LA-UR-02-3803

*Approved for public release;*
*distribution is unlimited.*

*Title:*

# Oxidation of Tritium Gas Under Accident and Transport Conditions

*Author(s):*

Jofu Mishima and Christopher M. Steele

*Submitted to:*

http://lib-www.lanl.gov/cgi-bin/getfile?00796853.pdf

# Oxidation of Tritium Gas Under Accident and Transport Conditions

Jofu Mishima, Senior Scientist
Pacific Western Technologies, Inc.
Spokane, Washington

and

Christopher M. Steele
Senior Authorization Basis Manager
Office of Los Alamos Site Operations
National Nuclear Security Administration

U.S. Department of Energy
Los Alamos, NM

July 2002

## Abstract - "Oxidation of Tritium Gas Under Accident and Transport Conditions"

Tritium, the radioactive isotope of hydrogen, is found in various LANL facilities (WETF, TSTA, TSFF, TA-54, TA-33). In gaseous form, tritium does not present a significant radiological hazard. When converted into the form of tritiated water or hydrocarbon, the material can be absorbed and its weak β emission releases all its energy into the human body.

Various mechanisms for this conversion of tritium gas into tritiated water are known (e.g. isotopic exchange between tritium and protium ($^1H$), combustion, microbial and vegetative processes, long-term reaction between residual oxygen during storage, etc.). The results of experimental investigations into the fraction of tritium converted to tritiated water by the processes are reviewed to determine the effectiveness of each mechanism. There appears a correlation between the tritium concentration in air and the fraction converted that is attributed to the activation of the conversion by the energy provided by the β-decay.

The most significant accident condition that could result in the large-scale oxidation of tritium gas to tritiated water (typically in vapor form) is termed combustion. Due to the many potential physical configurations and sequences for such an event, the only conservative "bounding" assumption is complete conversion (100%). Under storage conditions that shield the tritium gas from contact with air, the long-term conversion by residual oxygen in the container is conservatively bounded by a value of 1% conversion that is a factor of 10 greater than the measured values within a facility. Release of $^3H$ into an enclosure without ignition and transport within the enclosure (e.g. glove-box, room, etc.) is included in this value.

Data for the ignition of liquefied combustible gases and hydrogen under Boiling-Liquid, Expanding-Vapor, Explosion (BLEVE) conditions indicates that less than 10% of the energy available is converted to explosive forces by ignition. The partial energy conversion is attributed to the stratification of the physical forms involved (the vapor from the "flash" evaporation of the liquefied fuels are cold and, for hydrocarbon fuel, heavier than air) and the flame speed of the unconfined, flammable mixtures. It is uncertain whether this behavior is attributable to non-BLEVE conditions that are found for most releases of tritium gas at LANL.

## Table of Contents

| | | Page |
|---|---|---|
| Table of Contents | | 3 |
| List of Tables | | 6 |
| 1.0 | INTRODUCTION. | 7 |
| 2.0 | SUMMARY and CONCLUSIONS. | 8 |
| 3.0 | HYDROGEN. | 9 |
| 3.1 | Physical and Chemical Properties of n-Hydrogen Gas. | 10 |
| 3.2 | Combustion. | 12 |
| 3.2.1 | The determination of the Lower Flammability Limit | 14 |
| 3.2.1.1 | Flammable Limits - A function of direction of flame travel. | 14 |
| 3.2.1.2 | Effect of pressure and temperature on Flammable Limits | 15 |
| 3.2.1.3 | Effects of water on ignition of Hydrogen. | 15 |
| 3.2.1.4 | Detonable limits. | 16 |
| 3.2.2 | Ignition. | 16 |
| 3.2.2.1 | Ignition temperature. | 16 |
| 3.2.2.2 | Ignition energy. | 16 |
| 3.2.2.3 | Ignition sources. | 16 |
| 3.3 | Hazardous Properties of Liquid Hydrogen. | 17 |
| 3.4 | Solid Air or Oxygen, Other Oxidants. | 17 |
| 3.5 | Energy Yields and Occurrence Analysis. | 18 |
| 3.6 | Studies Pertaining to Vapor-Cloud Explosion. | 22 |
| 3.6.1 | Dispersion and delay effects. | 22 |
| 3.6.2 | Ignition studies, detonability. | 22 |
| 3.6.3 | Flame and detonation propagation in the cloud. | 23 |
| 3.7 | Hydrogen Storage | 23 |
| 3.7.1 | Low- to moderate pressure hydrogen gas storage. | 23 |
| 3.7.2 | Hydrogen gas storage on Inter-Metallic compounds. | 24 |
| 3.7.2.1 | Basic chemistry and thermodynamics. | 24 |
| 3.7.2.2 | Engineering properties of hydride storage. | 25 |
| 3.7.2.3 | Families of rechargeable metal hydrides. | 26 |
| 3.7.2.4 | Comparison of hydride storage with liquid hydrogen storage. | 27 |
| 3.7.2.5 | Purification/Separation. | 27 |
| 3.7.3 | Metal hydrides in the DOE Complex. | 27 |
| 3.7.3.1 | Savannah River Site. | 28 |
| 3.7.3.2 | Miamisburg Environmental Management Program. | 28 |
| 3.7.3.3 | Los Alamos National Laboratory. | 29 |
| 4.0 | TRITIUM. | 29 |
| 4.1 | Sources of Tritium. | 29 |
| 4.2 | Properties of Tritium (3.3.3 lead-in). | 29 |
| 4.2.1 | Physical properties. | 30 |
| 4.2.1.1 | Solubility. | 30 |

4.2.1.2 Diffusivity. 30
4.2.1.3 Permeability. 30
4.2.2 Chemical properties. 30
4.2.2.1 Reactivity. 30
4.2.2.2 Oxidizing reactions. 30
4.2.2.3 Radiolytic reaction. 31
4.2.2.4 Formation of Hydrides. 31
4.2.2.5 Corrosiveness. 31
4.2.2.6 Cleavage and cross-linking of polymers and oils. 31
4.2.2.7 Formation of Organically-Bound Tritium (OBT). 31
4.2.3 General characteristics of transport and atmospheric removal 32
4.3 Radiological Characteristics (4.2 + 4.1 + 3.3.4). 32
4.3.1 Tritium decay and associated properties. 33
4.4 Radiological Impacts from exposure. 33
4.4.1 Internal exposure. 33
4.4.1.1 Inhalation. 33
4.4.1.2 Absorption. 33
4.4.1.3 Ingestion. 33
4.4.1.4 Biological Half-life. 33
4.4.1.5 Annual Limit of Intake (ALI). 33
4.4.1.6 Derived Air Concentration (DAC). 34
4.4.1.7 Exposure hazard of tritium gas and Tritiated water vapor. 34
4.4.1.8 Estimating dose from Tritium gas 34
- Estimating dose from Tritium gas exposure. 34
- Estimating dose from Tritiated water vapor exposure. 34
- Estimating dose based on urine analysis. 34

4.4.1.9 Tritium elimination. 34
4.5 Biological Behavior. 34
4.5.1 Tritium in the DOE Complex. 35
4.5.1.1 Common forms of Tritium. 35
4.5.2 Tritium in the DOE Complex, Tritiated water 35
4.6 Potential Accidents. 35

5 CONVERSION OF TRITIUM GAS ($^3H_2$) TO TRITIATED WATER (HTO) - in storage, release to atmosphere, accident conditions. 36
5.1 Conversion of Tritium during Storage in Stainless Steel Containment Systems. 39
5.2 Conversion of Tritium after Release. Can be converted by β-decay induced conversion or by combustion. 39
5.2.1 No ignition source (β-energy Activated Conversion). 39
5.2.1.1 Dorfmann and Hemmer. 39
5.2.1.2 Yang and Gevantman. 39
5.2.1.3 Yang and Gevantman. 40
5.2.1.4 Eakins and Hutchinson. 40
5.2.1.5 Noguchi, Easterly, and Bennett. 43
5.2.1.6 Albenesius. 45

5.2.1.7 Easterly and Bennett; Easterly, Noguchi, and Bennett; Noguichi, Easterly, and Bennett. 47
5.2.2 Presence of ignition source 49
5.2.2.1 At point of release - "flaring" 50
5.2.2.2 Delayed ignition 50
A. Unconfined volume 50
B. Confined volume - explosive reaction in containment 50
6. RECOMMENDED CONVERSION VALUE FOR ACCIDENTALLY RELEASES OF TIRIUM GAS. 50
6.1 Conversion Values Used in Safety Analyses. 50
6.1.1 Fraction Tritium Converted by β-activated processes, indoors. 50
6.1.2 β-activated conversion, outdoors. 52
6.1.3 Fraction hydrogen burned in combustion. 55
6.2 Conversion Values Recommended in this Report. 61
6.2.1 Fraction Tritium converted by β-Activated processes (Simple Release of Low/Moderated Pressure Gas, continuous or puff, no ignition) 61
6.2.2 Fraction Hydrogen burned in combustion (from Releases of Low/Moderated Pressure, Gas continuous or puff, ignition). 61

7. REFERENCES 62

## List of Tables

| | | Page number |
|---|---|---|
| 1a | Gaseous n-Hydrogen Properties | 11 |
| 1b | Properties of n-Hydrogen | 11 |
| 2. | Liquid para-Hydrogen Properties | 12 |
| 3. | Slush para-Hydrogen Properties | 12 |
| 4. | Dissociation Pressure Data for Uranium Hydride, Deuteride, & Tritide | 28 |
| 5. | Penetration Depth (Ranges) of Tritium Beta | 32 |
| 6. | Conversion of Tritium to Water | 37 |
| 7. | Reaction Rates for Tritium Conversion | 37 |
| 8. | Catalytic Effect of Metals | 38 |
| 9. | Oxidation of Tritium in Dry Air | 42 |
| 10. | Conversion of Tritium to Tritiated Water in Air at 100% Relative Humidity | 42 |
| 11. | Conversion of Elemental Tritium to Tritiated water in the Presence of a Catalyst | 43 |
| 12. | Half-times of Reaction for 10 $MPC_{air}$ of Tritium | 43 |
| 13. | Rate Constants for the Tritium conversion reaction in the presence of a Catalyst | 44 |
| 14. | Tritium Releases at Savannah River Site | 53 |

## 1.0 INTRODUCTION.

Tritium is the radioactive member of the three isotopes of hydrogen. The three isotopes are:

1) protium (normal hydrogen, $n$-$H_2$) with a mass of 1 atomic mass unit (amu) and stable;
2) deuterium ($^2H_2$) with a mass of 2 amu and also stable; and,
3) tritium ($^3H_2$) with a mass of 3 amu and a β-particle emitter (average β-energy 5.7 keV, maximum β-energy of 18.6 keV).

All the isotopes of hydrogen behave in a similar manner, physically and chemically, to $n$-$H_2$ (also called "protium") with some differences due to greater mass and presence of energy due to β-decay. The relative abundance in atmospheric air is:

1) $n$-$H_2$ ($^1H_2$) 99.985%;
2) deuterium ($^2H_2$) 0.015%; and,
3) tritium ($^3H_2$) 1 x $10^{-18}$ fraction (O'Kula & East, 2000).

As a form of hydrogen gas, tritium is a combustion (i.e. fire and explosion) hazard.

Tritium gas is produced, handled, and used within the DOE Complex. Tritium gas and solids containing tritium are found in facilities at the Los Alamos National Laboratory. Typically, the gas is handled and stored at low to moderate pressures (<100-psig) in welded, stainless steel containers or as tritium absorbed on a solid (e.g. stable hydride, tritiated water on silica gel or zeolite). Small volumes may be temporarily under greater pressure such as in compressor stages.

Accident scenarios postulate the release of the gas within an enclosure (e.g. glove box), facility, or outdoors in the ambient environment. The gas may contain some small fraction (<1%) tritiated water vapor from oxidation of tritium gas during storage with residual oxygen/air in the containers. Once release, tritium gas can be oxidized by ignition or by other, slower processes that affect a lesser fraction of the gas. The behavior of the tritium gas is dependent on local environmental conditions. Since the downwind radiological impact is directly related to the fraction of tritium gas converted to tritiated water (oxide), the fraction of the tritium gas that oxidizes is of critical importance in estimating the downwind radiological impact from accidents involving tritium gas.

This document covers:

- the physical and chemical properties and behavior of n-hydrogen with respect to its potential for fire and explosion;
- storage practices for n-hydrogen and safety considerations during storage;
- the radiological characteristics of tritium;
- potential accidents within the DOE complex;

- the experimental data on the oxidation of tritium gas under various environmental conditions; and,
- conservative (grossly overstates impacts in most cases) estimates of (bounding) fractions of tritium that may be converted under accident condition and during transport.

## 2.0 SUMMARY and CONCLUSIONS.

Tritium is an isotope of hydrogen. Extensive information exists on the properties of *n*-hydrogen gas typically utilized in industry and its behavior in large spills (as a liquid). Information on the potential accidents involving tritium in DOE complex facilities is presented. The greatest potential source for a tritium gas release is during storage and processing. Storage practices and forms are addressed. The data cited for accident behavior, especially the energy yield, for accidents involving the release of large quantities of liquid *n*-hydrogen outdoors and its reaction under Boiling Liquid Expanding Vapor Explosion (BLEVE) conditions and are not representative of indoor releases of low- or moderate-pressure gas that are confined or partially confined.

Tritium gas has minor radiological impacts but converted to tritiated water the radiological impacts increase by greater than four orders of magnitude. The fraction of $^3H_2$ that is converted to tritiated water during storage, upon release to a structure or ambient environment, and by response to local environmental conditions are the significant factors controlling downwind radiological consequences.

The results of experimental studies and evaluations that have been performed to define the conversion to oxide (tritiated water) are covered. A single measurement of $^3H_2$ taken from an all-welded, stainless steel system showed a tritiated water level that was under the Lower Detection Limit for the sample and instrument (mass spectrometer) used indicating a conversion of less than 0.1%. For $^3H_2$ concentrations of >10 Ci/m$^3$ (~1 mg $^3H_2$/m$^3$), the β-induced conversion to tritiated water shows a 1st -order reaction rate constant and indicates a 1%/hr conversion to tritiated water. Most releases of tritium gas to an enclosure would result in initial mass concentrations greater than 1 mg $^3H_2$/m$^3$. With the exception of platinum/platinum black surfaces, all metal have a limited catalytic effect. The presence of water vapor also has a minor effect on the amount of $^3H_2$ converted.

Recommended values for conversion of tritium gas to tritiated water on release and under accident conditions are:

Simple Release of Low/Moderate Pressure Gas, continuous or puff, no ignition:

A. Outdoors - fraction of $^3H_2$ gas converted to tritiated water during transport from facility to ambient environment - bounding value 1% conversion to HTO.

From Releases of Low/Moderated Pressure, Gas continuous or puff, ignition:

*B.* Outdoors - due to oxidation by atmosphere, isotopic exchange, and oxidation due to absorption in the ground with conversion due to bacterial action & subsequent re-emission from ground or absorption by vegetation - bounding value <1%/day.

*C.* Confined
  1. Release into enclosure:
     - immediate ignition, gas flares to source - bounding value 100% conversion to tritiated water;
     - delayed ignition until essentially all gas is released, results in fire/deflagration/detonation - bounding value 100% conversion to tritiated water.

3. HYDROGEN (*n*- Hydrogen Gas - Physical and Chemical Properties, Combustion, Energy Yields).

Hydrogen isotopes are a combustion hazard. At atmospheric pressure and ambient temperatures, hydrogen is a gas (boiling point $-253^0$ C, Weast, 1975). Combustion, a chemical process, requires three elements - a fuel, an oxidant, and an ignition source. There are two forms of combustion, homogeneous and heterogeneous. The former involves pre-mixed fuel and oxidant (typically air) in gaseous form. The latter requires that a combustible vapor is generated from the solid fuel and mixed with oxidant to form a flammable mixture. Combustion involving hydrogen falls into the 1st category of combustion - homogeneous.

Homogeneous combustion typically results in deflagration (rapid burning). Turbulence has an effect on the completeness of burning and, therefore, on the over-pressure that may result (McKinley 1980). For large volumes of confined flammable mixture with sufficient turbulence and a strong ignition source, deflagrations may transition into a detonation (Deflagration to detonation transition, DDT)(NASA, 1996).

The behavior of normal gaseous hydrogen (*n*-hydrogen, *n*-$H_2$) that is 99.985% $^1H$ has been studied extensively. Gaseous forms of the other two isotopes (deuterium, $^2H_2$, and tritium, $^3H_2$) are anticipated to behave under the same conditions in a similar manner with some difference due to mass differences and, in the case of tritium, energy provided by the $\beta$-decay.

Three elements are required to begin the combustion process (i.e. fire and explosion) - fuel, oxidizer, and ignition source. Physical and chemical properties of the three forms of *n*-hydrogen found (gaseous, liquid, "slush") in the commercial sphere are presented. Gaseous $^3H$ or tritides are the forms typically encountered in the DOE complex.

Hydrogen gas is mobile and diffuses 10 times faster than air-in-air. The gas ignites readily with the smallest ignition energy required of most gases, spark energy of 0.015 milli-joule (<1/10th the spark ignition energy for hydrocarbons). Hydrogen has the widest flammability limits of all the flammable air mixtures (4 vol% to 75 vol%). But the Lower Flammable Limit is for flame propagation in the upward direction and higher concentrations are required for flame propagation in any direction (9 to 9.5 vol%). The temperature and pressure can affect the Flammability Limits. At the reduced atmospheric pressure found at Los Alamos, the flammability limits are narrower than those cited, above. The Concentration Limits for hydrogen-air mixtures that can detonate (18 vol% to 59 vol%) are significantly narrower than the Flammability Limit.

$^3H_2$ may be more readily ignited than *n*-hydrogen at high Ci-levels due to the potential activation of the gas by the ionization energy generated by the β-decay.

Extensive studies are cited that demonstrate that for outdoor (un-confined) releases of liquid n-hydrogen and oxidation under BLEVE-like conditions, the amount of gas that can react is limited by physical and chemical interactions to less than 10% theoretical explosive energy released for total combustion. It has not been demonstrated that the same phenomena will limit the oxidation of hydrogen to this level for a low/moderate-pressure release of gas indoors.

Tritium is be more readily converted to tritiated water due to the presence of β-decay energy in large quantities as shown by the increase to 1st-order reaction rates cited by Easterly, Noguchi, and Bennett (1985) at tritium concentrations $>10^{-3}$ Ci/m$^3$. The energy to activated the reaction between *n*-hydrogen and atmospheric oxygen is small (0.015 milli-Joule) and the conversion may be activated by the residual heat remaining in the containment and gaseous combustion products.

### 3.1 Physical and Chemical Properties of *n*-Hydrogen Gas.

There are two forms, based on the direction of rotation of the atoms within the molecule, for *n*-hydrogen. In the gaseous state, the molecules are 75% ortho- (the atoms rotate in opposite directions) and 25% para-hydrogen (the atoms rotate in the same direction) (NASA, 1996). Upon condensation, the fraction in the two forms change until 75% is in the form of para-hydrogen and 25% in the form of ortho-hydrogen in liquid hydrogen and "slush" (a mixture of solid and liquid hydrogen).

At ambient temperatures and atmospheric pressure, *n*-hydrogen is a colorless, odorless gas. Small hydrogen fires are especially hazardous, since, the flames from the pure gas are a light blue and nearly invisible to the naked eye (McKinley, 1980).

