PNNL-24194 Rev. 1
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Self-Flammability of Gases Generated by Hanford Tank Waste and the Potential of Nitrogen Inerting to Eliminate Flammability Safety Concerns

October 2015

LA Mahoney

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
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Test Specification: None
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Test Plan: TP-WTPSP-140, Rev 0
Test Exceptions: None

Prepared for
the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99352

Completeness of Work

This report describes the results of work specified in TP-WTPSP-140 Rev 0 "*Test Plan for Hydrogen Gas Release from Vessels Technical Issue Support*." All work was performed and reviewed in accordance with the quality assurance procedures applicable to the Waste Treatment Plant Support Program.

Approved:

Reid A. Peterson, Manager
WTP R&T Support Project

10/9/15
Date

Revision History

Revision Number	Interim Change No.	Effective Date	Description of Change
0	0	6/2015	Initial issue.
1	0	10/2015	Text changes for clarification throughout the document. Added Figure 3.1 and related text. Revised Equation (5.3) and the calculations made with it. Added Table 5.1. Added information in Section 5 about the H_2/N_2O ratio that gives mixtures that are denser than N_2. Added Appendix A to show the derivation of Equations (5.2) and (5.3).

Summary

Through radiolytic and thermolytic reactions, Hanford tank wastes generate and retain a variety of gases, including hydrogen, nitrous oxide, methane (and other hydrocarbons), ammonia, and nitrogen. This gas generation can be expected to continue during processing in the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The generation rates in the WTP will change from those for the in-situ tank waste because of different process temperatures, different dose rates produced by in-process changes in the proportions of solid and liquid, and dilution of the waste liquid.

The flammability of the generated gas that is continuously released, and of any retained gas that might be released into a vessel headspace in quantity due to a spontaneous release, depends on the concentrations not only of the fuel gases—primarily hydrogen (H_2), methane, other hydrocarbons, and ammonia—but of the oxidizer nitrous oxide (N_2O). As a result of high concentrations of N_2O, some gas mixtures are "self-flammable" (i.e., ignition can occur when no air is present because N_2O provides the only oxidizer needed). Self-flammability could potentially reduce the effectiveness of using a nitrogen (N_2) purge in the headspace as a flammability control, if its effects are not accounted for. A given amount of inertant gas (N_2) can accommodate only a certain amount of a generated self-flammable gas before the mixture with inertant gas becomes flammable.

Gases produced from laboratory-tested samples of Hanford wastes from several tanks have contained enough fuel (primarily H_2) and N_2O oxidizer to be self-flammable. There is not enough evidence to determine how the N_2O:H_2 ratio and amount of self-inerting by waste-generated N_2 will vary with modest amounts of water dilution of the tank waste or with other aspects of WTP waste processing that change the waste liquid composition.

Example calculations of flammability at 25°C indicated that a release gas fraction of about 0.3 in a well-mixed, initially N_2-inerted headspace could produce marginal self-flammability for a release gas composition of 15% N_2, 25% H_2, and 60% N_2O, a composition that is not outside the realm of possibility. Higher release gas fractions in the range of 0.5 to 0.6 would be needed to reach self-flammability at a broader range of H_2 fractions for this N_2 fraction, or to reach marginal self-flammability for a higher-N_2 release gas (i.e., 30% N_2, 21% H_2, and 49% N_2O). Given high enough in-situ pressures on the retained gas, small enough headspace volumes, and outflow of gas from the headspace during the gas release, a retained gas volume fraction of 0.3 could produce release gas fractions that would make an initially N_2-inerted well-mixed headspace self-flammable. A retained gas fraction of 0.3 has been observed in laboratory tests of retention in gas-generating simulant layers of 16 to 33 Pa.

S.1 Objective

The objective of this report is to summarize literature reports relating to the flammability of H_2 in N_2O/N_2 mixtures and the generation of H_2 and N_2O by Hanford waste, and to define conditions under which the generated gases are self-flammable. Table S-1 summarizes the work objective that applies to this task.

Table S.1. Summary of Work Objective and Results

Work Objective	Objective Met?	Discussion
Test/Analysis Objective 17: *Provide technical evaluations and analyses to support Bechtel National, Inc. (BNI) Engineering Studies.*	Yes	The report provides supporting information for evaluating the effectiveness of a N_2 purge for inerting WTP process headspaces in situations where the generation rate of N_2O is of the same order of magnitude as the generation rate of H_2.

S.2 Work Exceptions

No work exceptions are applicable to this report.

S.3 Results and Performance Against Success Criteria

Table S.2 presents the success criterion for achieving the work objective.

Table S.2. The Success Criterion for the Self-Flammability Summary Task

Success Criterion	How Work Did or Did Not Meet the Success Criterion
Objective 17 – Support to BNI Engineering Studies: *Complete requested technical evaluations and analyses, and required Pacific Northwest National Laboratory (PNNL) Quality Assurance (QA) reviews, consistent with BNI/WTP expectations, without significant QA problems, compliantly, on time, and within budget.*	This success criterion was met. The report summarizes literature and reports, providing data on (a) the flammability of H_2 in an N_2O atmosphere, (b) conditions under which N_2 inerting suppresses H_2/N_2O flammability, and (c) H_2 and N_2O generation in tests carried out on waste samples and simulants.

S.4 Quality Requirements

The PNNL QA Program is based upon the requirements as defined in the U.S. Department of Energy (DOE) Order 414.1 D, Quality Assurance and Part 10 of the Code of Federal Regulations (CFR) Part 830, Energy/Nuclear Safety Management, Subpart A -- Quality Assurance Requirements (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, Quality Assurance Requirements for Nuclear Facility Applications, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities
- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications
- ASME NQA-1-2000, Part IV, Subpart 4.2, Graded Approach Application of Quality Assurance Requirements for Research and Development.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…?" (HDI), which is a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The work described in this report was conducted under the current QA program document revision previously submitted to BNI: QA Manual QA-WTPSP-0002 Rev 1.1; QA Plan QA-WTPSP-0001 Rev 2.0; QA Requirements Matrix (QARM) QA-WTPSP-0003 Rev 2.0. The QA plan for the Waste Treatment Plant Support Program (WTPSP) implements the requirements of ASME NQA-1-2000, Part 1: Requirements for Quality Assurance Programs for Nuclear Facilities, presented in two parts. Part 1 describes the graded approach developed by applying NQA-1-2000, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development to the requirements based on the type of work scope the WTPSP is facing. Part 2 lists all NQA-1-2000 requirements the project is implementing for the different technology levels of research and development work. Requirements are clearly listed by applicable technology level.

