

MATHEMATICAL ANALYSIS OF HYDROGEN MIXING IN THE VAPOR SPACE OF A HIGH-LEVEL NUCLEAR WASTE TANK

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ABSTRACT

This paper presents mathematical analyses of the possible accumulation of radiolytically produced hydrogen in the vapor space in a tank storing liquid high-level radioactive waste. Under normal operating conditions, these tanks are continuously ventilated with air to ensure that the concentration of hydrogen never reaches its lower flammability limit (4%). Three scenarios are considered in which it is postulated that hydrogen may accumulate and present a flammability hazard. These scenarios are stratification due to gravity, slow mixing when the ventilation system is operating, and slow mixing when the ventilation system is not operating. In all three cases, the analyses indicate that the accumulation of hydrogen is not likely and thus does not present a flammability problem so long as controls are in place to dilute its concentration to less than 4%.

INTRODUCTION

The flammable gas hydrogen is continuously produced by the radiolysis of water in radioactive high-level waste tanks. This hydrogen diffuses from the waste to the vapor space in the tanks. At the Savannah River Site (SRS), the concentration of hydrogen is continuously monitored in vapor space of each of the tanks and measures taken to dilute it with air by ventilation techniques. In this way, it is ensured that the hydrogen never reaches its lower flammability limit (4% in air) and thus never presents a safety hazard. At SRS, the action limit for the monitors is set at 0.4% hydrogen. Three scenarios have been suggested in which it may be possible for hydrogen to accumulate in specific volumes in the vapor space where its concentration may approach the flammability limit. This paper presents mathematical analyses of these three scenarios. The scenarios are the possible accumulation of hydrogen due to

- stratification resulting from gravity
- slow mixing immediately above the waste slurry during normal ventilation conditions
- slow mixing immediately above the waste slurry during periods when the ventilation system is not operating.

In all three cases the mathematical analyses indicates that the diffusion and mixing of the hydrogen are sufficient so that its lower flammability limit is never reached in the vapor space of a high level waste tank.

STRATIFICATION OF HYDROGEN DUE TO GRAVITY

It has been suggested that, because hydrogen gas is less dense than air, hydrogen will tend to accumulate near the top of the vapor space of high-level waste tanks in which it is formed. This view is contrary to the laws of physics as shown below.

Hydrogen that is generated in the high-level waste and escapes from the surface must diffuse through the layer of air in the vapor space before it reaches the top of the tank. By that time, it will be thoroughly mixed with the air. If hydrogen is to be stratified in the top of the tank, it must be separated from air by the influence of gravity.

In this analysis, hydrogen and air are assumed to behave as ideal gases; thus, the effect of gravity on each of them will be independent of its effect on the other. The variation of pressure with height for any fluid is given by (1):

$$\frac{dP}{dh} = \rho g \quad (\text{Eq. 1})$$

where

- p = pressure (dynes/cm²)
- h = height (cm)
- ρ = density (grams/cm³)
- g = acceleration of gravity (980 cm/sec²)

From the ideal gas law:

$$p = \frac{\rho RT}{M} \quad (\text{Eq. 2})$$

where

- R = gas constant (8.31E+07 ergs/°K mol)
- T = temperature (°K)
- M = molecular weight (grams/mol)

Combining Eqs. (1) and (2)

$$\frac{dp}{dh} = \frac{M g \rho}{R T} \quad (\text{Eq. 3})$$

Solution of Eq. (3) yields:

$$\rho = \rho_0 \text{Exp} \left(- \frac{M g h}{R T} \right) \quad (\text{Eq. 4})$$

where

$$\rho_0 = \text{density at } h = 0.$$

Equations similar to (4) can be written for both hydrogen and air. If the ratio of these equations is taken one obtains:

$$\frac{\rho_H}{\rho_A} = \frac{\rho_{H0}}{\rho_{A0}} \text{Exp} \left(- \frac{(M_H - M_A) g h}{R T} \right) \quad (\text{Eq. 5})$$

where ρ_H/ρ_A is the ratios of the densities of the gases at height h while ρ_{H0}/ρ_{A0} is the corresponding ratio at zero height. $M_H = 2$ and $M_A = 29$ are the molecular weights of hydrogen and air respectively.