Relevant properties for the various forms of *n*-Hydrogen are given in Tables 1a and 1b for gaseous *n*-hydrogen, Table 2 for liquid *n*-hydrogen, and Table 3 for "slush" *n*-hydrogen:

## Table 1a
## Gaseous n- Hydrogen Properties
## (after NASA, 1996)

| | | |
|---|---|---|
| Reference temperature, F [R] K | | 68 [527.7] 293.15 |
| Standard pressure (1 atm.) psia (kPa, abs.) | | 14.69 (101.325) |
| Density (@ 527.1R & 1 atm.) lb/ft$^3$ (g/m$^3$) | | 0.00523 (83.7) |
| Specific volume (@ 527.7R & 1 atm.) ft$^3$/lb (m$^3$/g) | | 191.4 (0.0119) |
| Specific heat, a Btu/lb-R (J/g-K) | $C_p$ | 3.425 (14.33) |
| | $C_v$ | 2.419 (10.12) |
| Velocity of sound, ft/sec (m/sec) | | 4246 (1294) |
| Heat of combustion, BTU/lb (kJ/g) | low | 51 596 (119.93) |
| | High | 61 031 (141.86) |
| Stoichiometric composition in air, vol% | | 29.53 |
| Stoichiometric flame temperature, F (K) | | 3712 (2318) |
| Autoignition temperature, F (K) | in air | 1084 (858) |
| | In oxygen | 1040 (833) |
| Flammability limits, lower and upper, vol% | $H_2$-air mixture | 4.0 and 75 |
| | $H_2$-$O_2$ mixture | 4.0 and 95 |
| Explosive limits | $H_2$-air mixture | 18.3 and 59 |
| | $H_2$-$O_2$ mixture | 15.0 and 90 |
| Minimum spark ignition energy @ 1 atm, Btu (mJ) | in air | $1.9 X 10^{-8}$ (0.02) |
| | In oxygen | $6.6 X 10^{-9}$ (0.007) |

## Table 1b
## Properties of n-Hydrogen
## (after McKinley 1980, pg. 222)

| | |
|---|---|
| Molecular weight | 2.0159 |
| Triple-point temperature | 13.957 K |
| Triple-point pressure | 0.0711 atm. |
| Triple-point liquid density | 38.3 mol/liter |
| Triple-point solid density | 43.10 mol/liter |
| Triple-point vapor density | 0.0644 mol/liter |
| Normal boiling point | 20.39 atm. |
| Normal boiling-point liquid density | 35.2 mol/liter |
| Normal boiling-point vapor density | 0.6604 mol/liter |
| Critical temperature | 33.19 K |
| Critical pressure | 12.98 atm. |
| Critical volume | 14.94 mol/liter |
| Latent heat of fusion at triple point (p-$H_2$) | 28.08 cal/mol |
| Latent heat of vaporization at nbp | 214.5 cal/mol |
| Heat of combustion, gross | 68317 cal/mol |
| Heat of combustion, net | 57798 cal/mol |
| Limits of flammability in air | 4.0 to 75 vol % |
| Limits of detonability in air | 18 to 59 vol % |
| Burning velocity in air | Up to 2.6 m/sec |
| Burning velocity in oxygen | Up to 8.9 m/sec |
| Limits of flammability in oxygen | 4.0 to 95 vol % |
| Limits of detonability in oxygen | 15 to 90 vol % |
| Detonation velocity of $H_2$-$O_2$ mixture:<br>15% $H_2$ in oxygen | 1400 m/sec |

| | |
|---|---|
| 90% $H_2$ in oxygen | 3600 m/sec |
| Spontaneous ignition temperature | 520$^o$ to 580$^o$ C |

Table 2
Liquid para-Hydrogen Properties
(after NASA, 1996)

| | | |
|---|---|---|
| Boiling point @ 1 atm. F [R] (K) | | -423.3 [36.49](20.27) |
| Vapor pressure at F [R], psia (kPa) | -402 [57.7] | 163.0 (1124.3) |
| | -420 [39.7] | 23.7 (163.5) |
| | -423 [36.5] | 14.7 (101.4) |
| | -433 [26.7] | 1.9 (13.1) |
| Density (@ 36.49R & 1 atm.), lb/ft$^3$ (kg/m$^3$) | | 4.42 (70.79) |
| Criticality density, lb/ft$^3$ (g/m$^3$) | | 1.99 (31.49) |
| Critical pressure, psia (kPa) | | 187.5 (1292.7) |
| Triple point temperature, F [R] (K) | | -434.8 [24.84](13.80) |
| Specific heat, a Btu/lb-R (J/g-K) | $C_p$ | 2.32 (9.69) |
| | $C_v$ | 1.37 (5.74) |
| Heat of vaporization, Btu/lb (J/g) | | 191.7 (445.59) |
| Heat of fusion, Btu/lb (J/g) | | 25.1 (58.23) |

Table 3
Slush (para-) Hydrogen Properties
(after NASA, 1996)

| **State of hydrogen** | **Temperature, R (K)** | **Vapor Pressure, Psia (kPa)** | **Density, lb$_m$ Kg/m$^3$** |
|---|---|---|---|
| Liquid | 36.49 (20.27) | 14.69 (101.28) | 4.42 (70.79) |
| Liquid at triple point | 24.84 (13.80) | 1.02 (7.04) | 4.81 (77.04) |
| Slush 50 max % solid | 24.84 | 1.02 (7.04) | 5.09 (81.50) |
| Slush, 50 vol% solid | 24.84 (13.80) | 1.02 (7.04) | 5.11 (981.7) |
| Solid at triple point | 24.84 (13.80) | 1.02 (7.04) | (86.50) |

3.2 Combustion. - The major hazards associated with *n*-hydrogen are fire and explosion. The determination of the mode of combustion, fire or an explosive reaction, depends on local environmental conditions such as:

- presence or absence of an ignition source;
- the location of the ignition source relative to the point of release; and,
- the degree of mixing prior to ignition (within the flammable limits for the gas, turbulence).

*n*-Hydrogen can explode in two modes - deflagration & detonation:

a. Deflagration. The ordinary mode of burning; flame travels through the mixture at subsonic speeds. Unconfined vapor clouds of hydrogen-air mixtures can be ignited by a small ignition source. Flame speed is typically tens to hundreds of ft/s. Rapid expansion of hot gases produces a pressure wave that is not extremely severe but can damage nearby structures (NASA, 1996) and disperses unburned flammable material. Most mixtures of large quantities of gases deflagrate (Strehlow, undated)

b. Detonation. Flame and shock waves travels through mixtures at local sonic/super-sonic speeds. Pressure ratios across a detonation wave are considerably greater than for deflagration. Over-pressures generated are a hazard to personnel, structures, and nearby facilities (NASA, 1996).

Detonation often builds up from an ordinary deflagration that is ignited in a confined or partly confined mixture; even when ignited by a minimal ignition source. Typically a powerful ignition source is required to transition from a deflagration to a detonation in unconfined (typically outdoors) hydrogen-air mixture. Confined hydrogen-air or hydrogen-oxygen mixtures can be detonated by relatively small ignition sources (NASA, 1996).

The pressure ratio across detonation wave in hydrogen-air mixture is approximately 20 (300 psi if mixture is at atmospheric pressure). When a wave strikes an object, the pressure ratio seen by the object can be between 40 & 60. Pressure ratios are even larger where Deflagration Detonation Transition (DDT) occur (NASA, 1996).

Some of the considerations in the combustion of gaseous *n*-hydrogen are:

a. Leakage. In both liquid & gaseous state, hydrogen particularly is subject to leakage due to low viscosity and low molecular weight (leakage is inversely proportional to molecular weight). Leakage rates are 100 times greater than for JP-4 fuel, 50 times greater than for water, and 10 times greater than for liquid nitrogen from the low viscosity alone.

b. Diffusion and buoyancy. Diffusion rate of hydrogen in air is 10 times greater than for air in air. In a 500-gallon spill demonstration, hydrogen diffused to non-explosive (approximately 15 vol%) mixture in 1-minute. Air turbulence will increase the rate of hydrogen diffusion.

   Buoyancy limits the spread of the flammable mixture resulting from hydrogen release. *n*-Hydrogen is initially heavier than air at existing temperature after evaporation from liquid spill. At a temperature of -418$^{o}$ F (-214$^{o}$ C), hydrogen vapor are lighter than air and the cloud becomes buoyant.

c. Flammability. *n*-Hydrogen is flammable over a wide range of compositions in mixtures with air, oxygen, or other oxidizers (NASA, 1996). The Upper & Lower Flammability Limits for *n*-hydrogen are shown in Tables 1a and 1b. Note that the Lower Flammability Limit (sometimes referred to as the Lean Flammability limit) is for the propagation in an upwards direction.

3.2.1 The Determination of the Lower Flammability Limit - The definition of the flammability limits are not sufficiently precise. The concentration may show a variation of 0.1% concentration for 0%-100% propagation range. The concentration for *n*-$H_2$ for 100% propagation increases from 4.2% $H_2$ at a temperature of $25^o$ C to 6.3% *n*-$H^2$ at a temperature of $130^o$ C. 100% flame propagation concentration may be a more appropriate limit; a probabilistic view for the Flammability Limits may be more realistic and fundamental. Lean limit for 0% propagation at $25^o$ C is 4.13 vol% *n*-$H_2$ but is cited in literature as 4.0 vol% (McKinley, 1980).

The presence of diluents affects thermodynamic and transport properties and kinetics. Addition of diluent increases lean limit almost linearly.

3.2.1.1 Flammable Limits – as a function of direction of flame travel.
"Hydrogen Flammable Limits" are peculiar. The heat of combustion of a Lower Flammable Limit mixture of most gases will result in a flame temperature much higher than the ignition temperature of the mixture. The lower limit for hydrogen in air, 4.0 vol% for upwards propagation, produces a calculated average flame temperature of less than $350^o$ C, whereas the ignition temperature of hydrogen in air is $585^o$ C. This is a very low average temperature that can be understood from observations that the rising flame in a limit mixture rises as luminous balls, consuming only a part of the hydrogen. Fresh hydrogen diffuses into the burning ball and yields a higher effective concentration of hydrogen than the hydrogen that was present initially. It has been observed that not all the hydrogen is consumed in an upward propagating flame in a 2-in. tube until a concentration of 10 vol% hydrogen was present. Similar experiments with a horizontal tube resulted in a lower flammability of 6.5 vol% in air; downward propagation requires about 9.0 vol% hydrogen in air. The upper limit is about 75 vol% for propagation in all directions." (McKinley, 1980)

Consistent data for Flammability Limits of homogeneous mixtures of hydrogen gas in air at atmospheric pressure are presented for temperatures down to $-130^o$ C (Karim, Wierzba, and Boon, undated). Also, it considers retardation of the combustion of lower homogeneous hydrogen-air mixture due to dilution by inert gases such as $CO_2$, $N_2$ and He. Enhancement of Flammability Limits in mixtures of air & CO, $CH_4$, $C_3H_8$, and $C_2H_4$ is due to the presence of some hydrogen.

The Lower Flammable Limit is a minimum fuel concentration in air allowing propagation of flame from adequate ignition source. These values need to be carefully assessed relevant to accuracy and limitations particularly when a substantial concentration of inert gases are present.

Excellent literature reviews on Flammability Limits are available. Still some uncertainties need to be considered especially for hydrogen with the wide ranges of apparatuses and procedures being used to determine these values. There is a need consistent data from a single apparatus for wide range of fuel and diluent gases, especially combustion by-products.

The experiments used hydrogen with methane, carbon monoxide, propane & ethylene; inert gases nitrogen, carbon dioxide, and helium. Upward propagation generates the lowest Flammability Limit for the temperature range from ambient to $-120^{o}$ C.

A flammable mixture is not associated with constant flame temperature; only approximated.

Conclusions -

a) "The Lower Flammability Limits of a fuel such as hydrogen and their mixtures should be considered on a probabilistic basis. For safety considerations, the zero probability figure needs to be quoted, while for fuel utilization by combustion, the 100% probability figure needs to be considered." (McKinley, 1980)

b) "The concept of constant flame propagation temperature for judging the flammability limits at different initial temperatures and the extent of inert addition should be used only to yield approximate values. The flame temperature, when mixtures of fuels are involved, depends on the kind of fuel and their proportions in the mixture used. For fixed composition of fuel mixture, the concept of constant flame temperature gives adequate prediction of the lean limit of such a mixture with the addition of nitrogen or carbon dioxide." (McKinley, 1980)

c) "The Lower Flammability Limits of fuel mixtures containing hydrogen, with the addition of diluents can be predicted accurately on the basis of a knowledge of the corresponding flammability limits of the components under the same conditions using le Chatelier's formula." (McKinley, 1980)

3.2.1.2 Effect of pressure and temperature on Flammable Limits
Pressure has little effect on lower flammable limits in oxygen for propagation in any direction (from atmospheric to 122 atmospheres); 8 vol% to 10 vol%. The temperature of the pre-ignition mixture has a marked effect. At ambient temperature, the Flammability Limits are 9.5 vol% and 75 vol% for flame propagation in any direction; the limits broadens linearly with temperature to 6.3 vol% and 81.5 vol% (McKinley, 1980).

Reducing the pressure tends to narrow the Flammable Limits (raise lower limit and reduces the upper limit). This is of some consequence for events involving *n*-hydrogen at Los Alamos that has an atmospheric pressure of approximately 0.76 atmosphere. No mixture of hydrogen & air has been found to be flammable below 1.1 psia (NASA, 1996).

3.2.1.3 Effects of water on ignition of Hydrogen. A dense fog of small droplets of water at ambient temperature have little effect on $n$-$H_2$ flammability limits. The effect is larger at higher fog temperature due to increased dilution with $H_2O$ vapors/droplet vaporization.

The fog concentration to obtain inerting is a strong function of water droplet size. Experimental studies have shown that water vapor has small effect on lower flammability limit until >55% inerting is achieved; higher ignition temperatures are required as steam concentrations increase (Thompson, undated).

3.2.1.4 Detonable limits (McKinley, 1980):

- in air –
  Lower Detonation Limit (LDL) 18 vol%,
  Upper Detonation Limit (UDL) 59 vol% (velocities 1 m/sec to 8.9 m/sec)
- in oxygen –
  LDL 15 vol%
  UDL 90 vol% (with strong ignition sources or strong confinement, mixtures may pass over relatively slow burning velocities to detonation velocities up to 3600 m/sec).

### 3.2.2 Ignition

3.2.2.1 Ignition Temperature. The auto-ignition temperature for self-sustained Combustion, 1065 ° F (874 K/574° C) for a stoichiometric mixture of *n*-hydrogen-air, is high compared to 484.1° F (523 K) for kerosene and 438.2° F (499 K) for aviation fuel such as octane. Although the auto-ignition temperature is higher than for most hydrocarbons, hydrogen's lower ignition energy makes ignition of hydrogen-air mixture more likely. Minimum energy for spark ignition at atmospheric pressure is 0.015 milli-joule (NASA, 1996; McKinley, 1980).

At 3 to 8 psia, the auto-ignition temperature of a flammable hydrogen-air mixture is 650° F. Pressure at Los Alamos is approximately 11.2 psia indicating an auto-ignition temperature <1050° F (approximately 566° C) and > 650° F (approximately 434° C). Flammable hydrogen-air mixtures ignited at low ignition energy, 1/10th the energy that is required to ignite gasoline-air mixture. Invisible spark or static spark from person can ignite flammable *n*-hydrogen-air mixtures.

3.2.2.2 Ignition Energy. The ignition energy must be sufficient to establish a flame of a minimum critical size. If the flame is less than critical size, the flame is quenched by ambient unburned gas. The minimum ignition energy for a 30 vol% hydrogen in air (slightly greater than a stoichiometric mixture) is a spark ignition of 0.015 milli-joule. (The minimum spark ignition for a stoichiometric mixture of hydrocarbons $C_1$ to $C_6$ in air are in the range of 0.25 milli-joule; >10 times that required for hydrogen). Thus, *n*-hydrogen is relatively easy to ignite by spark (McKinley, 1980).

3.2.2.3 Ignition Sources. Elimination of ignition sources should be considered a second line of defense. All likely ignition sources should be eliminated; especially near hydrogen hazard areas. Hydrogen is easily ignited by unexpected means, and the presence of unknown ignition sources should always be considered. Any necessary ignition sources in hydrogen area should be surrounded locally with inert gas and non-combustible heat sinks (NASA, 1996).

A potential ignition source are electrical sparks caused by sudden electrical discharges between objects having different electric potential (e.g. breaking electric circuits or discharge of static electricity).

Thermal ignition is caused by burning materials or hot objects:

- Sparks which are caused by hard objects coming in forcible contact with each other such as metal striking metal or stone (sparks are particles of burning material that have sheared off as a result of contact). In liquid hydrogen atmospheres, even spark-proof tools can cause ignition. Nylon clothing and certain kinds of electrically insulated shoes have generated large static electricity build-up and produced significant sparks (NASA, 1996);
- Objects at temperature of $1065^o$ F (847 K) that will ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure; substantially cooler objects (approximately $600^o$ F, 590 K) may cause ignition under prolonged contact at less than atmospheric pressure. Metal-to-metal, metal-to-rock, even spark resistant tools are not immune to spark generation (McKinley 1980);
- Thermite Sparks. Aluminum particles impacting iron oxide ($Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$) are highly exothermic; and,
- Open flames or smoking readily ignite hydrogen mixtures.

Other potential ignition sources are:

- Lightning;
- Static electricity; and,
- Hot Hydrogen and Flash Fire. Leak of hydrogen at a temperature of $1050^o$ F to $6000^o$ F always results in a flash fire.

3.3 Hazardous properties of liquid hydrogen. All hazards associated with gaseous hydrogen exists for liquid hydrogen. Additional hazards (e.g. Hydrogen Embrittlement (for liquid hydrogen) and effect on materials used for storage and handling), and cited in NASA (1996) and McKinley (1980). Use of quantity-distance concept as a protective measure is also discussed in NASA (1996).

3.4 Solid air or oxygen, other oxidants. The effect of solid oxidants in liquid hydrogen appears to be generating a higher enrichment of oxygen that may cause explosion. Fracture of solid oxygen particles in liquid hydrogen are believed to provide sufficient energy to initiate explosion. Nitrous oxide solid in liquid hydrogen and other mild ignition energy are sufficient to result in explosion with high pressure hydrogen down to $-300^o$ C (McKinley, 1980).

3.5 Energy Yields and Occurrence Analysis. The literature cited provides information on and estimates of the explosive energy yield from unconfined (outdoors) spills of liquid fuel with the resultant Boiling Liquid Expanding Vapor Explosions (BLEVE). Typically, after-the-fact estimates of the explosive energy yields are based on estimates of structural damage (or the absence of such damage) as a function of distance from the source compared to known pressure values for structural damage of the structure and materials-of-construction. The explosive energy release at the point of origin is estimated by the Scaled-Distance correlation for TNT. As such, the estimates apply to the energy released by the reaction during the very brief period (seconds) when the pressure impulse is formed. Reactions outside this period are not accounted for and, for estimates of explosive potential, are of little concern. The estimates are not of the fraction of reacting flammable/combustible gas converted to oxide over the entire duration of the event.