The WTPSP uses a graded approach for the application of QA controls, such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life cycle state of work, or programmatic mission. The work described in this report has been completed under the QA technology level of Developmental Work, which is the highest QA technology level. WTPSP addresses internal verification and validation activities by conducting an independent technical review of the final data report in accordance with WTPSP procedure QA-WTPSP-601, *Document Preparation and Change*. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and that the reported work satisfies the test plan objectives.

S.5 R&T Test Conditions

This report summarizes literature and government-sponsored reports that describe $H_2/N_2O/N_2$ flammability and H_2 and N_2O generation from Hanford waste samples. No experimental testing was required to complete this review. Accordingly, the fields for summary of R&T Test Conditions, Table S.3, are N/A for “not applicable.”

Table S.3. Summary of R&T Test Conditions

R&T Test Condition	Discussion
N/A	N/A

S.6 Simulant Use

No simulants were used in this literature review.

S.7 Discrepancies and Follow-On Tests

This report only summarizes historical literature and government-sponsored reports that describe $H_2/N_2O/N_2$ flammability and H_2 and N_2O generation from Hanford waste samples. No laboratory testing was performed in pursuit of this review. Accordingly, no discrepancies were found and no follow-on tests are required.

Acronyms and Abbreviations

ASME	American Society of Mechanical Engineers
BNI	Bechtel National, Inc.
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
HDI	“How Do I...?”
HEDTA	hydroxyethyl ethylenediamine triacetic acid
HGR	hydrogen generation rate
LFL	lower flammability limit
NQA	Nuclear Quality Assurance
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&T	Research and Technology
TOC	total organic carbon
UFL	upper flammability limit
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Program

Nomenclature

f	volume fraction of release gas in the release gas/inertant mixture in the headspace
f_{open}	volume fraction of release gas in the headspace if the headspace is open to outflow (no pressurization)
f_{closed}	volume fraction of release gas in the headspace if the headspace is closed to outflow (pressurization)
$[N_2]$	volume fraction of N_2 in the headspace after release
$[N_2]_R$	volume fraction of N_2 in the release gas
R_P	ratio of in-situ retained gas pressure to the headspace pressure before release
R_V	ratio of headspace volume after release to the non-gas volume of the gas-retaining layer
α	retained gas volume fraction in the gas-retaining layer
φ	$\alpha / (1 - \alpha)$, ratio of retained gas volume to the non-gas volume of the gas-retaining layer

Contents

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1.0 Introduction

Through radiolytic and thermolytic reactions, Hanford tank wastes generate and retain a variety of gases, including hydrogen (H_2), nitrous oxide (N_2O), methane (CH_4) and other hydrocarbons, ammonia (NH_3), and nitrogen (N_2). This gas generation can be expected to continue during processing in the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The generation rates in the WTP will change from those for the in-situ tank waste because of different process temperatures, different dose rates produced by in-process changes in the proportions of solid and liquid, and dilution of the waste liquid.

The combination of high N_2O and H_2 generation rates from Hanford tank wastes is the result of the types of organics (e.g., chelating agents and breakdown products) that were used in Hanford processing. Most N_2O generation derives from the reduction of nitrite ions, but requires a low threshold concentration of certain organic compounds (e.g., hydroxyethyl ethylenediamine triacetic acid [HEDTA]) to provide a reducing agent (Bryan and Pederson 1994).

The flammability of the generated gas that is continuously released, and of any retained gas that might be released into a vessel headspace in quantity due to a spontaneous release, depends on the concentrations not only of the fuel gases—primarily H_2, CH_4, and NH_3—but of the oxidizer N_2O. As a result of high concentrations of N_2O, some gas mixtures are "self-flammable" (i.e., ignition can occur when no air is present because N_2O provides the only oxidizer needed). Self-flammability could potentially reduce the effectiveness of using a nitrogen (N_2) purge in the headspace as a flammability control, if its effects are not accounted for.

The possibility of concentrations of self-flammable gas in vessel headspaces, whether well-mixed throughout the headspace or localized in plumes, potentially produces a different inerting design criterion than the one typical in commercial facilities (i.e., where fuel gases are the only release and air the only oxidant). A given amount of inertant gas (N_2) can accommodate only a certain amount of a generated self-flammable gas mixture before the combination of waste gas and inertant gas becomes flammable. This report summarizes information on the potential for self-flammability in gases generated by Hanford waste and in mixtures of such gases with inertant N_2.

Section 2 describes flammability characteristics, primarily those of the $H_2/N_2O/N_2$ system, and Section 3 briefly discusses the flammability of tank waste gases. Section 4 summarizes information on how composition changes that occur during WTP processing will affect self-flammability of waste gases, and concludes there is not enough information to assess the effect of processing on self-flammability. Section 5 provides two examples to suggest the effect of N_2 inerting on self-flammability in WTP process headspaces. A more exhaustive determination could be carried out, considering the possible releases and headspace volumes of specific process vessels; however, that was not in the scope of this report. Sections 6 and 7 provide conclusions and references, respectively. Equations used in the calculations in Section 5 are derived in Appendix A.

2.0 Flammability Characteristics

Ross (1997) reported that, for an ignition energy of 8 J, N_2O does not participate in combustion of lean mixtures of H_2-air-N_2O, at an H_2 concentration of 8%. However, this study does not exclude the possibility of H_2-N_2O flammability because it did not include tests under conditions where the only oxidant present was N_2O. A subsequent study by Pfahl and Shepherd (1997) reviewed literature data for H_2 flammability in H_2-N_2O-N_2 mixtures and tested the flammability of more complex mixtures representing gases retained in Hanford tanks.

Figure 26 of Pfahl and Shepherd (1997) provides a plot based in part on $H_2/N_2O/N_2$ combustion tests performed by others (Posthumus 1930; Smith and Linnett 1953; van der Wal 1934; Scott et al. 1957), of the flammability limits in various H_2-oxidizer-N_2 systems at 25°C and 1 atm pressure. That plot is reproduced here as Figure 2.1, where the axes, being expressed in kPa in a system at 101.3 kPa (1 atm), can also be read as mole percentages of the initial mixture, because 1 atm is equal to 100 kPa within the accuracy to which the plot can be read. The y-axis is mole percent H_2, and the x-axis mole percent N_2. Flammable conditions exist only in the roughly triangular region between the upper sloping part of the curve (the upper flammability limit [UFL]) and the lower, nearly horizontal part (the lower flammability limit [LFL]). The flammability limits depend not only on composition, but on ignition energy and the turbulence (mixing) already existing at the time of ignition; these factors can lead to different limits being obtained by different experimenters.

