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HANFORD GROUT TECHNOLOGY PROGRAM

GAS GENERATION AND RELEASE FROM DOUBLE-SHELL SLURRY FEED (DSSF) GROUT VAULTS

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SUMMARY

The low-level fraction of liquid, radioactive wastes stored in double-shell tanks on the Hanford Site will be disposed of as a grouted waste in large, subsurface concrete vaults. This report describes the potential for generation and release of gas from vaults containing double-shell slurry feed (DSSF) grout.

The majority of the radiolytically produced gas in DSSF grout is expected to be hydrogen. Because of the quantity of hydrogen that may be produced, the grout vault design must provide a means for venting. It is recommended that a passive approach to hydrogen venting be pursued to show that the hydrogen can diffuse through the diffusion barrier without the presence of a vent. Tests to measure the diffusivity of hydrogen in the solid barrier would be required to support such an approach.

If a passive vent is not feasible, it is recommended that a vent with a design life of 250 years and a minimum 0.1-in.-diameter clear opening be installed through the solid diffusion barrier of the grout vault to prevent pressurization. The gas will flow through this small vent with only small backpressures. The penetration of the diffusion barrier should have a total cross-sectional area of less than 1.2 in.^{2} to limit long-term water vapor diffusion and to minimize the impact on the performance assessment.

Based on currently available information, there is confidence that after 250 years the rate of gas generation will be slow enough so that if the vent closes, the hydrogen can be released by diffusion through the solid asphalt/diffusion barrier that surrounds the grout vault.

A potential exists for the formation of explosive mixtures of hydrogen in the porosity of the soil near the vent and in the porosity of the gravel in the catch basin of the vault. It is recommended that ignition sources be excluded from the catch basin of the vault and from the soil. Tests are recommended to determine whether the hydrogen can burn in the porosity of the gravel, and to further define the quantity and type of gas generated in the grout.

An analysis of radon generation was performed. Using conservative assumptions, the maximum annual effective dose equivalent to someone living downwind at the edge of the grout site would be 8.1E-3 mrem/yr.

An analysis of tritium release in the form of hydrogen was performed. Using conservative assumptions, the annual effective dose equivalent to a person living downwind at the edge of the grout site would be 1.8E-2 mrem/yr[a].

No need for vents in the closure cover of the vault has been identified. The quantity of gas generated is fairly small, and the gas should dissipate after escaping from the diffusion barrier. Pressurization is not a concern since the closure cover is not a sealed system.

(a) In DOE Order 5480.1A, derived concentration guidelines are provided based on a 100 mrem/yr dose under a specified exposure scenario. Although the specific exposure assumptions were not used in the dose calculation, the estimated dose is well below 100 mrem/yr.

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INTRODUCTION

The low-level fraction of liquid radioactive wastes stored in double-shell tanks on the Hanford Site will be disposed of in grout. The liquid waste will be mixed with dry cementitious solids and pumped into engineered concrete vaults where the mixture will solidify, thereby reducing the mobility of the waste. The concrete vault and leachate collection basin below the vault will be completely encased in a solid asphalt/aggregate barrier or cocoon designed to prevent ionic diffusion of contaminants to the soil and to prevent vapor diffusion of water from the soil to the waste. Additional barriers will be placed over the top of the system to reduce advection of water in the soil surrounding the vault.

The grout considered in this report is produced by mixing double-shell slurry feed (DSSF) with a dry blend of materials consisting of 28% blast furnace slag, 28% class F fly ash, 4% type I,II Portland cement, and 40% calcium carbonate. The waste has a high pH and contains a high nitrate (NO_3^-) concentration. The majority of the radioactivity in the waste results from ^{137}Cs decay. Radiolysis of grout components will produce gases, potentially causing pressurization or other problems. The primary gas produced is expected to be hydrogen. Because tritium (^3H) exists in the waste, venting of hydrogen gas provides a potential pathway for the release of radioactive ^3H from the vault to the surface. In addition, the radioactive gas radon is produced through the decay chain of uranium. Radon provides another potential pathway through which radiation could reach the surface. These potential problems are evaluated and discussed in this report.

The report begins with a description of the analysis completed in order to estimate the gas generation rate in the grout. The impacts of hydrogen generation and radon and tritium release are then discussed. Next, the need for vents in the closure cover is evaluated. Conclusions from the analysis are then presented. Finally, tests which would provide useful information for the design of the disposal system are recommended.

ANALYSIS OF GAS GENERATION

SELECTION OF A RADIOLYTIC GAS YIELD

A key factor in a gas generation analysis is the gas generation rate. Previous work on the radiolytic generation of gas was examined to select a reasonable gas generation rate for the work reported here. Normally, the yield of a gas (or other product) from radiation is expressed as a "G" value, which is the number of molecules of gas produced per 100 electron-volts of energy absorbed. In order to make the results easier to interpret in terms of the grout vault, an equivalent term was used with the units (moles of gas produced)/[(grams of material)(dose in rad received)].

A review of the literature identified several previous experiments in which the radiolytic production of gas was examined. Matherson and Ritter (1971) irradiated water using ^{60}Co to determine the gas generation rate. The rate of hydrogen generation in pure water was approximately 4.51E-13 mol/(g H_2O rad). When nitrate solutions >1.3 molar were irradiated, the hydrogen generation rate decreased to 1.385E-14 mol/(g soln rad).

Work by Gray and Simonson (1985) indicates a value of 7.14E-13 mol/(g H_2O rad) for gamma radiation of water. Gray and Simonson also measured the rate of gas generation from alpha irradiation of water and found it to be 2.32E-12 mol/(g H_2O rad). In pure water, oxygen is produced in a stoichiometric ratio along with the hydrogen. As the mixture becomes more complex, the reactions become more complex.