The event of concern represents the outdoor scenario where the gases are un-confined. The buoyancy of the gases (especially hydrogen) and the turbulence generated by the reaction resulting in rapid dispersal of the unburned gases in front of the flame front (especially for a gas with high mobility as hydrogen). The stored materials are cryogenic liquids and initially result in a cold, dense, layer of gas near the surface. The rapid dispersal of gases can not occur in confinement that leads to the additional concern for Deflagration Detonation Transition (DDT). The unburned hydrogen remaining may continue to undergo oxidation (albeit at a much reduced rate) until released. The effect of the residual heat to activate the conversion has not been determined by experimentation but is indicated by the activation of oxidation as a function of concentration due to the energy associated with β-decay.

The information is illustrative but should not be applied to low-pressure releases of tritium gas indoors (confined/partially confined) without careful consideration.

Ordin (undated) reviewed 96 mishaps from primarily NASA centers & contractors to provide overall safety of hydrogen. He categorized these causes of the events and occurrences involving liquid hydrogen fuel used as a propellant as:

(1) Procedural deficiencies: failure to follow or prepare proper procedures (25%).
(2) Planning deficiencies: limited planning/ failure to perform hazard studies (14%).
(3) Material failures: failure of materials and components due to stresses that had been considered within design limits (3%).
(4) Design deficiencies: inadequate component or system design, including failure to specify safety devices and omission of essential information, failure to determine stress and fatigue, errors in material selection (such as cleric errors in drawing & specifications)(22%).
(5) Operation and work area deficiencies: inadequate working conditions (26%).
(6) Malfunctions: any anomaly, including components in a system which failed to function as intended (8%).
(7) Material incompatibility (3%).

(8) Contamination.
Ninety-six (96) mishaps are briefly described in an Appendix (Ordin, undated). Valve malfunctions/leaks were responsible for 20%. The reference cited discusses various factors that contributed to accidents.

Ignition occurred 62% of time when hydrogen was released to atmosphere and every time hydrogen was released to containment (e.g. tank, line) (the ambient temperature resulting from the release of liquid *n*-hydrogen is low).

Source of ignition when hydrogen-air mixture ignited:
30% unknown;
24% electrical shorts/sparking;
17% static electricity;
5% each for welding/cutting torches, metal fracture, and impingement of high-velocity gas.

Unconfined (in open-air) releases can be very dangerous because large amounts of material now involved. The mechanism is not well understood.

Strehlow (undated) reviewed accidental, unconfined vapor cloud explosions that occurred over a 42-yr (1930-72) period in the U.S. and Germany. The explosions were categorized by the type of condensed fuel involved. The time period of occurrence versus estimates of dollar of damage are reported. The majority of explosions are from spills of combustible gases with vapor density greater than air. Pressures were greater than ambient but <100 psig at ambient temperature.

The nature of the resultant fire/explosion depends on:

- nature of fuel;
- rapidity of spill coupled with wind conditions, terrain, and/or location of nearby building;
- delay before ignition; and,
- the nature of ignition source.

Explosion (with strong blast wave) are less likely with fuels having lower vapor pressures and higher vapor densities; in stable atmospheric conditions (calm winds) the vapors generated hug the ground and flammable concentrations are present only at fuel vapor-air interface. A very strong ignition source is need for explosion. Simple flash-over and ignition of the rest of fuel by mixing driven by buoyant hot product gases are typically the consequences.

Materials with high vapor pressures tend to form explosive clouds. At high flow velocities, flash evaporation of the liquid occurs when local pressures drop below vapor pressure of liquid. The phenomenon produces large amounts of vapor at high velocity that entrains air producing air-fuel mixtures at leak location resulting in a larger portion of vapor cloud at explosive concentration. Coupled with proper wind speed, terrain or building configuration at the site, and delayed ignition, very large vapor clouds may form.

A large, pre-mixed cloud of combustible mixture can detonate depending on strength and characteristics of ignition phenomenon. Proof of the mechanism responsible is lacking. More commonly, mixtures that deflagrate can have high velocities and extensive blast wave damage (for large clouds of gas before an explosion).

Reider, Otway, and Knight (1965) reported on the inadvertent auto-ignition of liquid *n*-hydrogen release during experiment (1/9/64 LANL experiments at NTS) to measure sound levels from release of gaseous hydrogen at high flow rates. Three-seconds after shut down, the mixture auto-ignited. Deflagration shock wave was of near-sonic velocity. The amplitude of negative phase of pressure impulse was equal to positive phase (amplitude negative phase 0.25 psig).

Reider, Otway, and Knight (1965) considered an auto-ignition from the following three initiations (the 4th becoming a possibility following the experiment):

1. Electrification of gas. Large mass flow can build up substantial potential difference between grounded nozzle and any point in gas. The phenomenon is unlikely without entrained droplets or particles. Thought the gas is unlikely to electrify in pure state (gas used was of cryogenic origin).

2. Electrification of particles carried in gas. The gas storage system was blown-down prior to use to clean the system. Higher flows were used than in previous runs with the possibility of dislodging new scale formation. Electrification of small diameter particles can be a significant ignition source.

3. Incandescence of large particles. Exit velocity was estimated to be approximately 4,000-ft/s, possibility of impact of metal or oxide particles on metal resulting in sparks.

4. Rupture of metal rod (welded across mouth of nozzle).

Shortly after down ramp hydrogen flow, fire was observed at nozzle followed by a fireball of modest luminosity. Infra-red imaging showed a cloud ~30ft diameter X 150-ft high. The explosion followed immediately. 2,000-lb of hydrogen was released; and an estimated 200-lb of the hydrogen gas released appears to have contributed to the explosion (theoretical yield 10% of TNT Eq.). The flame speed was estimated at approximately 100-ft/s.

The damage was widespread but superficial. At first glance, all damage was produced by the negative phase of the pressure pulse (walls of light building & heavy doors bulged outward). Two glass windows were blown in. A reasonable engineering estimate of the over-pressure for the event was 25-49 psig.

Burgess, Murphy, Zabetakis, and Perlee (undated) reported unconfined gas explosion range from 5% to 10% TNT Eq. of energy available. The paper attempts to show that the yields were probably due to the fact that only a small fraction of atmospheric dispersed gas mixture can be in the flammable range. The paper further compares the measurement of atmospheric dispersion to bi-variate Gaussian distribution with standard deviations, $\sigma_y$ (cross-wind dispersion) and $\sigma_z$ (down-wind dispersion) from air pollution literature. Three observations in relation to dispersion of flammable gas are:

(1) The concentrations of interest (flammable limits) are much higher than most critical pollutant concentrations;

(2) Concentration peaks may well be an order-of-magnitude higher than time-averaged concentration that are derived from statistical treatment; and,

(3) Most flammable vapors are heavier than air and form ground-hugging layers that extend the distance of the ignition hazard.

Calculation of the volume of vapor-air mixtures within surfaces of equal concentrations was performed. Figures in the cited document show most flammable vapors quickly disperse to concentrations below flammable limits.

The authors accepted the Pasquil concept of atmospheric dispersion (horizontal and vertical Gaussian distribution) for their calculations. They used a release rate of 25 $m^3/s$ (loss from broken propane gas line which exceed loss of Liquid Natural Gas from tanker truck) for calculations with a D category and 2 m/s wind speed.

The calculations show 25 times more fuel vapor in the concentration range between 0.1% and 1% than from 1% and 100% within 1 minute. During neutral or unstable conditions, the plume approaches steady state conditions in approximately 10 minutes. At 25 $m^3/s$ release rate for 15,000 $m^3$ gas release, tens of $m^3$ may be in flammable concentration range; representing 0-15% of theoretical yield. These values would decrease if ignition is delayed.

Some observations from the study:

A. Fire Hazard - It is assumed that the fuel-air mixture below the flammable limit that is present may be neglected. Fuel concentrations above the flammable limits can eventually burn by admixture of air. Thermal output and radiation therefore relate to total fuel concentration that is above lower flammable limit.

B. Effect of Rate of Release of Flammable Material – For releases much above the rate of 25 $m^3/s$, gravitational settling of the vapors becomes a problem for vapors that are heavier than air.

In principle, a large volume of flammable gas can instantaneously be generated and move down-wind as an expanding "puff". Actually, typically more likely to ignite at source. If

189 $m^3$ of liquid propane is released at $0^o$ C, 25% of the volume will flash to vapor (representing approximately 15,000 $m^3$ vapor) while the remainder cools to below the boiling point ($-42^o$ C). All concentrations >15% are gone in 15 s, all concentration >6% in 34 s, all concentration >4% in 44 s. At the moment of the greatest potential hazard, approximately 50% of the fuel will be found within the flammable limits.

### 3.6 Studies Pertaining to Vapor-Cloud Explosion.

3.6.1 Dispersion and delay effects. Two types of spills were noted - (1) single massive spill; and (2) continuous spills. The dispersion of both toxic vapors and combustible vapors has been modeled successfully. The modeling of surface spills considers the wind velocity and direction, the presence of an atmospheric inversion, and the neutral or unstable lapse-rate.

James (1948) reported on the distance between spill and ignition for 81 rail-car spills: 58% of the incidents ignited within 50 feet; 76% of the incidents ignited within 100 feet; and all incidents ignited within 300 feet.

Burgress (1971) reported that for continuous spills one should consider the nature of the flow at spill location.

Burgress studied three special fuels:

- Hydrogen fuels which disperse rapidly but less dangerously than heavy fuels;
- Liquid rocket fuel/propellants (e.g. hypergolic fuels which auto-ignite upon exposure to air and possess the unique characteristic of having the oxidizer present with the fuel.)
- Liquid Natural Gas (mostly methane) in which evaporation from spills off of the ground can be predicted by ordinary heat-transfer considerations. The evaporation process starts rapidly and then decreases with time as earth is cooled by evaporation process. Spills on water exhibit "explosive" evaporation rates and are hence extremely dangerous.

3.6.2 Ignition studies, detonability. As cited, above, there is a long and varied list of potential ignition sources (including electrical and frictional sparks). Removing or covering all potential ignition sources may result in more severe events when ignition does occur (delays as great as 15-min have been reported that allow formation of enormous combustible volumes). Ignition of most flammable mixtures is relatively easy. Direct initiation of detonations can occur using a sufficiently strong ignition.

Benedict (1970, 1971) studied ignition of hydrocarbon fuels using sheet explosives and flying-plate(s). Benedict cited a relationship between fuel concentration and the amount of explosive required to initiate the detonation at the upper explosive limits. Direct initiation of near-stoichiometric mixtures was produced by 8-in diameter x 0.25-in thick plate(s) traveling as a blunt body (<$30^o$ cant to flow direction) at 7500-ft/s. Benedict also cited other experiments on detonation scenarios.

Cassutt (1961) used 2 grams of explosive to initiate a detonation of a hydrogen-air mixture and a 6 gram squib to result in an immediate detonation of stoichiometric hydrogen-oxygen mixture.

Bach et al. (1971) analyzed the rate of energy deposition into gas and found this rate important for the direct initiation of a spherical detonation wave and indicated that the geometry of the explosive charge was important for wave development. They further indicated that a DDT can not be completely discounted as a possible outcome.

3.6.3 Flame and detonation propagation in a gaseous cloud. No experiments appear to have been performed for this area, however:

Woolfolk (1971) used a 15- & 90-ft$^3$ spherical balloons filled with a stoichiometric hydrogen-oxygen mixture centrally ignited, average flame velocities were produced one order of magnitude greater than prediction. (0.9-cm/millisecond using a Bunsen burner, 6.8 – 12 cm/millisecond using balloons). Buoyancy driven augmentation of flame velocity was noted.

Two areas not investigated: (1) effect of composition fluctuations on flame or detonation wave; (2) the behavior of truly unconfined clouds during deflagration (all experiments in balloons or bags).

*A.* Blast Effects. Ideal blast wave theory for application to a point source; instantaneous energy releases using TNT equivalence from accidental explosion, correlating blast damage vs. distance data. The use of % yield curves applied to a spill for a yield range from 0.75% to 16%. Ideal blast wave theory was found to be adequate for detonations but the characterization of the deflagration reaction was not simple. Evidence that scaled TNT equivalents increases with distance for a deflagration was noted.

Doyle (1971) 3000-lb cryogenic ethylene: 2% TNT Eq. nearby; 10% TNT Eq some distance away.

3.7 Hydrogen Storage.

Typically, tritium is stored within the DOE complex as a moderate to low pressure gas within welded stainless steel vessels. Tritium is held as a stable-tritide (MEMP, SRS, LANL) at single locations but *n*-hydrogen is also stored as unstable (readily released upon slightly elevated temperature) hydrides. Under both storage forms, the hydrogen would be released under low to moderate pressures under accident conditions for simple leaks. Catastrophic rupture of the vessels could result in a high pressure release dependent upon the burst pressure of the vessel.

3.7.1 Low to moderate pressure hydrogen gas storage. The storage as moderate to low pressure gas is not covered in detail here, since, the practices and equipment (all-welded stainless steel piping and vessels) are similar to other gas storage processes used throughout the industry. The industry use of inter-metallic compounds to store hydrogen as hydrides (or tritides for the DOE complex) is increasing and is addressed, below.

3.7.2 Hydrogen Gas Storage on Inter-Metallic Compounds. General information is provided on this hydrogen storage form to provide a comprehensive coverage of the area.

Typically 50-50 atom ratio of titanium and iron ($TiFeH_x$) is used commercially for $n$-$H_2$, due to cost and convenience of use. The working storage capacity is 1.5% hydrogen. De-hydriding occurs near ambient temperature but heat must be supplied to decompose metal hydride and free hydrogen. The reaction is fast but limited by heat transfer. It can be cycled 1000s of times but are susceptible to poisoning by impurities. Magnesium hydride can store several times as much hydrogen as TiFe (5.5 wt.% hydrogen) but is a stable metal hydride (SMH) requiring heating to $300^o$ C ($572^o$ F) to dehydride. (Salzano et al., 1980).

Many inter-metallic compounds absorb hydrogen extensively. The hydrogen capacity is extraordinary showing remarkable speed in dissolving and release of hydrogen [95% complete in 200 s at room temperature]. For hydrogenated rare earth, pressure increases systematically with atomic number. For RET [RE = rare earth and T = Fe, Co, Ni], pressure increases from Fe to Co to Ni. Hydrogenation often significantly influences superconductivity (Wallace, Craig, and Rao, 1980).

$ZrH_2$ & $UH_3$ have high capacities for hydrogen but are too-stable for practical commercial use; although they are used as a storage medium within DOE. Hydrogenated inter-metallic requires less heat to desorb than related binary hydrides (Wallace, Craig, and Rao, 1980).

3.7.2.1 Basic chemistry and thermodynamics of hydrogen storage on inter-metallic compounds (Sandrock and Snape, 1980). A simple reversible reaction governs the reaction between solid metal (Me) with gaseous $H_2$:

$$Me + 2[H_2] \leftrightarrow MeH_2$$

Not all metals react directly with gaseous hydrogen, and, some of those that do, are not readily reversible. Many metals do react reversibly with $H_2$ at ambient temperatures and pressure. Metals that react reversibly include elements, solid-solutions alloy, and especially inter-metallic compounds. Such metals/compounds are termed "rechargeable metal hydrides"; solid sponges that can be repeatedly be charged and discharged at will. Inter-metallic compounds have many advantages for storage of hydrogen; the principal advantages are extremely high volumetric packing density for hydrogen.

At ambient temperature and atmospheric pressure, hydrogen absorption is small. As hydrogen pressure increases, small amounts of $H_2$ are absorbed. At some pressure, the hydride reaction is initiated and the metal begins to absorb large amounts of $H_2$ at constant pressure ["plateau pressure", 2-phase mixture of metal and hydride]. Upon complete conversion to hydride, only a small addition of $H_2$ absorption occurs with increased pressure. In theory, the absorption-desorption curve is completely reversible but, in reality, complete reversibility only occurs occasionally. Hysteresis ["memory"] is the deviation from ideal absorption-desorption curves.

The hydriding reaction is exothermic [generates heat] and de-sorption reaction endothermic [absorbs heat]. The plateau pressure is related to absolute temperature by Van't Hoff eq.:

$$\ln P_p = [2/x][\Delta H/RT] + C$$

where: x from Eq. 1;
$\Delta H$ = enthalpy change (heat) of hydriding reaction;
R = Universal Gas Constant;
C = Entropy change of hydriding reaction

3.7.2.2 Engineering Properties of Hydride Storage (Sandrock and Snape, 1980).

- Plateau Pressure or Temperature. The Plateau Pressure or Temperature depends on the application and is a strong function of metal composition. A wide variety of data is available. Knowledge of the data can be used to effectively "tailor design" plateau pressure or dissociation temperature using the Van't Hoff plot so for representative materials can be chosen.

- Plateau Slope. Functional metallurgical segregation occurs in the production of a metal. A reasonably flat plateau is desired. The plateau slope may be varied and/or eliminated by heat treatment techniques.

- Hysteresis. Pressure differences between absorption and de-sorption should be small for use and will vary markedly between alloys, but is not understood. Empirical knowledge is typically applied to keep hysteresis values small.

- Heat of Reaction. The most important parameter for container design is the heat of reaction. The container must be an efficient heat exchanger; fast thermal cycling needs an effective heat exchanger.

- Hydrogen Capacity. $H_2$ capacity is a function of crystal structure [i.e. the available sites for $H_2$] and subtle metallurgical factors during alloy preparation. It is not a critical property [on a weight basis] for practical applications.

- Decrepitation. Most alloys that are used are brittle. The alloys break-down into finer powders that can cause problem. In order to prevent fine powder from being blown out, micron sized filter are provided for the exit lines; and, powder can pack resulting in severe bed impedance and expansion concerns. Expansion of the materials leads to stresses on container many times greater than from gaseous hydrogen, typically materials then plastically deform and rupture.

- Activation of Hydride Forming Alloy. Activation typically occurs prior to service. In some cases, evacuation of air and exposure to a suitable over pressure of hydrogen (a strong function of composition) at room temperature for a few minutes to an hour results in highly cracked structure, 0.1-0.2 $m^2/g$ active area. Room temperature activation is desirable.

- Kinetics. After activation, kinetics occurs extremely fast, even at room temperatures; often too fast to measure. Practically kinetics depends on the effectiveness of the heat exchanger – absorption as rapid as heat of reaction removed and de-sorption as rapid as heat can be supplied.

- Tolerance to Gaseous Impurities. Very important to use. Gaseous $O_2$, $H_2O$, $CO_2$, $H_2S$, etc. are "poisons" [interfere with sites] resulting in loss of kinetics and, ultimately, capacity. It remains dependant on the resistance of the alloy to poisoning and the purity of $H_2$. Present knowledge of this phenomenon is limited.

- Chemical Stability. An important property for high-temperature applications is the lack of stability may cause undesirable reactions ($CaNi_5 + 3H_2 \leftrightarrow CaNi_5H_6$). Repeated use at room temperatures may result in disproportionation into thermodynamically preferred $CaNi_5 + H_2 \rightarrow CaH_2 + 5Ni$. At 200° C, where diffusion of metal atoms is significant, the latter reaction begins and results in loss of reversible capacity.

- Thermal Conductivity and Specific Heat. Specific heat for metals and hydrides typically are in the range of 0.1-0.2 cal/g °C. The thermal conductivity of metal and hydride may not be sufficient for heat transfer requirements. The effective thermal conductivity of the bed depends on alloy, particle size, packing, void space, etc. and knowledge is limited in these areas.