Consider the case where $h = 1000 \text{ cm}$ ($\sim 33 \text{ ft}$) and $T = 308^\circ\text{K}$ (35°C) then $\rho_H/\rho_A = 1.001 \rho_{H0}/\rho_{A0}$

For a 1000 cm tall tank, the difference between the hydrogen concentration at the top and the bottom of a tank is quite small. On this basis, stratification due to gravity is not significant. In fact the difference would be even smaller because of convective mixing. Convective mixing is the dominant process for atmospheric mixing. The composition of the atmosphere is quite constant up to an altitude of about 100 kilometers while Eq. (5) would predict substantial changes in composition at that altitude. Above 100 kilometers, the average molecular weight of the atmosphere does decrease markedly due to gravitational effects.

ACCUMULATION OF HYDROGEN DUE TO SLOW MIXING DURING NORMAL VENTILATION CONDITIONS

Mathematical Approach

A second way in which hydrogen might be stratified in a waste tank is the following. Hydrogen is generated in the liquid waste and enters the vapor space of the tank at the waste interface. If it is not transported rapidly enough to the top of the tank, hydrogen would tend to accumulate near the interface. Here it might exceed the lower flammability limit while the concentration at the top (where hydrogen is monitored) was still far below it.

Molecular diffusion is, by far, the slowest of the transport processes. If it can be shown that diffusion alone is sufficient to keep the hydrogen concentration well below the flammability limit at the interface, there should be no reason for concern. Under normal operating conditions hydrogen leaves the interface, is transported to the top of the tank where it encounters an air stream that carries it out of the tank. Because hydrogen will ultimately be removed as fast as it is formed, this can be considered as a steady state diffusion process. In such cases the concentration gradient is constant and the problem can be formulated as follows:

$$F = -D \frac{\Delta C}{\Delta x} \quad (\text{Eq. 6})$$

where:

F = flux of hydrogen at the interface (mmols/sec cm^2)

D = diffusion coefficient (cm^2/sec)

Δx = distance from interface to top of tank (cm)

ΔC = concentration difference between top of tank and interface (mmols/cm^3)

Then, $\Delta C = C_1 - C_s$

where:

C_1 = concentration of hydrogen at the top

C_s = concentration of hydrogen at the surface of waste

C_s can be calculated from Eq. (7) because all of the other quantities are known.

$$C_s = C_1 + F \frac{\Delta x}{D} \quad (\text{Eq. 7})$$

Calculation of Hydrogen Flux at the Waste-Air Interface

The maximum hydrogen generation rate in a tank at SRS is estimated to be $3.8 \text{ ft}^3/\text{hr}$. This estimate is based on the tank

with the highest fission product inventory at SRS (Tank 35 which has a radioactive heat generation rate of $6.3\text{E}05 \text{ BTU/hr}$) (2) and the hydrogen generation rate of $6 \text{ ft}^3/\text{hour}$ for every 10^6 BTU . (3) The generation rate of $3.8 \text{ ft}^3/\text{hr}$ corresponds to 108 L/hr or 4.82 mols/hr or 1.34 mmols/sec . The surface area of waste in the tank is 523 m^2 or $5.23\text{E}+06 \text{ cm}^2$; therefore, $F = 1.34/5.23\text{E}+06 = 2.56\text{E}-07 \text{ mmols/sec/cm}^2$.

