DEFENSE NUCLEAR FACILITIES SAFETY BOARD

March 27, 1995

MEMORANDUM FOR: G. W. Cunningham, Technical Director

COPIES: Board Members

FROM: David T. Moyle

SUBJECT: Radiolytic Hydrogen Generation in Rocky Flats Plutonium-Nitric Acid Solution Tanks

1.   **Purpose:**   This report documents an independent Defense Nuclear Facilities Safety Board (Board) staff review of hydrogen generation in actinide solution tanks at the Rocky Flats Environmental Technology Site (RFETS). This is a follow-up action to concerns raised in a recent Board staff visit to Rocky Flats (November 28-December 1, 1994). The staff intends to evaluate whether passive venting of tanks is sufficient to prevent hydrogen accumulation and potential risk of hydrogen explosions in the tanks.

2.   **Summary:**   Assuming diffusion limited transport as a bounding calculation, analysis shows that even though vent lines to the actinide solution tanks are open, hydrogen and oxygen will accumulate in tank headspaces. Without headspace sampling, all tanks may be assumed to contain explosive mixtures of hydrogen and oxygen. Detonations and/or deflagrations may occur in vent lines and tanks if ignition sources arise. Detonation effects are similar for a wide range of hydrogen concentrations where the maximum reflected pressures at tank walls could exceed the failure pressure by a factor of two. Even if the tank wall remains intact, fittings and sight glasses may likely fail, breaching containment. The analysis indicates that within relatively short times hydrogen gas can build up to explosive concentrations. Due to the relatively long stagnant storage of these solutions, a hydrogen detonation in a tank is believed to be a credible hazard.

3.   **Background:**   Alpha decay of plutonium isotopes causes radiolysis reactions in solutions which produce hydrogen and oxygen gases as major products. Build up of this flammable gas mixture in tank void spaces poses several hazards to the facility, resulting from possible explosions, including:

   a.   Loss of containment which could cause spills and airborne releases from vaporization.
   b.   Missiles / Shrapnel.
   c.   Criticality from settling of broken Raschig rings, geometry changes.

The Board trip report dated December 8, 1994, discussed Rocky Flats' past efforts to resolve this issue.[1] In 1993, Los Alamos Technology Office at Rocky Flats (LATO) performed a safety study of plutonium and uranium solutions at RFETS, which concluded that in unvented high plutonium concentration tanks, sufficient hydrogen could be generated to reach the lower flammability limit (LFL) in about 12 hours. Further, LATO recommended that it was "extremely important that ventilation be maintain on all solutions in tanks." At Department of Energy / Rocky Flats Office (DOE/RFO) request, vent line outlet hydrogen concentrations were measured for tanks in building 771. All readings were zero except one at 17% of LFL. LATO assumed that outlet concentrations through several meters of vent line reflected the status of the tank void spaces, and concluded, "these measurements indicate that the potential for an explosion in a tank is extremely low." Furthermore, they concluded that the consequences of a tank explosion would be minimal, possibly blowing out gaskets and causing a leak, but not breaching the tank itself.[2] In response to Board staff questions about the hydrogen explosion scenario, EG&G representatives stated that there would be no off site consequences, and since only workers would be affected, EG&G considered it was not necessary to pursue.[1]

Occurrence report numbers RFO-EGGR-371OPS-1995-0037 and RFO-EGGR-771OPS-1995-0064 referenced a potential unreviewed safety question regarding hydrogen gas generation and buildup in stagnant actinide solution tanks in buildings 371 and 771.[3][4] More details were offered in Operating Experience Weekly Summary Report 95-09, reporting the completion of a draft Unreviewed Safety Question Determination (USQD) on February 28, 1995. The study concluded that a detonation could rupture the tanks if they were not vented and an ignition source was present. If vented, however, hydrogen accumulation was determined to be a manageable hazard. Further, an ignition source could not be identified.[5]

The Board staff is concerned that this draft USQD does not adequately address the hydrogen accumulation and explosion issue, and this paper summarizes results of an independent staff analysis. Diffusion calculations, presented in Appendix A, determine theoretical worst case concentrations of hydrogen in tanks and vent lines, while the explosion analysis in Appendix B estimates maximum pressures that could be experienced by containment in event of an explosion.

4. **Discussion:**

    a. Industry Standard Design and Operating Requirements: National Fire Protection Association (NFPA) 69, Standard on Explosion Prevention Systems, states that, "The combustible concentration shall be maintained below 25 percent of the lower flammability limit," when no automatic safety interlocks are provided.[6] Implicit in this requirement is the general assumption that an ignition source will be present. It is generally not acceptable practice to rely on the lack of an obvious ignition source unless a safety system is in place to assure suppression of ignition sources.

b. Identification of Tanks: This analysis assesses hydrogen generation in a total of 14 actinide solution tanks in buildings 371 and 771. Building 371 contains four of these tanks (D49B, D49C, D55A, D134C), while building 771 houses the remaining ten tanks (D452, D472, D550, D931, D933, D971, D972, D974, D1007, D1810).

c. Hydrogen Generation Rates: Hydrogen generation rates (G-values) for the alpha radiolysis of nitric acid solutions are taken from N.E. Bibler's experimental work at Savannah River.[7],[8] Oxygen G-values are estimated by relative trends observed at Rocky Flats in Kazanjian's research with actual plutonium nitric acid solutions.[9] See Appendix A for more details.

d. Diffusion Analysis: A Rocky Flats report has established that all solution tanks are vented, i.e. the vent lines are not blocked.[10] However, the vents are "passive", and in the absence of pressure variations, the escape of hydrogen from tank vapor spaces is limited by diffusion down the vent line. Concentration measurements at the vent line outlet are not representative of the tank vapor concentration, because diffusion limitations will cause a concentration gradient to develop down the length of the vent line.