Hyder (1965) measured the rate of oxygen generation in water with nitrate concentrations of 1E-3 molar to 4 molar and pH between 7 and 13. Elevated pH tended to increase the conversion of nitrate to nitrite, resulting in the release of oxygen. A tracer study using ^{18}O determined that up to 39% of the oxygen released from the solution is from nitrate at 4 molar concentration. Lower concentrations result in a lower fraction of the oxygen being generated from nitrate. The total oxygen generation rate was up to 3.9E-12 mol/(g soln rad). Hydrogen generation was not discussed.

Three articles were located in which the generation of gases in mortars was reported. Lewis and Warren (1989) studied the rate of gas generation

from mortars consisting of Portland cement, class F fly ash, and ground blast furnace slag. Red clay and glass beads were added to some mortars. The study examined the effect of dry constituents, KCl content, temperature of irradiation, and additives CaS and FeS. It was also found that, in any mix containing blast furnace slag, oxygen was not produced. In addition, oxygen that was initially in the air above the grout was consumed. Oxygen was produced when slag was not present, but was eliminated when CaS or FeS was added to the mix. It was found that an elevated temperature (120°C) decreased the rate of gas generation. It was found that Cl^- can increase the hydrogen generation rate, but, at an elevated temperature, the rate is reduced by up to a factor of 7. The greatest reported hydrogen generation rate was 3.65E-13 mol/(g mortar rad).

A second article by Bibler (1978) examined numerous mortar compositions. The compositions most applicable to the grout vault consisted of Fe_2O_3, NO_3, NO_2, water, and cement. These mortars were exposed to 8.9E4 rad/h of gamma radiation at 41°C. It was found that oxygen was consumed and not produced. Hydrogen was produced at a rate of 1.45E-13 mol/(g mortar rad). A small amount of N_2O was also produced. The rate of N_2O production was dependent on the nitrite concentration in the mortar. Additional tests using alpha radiation found that over a long time period, both oxygen and hydrogen were produced in a ratio of 0.5:1. Equilibrium pressures at a dose rate of 2.8E7 rad/h for mortar containing Fe_2O_3 and MnO_2 were measured at 120 and 66 psi, respectively.

In a report by Friedman et al. (1985), the grout studied was produced from a dry blend consisting of 38.5% type I-II Portland cement, 38.5% Class "F" fly ash, 7.7% Indian red pottery clay (IRPC) and 15.3% attapulgite. This formulation is very similar to the formulation used for phosphate/sulphate waste (PSW) grout. The waste used for the grout was a simulant for double-shell slurry (DSS) consisting of 1.1 M $NaAlO_2$, 2.6 M NaOH, 2.0 M $NaNO_3$, 1.6 M $NaNO_2$, 4.8 g/L of TOC and several minor components in concentrations <0.1 M. The grout, consisting of 42 wt% dry blend and 58 wt% DSS simulant, was exposed to 8E5 rad/h of gamma radiation for periods up to 11 days. The gas generated from one test consisted of 24% hydrogen, 63% N_2O, and 13% N_2. The total gas yield was 3.0E-14 mol/(g rad). Tests using alpha radiation produced primarily

hydrogen, with smaller amounts of N_2O. Oxygen and nitrogen were either consumed or produced, depending on the length of the test.

The gas generation rates obtained from the literature for various conditions are summarized in Table 1. A conservative estimate for the rate of hydrogen generation while gamma radiation dominates the dose was selected as 3.7E-13 mol/g rad. For this analysis it was assumed that oxygen will not be produced in the grout since the dry blend contains 28% blast furnace slag. The N_2O production was ignored. The production of N_2O is influenced by the presence of nitrate and nitrite in the waste, as well as by the dry blend composition. It is possible that N_2O will be produced. However, with the exception of the rates reported by Friedman, the rate of N_2O generation was much less than the rate of hydrogen generation. If the results from the Friedman report are representative of the gas produced, then the total gas generated will be somewhat less than the selected generation rate. In the work by Bibler (1978), it was found that the rate of hydrogen generation decreased with the addition of nitrates. There is a reasonable chance that the actual generation rate may be lower than the value assumed. Since the value selected is more than 50% greater than the number from Bibler for alpha irradiation of mortar, and exceeds the value for alpha radiation as given by Friedman et al. (1985), the gamma radiation gas yield will be used for alpha, beta, and gamma radiation.

DETERMINATION OF DOSE RATE

The radionuclide inventory for the DSSF grout was entered into a spread sheet calculation to determine the total dose from all radionuclides over time. An example of the spread sheet is shown in Table 2. The inventory was chosen as the upper-bound inventories developed for use in the performance assessment of grouted double-shell tank waste (Hendrickson 1990).
Table 2 indicates the radionuclide content and dose rate after 30 years of decay. The initial dose rate is 310 rad/h. The calculated dose rate as a function of time is shown in Figure 1. The data from this plot were generated from the spread sheet by entering different decay times and calculating the dose rate.