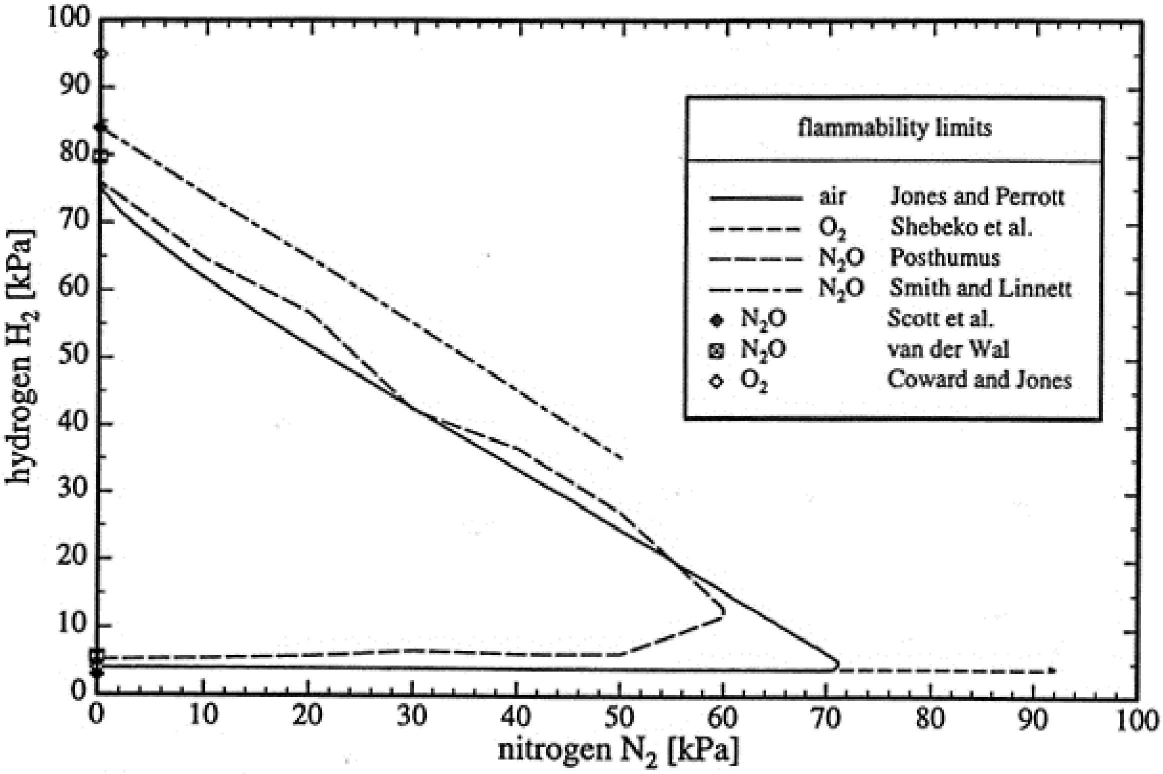

Figure 2.1. Flammability Limits for $H_2/N_2O/N_2$, $H_2/O_2/N_2$, and H_2/Air/Non-Air-N_2 at 100 kPa Total Pressure and 25°C. Reproduced from Pfahl and Shepherd (1997).

Figure 2.1 shows that the low-ignition-energy behavior of flammability in H_2-N_2O-N_2 (Posthumus 1930) is similar to that in H_2-air-N_2 (Jones and Perrott 1927), except that for H_2-N_2O-N_2 the LFL is slightly higher and the minimum inerting N_2 is lower. Under the conditions of the Posthumus (1930) test, the H_2 LFL in N_2O was 4.5 to 5% in the absence of N_2. The LFL increased from there to about 7% with 50% N_2 inerting (data labeled as Posthumus in Figure 2.1). As N_2 inerting was further increased, the LFL rose to reach about 12% H_2 at the minimum inerting N_2 fraction of 60%, and the LFL and UFL were equal. The UFL of H_2 in N_2O, without N_2 inerting, was between 75% (at a low ignition energy, Posthumus [1930]) and 84% (at 20 J for ignition, Smith and Linnett [1953]). The UFL measurements indicate that the minimum N_2O required for flammability was 16 to 25% with zero N_2 and 28% (for a low ignition energy) at 60% N_2.

For comparison, Pfahl et al. (2000) carried out tests on H_2-N_2O-N_2, running a fan to provide turbulence near the ignition location and typically using an ignition energy of 8 J (note that energies as low as 40 mJ were used to determine the effect of ignition energy on LFL). Pfahl et al. (2000) obtained a higher minimum inerting concentration than that of Posthumus (1930): the inerting concentration was 76% N_2, at which point the LFL and UFL were equal at about 7% H_2, giving a wider range of flammability than for the Posthumus (1930) tests, similar to that of H_2-air-N_2. In the absence of N_2, the LFL was 5% and the UFL 76%, similar to the values obtained by Posthumus (1930).

A specific ratio of N_2O to H_2 in the release gas can be defined that maximizes the potential for self-flammability by maximizing the range of release gas fractions over which the headspace could be flammable. On a plot of flammability limits (e.g., Figure 2.1), any dilution of release gas with inertant N_2 falls on a line between the composition of the release gas and the composition at infinite dilution (i.e., 100% N_2). The fraction of such a line that is within the flammability limits is longest when the line passes through the H_2 concentration that is flammable when N_2 is at the minimum inerting point. If this point is defined as having coordinates ($[N_2]_i$, $[H_2]_i$), then the N_2O/H_2 ratio of maximum potential for self-flammability can be expressed as $((100 - [N_2]_i) / [H_2]_i) - 1$, where all concentrations are in mole percent. The ratio is $(40/12 - 1) = 2.3$ for the Posthumus (1930) flammability data and $(24/7 - 1) = 2.4$ for the Pfahl et al. (2000) flammability data. The ratio is significant as a sign of release gases where the effectiveness of N_2 inerting is most affected by release gas self-flammability.