Appendix A develops a three component, one dimensional model for radiolytic hydrogen and oxygen diffusing through non-diffusing air in a horizontal vent line. This model predicts that vent lines longer than approximately 1 meter will result in a flammable tank atmosphere (4 volume % hydrogen). For realistic vent line lengths, equilibrium concentrations in several tanks may approach the stoichiometric ratio of hydrogen and oxygen. Hydrogen is quite easy to ignite over a wide range of concentrations, requiring less energy than most other flammable gases. In oxygen, hydrogen concentrations between 4 and 94 volume % are flammable, with a detonable range between 15 and 90 volume%.[11a] All tanks are expected to have equilibrium concentrations in the detonable range for hydrogen-oxygen mixtures.

Appendix A also gives diffusion results and hydrogen buildup times for Kazanjian's hydrogen generation rate data (less conservative than Bibler's), as estimated in the Rocky Flats draft USQD calculation.[12] With these generation rates, explosive mixtures are still expected in all solution tanks.

e. Flammable Gas Buildup Time: Using the hydrogen generation rates from Bibler's research, worst case hydrogen gas build-up times were approximated, neglecting diffusion. Results in Appendix A show that LFL (4 volume %) can be reached in 1 to 10 days in some tanks, and equilibrium concentrations are reached in 1 month to 8 years. Based on the number of years that the tanks have remained idle, it could be assumed that all tanks are currently at explosive concentrations.

f. Explosion Analysis: The method followed for the explosion analysis in Appendix B primarily came from references used in a seminar on the calculation and evaluation of fire and explosion hazards sponsored by the American Institute of Chemical Engineers. For confined gas explosions, the deflagration pressure wave is generally assumed to be 10 times the initial pressure. Calculations for a stoichiometric hydrogen-oxygen mixture show the deflagration pressure is approximately 143psia. When a pressure wave strikes a surface, a reflected pressure wave is developed. This reflected pressure is greater than the incident pressure and results from a momentum change, due to a change in direction when the moving air strikes a dense surface. The reflected pressure of a deflagration wave striking a surface normal to the incident pressure wave is approximately twice the deflagration pressure or, 285psia.[11],[13]

The detonation pressure for a confined gas can be estimated as twice the deflagration pressure or, 285psia in this case. The maximum reflected pressure from the detonation shockwave striking a surface, such as the inner tank wall, normal to the direction of propagation, will be approximately 1800psia.[11],[13a] This worst case reflected pressure results in a tensile stress nearly twice the ultimate stress of a 42 inch diameter, 1/4 inch thick wall, 304L stainless steel cylindrical tank. Due to the ductility of 304L stainless steel,[14] it is difficult to determine if the impulse of a reflected detonation pressure will rupture the tank, but it is likely to cause deformation and blow out fittings.

The calculated detonation pressure for a stoichiometric hydrogen-oxygen ratio corresponds to that reported in Bureau of Mines Bulletin 627. Further, a graph of detonation pressures shows that the effects of a hydrogen detonation will be essentially the same for much of the explosive range (20 to 80 volume %).[15]

g. Deflagration Versus Detonation: By definition, deflagrations propagate at subsonic velocities, and detonations propagate at supersonic velocities. Deflagrations transition to detonations when the reaction front accelerates to the speed of sound. If a deflagration were to occur in a storage tank, it is possible that pressures could be vented enough to avoid extensive damage to system components. However, 90 degree elbows in vent lines and large length to diameter ratios will limit the effectiveness of venting.[11],[13] Therefore, deflagrations may cause some structural damage.

Based on current analyses, the possibility of a detonation can not be ruled out. Acceleration to detonation in horizontal pipes generally occurs in distances proportional to the square root of the pipe diameter. However, depending on the strength of the ignition source, detonation can be almost instantaneous.[11],[13] Therefore, a hydrogen detonation in an actinide solution tank or vent line can not be ruled out. Furthermore, deflagrations and/or detonations are likely to affect other tanks connected through common vent lines. See appendix B for further discussion.

5. References

[1]   Bamdad, F., memorandum for G. W. Cunningham, "Nuclear and Criticality Safety at Rocky Flats", Trip Report (November 28-December 1, 1994), December 8, 1994.

[2]   Los Alamos Technology Office at Rocky Flats, "Plutonium and Uranium Solutions Safety Study", October 14, 1993. DNFSB Control # RF: 94-3523.

[3]   Occurrence Report RFO-EGGR-371OPS-1995-0037.

[4]   Occurrence Report RFO-EGGR-771OPS-1995-0064.

[5]   "Operating Experience Weekly Summary 95-09", February 24 through March 2, 1995.

[6]   "NFPA 69, Standard on Explosion Prevention Systems", 1992 Edition.