TABLE 1. Yields of Radiolytic Gas from Various Compositions as Reported in the Literature

mol/g rad	Summary of Conditions
4.51E-13	^{60}Co source irradiating water (Matherson and Ritter 1971)
1.39E-14	^{60}Co source irradiating 1.3 M nitrate solution (Matherson and Ritter 1971)
7.14E-13	Gamma irradiation of water (Gray and Simonson 1985)
2.32E-12	Alpha irradiation of water (Gray and Simonson 1985)
1.45E-13	Cement/Fe_2O_3 highest rate reported, mix contains no nitrate (Bibler 1978)
2.90E-14	Cement/Fe_2O_3, nitrate, nitrite - highest rate reported, mix contains ≈2 wt% NO_3, NO_2 (Bibler 1978)
1.33E-13	Cement/Fe-Mn waste, no nitrate, ^{244}Cm alpha source (Bibler 1978)
3.65E-13	Slag/fly ash/cement mix - highest rate reported (6% KCl) (Lewis and Warren 1989)
2.49E-13	DSS simulant-fly ash/cement/IRPC/attapulgite: alpha radiation, primarily hydrogen with N_2O (Friedman et al. 1985)
3.00E-14	DSS simulant-fly ash/cement/IRPC/attapulgite: gamma radiation, primarily N_2O with hydrogen. O_2 partially consumed (Friedman et al. 1985)

GAS GENERATION RATE

In the previous two sections a gas generation yield has been selected (3.7E-13 mol/(g rad)) and the dose rate has been determined over time. Initially the dose rate is 310 rad/h, after which it decreases following the decay of ^{137}Cs. To calculate the gas generation from a single vault, the yield is multiplied by the dose rate and mass of grout as follows:

$$[3.7E\text{-}13 \text{ mol/(g rad)}][310 \text{ rad/h}][8.8E9 \text{ g grout}] = 1.01 \text{ mol/h}$$

TABLE 2. Spread Sheet Used for Calculation of Dose Rates Over Time

ISOTOPE	T 1/2 (HRS)	DECAY CONSTANT (HR-1)	INITIAL ACTIVITY (Ci/L)	FINAL ACTIVITY (Ci/L)	WATT PER CURIE	139.172 WATT PER LITER	5.32E+07 rad Integrated Dose, rad
3H	1.07E+05	6.48E-06	1.14E-05	0.00E+00	1.10E-04	0.00E+00	4.20E+01
14C	5.02E+07	1.38E-08	7.86E-07	7.83E-07	2.93E-04	2.29E-10	1.31E+01
60Co	4.62E+04	1.50E-05	2.00E-05	3.87E-07	1.54E-02	5.96E-09	4.36E+03
79Se	5.69E+08	1.22E-09	1.80E-05	1.80E-05	2.49E-04	4.47E-09	2.55E+02
90Sr	2.51E+05	2.77E-06	7.90E-03	3.82E-03	1.16E-03	4.43E-06	3.71E+05
90Y	6.41E+01	1.08E-02	7.90E-03	3.82E-03	5.53E-03	2.11E-05	1.77E+06
94Nb	1.75E+08	3.96E-09	2.50E-05	2.50E-05	1.02E-02	2.54E-07	5.10E+00
99Tc	1.87E+09	3.71E-10	6.40E-05	6.40E-05	5.01E-04	3.21E-08	1.83E+03
106Ru	8.84E+03	7.84E-05	1.20E-02	1.34E-11	5.95E-05	7.97E-16	1.97E+03
106Rh	8.31E-03	8.34E+01	1.20E-02	1.34E-11	9.55E-03	1.28E-13	3.17E+05
129I	1.38E+11	5.04E-12	2.20E-07	2.20E-07	4.68E-04	1.03E-10	5.87E+00
134Cs	1.81E+04	3.84E-05	3.40E-03	1.42E-07	1.02E-02	1.45E-09	1.96E+05
137Cs	2.64E+05	2.62E-06	2.60E-01	1.31E-01	1.01E-03	1.32E-04	1.08E+07
137m Ba	4.20E-02	1.65E+01	2.46E-01	1.23E-01	3.92E-03	4.84E-04	3.97E+07
238U	3.91E+13	1.77E-14	1.14E-08	1.14E-08	2.49E-02	2.84E-10	1.62E+01
239Pu	2.11E+08	3.28E-09	1.20E-06	1.20E-06	5.87E-02	7.04E-08	4.01E+03
241Am	3.79E+06	1.83E-07	1.40E-06	1.33E-06	3.28E-02	4.38E-08	2.56E+03
					Totals:	6.42E-04	5.32E+07 rad

139.172 rad/hr

year 30

Cm244 neglected (t1/2=18yr, 1.7e-7 Ci initial)
Pu 239/240 treated as 239
U234 combined with U238, (note long half lives)
U235 neglected
W/Ci for 94Nb, 79Se from Urbin Jenquin to agree with Origen Code