- Safety. Hydrides are inherently safe; small void spaces and low pressures mean that little gaseous $H_2$ is present. De-sorption is endothermic which means it is also self-limiting. Self-limiting systems tend to limit accidental discharge after loss containment. Care is necessary for storage – hydride powder is pyrophoric when exposed to air [$AB_5$ compound begins to glow like ignited coal after a few minutes exposure to air]. One must avoid expansion problems due to high internal pressure that can be generated if hydride bed is over-heated. The hydride container should also have a pressure relief valve.

3.7.2.3 Families of Rechargeable Metal Hydrides (Sanrock and Snape 1980). The following subsection is a review of the main classes available. Most near room temperature (hydride-former) are inter-metallics with at least one element with a high affinity for hydrogen and one element with a relatively low affinity for hydrogen. The three classes of inter-metallics are - AB, $AB_5$, $A_2B$.

- AB Compounds. FeTi is the best known and maintains a favorable hysteresis loop.

Two plateaus are present and are represented by FeTi + ½ $H_2$ ↔ FeTiH and FeTiH + ½ $H_2$ ↔ $FeTiH_2$. These species are the lowest cost room temperature hydrides available. Disadvantages: high hysteresis; low poison resistance to $O_2$; and a high heat requirement for activation. The materials can be effective if carefully handled. Partial tertiary substitution to change plateau is possible which would increases versatility.

- $AB_5$ Compounds. $LaNi_5$ is a classic example.

Very attractive hydrogen storage properties: 1) convenient plateau pressure; 2) low hysteresis; 3) excellent kinetics; 4) easy activation; 5) relatively good resistance to poisoning. High cost is a disadvantage.

$CaNi_5$ for use when $H_2$ pressure exceeds 1 atm. at room temperature. $CaNi_5$ & $MNi_5$ [M is low-cost rare-earth mixture] form continuous solid solutions.

- $A_2B$ Compounds. An important compound is $Mg_2Ni$; a light-weight hydride. Has a very flat plateau and small hysteresis. Mobile applications. High temperature is required for H-desorption [approximately $300^o$ C]; ΔH high, -15 kcal/mol $H_2$.

3.7.2.4 Comparison of Hydride Storage with Liquid Hydrogen Storage (Sandrock and Snape, 1980).

- Hydride more energy efficient;
- cryogenic liquefaction requires upwards of 33% of combustion energy of $H_2$ for the process; hydriding only requires 10-15% of the combustion energy;
- low waste heat [e.g. room temperature heat];
- liquid hydrogen requires insulated tanks; liquid hydrogen can not be stored long period due to boil-off losses [could use hydride to collect boil-off losses]; and,
- costs of complex heat exchanger tanks and alloy disadvantage.

3.7.2.5 Purification/separation. Hydrides absorb only hydrogen and could be used as a purification process. Most alloys have similar absorption/desorption for the isotherms of hydrogen and deuterium; some show different plateau pressures for the gaseous state (e.g. vanadium, TiNi).

3.7.3 Metal Hydrides in the DOE Complex. Metal hydrides are used for tritium storage at three locations within the DOE Complex - at the Savannah River Site (SRS), Los Alamos National Laboratory (LANL), and at the Miamisburg Environmental Management Program (MEMP).

3.7.3.1 Savannah River Site. Hydrides of U, Pd, Ti (typically U or Pd are used because they are stable tritides) are used as storage to provide volume reduction and solid phase storage. Some concerns with this technology are:

- the finely divided metals used (e.g. U) can be pyrophoric;
- elevated temperature are necessary to release tritium; and,
- hydrides can be subject to fire & seismic-induced release.

The dissociation pressure is a function of temperature:

$$\text{Log } P_{mm} = -AT + B$$
$$P_{mm} = 10^{-[AT(K)] + B}$$

Table 4
Dissociation Pressures Data for Uranium Hydride, Deuteride, & Tritide.
(After O'Kula and Esat, 2000)

| Metal Tritide | Reference | Temperature Range, °C | A, (Kelvin) | B | Temperature Required to Generate Pressure of 1 Atmosphere |
|---|---|---|---|---|---|
| $UH_3$ | Spedding et al. | 260 to 430 | 4500 | 9.28 | 430° C |
| | Destriau & Seriot | 243 to 412 | 4255 | 9.08 | 415° C |
| | Wicke & Otto | 200 to 430 | 4450 | 9.20 | 434° C |
| | Mogard & Cabane | 500 to 650 | 4480 | 9.20 | 435° C |
| | Libowitz & Gibb | 450 to 650 | 4410 | 9.14 | 432° C |
| $UD_3$ | Spedding et al. | Unspecified | 4500 | 9.43 | 414° C |
| | Destriau & Seriot | Unspecified | 4401 | 9.01 | 445° C |
| | Wicke & Otto | Unspecified | 4500 | 9.40 | 417° C |
| $UT_3$ | Flotrow & Abraham | Unspecified | 4471 | 9.461 | 408° C |
| | WSRC | Unspecified | 4038.2 | 6.074 | Unspecified |

3.7.3.2 Miamisburg Environmental Management Program (Reis, 1999). Dose from intake of a particular type of SMT may be many times greater than for HTO.

ICRP-7-1 does provide Dose Conversion Factors for tritium particulate aerosols. DOE found no dose assessment methodology and no dosimetry model for low-molecular-weight organic compounds. Dose consequence for a particular SMT used and organic-bound tritium (OBT) is greater than for HTO.

3.7.3.3 Los Alamos National Laboratory (LANL). The Tritium Science and Engineering Group operates three tritium facilities - WETF, TSTA, & TSFF (LANL, 1996):

- Weapons Engineered Tritium Facility (WETF) - stable tritides and storage of waste as water vapor on solid sorbants;
- Tritium Systems Test Assembly (TSTA);
- Tritium Science and Fabrication Facility (TSFF);
- Waste Disposal Site (TA-54)(approximately 200 grams of $^3$H waste is buried at TA-54); and,
- HP site at TA-33 was the site of high-pressure tritium-handling facility being decontaminated and decommissioned

## 4.0 TRITIUM

The three isotopes of hydrogen are:

1. "Protium" - $^1_1$H [1 proton, 1 electron], 1.007825 amu, stable, comprises 99.985% of natural hydrogen;
2. Deuterium - $^2_1$H or D [1 proton, 1 neutron, 1 electron], 2.01400 amu, stable, comprises 0.015% of natural hydrogen; and,
3. Tritium - $^3_1$H or T [1 proton, 2 neutrons, 1 electron], radioactive (beta decay), 3.01605 amu, comprises approximately $10^{-18}$ parts of natural hydrogen

4.1 Sources of Tritium (LANL, 1996). The sources of tritium gas in the atmosphere are:

- MCi/year by cosmic radiation + $^{14}N_2 \rightarrow {}^{12}C + {}^3H$;
- Material from Nuclear weapons tests (in 1945-1980) that has decayed or oxidized to tritiated water and accumulated in oceans; and,
- nuclear power stations, and defense industries (1-2 MCi/year); LANL nominally releases 1 kCi/year to the atmosphere.

Oceans contain 100 MCi from natural sources and 100 MCi from man-made sources. The "typical" atmospheric concentration is approximately 15 pCi/m$^3$ resulting in a "typical" concentration in rain and ground water 30 pCi/liter.

Radioactive reactions generating tritium in various types of processes are:

- Fusion reactor: $2\,{}^2H \rightarrow {}^3H + {}^1H$;
- Fission reactor: $^6$Li + neutron $\rightarrow$ $^3$H + $^4$He; and,
- Accelerator: $^3$He + neutron $\rightarrow$ $^3$H + proton.

4.2 Properties of Tritium. All hydrogen isotopes behave in a similar manner with some deviations from *n*-Hydrogen due to mass differences (permeability & buoyancy) and the presence of β-decay energy (provides activation energy for reaction).

### 4.2.1 Physical properties (LANL, 1996)

4.2.1.1 Solubility: Defined as the ability of one material to dissolve into another; solutions of gas or liquid in a solid are common. Hydrogen dissolves in almost all materials to some extent and can be released at a later time making decontamination of tritium-contaminated surfaces is very difficult.

4.2.1.2 Diffusivity: Because $H_2$ represents a small molecule, hydrogen moves faster than other materials (i.e. hydrogen diffuses rapidly).

4.2.1.3 Permeability: The ability of one material to pass through another. Factors that affect permeability are:

a) type of materials; thickness of material, surface conditions;
b) materials that are permeable (in order of decreasing permeability) are: ceramic; metals (e.g. 304L and 316L stainless steel, aluminum, copper) and polymers (plastics);
c) polymers (plastics): Most gloves are made of polymers; thicker gloves are less permeable than thinner gloves; material such as butyl and Viton are less permeable; when working with tritium change gloves often (several times per hour); and,
d) Surface-conditions are important. The permeability of tritium through metal oxide (e.g. $Al_2O_3$, aluminum oxide) is often orders of magnitude lower than through the metal. Even a thin layer of some oxide can significantly reduce permeability.

### 4.2.2 Chemical properties (LANL, 1999; O'Kula and East, 2000).

4.2.2.1 Reactivity: The ability of an atom or molecule to combine chemically with an other atom or molecule; tritium is reactive over a wide range of compounds and materials, either directly or by isotopic exchange. Reactions may cause structural changes that can result in leaks:

1) High-temperature and high-pressure can be a problem - strength of 304L stainless steel is reduced by factor of 6 when exposed to tritium at $150^o$ C & 6 atmospheres for 2-years; and,
2) Any gas trapped in metal may result in embrittlement. $^3$He from the decay of $^3$H also weakens metals.

4.2.2.2 Oxidizing Reactions:

1. Hydrogen ("protium", deuterium, tritium) in the presence of oxygen (e.g. air) can react slowly, burn rapidly, or explode to form $H_2O$/HTO.
2. HT is also slowly converted to HTO through isotopic exchange with moisture (water vapor in air & absorbed in materials). Formation of HTO is favored in isotopic exchange ($HT + H_2O \rightarrow H_2 + HTO$).
3. Tritiated hydrocarbons and organic materials can also be formed by isotopic exchange.

4.2.2.3 Radiolytic Reactions: More reactive than stable isotopes of hydrogen due to ionization of molecules by the β-decay. Supplies activation energy for chemical reactions:

1. β-particle (average energy 5.7 keV) carries 1000X energy required to break chemical bond;
2. Accelerate chemical reactions.

4.2.2.4 Formation of Hydrides:

1. Some metals (e.g. uranium, titanium) form hydrides readily that can be used to store tritium (in a uranium bed).
2. Other metals do not form hydrides readily (e.g. 304L & 316L stainless steel, aluminum, copper) and may be used to contain tritium.
3. Hydrogen/tritium disrupt the structure of metals.

4.2.2.5 Corrosiveness:

1. Highly tritiated water acts aggressively with metal causing severe corrosion. The corrosion is partially due to the formation of hydrogen peroxide ($H_2O_2$); and therefore, it is important to minimize use of $O_2$ or $H_2O$ in tritium/HT systems.
2. Tritium reacts with materials used for seals (e.g. Teflon, Viton, Kel-F, PVC) that contain chlorine (Cl) or fluorine (F) to produce *T*F (tritium fluoride) or *T*Cl (tritium chloride). Such materials may degrade within a year.

4.2.2.6 Cleavage and cross-linking of Polymers and Oils:

1. Polymers are readily permeated by tritium.
2. Energy from β-decay may break polymer chain or result in cross-linkage.
   a) May result in softening (becomes "gummy") or embrittlement.
   b) Generally, use metal gasket/welded joints rather than elastomer seals.
   c) Energy from β-decay may result in elongation of hydrocarbon chain in oils increasing viscosity. If tritium concentration >few Ci/liter, oil may begin to solidify causing pump to seize.

4.2.2.7 Formation of Organically-Bound Tritium (OBT).

1. Plants and animals can incorporate some fraction of HTO into organic compound.
2. Tritium bound organically in isotopic exchange reaction or in enzyme-catalyzed reaction.
3. Organic compounds can have exchangeable hydrogen (exchange with cellular-water).
4. Stable H-C bond via enzymatically-catalyzed reaction.
5. Organically bound tritium has significantly longer residence time in humans.

4.2.3 General characteristics of transport and atmospheric removal

- Tritium is transported through the environment at approximately the same rate as hydrogen; tritium possesses a greater isotopic exchange rate at low humidity.
- Atmospheric half-life HT via oxidation effects approximately 7-years (atmosphere and surface effects).
- Wet deposition (rain-out & wash-out) of HTO greater than dry deposition (lower solubility).
- Dry deposition:
  - Half-life HTO 21-days to 41-days; 0.4 cm/s to 0.8 cm/s;
  - Half-life HT: approximately 5-years; 0.04 cm/s to 0.05 cm/s.
- Re-entry into atmosphere possible

4.3 Radiological Characteristic of Tritium ($^3H$). Tritium is a weak β-emitter with a maximum energy of 18.6 keV and an average emission energy of 5.7 keV. In the form of a gas, tritium has minimal radiological impact due its immersion and inhalation doses. Converted to tritiated water increases its radiological impact by a factor of >20,000. The following the subsection provides some basic information about tritium found in processing and the environment at Los Alamos.

Due to the aforementioned radiological properties of tritium (a weak β-emitter), the direct radiological consequences of direct exposure to tritium gas is minor. The weak β particle cannot penetrate skin and inhalation does not convert a significant fraction of the gas to tritiated water by oxidation nor isotopic exchange with water (see table 1, below). Significant radiological impacts result only due to ingestion of tritiated water that has a dose impact approximately 25,000 greater than from tritium gas.

Table 5
Penetration Depth (Ranges) of Tritium Beta
(after O'Kula & East, 2000)

| **Medium** | **E(β) [keV]** | **Range** |
|---|---|---|
| $T_2$ gas, STP | 5.7 | 0.26 cm |
| $T_2$ gas, STP | 18.6 | 3.2 cm |
| Air, STP | 5.7 | 0.036 cm |
| Air, STP | 18.6 | 0.45 cm |
| Water, Soft tissue | 5.7 | 0.42 μm |
| Water, Soft tissue | 18.6 | 5.5 μm |
| Stainless steel | 5.7 | 0.06 μm |

Thus, significant radiological impact to workers and public depends greatly on the fraction of tritium gas ($^3H_2$) that is converted into tritiated water ($^1H \cdot {}^3HO$ = HTO or $^3H_2O$) during release from containment/confinement, by accident conditions and during intra-facility and atmospheric transport.

4.3.1 Tritium decay and associated properties (LANL 1996; O'Kula and East, 2000).

- ${}^{3}_{1}H \rightarrow {}^{3}_{2}He + {}^{0}_{-1}\beta + \upsilon$ + energy (max. 18.6 keV, average energy 5.7 KeV). Tritium is not an external hazard;
- Nuclear properties of tritium -
  - Half-life: 12.32-12.43 years;
  - Specific activity: 9545-9640 Ci/g ($T_2$);
  - Power density: 0.328 W/g ($T_2$);
  - Activity density: 2.372 Ci/cm$^3$ to 2.589 Ci/cm$^3$ ($T_2$ gas, 1 atmosphere and 0$^o$ C), HT is approximately 1/2 of value [approximately 30,000 Ci/mole $^3H$, 3 gram/mole $^3H$, 10,000 Ci/gram $^3H$];
  - Daughter is $^3He$ (helium), monatomic gas [can build-up pressure in vessel (1 mole of $^3H_2$ yield 2 mole of $^3He$);
  - Maximum distance $^3H$ $\beta$ can travel in air is 5-μm (a minute fraction of an inch); tissue density is 1000X of air, range in tissue is 5 X $10^{-3}$ μm in tissue;
  - Will not penetrate sheet of paper or dead layer of skin; therefore, $^3H$ is not an external hazard (immersion dose);
  - Key to protection from $^3H$ is to prevent entry into the body;
  - $^3H$ $\beta$ cannot penetrate windows of most radiation monitoring instruments; and, therefore, it requires specially designed detectors.

4.4 Radiological Impact from Exposure (LANL, 1996).

4.4.1 Internal exposure.

4.4.1.1 Inhalation: HT slightly incorporated into body (almost all exhaled in a few minutes). Approximately 0.005% is converted to HTO via isotopic exchange or bacteria in GI tract. HTO vapor readily taken up by the lung (approximately 99%) and retained (in soft tissue within 1-2 hours).

4.4.1.2 Absorption: through intact skin and open wounds.

4.4.1.3 Ingestion: tritium can be ingested (especially as HTO).

4.4.1.4 Biological Half-life. Eventually flushed out of body, half-life time required for elimination of intake by natural processes. Approximately 10-days (4- days to 15-days depending on fluid intake).

4.4.1.5 Annual Limit of Intake (ALI) - the quantity of radionuclide that results in 5 rem dose when taken into the body:

1. Tritium: 80 mCi (dose equivalent when expressed in rem);
2. Approximately 1 Ci = 60 rem

4.4.1.6 Derived Air Concentration (DAC) - Airborne concentration that when breathed for 2,000-hours work-year equals effective dose of 5 rem

1. Tritium (HTO & $T_2O$) 20 µCi/$m^3$;
2. DAC derived from ALI (average worker breathes [2,400 $m^3$/year][ 20 µCi/$m^3$ ] = 48 mCi, plus 30 mCi absorption through skin, total represents approximately 80 mCi);
3. DAC for tritium gas: (based on direct exposure to inner lining of lung since tritium gas not readily absorbed) = 500 mCi/$m^3$

4.4.1.7 Exposure Hazards of Tritiated Water Vapor and Tritium Gas. Exposure hazards for the two physical forms are very different. The relative hazard [HT 500 mCi/$m^3$]/[HTO 20 µCi/$m^3$] = 25,000.

4.4.1.8 Estimating Dose from Tritium Gas.

1. Tritium Gas Inhalation: 1 DAC for 1-hour (1/2000th ALI) = 2.5 mrem.
2. Estimating Dose from Tritiated Water Vapor: Tritiated Water Vapor inhalation: 300 mCi/$m^3$ for 30-min = [exposure 300 mCi/$m^3$][DAC 20 µCi/m] = 15,000 DAC; [15,000 DAC][0.5-hr] = 7,500 DAC-hour; [1 DAC-hour = 2.5 mrem][7,500 DAC-hour] = 18,750 mrem (18.75 rem).
3. Estimating Dose based on Tritium Concentration in Urine:
   - Chronic exposure - 1 µCi/liter in urine is 0.2 mrem/day
   - Acute exposure: - 1 µCi/liter in urine in 1st 24-hours = 0.2 mrem/day for 1st few days falling to 0.1 mrem/day after 10 days

4.4.1.9 Tritium Elimination. Depends on turnover rate of body water. Elimination can increase by drinking more water, use of diuretics. Biological half-life can be reduced by a factor of 2 to 4 using methods, above.