[7]   Bibler, N.E., "Curium-244 Alpha Radiolysis of Nitric Acid. Oxygen Production from Direct Radiolysis of Nitrate Ions", Savannah River Laboratory, E.I. duPont Nemours & Co., DP-MS-72-68. DNFSB Control # SR:94-257.

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[9]   Kazanjian, A.R., & D.R. Horrell, "Radiologically Generated Gases in Plutonium-Nitric Acid Solutions", Radiation Effects 1972, Vol 13, pp. 277-280, Gordon and Breach Science and Publishers Ltd., Glasgow, Scotland.

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[11a]   Handbook of Compressed Gases, Third Edition, Compressed Gas Assn., Inc., Van Nostrand Reinhold, NY, 1990.

[11b]   Kuchta, Joseph M., Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - A Manual, U.S. Department of the Interior,

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[12]   Colwell, R.G., "Analysis of Hydrogen Generation, Explosivity and Pressure Rise in Unvented Pu-HNO$_3$ Solution Tanks Due to Radiolysis", (DRAFT) Calc. No. CALC-RFP-95.0386-RGC-USQD.

[13]   Grelecki, Dr. Chester, "Fundamentals of Fire and Explosion Analysis", AIChE Today Series. Course notes and excerpts, including:

[13a]   Glasstone, Samuel (Editor), The Effects of Nuclear Weapons, Chapter III: "Air Blast Phenomena", United States Atomic Energy Commission, April, 1962.

[13b]   Cook, Melvin A., The Science of High Explosives, Appendix II, American Chemical Society Monograph Series. Reinhold Publishing Corp., New York, 1958.

[14]   Perry, Robert H., & Don Green (Editors), Perry's Chemical Engineers' Handbook, Sixth Edition, McGraw-Hill Book Company, New York, 1984.

[15]   Zabetakis, Michael G., Flammability Characteristics of Combustible Gases and Vapors, U.S. Department of the Interior, Bureau of Mines, Bulletin 627, 1965.

[16]   Bird, Stewart, & Lightfoot, Transport Phenomena, John Wiley & Sons, Inc., 1960.

Appendix A
Radiolytic Gas Generation and Diffusion Analysis

1. Assumptions

For all calculations, ambient temperature is assumed to be zero Celsius (273 K), and ambient pressure is 1 atmosphere (14.7 psia). All pressure variations and buoyancy affects are neglected, and the horizontal vent line system is assumed to be diffusion limited. It is recognized that pressure fluctuations within the system may induce flows which could affectively flush the vent lines and tank vapor spaces. However, such detailed effects are beyond the scope of this worst case safety analysis.

Information on exact vent line lengths and diameters for specific tanks were not obtained, because they vary for each tank, therefore, approximations are used. A report on the status of vent valves in building 771 states that of the 10 tanks of concern, 2 have 1/2 inch lines, 6 have 3/4 inch lines and 2 have 1 inch lines.[10] Assuming schedule 40S pipe, the inner diameter of a 3/4 inch vent line is 0.824 inches.[14] Diffusion calculations use this average diameter.

A representative vent line system is assumed to be a "dead-ended" extension of a glove box system. Each vent line extends approximately one foot vertically from the top of a tank, connecting to a horizontal line, common to several tanks. The vent line then extends for 10-15 meters, with one or more 90 degree turns in the horizontal plane. Finally, a 90 degree turn down connects the vent line to an opening in the top of a glove box, approximately one foot below.

2. Radiolytic Gas Generation Rates

Data for radiolytic gas generation rates from nitric acid solutions exists from several researchers. Experimental techniques vary in the determination of G-values (molecules of gas produced / 100 eV of exposure) making it difficult to conclude which method is the most appropriate. N.E. Bibler at Savannah River conducted several experiments and generated a representative curve fit for hydrogen G-value dependence on nitrate concentration, which agrees well with the data of Savel'ev, another researcher.[7],[8] Two researchers at Rocky Flats, A.R. Kazanjian and D.R. Horrell, observed similar trends in hydrogen generation rates, but the magnitudes measured were much lower than recorded by Bibler.[9]

Bibler's data should be used to determine hydrogen generation rates for a safety analysis because his numbers are the most conservative. However, important trending information can still be gained from the work of Kazanjian. Kazanjian's experiments were run with plutonium-239 as an alpha source, while Bibler used curium-244 and Savel'ev used polonium-210 as alpha sources. Similar decreasing trends were seen in all three cases for hydrogen G-values as nitrate concentration increased. However, Kazanjian's G-values were nearly one fifth of the magnitude documented by the other researchers. The reasons for this difference are likely do to different

experimental techniques. Bibler ran a few samples in the presence of plutonium and found that there was no effect on measured hydrogen G-values. For oxygen G-values, however, it seems that plutonium has some effect on reducing the oxygen released. Experiments with Cm-244 and Po-210 alpha sources showed oxygen G-values increasing with increasing nitrate concentration. On the other hand, Kazanjian, who used plutonium in solution as an internal alpha source, observed oxygen G-values following the same decreasing trend as hydrogen G-values, but at approximately half the magnitude. It seems that plutonium may have a significant effect on the chemistry of radiolytic oxygen production.[8]

As Bibler's data is more conservative for hydrogen G-values, Kazanjian's data on the trend of oxygen generation rates should be applied in determining oxygen G-values in plutonium-nitric acid solutions. This results in oxygen G-values of one-half the magnitude of hydrogen G-values for given nitric acid concentrations. As will be seen in the diffusion section below, this is the most conservative case, allowing for buildup of stoichiometric mixtures of hydrogen and oxygen in solution tanks.

