period of 1944 to 1989, wastes were generated from the reprocessing of nuclear fuel and the recovery of radioisotopes. The acidic liquid wastes were neutralized with sodium hydroxide for storage in mild steel, underground storage tanks. The radioactive waste in the tanks at the Hanford Site is composed mostly of water, sodium nitrate, sodium nitrite, sodium aluminate, and sodium hydroxide, with many other compounds in lesser amounts. The waste also contains organic molecules resulting from chelating agents used to recover fission products or solvents that became entrained in the waste through liquid-liquid extraction processes. These organic compounds appear to play a large role in the tanks’ headspace compositions.

Two major classes of waste tanks exist at the Hanford Site: double-shell and single-shell tanks. The 28 double-shell tanks have positive ventilation. Although a few of the 149 inactive single-shell tanks have positive ventilation, most are passively ventilated.

It has always been expected that the waste in the tanks will produce hydrogen gas from the radiolysis of water. It should be pointed out that nitrate ion, which is plentiful in the waste, provides some protection to the water from the radiolysis. The result is that all tanks are assumed to generate hydrogen at some low rate. Evaluations and measurements have been performed to determine if radiolytically-produced hydrogen can accumulate in the tank headspaces. As expected, the measurements show values of hydrogen well below the lower flammability limit.

In the early 1980s, waste tank surface levels were observed to rise, which led to the conclusion that gas was accumulating within the waste. A few of the double-shell tanks released this accumulated gas in a short period of time in what is termed a gas release event or a "burp." In one tank, 241-SY-101, enough hydrogen-containing gas was released that on brief occasions, the tank’s headspace exceeded the lower flammability limit for hydrogen. This tank was deemed hazardous enough that it has since been mitigated by using a pump to periodically force jets of liquid through the waste to cause a controlled release of the accumulated gas. Additional tanks are being evaluated as potentially storing gas.

In addition to the hydrogen problem, certain tanks give off foul-smelling or noxious vapors. Since 1980, a number of workers have complained of adverse health effects from these noxious vapors. This issue did not surface prior to 1980 because most tanks were ventilated. Most of the single-shell tanks were removed from active ventilation after 1980, and the foul-smelling vapors accumulate in the tanks and are released when workers access the tanks and when the tanks "breathe." Ammonia seems to be a major contributor when a foul smell is reported.

Certain tanks were also identified as having the potential for a separable-phase-organic layer on the waste. One tank, 241-C-103, has been shown to have a liquid organic layer about 5 cm (2 in.) deep. The organic layer has been determined to be predominately tributyl phosphate in solution with semivolatile normal paraffin hydrocarbons. There was a concern that the organic liquid may have a high enough vapor pressure that a flammable atmosphere may be created in the tank headspaces.
The potential problems of hydrogen generation, noxious vapors, and liquid organics have led to the current tank headspace sampling program at the Hanford Site. The first two tanks that received extensive vapor sampling were tank 241-SY-101 and tank 241-C-103. Tank 241-SY-101 became the test bed for a number of on-line instruments. At various times, a gas chromatograph, on-line mass spectrometer, solid state hydrogen monitor, FTIR (Fourier Transform Infrared spectrometer), and radio acoustic ammonia monitor have been installed on tank 241-SY-101. In addition, grab samples have been used extensively for off-line analysis. Tank 241-C-103 has had grab samples taken cryogenically and with heated sample lines.

Currently, standard hydrogen monitors have been installed on those tanks that have the potential for hydrogen storage in the waste. The monitors are continuous, and provisions have been made to take grab samples for calibration.

Grab samples from the tank headspaces are also collected from tanks that do not have continuous monitoring equipment. These samples allow identification and quantitation of the priority inorganic and organic gases and vapors for tank safety screening, tank farm industrial hygiene worker protection, and environmental regulatory compliance.

Currently, 47 (about one third) of the tank headspaces have been characterized. Results confirm that the predominant waste gases and vapors present are ammonia, carbon dioxide, hydrogen, and nitrous oxide. Nitrogen gas, also expected to be released from the waste, cannot be differentiated from the natural levels of nitrogen in the air. The presence of hydrogen, ammonia, and nitrous oxide are important to flammability concerns. Table 1 shows the gases that have been found in the largest quantities. These tend to be inorganic gases such as carbon dioxide, nitrous oxide, ammonia and hydrogen. The organic gases are generally solvents or degradation products of the solvents used at the Hanford Site.

Vapors and gases that are flammability concerns are hydrogen, ammonia and nitrous oxide. Nitrous oxide is of concern because it provides an oxidant commingled with the gases from the waste. Nitrous oxide was found in 39 of 47 tanks, while hydrogen was above detection limits in only 27 tanks. Figure 1 shows the concentrations of hydrogen and nitrous oxide found in these tanks. Each species was sorted from highest to lowest. Hydrogen was not detected anywhere close to the lower flammability limit. Nitrous oxide was found in greater quantities.

Ammonia was one of three chemical species that were found in every tank sampled. The other two chemical species were water and 1-propanone (acetone). Ammonia is of concern because it was the noxious vapor found in the greatest quantities. Figure 2 shows the ammonia concentrations sorted from low to high. Many tanks had quantities great enough to require caution when working near an opening in the tank.