4.5 Biological Behavior (O'Kula and East, 2000).

- For an acute exposure, inhalation: small amount dissolves in blood stream; eventually exhaled with waste products
- Longer term inhalation exposure: $^3H$ reaches other body fluids
- Small amount (0.003%-0.005%) converted to HTO due to bacterial/enzyme action
- Dose:
  - Lung dose from HT
  - Whole body dose from conversion to HTO
- Tritiated water vapor:
  - Airborne up-take is 99% efficient
  - Ingestion up-take by GI tract
  - Absorption begins within minutes into organs, fluids, and tissue
- Skin absorption important (approximately 50% inhalation rate)
- Uniformly distributed in all biological fluids within 1-2 hours
- Typical human body model:
  - Approximately 10-day half-life characteristic of body water

  - One or more long-term components (organic hydrogen sites), half-life in 100s of days.

4.5.1 Tritium in DOE Complex (O'Kula and East, 2000).

4.5.1.1 Common Forms of Tritium:

Gaseous tritium: 22.4 l/mol @ $0^o$ C; general storage (little embrittlement at low pressures). Gas subject to leakage or catastrophic vessel failure;
Metal tritides;
Tritiated water; and,
Other forms and species exist.

4.5.2 Tritium in DOE Complex, tritiated water. Some characteristics are:

- Tritiated water may be difficult to store for long periods - subject to spills and leakage;
- Likely due to tritium oxide generation of free radicals ($OH^-$, $OD^-$) from radiolytic decomposition of water; and,
- Tritium beta energy impinging on surrounding molecules.

4.6 Potential Accidents Within the DOE Complex.

Hydrogen/air or hydrogen/oxygen mixtures are flammable for a wide range of hydrogen concentration (4-vol% to 75-vol% flammable limits in air, Zabetakis 1924; Coward and Jones 1952; Bodurtha 1980; Thompson 1964; Stull 1977; Strehlow 1979; Drysdale 1985; Glassman 1996). Hydrogen is a gas at normal temperature and atmospheric pressure. With immediate ignition for leaking gas, the gas typically flares (produces a jet-flame). Delayed-ignition typically results in a deflagration (rapid burning) but can transition to a detonation (DDT) under some circumstances that are difficult to define precisely.

Fire and explosion are principal hazards during processing and storage of tritium gas due to the inadvertent releases during processing, storage, leaks, and mishandling. ${}^3H_2$ is typically stored/held under moderate- or less than- atmospheric pressure in stainless steel systems but can also be stored as unstable or stable metal hydrides (called Stable Metal Tritide, SMT)( Reis 1999). Typically tritium is found within DOE facilities as ${}^3H_2$ (tritium gas) but may be found as HT (mixture of tritium and *n*-hydrogen), ${}^1H^3HO/{}^3H_2O$ (tritiated water), Organically-Bound Tritium (OBT) due to isotopic exchange with *n*-hydrogen in hydrocarbons/organic materials.

If released as a gas, ${}^3H_2$ could be oxidized:

- while stored as gas (residual atmospheric oxygen in storage vessels);
- during transport and residence in enclosure into which it has been released that contains atmospheric air/oxygen;

- by ignition of flammable tritium/air mixtures upon or following release (fire and explosion); and,
- during atmospheric transport and dispersion.

## 5. CONVERSION OF TRITIUM GAS ($^3H_2$) TO TRITIATED WATER (HTO) - in storage, release to atmosphere, and accident conditions.

Tuggle (2000) reports a single datum of the presence of HTO in the WETF stainless steel storage system via mass spectroscopy of approximately 0.1% (the Lower Level of Detection of the instrument). SRS (O'Kula and East 2000) assumes a similar value.

Laboratory experiments have shown that the conversion of tritium gas ($^3H_2$) to tritiated water ($^1H^3HO$ or $^3H_2O$) is a 1st-order reaction (a linear function of the concentration) at higher $^3H$ concentrations and follows the equation:

$$N - N_oe^{-At};$$

where N = fraction as HT and A = 0.01/hr (total conversion rate). Using the equation, approximately 1 percent of the $^3H_2$ will have been converted to tritiated water after 1-hour. The oxidation of $^3H$ is controlled by the ions generated by radioactive decay that combine with atmospheric oxygen to form tritiated water. The rate constant is a function of the $^3H$ concentration (McSweeney and Cybulkis 1995).

Over the range of $^3H$ concentrations from $10^{-3}$- to $10^6$-Ci/m$^3$, there appears to be 3 reaction rate regimes (Easterly, Noguchi, and Bennett 1985):

| | |
|---|---|
| $10^{-3}$- to 10-Ci/m$^3$ | 1st-order |
| 10- to $10^4$-Ci/m$^3$ | 2nd-order |
| >10-Ci/m$^3$ | 1st-order |

The rate constants measured were:

| | |
|---|---|
| 1.4-Ci/m$^3$ | 1.5 X $10^{-9}$/s; |
| 0.10-Ci/m$^3$ | 1.8 X $10^{-9}$/s; |
| 0.012-Ci/m$^3$ | 1.9 X $10^{-9}$/s; |
| 0.0025-Ci/m$^3$ | 2.8 X $10^{-9}$/s; and, |
| 0.000086-Ci/m$^3$ | 4.8 X $10^{-10}$. |

Typical metals found in nuclear facility equipment and systems (e.g. stainless steel, steel, brass, aluminum) have minor catalytic effect (Eakins and Hutchinson, 1973). Surface area, concentration, and presence/absence of water vapor are not significant factors. Platinum and platinum-black have significant catalytic effects.

Albenesius (1974) tabulated the conversion of $^3H_2$ to tritiated water and the effects of metals to catalyze the conversion reported by others previous to that date:

## Table 6
## "Conversion of Tritium to Water" (after Albenesius 1974)

| Reference | Initial $^3H$ Conc, mCi/ml | Reaction | Reaction Rate Constant | Initial Reaction Rate[c] |
|---|---|---|---|---|
| Dorfman & Hemmer 1954 | 94 to 324 | Oxidation | 7.1E-3[a] | 0.17 |
| Casaletto et al. 1962 | 0.26 | 1 | 6.2E-4[a] | 0.0039 |
| Yang & Gevantman 1964 | 0.05 to 0.70 | 2 | 1.5E-3[b] | 0.0018<br>0.025 |
| Eakins & Hutchinson 1973 | 0.02 | 1 | 5.6E-4[b] | 0.0003 |
| Eakins & Hutchinson 1973 | 0.02 | 3 | 2.9E-3[b] | 0.0014 |

1 Oxidation in dry air
2 Isotopic exchange
3 Isotopic exchange + oxidation in 100% RH air

[a] 1st-Order constant, per hr.
[b] 2nd-Order constant, ml/[mCi][hr]
[c] Initial reaction rate, initial concentration $^3H$/day

## Table 7
## "Catalytic Effect of Metals"
## (after Albenesius 1974)

| | $K_1$, ml/[mCi][hr] | |
|---|---|---|
| Metal | Dry Air | Humid Air |
| Brass | 6.0E-4 | 8.6E-2 |
| Steel | 4.2E-3 | 6.1E-23 |
| Aluminum | 3.9E-3 | 9.6E-3 |
| Platinum | 2.4E-2 | 8.4E-1 |

O'Kula and East (2000) tabulated the Reaction Rates (presented on the following page).

Table 8
Reaction Rates for Tritium Conversion
(after O'Kula and East 2000)

| **Reaction Type** | **Environment** | **Rate** |
|---|---|---|
| Oxidation in dry air | No metal surfaces | 0.03%/day |
| | Al metal surfaces | 0.2%/day |
| | Pt metal surfaces | 1.1%/day |
| Isotopic exchange with $H_2O$ in air | No metal surfaces | 0.1%/day |
| | Al metal surfaces | 0.3%/day |
| | Pt metal surfaces | 28%/day |
| Photo-chemical reaction | | 0.06%/day |
| Oxidation in soil | 32% water content | 20%/min. |
| | 28% water content | 5%/min |
| Oxidation by plants | Pine needles | 0.001%/min |
| | Pine branches | 0.008%/min |
| | Lawn grass | 0.1%/min |

The radiological impacts of $^3H$ have been a concern since at least 1950 (Roesch 1950). LANL (Tritium Working Group undated) reviewed the relevant information on *n*-hydrogen large scale, outdoor fires/explosions to define the maximum fraction that could be oxidized under these conditions. Their concerns were for outdoor events and the information for outdoor release of *n*-hydrogen under BLEVE (Boiling Liquid Expanding Vapor Explosion) conditions appears to some extent applicable (the value defines the energy release as explosive energy). From outdoor events involving many types of fuel (including *n*-hydrogen), the fraction of the fuel inventory burned was determined to be <10%. Subsequently others (Edusky and Pan 1996, Tuggle 2000) attempted to apply this value to indoor releases without due consideration for the differences:

- in physical configuration (an unlimited ceiling outdoors);
- the reflection of un-burned fuel in partial or total confinement;
- the effects of BLEVE-like situations on turbulence and mixing; and,
- the relatively ease of activation of the oxidation reaction.

Other sites (SRS 1998) apply only two values - (1% conversion to tritiated water for release without ignition and 100% conversion for fire/explosion) and these values are accepted by the DNFSB (Bamdad, 1995).

Conversion after the release of gaseous tritium without ignition appears to be bounded by a value of 1%/day due to all mechanisms. The absorption of $^3H_2$ into the biosphere, conversion to tritiated water by microbial/enzymatic action, and subsequent desorption of the tritiated water may result in a local elevated concentration of tritiated water at/near the surface.

Due to the uncertainty of configuration and conditions, a conversion rate of 100% is used to bound conversion of $^3H_2$ to tritiated water from involvement in fire or explosion.

### 5.1 Conversion of Tritium during Storage in Stainless Steel Containment Systems.

Tuggle (2000) reports a single datum of the presence of HTO in the WETF stainless steel storage system via mass spectroscopy of approximately 0.1% (the Lower Level of Detection of the instrument). SRS (O'Kula and East 2000) assumes a similar value. Both are approximately and order of magnitude less than the value of 1% that is applied for the entire conversion of tritium gas in the absence of an ignition source during its transit through enclosed volumes prior to release to the ambient atmosphere.

### 5.2 Conversion of Tritium After Release.

#### 5.2.1 No ignition source (beta-activated conversion of Tritium gas to tritiated water; includes experiments to measure isotopic-exchange and conversion in air).

5.2.1.1 Dorfman and Hemmer. The results and observations from 11 runs performed using varying fractions of *n*-$H_2$ and $^3H_2$ are reported by Dorfman and Hemmer (1954). Some observations from preliminary experiments that were performed are: a thin yellowish deposit accumulated on walls of Pyrex™ reaction tube and mercury in a manometer became dis-colored (probably due to oxidation) with aging. Tritiated water formed from reduction of mercury oxide after a week with tritium gas stored in cell - $H_2O + T = H_g + OT$. $H_2$-$T_2$ mixture ($T_2$ stored on uranium bed) was analyzed using GE mass spectrometer.

The rate of reaction of tritium and oxygen, initiated by the tritium beta radiation, has been investigated at 25° C, in the absence of mercury vapor, by using a sensitive Bourdon gauge as the manometer. The rate is not linear with time, but shows a small continual decrease as the reaction proceeds. The initial reaction rate was found to be proportional to the tritium pressure, and hence proportional to the radiation intensity. The reaction rate shows a slight dependence on the isotopic composition of the hydrogen reactant, tending to rise with increase in the mole fraction of protium (n-hydrogen). The initial reaction may be represented by:

$$R_o = 1.9 \text{ X } 10^{-4}[C_{T2}][1 + 0.3m_H]$$

Where: $C_{T2}$ = tritium concentration in mole/liters or other absolute concentration unit; and,
$M_H$ = mole fraction of protium in the hydrogen reactant.

On the basis of a requirement of 33 ev/ion pair in the reactant mixture, the initial ion pair-yield for tritium disappearance or water formation is $(M/N)_o = 3.2$ for the reaction of pure hydrogen with oxygen. Material balance measurements indicate that little or no peroxide appears in the product.

5.2.1.2 Yang and Gevantman. The conversion of tritium to tritiated water through its β-radiation-induced isotopic exchange with water vapor was investigated by Yang and Gevantman 1960. It was found that, under simulated normal atmospheric condition with tritium concentrations in the range of 0.05 to 0.7 Ci/liter, the rate of conversion of tritium to tritiated water is independent of water vapor density. On the other hand, a second order dependency on the initial tritium concentration was observed. The isotopic exchange rate, R, expressed in mCi/[liter][day] may be approximated by the following equation:

$$R = 4 \text{ X } 10^{-5}[{}^3H_2]^2$$

Where: ${}^3H_2$ = Initial tritium concentration, mCi/liter.

Results from the x-ray irradiation of the reaction mixture indicate that the exchange rate is essentially proportional to radiation absorption. Lowering of the reaction rate by dilution of tritium with "protium" (n-hydrogen) was observed. To account for the marked inhibiting effect of nitric oxide, a reaction mechanism involving radical intermediaries is proposed.

The rate of conversion to HTO varies with square of tritium concentration. The release of gram quantities of tritium into a volume equivalent to an average sized room resulted in a conversion <1%/day. Considering the reaction mechanism, a rate even less is expected in the atmosphere.

Rate Dependency on Initial Tritium Concentration. 2nd-order dependence (on ${}^2H_2$ concentration) commonly observed in tritium β-decay initiated labeling of organic compounds; "G" values for tritium incorporation in benzene, hexane, and cyclo-hexane increase roughly proportionally to the pressure (or mole ratio) of the ${}^3H_2$.

Effect of X Irradiation. Increases induced ${}^3H_2$ - $H_2O$ exchange rate.

Competition by Protium. Dilution with *n*-hydrogen resulted in pronounced reduction in exchange rate.

5.2.1.3 Yang and Gevantman (1964) found that the rate of tritium β-decay-induced isotopic exchange between tritium gas and water vapor is found to be a constant within a four-fold variation in water vapor density, but to increase as a second-order function of the tritium concentration. Inert gas present in large excess, appeared to function purely as a moderating media for the tritium β-energy. With helium gas as the moderator and tritium concentrations in the range from 0.05 to 0.7 Ci/liter, the reaction rate in mCi/[liter][day] at the ambient temperature of $22 \pm 2^o$ C is observed as d/(HTO)/dt = 3.6 E-5 $({}^3H_2)^2$, where ${}^3H_2$ is the initial tritium concentration in mCi/liter. This exchange is strongly inhibited by the presence of nitric oxide in the reaction mixture. The results are consistent with the reaction mechanism involving radical intermediaries.

5.2.1.4 Eakins and Hutchinson (1973) investigated the effects of moisture and commonly found metal surfaces on the conversion rate of tritium to tritiated water. The ICRP Maximum Permissible Concentration$_{air}$ for ${}^3H_2$ is 2 nCi/ml and for tritiated water is 5 pCi/ml. Considering quality factor modification for low-energy β-emitters reduces the $MPC_{air}$ to:

- ${}^3H_2$ 3.4 X $10^{-3}$ µCi/ml; and,
- tritiated water 8.5 X $10^{-6}$ µCi/ml.

It is evident that tritiated water is the greater hazard. Releases of gaseous ${}^3H$ need to consider its conversion to tritiated water by oxidation and/or isotopic exchange.

Previous studies cited indicate:

- Dorfman & Hemmer (1954): 1st-order rate constant 1.2 X $10^{-4}$/min, halftime for reaction 96-hr;
- Casaletto et al. (1962): at lower ${}^3H$ ($10^{-2}$ to 1.0 mCi/ml) concentrations, 2nd-order reaction rate constant 6.2 X $10^{-4}$ ml/[mCi][hr] in dry air; and,
- Yang & Gevantman (1964) isotopic exchange ${}^3H$ & HTO: in inert atmosphere with an initial concentration of 1 µCi/ml, 2nd-order reaction rate constant 1.5 X $10^{-3}$ ml/[mCi][hr]; oxidation reaction halftime 6.4 X $10^4$ days (approximately 175-yr); isotopic reaction halftime 2.8 X $10^4$ days (76.6-yr); both oxidation & isotopic exchange rate are independent of $O_2$ or water vapor concentration.

Experimental. Glass bulbs (glass type not specified) with metal catalysts (foils of mild steel, brass, platinum, & aluminum - 92 $cm^2$ surface area).

Results. Initial experiments were performed in the absence of catalyst. Initial ${}^3H$ concentration was 2 X $10^{-2}$ $mCi/cm^3$. Casaletto et al. (1961) reported an initial rate of tritium oxidation ($R_o$) proportional to square of tritium concentration, $(T_2)2_o$, and rate constant $k = R_o/(T_2)_o(T_2)_t$. This fits the data by Yang and Gevanmtman (1964). Casaletto et al. (1961) initial concentration represents radiation intensity:

$$K = (T_2)_o - (T^2)_t/t(T_2)_o(T_2)_t$$

where: t = reaction time, hr;
$(T_2)_o$ = initial tritium gas concentration, $mCi/cm^3$;
$(T_2)_t$ = final tritium gas concentration, $mCi/cm^3$.

Table 9
Oxidation of Tritium in Dry Air
(after Eakins and Hutchinson, 1973)

| Reaction time, hr | Rate Constant k, ml/[mCi][hr] |
|---|---|
| 24 | 1.4E-3 |
| 96 | 7.1E-4 |
| 768 | 3.5E-4 |
| 1464 | 6.2E-4 |
| Mean of last three, k = 5.6E-4 | |

Table 10
Conversion of Tritium to Tritiated Water in Air at 100% Relative Humidity
(after Eakins and Hutchinson, 1973)

| Reaction time, hr | Rate constant k, ml/[mCi][hr] |
|---|---|
| 24 | 8.1E-3 |
| 72 | 2.8E-3 |
| 168 | 3.5E-3 |
| 336 | 3.1E-3 |
| Mean of last three k = 2.9E-3 | |

The 1st result was omitted since it was much higher than others (assumed that a small amount of tritiated water in $^3H_2$ was present in the source material) could skew the results. Mean value for oxidation in dry air, 5.6E-4 ml/[mCi][hr], agrees with Casaletto et al. (1961), k = 6.2E-4 ml/[mCi][hr]. Value for oxidation in 100% Relative Humidity air has two components:

1. oxidation rate to HTO (6.3E-4 ml/[mCi][hr]);
2. isotopic exchange rate $^3H_2 \leftrightarrow$ HTO, 1.5E-3 ml/[mCi][hr] (Yang & Gevantman (1964); and,
3. $\sum$ 2.1E-E-3 ml/[mCi][hr] versus measured mean 2.9E-3 ml/[mCi][hr]

<u>Reaction rate constants in the presence of metal catalysts</u>. Assumed catalysts accelerate reaction but do not change order. Confirmed by 3 experiments using mild steel in dry air using different reaction times; similar 2nd-order reaction rate constants.

Table 11
Conversion of Elemental Tritium to Tritiated Water in the Presence of a Catalyst
(after Eakins and Hutchinson, 1973)

| Catalyst (metal) | Rate Constant k, ml/[mCi][hr] | |
|---|---|---|
| | Dry air | Humid air |
| Brass | 6.0E-4 | 8.6E-2 |
| Steel | 4.2E-3 | 6.1E-2 |
| Aluminum | 3.9E-3 | 9.6E-3 |
| Platinum | 2.4E-2 | 8.4E-1 |

In dry air for the metals tested, all but brass accelerates the reaction. In humid air, all metals appeared to catalyze oxidation; platinum had the greatest effect. Further experiments were performed using oxidized brass & steel in humid air but had no effect.