3. Diffusion Theory

Rocky Flats presents a relatively convincing argument that all solution tanks are constantly vented such that there will be no increase in static pressure due to buildup of radiolytic gases.[10] This venting, however, does not imply forced flow. The vents are "passive", such that the pressure in the tanks and lines remains at ambient. If this ambient pressure does not fluctuate, it can be expected that diffusion will limit the transport of gases down the vent line. Thus, with hydrogen and oxygen being generated by radiolysis, the tank headspace may develop a flammable mixture, dependant on the steady state concentration profiles as the gases diffuse down the vent line.

A. Two Component, One Dimensional Model

A one dimensional diffusion model can be developed that assumes the tank head space is well mixed at a uniform hydrogen concentration, and the hydrogen diffuses down the vent line through non-diffusing air, neglecting elbows and elevation effects. This is a first approximation that can be enhanced as discussed in section B. Given a vent line length and cross section, an outlet concentration, and a hydrogen generation rate, the equilibrium tank concentration can be determined. Further, a minimum vent line length can be determined that results in a flammable tank atmosphere. The following development is based on theory presented in Transport Phenomena by Bird, Stewart, and Lightfoot (reference [16]).

Starting with Fick's first law of diffusion as:

$$J_A^* = c_A(v_A - v^*) = -cD_{AB}\nabla x_A \qquad (eqn.1)$$

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Where: J_A^* = Molar flux of A relative to molar average velocity [mol/cm²*sec]
c_A = Molar concentration of component A [mol/cm³]
v_A = Velocity of component A [cm/sec]
v^* = Molar average velocity of mixture [cm/sec]
c = Total molar concentration of mixture [mol/cm³]
D_{AB} = Binary diffusion coefficient [cm²/sec]
x_A = Mole fraction of component A

The molar flux of component i relative to stationary coordinates is:

$$N_i = c_i v_i \quad (eqn.2)$$

In a binary system, the molar average velocity is:

$$v^* = x_A v_A + x_B v_B \quad (eqn.3)$$

With use of equations 2 and 3, equation 1 becomes:

$$N_A = x_A(N_A + N_B) - c D_{AB} \nabla x_A \quad (eqn.4)$$

At steady state, we assume that component A (hydrogen) is diffusing through non-diffusing component B (air). Therefore $N_B = 0$ and N_A = constant = generation rate/vent line area. Then, equation 4 can be simplified to the following one dimensional form:

$$\frac{N_A}{c D_{AB}} = \frac{-1}{1-x_A} \frac{dx_A}{dz} \quad (eqn.5)$$

This equation can be integrated directly giving:

$$\frac{N_A}{c D_{AB}} z = \ln(1-x_A) + K \quad (eqn.6)$$

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The integration constant, K, can be evaluated with the use of a boundary condition at the outlet to the glove box, $x_A = x_{Ah}$ at $z = h$. This gives:

$$K = \frac{N_A h}{c D_{AB}} - \ln(1 - x_{Ah}) \qquad (eqn.7)$$

Equation 6 can now be solved for the mole fraction of component A at position z:

$$x_A(z) = 1 - (1 - x_{Ah}) e^{\frac{N_A}{c D_{AB}}(z - h)} \qquad (eqn.8)$$

B.   Three Component, One Dimensional Model

The result in the above development is not accurate because it fails to account for other gases produced by radiolysis, which also will diffuse down the vent line. Kazanjian found oxygen, nitrogen, and other trace gases released in his experiments. By far, oxygen was the next most prevalent gas after hydrogen. G-values for oxygen were approximately half of the G-values for hydrogen.[9] For simplicity and conservatism, only hydrogen and oxygen generation are considered in the following development.

Three components will be considered: hydrogen, oxygen, and air. Hydrogen and oxygen will diffuse down the vent pipe through non-diffusing air. Fick's law still applies as shown in equation 1, except the diffusivity of hydrogen is now related to two other components and compositional changes will affect the diffusivity of hydrogen through the medium. Diffusivity is based on molecular weight ratios, and since the molecular weights of air, oxygen, and nitrogen are similar, we can assume a constant diffusivity of hydrogen in the medium, equal to its value in air ($0.611 cm^2/sec$).[14]

The molar average velocity for three components is:

$$v^* = x_A v_A + x_B v_B + x_C v_C \qquad (eqn.9)$$

With the use of equations 2 and 9, Fick's law becomes:

$$N_A = x_A(N_A + N_B + N_C) - cD_{A-BC}\nabla x_A \qquad (eqn.10)$$

At steady state, we assume that components A (hydrogen) and B (oxygen) are diffusing through non-diffusing component C (air). Therefore, $N_C = 0$, N_A = constant = generation rate/pipe area, and N_B = constant = generation rate/pipe area. With an integrating factor and the boundary condition at the outlet of the vent line, $x_A = x_{Ah}$ at $z = h$, the one dimensional form of equation 10 can be solved to give:

$$x_A(z) = \frac{N_A}{N_A + N_B} - \left(\frac{N_A}{N_A + N_B} - x_{Ah}\right) e^{\frac{N_A + N_B}{cD_{A-BC}}(z-h)} \qquad (eqn.11)$$

