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7. Abstract
Hydrogen and nitrous oxide are formed from radiolytic breakdown of water and organic materials in the disposal facility grout block. Gas retention and release from grout and subsequent time-dependent compartment concentrations are modeled.

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EXECUTIVE SUMMARY

Hydrogen and nitrous oxide gas generation is recognized as a consequence of radiolytic decomposition of liquid and other materials in the grout mix. Oxygen may also be formed radiolytically in some grout mixes. The generation of these gases does not create a safety concern from the standpoint of toxic or radioactive hazards. The presence of these gases is a potential hazard for flammability impact on structural and radioactive retention integrity of the disposal facility must be addressed as part of the design justification for the grout disposal facility. Quantitative models were developed for the time-dependent presence of these gases in the grout disposal facility regions to support the safety analysis studies that address the hydrogen flammability issues.

The modeling approach involved two major tasks. One task was to develop engineering models of gas buildup, retention, and release from the grout block where the gases are formed by radiation from radioactive decay. The migration of these gases into compartment regions were modeled to determine time-dependent concentrations in the grout disposal facility. These concentrations are needed to support safety analysis studies that address potential structural damage or release of radioactive vapors or liquids as a consequence of potential flammability incidents.

The second task was to collect physical data used by the calculational models. These data include gas generation rates, diffusion coefficients, gas solubilities, and other data. The availability of these data were fragmented in the open literature. Information is particularly lacking to limit the extremes of uncertainty on gas generation dose conversion factors. In those cases where specific data did not exist for the gas conversion factor, best estimates and bounding case levels were identified which present average values and limits of uncertainty, respectively. The dose rate in the grout material was based on a 95% confidence level of the concentrations reported on tank measurements. This conservative dose rate was used for both the reference and bounding case calculations. Based on these dose conversion factors and the conservative dose rate, a reference case and a bounding case were established. The reference calculation is believed to conservatively

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characterize the hydrogen and nitrous oxide distributions in the grout disposal facility regions and compartments. The bounding case represented extreme limits in the dose conversion factors for gas generation rates.

The results of modeling for the reference case indicated that the hydrogen levels in the vault compartments may be acceptable before final closure. The hydrogen levels in the unfilled vault vapor space were very low and will not require active ventilation or mitigation systems to prevent hydrogen flammability during phase I filling of the vault. The levels of hydrogen in the leachate sump were below the level of concern and do not require active ventilation to prevent potential flammability before final closure.

Due mainly to uncertainty in data that relates gas formation to radioactive dose rate, the gas generation rate of the bounding case may potentially be much higher than the reference case cited above. A discussion of these data uncertainties, their effects on hydrogen concentrations, and suggestions for resolving adverse uncertainties are discussed in this report.

Sensitivity studies were made to quantitatively evaluate the effects of uncertainty of these data. These studies provided a range of results on which to either base the safety studies or to identify areas where more defined measurements are needed. Suggestions were made which identified data that may be upgraded to avoid restrictive conservatism in the results.

The basis of the models used are fully documented in this report. A discussion is presented of the models to provide understanding of the factors that must be considered in the calculations. The cases evaluated in this report identify uncertainties in data that are known and the results reported cover the range of these uncertainties. These results provide input to evaluate the facility design from the hydrogen flammability issue as intended.

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GROUT DISPOSAL FACILITY GAS CONCENTRATIONS

1.0 PURPOSE

This report provides a quantitative analysis which may be used for evaluating the acceptability of the current grout disposal facility design from the standpoint of potential hydrogen and other gas generation, and associated safety issues such as hydrogen flammability. The results of this study provide quantitative levels of production rates and concentrations of hydrogen and other potentially reactive gases, such as oxygen and nitrous oxide, that are used to support follow-on studies that establish the risk of chemical reaction and associated radiological consequences. In addition, these results may be used to determine the functional requirements of mitigation systems that reduce the risk of potential flammability to acceptable levels. The quantitative results of this study provide a basis for evaluating contingencies for operation of safety equipment.

Additionally, this report documents the modeling basis and identifies areas where further modeling refinement is necessary.

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2.0 OBJECTIVE

The objective of this report is to provide technical support on which to evaluate the grout disposal facility design with respect to hydrogen flammability and safety. This report provides a quantitative model of a reference case of hydrogen and nitrous oxide generation. The reference case is based on both available data and engineering estimates of less certain data. The engineering estimates are identified where appropriate and the impact of uncertainties on design are evaluated in a sensitivity study.

The specific applications of this reference case and sensitivity study will be to determine the release rates of gases from the grout and the related time-dependent concentrations of gas compositions in the facility regions. The time-dependent concentrations will be used to determine safety-related consequences if mitigation systems are not present or functioning. The release rates of gases from the grout may be used in other studies to design and evaluate the effectiveness of proposed mitigation systems.

An investigation of the permeation of hydrogen and other gases through the asphalt diffusion barrier is also included in this report. Permeation is evaluated to quantify the amount of venting hydrogen and other generated gases to the soil.

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3.0 MODEL DESCRIPTION

The following descriptions cover facility features and conditions that are relevant to the physics of modeling the generation and transport of hydrogen, oxygen, and nitrous oxide in the materials and regions of the grout disposal facility. They are listed here to record the basis of modeling and results presented in this report.

3.1 FACILITY DESCRIPTION

3.1.1 Physical

The regions of the grout disposal facility are shown in Figure 3-1. These vaults represent vaults 102, 103, 104, and 105 which are prototypes of the later disposal facilities. The dimensions of the grout block are 50.5-ft wide by 34-ft high by 123.5-ft long (15.4-m wide by 10.4-m high by 37.6-m long). The height includes an upper 4-ft-thick cold-cap grout layer containing no radioactive materials. The total volume of the grout is 1.4 M gal. The vault is designed to contain 1 M gal of liquid from the double-shell tanks.

The grout block is enclosed by a concrete vault which has an end thickness of 2.5 ft (0.76 m), bottom thickness of 4.5 ft (1.37 m), top thickness of 2.8 ft (0.85 m), and tapered sides with an average thickness of about 3 ft. (0.9 m). The inside walls and floor of the vault are coated with a 60-mil-thick elastomer which serves as a barrier to liquid flow. The top of the vault consists of concrete slabs that rest on the walls of the vault.

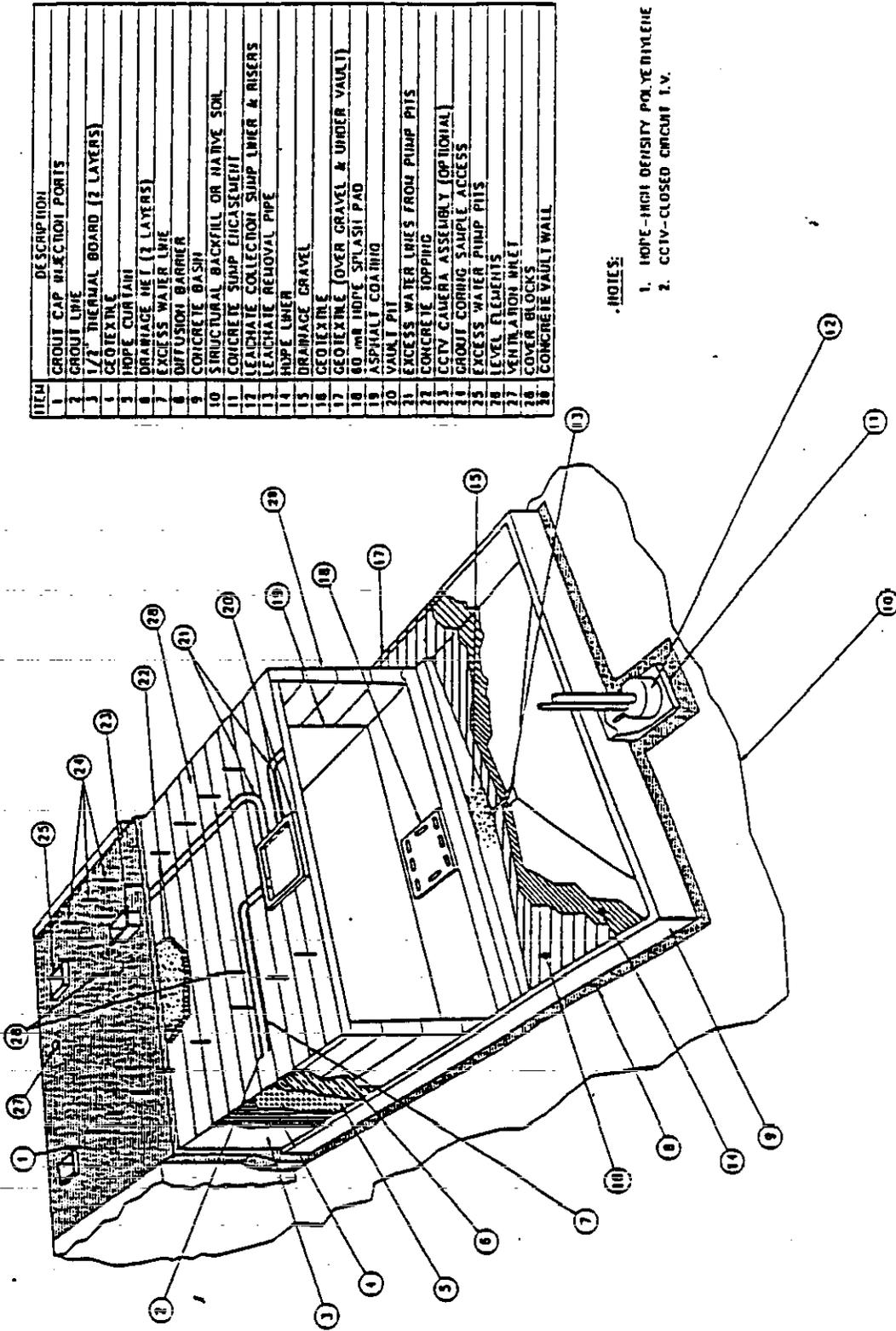
The vault rests on a gravel-filled leachate catch basin. The total volume of the catch basin is 14,730 ft³ (417,100 L) which is gravel-filled with 40 vol% void space. The catch basin drains to a leachate sump through a 107.5-ft (32.8-m) length of 4-in. Schedule 80 pipe whose volume is about 9.5 ft³ (269 L). The total estimated leachate sump volume is 888 ft³ (25,150 L). This volume includes a 26-in.-diameter vent pipe with a 162-ft³ (4,587 L) volume, and an 8-in.-diameter vent pipe with a 18-ft³ (509 L) volume.

The outside vertical surfaces of the vault are covered with a high density polyethylene liner, insulating material, and a coarse webbing (geotextile) that will allow gas and liquid to flow down the sides into the collection basin. The vault and collection basin are surrounded by an asphalt diffusion barrier which functions as a moisture barrier. The top and sides of the barrier are 40 in. (1.02 m) thick, the bottom is 18 in. (0.46 m) thick. The top of the barrier will be installed before pouring the grout block. Two 24-in. (0.61 m) ducts from the ventilation system inlet and exhaust penetrate the cover blocks to the grout volume during filling. A 12-ft (3.7 m) thick Resource Conservation and Recovery Act (RCRA) cover will be installed after the cold cap is poured.

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Figure 3-1. Grout Disposal Facility Used in Gas Modeling.

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ITEM	DESCRIPTION
1	GROUT CAP INJECTION PORTS
2	GROUT LINE
3	1/2" THERMAL BOARD (2 LAYERS)
4	GEOTEXTILE
5	HOPE CURTAIN
6	DRAINAGE NET (2 LAYERS)
7	EXCESS WATER LINE
8	DIFFUSION BARRIER
9	CONCRETE BASIN
10	STRUCTURAL BACKFILL OR NATIVE SOIL
11	CONCRETE SUMP ENCLOSURE
12	LEACHATE COLLECTION SUMP LINER & RISERS
13	LEACHATE REMOVAL PIPE
14	HOPE LINER
15	DRAINAGE GRAVEL
16	GEOTEXTILE
17	GEOTEXTILE (OVER GRAVEL & UNDER VAULT)
18	80 MB HOPE SPLASH PAD
19	ASPHALT COATING
20	VAULT PIT
21	EXCESS WATER LINES FROM PUMP PITS
22	CONCRETE TOPPING
23	CCIV CAMERA ASSEMBLY (OPTIONAL)
24	GROUT CORING SAMPLE ACCESS
25	EXCESS WATER PUMP PITS
26	LEVEL ELEMENTS
27	VENTILATION INLET
28	COVER BLOCKS
29	CONCRETE VAULT WALL

- NOTES:
1. HOPE-HIGH DENSITY POLYETHYLENE
 2. CCIV-CLOSED CIRCUIT T.V.

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3.1.2 Operational Periods

The operational periods of the grout disposal facility must be considered in the modeling design. The three periods considered are as follows: (1) phase I, filling; (2) phase II, surveillance, and (3) phase III, final closure. The filling period covers the first year. In this time, the portion of grout containing radioactive materials is poured in 4 to 8 months. This will be done in a number of lifts or partial fillings, which allows removal of the heat of hydration associated with grout hardening and curing. For design purposes, the filling period lasts 1 yr and ends when the cold-cap is poured, filling the remaining vapor region inside the grout vault.

The surveillance period extends from 1 yr until the draining of liquid to the sump is insignificant and the State of Washington allows closure. A 30-yr period is assumed for design purposes. During this time, excess liquid collected in the leachate catch basin will drain to and be pumped from the sump. Vapor concentrations in the catch basin and sump may be monitored for gas concentrations, and the vents from the sump pit to the atmosphere will remain open.

Final design closure occurs after 30 yr and extends indefinitely. For the purposes of hydrogen modeling, 300 yr will be the cutoff time. By that time, hydrogen production will be significantly reduced because of a decrease in radioactive material activities due to radioactive decay. Final closure will begin when the sump vents are filled with grout and capped off. Active surveillance will be discontinued after phase II. The radiolytically generated hydrogen and other gases will be discharged to the soil through two vent tubes penetrating the asphalt diffusion barrier near the top of the leachate catch basin. Release of gases directly through the asphalt diffusion barrier will be investigated as an alternative venting process during phase III.

3.2 HYDROGEN SOURCE TERM

Considerable investigation of hydrogen generation has been performed in the Hanford waste tanks. From these investigations, useful insight can be determined for the generation of hydrogen and other gases in the grout material. The sources of hydrogen generation are from the radiolytic decomposition of liquid in the grout and by associated chemical reactions that are believed to be initiated by the radiolytic decomposition (Meisel et al. 1991). Ionizing radiation, such as gamma rays, beta particles, and alpha particles, from radioactive materials in the grout cause liquid radical formation. These liquid radicals exist momentarily in volumes that appear sporadically throughout the grout region. Radiolytic hydrogen results from the recombination of a fraction of these radicals. These volumes of liquid-radicals recombine rapidly as liquid and other molecules. This partial recombination forms a molecule each of hydrogen and hydrogen peroxide in pure water.

The recombination of the fraction of liquid radicals forming hydrogen is affected strongly by materials in the grout mixture, such as nitrites and nitrates, that will chemically interact with the radicals. Typically, these interactions will reduce the hydrogen generation in grout when compared to the generation within pure water. A study of chemical reaction mechanisms in

tank 241-SY-101 (Babad et al. 1991) describes formation of hydrogen and nitrous oxide from interaction of other materials. The formation rate of hydrogen and nitrous oxide by chemical reaction of other materials is difficult to determine by predictive methods alone. Compared to chemical reactions initiated by radiation, the gas formed by non-radioactive decay is felt to be small. The formation rate of these gases is most reliably determined from measured values of a specific grout mix.

3.2.1 Gas Generation Dose Conversion Factors

The overall formation rates of hydrogen and other gases from measurements are expressed as dose conversion factors. These conversion factors are multiplied by the dose rate to determine generation rates. These gas generation conversion factors are considered equal for gamma and beta radiation. Gamma and beta radiation are prominent in the grout disposal facility. The initial level of dose rate and gas formation from alpha particles is over four orders of magnitude below the initial levels of gamma ray and beta particle radiation. This low generation rate of alpha particles does not significantly contribute to the gas production rate during the time of interest.

The hydrogen conversion from radiolytic decomposition is expressed as a yield "G", which is defined as the number of hydrogen or other molecules produced per 100 electron volts of radiation energy absorbed.

A listing of yield "G" values, and initial gas production rates is given in Table 3-1. The initial gas generation rates are the basis of the reference and bounding cases. The yield "G" value of gas production in a similar grout mix was found from measured data (Friedman et al. 1985). A discussion of this yield "G" value and its application to the double-shell slurry grout mix is discussed in Appendix A. The grout mix is still being developed and may be composed of the same ingredients as noted in Appendix A except 7% clay may be used instead of 14% clay. The mix identified in Appendix A is still applicable from the standpoint of gas generation. A conversion factor determined by measurement in a similar grout mix is used as the reference and bounding cases for hydrogen production in this study.

The upper limit or bounding case of hydrogen conversion is based on an earlier study (Whyatt 1991) that selected conservative conversion factors from available data of grout measurements in the literature. This bounding case was determined with a grout mixture that did not contain nitrates or nitrites. These materials are known suppressants to the formation of radiolytic gases. The bounding case is not meant to be a realistic estimate of gas generation rates for the grout mix proposed for the disposal facility; however, it provides the worst case hydrogen generation rates reported in literature. The nitrous oxide and oxygen values are also taken from literature and represent an additional conservative estimate, in that they were not produced with the bounding hydrogen generation rates, but were taken from other liquid generation data. Therefore the bounding case is an unrealistic worst case value. Further experimentation could determine a less conservative bound of these generation rates. The bounding case results in a combined gas generation rate that is about a factor of 30 above the reference case. This conversion factor value represents an upper limit on the hydrogen formation rate that is considered in this report.