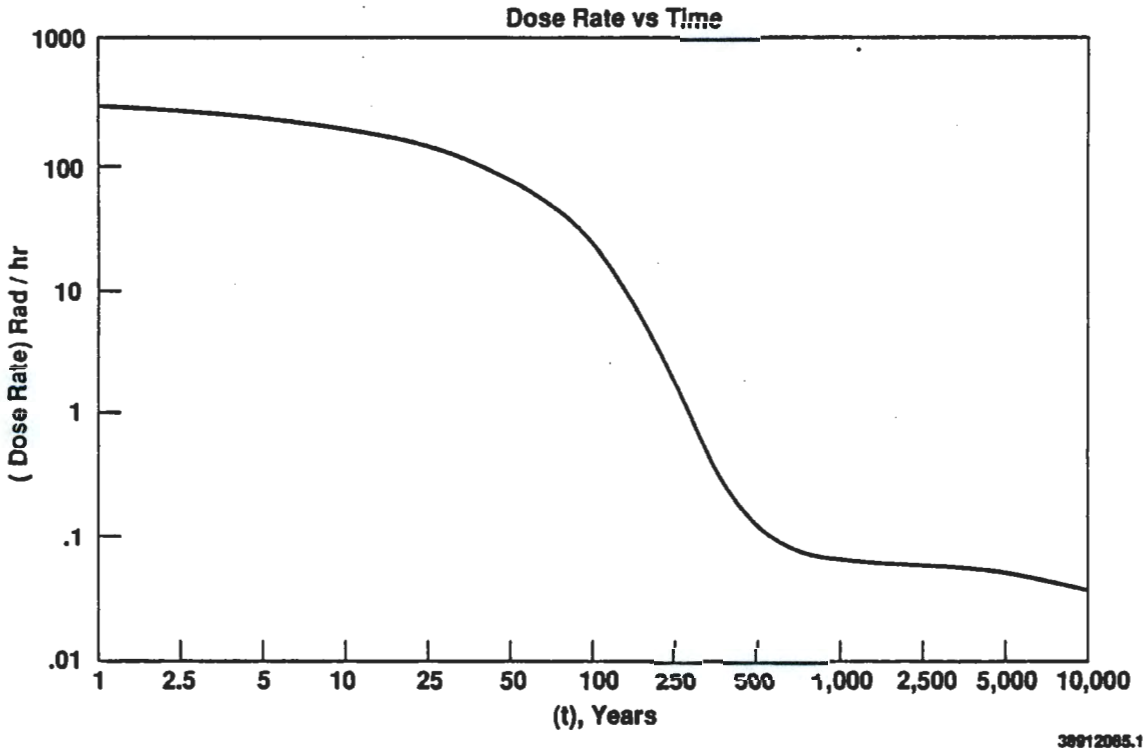

FIGURE 1. Dose Rate in Grout Over Time

EVALUATION OF HYDROGEN MIGRATION

ESCAPE OF HYDROGEN FROM THE GROUT AND CONCRETE VAULT

The escape of hydrogen from the grout mass itself has not been evaluated in detail. In the studies performed on concrete exposed to gamma radiation (Bibler 1978), it was found that an equilibrium hydrogen pressure is reached. The equilibrium pressure changes with mortar composition and is related to the dose rate, with higher dose rates producing higher equilibrium pressures. At dose rates of 0.1 Mrad/h, equilibrium pressures in two mortars were 20 and 40 psi, while at dose rates of 27 Mrad/h the pressures were 60 and 110 psi. In another mortar of a different composition, the gas generation was stopped at 36 psi at 0.89 Mrad/h, while at 14 Mrad/h the pressure was more than 200 psi. An alpha dose rate of 0.4 Mrad/h also produced pressures greater than 200 psi, indicating a different mechanism for gas generation from alpha radiation.

In the DSSF grout the initial dose rate will be only 3E-4 Mrad/h, which would likely result in a lower equilibrium pressure. It is possible that within the grout matrix, equilibrium pressures may be reached that will result in the production of less than the estimated quantity of hydrogen. However, the equilibrium pressure is difficult to predict due to the dependence on composition. In the event that equilibrium pressures are not reached, the entire quantity of hydrogen will diffuse through the grout and concrete and escape to the catch basin.

If the mobility of the hydrogen in the grout is too low, the pressures could potentially produce micro-cracks in the grout through which the hydrogen would easily vent. Such cracks would not have a detrimental effect on the performance of the system. Only if leaching under saturated conditions occurred would cracking have a detrimental effect. Such leaching is not expected to occur.

DIFFUSION OF HYDROGEN THROUGH THE DIFFUSION BARRIER

When the grout is poured, the gas generation rate for one vault is estimated to be approximately 1.01 mol/h. The diffusion barrier is not designed to contain gas pressures. It is likely that small imperfections introduced in the barrier during construction will allow some leakage of hydrogen under pressure. However, if it is assumed that the diffusion barrier is completely sealed and the vault becomes pressurized to 50 psi without damage, then the diffusivity of hydrogen that is required to prevent further pressurization can be calculated. This is only an order-of-magnitude estimate based on an overburden pressure on top of the catch basin of approximately 45 psi.

The transport of hydrogen through the solid barrier involves first a solubility of hydrogen in the asphalt phase and then diffusion through the asphalt. If the solubility is assumed to follow Henry's Law, then the effect of solubility can be lumped into a diffusion coefficient. Since the solubility of hydrogen in the barrier is not known, the diffusion coefficients will be calculated with the solubility effect included.

With a hydrogen pressure of 50 psi, the diffusivity must be >1E-5 cm^2/s in order to prevent further pressurization (see appendix for details). Unfortunately, data on hydrogen diffusion through asphalt are not available. For comparison, other data were obtained for other gases diffusing through asphalt. A diffusion-only value (not including solubility effects) for CO_2 was measured at 1E-5 cm^2/s (Mehrotra et al. 1987). Diffusivities of radon (including solubility effects at the interface) in different asphalts were measured at 4.4E-7 to 2.8E-6 cm^2/s (Baker et al. 1984). Therefore, in the absence of data for diffusion of hydrogen through the barrier, a small vent should be installed in the diffusion barrier to permit the escape of radiolytic hydrogen.[a]

(a) Diffusivity of hydrogen would be greater than diffusivity of CO_2 or radon. However, the observed diffusivity of the gas in asphalt will be a combination of the solubility of the gas in the asphalt (Henry's Law) and the diffusivity in the asphalt. Since the relative solubilities are not known, there is uncertainty in the comparison.