Note that equation 11 reduces to equation 8 when $N_B = 0$. Further, as the vent line length, h, increases, the tank concentration of component A at $z = 0$ approaches the limit ratio of the flux (or generation rate) of A to the total flux (or generation rate) of diffusing gases. Equation 11 can also be applied to oxygen if the diffusivity is assumed to be constant. The diffusivity of oxygen will actually lie somewhere between its value in hydrogen ($0.697cm^2/sec$) and its value in air ($0.178cm^2/sec$).[14] Therefore, if the line is long enough for hydrogen to reach its limiting concentration, then oxygen will also be at its limiting concentration. Regardless, explosion calculations will assume that there is always enough oxygen present to burn all of the hydrogen fuel. Furthermore, the model predicts that the composition of hydrogen can not exceed its limiting composition of 66.7% by volume, it's stoichiometric combustible concentration in oxygen.

Table 1 shows possible representative equilibrium concentrations for 3/4 inch lines with assumed lengths of 10 meters each, based on a recent facility visit and tour of building 771. Table 2 reports vent line lengths which result in LFL (4 vol % H_2) and 90% of the limiting concentration (or 60 vol % H_2) at equilibrium. Lengths in table 2 are obtained by manipulating equation 11. Setting $x_{Ah}=0$, specifying x(0), and solving for h gives:

$$h = \frac{-cD_{AB}}{(N_A + N_B)} \ln\left[1 - \frac{(N_A + N_B)}{N_A} x_A(0)\right] \qquad (eqn.12)$$

3. Gas Buildup Time

A conservative approach is used to estimate minimum times for hydrogen and oxygen to build up to flammable and/or equilibrium concentrations. The calculation involves dividing the volume fraction of the tank head space which corresponds to a particular composition by the volumetric generation rate. This is a limiting worst case time, not accounting for loss of hydrogen by diffusion. It simply assumes that all hydrogen produced displaces the air or oxygen in the tank head space. The results are shown in table 3.

Table 3 shows that in all cases, a detonable gas mixture can build up in approximately a year, some only requiring several days. Also recognize that several tanks require only a month or two to reach equilibrium concentrations approaching 67 volume % hydrogen. Noting that these tanks have remained "passively vented" for five years or more, all tanks should be assumed to contain explosive vapor concentrations.

4. Results Using Rocky Flats G-values

Rocky Flats draft USQD calculation CALC-RFP-95.0386-RGC-USQD[12] used Kazanjian and Horrell's data to obtain hydrogen generation rates.[9] A quadratic interpolating polynomial was developed from maximum G-values including uncertainty, as they relate to acid concentration. The polynomial was derived to give hydrogen generation rate in units of moles/hour/liter of solution at 50 g/liter plutonium concentration.[12] Noting that the alpha decay heat of a representative isotopic composition of plutonium is 5e19 eV/g/hr,[9] G-values in units of molecules/100eV can be obtained by multiplying the polynomial by the following factor:

$$(polynomial)\left[\frac{mol}{hr\;\ell}\right]*\left[\frac{1\,\ell}{50gPu}\right]\left[\frac{6.02e23\,molecules}{mol}\right]\left[\frac{hr\;gPu}{(5e17)(100eV)}\right]$$

Which gives the following expression for hydrogen G-value, dependent on acid molarity:

$$G_{H_2} = 24080*(9.56e\text{-}6-1.86e\text{-}6*M_{acid}+9.94e\text{-}8*M_{acid}^2)\left[\frac{molecules}{100eV}\right] \qquad (eqn.13)$$

Table 4 displays representative equilibrium tank concentrations for 10 meter long 3/4 inch vent lines and hydrogen G-values as in equation 13. Table 5 reports predicted buildup times. These tables show that even if Kazanjian's data is used, detonable hydrogen concentrations should be assumed in solution tanks.

Table 1: Representative case to determine equilibrium hydrogen concentrations in solution tanks

Alpha energy released from plutonium solutions:	5.00E+19 eV/g/hr	
Avagadro's Number:	6.02E+23 molecules/mole	
Molecular Diffusivity of Hydrogen in Air at 0 C:	0.611 cm²/sec	0.21996 m^2/hr
Molar Volume of Ideal Gas at 0 degrees C:	22.386 liters/mol	
Molar Concentration of Ideal Gas at 0 degrees C:	44.6707638 mol/m^3	