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Table 3-1: Conversion Factors and Initial Formation Rates of Radiolytic Hydrogen, Nitrous Oxide, and Oxygen.

Case	Initial Dose Rate (Gray/h)	Yield "G" value (molecule/100 eV)	Initial formation rate (mol/h)
Reference Case			
Hydrogen	3.10	0.0043	0.012
Nitrous oxide	3.10	0.011	0.031
Oxygen	3.10	0.0	0.0
Bounding Case			
Hydrogen	3.10	0.23	0.65
Nitrous oxide	3.10	0.23	0.65
Oxygen	3.10	0.07	0.20

3.2.2 Dose Rates

The rate of hydrogen formation is determined by multiplying the yield "G" value by an appropriate constant¹, 1.036×10^{-7} mol-100 eV/gray-kg-molecule, and the average dose rate and grout mass. The average dose rate in the grout mass was determined from 95% confidence interval concentrations of measurements in the feed tanks (Hendrickson 1990). A discussion of these concentrations and the corresponding initial dose rates was calculated to be 310 rad/h (Whyatt 1991) which is 3.10 gray/h.

The mass of the grout is 8.797×10^6 kg from that same reference. These factors give an initial hydrogen formation rate of:

Initial hydrogen formation rate = $0.0043 \text{ molecule}/100 \text{ eV}$
 $\times 1.036 \times 10^{-7} \text{ mol-100 eV/gray-kg-molecule}$
 $\times 3.10 \text{ gray/h} \times 8.797 \times 10^6 \text{ kg}$
 $= 0.012 \text{ mol/h.}$

3.2.3 Dose Rate Time-Dependence

The normalized time-dependent formation rate of hydrogen is shown in Figure 3-2. The reference curve fits the data, the fitted curve envelopes the reference curve and was used in the calculations. The time-dependent shape of this curve is based on well established radioactive decay characteristics of initial isotope concentrations. The time-dependent shape of the curve in the period of interest from 0 to 400 yr is dominated by the radiation from ¹³⁷Cs.

¹The conversion constant is found by: ("G" molecules/100eV)* (1 eV/1.6022 E-19 Joule)*(1 Joule/kg-gray)*(1 mol/6.022 E+23 molecules).

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The curves will not be significantly affected by uncertainties in concentration of other radioactive materials. Therefore, this normalized curve can be applied to any initial hydrogen formation rate to give the time-dependent reduction from decay of the radioactive materials in the grout.

3.2.4 Assumptions and Conservatism

The gas generation rates were based on the best available data or on conservative assumptions when data was not available. Examples of these conservative assumptions are the following:

1. The dose conversion factors for gas generation were based on measured values of similar grout mixtures or on a grout mixture that represents an upper bound conversion factor limit.
2. The gas generation was based on the total quantity of gamma ray and beta particle formation rates. The beta particles will terminate at their point of origin. Gamma radiation will penetrate into the walls of the vault for a short distance. Its mass attenuation coefficient for ^{137}Cs gammas is about 0.18 cm^{-1} which corresponds to the gamma flux being reduced by a factor of 10 about every 5 in. Gas formation in the vault concrete is not significant when compared to total production and was included with the grout block production.
3. Pressure buildup of gas has a reverse reaction on formation rate. Equilibrium concentrations can be reached at pressures much higher than will be realized in the grout materials. A minor reduction in gas formation is expected but its effect was ignored in the calculations.
4. Radioactive decay time dependence in the calculations was based on a simple curve that enveloped the curve representing more rigorous calculations. The total gas generation over time will exceed the actual amount produced due to the simplified approximation.

3.3 NITROUS OXIDE SOURCE TERM

Nitrous oxide formation is of concern because nitrous oxide has the potential to react with hydrogen. The reaction of nitrous oxide and hydrogen produces higher pressures than the reaction of equal quantities of hydrogen and oxygen because the reaction products will produce a greater gas volume than an equivalent reaction of hydrogen and oxygen. Nitrous oxide is formed from nitrites and nitrates in the grout mixture by both direct radiolytic formation and chemical reactions believed to be initiated by radiolytic radicals formation.

The mechanism of nitrous oxide formation is not well established at this time. In present practice, the nitrous oxide formation rate is established by comparing concentrations to hydrogen concentrations in tank vapors. The measurement of hydrogen and nitrous oxide concentrations in tank 241-SY-101 vapors (Babad et al. 1991) suggests that a formation rate of nitrous oxide

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equal to that of hydrogen is appropriate. Therefore, the bounding case estimate of the nitrous oxide conversion factor is assumed to be equal to hydrogen formation. The initial formation rate of the nitrous oxide bounding case is assumed to be 0.65 mol/h for the grout vault. Its time-dependent formation rate is represented by the fitted normalized curve in Figure 3-2.

The reference case conversion factor has been measured in a similar grout mixture (Friedman et al. 1985). A discussion of the conversion factor is given in Appendix A. The yield "G" value from this reference is 0.011 molecule/100 eV. The conversion factor results in initial generation rate of 0.031 mol/h for the reference case. Its time-dependent formation rate is related to the formation rate of hydrogen. Therefore, its time dependence is represented by the fitted normalized curve in Figure 3-2.

3.4 OXYGEN SOURCE TERM

Oxygen is not formed directly from radiolytic decomposition of water. More accurately, it is formed by the chemical decomposition of hydrogen peroxide that is a direct product of radical reformation. A possible mechanism for reduction of oxygen is oxidation of sulfides and organics. Oxygen formation is substantially reduced by the materials in grout mixtures, such as water-cooled blast furnace slag that can retard oxygen formation. The oxygen formation rate is determined in practice by measurement rather than by relying on predictive models.

Oxygen formation is based on the production of hydrogen similar to that for nitrous oxide formation in this report. A value for oxygen production that is 30% of the value for hydrogen production was given in Appendix A to establish an upper limit case to evaluate the impact of oxygen formation on the vault design. This ratio to hydrogen has been observed in some grout mixes which do not scavenge oxygen (see Appendix A). The initial bounding formation rate of oxygen corresponds to be 0.20 mol/h for the total grout disposal facility. This formation rate is considered to be extremely conservative. It is associated with the bounding generation rate of hydrogen which is discussed in Section 3.2.1. Since the oxygen formation rate is associated with the formation of hydrogen, time dependence is represented by the fitted normalized curve in Figure 3-2.

The reference case assumed no oxygen formation. A discussion of materials in the grout mixture is given in Appendix A. The measured values of a similar grout mixture (Friedman et al. 1985) indicate that oxygen formation would not occur. The contingency of assuming oxygen formation is considered in this report to cover the situation of having other grout mixtures chosen in the future. The impact of oxygen formation on design is evaluated in the sensitivity study in Chapter 5.0.

3.5 MATERIAL PROPERTIES

The material properties that affect hydrogen migration in the vault facility are discussed in this section. These materials are the grout, concrete, asphalt, and elastomer moisture barrier.

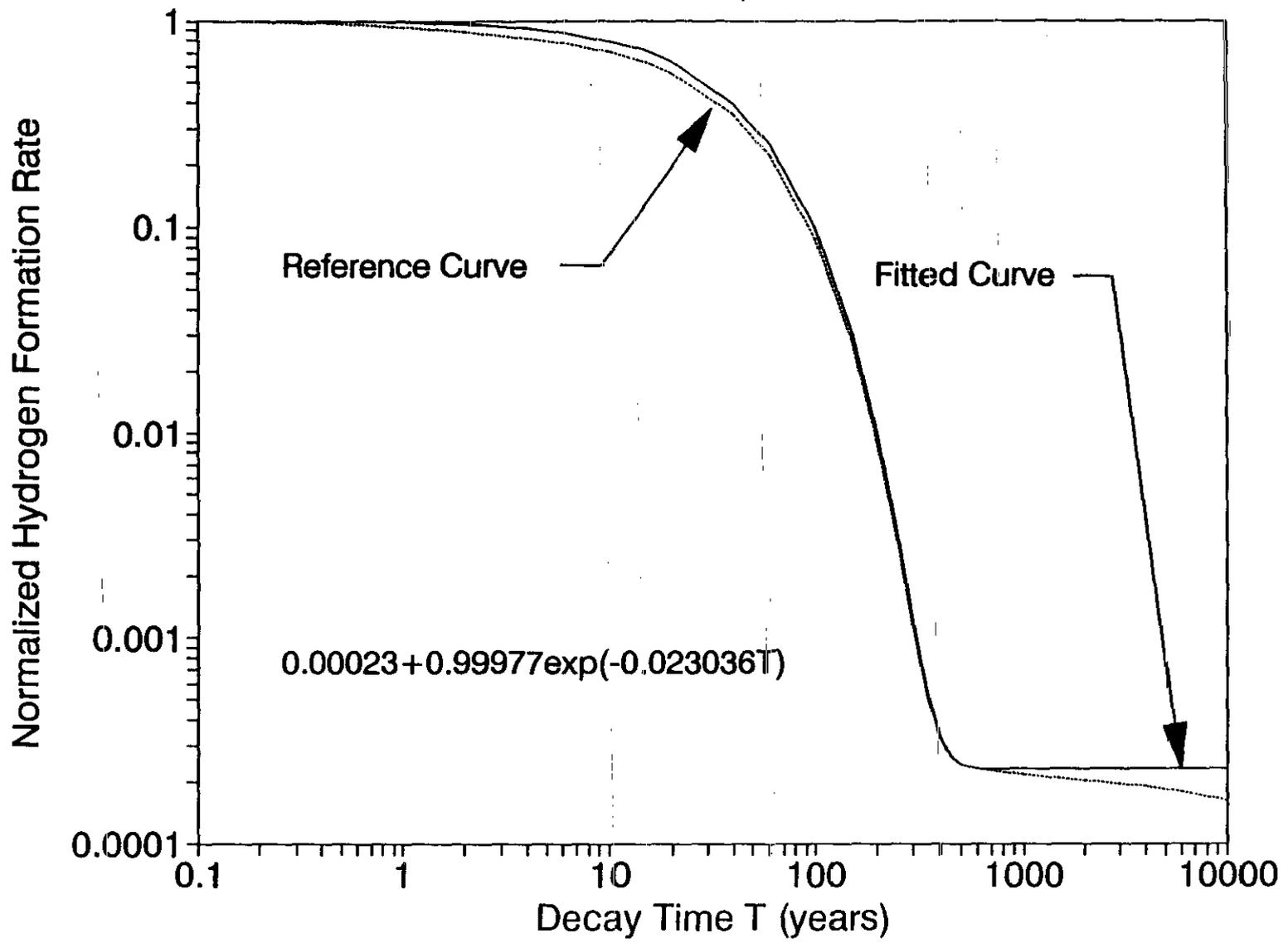


Figure 3-2. Normalized Hydrogen Source--Double-Shell Tank Grout Feed Facility.

3.5.1 Grout Material

A general description of cementitious material is contained in Kingery, et al. (1975). A description of grout material similar to that proposed for the grout facility is also given in Lokken, et al. (1988). Cementitious material is characterized by regions of solids and capillaries surrounding irregular-shaped pores (see Figure 3-3). This figure shows fracture surfaces of pilot-scale grout samples about 6 in. and 3 ft below the top surface (Lokken, et al. 1988). The pore regions are generally interconnected and can be partially or completely filled with liquid, depending on the extent of saturation of the grout.

The pore regions contain a limited amount of liquid solution that remains in place because of surface tension or capillary forces. Likewise, the fine capillaries of the solid regions contain liquid that will also remain bound by surface tension. This portion of the liquid, referred to as bound liquid, will not be moved by gas pressurization and flow. An average pore diameter of 10 microns was assumed in the calculations of unbound liquid in order to be conservative and to account for the distribution of larger pore volumes.

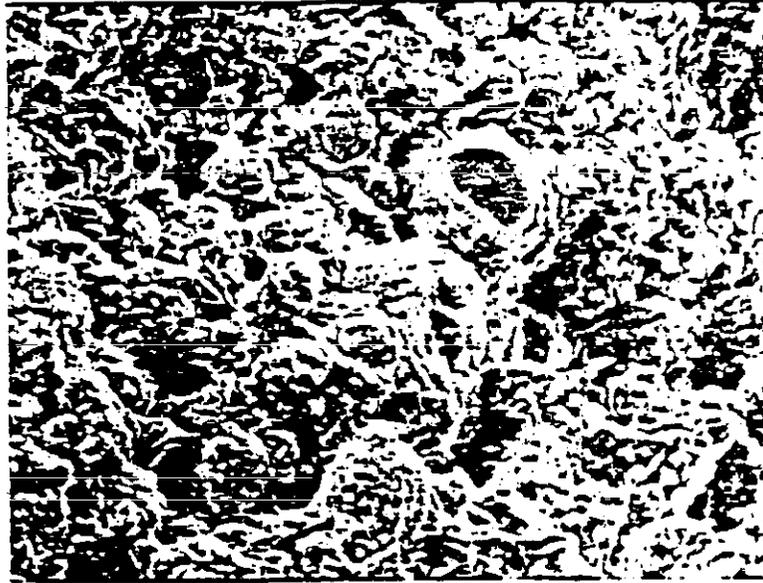
If the liquid content in the pores exceeds the quantity held by capillary forces, the excess is referred to as unbound pore liquid. Gas caused by radiation will form throughout the liquid in these regions. If the solubility of gas in the liquid is exceeded, gas bubbles will form that displace part or all of the unbound liquid. The displacement of unbound liquid will cause a combined two-phase flow of liquid and gas bubbles from the grout block. The liquid phase of the flow through capillaries and pores of the outer grout adds significantly to the flow resistance because of its higher viscosity.

A fully saturated grout material, such as the present grout design, will cause a high resistance to hydrogen migration by diffusion because of the low permeability of the saturated grout mix. In fact, the permeability of hydrogen gas in fully saturated grout is nearly zero. From the mechanism of diffusion, gas molecules will migrate in the water of the pore regions that constitute most of the grout volume. This migration in the liquid-filled grout pores is characterized by diffusion of gas molecules in water with dissolved salts. At low gas formation rates, a high retention of gas will be contained permanently in the grout material.

A gas generation threshold level exists in the grout called breakaway. This is the gas generation level at which the remaining liquid is held by capillary forces and the flow is dominated by the gas phase. The flow resistance of gas is much lower so the flow rate will increase. If this point is reached, gas pressures inside the grout will relieve and the fraction of retained gas will be reduced significantly. This effect is discussed further in Section 5.4.

Another gas generation threshold level exists called advection initiation. This is the level at which advection flow occurs. If the gas generation rate is below this level, the losses by diffusion will be adequate to prevent gas pressure inside the grout to reach the level to produce bubbles and liquid displacement. A discussion of this effect is given in Section 5.5.

Figure 3-3. Scanning Electron Micrographs of Pilot-Scale Grouts



Top of Sample

13 μm



Bottom of Sample

13 μm

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The grout material is required to have a compressive strength of 500 lb/in² (3.4 MPa). The level of tensile strength is not available but is expected to be significantly less than the compressive limit. It is very likely that pressurization of liquid and gases in the pores will exceed the tensile limit and cause fractures in the grout structure. If fracturing occurs, the flow resistance will decrease. Fracturing will effectively increase the volumes of the pores and increase the volume fraction of unbound liquid. Significant fracturing may cause swelling of the grout block. It is unclear with present knowledge what effect fracturing will have on gas migration. Since information on the effects of fracturing on gas flow is not available at this time, the fracturing is assumed to have no effect on the gas flow in this study. More sophisticated modeling, coupled with an experimental program (including microscopic studies), is required to resolve the effects of these issues that have been identified describing gas and liquid flow in the grout material.

3.5.2 Concrete

Concrete in regions such as the vault walls is characterized by micropore structure between solid regions similar to grout. However, the pore regions are assumed to have a low-degree saturation of unbound liquid due to ample drying time of the vault and its structures. The flow of gases through these materials is expected to be characterized by a high permeability (Atkinson et al. 1988). This high permeability will prevent high pressure gradients and associated stresses in the grout material. The compressive and tensile strength of concrete is higher than that of grout. The pressure buildup from gas migration is expected to be below the level that would cause microfractures in the concrete.

3.5.3 Asphalt

The permeability of gas flow in asphalt has not been fully quantified. Diffusion of gas in the asphalt is very low. However, the permeability is influenced significantly by the density of open and interconnected pores that may exist in the asphalt. If the open porosity is high enough to result in significant interconnection, then the permeability may be adequate to allow the flow of gases generated in the vault directly through the barrier during phase III without the need for special vent tubes.

3.5.4 Elastomer Barrier

An elastomer barrier is coated on the floor and inside walls of the concrete vault. This material is assumed to be a partial barrier to the diffusion flow of gases generated in the grout. However, the elastomer is assumed to be an effective barrier to liquid flow. The elastomer barrier will cause a preference of liquid flow towards the top of the vault because it is a flow path of least resistance. The elastomer barrier is assumed in the calculations to prevent the two-phase advection flow of liquid and gases from the bottom and sides of the grout block. A partial flow of liquid and gas through the elastomer barrier will not significantly affect the results.

3.6 TEMPERATURE DISTRIBUTION

A temperature of 60 °C was assumed as a steady-state temperature for the calculations. The short time periods during filling when temperatures are high because of the heat of hydration do not significantly affect the results of this study. A design temperature limit of 90 °C during the pouring stage was assumed. The steady-state temperature and its spatial profile may be an important factor in follow-on calculations using more sophisticated modeling. These models should include the driving force of temperature or liquid vapor pressure due to heat generated by radioactive materials during phases II and III.