Water vapor, as well as N_2, is an inertant of H_2 combustion reaction. No information was found for the inerting effect of water vapor on H_2-N_2O flammability. In the case of H_2-air, water vapor has more effect on the UFL than on the LFL between 20 and 71°C; according to Shapiro and Moffette (1957) the LFL increases from 4.6 to 5.4%, but the UFL decreases from 70 to 40%. At a temperature of 71°C, inerting of H_2-air mixtures is complete. Because H_2-N_2O-N_2 shows flammability characteristics similar to those of H_2-air-N_2, as already discussed, and because H_2O is a combustion product, and therefore an inertant for combustion reactions, in both H_2-N_2O combustion and H_2-air combustion, water vapor may have similar inerting effects in both systems. However, data are needed to confirm this hypothesis.

Besides H_2, the other main fuel gases in Hanford waste are CH_4 and NH_3, though they are typically present in much smaller concentrations than H_2. These two gases have also had their flammability in N_2O characterized. Pfahl et al. (2000) provide measurements of the flammability of these gases in N_2O-N_2 mixtures. CH_4 had an LFL of 2.5 to 3.0% and a UFL of 43 to 50% in the absence of N_2, and a minimum inerting concentration of 70.5% N_2 (at which the LFL and UFL were both 7%). NH_3 had an LFL of 5% and UFL of 68% in the absence of N_2, and a minimum inerting concentration of 61% N_2 (at which the LFL of was 11% and the UFL was 16%).

3.0 Self-Flammability of Tank Waste Gases

Section 3.6 of Mahoney et al. (2000) provided equations that approximate the behavior of the LFL and UFL of H_2, NH_3, and CH_4 in N_2O-N_2 as linear functions of the N_2 fraction, using the minimum inerting fraction of 60% N_2 for H_2-N_2O-N_2. The equations were used to produce Table 3.4 in Mahoney et al. (2000), which assessed whether there could be self-flammable gases retained in the non-convective layers of the 14 Hanford waste tanks that had been sampled for retained gas. Self-flammability was considered possible for retained gases in 4 of the 14 wastes (i.e., 241-SY-101 crust, S-102 nonconvective layer, U-103 nonconvective layer, and SX-106 nonconvective layer). Two additional wastes (i.e., AN-104 nonconvective layer and AX-101 nonconvective layer) retained gases that were near the minimum required N_2O limit and, thus, borderline self-flammable. In the fully self-flammable gases, the H_2:N_2 concentrations were 23%:36%, 33%:32%, 34%:27%, and 51%:20%; in these cases N_2O concentrations were in the range of 27 to 41%. Describing the gas compositions in another way, the N_2O:H_2 ratios were between 0.5 and 2, lower (more fuel-rich) than the ratios of 2.3 and 2.4 given by Posthumus (1930) and Pfahl et al. (2000), respectively, for maximum potential self-flammability.

Freshly generated gases may be more pertinent to WTP processes than gases retained in Hanford waste tanks, because process residence times are short and gas scavenging will play little part in the composition of retained gas in the process vessels. Self-flammable compositions have been observed previously in generated gases. Table 2-5 in Sherwood and Stock (2004) evaluated gases produced by five different tank wastes reacting at 90°C, both with and without an oxygen (O_2) atmosphere in the test vessel. In three of ten cases, H_2:N_2 concentrations were in a fuel-lean range between 11%:30% and 16%:33%, producing N_2O:H_2 ratios higher than the ratios of 2.3 and 2.4 for maximum potential self-flammability. However, these measured generation rates were purely thermolytic; no dose was applied, so there was no radiolytic contribution either from the organics or from water. Radiolytic generation (particularly from water) would likely increase the proportion of fuel in the generated gas. For example, the AW-101 waste is a case where gas compositions are available both for all mechanisms at in-tank conditions (81% H_2/11% N_2O/7% N_2, plus other gases) and for pure thermolysis at 90°C with O_2 present (18% H_2/2% N_2O/72% N_2, plus other gases).

Conversely, the estimated generated gases for A-101, S-106, and U-103 wastes (Tables 2.8 and 2.9 of Mahoney et al. [2000]) fell into a fuel-rich self-flammable range of H_2 and N_2 concentrations. These generated-gas compositions were estimated using in-tank temperatures and dose rates, as well as correlations based on data from laboratory tests of waste samples. Because release gases can be either fuel-rich or fuel-lean compared to the condition of maximum potential self-flammability, the maximum potential composition cannot be ruled out in gases generated by tank waste.

Figure 3.1 presents simplified versions of the H_2/N_2O/N_2 flammability curves discussed in Section 2 and the retained gas and generated-gas data discussed earlier in this section, normalized to include only H_2, N_2O, and N_2. Other gases, including fuel gases such as CH_4 and NH_3, were also present in many measurements and, for retained gases, were included in flammability assessments by Mahoney (2000). Therefore, conclusions that may be drawn about flammability of retained gases from Figure 3.1 are not necessarily the same as those drawn by Mahoney (2000). Figure 3.1 also shows the line of maximum potential self-flammability—drawn through the inerting points of the flammability curves and the 100% inertant point—and the stoichiometric composition for H_2/N_2O without N_2. This latter composition is significant in terms of approximately indicating the H_2/N_2O ratio where the least ignition energy is needed

(Pfahl et al. 2000). As Figure 3.1 shows, many historically-observed gas compositions have been within the flammability envelope.