Tank #	Plutonium Solution Conc. [g/l]	Tank Volume [liters]	Tank Capacity [liters]	Acid Strength [M]	Hydrogen G-value [molec/100eV]	Total mass Plutonium [grams]	Hydrogen Generation [mol/hr]	Oxygen Generation [mol/hr]	Line Diam. [cm]	Flux of H2 in Line [mol/m^2hr]	Flux of O2 in Line [mol/m^2hr]	Line Length [meters]	Tank H2 Conc. [vol %]
D49B	0.6	1483	2226	1.3	0.43	889.8	0.0003178	0.0001589	2.09	0.9263006	0.4631503	10	50.5%
D490C	0.83	1214	2395	1	0.5	1007.62	0.0004184	0.0002092	2.09	1.2197136	0.6098568	10	56.3%
D554A	0.6	755	1106	0.31	0.7	453	0.0002634	0.0001317	2.09	0.7679625	0.3838463	10	46.0%
D134C	0.4	1400	2235	1	0.5	560	0.0002326	0.0001163	2.09	0.6778742	0.3389371	10	43.0%
D452	5	495	520	7	0.1	2475	0.0002056	0.0001028	2.09	0.5991924	0.2995962	10	40.0%
D472	95	25	176	7.5	0.09	2375	0.0001775	8.877E-05	2.09	0.5174843	0.2587422	10	36.4%
D550	130	222	252	10	0.08	28860	0.0019176	0.0009588	2.09	5.5895569	2.7947784	10	66.7%
D931	96	260	334	7	0.1	24960	0.0020731	0.0010365	2.09	6.0427642	3.0213821	10	66.7%
D933	95	116	222	7	0.1	11020	0.0009153	0.0004576	2.09	2.6679191	1.3339596	10	65.5%
D971	40	74	525	8	0.08	2960	0.0001967	9.834E-05	2.09	0.5732879	0.2866439	10	38.9%
D972	40	63	545	8	0.08	2520	0.0001674	8.372E-05	2.09	0.4880694	0.2440347	10	35.0%
D974	95	27	230	7	0.1	2565	0.0002113	0.0001065	2.09	0.6209812	0.3104906	10	40.8%
D1007	90	36	190	8	0.08	3240	0.0002153	0.0001076	2.09	0.6275178	0.3137589	10	41.1%
D1810	140	146	262	3.5	0.18	20440	0.0030558	0.0015279	2.09	8.9072669	4.4536334	10	66.7%

Table 2:	Minimum vent line lengths to reach specified equilibrium hydrogen concentrations			
Vent line diameter =		2.09 cm	(3/4 inch schedule 40 pipe)	
			LFL condition Tank H2 Concentration 4%	90% of Max. Tank H2 Concentration 60%
Tank #	Flux of H2 In Line [mol/m^2hr]	Flux of O2 In Line [mol/m^2hr]	Vent line Length [meters]	Vent line Length [meters]
D49B	0.926	0.463	0.438	16.283
D49C	1.220	0.610	0.332	12.366
D55A	0.768	0.384	0.528	19.647
D134C	0.678	0.339	0.598	22.251
D452	0.599	0.300	0.676	25.172
D472	0.517	0.259	0.783	29.147
D550	5.590	2.795	0.073	2.698
D931	6.043	3.021	0.067	2.496
D933	2.668	1.334	0.152	5.654
D971	0.573	0.287	0.707	26.310
D972	0.488	0.244	0.830	30.904
D974	0.621	0.310	0.653	24.289
D1007	0.628	0.314	0.646	24.036
D1810	8.907	4.454	0.046	1.693

Table 3:	Worst case hydrogen gas build-up times				
Tank #	Time to 1 vol % [days]		Time to 4 vol % [days]		Time to Equilib. [years]
D49B	43.52		174.07		6.01
D49C	52.53		210.13		8.10
D55A	24.81		99.22		3.13
D134C	66.83		267.32		7.86
D452	2.26		9.05		0.25
D472	15.83		63.32		1.58
D550	0.29		1.16		0.05
D931	0.66		2.66		0.12
D933	2.16		8.62		0.39
D971	42.68		170.72		4.54
D972	53.58		214.32		5.14
D974	17.74		70.94		1.98
D1007	13.31		53.26		1.50
D1810	0.71		2.83		0.13

Table 4: Representative case to determine equilibrium hydrogen concentrations in solution tanks (Using Rocky Flats fit to Kazanjian's data)