3.7 HYDROGEN TRANSPORT MECHANISMS

3.7.1 Grout Material

Two mechanisms of gas release from the grout material are diffusion and advection. Diffusion is caused by the kinetic motion of molecules in a host material that results in that molecule mixing without movement of the material it is in. Flow of molecules occurs if a difference in concentrations exists that promotes flow in the direction of lesser concentrations. Advection is a two-phase flow of gas and liquid through the interlocking pores of the grout that is driven by a pressure gradient. The pressure gradient is determined by pressures of bubbles formed throughout the grout material that displace liquid.

The diffusion of hydrogen and other gases were modeled for the reference gas generation rate using the corresponding diffusion coefficients representing liquid in the grout pores. This model is documented (Watson 1993) and is described in Appendix B. The release of hydrogen by diffusion alone is slow in the saturated grout. The release of hydrogen by diffusion alone does not satisfactorily account for mass balance and pressure equilibrium for the level of gas generation produced by radiolytic formation. The chemical pressures of dissolved gas would become unreasonably high if diffusion were the only mechanism of gas release from the large grout block. A two-phase advection mass flow of liquid and gases driven by pressures from gas formation and displacement better explains pressure release and gas flow.

The liquid involved is that fraction of liquid not bound to the matrix by chemical or capillary forces. The displacement of the liquid is caused by the formation of gas bubbles throughout the grout whose pressures are equalized by the flow resistance of the liquid.

To determine the time history of gas concentrations in the grout disposal facility, an engineering model was devised to make these calculations. This model is documented (Watson 1993) and is described in Appendix D.

The radiolytic production of gases (H_2 , N_2O , and O_2) in the grout liquid-filled pore spaces continually build up their solution concentrations until the pressure of these dissolved gases exceeds the hydrostatic pressure of the earth fill and concrete overburden and grout liquid column. When this overpressure is reached, bubbles of gas form in the grout liquid that displace

liquid volume. The displacement of liquid may cause a flow of unbound liquid toward the top of the grout block. Both pore liquid, small gas bubbles, and dissolved gases will flow out of the grout. Fracturing of pore volumes by pressure gradients may likely occur (see Section 3.5.1), thus fracturing will reduce flow resistance and may affect the level of gas release. This effect was included in the present model by assuming a pore size of 10 micron instead of anticipated sizes of 0.1 micron (Harris 1992). This assumption will increase the rate of gas release, which is conservative. Liquid flow will continue until the production of gas diminishes, because of the decay of radioactive materials, to insignificant levels. A fraction of the generated gas will remain in the voided volume of the grout after significant gas generation has stopped. Beyond this time, a small quantity of this gas fraction will slowly diffuse through the vault walls and floor. The flow resistance of gas diminishes as the liquid volume decreases in the grout block. Higher generation rates will result in higher quantities of liquid being expelled and higher flow rates for gas.

The release of gas from the grout block is associated with comparatively high diffusion rates and lower advection rates for low initial gas generation rates. This permanent holdup fraction of gas in the grout material is also high for the low initial gas generation rates. For high initial gas generation rates, the gas diffusion is less significant, while the gas advection rate is high and the permanent gas holdup fraction is lower.

In the calculations of liquid loss, we assumed that the gas pressure may force up to 50% of the unbound liquid out of the grout matrix before the gases can flow freely. During the liquid voidance process, the liquid flow rate is governed by Darcy's Law modified to include surface tension forces. A detailed description of this mechanism is provided in Appendix B.

Another reference (Harris et al. 1992) has postulated the mechanism of advection and provided references to observations of this effect. A quote from page 157 of this report states "At sufficient excess internal pressure difference the gas should be able to expel a proportion of the pore water from the porosity of even fully-saturated material, allowing migration in what is effectively a small volume fraction of open porosity. This effect has been observed in other porous materials, in particular compressed bentonites, where 'critical' pressures of the order of 100K Pa to 2.4 MPa have been measured IAEA (1990) and Pusch et al. (1985). Under such conditions, the migration will in reality be a two-phase flow."

3.7.2 Facility Spaces

The release of hydrogen and other gases from the grout were modeled as diffusion through the side and bottom surfaces of the grout block and as advection through the top of the grout block. During the phase I filling stage, the release of gases is directly into the vault vapor space, the vault sides, and into the catch basin. The gases entering the vapor space will be isolated from the catch basin by ventilation removal. Gases will enter the catch basin only from diffusion through the vault sides and bottom during phase I.

During the phase II surveillance period, the flow path of gases will be by advection from the top of the grout block surface to the outer vault wall regions by a path through the vault ceiling. A diffusion flow will go from the grout into the vault sides and catch basin. The cold cap is a substantial barrier to diffusion flow of gas due to its thickness of saturated liquid which separates the source term. It will virtually stop diffusion flow from the top of the grout block. During this phase, the sump vent is open to the atmosphere so the generated gas will flow from the top of the grout block and diffuse down the vault sides into the catch basin, through the drain line, into the sump and to the atmosphere through the vent. An outside air mixing in the 26-in.-diameter vent pipe of the sump is included in the calculation. The driving force of this mixing is atmospheric pressure variations. Other potential mixing mechanisms such as temperature variation and winds were not considered. Buoyancy effects are not considered because the mixture of gases released from the grout block is slow when compared to diffusion mixing and its density is close to or greater than the density of air (see Appendix C).

During the phase III final-closure period, the sump compartment volume and vent will be filled in with grout. The two filtered vents penetrating the asphalt diffusion barrier near the leachate catch basin will be the only direct-release paths to the soil. The mass flow of gas will flow out this path to the soil. The source of gases from the grout are the same as those described during phase II. Diffusion of hydrogen and other gases at the top opening of the catch basin will enter the catch basin and migrate to the sump volume by the drain line in these stagnant volumes. A contingency calculation was run assuming that these vents are closed and that the effects of concentration and pressure will be determined in relation to the material permeability of the asphalt diffusion barrier. The results of this calculation are discussed in Chapter 5.0.

3.7.3 Asphalt

The calculations of gas flow and mixing in the compartments allow no flow through the asphalt diffusion barrier. One potential mechanism that can allow gas to flow through the asphalt after final closure is by permeation. Permeation is a fluid flow driven by pressure difference through a porous material. The ability of gas flow is described in units of permeability which depends on the density and interconnection of gas-filled pores in the asphalt. Measurements of asphalt permeability have been conducted by Pacific Northwest Laboratory to determine representative levels in the asphalt. This mechanism will be feasible if adequate open porosity exists in the installed asphalt. A sensitivity study (Section 5.5) identifies the relationship of permeabilities and internal pressure of the grout regions.

3.8 BEST-ESTIMATE VALUES

The objective of this study was to conduct a reference calculation of time-dependent concentrations of hydrogen and nitrous oxide based on best-estimate values of production rates and material properties which affect these results.

The preferred properties are derived from direct measurements made with materials that are unique to the grout disposal facility. Properties not available from direct measurement are estimated from a review of the literature. In these cases, estimates of uncertainty are made. The sensitivity study in Chapter 5.0 presents the impact on the results and the design justification. From these considerations, the need for further properties data will be determined.

The data used in the reference calculation are documented in Table 3-2. The references and uncertainties of these data are included in this summary.

Table 3-2. Data Used in Reference Calculations.

Item	Description	Best estimate	Estimated range of variation	Reference
1	Hydrogen generation	0.012 g mol/h	0.012 to 0.65	Friedman 1985
2	Nitrous oxide generation	0.031 g mol/h	0.031 to 0.65	Friedman 1985
3	Oxygen generation	0.0 g mol/h	0.00 to 0.20	Friedman 1985
4	Grout temperature	60 °C	NA	
5	Compartment atmosphere temperature	16 °C	NA	
6	Grout hydrogen advective permeability a. wet b. dry	1.0 E-20 cm ² 2.5 E-11 cm ²	2.5 E-12 to 2.5 E-10	Atkinson 1988
7	Grout liquid content in pores a. Total liquid volume b. Capillary (bound) c. unbound	64% 32% 32%	20. to 40%	
8	Gas diffusivity in wet grout	H ₂ = 1.15 E-5 cm ² /s N ₂ O = 2.46 E-6 cm ² /s O ₂ = 2.89 E-6 cm ² /s	5.76 E-6 to 2.30 E-5 1.23 E-6 to 4.93 E-6 1.45 E-6 to 5.78 E-6	Atkinson 1988
9	Henry's Law coefficients H ₂ = N ₂ O = O ₂ =	84.6 ^a 6.19 ^a 100.8 ^a		International Critical Tables
10	Gas diffusivity in dry concrete	H ₂ = 9.50 E-4 H ₂ O = 1.90 E-4 O ₂ = 2.54 E-4	NA NA NA	Atkinson 1988

^a Henry's coefficients were based on 92%, 97%, and 145% above levels in pure water due to dissolved salts for hydrogen, nitrous oxide, and oxygen, respectively.

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4.0 - MODEL RESULTS

The results of gas modeling require consideration of the following two problems: (1) to model the gas released from the grout block, and (2) to determine the gas transport and time-dependent gas concentrations in the compartments of the grout disposal facility. The release rate of gases from the grout block is required input for the second problem of transport and region buildup. The release rate of gases from the grout block is also needed to establish a basis for specifying and evaluating mitigation system designs if they are required.

4.1 GAS RELEASE FROM GROUT BLOCK

The release of hydrogen and other gases from the grout block involves a combination of established mechanisms to model. The mechanism of diffusion can only explain partial amounts of gas release from the grout block. Diffusion alone does not account adequately for the levels of gas release from the grout block or relief of dissolved gas pressure for the levels of radiolytic gas formation rates encountered by this study. The mechanism of advection described in Appendix B involves a model that approximates a two-phase flow of liquid and gas from the grout block. The driving force of this flow is the displacement of liquid by gas bubbles formed uniformly throughout the grout block. A calculational model that characterized this gas release mechanism is described also in Appendix B.

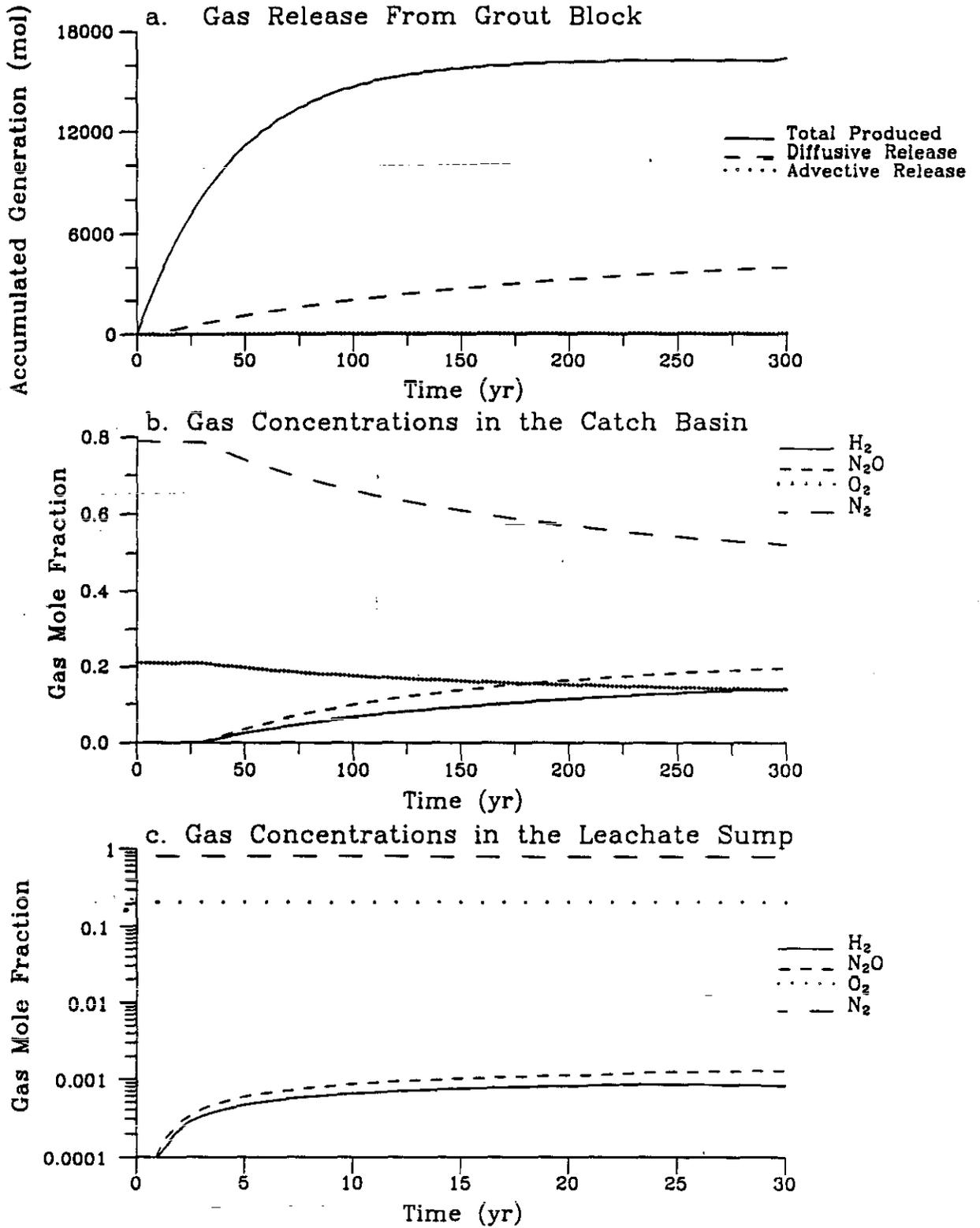
4.1.1 Reference Case Calculation (Case A)

The reference case calculation was based on the best estimate values of gas generation and material property data involving the combined release by diffusion and advection. The following cases B, C, and D use these best-estimate gas generation rate, but show the individual gas migration effects of no gas holdup, diffusion, and advection, respectively.

If the total formation of gases is below a threshold level which is described in Section 5.4.2, a significant quantity of hydrogen and other gases will be retained permanently in the grout block. These retained gases will not contribute to a potential safety problem because there is no method of flammability in the grout block. Due to radioactive decay, the production rate of gas decreases with time and a finite quantity of gas will be generated. In the case of the reference calculation (Case A), the total gas production volume at 1 atmosphere pressure is 6.8% of the total grout volume. This volume of gas will displace only a fraction of the unbound liquid. The results showing gas release by advection and diffusion from the grout block are illustrated in Figure 4-1, part a. A summary of the gas release from the grout block is listed in Table 4-1, part a.

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Figure 4-1. Gas Release from Grout Block and Compartment Concentrations--
Reference Case (Case A) (29% H₂, 71% N₂O, 0% O₂).
(Initial Gas Generation Rate 0.043 mol/h.)



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Table 4-1. Gas Release from Grout Block and Compartment Concentrations--
 Reference Case (29% H₂, 71% N₂O, 0% O₂).
 (Initial Gas Generation Rate 0.043 mol/h.)
 (sheet 1 of 2)

a. Summary of Gas Release from Grout Block

Case description	Advection start time (yr)	Total gas release ^a					
		Diffusion (mol)			Advection (mol)		
		H ₂	N ₂ O	O ₂	H ₂	N ₂ O	O ₂
Reference (diffusion & advection with holdup)	22	1.7 E+3	2.3 E+3	*--	2.2 E+1	5.9 E+1	2.2 E+0
Comparison (no holdup)	0.0	0	0	0	4.7 E+3	1.2 E+4	0
Diffusion only	N/A	1.7 E+3	2.4 E+3	*--	0	0	0
Advection only	20	0	0	0	4.7 E+1	1.2 E+2	3.4 E+0

*Diffusion O₂ was slightly negative due to model of gas concentrations and vapor pressure of liquid.

b. Compartment Gas Concentrations Versus Time--Reference Case (Case A).

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.1 E-3	1.4 E-3	2.1 E-1	7.9 E-1	6.5 E-4	8.6 E-4	2.1 E-1	7.9 E-1
30	1.4 E-3	2.1 E-3	2.1 E-1	7.9 E-1	8.3 E-4	1.3 E-3	2.1 E-1	7.9 E-1
100	6.6 E-2	9.8 E-2	1.8 E-1	6.6 E-1	--	--	--	--
200	1.1 E-1	1.6 E-1	1.5 E-1	5.7 E-1	--	--	--	--
300	1.4 E-1	2.0 E-1	1.4 E-1	5.2 E-1	--	--	--	--

^aaccumulated releases at 300 years.

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Table 4-1. Gas Release from Grout Block and Compartment Concentrations--
Reference Case (29% H₂, 71% N₂O, 0% O₂).
(Initial Gas Generation Rate 0.043 mol/h.)
(sheet 2 of 2)

c. Compartment Gas Concentrations Versus Time--Comparison Case (Case B).

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.0 E-2	2.8 E-2	2.0 E-1	7.6 E-1	6.3 E-3	1.8 E-2	2.1 E-1	7.7 E-1
30	6.6 E-3	1.8 E-2	2.1 E-1	7.7 E-1	4.0 E-3	1.1 E-2	2.1 E-1	7.8 E-1
100	1.6 E-1	3.9 E-1	9.6 E-2	3.6 E-1	--	--	--	--
200	1.8 E-1	4.4 E-1	8.1 E-2	3.0 E-1	--	--	--	--
300	1.8 E-1	4.4 E-1	7.9 E-2	3.0 E-1	--	--	--	--

d. Compartment Gas Concentrations Versus Time--Diffusion Case (Case C).