Table 12
Half-times of Reaction for 10 $(MPC)_{air}$ of Tritium
(after Eakins and Hutchinson, 1973)

| Catalyst | Reaction half-time, days |
|---|---|
| None | 4.2E+5 |
| Brass | 1.4E+4 |
| Steel | 2.0E+4 |
| Aluminum | 1.3E+5 |
| Platinum | 1.5E+3 |

Ratio metal surface to volume 0.36:1; initial $^3$H concentration 3.4 X $10^{-2}$ mCi/cm$^3$ (10 $MPC_{air}$). For room 20-ft$^2$ X 10-ft high completely lined with Pt, requires ~4.5-yr.

5.2.1.5 Noguchi, Easterly and Bennett. The conversion reaction of tritium gas ($^3H_2$) to tritiated water was studied experimentally at initial tritium concentrations between 2.6E-4 and 1.3 Ci/m$^3$ in air (Noguchi, Easterly and Bennett, undated). The effects of water vapor on the conversion rate were also examined. The potential catalyst, stainless steel, copper, paint and platinum black were used.

It was found that 1$^{st}$-order rate constants for the reaction in air are independent of the initial tritium concentration, and that there is no effect of water vapor on the reaction. The conversion was insensitive to the presence or absence of stainless steel and copper. Paint, which did not influence the rate constant, sorbed $^3H_2$ and tritiated water, but the latter was de-sorbed from the paint by heating. Platinum black produced a remarkable increase of the rate constant.

Conversion inside enclosure is different than in natural environment. In an enclosure, the conversion is mainly due to β-induced reactions and catalytic reactions; the dominant reaction in the environment is oxidation by micro-organisms in the soil.

$^3H_2$ concentrations in fusion reactor room were estimated at 1 Ci/m$^3$ under accident conditions. Adsorption/de-sorption of tritiated water at wall surface influences flow rate of air tritium removal system.

Conversion of $^3H_2$ in gas phase was studied by several investigators over range of 0.001 to 10$^6$ Ci/m$^3$.

- Dorfman & Hemmer (1954) conversion 1st-order $^3H$ concentration dependent between 9.4E+4 - 3.2E+5 Ci/m$^3$ (9.4 – 32 g $^3H/m^3$) on $^3H$ concentration. Casaletto et al. (1962) conversion in dry-air & $O_2$ 2nd-order $^3H$ concentration dependent between 10 to 10$^3$ Ci/m$^3$ (0.001- to 0.1 g $^3H/m^3$); due toβ-decay from $^3H$. Belovodskii et al. (1975) conversion dependence $[^3H]^{3/5}$ in range 1- to 600 Ci/m$^3$ (0.001 to 0.06 g $^3H/m^3$) in humid air and mixture $O_2$-Ar. At lower $^3H$ concentrations (range 1E-3 to 1 Ci/m$^3$), the rate constant for conversion in air and $N_2$ are independent of initial $^3H$ concentration.

- Catalytic conversion (Eakins & Hutchinson 1973) - increases the rate constant for Al 7.5X, steel 7.0X, Pt 43X at $^3H$ 20 Ci/m$^3$ (0.002 g $^3H/m^3$).

Measured rate constant for conversion at low initial $^3H$ conc. (2.6E-4 Ci/m$^3$) were 1E-3 and 1 Ci/m$^3$. This includes both the contribution from the isotopic exchange between $^3H$-water vapor and the catalytic reaction on surfaces of stainless steel, copper, platinum black, and paint.

Conversion of low concentration $T_2$ ($^3H_2$) in air. Initial $^3H_2$-in-air was 2.6E-4 Ci/m$^3$zero that was attributed to small amount of tritiated compounds that entered flask during preparations.

Current experiments indicate six (6) rate constants for a range of initial $^3H_2$ concentrations from 2.6E-4 to 1.3 Ci/m$^3$ measured.

Previous work indicated that rate constants for conversion were independent of initial $^3H_2$ concentrations at low $^3H_2$ concentrations; overall average rate constant 1.8±0.5 E-9/s. This is verified by present work to concentration of 2.6E-4 Ci/m$^3$ (2.6E-8 g $^3H/m^3$). Figure 4 in this document shows rate constant increase with initial $^3H$ >10 Ci/m$^3$ (0.001g $^3H/m^3$) but are constant below that value. This suggests a dominant mechanism different above and below 10 Ci/m$^3$; at high $^3H$ β-decay energy induces conversion. At low $^3H$, $^3H^3He$ important for production of HTO because physical $^3H$ decay constant (1.75E-9/s) and measured rate constant.

Conversion of $^3H$ in the presence of water vapor. Effect water vapor on rate constant studied at $^3H$ approximately 1.3 Ci/m$^3$ (10$^{-4}$ g $^3H/m^3$).

Calculated rate constants - RH 0% 1.3E-9/s; RH 40% 1.5E-9/s; RH 100% 1.5E-5/s indicate that water vapor has no effect; isotopic exchange does not proceed at low tritium concentrations (Casaletto et al. 1962). Water vapor in $O_2$ increased the rate constant X3 at relatively high $^3H$ concentration. The rate constant for breathing air is the same as dry air. Eakins and Hutchinson (1973) rate constant in humid air five times greater than in dry air at $^3H$ concentration of 20 Ci/m$^3$ (0.002 g $^3H/m^3$).

Effect of catalyst on the conversion. Insensitive to presence of stainless steel; rate constant 1.4E-9/s ≈ overall average, above. Foil did not de-sorb HTO upon heating to 600° C.

Table 13
Rate Constants for the Tritium Conversion Reaction in the Presence of Catalys*t*
(after Noguchi, Easterly, and Bennett, undated)

| Catalyst | Initial $^3H_2$ conc., Ci/m$^3$ | RH | Rate constant, s$^{-1}$ |
|---|---|---|---|
| Stainless steel | 0.22 | 60 | 1.4E-9 |
| Copper | 0.33 | 60 | 1.6E-9 |
| Enamel paint | 0.30 | 60 | 2.2E-9 |
| Platinum black | 0.33 | 60 | 2.8E-8 |
| Platinum black | 0.23 | 60 | 5.8E-7 |

Stainless steel and copper have no effect; rate constants are the same as for air (1.8E-9/s). Recovery of $^3H_2$ and HTO from paint low after 10-days. When heated to 250° C and collected in liquid $N_2$, HTO 2X but no additional $^3H_2$; possible $^3H$ forms stable compound with paint. Estimated rate constant for paint using total recovered HTO; no significant change in rate constant from dry air.

Significant increase in rate constant was observed for platinum black, 300X to 1600X; the behavior shows that the diffusion constant of $^3H_2$ to surface is not the rate-determining step. The conversion of 61%/4-day and 59%/18-days implies that the reaction is at equilibrium. Eakins and Hutchinson (1973) - steel, Al, and Pt increased rate constant for HTO conversion in dry air at $^3H$ concentration of 20 Ci/m$^3$ (100X used, above) and catalytic effect are further enhanced in humid air. The differences can be attributed to the use of different catalysts and $^3H$ concentration.

Rate constants were independent of the $^3H$ concentration to 2.6E-4 Ci/m$^3$; overall average 1.8±0.5 E-9/s. Isotopic exchange is negligible at these low $^3H$ concentrations. Stainless steel and copper showed no catalytic effect on HTO conversion @ $^3H \sim 0.2$ Ci/m$^3$. Platinum black shows a significant increase in rate constant. Oil-based enamel had no catalytic effect, but, absorption/de-sorption on painted surface may complicate behavior analysis of $^3H$ released into building.

5.2.1.6 Albenesius (1974) memo summarizes and interprets literature data on $^3H_2/^1H^3H$ to tritiated water. From the information available, it was concluded that the conversion rate was low. Lifetime in troposphere is approximately 10-yrs. Only 10%-15% of tritiated water in the atmosphere is deposited on land; the remainder deposits in ocean.

$^3H_2$ as a gas is converted to tritiated water by two processes: oxidation and isotopic exchange with water vapor existing in air both yielding HTO.

Previous studies cited and their results are:

- Dorfman & Hemmer (1954) studied reaction between $^3H_2$ & $O_2$ at high $^3H$ concentrations (94-324 mCi/ml). Concluded that initial reaction rate was proportional to $^3H$ concentration and the 1st-order with rate constant, $k_1 = 1.2 \times 10^{-4}$/min. Reaction halftime is approximately 96-hr. Reaction rate, R:

  $R = k_1C_T$ where $C_T$ = tritium concentration

- Caseletto et al. (1962) $^3H_2$ with dry air, $C_t = 0.26$ mCi/ml. Concluded the reaction rate was 2nd-order with a reaction rate constant $k_a = 10^{-4}$ ml/[mCi][hr]. Reaction rate independent of $O_2$ concentration with initial reaction rate varying as $[C_T]^2$.

  $R_o = K_a[C_T]^2_o$ where $[C_T]_o$ = initial tritium concentration

Reaction rate for atmospheric air ≈ dry air. Suggests that radiation intensity factor in determining the reaction rate.

- Yang and Gevantman (1964) studied isotopic exchange between $^3H$ and water vapor in inert atmosphere. The reaction rate is 2nd-order with a reaction rate constant $k_a = 1.5 \times 10^{-3}$ ml/[mCi][hr] with an initial $^3H$ concentration 0.05 to 0.7 mCi/ml. Rate independent of water vapor density. The Initial reaction rate is proportional to $[C_T]_o^2$.

- Eakins & Hutchinson (1971) reported the oxidation of $^3H_2$ in dry air and isotopic exchange at 100% RH. Both 2nd-order with rate constants of $5.6 \times 10^{-4}$ ml/[mCi][hr] for oxidation and $2.9 \times 10^{-3}$ m/[mCi][hr] for isotopic exchange (assumed included oxidation).

  Both oxidation and isotopic exchange are dependent on original $^3H$ concentration. At moderate $^3H$ concentrations, reaction proceeds with a 2nd-order rate constant. Rate constant for oxidation and isotopic exchange agrees reasonably well with oxidation in dry air (6.1E-4 ml/[mCi][hr]) and isotopic exchange (1.5E-3 ml/[mCi][hr]); isotopic exchange is approximately 3X greater than for oxidation. At higher concentrations of $^3H$ (greater than ~100 mCi/ml, Dorfman and Hemmer) the conversion is 1st-order rate independent of $^3H$ concentration.

  Both oxidation and isotopic exchange are induced/influenced by beta radiation from $^3H$. The primary step is ionization by beta particle. Rates are independent but similar. It needs to be pointed out that all data is from laboratory experiments; not in the atmosphere (confined space therefore are assumed to be a maximum rate).

A marked increase in the rate constant in presence of metal catalysts and humid air increases corrosion (initial conc. $^3H$ 2E-2 mCi/ml, metal surface to volume ratio = 0.36:1).

- Estimates of chemical half-life of $H_2$ in troposphere:
  - Levy (1973), Kummler and Bauer ((1973)2-yr.;
  - Schmidt (1974) 4-to 7-yr;
  - Mason (1974) 10-yr

  appear to be the most reliable and was taken from measurements of inter-hemispheric exchange times.

- Environmental measurements from unplanned release of 480,000 Ci $^3H$ from SRP on 5/2/74 indicated that <1% was released in form of water (>99% of the water was formed within 1st few minutes after release). Estimated $^3H$ concentrations from stack were 0.03 mCi/ml. Conversion rate after discharge from stack was 0.03%/day.

5.2.1.7 Easterly and Bennett; Easterly, Noguchi, and Bennett; Noguchi, Easterly, and Bennett. The information and results from Easterly and Bennett (1983); Easterly, Noguchi, and Bennett (1985); and, Noguchi, Easterly, and Bennett (1989) are combined; since, the three articles cover much of the same work.

- A survey of water production dependence on tritium concentration and external radiation fields has been made for tritium-in-air concentrations ranging from 0.01 to 2 Ci/m$^3$. Results of reaction taking place under static conditions (in a Pyrex™ flasks at 20° C) indicate that:

  1) Self-catalyzed rates may be 1st-order-dependent on tritium concentration; and,
  2) External radiation fields may cause a virtual steady-state condition to occur (in terms of additional self-catalyzed water production.

- Conversion rate of tritium gas ($^3H_2$) to tritiated water is reported for tritium in ambient air and in nitrogen mixtures for initial tritium concentrations between $10^{-3}$ and 1 Ci/m$^3$. Evidence suggests that, for air mixtures, production of condensable species, primarily HTO, occurs at a rate commensurate with the tritium decay rate. Nitrogen with less than 0.05% oxygen decreases this rate by a small (25%) amount. Irradiation with up to 10 Krad $^{60}Co$ does not measurably affect the conversion rate in ambient air. This new data, along with data from other authors, reveals that over the range $10^{-3}$ to $10^6$ Ci/m$^3$ [1E-7 to 1E+4 g $^3H$/m$^3$], there are three reaction regimes:

  (1) 1st-order between $10^{-3}$ to 10 Ci/m$^3$;
  (2) ~2nd-order between 10 & $10^4$ Ci; and,
  (3) 1st-order >$10^4$ Ci/m$^3$.

Author's previous experiments found a conversion rate constant 2E-4/s in air and independent of $^3$H concentration in the range of $10^{-2}$ and 1 Ci/m$^3$.

Metal (brass, steel, aluminum, and platinum) surfaces have catalytic effect on conversion rate at $^3$H concentration of 20 Ci/m$^3$ but effects of other structural material over wide range of $^3$H concentrations are not known.

The experimental equipment and procedures are the same in all experimental work reported. Two types of Pyrex™ vessels were used. Effects of Pyrex™ were studied; a 10-g fiber with 500 cm$^2$/g was used. External irradiation source was $^{60}$Co.

Self-irradiation with Air. 1st-order rate constants:

1.4 Ci/m$^3$ = 1.5E-9/s;
0.10 Ci/m$^3$ = 1.8E-9/s;
0.012 Ci/m$^3$ = 1.9E-9/s;
0.0025 Ci/m$^3$ = 2.8E-9/s; and,
0.00086 Ci/m$^3$ = 4.8E-10/s

These constants appear high when compared to extrapolations of data of Belovodskii et al. (1975) or Casaletto et al. (1962). The rate constants agree with both author's former data and extend $^3$H concentration order of magnitude lower. Confirm rate constant independent of $^3$H concentration at concentrations <10 Ci/m$^3$.

$^{60}$Co Irradiation of Tritium or Tritiated Water in Air Mixtures. $^3$H irradiated at a concentration of approximately 200 Ci/m$^3$ and resulted in increased HTO. Dose ranged from 10 rads to 10,000 rads. The experimental results were analyzed after twelve days. The average conversion rate constants were almost identical, 2.1±0.1E-9/s. External irradiation had no effect at low $^3$H concentrations. This confirms that external irradiation has no effect on conversion rate constants.

Effect of Pyrex™ Glass on the Tritium Conversion. Data indicated that pyrex™ glassware had a small effect but the data was preliminary and not final. There was a slight increase in HTO with increasing surface area. The rate constants: 500 cm$^2$ = 2.1E-10/s and 5,000 cm$^2$ = 5.0E-10/s. A 10X increase in surface area increased the rate constant by 2.4X – a notable small effect. The rate constants were less than the self-irradiation values. HTO may have absorbed in neoprene O-ring but it was uncertain.

Tritium Conversion in Nitrogen. Two series of experiments were conducted: $N_2$ <0.05% $O_2$ and $H_2O$. Rate constant 1.3E-9/s using $^3$H conc. 0.0056 & 0.0073 Ci/m$^3$. A rate constant within 25% that for ambient air that contains 20% $O_2$ & RH 40% was determined. The conversion appears to be relatively insensitive to $O_2$ concentration and the presence/absence of moisture.

Theoretical Calculations. At high $^3$H concentrations β-particle emission induces conversion. At low $^3$H concentrations, the density of tritium is so low that the probability of β-decay energy from 1 molecules resulting in tritium radical formation in another is very low; most of the decay energy was absorbed by the dominant gas, $N_2$. With <1 tritium molecule per $10^5$ of other gases, collisions that are energetic enough to result in tritium radical formation is diminishing few. Important reaction:

$$^3H_2 \rightarrow {}^3He^3H$$

$^3He^3H$ undergoes dissociation rapidly to form $[^3He^+ + {}^3H]$ and $[^3He + {}^3H^+]$. This results in production of HTO. Agreement of physical decay constant (1.78E-9/s) and measured rate constants suggest that $^3H_2$ decay process is the predominant factor in HTO formation for range $^3H$ concentration range of $10^{-3}$ to 1 Ci/m$^3$. The base rate constant is 1.78E-9/s with conversion reaction kinetics to calculate conversion rate in the $^3H$ concentration range of $10^{-4}$ to 10 Ci/m$^3$.

This indicates good agreement between measured and calculated rates.

The conversion of tritium gas ($^3H_2$) to tritiated water was studied experimentally at initial tritium concentrations between 9.6 and 48 GBq/m$^3$ (2.6 X $10^{-4}$ to 1.3 Ci/m$^3$) in air. The effect of water vapor and catalysts on the conversion rate constant was also examined. Stainless steel, copper, paint, and platinum black were used as potential catalytic surfaces.

First-order rate constants for the reaction in air are found to be independent of the initial tritium concentration, and there is no effect from water vapor on the reaction. The conversion is insensitive to the presence or absence of stainless steel and copper. Paint sorbs $T_2$ and HTO, but the latter is de-sorbed from the paint by heating. Platinum black produces the expected increase in the reaction rate.

5.2.2 Presence of ignition source (combustion). The ignition and combustion characteristics of *n*-hydrogen are cited in previous subsections. The limits of flammable gas concentration are exceptionally broad (4.1- to 75-vol%). The range of gas concentration for explosive reaction is narrower, 18.3- to 59-vol%. The Heat of Combustion ranges from 119.93 to 141.86 kJ/g of *n*-hydrogen (would vary due to the increased molecular weight of tritium). The auto-ignition temperature is for a stoichiometric concentration in air 1084$^o$ F (520$^o$ to 580$^o$ C) that is high compared to hydrocarbon fuels. The burning velocity in air can range to 2.6 m/s in air and 8.9 m/s in oxygen. The calculated average flame temperature is 350$^o$ C. The ignition energy is low (0.015 milli-Joule) and can readily be supplied by many common occurrences [e.g., static discharge from human activities, simple rupture of metal line may provide sufficient energy as shown by Reider, Otway and Knight (1965) provided concentration between LFL & UFL]. Experiments to determine LFL indicate that at this concentration, not all the hydrogen is consumed by the reaction (McKinley 1980).

5.2.2.1 At point of release - "flaring". If the hydrogen gas is ignited at or near the point of release and the flames are not extinguished by gas mass flow variations or other phenomena, hydrogen (and other combustible/flammable gases) can burn all the gas emitted.

5.2.2.2 Delayed ignition. If the ignition is delayed until a substantial fraction or all the hydrogen gas is released, the gas within the flammable concentration limits can burn, deflagrate or detonate dependent on quantity of fuel released and the configuration of the event:

A. Unconfined volume - burns or an explosive reaction depending on amount released and configuration (BLEVE for liquid fuel; deflagration or DDT for some configurations); conversion to tritiated water would be near the explosion energy release value; since, unburned gas can escape freely and be completely removed from reaction zone.
B. Confined volume burns or undergoes an explosive reaction in containment. The burned gases may be reflected by the walls of the containment and be subsequently converted to oxide. Given the apparent low activation energy for the reaction (the conversion increases with β-energy present and may indicate that additional conversion may occur from the energy available in the residual heat after combustion or an explosive reaction within containment). No experimental basis exists to limit the conversion of tritium gas under these conditions.