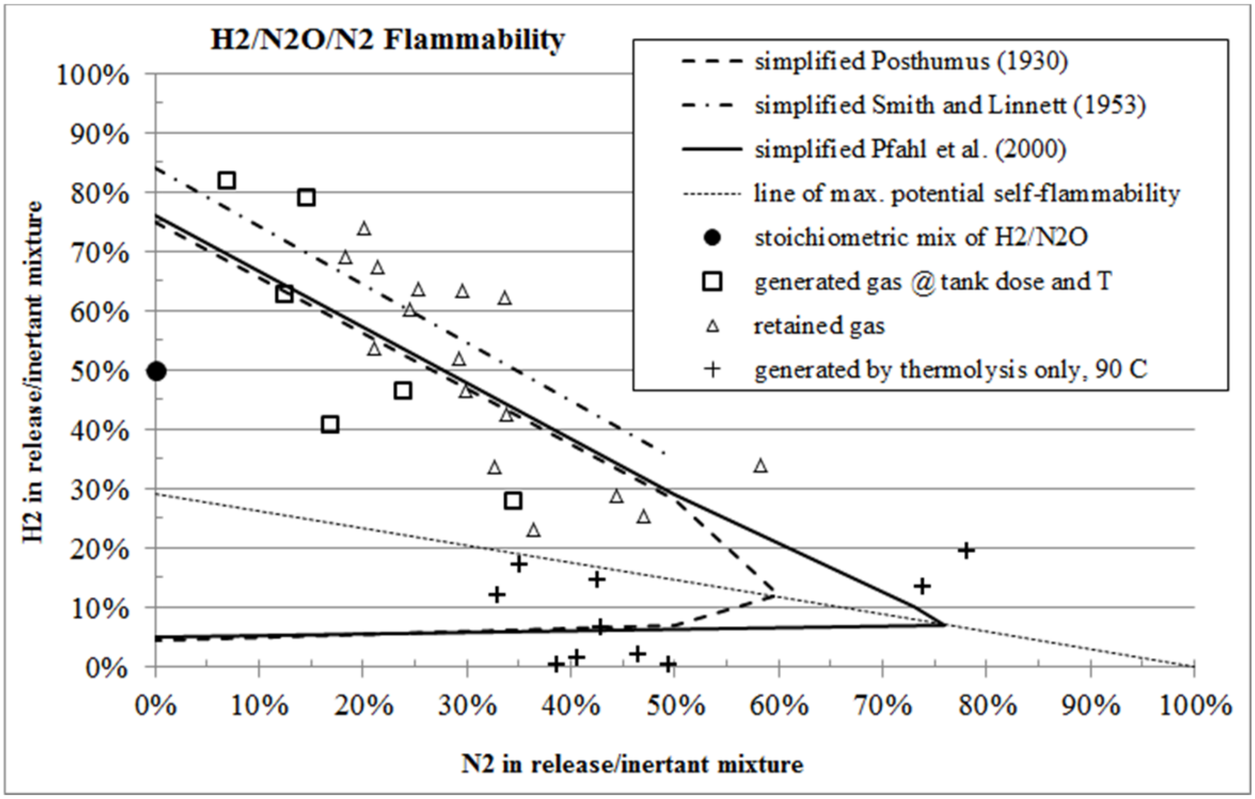

Figure 3.1. Waste Gas Composition in Relation to Self-Flammability Boundaries

4.0 Effect of Processing Tank Waste

The generation rates of the gases of interest will change from those in the in-situ tank waste because of different process temperatures, different dose rates produced by in-process changes in the proportions of solid and liquid, and dilution of the waste liquid.

For a limited set of wastes, the effect of temperature on generated-gas composition has been tested between (typically) 60 and 120°C. The fraction of N_2O in generated gas may decrease or increase between 60 and 90°C; N_2 and CH_4 fractions usually increase along with temperature; and the H_2 fraction holds steady or decreases as temperature increases, as discussed by Bryan et al. (1996), King et al. (1997), King and Bryan (1999), and other sources.[1,2,3] These data come from tests conducted at dose rates in the range of 80 to 286 rad/hr, depending which waste was being tested. No obvious, definite overall trend in self-flammability is apparent. Determining the combined effect of characteristic WTP dose rates and

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[1] Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste: Status Report*, TWS98.39, Pacific Northwest National Laboratory, Richland, WA.

[2] Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Status Report*, TWS96.17, Pacific Northwest National Laboratory, Richland, WA.

[3] Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste: Status Report*, TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

temperatures on self-flammability for this limited set of wastes would require a more complete analysis of the detailed gas-generation information given in those references.

The tank wastes will typically be diluted before reaching the WTP vessels. Washing of the leached waste solids during processing causes further dilution. Dilution affects the self-flammability by affecting H_2 generation and nitrogenous gas generation.

The effect that water dilution has upon H_2 generation, at a given temperature, has been thoroughly studied. The effect depends on the balance between water radiolysis, organic radiolysis, and organic thermolysis mechanisms, as discussed and modeled by Sherwood and Stock (2004). As water is added to a waste liquid, the decrease in dissolved NO_2^- and NO_3^- ions may lead to an increase in the H_2 generation rate (HGR) from water radiolysis. The direction in which the HGR is changed by water addition depends on whether the increase in the generation per unit dose (*G*-value) with increased dilution is offset by the decrease in the volumetric concentrations of the radionuclides that contribute dose. The same water dilution monotonically decreases the organics-related HGR because all the relevant concentrations decrease: organic radiolysis depends linearly on dose and on total organic carbon (TOC) concentration and organic thermolysis depends linearly on dose and on TOC concentration and on the 0.4 power of dissolved aluminum concentration.

Hence, the cumulative effect of dilution on organics-related HGR is to multiply the undiluted organic radiolysis HGR by the square of the concentration ratio (i.e., dilute/initial). However, the same dilution multiplies the undiluted organic thermolysis HGR by the concentration ratio to the 2.4 power—i.e., a power of 2 for the changes in TOC concentration and volumetric dose, as for radiolysis, plus a power of 0.4 for the change in Al concentration. The total effect of dilution on HGR over all three mechanisms might be a decrease or increase depending on the extent of dilution and on the dissolved reactant concentrations, dose, and temperature.

Fewer studies have analyzed the effect of water dilution on the generation rates of N_2O and N_2. Bryan and Pederson (1994) cited studies that determined that most N_2O generation derives from the reduction of nitrite ions once a low threshold concentration of certain organic compounds (e.g., HEDTA) is present to provide a reducing agent. In their own tests, Bryan and Pederson (1994) found that under combined radiolytic and thermal conditions the rate of N_2O generation from a solids-containing SY-101 simulant (with HEDTA organic) increased as dilution with 2 M sodium hydroxide (NaOH) increased (up to 30% dilution from an initial total sodium [Na] concentration of 13.5 M). The $N_2O:H_2$ ratio increased from 4 to almost 7 over this range of dilution. In the same tests, the ratio of $N_2:H_2$ generation rates remained nearly constant. The authors attributed this result to the dissolution of $NaNO_2$ solid during dilution, such that the dissolved nitrite concentration remained constant while the organic concentration decreased with dilution. Because the HGRs were low for this particular simulant and the H_2 concentration in product gas was <5%, no strong statement can be made about the effect of the tested modest amount of dilution on self-flammability. However, if enough dilution (or other processing) occurred to remove the TOC, and if the processed waste liquid were exposed to dose, the result would be the generation of H_2 (through water radiolysis) without N_2O and N_2. In that case, self-flammability would not be an issue.