A design life of 250 years for the vent is desirable. If the vent remains open for 250 years and then closes completely, 328 years will be required to reach 50 psi, assuming no leaks and no diffusion through the barrier. At this point, the rate of gas generation will be extremely small and it is reasonable to assume that the hydrogen can diffuse through the diffusion barrier. Assuming the vent closes at 250 years and using 50 psi pressure inside the barrier, the diffusivity of hydrogen through the barrier would have to be greater than 4E-9 cm^2/s to vent the gas. It is reasonable to assume that the diffusivity of hydrogen through the barrier will not be lower than this based on comparison to the diffusivities presented in the previous paragraph.

After 500 years, the rate of hydrogen production is extremely low such that pressurization from atmospheric pressure to 50 psi will require 3300 years assuming there are no leaks, diffusion, or reactions acting as hydrogen sinks.

SIZE OF THE HYDROGEN VENT

The amount of gas generated is fairly small from the standpoint of gas flow. The estimated initial rate of gas generation for the grout is 1.01 mol/h, which is equivalent to 20.6 ft^3/d at 20°C and 1 atm pressure. The vent was sized to handle more than the maximum rate of gas generation that will occur. Two factors control the sizing of the vent: it must be large enough to allow the gas to escape without producing excessive backpressure, and it must be small enough that the rate of water diffusion through the vent over long time periods will not significantly contribute to the rate of contaminant release. The vent was nominally sized at 0.10 in. dia. for a 6-ft section passing through the diffusion barrier. The end of the vent where the gas exits to the soil is assumed to be 1-in.-dia. and filled with pea gravel.

The backpressure produced by the venting gas is affected by contributions from the frictional pressure drop in the vent line and the backpressure produced in venting to the soil. Venting of gas into soil can be described by the equation (Rolston 1986):

$$P_v = \frac{r}{4 \pi R^2} \frac{Q \mu}{k_a K}$$

Where:

P_v = back pressure [g cm/(cm^2 s^2)]
r = unit length = 1 cm
R = vent exit radius = 1.27 cm
Q = gas flux cm^3/s = 8.36 cm^3/s @ 90°C, 1 atm
μ = H_2 viscosity, 90°C = 1E-4 g/cm s (Perry and Chilton 1973)
ka = soil relative air permeability = 0.92 (Cary et al. 1989)
K = soil intrinsic permeability = 3E-9 cm^2 (Fayer et al. 1985)

This equation describes a vent discharging into an infinite mass of soil and expanding in three dimensions. When solved and converted to psi, P_v = 0.22 psi. The gas is limited in expansion in that it cannot expand in the direction of the vault. However, the backpressure is clearly not significant.

The pressure drop through the vent line can be described by the Darcy formula shown below (Crane 1986, Eq. 1-4). The Darcy equation is accurate for the flow of gases when the molar volume is assumed to be that at the inlet if the pressure drop is less than 10% of the absolute pressure at the entrance (Crane 1986, pg 1-7). In this case the flow is laminar so the friction factor is defined as 64/(Reynolds #).

$$P = \frac{(\rho f L v^2)}{144 D 2 g}$$

where:

P = pressure drop in psi
ρ = density in lb/ft^3
f = friction factor
L = length of pipe in feet
v = mean velocity ft/s
D = diameter of pipe, feet
g = gravitational acceleration 32.2 ft/s

The calculated pressure drop is only 2.2E-4 psi. The initial pressure drop could be slightly higher since air will be forced out of the vent as hydrogen is produced. If the properties of air are used, the pressure drop is 0.05 psi, which is still an insignificant pressure drop.

The impact of this vent on the performance of the vault is estimated by assuming that the vent pipe has decayed, leaving a hole in the diffusion barrier. The water vapor is assumed to diffuse back through the vent under isothermal conditions at 13°C. The humidity in the catch basin is assumed to be in equilibrium with 4 M $NaNO_3$ solution. The porosity of the soil at the vent exit is assumed to be at 100% relative humidity. A diffusion distance of 3 feet is used since this distance is the minimum thickness of the barrier. All water diffusing through the vent is assumed to reach the waste concentration and immediately mix with the water drawn from a downgradient well. The contribution to release from a 1.2-in.^{2} penetration through the barrier is less than 1% of the current performance goals in the performance assessment for the disposal system. This area corresponds to the cross-sectional area of two standard 1/2-in. pipes passing through the barrier.

VENT DESIGN GUIDANCE

The proposed location of the vent would be at the end of the vault opposite the leachate collection tank and just above the lip of the concrete catch basin. The tube must be designed to maintain a 0.1-in.-dia. opening for a design life of 250 years. The wall thickness of the tube should be such that it will allow compaction of the asphalt barrier on top of the tube without collapsing the tube. Filters on the ends of the vent tube are advisable to prevent aerosol particles from settling in the tube. The environment of the vent tube is not particularly corrosive since it has asphalt outside the tube and likely will have an oxygen-starved gas flowing through it. However, care should be taken that corrosion scale does not plug the opening of the vent.

The ends of the tube can be connected to 1-in. pipe, with an abrupt entry of the tube into the pipe and a screen just beyond the tube ends to prevent clogging by soil. The pipe section should be filled with pea gravel before installation to prevent clogging of the pipe and to reduce the pressure drop in venting to the soil.

POTENTIAL EXPLOSION HAZARD

The generation of hydrogen may create flammable gas mixtures in the gravel of the catch basin and in the porosity of the soil surrounding the vault. Small amounts of N_2O may be produced by irradiation of the grout. It is uncertain whether oxygen will be produced or scavenged by reactions occurring as a result of the grout being irradiated. However, it is possible that at some time a flammable mixture of hydrogen will exist in the catch basin of the vault. Also, flammable concentrations of hydrogen may exist in the porosity of the soil near the vent. Whether or not hydrogen can burn in the porosity of the soil is unknown. It may be that the high heat capacity of the gravel or soil will prevent combustion of the hydrogen.