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.1 E-3	1.4 E-3	2.1 E-1	7.9 E-1	6.5 E-4	8.6 E-4	2.1 E-1	7.9 E-1
30	1.4 E-3	2.0 E-3	2.1 E-1	7.9 E-1	8.1 E-4	1.2 E-3	2.1 E-1	7.9 E-1
100	6.4 E-2	9.5 E-2	1.8 E-1	6.7 E-1	--	--	--	--
200	1.1 E-1	1.6 E-1	1.5 E-1	5.8 E-1	--	--	--	--
300	1.4 E-1	2.0 E-1	1.4 E-1	5.3 E-1	--	--	--	--

e. Compartment Gas Concentrations Versus Time--Advection Case (Case D).

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	0	0	2.1 E-1	7.9 E-1	0	0	2.1 E-1	7.9 E-1
30	5.9 E-5	1.6 E-4	2.1 E-1	7.9 E-1	3.5 E-5	9.9 E-5	2.1 E-1	7.9 E-1
100	3.6 E-3	8.8 E-3	2.1 E-1	7.8 E-1	--	--	--	--
200	4.8 E-3	1.2 E-2	2.1 E-1	7.8 E-1	--	--	--	--
300	5.0 E-3	1.2 E-2	2.1 E-1	7.8 E-1	--	--	--	--

H₂ = Hydrogen
 N₂O = Nitrous oxide
 O₂ = Oxygen
 mol = Moles
 Mol = Moles
 mol/h = Moles per hour
 yr = Years

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4.1.2 Comparison Calculation (Case B: No Holdup)

A comparison calculation was performed to demonstrate the impact of having no holdup of gases in the grout block. This calculation does not represent a realistic case. The release of gas from the grout block is shown in Figure 4-2, part a. A summary of the gas release from the grout block is listed in Table 4-1, part a.

4.1.3 Intermediate Mechanisms Calculation (Cases C and D)

Two calculations were performed to show the isolated effects of diffusion and advection of gas flow. This source of diffusion through the sides and bottom of the grout block (Case C) are shown in Figure 4-3. The advection source of gases from the top of the grout block (Case D) are shown in Figure 4-4. A summary of the gas release from the grout block for these cases is listed in Table 4-1, part a.

These intermediate calculations do not represent a realistic case. They are included in this report to demonstrate the independent effects of these source mechanisms.

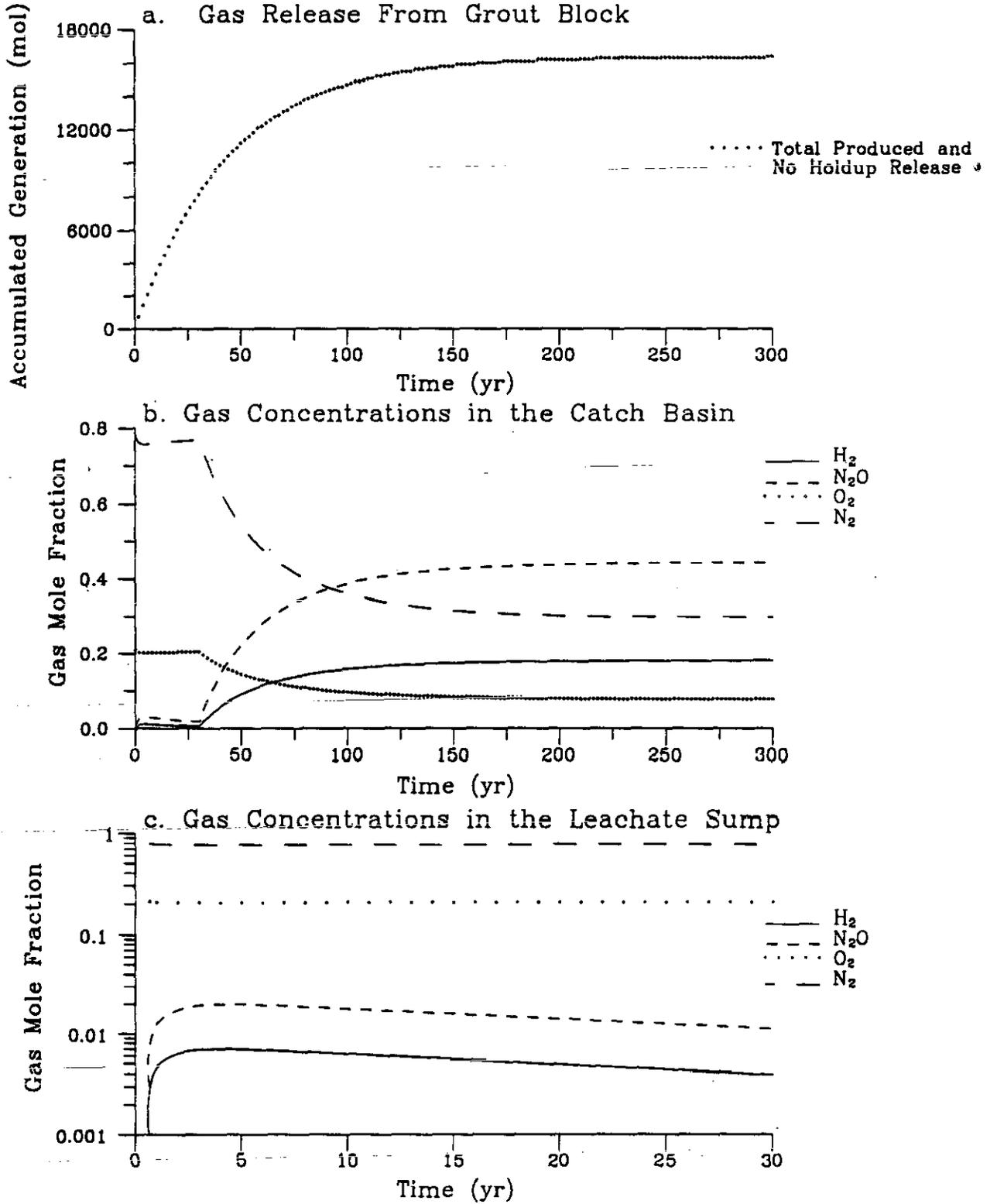
4.1.4 Release of Gas into Vault Vapor Space

A calculation was made of the gas release into the unfilled portion of the grout vault to be applied to the vault vapor volume during the phase-I filling. This release rate is shown in Figure 4-5, part a. A summary of the gas released is listed in Table 4-2, part a. This calculation, based on the minimum free volume in the vapor space, provides the most conservative gas concentration levels. The calculation of this release is given in Appendix B. After the cold cap is applied, only gas flow by advection will occur in the vertical direction. Potential diffusion through the extra 4 ft of grout on top of the grout block will be virtually stopped by the high resistance to diffusion of the cold cap that has no formation source of gases. However, diffusion through the floor and sides of the vault will occur. This diffusion source has been included in the other calculations in this section.

4.2 GAS CONCENTRATIONS IN GROUT DISPOSAL FACILITY REGIONS

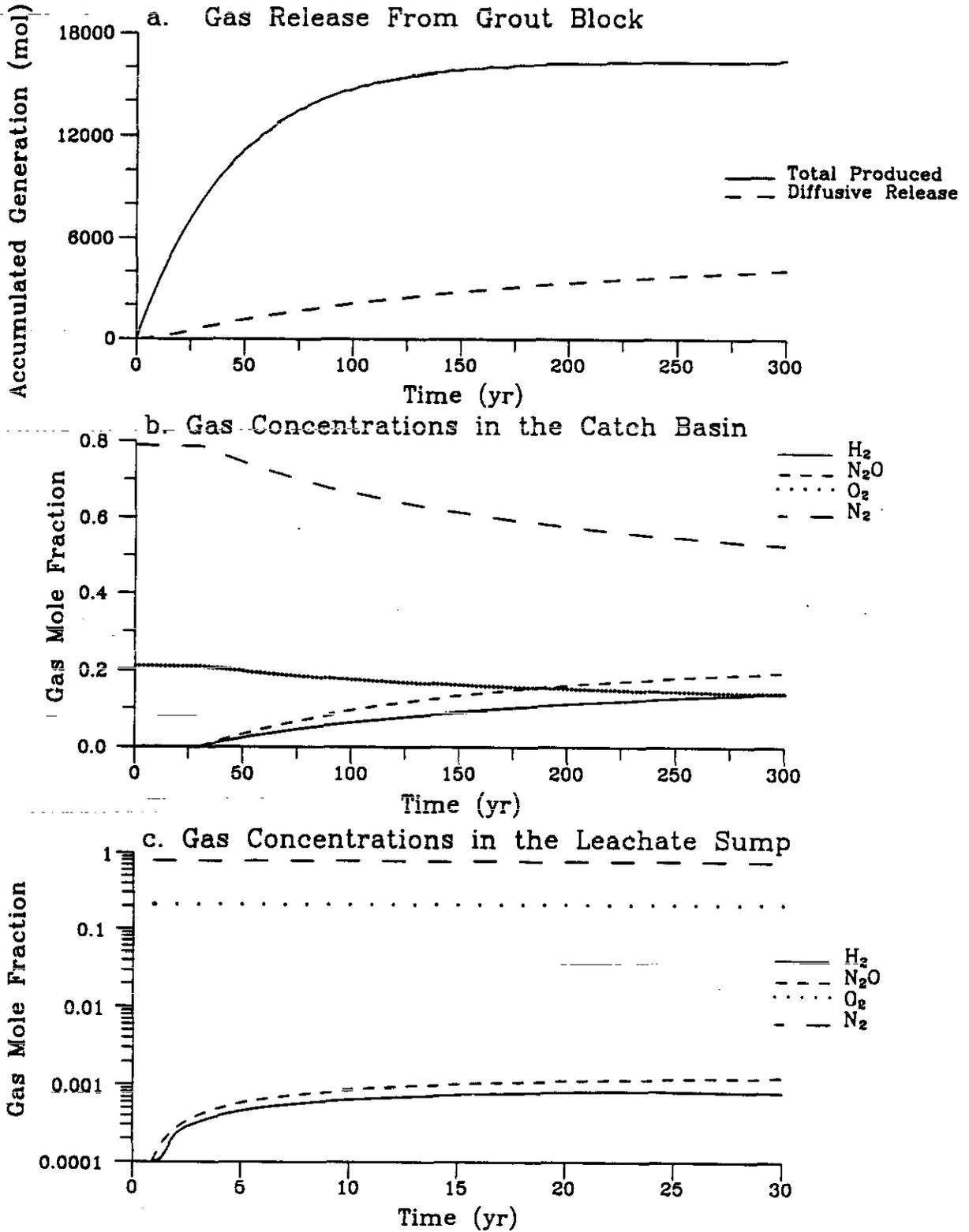
The gas release rates described in Section 4.1 were used as input into models producing time-dependent concentrations of the grout regions. The regions were assumed to be air-filled before grout filling with oxygen and nitrogen concentrations of 21 vol% and 79 vol%, respectively. An engineering calculational model (see Appendix D) was set up to calculate the following: (1) time-dependent concentrations of hydrogen, nitrous oxide, oxygen, and nitrogen in the vault vapor space during phase I operation, and (2) catch basin and leachate sump volumes during phase I, phase II, and phase III operation. This model accounts for the gas diffusion, and the exchange rate of outside air driven by atmospheric pressure variation (Garfield 1975). It

Figure 4-2. Gas Release from Grout Block and Compartment Concentrations--
 (Case B: No Holdup) (29% H₂, 71% N₂O, 0% O₂).
 (Initial Gas Generation Rate 0.043 mol/h.)



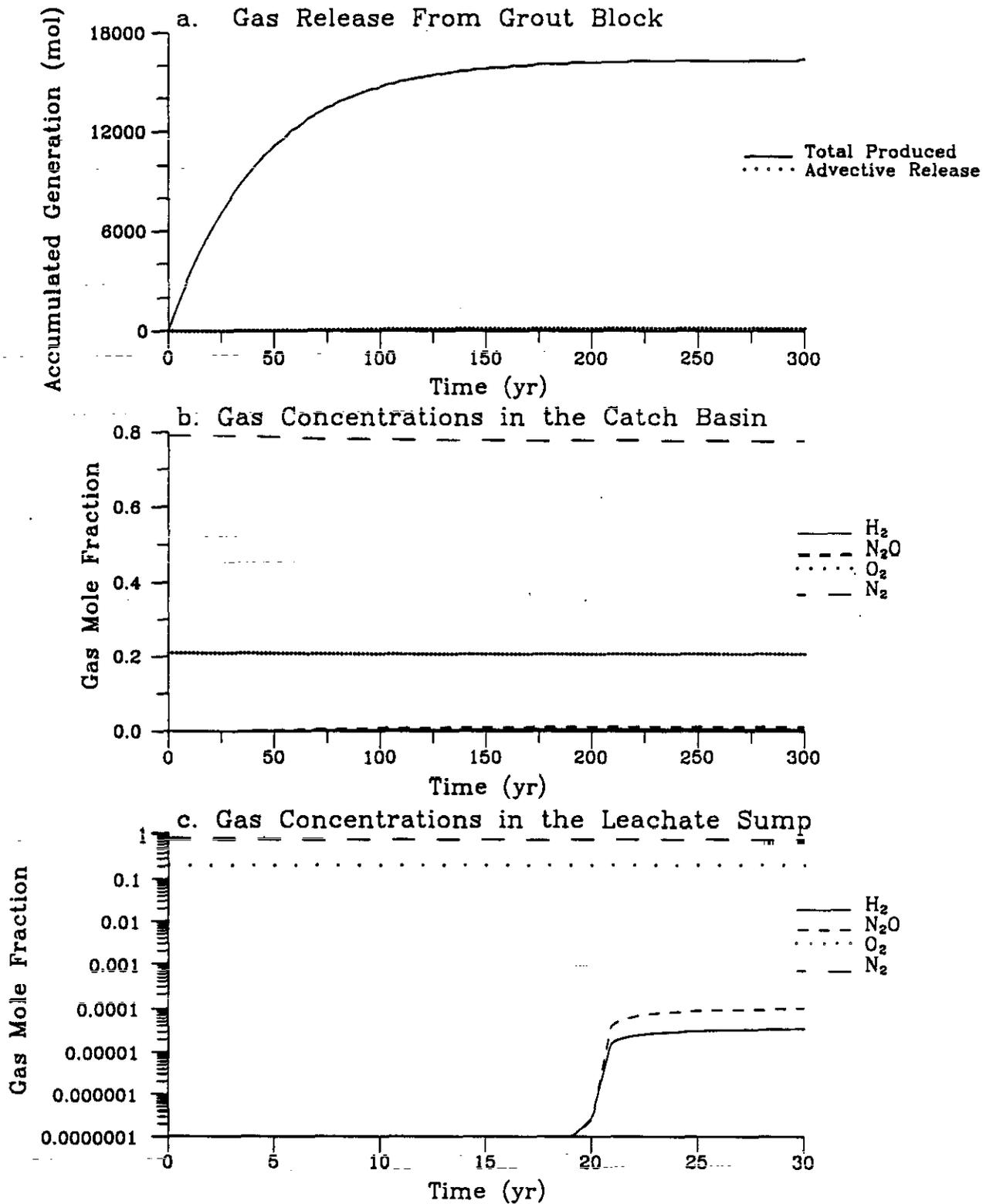
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Figure 4-3. Gas Release from Grout Block and Compartment Concentrations-- Diffusion-Only Case (Case C) (29% H₂, 71% N₂O, 0% O₂). (Initial Gas Generation Rate 0.043 mol/h.)