Concentration of Hydrogen in the Air at the Top of the Tank

At SRS, ventilation is set so that the rate of air entering and leaving the tank is $150 \text{ ft}^3/\text{min}$ or 71 L/sec . or $71,000 \text{ cm}^3/\text{sec}$. The rate of hydrogen generation is 1.34 mmols/sec ; therefore,

$$C_t = 1.34/71000 = 1.89\text{E}-05 \text{ mmols/cm}^3 \text{ (or mols/L)}$$

Diffusion Coefficient of Hydrogen in Air

The diffusion coefficient of hydrogen in air is reported to be (4) $D = 0.611 \text{ cm}^2/\text{sec}$ at 0°C . The value at the tank temperature should be somewhat higher. To be conservative, a value of 0.6 in will be used in subsequent calculations.

Diffusion Distance

The distance between the waste and the top of the tank was assumed to be 75 in or 190 cm.

Calculation of the Hydrogen Concentration at the Waste-Air Interface

From these data we calculate

$$C_s = 1.89\text{E}-05 + \frac{2.56\text{E}-07 \times 190}{0.6} = 1.00\text{E}-04 \text{ mmol/cm}^3$$

This concentration can be represented as, f_v , a volume fraction of the space:

$$f_v = RTC_s = 0.082 \times 298 \times 1.00\text{E}-04 = 2.44\text{E}-03$$

or in volume percent, 0.244%.

Based on this analysis assuming only molecular diffusion to be occurring, the volume percent of hydrogen at the interface is less than one tenth of the lower flammability limit (4%). Again, convective mixing and mixing caused by the ventilation would make this concentration lower.

ACCUMULATION OF HYDROGEN DUE TO SLOW MIXING WHEN THE VENTILATION SYSTEM IS NOT OPERATING

Another problem that has been posed is: If ventilation were lost in a waste tank, how long would it take for the hydrogen concentration to reach the lower flammability limit? And, since the hydrogen monitors are located near the top of the tanks, would it be possible to approach the flammability limit near the bottom before an unsafe condition was detected at the top?

Again a one dimensional diffusion model will be assumed. As before, the assurance that the results will be conservative in that convective mixing is not considered. The following equation must be solved:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (\text{Eq. 8})$$

with the boundary conditions such that the flux at one surface is constant and that at the opposite surface is zero. This problem has been solved by Crank (5) who gave the following solution:

$$C - C_0 = \frac{FL}{D} \left\{ \tau + \frac{3x^2 - L^2}{6L^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \text{Exp}(-\pi^2 n^2 \tau) \text{Cos}\left(\frac{n\pi x}{L}\right) \right\} \quad (\text{Eq. 9})$$

where

$$\tau = \frac{Dt}{L^2}$$

and C = concentration at any t and x

C_0 = initial concentration

F = flux at surface L

L = the distance of one surface from the origin

x = any distance between 0 and L

t = time

D = diffusion coefficient.

There are two values of x of interest in a waste tank. When $x = L$ in this equation, this corresponds to the waste-air interface in the tank. When $x = 0$, this corresponds to the top of the tank where initially the hydrogen concentration is zero. It is assumed that this is where the air is sampled for hydrogen. Tables I and II show the calculated hydrogen concentrations at various times at these locations for two tank heights assuming that the tank initially contained no hydrogen and that only molecular diffusion causes the hydrogen and air to mix. Table I contains calculations for a freeboard of 190 cm (~ 6 ft) and Table II contains similar calculations for a freeboard of 380 cm (~ 12 ft). In both cases a flux of $2.56E-07$ mols/sec cm^2 was

TABLE I

Hydrogen Concentrations at the Waste-Air Interface and at 190cm (~ 6 ft.) Above the Waste when the Tank Ventilation System is not Operating. Only Molecular Diffusion is Assumed to Contribute to the Mixing Process^a

Time, Time, Hours	Volume % at Waste Surface	Volume % at 190 cm.
20	0.30	0.20
40	0.54	0.44
60	0.78	0.68
100	1.25	1.15
150	1.85	1.75
200	2.44	2.34
250	3.03	2.93
300	3.62	3.52
350	4.22	4.12
400	4.81	4.71

^aHydrogen flux from the waste surface was $2.5E-07$ mols/sec cm^2 .