The best way to ensure that the hydrogen does not burn is to exclude ignition sources. Potential ignition sources should be excluded from the grout vault catch basin, leachate collection tank, and surrounding soil. If ignition sources cannot be excluded, additional study of the flammability of hydrogen in the porosity of sand and gravel and study of the type and quantity of gases produced should be performed.

RADON GENERATION AND RELEASE

Double-shell slurry feed waste contains large quantities of ^{238}U, which ultimately decays through the radioactive gas ^{222}Rn (radon). Radon has a half-life of 3.825 days. The decay process is shown in Figure 2. The decay passes through ^{234}U, ^{230}Th, and ^{226}Ra before decaying to radon. Therefore, the best estimates of radon generation would be obtained from the concentration of these isotopes.

Information was not available on the concentration of ^{230}Th or ^{226}Ra in the waste. Lacking any information with which to estimate the radon generation rate, the radon generation was assumed to be in equilibrium with ^{234}U decay. This assumption is conservative since most of the ^{230}Th and ^{226}Ra is removed in processing the uranium ore.

The quantity of radon gas that will exist at any one time in equilibrium with the decay of ^{234}U is only 3.6E-9 moles. Therefore, from the standpoint of pressurization, the volume of radon is negligible. In the absence of a vent or if the vent eventually closes over a long period of time, radon release from the vault will be negligible. The diffusivity of radon through an asphalt hydraulic mix has been measured at 3E-6 cm^2/s (Baker et al. 1984). The asphalt hydraulic mix that was used was very similar to the material used to construct the diffusion barrier surrounding the grout vault. Therefore, diffusion through the diffusion barrier will be slow enough that the radon will decay before escaping the vault. However, with a vent that allows release of radiolytic hydrogen, the radon can escape from the vault system to the soil where it will then diffuse to the surface. An attempt has been made to quantify the radon release in a conservative calculation to eliminate concern over this issue.

Equations have been developed to estimate the release of radon from uranium mill tailings piles (Rogers et al. 1980). In order to estimate the amount of radon that might escape from the vault, the surfaces on the bottom and sides of the grout were assumed to represent the surface of an infinitely

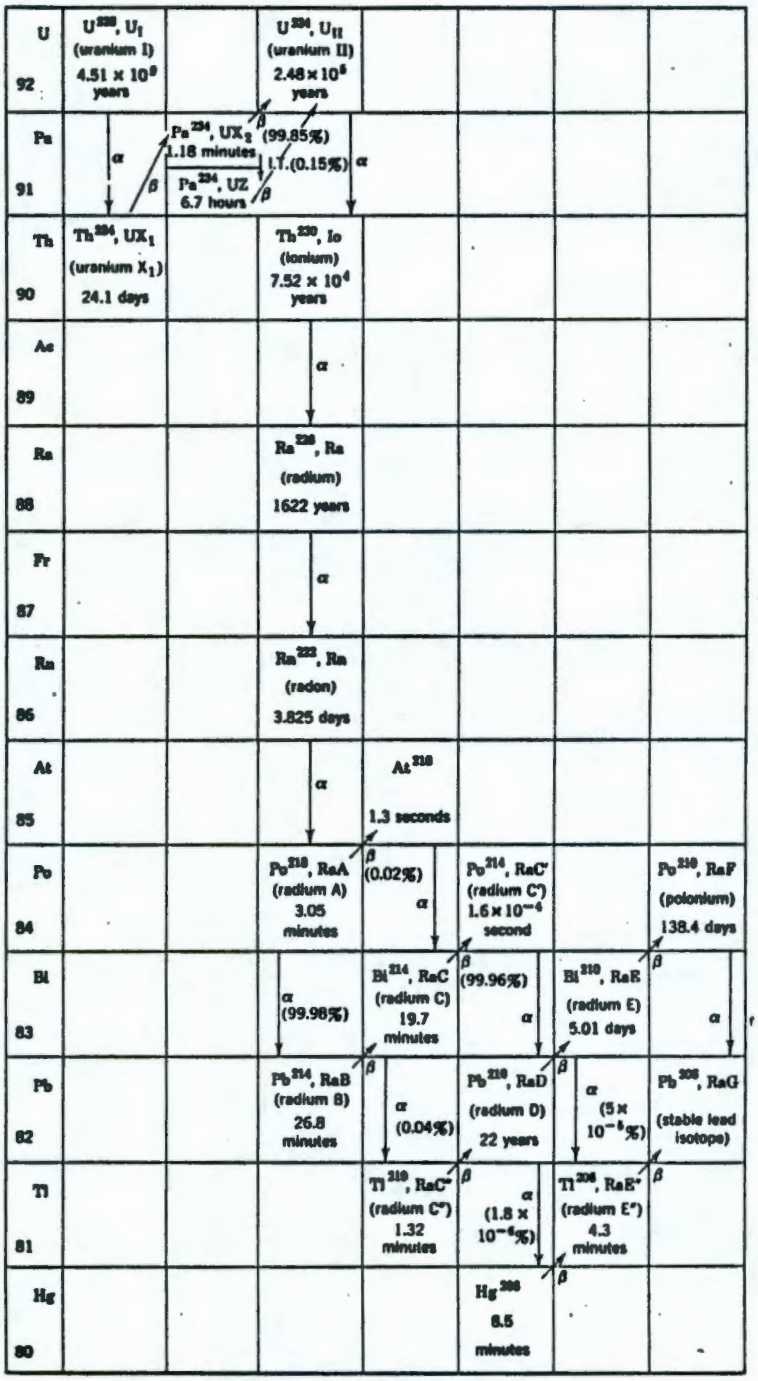

FIGURE 2. Decay Chain of Uranium (from Friedlander et al. 1964)

deep uranium mill tailings pile. For purposes of calculation, the transport within the grout was assumed to be similar to that in a soil used as backfill for the vault (porosity = 0.38). The equation that describes release from a tailings pile is shown below (Rogers et al. 1980).