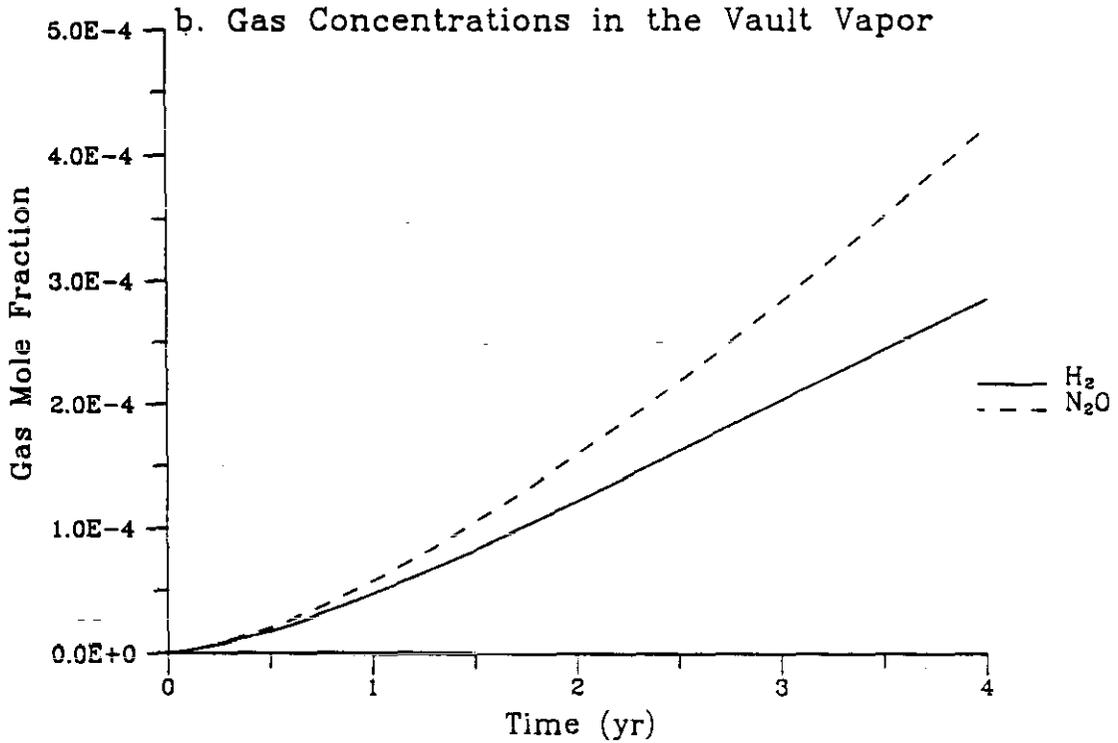
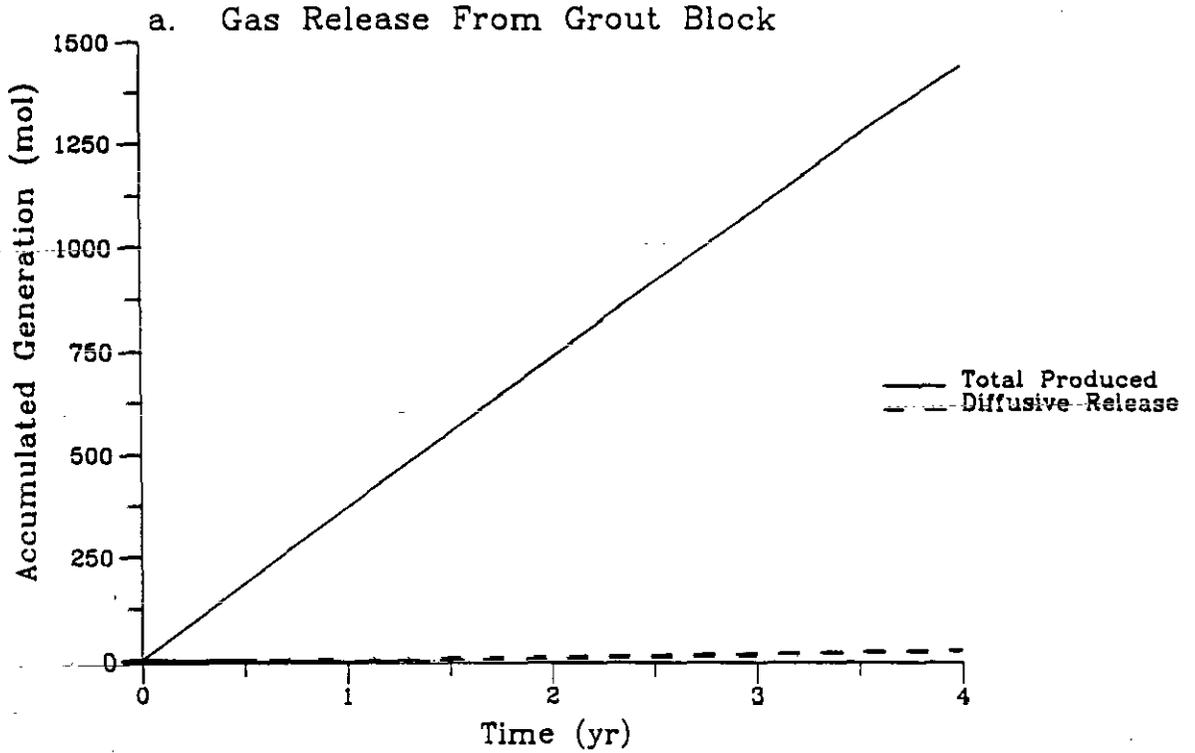
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Figure 4-4. Gas Release from Grout Block and Compartment Concentrations--
 Advection-Only Case (Case D) (29% H₂, 71% N₂O, 0% O₂).
 (Initial Gas Generation Rate 0.043 mol/h.)



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Figure 4-5. Gas Release Source Term Rate and Compartment Concentrations--
Reference Case (Case A) (29% H₂, 71% N₂O, 0% O₂).
(Initial Gas Generation Rate 0.043 mol/h.)



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Table 4-2. Gas Release from Grout Block and Vault Vapor Space Concentrations--Reference Case (Case A)(29% H₂, 71% N₂O, 0% O₂). (Initial Gas Generation Rate 0.043 mol/h.)

a. Gas Release from Top Surface of Grout Block

Time (yr)	Accumulated gas release (mol)		
	H ₂	N ₂ O	O ₂
0.1	5.0 E-2	5.7 E-2	-6.6 E-1
0.2	1.4 E-1	1.6 E-1	-9.4 E-1
0.4	4.0 E-1	4.5 E-1	-1.3 E+0
1.0	1.6 E+0	1.8 E+0	-2.1 E+0
2.0	4.4 E+0	5.0 E+0	-3.0 E+0
4.0	1.2 E+1	1.4 E+1	-4.2 E+0

b. Vapor Space Gas Concentrations Versus Time--Reference Case (Case A).

Time (yr)	Vault vapor space (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂
0.1	1.7 E-6	1.9 E-6	2.1 E-1	7.9 E-1
0.2	4.6 E-6	5.3 E-6	2.1 E-1	7.9 E-1
0.4	1.3 E-5	1.5 E-5	2.1 E-1	7.9 E-1
1.0	4.8 E-5	5.8 E-5	2.1 E-1	7.9 E-1
2.0	1.2 E-4	1.6 E-4	2.1 E-1	7.9 E-1
4.0	2.9 E-4	4.2 E-4	2.1 E-1	7.9 E-1

does not model buoyancy effects of hydrogen because the mixture of hydrogen and nitrous oxide is near or heavier than the density of air (see Appendix C), and the slow rate of gas entry into a region will allow complete mixing by diffusion.

4.2.1 Grout Vault Compartments Gas Concentrations

The time-dependent concentrations of the gas from the reference case (case A) in the catch basin and leachate sump, are given in Figure 4-1, parts b and c, respectively, for all phases of operation. These cases are for the catch basin and leachate sump with holdup of gas in the grout block. These concentrations also are listed in Table 4-1. part b.

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The comparative case for nonholdup of gas release (case B) in the grout block is also considered as an extreme example of compartment concentration buildup. The results of this calculation are shown in Figure 4-2, parts b and c for the catch basin and leachate sump volumes, respectively. These concentrations are also listed in Table 4-1, part c.

The calculations of the compartment gas concentrations for the intermediate sources for diffusion only (case C) and advection only (case D) are also included. The gas concentrations are shown in Figure 4-3, parts b and c for the catch basin and leachate sump, respectively, for the diffusion-only calculation. The gas concentrations are shown in Figure 4-4, parts b and c for the catch basin and leachate sump, respectively for the advection-only case. At the gas generation rates for this case, advection is very low and retention of gases in the grout material is high. The concentrations in the catch basin and leachate sump is very low for this case.

4.2.2 Vault Vapor Space Gas Concentrations

The results of the time-dependent concentrations for the reference case (case A) are given in Figure 4-5, part b and Table 4-2, part b for the vault vapor space during phase I. These results indicate very little gas release and very low concentrations during this time. No supplemental ventilation was assumed for these calculations.

4.3 HYDROGEN MITIGATION

Hydrogen mitigation or flammability control may be needed in the catch basin. It is apparent from the results in Section 4.2 that the hydrogen levels will be below the level of concern in the leachate sump. The effectiveness of two mitigation mechanisms, ventilation and a vault diffusion barrier, was investigated.

4.3.1 Ventilation

If required, removal of hydrogen and nitrous oxide by ventilation is the simplest approach to hydrogen control. The source term release rate is less than 0.001 cfm. At this release rate, a ventilation flow of 1 cfm will be adequate to maintain a level of hydrogen and nitrous oxide concentrations below 0.1 vol%.

4.3.2 Gas Diffusion Barrier

The diffusion of gas from the sides and bottom of the vault represents a significant source of hydrogen and nitrous oxide. This source may be eliminated or significantly reduced by placement of a diffusion barrier on the sides and bottom of the grout vault. The case D calculation discussed in Section 4.1.3 represents the situation of a completely effective diffusion barrier.

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4.4 GAS RELEASE TO ENVIRONS

The grout disposal facility design has vent systems which allow release of generated gas to the environs. These release paths are a filtered vent system on the leachate sump compartment and two tubes from the top of the catch basin compartment to the soil. The release of gases from these vent systems are discussed below.

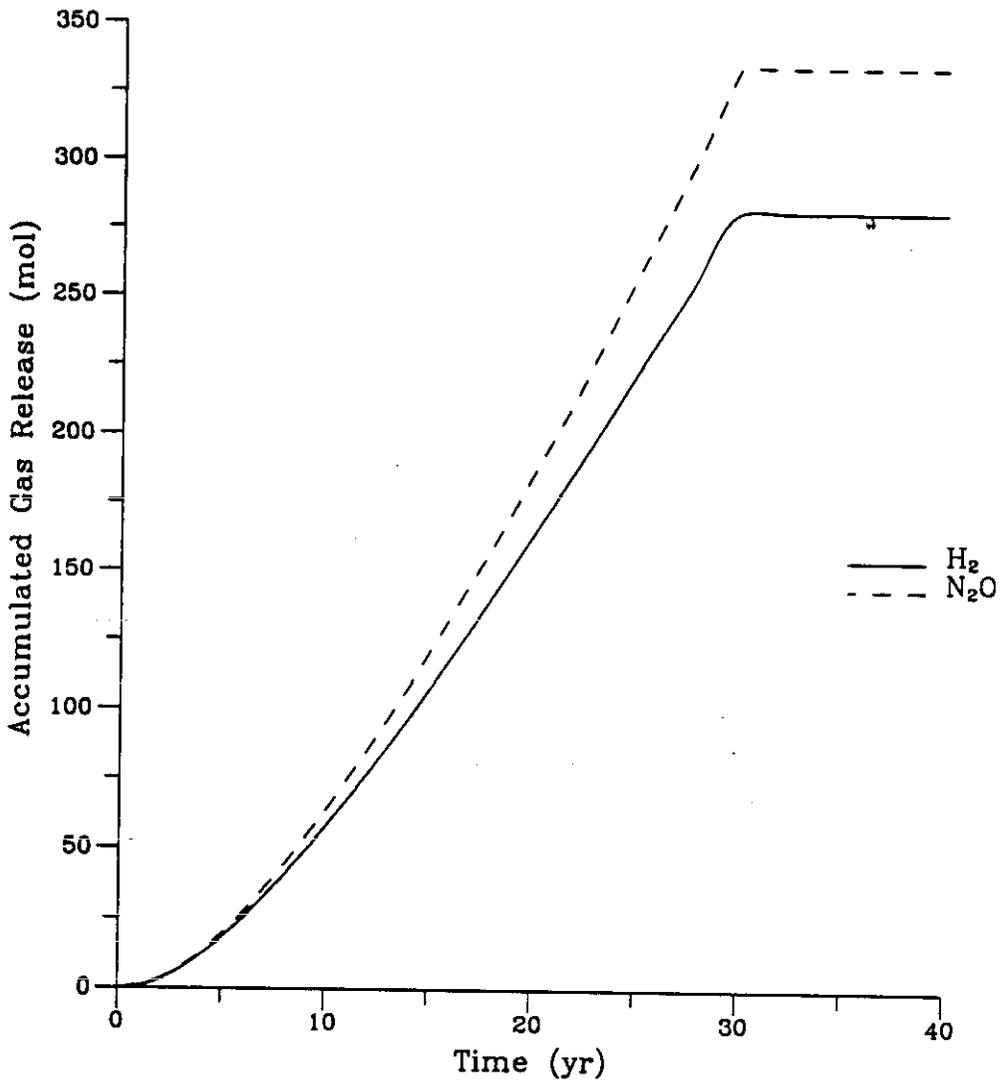
4.4.1 Gas Release to Atmosphere

During phases I and II, the filtered vent in the leachate sump compartment is open to the atmosphere. During this time, part of the hydrogen and nitrous oxide in the leachate sump compartment will be emitted to the atmosphere by diffusion and migration with air flow driven by barometric pressure variations. The exchange rate by diffusion was determined by minimum area and length of pipe from the sump compartment to the outside. These loss mechanisms are adequate to maintain the concentrations of hydrogen and nitrous oxide in the leachate sump to negligible levels. A summary of the gas losses of hydrogen and nitrous oxide from the leachate sump vents to the atmosphere for the reference case (case A) are shown in Figure 4-6 and Table 4-3.

The major driving force for gas release to the atmosphere was determined to be barometric pressure variations.

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Figure 4-6. Gas Release to the Atmosphere.



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Table 4-3. Gas Release from Leachate Sump into the Atmosphere--Reference Case (Case A)
(29% H₂, 71% N₂O, 0% O₂).

(Initial Gas Generation Rate 0.043 mol/h.)

Time (yr)	Accumulated Gas Release (mol)	
	H ₂	N ₂ O
10	5.8 E+1	6.3 E+1
30	2.8 E+2	3.3 E+2

4.4.2 Gas Release to Soil

During phase III, the vents from the leachate sump compartment to the atmosphere is closed. At this time, the flow of excess gas, equal to displacement volume of gas released from the grout block, will flow through the vent tubes in the catch basin to the soil. The flow of these gases for the reference case is shown in Figure 4-7 and Table 4-4.

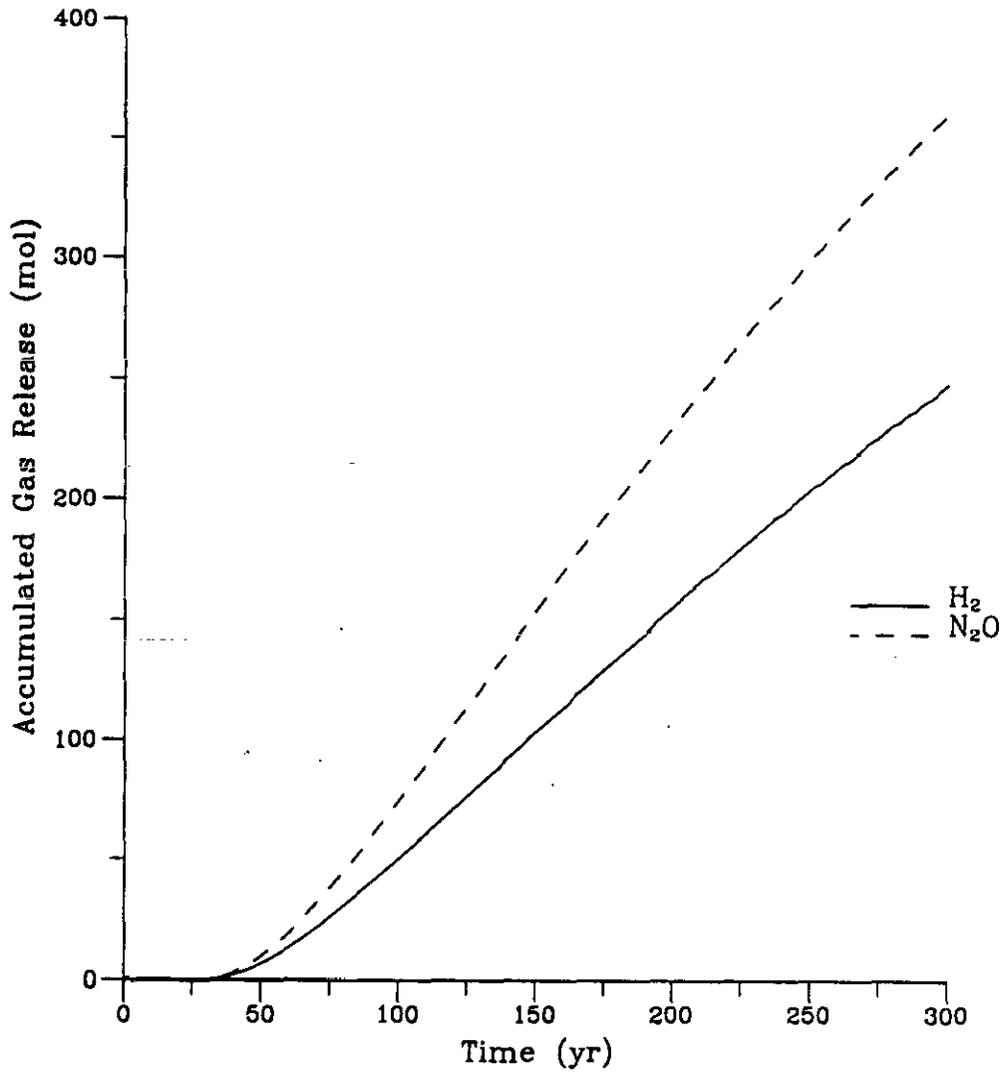
Table 4-4. Gas Release from Catch Basin Vent to Soil--Reference Case (Case A)
(29% H₂, 71% N₂O, 0% O₂)

(Initial Gas Generation Rate 0.043 mol/h.)

Time (yr)	Accumulated Gas Release (mol)		
	H ₂	N ₂ O	O ₂
10	0	0	0
30	0	0	0
100	5.0 E+1	7.4 E+1	2.8 E+2
200	1.6 E+2	2.3 E+2	4.7 E+2
300	2.5 E+2	3.6 E+2	5.7 E+2

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Figure 4-7. Accumulated Gas Release to Soil.



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5.0 SENSITIVITY STUDY RESULTS

The purpose of this sensitivity study is to quantitatively show the impact on the current design of variations in data within established boundary limits. The acceptability of the current design can be evaluated on the basis of these results. If the results exceed limits of acceptability, upgrades in measured data may be made to reduce conservatism and uncertainties.