Ions other than TOC, nitrate, and nitrite also affected the relative generation rates of H_2, N_2O, and N_2. Thus, their dilution could also affect self-flammability. Bryan and Pederson (1994, Section 4.6) found that after about 100 hours of reaction, the thermal production of N_2O from SY-101 simulant (i.e., 0.3 M

HEDTA, 90°C) peaked strongly at 0.5 M chloride compared to lower and higher Cl concentrations. If this pattern holds for other wastes, diluting chloride concentration from the value where N_2O generation is at its peak would decrease N_2O concentration in the release gas, which would make self-flammability less likely in a fuel-rich release gas and more likely in a fuel-lean release gas. However, diluting chloride from a starting Cl concentration that was higher than that at which N_2O production peaked would increase N_2O concentration and have opposite effects on self-flammability. Transition metal concentration in the simulant had relatively little effect on thermal H_2 generation; however, decreasing the transition metal concentration increased the thermal N_2O generation and decreased the thermal N_2 generation (Bryan and Pederson 1994, Section 4.7). A dilution of the transition metals could decrease N_2 generation, and increase the chance of self-flammability. Considering the limited data and the variability of gas-generation response to dilution, the available information does not allow a conclusion as to whether a moderate dilution increases or decreases the potential for self-flammability.

The caustic leach process in the WTP raises the hydroxide concentration in the waste liquid, which is another potential cause of a change in self-flammability. The results in Bryan and Pederson (1994, Section 4.4) indicate a dependence of the N_2:H_2 and N_2O:H_2 ratios on the concentrations of hydroxide ions. For thermal reaction tests at 90°C with an SY-101 simulant that included 0.3 M HEDTA as the organic, the ratio of N_2:H_2 increased consistently as the hydroxide concentration increased from 1 to 6.5 M, while the ratio of N_2O:H_2 peaked at 4 M OH (see Table 4.4 of Bryan and Pederson 1994). A similar pattern of behavior was followed by SY-101 simulant containing 0.3 M ethylenediamine triacetic acid (EDTA); however, when 0.5 M citrate was used as the organic, the peak N_2O:H_2 ratio occurred at 5.3 M NaOH. The non-monotonic dependence of N_2O:H_2 on hydroxide, and the different hydroxide concentrations at which the N_2O:H_2 peaks occurred for different organic species, suggest that the relation of self-flammability to hydroxide concentration cannot be simply defined.

5.0 Flammability of Releases

Two distinct sets of properties govern the self-flammability of a waste gas release into an inerted headspace. First, the composition of the waste gas may tend to increase or decrease the chances of self-flammability; higher N_2 (too close to inert), very low H_2 (too lean), or very high H_2 (too rich) can put the gas outside the flammable region when it is mixed with inertant. Second, the volume of gas released may be insufficient to produce a self-flammable mixture; the volume release is controlled by process parameters and the physical properties of the waste. The N_2 concentration in any mixture of N_2 and release gas, whatever the release fraction, is

$$[N_2] = (1 - f) + f[N_2]_R \tag{5.1}$$

where f is the volume (or mole) fraction of release gas in the mixture, $(1 - f)$ is the fraction of N_2 inertant, and $[N_2]_R$ is the fraction of N_2 in the release gas.

First, consider two examples of the effect of the composition of a waste gas release into a headspace that initially contains pure N_2. In Example 1, the release gas has a composition similar to that of the generated gas estimated for S-106 under in-tank conditions (Mahoney et al. 2000): 15% N_2, 40% H_2, and 45% N_2O. In Example 2, the gas has a composition similar to that in several gas mixtures listed in Section 3: 30% N_2, 35% H_2, and 35% N_2O. In addition, consider two different models of flammability behavior. The flammability curve in Figure 8 of Pfahl et al. (2000), which gives a wider flammable range, will be used to show the effect of the more flammable (low-N_2) gas in Example 1, as a higher-flammability example. The Posthumus flammability curve shown in Figure 2.1 has a narrower flammable range and will be used to show the effect of the less flammable gas in Example 2, as a lower-flammability example.

For Example 1, if the inerting effect of water vapor is not included, the fraction of release gas (back-calculated from Eq. [5.1]) must equal at least (1 – 0.76) / (1 – 0.15) = 0.28 for the inerting constraint to be removed. At this release gas fraction, the H_2 concentration in the mixture is (0.28)(0.4), or 11%, which is higher than the 7% UFL of H_2 at 76% N_2. Although this particular gas contains enough H_2 to be too rich for self-flammability, it becomes borderline self-flammable when mixed with enough inertant to put the mixture at the minimum inerting concentration of N_2. At the point where the N_2 concentration in the release/inertant mixture is 65% and the potentially flammable H_2 concentration ranges from about 7 to 16% (estimated from Figure 8 of Pfahl et al. 2000), the fraction of release gas (calculated in the same way) is 0.41. At this release gas fraction the H_2 concentration in the mixture is 16%, on the borderline of being too rich to be flammable. At a higher release gas fraction, this particular release gas would produce a flammable mixture with N_2.

Note that if the release gas composition had been 25% H_2 with the same N_2 concentration of 15%, it would have been near the line of maximum potential for self-flammability and could have produced flammable mixtures for any release gas fraction greater than 0.28. Because the compositions of retained and measured gases from tank waste have fallen on both the fuel-rich and fuel-lean sides of the line of maximum potential for self-flammability, a composition of 25% H_2 and 15% N_2 may be possible. However, a more comprehensive examination of existing gas-generation test data, and the existing correlations based on those data, would be needed to test this.

For Example 2 (30% N_2), assume the flammability behavior found by Posthumus (1930), where the minimum inerting concentration of N_2 was 60% and the UFL of H_2 at that point was 12%. In this case, the fraction of release gas must equal at least (1 – 0.60) / (1 – 0.30) = 0.57 for the inerting constraint to be removed. At this release gas fraction, the H_2 concentration in the mixture is (0.57)(0.35), or 20%, which is higher than the 12% UFL of H_2 at 60% N_2 (according to Posthumus [1930]), and is too rich to be flammable. If the release gas composition had been 21% H_2 with the same N_2 concentration of 30%, it could have produced flammable mixtures for any release fraction greater than 0.57.

The above examples, summarized in Table 5.1, show that realistic generated-gas compositions can produce self-flammable conditions in a well-mixed initially inerted headspace, but that the release gas fraction in the headspace probably has to be greater than 0.30, and possibly greater than 0.50. A large volume of gas must be released, and it follows that a large volume of retained gas must be present before the release. This report does not include a comprehensive discussion of the generation rate of total gas (not solely H_2) and event duration that are necessary to produce high volume fractions of retained gas. Only a brief discussion of observations of the relation between waste properties and high gas retention is included.