Alpha energy released from plutonium solutions: 5.00E+19 eV/g/hr

Avagadro's Number: 6.02E+23 molecules/mole

Molecular Diffusivity of Hydrogen in Air at 0 C: 0.611 cm^2/sec   0.21996 m^2/hr

Molar Volume of Ideal Gas at 0 degrees C: 22.386 liters/mol

Molar Concentration of Ideal Gas at 0 degrees C: 44.6707638 mol/m^3

Tank #	Plutonium Conc. [g/l]	Solution Volume [liters]	Tank Capacity [liters]	Acid Strength [M]	Hydrogen G-value [molec/100eV]	Total mass Plutonium [grams]	Hydrogen Generation [mol/hr]	Oxygen Generation [mol/hr]	Line Diam. [cm]	Flux of H2 in Line [mol/m^2hr]	Flux of O2 in Line [mol/m^2hr]	Line Length [meters]	Tank H2 Conc. [vol %]
D49B	0.6	1483	2226	1.3	0.176	889.8	0.0001301	6.504E-05		0.3791897	0.1895948	10	29.3%
D49C	0.83	1214	2395	1	0.188	1007.62	0.0001572	7.859E-05		0.4894777	0.2290739	10	33.5%
D554	0.6	755	1106	0.31	0.217	453	8.148E-05	4.074E-05	2.09	0.2374915	0.1187457	10	20.3%
D134C	0.4	1400	2235	1	0.188	560	8.735E-05	4.368E-05	2.09	0.2546225	0.1273112	10	21.5%
D452	5	495	520	7	0.034	2475	6.982E-05	3.491E-05	2.09	0.2035292	0.1017646	10	17.8%
D472	95	25	176	7.5	0.029	2375	5.706E-05	2.853E-05	2.09	0.16632	0.08316	10	14.9%
D550	130	222	252	10	0.022	28860	0.0005195	0.0002597	2.09	1.514211	0.7571055	10	60.1%
D931	96	260	334	7	0.034	24960	0.0007042	0.0003521	2.09	2.0525607	1.0262804	10	63.8%
D933	95	116	222	7	0.034	11020	0.0003109	0.0001554	2.09	0.9062187	0.4531094	10	50.0%
D971	40	74	525	8	0.025	2960	6.166E-05	3.080E-05	2.09	0.1797381	0.0898691	10	16.0%
D972	40	63	545	8	0.025	2520	5.25E-05	2.625E-05	2.09	0.1530203	0.0765102	10	13.9%
D974	95	27	230	7	0.034	2565	7.236E-05	3.618E-05	2.09	0.2109302	0.1054651	10	18.4%
D1007	90	36	190	8	0.025	3240	6.75E-05	3.37E-05	2.09	0.1967404	0.0983702	10	17.3%
D1810	140	146	262	3.5	0.103	20440	0.0017446	0.0008723	2.09	5.0835077	2.5425638	10	66.9%

Table 5:	Worst case hydrogen gas build-up times (Using Rocky Flats fit to Kazanjian's data)				
Tank #	Time to 1 vol % [days]		Time to 4 vol % [days]		Time to Equilib. [years]
D49B	106.31		425.23		8.53
D49C	139.85		559.42		12.84
D55A	80.18		320.74		4.45
D134C	177.92		711.67		10.46
D452	6.66		26.66		0.32
D472	49.26		197.03		2.02
D550	1.07		4.30		0.18
D931	1.96		7.82		0.34
D933	6.35		25.38		0.87
D971	136.13		544.54		5.96
D972	170.89		683.58		6.50
D974	52.21		208.86		2.62
D1007	42.47		169.87		2.01
D1810	1.24		4.95		0.23

Appendix B
Explosion Analysis

1. Thermodynamics of Detonation or Deflagration

For gaseous explosions in confined spaces, a simple approximation can be made for the deflagration pressure. This involves determining the final pressure from a constant volume, adiabatic burn of the gas mixture.[11b] The equation for hydrogen combustion in pure oxygen is the following:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (eqn.14)$$
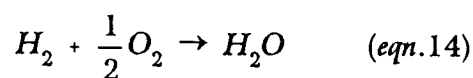
$$\Delta H_{rxn} = 57.8 \ kcal/mol \ H_2 \qquad (reference\,[14])$$

For complete combustion, the final temperature, or flame temperature will depend on the constant volume heat capacity of the products, in this case water. Appendix II of The Science of High Explosives lists average constant volume heat capacities for combustion products over temperature ranges from an initial 300K to the applicable final temperature. An iterative process was used to obtain the correct average heat capacity applicable to the calculated temperature rise. Over the temperature range from 300K to 5900K, the average constant volume heat capacity of products is:[13b]

$$\overline{C}_v = 10.26 \ cal/mol \ H_2/K$$

The temperature change can then be calculated:

$$\Delta T = \frac{\Delta H_{rxn}}{\overline{C}_v} = \frac{57,800 \ cal/mol\,H_2}{10.26 \ cal/mol\,H_2/K} = 5634 \ K \qquad (eqn.15)$$

The assumed initial temperature is 273 K, thus the calculated flame temperature equals 5634°C (5907K). This calculated flame temperature does not account for dissociation of products which is observed as calculated flame temperatures exceed 2100°C. The actual flame temperature can be estimated from a curve relating flame temperatures without dissociation to flame

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temperatures with dissociation. From this curve, the predicted actual flame temperature with dissociation for constant volume, adiabatic combustion of a stoichiometric hydrogen-oxygen mixture is 2797°C (3070K).[11]

Some of the energy released goes into the endothermic dissociation of water into O_2, H_2, and OH. For simplicity, we will neglect OH and assume dissociation as the reverse combustion reaction. This implies that the resultant product is an incomplete combustion, and the reaction can be written:

$$(x+1)H_2 + \left(\frac{1}{2}x+\frac{1}{2}\right)O_2 \rightarrow H_2O + (x)H_2 + \left(\frac{1}{2}x\right)O_2 \qquad (eqn.16)$$
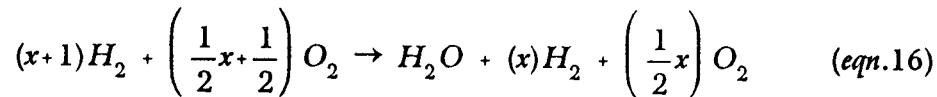
$$\Delta H_{rxn} = 57.8 \ kcal/mol \ H_2O \ produced$$

The unknown, x, in the stoichiometry can be determined by relating the known flame temperature to the ratio of the heat of reaction and the average constant volume heat capacity of the products. For the temperature range of 300K to 3100K the average constant volume heat capacities for each of the products are as follows:[13b]

$C_{v,H2O}$ = 9.111 cal/mol H_2O/K
$C_{v,H2}$ = 5.879 cal/mol H_2O/K
$C_{v,O2}$ = 6.724 cal/mol H_2O/K