5.1 RADIOLYTIC GAS GENERATION

The variation in the formation rate of gases by radiolytic decomposition of liquid and other materials has a significant impact on the grout disposal facility design. The range of initial gas generation is bounded by the limits of the reference case and an upper limit case which are discussed in Chapter 3.0. The sensitivity study will show the effects of intermediate levels in this range of initial gas generation rates.

The three gases of interest are hydrogen, nitrous oxide, and oxygen. The magnitude of total gas production in the grout block ranges from 0.043 mol/h for the reference case to 1.3 mol/h for the bounding case. The generation rates for the sensitivity study covered intermediate levels and upper bounds of this gas production range. Three relative gas mixtures were selected for the sensitivity study. These mixtures are based on representative and limiting concentration ranges. The relative gas concentrations of these mixtures are listed in Table 5-1.

Table 5-1. Relative Gas Mixtures in Sensitivity Study.

Gas component	Mixture 1 (%)	Mixture 2 (%)	Mixture 3 (%)
Hydrogen	29	50	43
Nitrous oxide	71	50	43
Oxygen	0	0	14

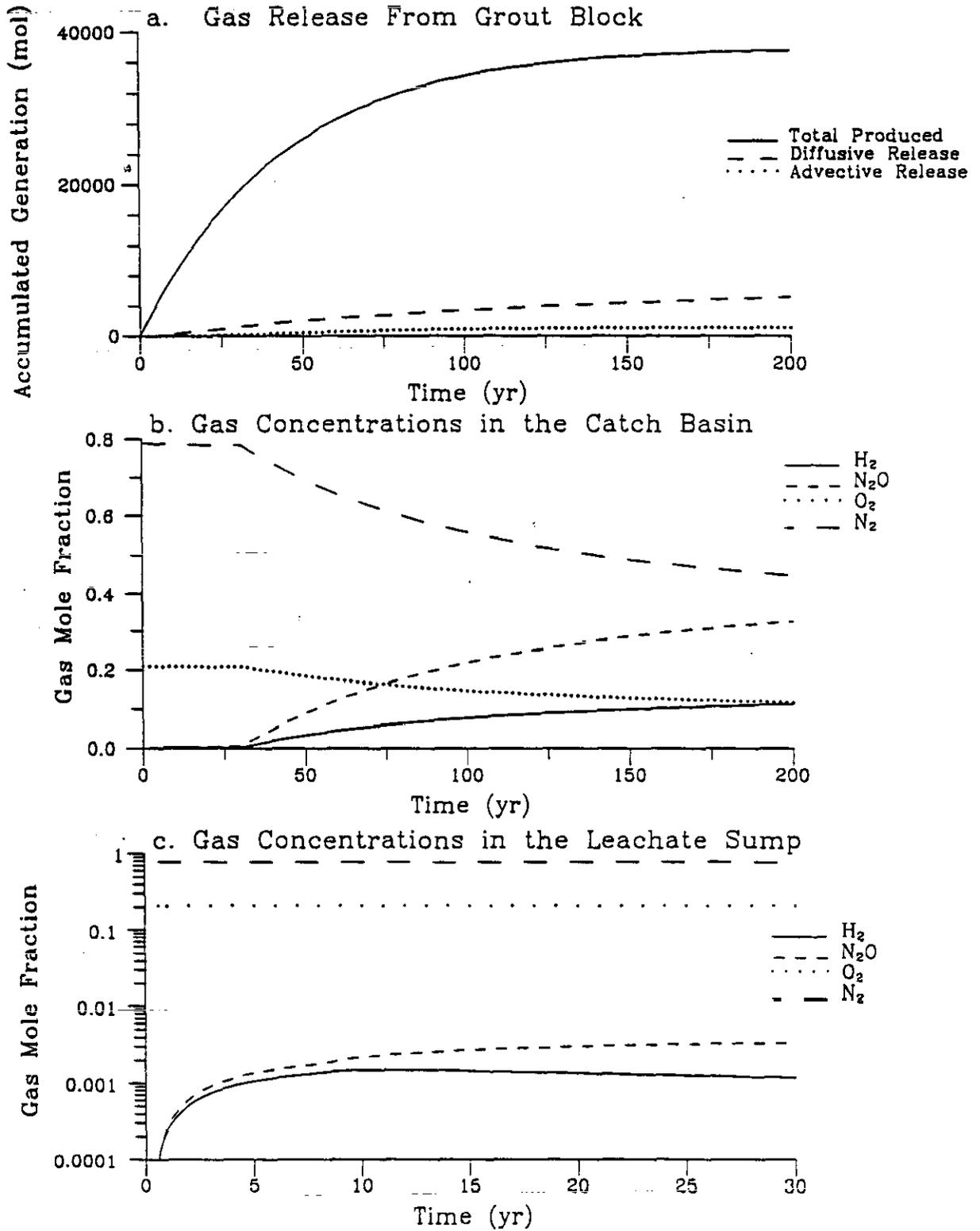
The initial generation rates of 0.1, 0.2, 0.4, 1.0, and 1.4 mol/h for these gases were used in the calculations.

The results of these calculations are shown in a three-part figure for each mixture and formation rate as follow: (1) part A--release rate from the grout block, (2) part B--time-dependent concentrations in the catch basin, and (3) part C--time-dependent concentrations in the leachate sump volume. The corresponding figures for mixture 1 are Figures 5-1 through 5-5. The corresponding figures for mixture 2 are Figures 5-6 through 5-10. The corresponding figures for mixture 3 are Figures 5-11 through 5-15.

The results of these calculations are also listed in the following tables: (1) summary of gas release from grout block for mixtures 1, 2, and 3, in Tables 5-2, 5-3 and 5-4, respectively, and (2) compartment gas concentrations for mixtures 1, 2, and 3 in Tables 5-5, 5-6, and 5-7 respectively.

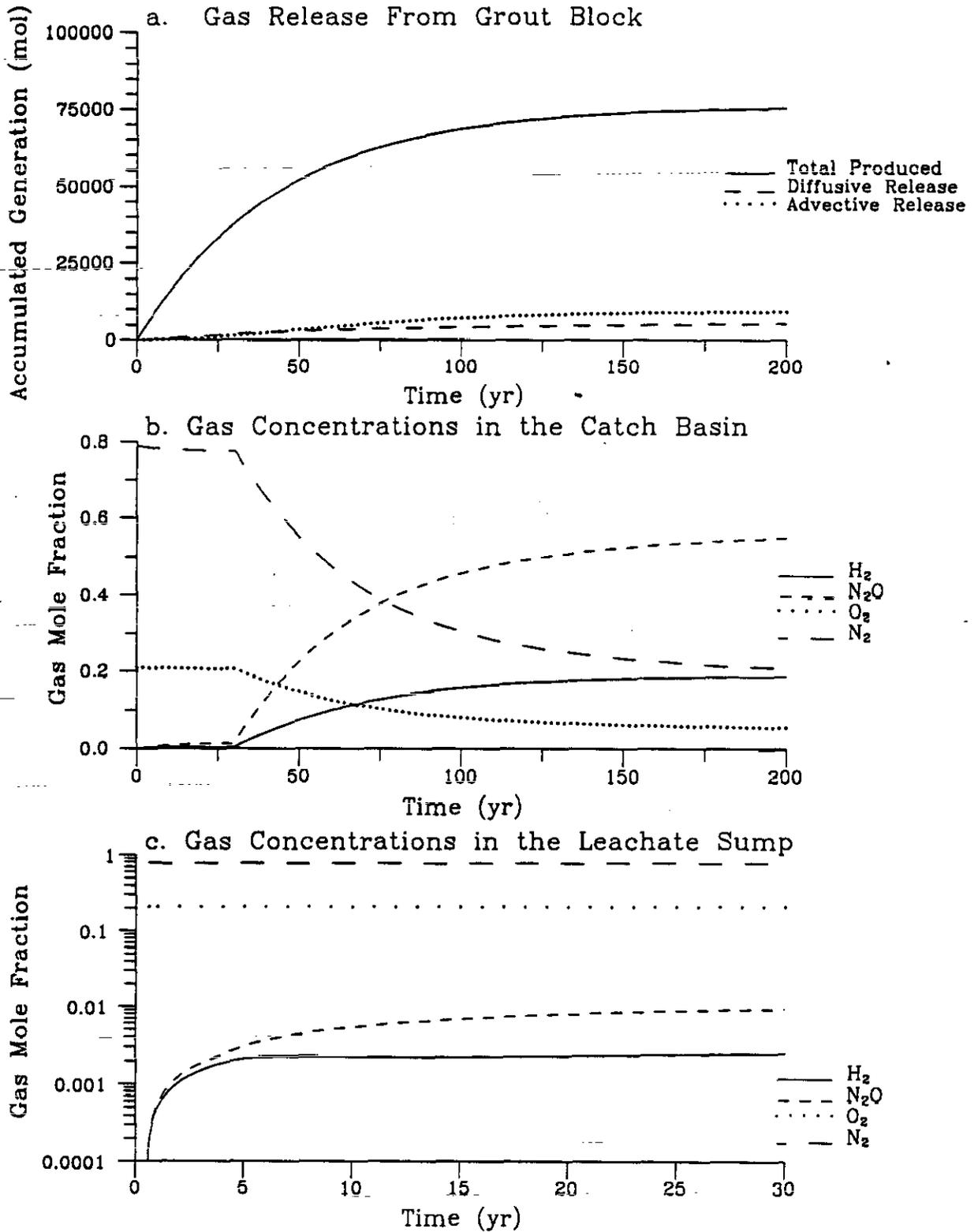
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Figure 5-1. Gas Release Source Term and Gas Concentrations--Mixture 1.
(Initial Gas Generation Rate = 0.1 mol/h.)



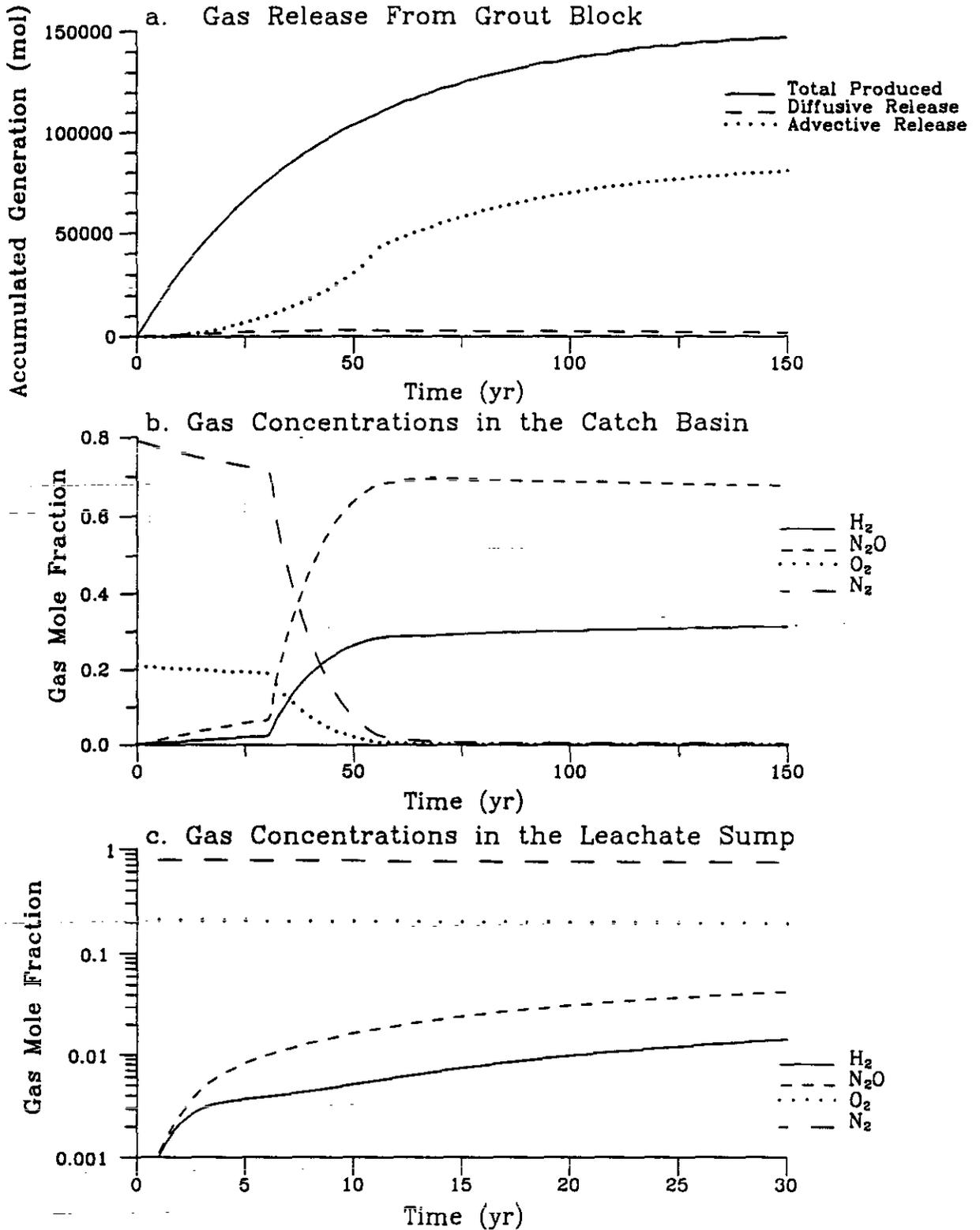
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Figure 5-2. Gas Release Source Term and Gas Concentrations--Mixture 1.
(Initial Gas Generation Rate = 0.2 mol/h.)



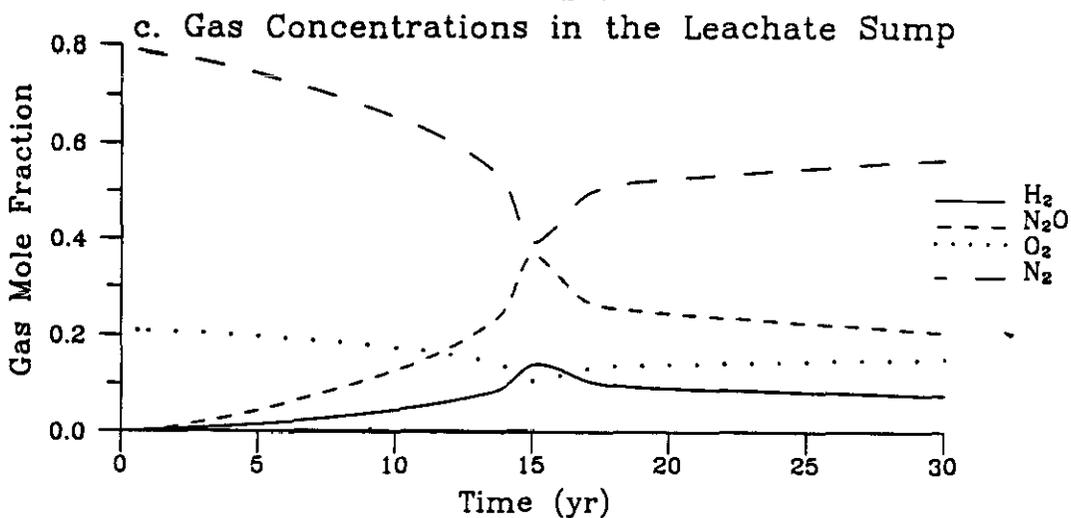
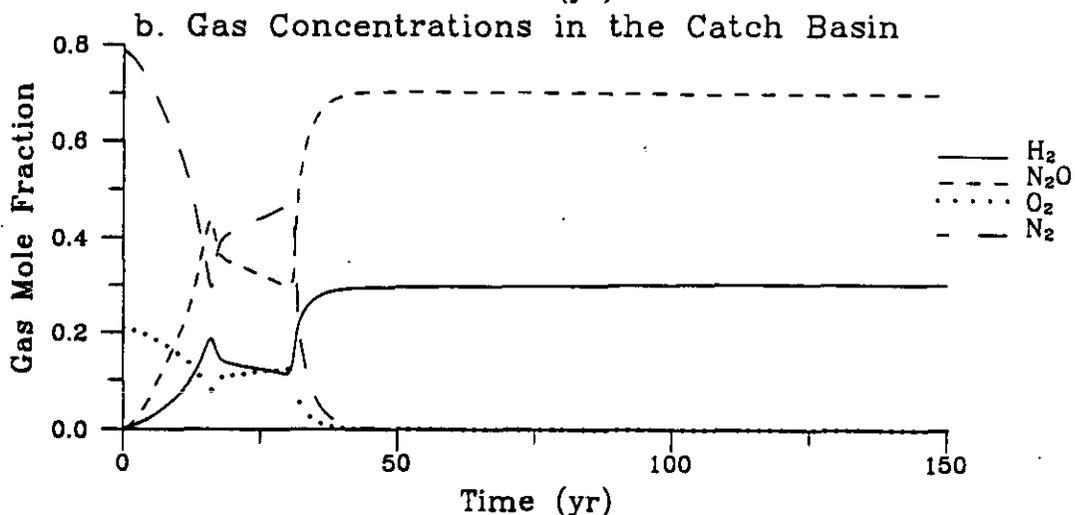
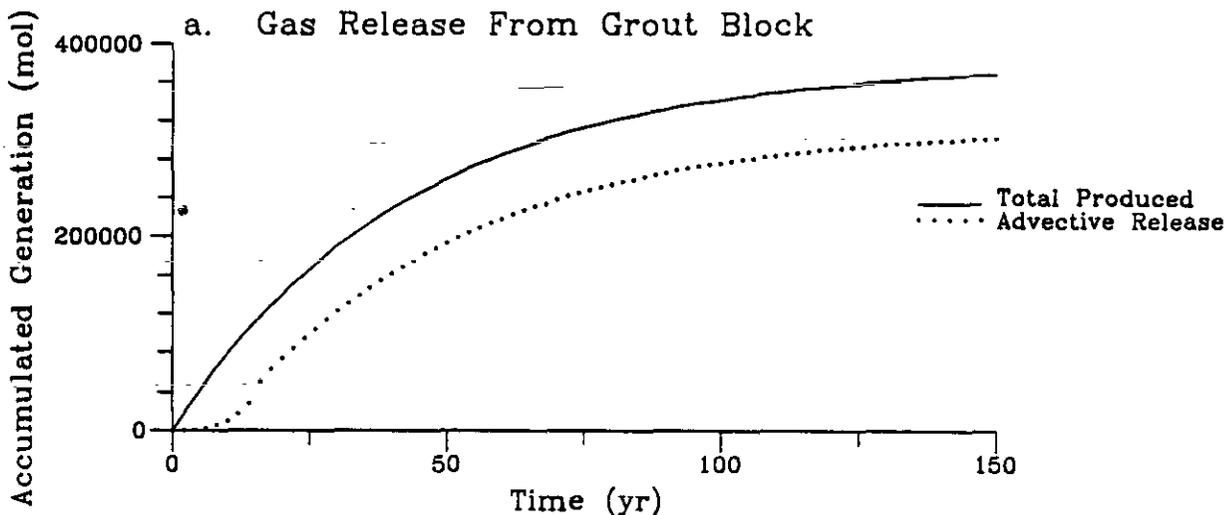
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Figure 5-3. Gas Release Source Term and Gas Concentrations--Mixture 1.
(Initial Gas Generation Rate = 0.4 mol/h.)