Table 5.1. Examples of Waste Gas Self-Flammability and Inerting When Mixed With N_2

Waste Gas	Minimum N_2 for Inerting (Inerting Concentration)	Source for Flammability Behavior	Minimum Fraction of Release Gas in Headspace To Prevent N_2 Inerting	H_2 LFL and UFL when N_2 is at the Inerting Concentration	H_2 Concentration in Headspace at the Minimum Fraction of Release Gas To Prevent N_2 Inerting	Minimum Fraction of Release Gas in Headspace To Enter Flammable Region	H_2 LFL and UFL when Flammable Region is Entered	H_2 Concentration in Headspace at the Minimum Fraction of Release Gas to Enter Flammable Region
Example 1: 15% N_2, 40% H_2	76%	Pfahl et al. (2000)	0.28	LFL = 7% UFL = 7%	11%	0.41	LFL: 7% UFL: 16%	16%
Example 1, less H_2: 15% N_2, 25% H_2	76%	Pfahl et al. (2000)	0.28	LFL = 7% UFL = 7%	7%	0.28	LFL: 7% UFL: 7%	7%
Example 2: 30% N_2, 35% H_2	60%	Posthumus (1930)	0.57	LFL = 12% UFL = 12%	20%	0.68	LFL = 8% UFL = 24%	24%
Example 2, less H_2: 30% N_2, 21% H_2	60%	Posthumus (1930)	0.57	LFL = 12% UFL = 12%	12%	0.57	LFL = 12% UFL = 12%	12%

Rassat et al. (2014) performed tests of gas retention in, and release from, layers of gas-generating bentonite-Min-u-Sil simulant slurry in vessels of 58 cm (23 in.) and 178 cm (70 in.) diameter. In these tests, the slurry layer thickness was 17% of the diameter and the thickness of the supernatant liquid (water) layer was, in most tests, approximately one-fourth of the slurry thickness. In those tests where the shear strength of the slurry was 16 to 33 Pa, the retained gas fraction at the time of release was consistently about 30%, and 90% or more of the gas inventory was released.

A large gas release causes the headspace volume to increase significantly because of the subsidence of the waste surface. The released gas expands from its hydrostatic in-situ pressure to the lower pressure of the headspace, which may be pressurized[4] by the release if outflow is limited. The release gas fraction in the well-mixed vessel headspace after release can be calculated for a release of all retained gas at isothermal conditions on two bases, one where there is no headspace pressurization (open unrestricted outflow after release) and one where all gas remains in the headspace (closed to outflow after release). Both cases are assumed to start at the same initial headspace pressure and volume (initial meaning just before the waste gas release).

In the open-headspace case, the gas release is assumed to be plug flow, which expels an equal volume of inertant gas from the headspace before mixing with the portion left behind. In the closed-headspace case, the release gas is assumed to mix with all of the inertant gas that is initially in the headspace before any gas is expelled, giving a lower value of f than for the open-headspace case. The two conditions bound the effect of headspace pressurization on the release gas fraction in the headspace.

The expressions for release gas fraction under open and closed conditions can be derived:

$$f_{open} = \frac{\varphi R_P}{R_V} \tag{5.2}$$

$$f_{closed} = \frac{\varphi R_P / R_V}{\varphi R_P / R_V + 1 - \varphi / R_V} = \frac{f_{open}}{1 + (R_P - 1)\varphi / R_V} \tag{5.3}$$

where R_P is the ratio of in-situ gas pressure divided by the headspace pressure before release, R_V is the ratio of headspace volume after release to the non-gas volume of the gas-retaining layer, and φ is equal to $\alpha/(1-\alpha)$, α being the retained gas volume fraction in the gas-retaining layer. Depending on the waste properties, the gas-retaining layer may be the whole slurry volume or a smaller volume of settled solids.

The experimentally observed retained gas fraction, α, of 0.3 corresponds to a specific gas ratio, φ, of 0.3/0.7, or 0.43. If this gas fraction is present and R_V is 1 (i.e., the non-gas volume in the gas-retaining layer equals the headspace volume), then under both closed and open conditions the total release of retained gas at an R_P of 1 (no hydrostatic head) will produce a release gas fraction of 0.43, which would be self-flammable for some release gas compositions (e.g., Example 1). The presence of hydrostatic head would increase both the open-headspace and closed-headspace release gas fractions, but the open-headspace release gas fraction would increase more rapidly.

For comparison, a release gas fraction of 0.6 could not be produced at $R_V = 1$ and $\alpha = 0.3$ unless there was an R_P of 1.4 under open conditions or an R_P of 2.0 under closed conditions. The closed-condition R_P

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[4] Note that flammability limits are a function of pressure but do not change significantly in the pressure range of 1-2 atm (Shapiro and Moffette 1957).

value may be too high a hydrostatic pressure to be plausible, but the open-condition value might be possible. A determination of the values for R_V and R_P that are plausible in actual WTP vessels, including the possibility that solids settle and produce relatively small gas-retaining layers, could be carried out, as could an evaluation of the possible extent of headspace pressurization.

The discussion in this section has assumed that all of the release was well-mixed in the headspace. As in the case of releases of pure H_2, localized plumes of potentially self-flammable release gas would increase the chance of flammable regions in the headspace, although these regions would be smaller volumes.

In addition, there is a possibility of a layer of release gas denser than N_2 and self-flammable, where the higher density opposes buoyancy-driven mixing with the inerting N_2 in the headspace. For example, if the release gas composition was 15% N_2, 25% H_2, and 60% N_2O (i.e., the case of Example 1 with less H_2 discussed previously), the molecular weight of the mixture would be greater than the molecular weight of N_2 when the release/inertant mixture is in the flammable zone (i.e., a release gas fraction greater than 0.28). More generally, mixtures of $H_2/N_2O/N_2$ are denser than N_2 when the H_2/N_2O ratio is less than 0.616, or an H_2 concentration of 38% in the absence of N_2. However, the initial momentum of the release gas, plus the free convection caused by even small temperature differences within the headspace, would assist with mixing a denser gas layer into the N_2 inertant.

Note also that the discussion in this section has conservatively assumed that N_2 is the only inertant. As mentioned in Section 2, water vapor in sufficient quantity (i.e., at high enough temperature) is also an inertant, though its effect has not been quantified for the $H_2/N_2O/N_2$ system.

6.0 Conclusions

Gases produced from laboratory-tested samples of Hanford wastes from several tanks have contained enough fuel (primarily H_2) and N_2O oxidizer to be self-flammable (i.e., flammable in the absence of air). Insufficient evidence is available to determine how the $N_2O:H_2$ ratio and amount of self-inerting by waste-generated N_2 will vary with modest amounts of water dilution of the tank waste or with other aspects of waste processing in the WTP that change the waste liquid composition.