The average for the products is then:

$$\overline{C_v} = 9.111 + 5.879x + \frac{6.724}{2}x = 9.111 + 9.241x \ [cal/mol\,H_2O/K] \qquad (eqn.17)$$

Relating $\Delta T = \Delta H_{rxn} / C_v$ gives:

$$2797K = \frac{57,800\,cal/mol\,H_2O}{(9.111+9.241x)\,cal/mol\,H_2O/K} \qquad (eqn.18)$$

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Equation 18 can be solved to give x = 1.25. Plugging this into the chemical equation above, the stoichiometry predicts 3.375 moles of reactants and 2.875 moles of products. The final explosion pressure can be determined by the following equation:[11b],[13]

$$P_f = \left(\frac{T_f}{T_o}\right)\left(\frac{n_f}{n_o}\right) P_o \qquad (eqn.19)$$

This gives:

$$P_f = \left(\frac{3070\ K}{273\ K}\right)\left(\frac{2.875}{3.375}\right) P_o = 9.58\ P_o \qquad (eqn.20)$$

which corresponds to the thumb rule of $P_f/P_o = 10$ for contained gaseous deflagrations. For pressure vessel design, dead-ended surfaces should be able to withstand twice this pressure to account for reflected pressure of a deflagration.[11] With initial pressure equal to atmospheric, the tank walls must be able to withstand 19.16 atm of reflected pressure or 282 psia.

The detonation pressure of a gas is generally assumed to be twice the deflagration pressure, or in this case, 19.16 atm.[11],[11b] Shock waves generated by detonation of hydrogen in air give rise to reflected pressures related to the incident pressure, normal to the surface as:[11],[13a]

$$P_r = 2P_i \frac{(7P_o + 4P_i)}{(7P_o + P_i)} \qquad (eqn.21)$$

Substituting for atmospheric and incident pressures gives:

$$P_r = 2*19.16 \frac{(7*1 + 4*19.16)}{(7*1 + 19.16)} = 122.5\ atm \qquad (eqn.22)$$

If a detonation occurs, the tank and/or lines and fittings must be able to withstand 122.5atm (1800psia) of peak reflected pressure.

Bulletin 627 of the Bureau of Mines charts experimental incident detonation pressure for hydrogen-oxygen mixtures. The pressure varies along a smooth curve between 15 and 19 atm for a range of hydrogen concentrations between 25 and 80 volume %, with a maximum at 67%

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hydrogen.[15] This data agrees with the above calculations, and predicts that the damage potential of a hydrogen detonation depends little on the actual concentration of hydrogen as long as it is within the detonable range. There is no data to refute the conclusion that vapor spaces in actinide solution tanks at Rocky Flats are currently at detonable concentrations. Furthermore, based on predicted hydrogen generation rates, it may take only a few days to several months to build up to a detonable hydrogen mixture in solution tanks.

2. Explosion Containment / Tank Structure

The failure pressure of a cylindrical tank can be estimated by the following equation:[11]

$$P_{fail} = \frac{2*s*t_w}{d} \qquad (eqn.23)$$

Where: P_{fail} = Failure overpressure (gauge)
   s = Ultimate tensile strength
   t_w = Wall thickness
   d = Internal diameter

Los Alamos Technology Office (LATO), conducted a safety study on plutonium and uranium solutions and reported that most storage tanks are type 304L stainless steel.[2] Perry's Handbook reports an ultimate tensile strength of 79,000 psi for this material.[14] Tank 1810 is an annular tank has a 1/4 inch thick wall, and a 42 inch diameter.[2] The dimensions of other tanks were not obtained for this analysis, but LATO chose 1810 as a representative tank, and observations from facility tours suggest that the other tanks have similar dimensions. The failure overpressure for tank 1810 is 64 atm (940psig), which corresponds to an absolute failure pressure of 65 atm. Based on peak pressures estimated above, this tank would likely fail in event of a hydrogen detonation, but not for a deflagration.

3. Explosion Venting

Deflagrations can be successfully vented if a large enough vent area is available.[11] For hydrogen deflagrations in Rocky Flats actinide solution storage tanks, venting may be complicated by the fact that the vent line itself is likely filled with an explosive mixture. Furthermore, based on facility tours it was observed that vent lines have several 90 degree elbows before they reach the discharge point at their respective glove boxes. Such severe angles and long line distances greatly reduce the venting capability in event of a hydrogen deflagration. Formal guidance exists in estimating vent sizes, but due to the reasons stated above, successful venting is not likely. Damage can be expected for sight glasses/level gauges, gaskets, and fittings even if the tank itself can handle the deflagration pressure.[11],[13]

In general, detonations can not be successfully vented due to extremely fast reaction rates. With moderate ignition sources, hydrogen explosions in horizontal pipes generally accelerate to detonations in a lengths proportional to the square root of the pipe diameter. In the long vent lines on Rocky Flats tanks, acceleration to detonation is possible. Furthermore, Bureau of Mines Bulletin 627 states that depending on the strength of the ignition source, hydrogen detonations can occur with essentially zero acceleration distance.[15] For these reasons, a hydrogen detonation in an actinide solution tank can not be ruled out. Since such an event can not be successfully vented, a vent size analysis is not included in this review.