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Figure 5-4. Gas Release Source Term and Gas Concentrations--Mixture 1.
(Initial Gas Generation Rate = 1.0 mol/h.)



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Figure 5-5. Gas Release Source Term and Gas Concentrations--Mixture 1.
(Initial Gas Generation Rate = 1.4 mol/h.)

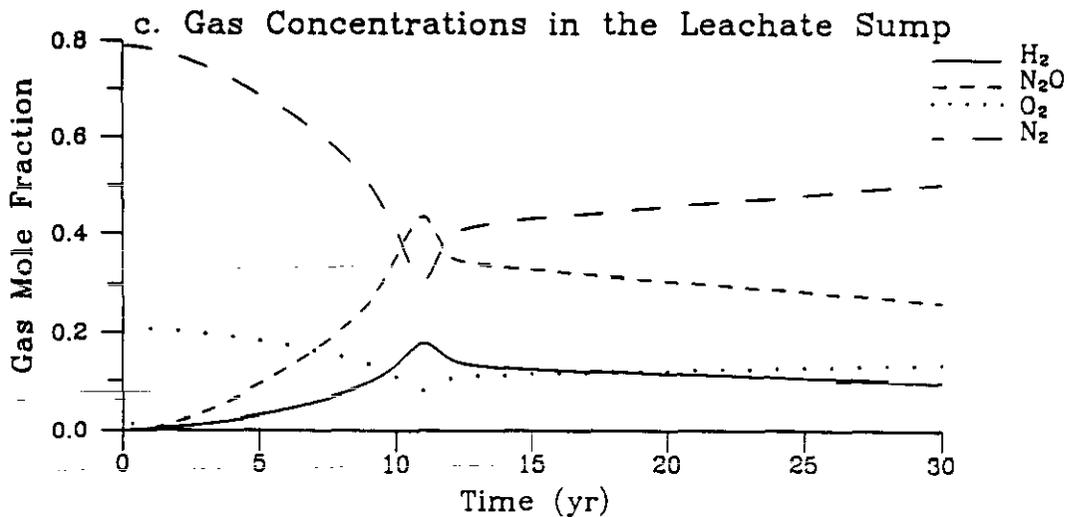
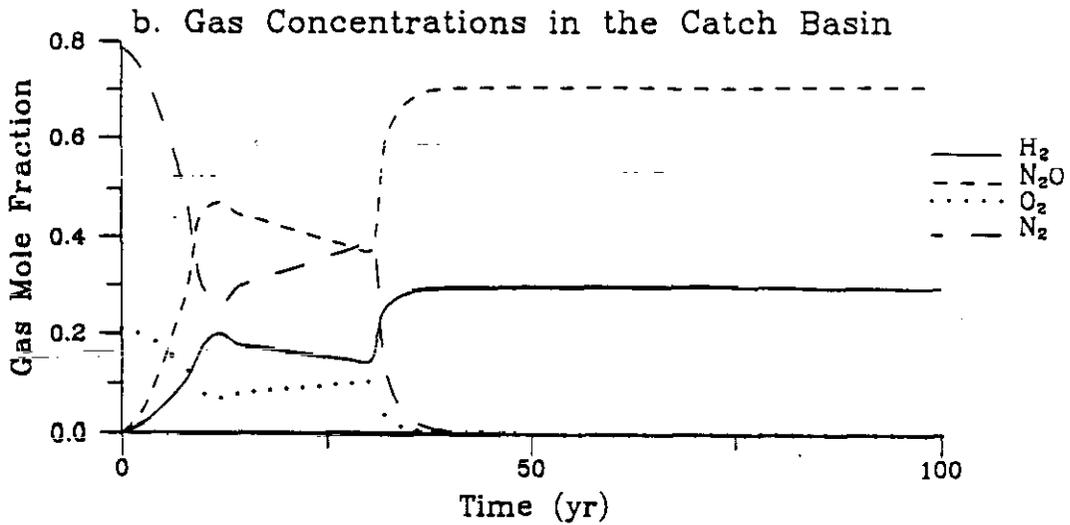
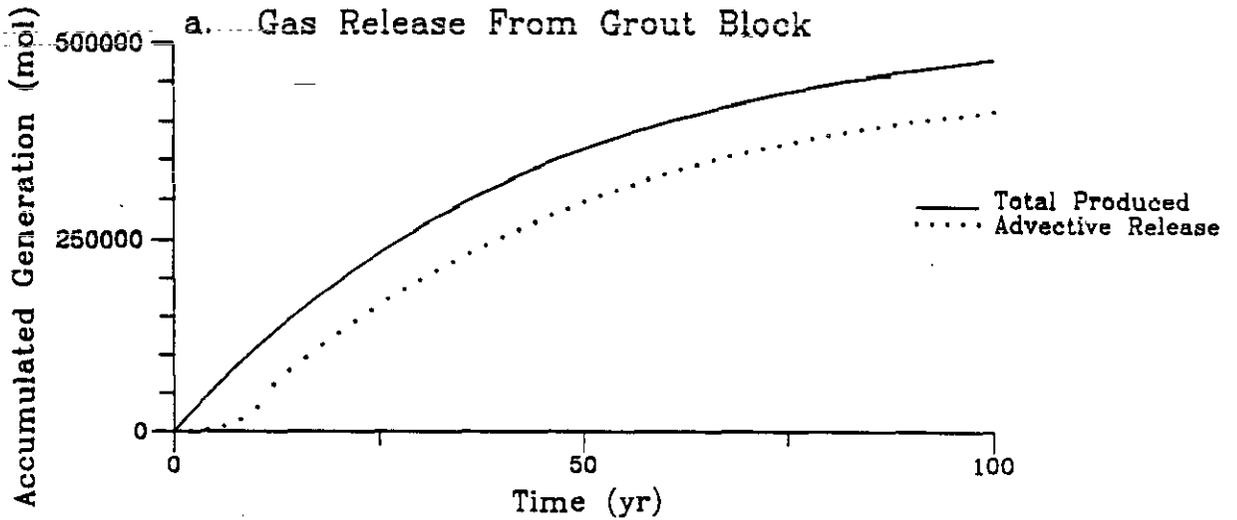
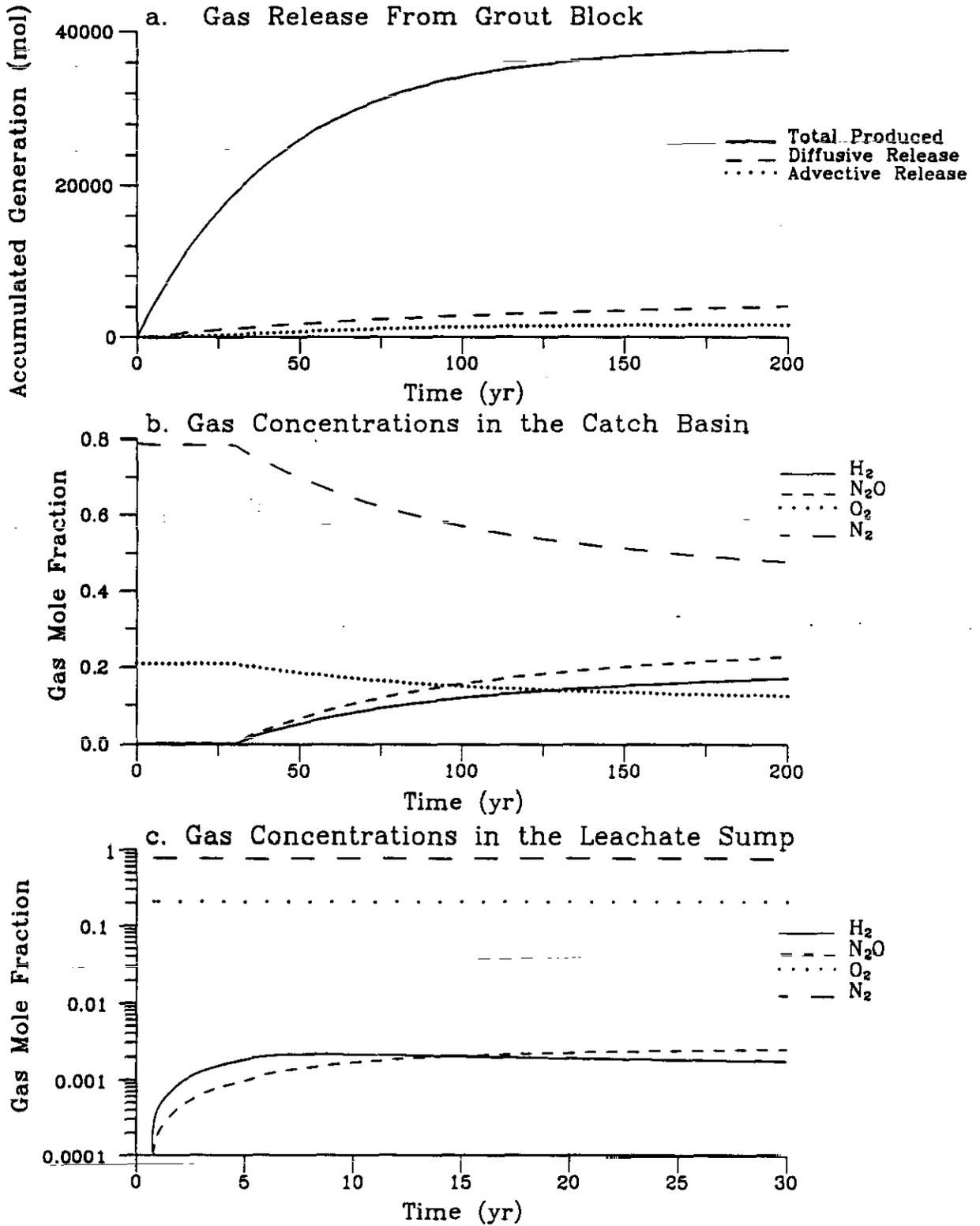
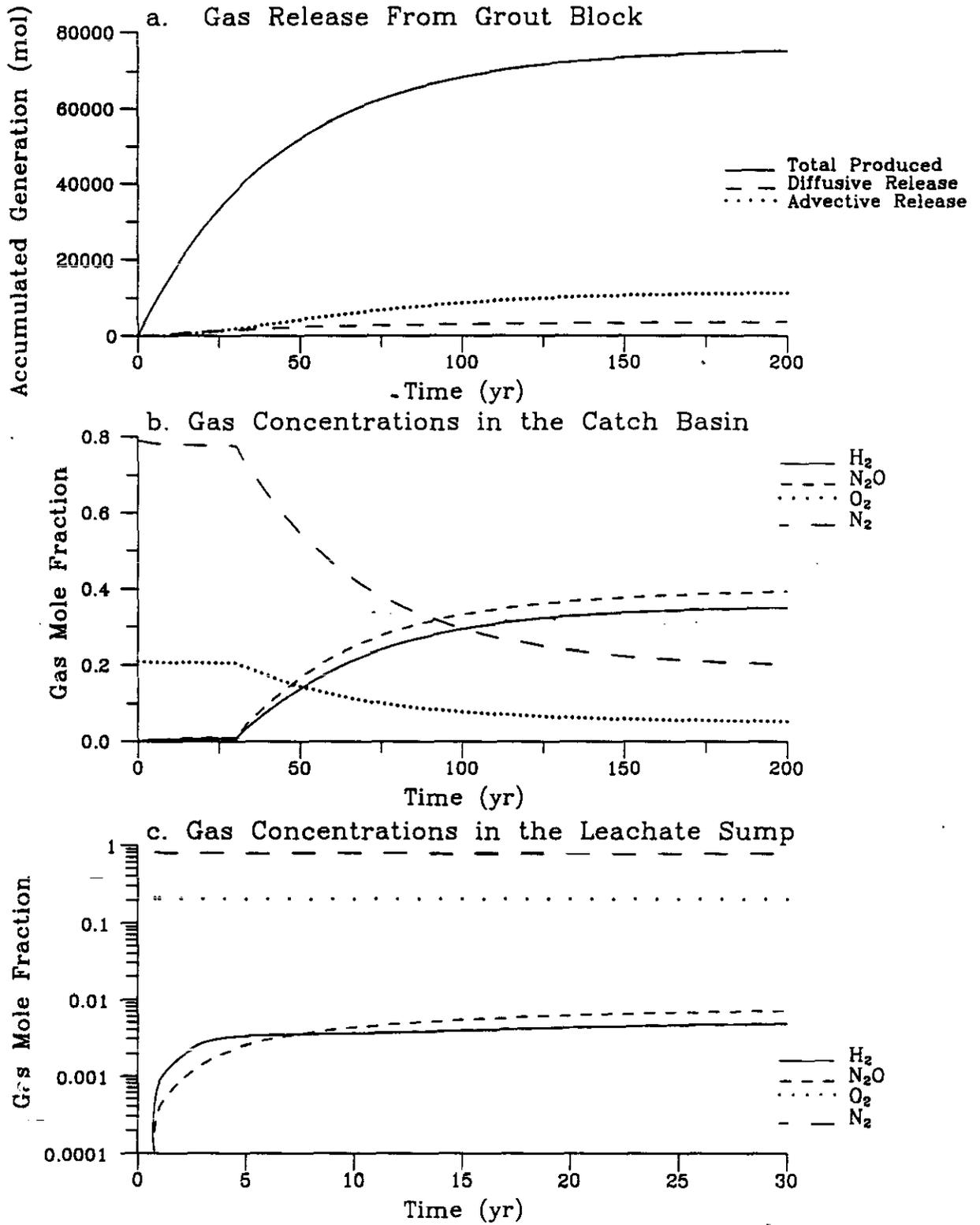


Figure 5-6. Gas Release Source Term and Gas Concentrations--Mixture 2.
(Initial Gas Generation Rate = 0.1 mol/h.)



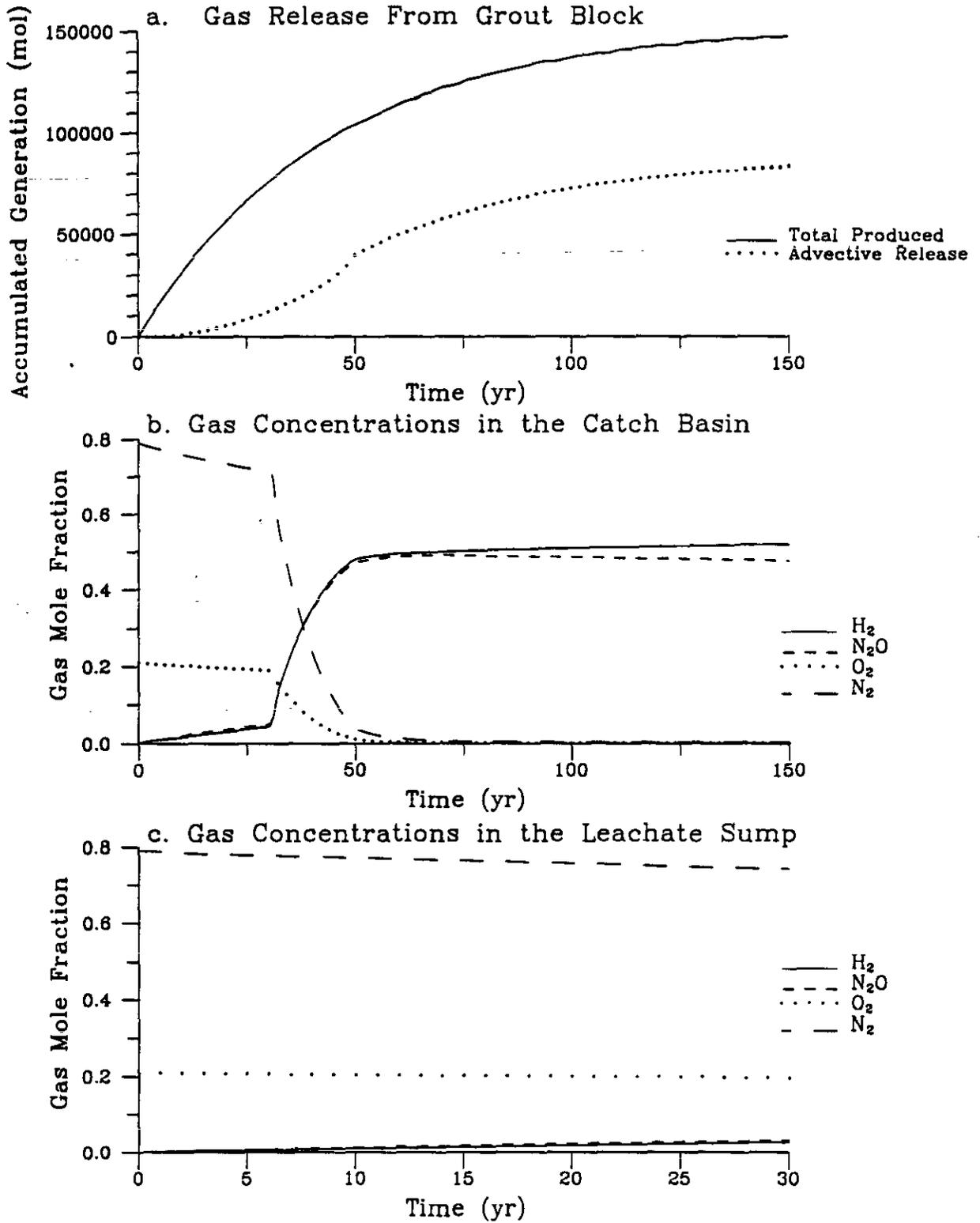
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Figure 5-7. Gas Release Source Term and Gas Concentrations--Mixture 2.
(Initial Gas Generation Rate = 0.2 mol/h.)