TABLE II

Hydrogen Concentrations at the Waste-Air Surface and at 380cm (~ 12 ft) Above the Waste When the Tank Ventilation is not Working. Only Molecular Diffusion is Assumed to Contribute to the Mixing Process^a

Time, Volume % at Hours	Volume % at Waste Surface	Volume % at 380 cm.
20	0.25	0.06
40	0.37	0.17
60	0.49	0.29
100	0.73	0.53
200	1.32	1.12
300	1.91	1.71
400	2.50	2.31
500	3.10	2.90
600	3.69	3.49
700	4.28	4.08
800	4.88	4.68

^aHydrogen flux from the waste surface was $2.5E-07$ mols/sec cm^2 .

assumed. The data are presented graphically in Figs. 1 and 2, respectively.

Table I and Fig. 1 show that 340 hours (~ 14 days) are required for the lower flammability limit (LEL) of hydrogen (4.0%) to be achieved. Figure 1 clearly shows that the hydrogen concentration at 190 cm is only slightly higher than the concentration at the waste-air interface. When the concentration at the top has risen to 0.4% H_2 (the action limit for the tank farm), the concentration at the interface is about 0.5% H_2 , which is far below the flammability limit. Doubling the freeboard (see Table II and Fig. 2) doubles the time to reach the LEL and slightly increases difference between the concentrations at the top and at the interface. Again, when 0.4% is reached at the top, the concentration at the interface is still far below the LEL for hydrogen.

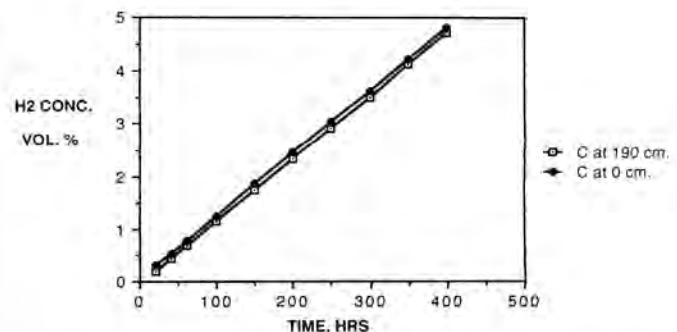


Fig. 1. Calculated hydrogen concentrations at the waste surface and at 190 cm when the ventilation system is not operating and the tank freeboard is 190 cm. Only molecular diffusion is assumed to cause the mixing process.

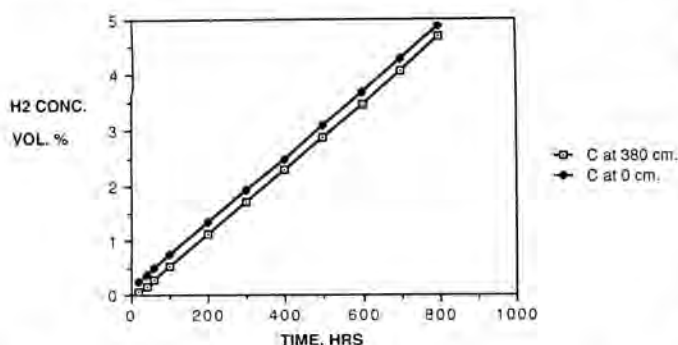


Fig. 2. Calculated Hydrogen Concentrations at the Waste Surface and at 380 cm when the Ventilation System is not Operating and the Tank Freeboard is 380 cm. Only molecular diffusion is assumed to cause the mixing process.

CONCLUSIONS

The mathematical analyses presented in this paper indicate that during normal ventilation conditions it is impossible for radiolytically produced hydrogen to accumulate in the vapor space of a waste tank and present a flammability hazard. During periods when the ventilation system is not operating,

the times necessary for hydrogen accumulation can be calculated. For SRS tanks, these times are nominally several days. The analysis also shows that, during these times, the hydrogen concentration at the top of the vapor space is essentially the same as that at the waste-air interface; thus, detectors at the top are analyzing hydrogen concentrations representative of those at the waste-air interface.

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