## 6.0 RECOMMENDED CONVERSION VALUE FOR ACCIDENTALLY RELEASES OF TIRIUM GAS.

### 6.1 Conversion Values Used in Safety Analyses.

### 6.1.1 Fraction Tritium Converted by β-Activated Processes, Indoors

(Tuggle, 2000) states that $^3H$ at the WETF contains less than 0.1% $^3H_2O$ measured by mass spectroscopy (lower detection limit). Conservatively assume $^3H_2O$ at WETF 1% (at least factor of 10 overestimate).

Roesch (1950) assessed the hazards of the P-10 system at Hanford. The product of the P-10 system is $^3H$; the principal hazard is HTO. Most $^3H$ exchanges if a suitable catalyst is present. At 20$^o$ C, 1.7E-5 g/cm$^3$ of water in saturated air; 9.45 moles/cm$^3$. Allowable human tolerance for $^3H$ is 10E-11 Ci/cm$^3$; 1.5E-16 moles/cm$^3$. Consider reaction: $^3H_2 \leftrightarrow$ HTO + HT. If K = equilibrium constant for reaction and X = number of moles HTO formed:

$$K = X^2/[a-X][b-x] \quad \text{where:} \quad a = \text{moles}_{H20}/cm^3; \quad b = \text{moles } ^3H \text{ tolerable}$$

Solution for a/b:

$$X = b[1-b/K_a]$$

This indicates that all $^3H$ is exchanged; which is true for wide variation in a, b, & K. Accurate knowledge of K not essential; K = 1; depends on the presence of a catalyst. It is doubtful if reaction will proceed in the absence of a catalyst. No exchange in a vacuum system takes place but the presence of charcoal, nickel makes reaction proceed rapidly. Do not know of presence of catalyst in lung. Determine by sampling P-10.

SAR for facility at Pantex site used the following assumptions (McSweeney and Cybulskis, 1995):

"The conversion rate of hydrogen tritide (HT) to tritiated water (HTO) follows the formula:

$$N - N_oe^{-At}$$; where N = fraction as HT and A = 0.01/hr.

Using the equation, approximately 1 percent of the HT will have been converted to HTO after 1-hour. Since the personnel exposure time is much shorter than an hour, only HT will be considered in the assessment." No references were provided for "A" value.

References were reviewed to provide additional support. Major conclusions from review:

- Oxidation of $^3H$ is controlled by ions generated by radioactive decay that combine with atmospheric oxygen to produce water. Rate constants are a function of $^3H$ concentration. The conversion was more efficient at high concentration due to the higher concentration of ions.

- At high concentrations, 94 to 324 mCi/ml, Dorfman and Hemmer (1954) found the reaction to be 1st-order with reaction rate constants in the range of 1.2E-4/min - 1.4-hr for 1% conversion. At lower concentrations, the reaction was found to be 2nd-order with respect to $^3H$ concentration. Yang and Gevantman (1964) measured isotopic exchange the $^3H$ concentration range of 0.05- to 0.7-mCi/ml, a rate constant 1.5E-3 ml/[mCi][hr] at a 0.1 mCi/ml $^3H$ concentration was measure; 66-hrs required to convert 1%. At a $^3H$ concentration of 0.01 mCi/ml, 666-hr (~1-mo) would be required for 1% conversion. Eakins and Hutchinson (1971) measured oxidation in dry and 100% RH air. For dry air oxidation, a rate constant of 5.6E-4 ml/[mCi][hr] and 2.9E-3 ml/[mCi][hr] are reported. At these rates at 0.1 mCi/ml, 1% oxidation would occur in 180- and 35-hr, respectively. At 1/10th the tritium concentration, the time spans are ten times greater.

- Ionization still catalyzes the conversion in atmosphere. Initially the rate is controlled by ionization of $^3H$, when beta ionization becomes an ineffective source of free-radicals, ultra-violet radiation becomes dominant mechanism. The rate is small and only 10%-15% HTO deposited on land prior to decay to $^3He$.

Cited letter from Cornman & Albenesius, SRL, 8/16/74:

"*Environmental Measurements after an unplanned release of 480,000 Ci of tritium gas from SRP on May 2, 1994 (1974 in Albenesius' memo, above), showed that only a small fraction of the tritium, less than 1%, was in the oxide form. As described previously in this report, the conversion rate is directly related to the concentration of tritium in air, except after considerable dilution in the environment where it is influenced primarily by photochemical effects. In the May 2 release, most of the oxide (>99%) was observed in environmental samples was probably formed within the 1st minute after the gas leaked from a failed process valve. Only during this short period, were tritium concentrations sufficiently high to result in the small amount of oxide observed. In the stack, the tritium was diluted in 540,000 ft$^3$ of air to an average concentration of 0.03 mCi/ml. During the rapid passage through the stack, at this concentration less than $10^{-6}$ of the gas would be converted to oxide. After discharge from the stack, the gas was substantially diluted further and is being converted to HTO at a rate of 0.03%/day*."

Savannah River Site SARs (SRS July 1988) apply a conversion value of 1% for tritium gas released into an enclosure with atmospheric oxygen and no ignition source prior to release to the ambient environment.

### 6.1.2 β-Activated Conversion, Outdoors

The environmental processes cited for the conversion of tritium gas released are (O'Kula and East, 2000):

- Environmental Processes Converting HT to HTO
    - Oxidation in air (slow)
    - Isotopic exchange reaction with $H_2O$
    - Photo-chemical oxidation in air/sunlight
    - Oxidation in soil (bacteria/enzyme)
    - Oxidation in plants

Experimentation indicates little air or plant conversion to HTO. The major conversion by soil - HTO released from soil as water vapor; transfer of HTO as released by plants. Major long-term exposure due to HTO.

Pan and Rigdon (undated) report that measured tritiated water/tritium show that HTO/HT conversion ratio of 0.01 (1%) would bound measured data by a factor of 2 to 500.

Recommends use of above ratio with site-specific or conservative meteorological data for three Los Alamos tritium facilities to bound dose calculations from sophisticated tritium transport codes and provide an upper-bound off-site dose.

Tritiated water and organic compounds remain in body in both forms. Biological half-life $^3$H 9.7-days, and organic compound half-lives of 30-day and 450-days.

Major $^3H$ production is as a by-product of nuclear reaction and from atmospheric atoms interaction with cosmic rays in upper atmosphere. Minor $^3H$ production is by neutron capture by $^6Li$ in rocks in the earth's crust where neutrons from uranium give (α, n) reaction. Man-made $^3H$ from weapons testing and nuclear facilities (nuclear power plants and $^3H$ production facilities) that have produced 50X the natural $^3H$.

$^3H$ specific activity 9.6 X $10^3$ Ci/gram. Radiological impact depends on rate of formation to tritiated water (HTO). Radiation impacts depend on rate of formation HTO vapor (approximately 22,000 X's greater radiological impact than $^3H_2$ - dose conversion factor HTO 95-rem/Ci versus HT 3.5 X $10^{-3}$ rem/Ci). Various processes for conversion of HT to HTO: oxidation in air; exchange with $H_2O$; photochemical oxidation in air; oxidation in soil; and oxidation in plants.

Cited three experiments to investigate $^3H_2$ conversion in atmosphere:

08/25/86 - Canadian outdoor release of 18.5-Ci;
10/15/86 - French outdoors release 7,000-Ci; and,
06/10/87 - Canadian outdoor release 95.7-Ci.

Little $^3H_2$ conversion occurs in air and plants. The major conversion occurs in the ground that re-emits HTO to air and plant up-take from soil that is subsequently emitted to air.

Subsequently, dispersion codes were developed from the information - ETMOD, UFORTI, H3DISP.

Based on data from three studies cited, above, and SRS accidental release (1974). The majors findings are:

- amount of HTO formed in atmosphere provides a negligible fraction; the formation through chemical kinetics is extremely small;
- surface soils oxidize HT by microbial action;
- part of HTO formed in soil is directly re-emitted to the atmosphere with soil emissions dominating the source of HTO after HT plume passage;
- deposition velocities estimated for HT to soil are approximately $10^{-4}$ to $10^{-3}$ m/s with good agreement among all measuring devices;
- soil $^3H$ re-emission rates are approximately a few percent per hr for duration of 1-day; and,
- wind speed, humidity, release height, and soil properties dictate conversion rate.

HTO/HT ratio of 0.01 (1%) bounds all measurements cited in experiments, above; mean value 8.8 X $10^{-4}$, median value 2.3 X $10^4$; 99.7% value is 6.1 X $10^{-3}$.

The measured conversion ratios ranged from $10^{-5}$ to $10^{-3}$ up to 15 km downwind;
the dose conversion factor, rem/gram, of $^3H$ released can be calculated. Meteorological parameters applied are:

- Semi-empirical correlation for key-parameters from three tests cited. Doses from mechanistic models (H3DISP & UFORTI) good agreement; both codes use conservative meteorological conditions. Dose for 5% re-emission in 8-hr realistic and recommended for short-term exposure.

- Simpler models extrapolations of test results are overly conservative to bound experimental uncertainties. 2X to 25X from mechanistic models.

- Currently 0.05 rem/g-HTO being applied for accidental release for environmental impacts for European and U.S. new facilities; values are between factor calculated by simple and mechanistic models.

Dose, as TEDE (Total Effective Dose equivalent) can be calculated from a short-term accidental exposure based on measured data or predicted by analysis outlined. No credible accident at most DOE facilities would involve sufficient $^3H$ to reach off-site dose evaluation guideline, 25 rem. Typical releases from SRS past 20-yr in Murphy, Bauer, and Hoel (1992).

Table 14 - "Tritium Releases at Savannah River Site"
(after Pan and Rigdon, undated)

| **Date** | **Release, Ci** | **HTO, %** | **HTO, Ci** |
|---|---|---|---|
| 05.02.74 | 479,000 | 1.0 | 4,790 |
| 12.31.75 | 182,000 | 0.6 | 1,092 |
| 03.27.81 | 32,934 | 100.0 | 32,934 |
| 07.16.83 | 56,000 | 1.0 | 560 |
| 03.24.84 | 7,500 | 70.0 | 5,250 |
| 09.07.84 | 43,800 | 100.0 | 43,800 |
| 01.31.85 | 9,300 | 50.0 | 4,650 |
| 03.27.85 | 19,422 | 99.9 | 19,403 |
| 07.31.87 | 172,000 | 2.7 | 4,644 |
| 03.01.88 | 20,000 | 15.0 | 3,000 |
| 06.07.88 | 3,650 | 4.0 | 146 |
| 10.06.88 | 7,086 | 10.0 | 700 |
| 12.07.88 | 3,082 | 99.5 | 3,050 |
| 01.03.89 | 500 | N/A | N/A |
| 03.30.89 | 1,100 | 97.0 | 1,067 |
| 10.19.89 | 800 | 100.0 | 800 |
| 02.07.90 | 100 | 100.0 | 100 |

Based on the conversion factors, approximately 700-gram (or approximately 7 X $10^6$ of HTO) or approximately 150,000-grams HT (approximately 1.5 X $10^9$ Ci) would result in exceeding the off-site MOI evaluation guideline of 25 rem. Using sophisticated models is not justified.

Propose direct application of HTO/HT conversion ratio with site-specific weather data viable method to reasonably calculate TEDE for accidental short-term exposures. If no site-specific weather data available, use Gaussian straight-line dispersion.

Sensitivity Study. Calculate dose using basic equation:

$$D = [M][SP][DCF][\chi/Q][BR]$$

Where: D = 50-yr TEDE, rem;
M = material released, g either as HTO or HT;
SP = specific activity, 9.6E3 Ci/g;
DCF = Dose Conversion Factor - (HT 3.5E-3 rem/Ci; HTO 95 rem/Ci;
$\chi/Q$ = atmospheric dispersion factor, s/m$^3$; and,
BR = Breathing Rate, 3.5E-4 m$^3$/s.

For all combinations of HT and HTO in the initial release, off-site doses calculated using 0.01 were estimated to be ≥ (by a factor of 10) using dose factors from sophisticated tritium codes.

Tritiated water/$^1H^3H$ atmospheric conversion factor of 0.01 (1%) bounds all measured values by a factor of 2 to 500 for all downwind distances to 15-km. 99.7% value for measured data is $6.1 \times 10^{-3}$. Use of conversion ratio, above, bounds all doses for accidental releases from three LANL $^3H$ facilities using dose factors calculated from sophisticated tritium transport codes using conservative meteorology and physical conditions. Use of ratio proposed bounds off-site doses.

### 6.1.3 Fraction Hydrogen Burned in Combustion

Tritium Working Group (undocumented). The document poses the following question, "*In an accident involving the release of tritium to the atmosphere, what fraction of the released tritium will be oxidized*?" Scope - limited to likelihood of tritium ignition during/following release and the fraction of gas that will burn. The document gives guidance as to what to expect.

The paper is mostly concerned with outdoor accidents.

Comments on relevant articles (also cited in Pan and Rigdon undated, Edusky and Pan 1996):

R.A. Strehlow (1973) in "Unconfined Vapor Explosions - An Overview (***14th International Symposium on Combustion***, Combustion Institute, Pittsburgh, PA) - 109 vapor cloud explosions (2 involving hydrogen); the combustion involved <10% of fuel involved; exception detonation of liquid propane spill that consumed 16%.

J. Hord (1976) "Is Hydrogen Safe?" (NBS Technical Note 690) - <10% accidental releases of combustible gases burn; sources include unpublished report - Strehlow; Burgess et al., below.

D. Burgess, J.N. Murphy, M.G. Zabetakis, & H.E. Perlee (1977) in "Volume of Flammable Mixture Resulting from Atmospheric Dispersion of Leak or Spill" (***15th International Symposium on Combustion,*** Combustion Institute, Pittsburgh, PA) - calculations to show that in an equilibrium situation (a maximum vapor cloud has been established), <1% to 10% released gases will burn. In an instantaneous release (no ignition time has been specified by Burgess) 50% burn of the vapor is estimated. Intermediate cases, intermediate results.

R.A. Strehlow & W.E. Baker (1975) in "The Characterization and Evaluation of Accidental Explosions" (NASA Report NASA CR 134770) - explosion including vapor cloud explosions. Example of vapor cloud explosion - massive release of combustible gas, 30-seconds to 30-min delayed ignition. Data verifies that that a combustion of 10% is a maximum value as predicted by Burgess et al. If combustible gas continues to be released, flames travels back to source igniting the gas (presumes subsequent combustion nearly complete).

R. Reider, H.J. Otway, & H.T. Knight (1965) in "An Unconfined, Large-Volume Hydrogen/Air Explosion (***Pyrotechnics***) – 2000-lb hydrogen planned release. The experimenters did not plan on ignition of the gas however, ignition occurred after ~26-seconds from start of experiment. Estimate 200-lb. (10%) involved in explosion.

R.H. Raring, W.F. Brown, C.E. Cataldo, J. Lombardo, & W. Rowe (1967), ***Report of NASA Working Group on Storage of Hydrogen at High Pressure*** - failures of 3500-6000 psi vessels. Six non-catastrophic failure (no ignitions identified). Crack repaired in-place and returned to service - evidence that non-catastrophic failures of high-pressure hydrogen vessels do not necessarily lead to ignition. Report on failure of pressure (Bourdon tube ruptures) gauges that ignited gas.

Factory Mutual Research Corp. (1984) ***Loss Prevention Data Sheet 7-91*** - Under proper wind conditions (not defined), spill of 500-gallons (300-lb) of liquid hydrogen, entire mass will diffuse to less that the lower flammable limit for hydrogen/air (4%) within 1-minute and would be not burn.

M.G. Zabetakis (1974). ***Safety in Cryogenic Fluids***, Plenum Press - stability of flare stacks. Flame may extinguish if velocity gradient is too-great (author deduce that would result in incomplete combustion).

P.M. Ordin (1974) "Review of Hydrogen Accidents and Incidents in NASA Operations", ***Proceedings of the 9th Intersociety Energy Conversion Engineering Conference*** - reviewed 96 hydrogen accidents/incidents that have occurred in NASA operations, 80 released hydrogen gas to the atmosphere. The hydrogen/air mixture was ignited in 61/80 (76%). Ordin did not state fraction of release gas that was burned.

R.G. Zalosh & T.P. Short (1978) ***Compilation and Analysis of Hydrogen Accident Reports***, Factory Mutual Research Corp. Report to U.S. DOE COO-4442-4 - Reviewed report for 409 hydrogen accidents in U.S., England, & Germany. Fire/explosion occurred in 328/409 (80%) of events. Fraction of release hydrogen burned not stated by Zalosh.

L. Thompson (1984) "EPRI Research on Hydrogen Combustion and Control for Nuclear Safety", ***Proceedings of the World Hydrogen Energy Conference IV***, Pergamon Press - Uniform mixture of hydrogen-air in the concentration range of 4% to 8% only burn partially. For a hydrogen concentration of <4% (lower flammable limit for hydrogen-air mixtures), the mixture does not burn. For the hydrogen concentrations in air between 4% and 8%, the mixture will only burn in an upwards direction. At a hydrogen concentration in air >8%, the mixture will burn in any direction and approaches 100% consumption.

To utilize the proceeding information for accident analyses, additional information is needed:

- Total quantity of hydrogen released;
- Ratio of volume released to the volume of the enclosure into which the hydrogen is released; and,
- Knowledge of the air velocity in and ventilation rate of the enclosure.

Three types of accident situations can be considered:

1. Instantaneous release of massive quantity ("massive" not defined by authors) of hydrogen with/without immediate ignition;
2. Continuous release of hydrogen gas until the maximum combustible cloud is formed followed by ignition; and,
3. Release of hydrogen gas with delayed ignition prior to formation of a maximum combustible cloud.

For Case #1 - Ignition may or may not occur. For a gentle release (gentle" not defined by authors, possibly a low pressure vent), the probability of ignition appears small. But for the release of high pressure hydrogen gas ("high-pressure" not defined by authors of the cited document) the probability appear to be >50%. If the release results from an event involving rending of metal (vessel rupture), ignition is likely. Author estimates that 50% of the hydrogen vented would be burned.

For Case #2 - Most of the gas would diffuse out of the flammable range (<1% in the Flammable Range) have been calculated, (Author’s comment - appears to depend on the height of the enclosure, remains valid for outdoor use). Data

> indicates <10% burned (Author's comment – valid for outdoor diffusion only). A release duration of greater than a few minutes is necessary to establish a equilibrium sized gas cloud prior to finding an ignition source. If the gas release is continuing, the flames could propagate back to the source where the gas would continue to burn until exhausted.
>
> For Case #3 - Release of gas persists until ignition source is found. Duration of release must be less than for Case #2. The fraction burned depends on the approach to Case #1 or #2, estimate between 10% to 50%. As in Case #2, the flame may propagate back to the release point and burning would continue until the hydrogen gas is turned off or exhausted.
>
> If the total release is small ("small" not defined by authors) compared to the volume in which it is released, it can be concluded that the fraction burn ranges from 1% to >50%.

DNFSB staff accepted that seismic event followed by a fire bounds risk for SRS Replacement Tritium Facility (RTF) (Bamdad 1995). MOI at site boundary dose of 5.1-rem (2-hr exposure, 50% meteorology, 100% conversion to HTO). Within 10CFR100 guidelines of 25-rem for site boundary for commercial nuclear industry.