Example calculations of flammability at 25°C (see Section 5) indicated that a release gas fraction of approximately 0.3 in a well-mixed, initially N_2-inerted headspace could produce marginal self-flammability for a release gas composition of 15% N_2, 25% H_2, and 60% N_2O, a composition that is not outside the realm of possibility. Higher release gas fractions (i.e., in the range of 0.5 to 0.6) would be needed to reach self-flammability at a broader range of H_2 fractions for this N_2 fraction, or to reach marginal self-flammability for a higher-N_2 release gas (30% N_2, 21% H_2, and 49% N_2O). Given high enough in-situ pressures on the retained gas, small enough headspace volumes, and outflow of gas from the headspace during the gas release, a retained gas volume fraction of 0.3 could produce release gas fractions that would make an initially N_2-inerted well-mixed headspace self-flammable. This retained gas fraction has been observed in laboratory tests of retention in gas-generating simulant layers of 16 to 33 Pa.

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Appendix A

Derivation of Release Equations

Appendix A

Derivation of Release Equations

This appendix contains the derivation of Eq (5.2) and Eq (5.3) as they appear in the main body of the report.

The volume of the headspace is V_0 both before any gas is retained and after the (assumed complete) gas release. The gas-retaining portion of the waste has a non-gas volume of V_W, which is its solids/liquid volume before any gas retention. The maximum retained gas volume fraction, volume of gas per volume of gas plus solids and liquid, is α.

Define V_1, the volume of headspace just before release (minimum headspace volume) as

$$V_1 = V_0 - \frac{\alpha}{1-\alpha} V_W$$

This volume V_1 consists entirely of inertant N_2. Define the specific gas ratio $\varphi \equiv \alpha/(1-\alpha)$, and the above equation becomes

$$V_1 = V_0 - \varphi V_W$$

The pressure in the headspace just before release is assumed to be P_0 and the average in-situ pressure in the gas-retaining layer just before release is P_W. No assumption is made about whether flow from the headspace was open or closed before gas retention and headspace shrinkage began, which would affect whether P_0 is the same as the headspace pressure that existed before any gas retention.

For simplicity in carrying through the ideal-gas assumption, it is further assumed that the vessel contents, whether headspace or slurry, are all at the same temperature.

If there is unrestricted flow out of the headspace during release (open condition), and inertant gas is preferentially expelled by plug flow caused by the gas release, then the headspace pressure remains at P_0 and the release gas fraction in the headspace is

$$f_{open} = \frac{\varphi V_W P_W}{V_0 P_0}$$

The above expresses the ratio between the retained gas volume after expansion to P_0 (i.e., $\varphi V_W P_W / P_0$) and the total post-release (and pre-retention) headspace volume V_0. The value of f_{open} may be calculated as greater than 1, but this only indicates that the release was large enough to expel all the inertant gas (by plug flow) as well as some of the release gas. Because f_{open}, by definition, is a fraction of the headspace volume (or moles), it cannot exceed 1.

If there is no flow out of the headspace during release (closed condition), then the headspace after release has a volume of V_0, as in the open condition, and a pressure P_2 that is greater than P_0. The volume of inertant present in the headspace before release is V_1; after release, it is P_0V_1/P_2. The volume of release gas present is equal to $\varphi V_W P_W/P_2$.

Under isothermal conditions, this new pressure is

$$P_2 = P_0(mole\ ratio\ new/old)(volume\ ratio\ old/new)$$

$$P_2 = P_0\left(\frac{V_1P_0 + \varphi V_W P_W}{V_1P_0}\right)\left(\frac{V_1}{V_0}\right) = \left(\frac{(V_0 - \varphi V_W)P_0 + \varphi V_W P_W}{V_0}\right)$$

Define two ratios to simplify the equation.

$$R_P = \frac{P_W}{P_0}$$

$$R_V = \frac{V_0}{V_W}$$

Substituting these into the equation for P_2 gives

$$P_2 = P_0(1 + (R_P - 1)\,\varphi/R_V)$$

Because $R_P \geq 1$, it is impossible for P_2 to be less than P_0.

The closed-headspace release gas fraction is

$$f_{closed} = \frac{\varphi V_W P_W}{\varphi V_W P_W + V_1 P_0} = \frac{\varphi V_W P_W}{\varphi V_W P_W + (V_0 - \varphi V_W)P_0}$$

This closed-headspace release gas fraction can be expressed as

$$f_{closed} = \frac{\varphi V_W P_W}{\varphi V_W P_W + V_1 P_0} = \frac{\varphi V_W P_W}{\varphi V_W P_W + (V_0 - \varphi V_W)P_0} = \frac{\varphi R_P}{\varphi R_P + R_V - \varphi} = \frac{\varphi R_P/R_V}{\varphi R_P/R_V + 1 - \varphi/R_V}$$

$$f_{closed} = \frac{\varphi R_P/R_V}{1 + (R_P - 1)\,\varphi/R_V}$$

Using the same pressure and volume ratio definitions,

$$f_{open} = \frac{\varphi V_W P_W}{V_0 P_0} = \frac{\varphi R_P}{R_V}$$

Because $R_P \geq 1$, it is impossible for f_{closed} to be greater than $\varphi R_P/R_V$, and it follows that for the same values of φ, R_P, and R_V it must be the case that $f_{open} \geq f_{closed}$.

If there is a particular value of gas release fraction, f_T, to be targeted, then it is necessary to find the relation between R_P and R_V that must be present to produce this value of f.

Open condition:

$$f_T = \frac{\varphi R_{Popen}}{R_V}$$

$$R_{Popen} = \frac{f_T R_V}{\varphi}$$

Closed condition:

$$f_T = \frac{\varphi R_{Pclosed}/R_V}{1 + (R_{Pclosed} - 1)\,\varphi/R_V}$$

$$f_T + f_T(R_{Pclosed} - 1)\frac{\varphi}{R_V} = \frac{\varphi R_{Pclosed}}{R_V}$$

$$f_T - f_T\frac{\varphi}{R_V} = \frac{\varphi R_{Pclosed}}{R_V} - f_T\frac{\varphi R_{Pclosed}}{R_V}$$

$$R_{Pclosed} = \frac{f_T}{1 - f_T}\left(1 - \frac{\varphi}{R_V}\right)\frac{R_V}{\varphi}$$

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