$$J_0 = \frac{D_e (S - C_0 a^2)}{a}$$

Where:

J_0 = radon flux (pCi/ m^2 s)
C_0 = surface concentration (assume ≈0)
D_e = effective diffusivity = Dp, p = porosity = 0.38
radon in air = 0.12 cm^2/s
= 4.56E-6 m^2/s
a = $(L\ p\ /\ D_e)^{0.5}$
L= decay constant for radon = 2.10E-6 s^{-1}
= 0.4183 m^{-1}
S = (R rho L E)/D_e
R = radium activity per gram of grout = 13.86 pCi/g
rho = density of grout = 1.66E6 g/m^3
E = emanating power: fraction of radon that escapes from grains of matrix. Can vary from 0.01 to 0.91 for ores. Typical value is 0.20.
E = 0.20.

When J_0 is calculated and multiplied by the area of the bottom and sides of the grout, 38,946 pCi/s of radon is released from the grout. This quantity represents approximately 15% of the total radon generated within the grout. The diffusivity of radon through concrete is on the order of 2E-5 cm^2/s (Rogers et al. 1980), which would greatly reduce radon release from the vault. However, it is possible that the radon could be carried by radiolytic hydrogen through small cracks in the concrete. Therefore, no credit has been taken for the concrete vault.

The volume of the vapor space of the catch basin is 2225 ft^3 (based on KEH design analysis #WO ER9089 with gravel porosity = 0.26). The maximum hydrogen generation rate is approximately 26 ft^3/d (90°C, 1 atm). If there was not a gas vent and the radon reached an equilibrium concentration, it would reach a concentration of 8.34E6 pCi/ft^3. The 26 ft^3/d of hydrogen is assumed to exit the gas vent with this concentration of radon gas and enter

the soil, thus providing a source of radon of 2508 pCi/s at the exit of the vent.

The vent is assumed to be located on the end of the vault. The spacing between ends of vaults is assumed to be 40 feet. The gas is assumed to spread to the width of the vault only so that the flux occurs over an area of 186 m^2 (40 x 50 ft). The selection of an area will affect only the flux per unit area at the surface, and not the total release of radon to the air or the calculated dose. The flux of radon through cover material has been studied (Rogers et al. 1980); an equation describing this flux is shown below.

$$J=J_0 \exp[-(L\ p/D_a)^{0.5}\ b]$$

where:

J = flux from surface of the soil pCi/(m^2 s)
J_0 = flux into cover material, in this case from the vent
= (2508 pCi/s)/186 m^2 = 13.48 pCi/(m^2 s)
b = cover soil thickness = 17 m
D_a = D_e h(b): h(b)≈1.0 for thick soil covers
J_b : (for definition see Rogers et al. 1980)
(other notation is the same as the previous equation)

When calculated, this gives a flux at the soil surface = 1.1E-2 pCi/m^2 s. This value will decrease with the half-life of ^{137}Cs since the hydrogen gas is required to carry the radon through the vent. If all 44 vaults are assumed to be poured with a site area of 2033 m^2 per vault, and all vaults are releasing at the maximum rate, the radon emission for the site is 1.01E-3 pCi/(m^2 s). The dose was estimated using the GENII code assuming that radon is in equilibrium with its daughter products and that the wind travels along the long dimension of the site (442 m) at a speed of 1 m/s with mixing in the air occurring to a height of 1 m. For a person living downwind at the edge of the site, the annual effective dose equivalent for inhalation and external exposure is 8.1E-3 mrem/yr. Therefore, the release of radon is not a concern[a].

(a) In DOE Order 5480.1A, derived concentration guidelines are provided based on a 100 mrem/yr dose under a specified exposure scenario. Although the specific exposure assumptions were not used in the dose calculation, the estimated dose is well below 100 mrem/yr.

TRITIUM RELEASE

The DSSF waste contains tritium that will be converted to a hydrogen gas by the radiolysis of tritiated water. The upper bound inventory of tritium in each vault is 59 Ci (6.08E-3 g). Assuming that tritium and hydrogen gases are produced at the same rate by radiolysis, 1.021E-5 Ci/d of tritium as hydrogen gas will be produced in the grout. Some of this tritium will be released through the vent. Tritium containing hydrogen gas will be produced only in the early life of the vault because of the 12.3-year half-life of tritium. Over the first 30 years, the release will fall by roughly a factor of 12 due to decay of the tritium and decay of the radionuclides causing radiolysis. Tritium is not generated in the waste.

It was conservatively assumed that all of the tritium generated in the grout reaches the surface. A dose was estimated using the GENII code. GENII does not calculate dose from tritium in hydrogen gas. Therefore, the tritium was treated as tritiated water, which is conservative. Only the inhalation pathway was evaluated. It was assumed that all 44 vaults were releasing hydrogen at their maximum rate. A wind speed of 1 m/s travelling along the longest dimension of the site (442 m) with mixing occurring to a height of 1 m was assumed. The annual effective dose equivalent resulting from tritium release to a person living downwind at the edge of the site is 1.8E-2 mrem/yr. Therefore, tritium release should not be a problem.