Two hundred chemical species have been found in six or more tanks, most in trace quantities. A larger list was identified for species occurring in five or less tanks. However, these species could also represent species misidentified when the mass spectrometer library is used to identify species.

It is probable that the gases found in the tank headspaces are products of the slow chemical and radiolytic reactions occurring in the waste. All of the waste contains nitrates and nitrites. Laboratory work has shown that ammonia and nitrous oxide can come from the nitrites. The nitrates and nitrites are good oxidizers and may slowly be reacting with organic molecules in the waste. The effect of radiation seems to increase the reactivity of the organic molecules. The slow chemical reactions and the radiation account for the many chemical species found in trace quantities. It should be pointed out that these are very slow reactions with half lives measured in decades. The waste will continue to produce gases for the foreseeable future but at a low enough rate so as not to present a major problem.

The headspace gas sampling activities will continue for the next few years. The current goal is to sample the headspace of all the tanks. Some tank headspaces will be sampled several times to see if the data vary with time. Other tanks will have continuous monitors installed to provide additional data. A sampler was recently deployed that can trap and sample gases within the waste.

At present, the tank headspace composition data have helped provide a greater understanding of the reactions within the waste. Sampling data have helped provide a better understanding of the flammability issues of the tank headspaces. For all of the single-shell tanks sampled so far, none have had an atmosphere close to 25 percent of the lower flammability limit. The headspace sampling program has provided valuable information that has increased the understanding of the true nature and safety of the tanks.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Toxicity</th>
<th>Log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hexadecane</td>
<td>C16H34</td>
<td>15</td>
<td>-3.7</td>
</tr>
<tr>
<td>1-Heptadecane</td>
<td>C17H36</td>
<td>15</td>
<td>-2.9</td>
</tr>
<tr>
<td>1-Undecane, 2,6-dimethyl</td>
<td>C21H42</td>
<td>19</td>
<td>-3.6</td>
</tr>
<tr>
<td>1-Undecane, 2,11-dimethyl</td>
<td>C21H42</td>
<td>19</td>
<td>-3.6</td>
</tr>
<tr>
<td>1-Dodecane, 4,6-dimethyl</td>
<td>C22H46</td>
<td>22</td>
<td>-3.9</td>
</tr>
<tr>
<td>1-Dodecane, 4,11-dimethyl</td>
<td>C22H46</td>
<td>22</td>
<td>-3.9</td>
</tr>
<tr>
<td>1-Dodecane, 6,10-dimethyl</td>
<td>C22H46</td>
<td>22</td>
<td>-6.1</td>
</tr>
<tr>
<td>1-Dodecane, 6,11-dimethyl</td>
<td>C22H46</td>
<td>22</td>
<td>-6.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>87</td>
<td>20.8</td>
</tr>
<tr>
<td>n-Heptadecane</td>
<td>C17H36</td>
<td>15</td>
<td>-4.0</td>
</tr>
<tr>
<td>Butanal</td>
<td></td>
<td>94</td>
<td>0.3</td>
</tr>
<tr>
<td>1-Butanol</td>
<td></td>
<td>94</td>
<td>0.3</td>
</tr>
<tr>
<td>n-Butyric acid</td>
<td>C6H10O</td>
<td>13</td>
<td>2.3</td>
</tr>
<tr>
<td>n-Butynoic acid</td>
<td>C6H9O</td>
<td>13</td>
<td>2.3</td>
</tr>
<tr>
<td>Ammonia</td>
<td></td>
<td>0</td>
<td>9.5</td>
</tr>
<tr>
<td>Nitrogen oxide (N2O)</td>
<td></td>
<td>0</td>
<td>8.9</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td></td>
<td>0</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 1: Cages Found in Headspaces of Waste Tanks in General Quantities.
Figure 1: Hydrogen and Nitrous Oxide in Tank Vapor Space.

- Nitrogen Oxide (N$_2$O)
- Hydrogen (H$_2$)
Figure 2. Ammonia in Single-Shell Tank Headspace.
## DISTRIBUTION

**Number of Copies**

**OFFSITE**

1  Pacific Northwest National Laboratory

<table>
<thead>
<tr>
<th>Pacific Northwest National Laboratory</th>
<th>K6-80</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. L. Huckaby</td>
<td></td>
</tr>
</tbody>
</table>

**ONSITE**

8  Westinghouse Hanford Co.

<table>
<thead>
<tr>
<th>Westinghouse Hanford Co.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L. L. Buckley</td>
<td>R2-12</td>
</tr>
<tr>
<td>C. S. Homi</td>
<td>R2-12</td>
</tr>
<tr>
<td>T. J. Kelly</td>
<td>T7-37</td>
</tr>
<tr>
<td>N. W. Kirch</td>
<td>R2-11</td>
</tr>
<tr>
<td>D. A. Reynolds</td>
<td>R2-11</td>
</tr>
<tr>
<td>L. D. Pennington</td>
<td>S7-21</td>
</tr>
<tr>
<td>J. P. Sloughter</td>
<td>R2-54</td>
</tr>
<tr>
<td>DPC</td>
<td>A3-94</td>
</tr>
</tbody>
</table>

Distr-1