Doses calculated by proposed method using very conservative meteorology. For three LANL $^3H$ facilities (TSTA, TSFF, & WETF). Table indicates that:

- dose @ 1,000-m using HTO/HT = 0.01 + GENNI 95th weather (with/without building wake effect) ≥ (by as much as 10X) than those using HT & HTO dose factors; and,
- dose @ 1,000-m using HTO/HT and simple Gaussian dispersion with building wake effect ≥ (by as much as 4X) using HTO & HT dose factors.

A LANL document addressed the concerns of the possibility of combustion during/after release and completeness of combustion of $^3H_2$ stored at elevated pressure (Edusky and Pan, 1996). Do not have data on combustion of $^3H_2$-air mixtures. Pertinent data: combustible concentration range; ignition temperature, and flame velocities. Data is available for *n*-$H_2$ combustion and it is reasonable to assume that the properties and reactions do not vary significantly. Review of pertinent portions of recent investigations on completeness of burning $^1H_2$.

- Instantaneous Release. Rapid release of entire contents of container a $^3H_2$ initially at elevated pressure. Mixes with ambient air with concentration range from pure $^3H_2$ to nominal air. May or may not be ignited.

  Instantaneous release = initial velocity high. If ignited immediately, very difficult to predict fraction oxidized. Gas velocity higher than flame speed (a few m/s to <10-m/s). Guess that as much as 50% could burn but no data/investigations to support.

- Delayed ignition - released gases expand and mix with the atmosphere. An ignition source is needed. Also, at least a sufficient volume that the gas/air mixture is within a flammable concentration range (for *n*-$H_2$/air 4% to 75% is needed, stoichiometric ~29%) when contact ignition source (Author's comment - not true, can ignite when some local concentration within flammable range and turbulence created by burning will dilute remainder; may be scenario for DDT). Combustion very incomplete at 4%; >8% combustion almost complete (none of gas <4% when ignition occurs and little of gas between 4% and 8% burns). Investigation of prolonged releases lead to estimates of 1% to 10% of released $H_2$ consumed. (References - Burgess, Murphy, Zabetakis & Perlee 1977; Reider, Otway, & Knight, 1965).

- Prolonged Release (from slower leak or partial valve opening). Mixes with atmosphere under more controlled manner. Immediate ignition less likely but still possible. Delayed ignition - <10% $H_2$ consumed (Author's comment - the energy yield value is only valid for the release of liquid fuel outdoors and BLEVE reaction)(References - Burgess, Murphy, Zabetakis & Perlee 1977; Strehlow 1973) but flame can propagate back to source (100% $H_2$ consumed under this circumstance).

- Release into a Closed Volume. Release of fixed quantity into closed volume (poorly ventilated room), ignition after release and mixing is completed. If concentration <4%, no combustion (Author's comment - this statement may not be true for tritium conversion due to the enhancement of the oxidation reaction by the β-decay energy emitted or other energy sources). Concentration between 4% and 8%, combustion incomplete - varies linearly from 0 @4% to 1.0 (>0.75) @ 8% (References – Thompson, 1984; Wong, 1988). *n*-$H_2$ at a concentration >75% is not combustible (in air).

- Ignition Considerations. Cannot predict with 100% assurance whether or not $H_2$ released can be ignited. Ignition source must be present for combustion. Different values for ignition temperatures cited for $H_2$/air mixtures. Ignition temperature depends on ways $H_2$ ignited (a function of atmospheric pressure)(Reference - Hansel, Mattern, & Miller 1993). Ignition temperature (1023 K/750° C) for contact of $H_2$/air mixture contacting hot surface most appropriate (not for all cases).

  Ignition energy required very low. For the stoichiometric mixture (approximately 29% $H_2$/air) at atmospheric pressure and ambient temperature, ignition takes only 0.015 milli-joule; 1/10th energy for ignition of common hydrocarbon fuels. Ignition is highly dependent on $H_2$ concentration initial temperature and pressure. As concentration deviates from the stoichiometric concentration, the energy required to ignite the mixture increases.

  At room temperature (300 K), *n*-$H_2$ above inversion temperature and gas will expand freely and temperature increases (especially at Los Alamos where atmospheric pressure is approximately 0.76 atm.). Expansion and heating mentioned as a possible ignition source. Heating during expansion is not adequate to raise the temperature of $H_2$ to anywhere near ignition temperature. The source does not provide an auto-ignition temperature for $H_2$.

Possible ignition sources:

- open flames;
- hot spots;
- electric sparks (removing a coat made of synthetic material may generate a spark sufficient to ignite $H_2$);
- static electricity generated by flowing gas stream, especially streams containing solid particles;
- if flow approaches sonic velocity, impact of a solid particle on a solid surface (e.g. wall during transmission through a bend in piping) may generate a hot spot adequate to ignite $H_2$/air mixture; and,
- the energy generated by the tearing/rupturing during the catastrophic failure of a vessel may generate a hot spot adequate to ignite a $H_2$/air mixture.

The absence of an ignition source cannot be ensured.

Conclusions.

- Estimates of fraction of released tritium gas reacted can only be made for accident type.
- Slow leak through a thick-wall vessel (did not define thick-wall) would not ignite immediately. If no subsequent ignition, no combustion (conversion to tritiated water). If ignited subsequent to release, fraction reacted would depend on fraction that can be diluted to 4% (or 8%) by diffusion and convection prior to ignition.
- "Worst case scenario" - moderate release rate with immediate ignition (e.g. like "flare-off"); near 100% conversion to tritiated water.
- Catastrophic rupture of vessel would probably result in immediate ignition of tritium gas. Fraction converted is probably >50%.

The Savannah River Site (SRS July 1998) applies a bounding value of 100% conversion for accident scenarios involving fire or explosion for all tritium facilities.

The Draft FSAR for LANL's Weapons Engineering Tritium Facility (Tuggle 2000) assumes 10% of $^3H$ is oxidized for a catastrophic failure scenario involving as stainless steel vessel containing tritium that could throw shrapnel/fragments that provides potential ignition source. The assumption is based that the ratio of the amount of $^3H_2$ to the enclosed volume (123 liter/3,000-liters = 0.41%; >lower flammable limit) makes the assumption that this configuration is equivalent to an un-confined gas volume. Applies fact that 10% $H_2$ in un-confined vapor cloud (outdoors BLEVE) is converted to explosive energy as an indice of the fraction of tritium gas converted to tritiated water (factor for hydrocarbon fuels but has not been established for $H_2$ that requires less than 0.1 ignition energy than hydrocarbon fuels; also not basis for assumption that cloud is un-confined).

Amount $^3H$ in TGHS at WETF is 400 grams (2,000-liters). Released into glove-box where $O_2$ concentration is <5%. $H_2$ is not flammable in $O_2$ concentrations that are <5%. If both the TGHS and glove-box fail, $^3H$ released into room [volume of room 50-$m^3$ (50,000-liters)]. Assuming uniform mixing, $^3H_2$ concentration is 4% with a pressure of 600 torr. (600-mm Hg). Smallest room volume is not designated but assume all are un-confined vapor clouds and 10% $^3H_2$ oxidizes.

If $^3H$ released into fire, 100% oxidized.

## 6.2 Conversion Values Recommended in this Report

### 6.2.1 Fraction Tritium Converted by β-Activated Processes (Simple Release of Low/Moderated Pressure Gas, continuous or puff, no ignition)

D. Outdoors - fraction of $^3H_2$ gas converted to tritiated water is fraction oxidized while in storage - bounding value 1% conversion to HTO.

E. Confined - Release into enclosure with air atmosphere; same as outdoors - bounding value 1% conversion to HTO (includes the conversion during transit through the facility that is assumed to be rapid due to the mobility of the tritium).

### 6.2.2 Fraction Hydrogen Burned in Combustion (from Releases of Low/Moderated Pressure, Gas continuous or puff, ignition)

- Outdoors
  - Immediate Ignition: Ignited at or near source; flames anchors to site and gas "flares".
    Bounding Value 100%
  - Delayed Ignition: Ignited after essentially all gas is vented; burns/explodes.
    Bounding value 100% (Other values may apply with adequate technical support to demonstrate tritium conversion to tritiated water under specific conditions)
- Confined
  - Immediate Ignition: immediate ignition of gas at or near to point of release; gas flares (burns).

Bounding value 100% conversion to tritiated water.

- Delayed Ignition: Ignition after essentially all gas is released; results in fire/deflagration/detonation.
  Bounding value 100% conversion to tritiated water.

- Delayed Ignition: Gas released into volume where can not ignite (e.g. inert atmosphere, no ignition source) with failure of containment after complete release and ignition.
  Bounding Value on case-by-case basis (requires substantial technical support)

## 7.0 REFERENCES.

Albenesius, E.L. 1974. "Conversion of $T_2$ to HTO", memo to W.R. Corman, Savannah River Laboratory/Technical Division, Aiken, SC.

Bamdad, F. 1995. Excerpt from paper "8. Safety Envelope", (undocumented).

Bodurtha, F.T. 1980. ***Industrial Explosion Prevention and Protection***, McGraw-Hill Book Company, New York, NY.

Burgess, D., J.N. Murphy, M.G. Zabetakis, and H.E. Perlee. (undated) "Volume of Flammable Mixture from the Atmospheric Dispersion of a Leak or Spill", ***Fire and Explosion Research*** (undocumented).

Coward, H.F. and G.W. Jones. 1952. ***Limits of Flammability of Gases and Vapors,*** Bureau of Mines Bulletin 503, U.S. Department of the Interior, Washington, DC.

Dorfman, L.M. and R.A. Hemmer. 1954. "Ion-Pair Yield of Tritium-Oxygen Reaction", ***J. of Chemical Physics***, 22:No. 9: pp 1555-1558.

Drysdale, D. 1985. ***An Introduction to Fire Dynamics***, John Wiley and Sons, New York, NY.

Eakins, J.D. and W.P. Hutchinson. (1973) "The Radiological Hazard from the Conversion of Tritium to Tritiated Water in Air by Metal Catalysts", ***Tritium*** (A.A. Moghissi and M.W. Crater, Ed.), Messenger Graphics, Phoenix, AZ.

Easterly, C.E., H. Noguchi, and M.R. Bennett. 1985. "Low-Concentration Conversion of Tritium Gas to Tritiated Water", ***Fusion Technology***, 8: pp 2564-2568.

Glassman, I. 1996. ***Combustion*** Third Edition, Academic Press, New York, NY.

Karim, G.A., I. Wierzba, and S. Boon. (undated) "Some Considerations of the Lean Flammability Limits of Mixtures Involving Hydrogen", ***Hydrogen Energy Progress - IV***, (undocumented).

LANL. 1996. ***Tritium Safety*** (Self Study Guide) LA-UR-99-5085, Los Alamos National Laboratory, Los Alamos, NM.

McKinley, C. 1980. “Safe Handling of Hydrogen”, pp 217-228, in ***Hydrogen: Production and Marketing*** (W.N. Smith and J.G. Stanangelo, Ed), ACS Symposium Series, American Chemical Society, Washington, DC.

McSweeney, T. and P. Cybulskis. 1995. "Conversion Rate of Tritium Gas to HTO", memo to Chris Steele dated July 14, 1995, Battelle Memorial Institute-Columbus Laboratory, Columbus, OH.

NASA. 1996. "Chapter 6 - Hydrogen Propellant" in ***NASA Glenn Safety Manual***, Glenn Research Center.

Noguchi, H., C.E. Easterly, and T.R. Bennett. (undated) ***Conversion of Tritium Gas to Tritiated Water at Low Tritium Concentrations***, HC-18, Oak Ridge National Laboratory, Oak Ridge, TN.

Noguchi, H., C.E. Easterly, and M.R. Bennett. 1989. "Conversion of Low-Concentration Tritium Gas to Tritiated Water", ***Fusion Technology***, 16: pp 137-142.

O'Kula, K.R. and J.M. East. 2000. ***Tritium Dispersion & Consequence Analysis***, course presented at EFCOG Safety Analysis Workshop Training, April 28, 2000, Santa Fe, NM.

Ordin, P.M. (undated) "Review of Hydrogen Accidents and Incidents in NASA Operations", (undocumented)

Ostlund, H.G. and A.S. Mason. 1974. "Atmospheric HT and HTO", ***Tellus XXVI***, pp 91-100.

Pan, P.Y. and L.D. Rigdon. (undated) ***Tritium Oxidation in Atmospheric Transport***, LA-UR-96-2953, Los Alamos National Laboratory, Los Alamos, NM.

Reis, V. 1999. "Review of Status of Stable Metal Tritium Compounds", memo to D. Minnema, DOE/DP-45, U.S. Department of Energy, Washington, DC.

Reider, R., H.J. Otway, and H.T. Knight. 1965. "An Unconfined, Large-Volume Hydrogen/Air Explosion", ***Pyrodynamics, Volume 2***, pp 249-261, Gordon and Beach, Science Publishers, Ltd., Northern Ireland.

Roesch, W.C. 1950. ***P-10 Chemical Equilibrium***, HW-17318, General Electric-Hanford Atomic Products Operation, Richland, WA.

Salzano, F.J., M.M. Beller, G. Strickland, and S. Srinivarsan. 1980. “Hydrogen Technology: An Overview” in ***Hydrogen: Production and Marketing*** (W.N. Smith and J.G. Stanangelo, Ed), ACS Symposium Series, American Chemical Society, Washington, DC.

Sandrock, G.D. and E. Snape. 1980. “Rechargeable Metal Hydrides: A New Concept in Hydrogen Storage, Processing, and Handling”, pp 293-322 in ***Hydrogen: Production and Marketing*** (W.N. Smith and J.G. Stanangelo, Ed), ACS Symposium Series, American Chemical Society, Washington, DC.

SRS. July 1998. "Chapter 3 Hazard and Accident Analysis" of ***Tritium Facilities Safety Analysis Report***, WSRC-SA-1-2-Vol 1, Westinghouse Savannah River Company, Aiken, SC.

Strehlow, R.A. (undated). "Unconfined Vapor-Cloud Explosions - An Overview", ***Fire and Explosion***, (undocumented).

Strehlow, R. 1979. ***Fundamentals of Combustion***, Robert E. Kreiger Publishing Company, Huntington, NY.

Stull, D.R. 1977. ***Fundamentals of Fire and Explosion***, AIChE Monograph Series, Vol. 73, No. 10, American Institute of Chemical Engineers, New York, NY.

Thompson, L. (undated) "EPRI Research on Hydrogen Combustion and Control for Nuclear Reactor Safety, ***Hydrogen Energy Progress - IV***, (undocumented).

Thompson, N.J. 1964. ***Fire Behavior and Sprinklers***, National Fire Protection Association, Boston, MS.

Tritium Working Group. (undated) "Oxidation of Tritium", (undocumented).

Tuggle, D. 2000. "Oxidation of Tritium to Water in WETF SAR Accident Scenarios", memo to Greg Rand dated March 13, 2000, Los Alamos National Laboratory, Los Alamos, NM.

Wallace, W.E., R.S. Craig, and V.U.S. Rao. 1980. “Hydrogen Absorption by Intermetallic Compounds” in ***Solid State Chemistry: A Contemporary Overview*** (S.L. Holt, J.B. Milstein, and M. Robbins, Ed.) Advances in Chemistry Series, American Chemical Society, Washington, DC.

Weast, R.C. (Ed). 1975. ***CRC Handbook of Chemistry and Physics***, 75th Edition, CRC Press, Cleveland, OH.

Witcofski, R.D. and J.E. Chirivella. (undated). Experimental and Analytical Analyses of the Mechanism Governing the Dispersion of Flammable Clouds Formed by Liquid Hydrogen Spills", ***Hydrogen Energy Progress - IV***

Yang, J.Y. and L.H. Gevantman. 1960. ***Tritium β-Radiation Induced isotopic Exchange in the $T_2$-$H_2O$ System***, USNRDL-TR-471, U.S. Naval Radiological Defense Laboratory, San Francisco, CA.

Zabetakis, M.G. 1924. ***Flammability Characteristics of Combustible Gases and Vapors***, Bureau of Mines Bulletin 627, U.S. Department of the Interior, Washington, D.C.

**References not cited in document on the outdoor experimental release of tritium and its conversion to HTO.**

Brown, R.M., G.L. Ogram, and F.S. Spenser. September 1988. "Field Studies of HT Behavior in the Environment: 1. Dispersion and Oxidation in the Atmosphere", ***Fusion Technology***, 14: pp 1165-1169.

Burnham, C.D., R.M. Brown, G.L. Ogram, and F.S. Spencer. September 1988. "An Overview of Experiments at Chalk River on HT Dispersion in the Environment", ***Fusion Technology***, 14: pp 1159-1164.

Davis, P.A., w.j.g. Workman, B.D. Amiro, F.S. Spenser, H. Noguchi, H. Amano, Y. Ichimasa, and M. Ichimasa. October 1995. "Overview of the 1994 Chronic HT Release Experiment at Chalk River", ***Fusion Technology***, 28: pp 840-845.

Djerassi, H. and G. Werner. September 1988. "Overview of the Tritium Release experiments in France", ***Fusion Technology***, 14: pp 1216-1221.

Easterly, C.E., G.S. Hill, and J.B. Cannon. September 1989. "Environmental Effects of Fusion Power Plants. Part III: Potential Radiological Impact of Environmental Releases", ***Fusion Technology***, 16: pp 125-136.

Jalbert, R.A. and C.E. Murphy. September 1988. "U.S. Team Measurements During the June 1987 Experimental HT Release at the Chalk River Nuclear Laboratories, Ontario, Canada", ***Fusion Technology***, 14: pp 1182-1186.

Jalbert, R.A. and C.E. Murphy. September 1988. ***The Canadian Experimental HT Release of June 10, 1987, U.S. Measurements***, LA-11368-MS, Los Alamos national Laboratory, Los Alamos, NM.

Noguchi, H., T. Matsui, and M. Murata. September 1988. "Tritium Behavior Observed in the Canadian HT Release Study", ***Fusion Technology***, 14: pp 1187-1192.

Noguchi, H., S. Yokoyama, N. Kinouchi, M. Murata, H. Amano, Y. Ichimasa, and M, Ichimasa. October 1995. "Tritium Behavior on a Cultivated plot in the 1994 Chronic HT Release Experiment at Chalk River", ***Fusion Technology***, 28: pp 924-929.

Noguchi, H., T. Matsui, and M. Murata. September 1988. "Tritium Behavior Observed in the Canadian HT Release Study", ***Fusion Technology***, 14: pp 1187-1192.

Noguchi, H., S. Yokoyama, N. Kinouchi, M. Murata, H. Amano, Y. Ichimasa, and M, Ichimasa. October 1995. "Tritium Behavior on a Cultivated plot in the 1994 Chronic HT Release Experiment at Chalk River", ***Fusion Technology***, 28: pp 924-929.

Ogram, G.L. and F.S. Spenser. September 1988. "Field Studies of HT Behavior in the Environment: 2. The Interaction with Soil", ***Fusion Technology***, 14: pp 1170-1175

Spenser, F.S. and G.L. Ogram. September 1988. "Field Studies of HT Behavior in the Environment: 3. Tritium Deposition and Dynamics in Vegetation", ***Fusion Technology***, 14: pp 1176-1181.