CLOSURE COVER VENTS

No need for vents in the closure cover has been identified. The hydrogen expected to be released from the vent in the diffusion barrier is only about 20.6 ft^3/d. This quantity of hydrogen should easily disperse in the soil. Pressure cannot build under the closure cover since it is not a sealed structure. Vents would be required only if pressurization was a potential issue.

CONCLUSIONS

The conclusions of this analysis are as follows:

1. The rate of gas generation is expected to be approximately 3.7E-13 mol/(g rad). The gas is expected to be primarily hydrogen, but O_2 and N_2O may also be produced. The yield of gas (per rad) is expected to be roughly the same after alpha and beta radiation dominate the dose.

2. The maximum dose rate in the grout is 310 rad/h when the grout is first poured. The dose rate and gas generation follows the decay of ^{137}Cs until approximately 500 years, after which the dose is controlled by alpha and beta radiation. A breakdown of radionuclides was provided in Table 2.

3. It is possible that equilibrium gas pressures will be reached inside the grout matrix, which will decrease the amount of hydrogen generated. If equilibrium is not reached and the mobility of the hydrogen is insufficient to relieve pressure, microcracks in the grout might open to release the pressure. These cracks will not affect the performance of the grout disposal system.

4. It is recommended that a passive approach to venting hydrogen be pursued. It is possible that the hydrogen will diffuse through the barrier without a vent. Measurements of hydrogen diffusion through the solid asphalt barrier would be needed to support a design that does not include a vent. Also, the gas composition and generation rate for the specific waste and dry blend being used may need to be measured.

5. Based on currently available information, the rate at which hydrogen diffuses through the diffusion barrier may not be high enough to allow the hydrogen to escape during the first 250 years. There is reasonable confidence that, after 250 years, the hydrogen generation rate will decrease to a level that is low enough to permit escape of hydrogen from the vault by diffusion through the barrier.

6. If a passive approach is not feasible, a vent with a 250-year design life and a 0.1-in.-diameter clear opening is recommended for venting radiolytically generated hydrogen to the soil. It is also recommended that the cross-sectional area of the penetration of the asphalt barrier be less than 1.2 in^2.

7. Flammable mixtures of hydrogen may exist in the catch basin and in the soil near the vent exit during the life of the vault. The potential for hydrogen to burn in the porosity of the soil or gravel is unknown. In the absence of further information, ignition sources should be excluded from the vault catch basin, leachate collection tank, and surrounding soil.

8. Radon generated in the vault will decay to low levels before it reaches the surface. The release of radon is not a concern.

9. In the early life of the vault, approximately 1.02E-5 Ci/d of tritium in the form of hydrogen gas may be released to the soil by the vent. The quantity of tritium released is not a concern.

10. There is not a need for vents in the closure cover.

RECOMMENDED TESTS

The following tests could be conducted to provide useful information for the design of the disposal system. Each experiment is described along with the use for the resulting data.

1. Hydrogen diffusion tests should be performed to determine the hydrogen diffusion rate through the solid asphalt/aggregate barrier. This data could support a design using a passive approach to venting the radiolytically produced hydrogen. The test data might also change the required design life requirement for vents installed through the diffusion barrier.

2. The gas generation from DSSF grout should be studied using a representative waste and dry blend to determine the type and quantity of gases produced. Tests performed at low dose rates could be used to establish equilibrium pressures in the grout. Favorable results could support a passive design approach to venting or alter the required design life of the vent.

3. The flammability of hydrogen mixtures in the porosity of a gravel bed should be studied to determine if there is a potential for explosion in the catch basin or in the soil surrounding the vault. If it is determined that the hydrogen cannot burn in these media, the requirement for excluding ignition sources from the catch basin of the vault would be removed.

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APPENDIX

ASSUMPTIONS AND BASIS FOR VALUES IN REPORT

9 2 1 2 4 1 4 1 3 1 8

Below are listed several values from the report with a description of how the values were determined.

3.7E-13 mol/(g rad)- Radiolytic gas yield. See Table 1. Value is the largest generation rate obtained in the literature using a cementitious waste form. Value from Lewis and Warren (1989).

310 rad/h- The initial dose rate in the grout assuming upper bound inventory from the DSSF grout PA is distributed into 44 vaults of 1.4E6 gallons with a grout density of 1.66, and assuming that all radiation is absorbed in the grout.

1.01 mol/h- The initial rate of hydrogen generation. Value calculated = 3.7E-13 mol/(g rad) * 310 rad/h * 8.797E9 g

1E-5 cm^2/s- The diffusivity required to vent the initial hydrogen generation rate without a vent in the diffusion barrier. This assumes the diffusion barrier sides are 152.4 cm thick with an area of 1.1E7 cm^2 and the vault top and bottom are 96.5 cm thick with an area of 1.2E7 cm^2. The pressure in the vault is assumed to be 50 psi. Fick's law is used to determine the diffusivity required. Therefore, the concentration induced in the asphalt is implicitly assumed to have the same volumetric concentration for hydrogen as the gas contained inside the diffusion barrier. This is only a gross approximation. Therefore, the diffusivity effectively includes the effect of solubility at the gas/asphalt interface.

4E-9 cm^2/s- The diffusivity required to vent hydrogen by diffusion through the barrier if the vent closes after 250 years. The time required to pressurize the catch basin is included to determine the gas generation rate. The assumptions are the same as in the value above.