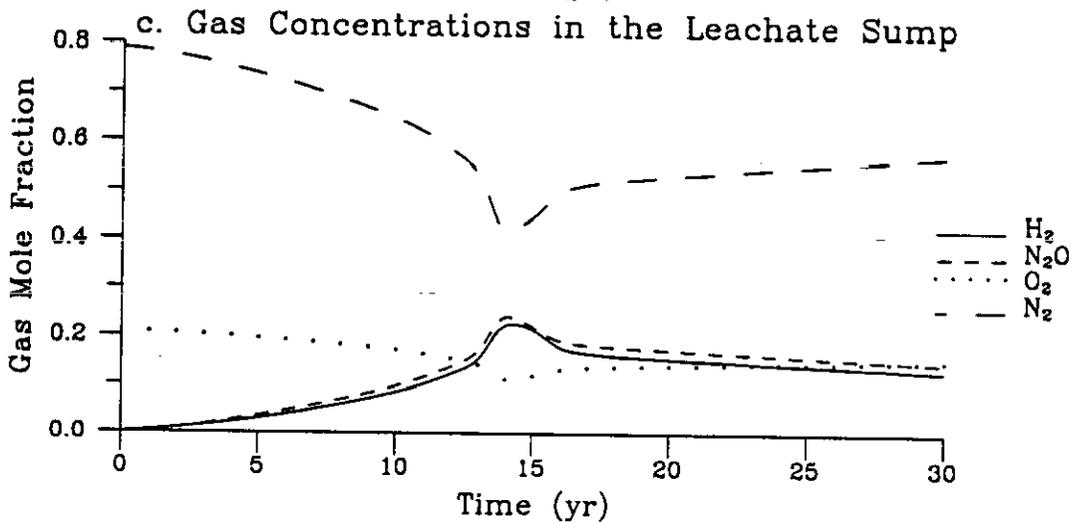
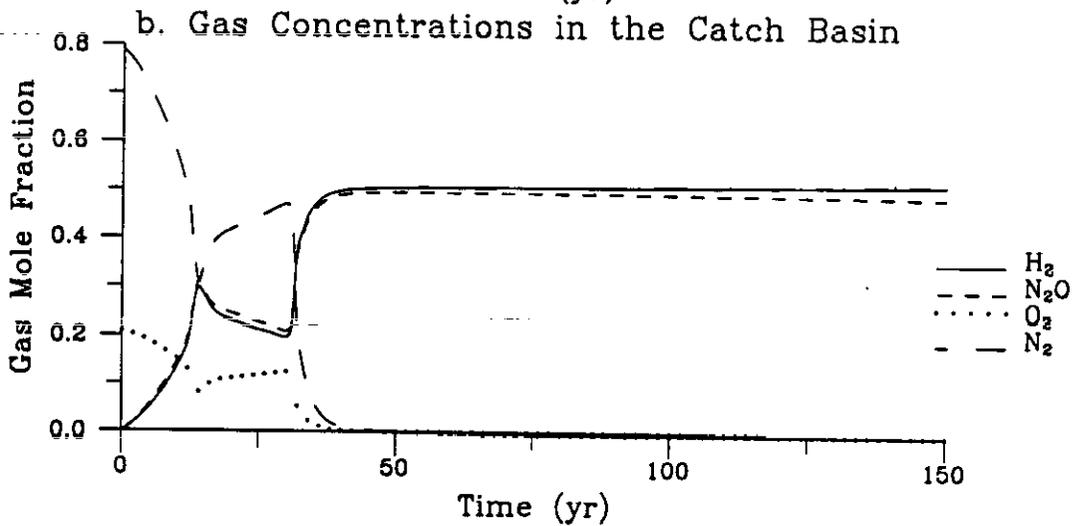
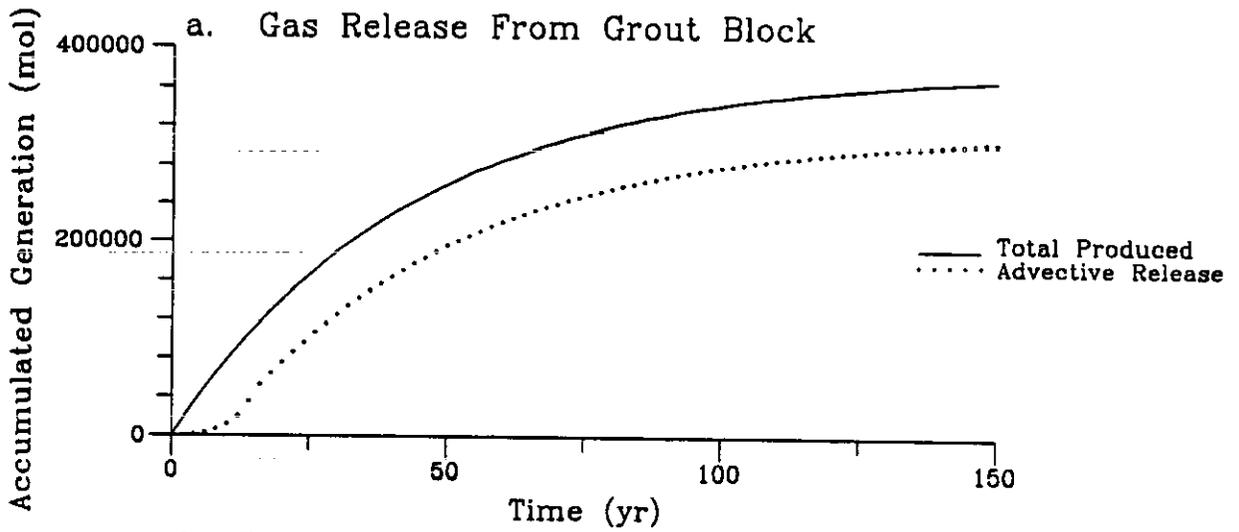
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Figure 5-8. Gas Release Source Term and Gas Concentrations--Mixture 2.
(Initial Gas Generation Rate = 0.4 mol/h.)



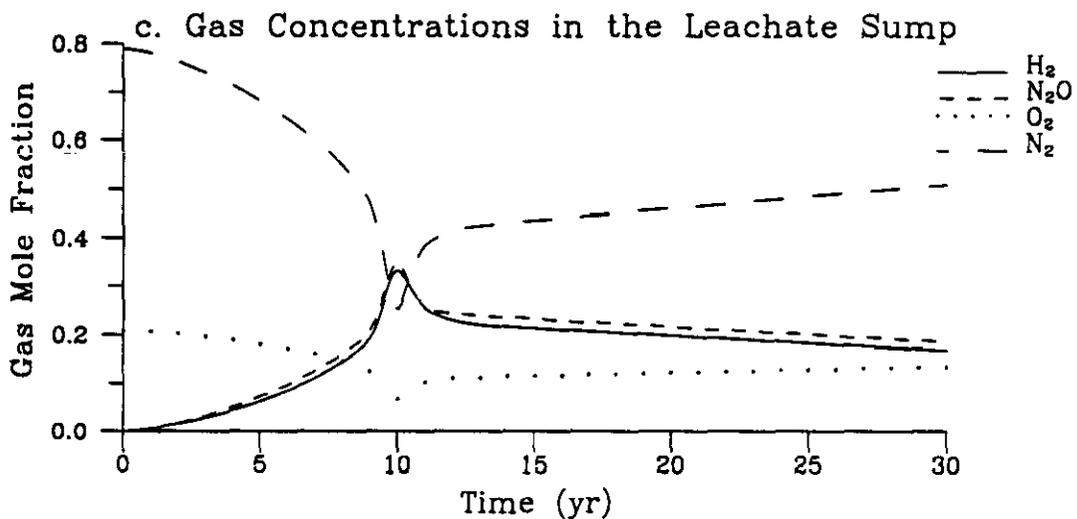
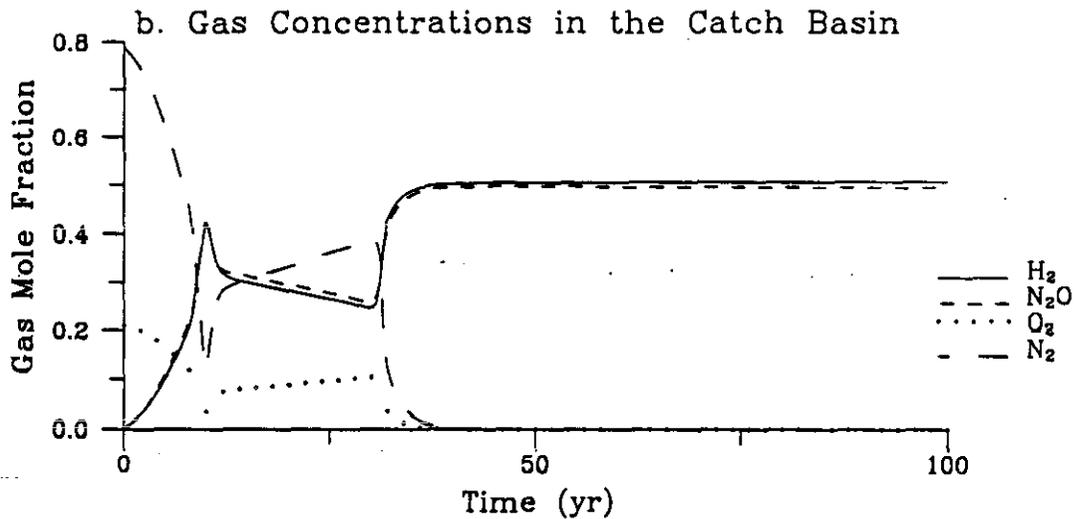
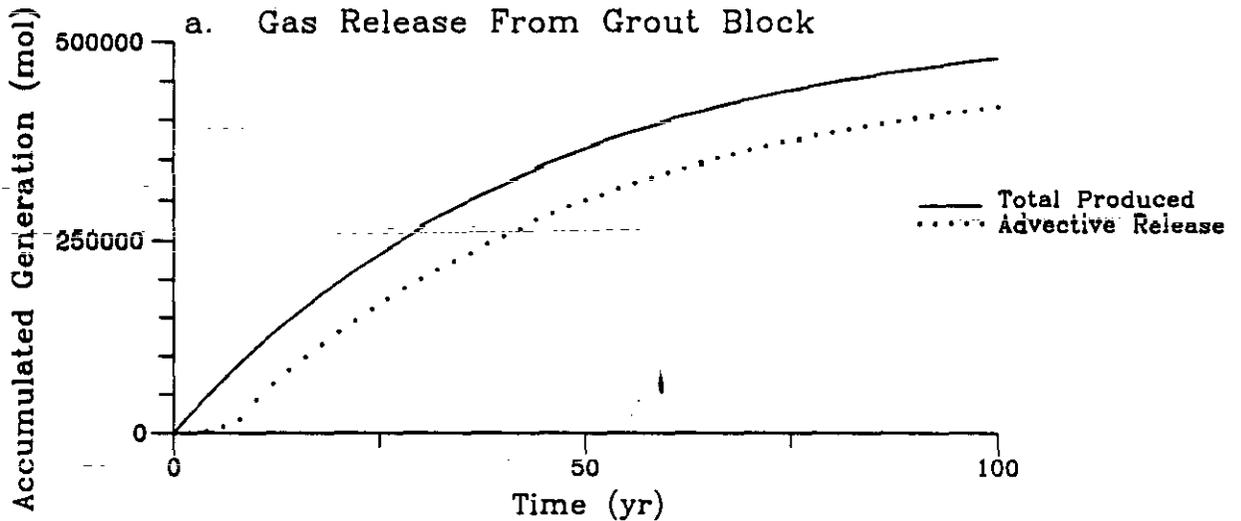
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Figure 5-9. Gas Release Source Term and Gas Concentrations--Mixture 2.
(Initial Gas Generation Rate = 1.0 mol/h.)



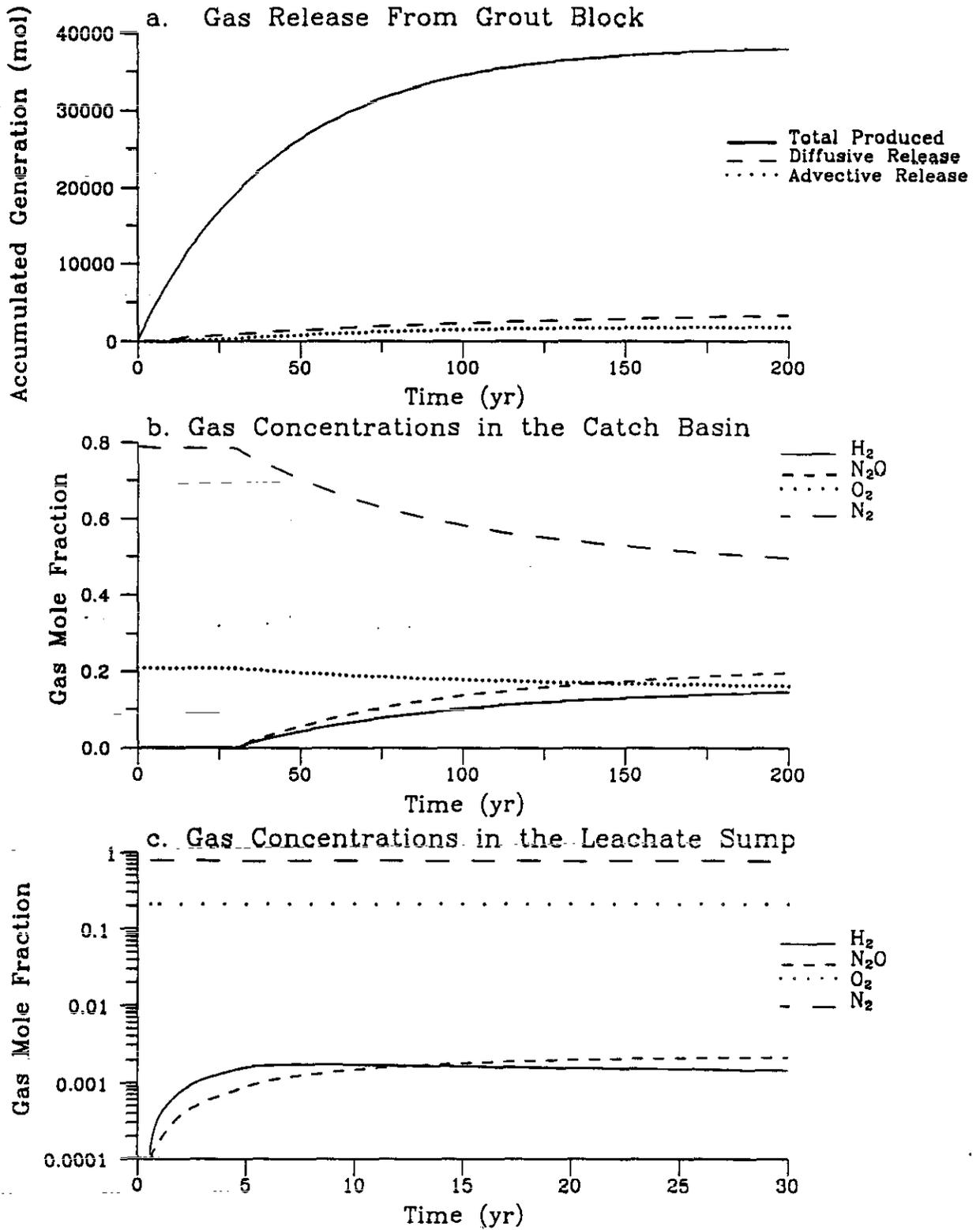
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Figure 5-10. Gas Release Source Term and Gas Concentrations--Mixture 2.
(Initial Gas Generation Rate = 1.4 mol/h.)



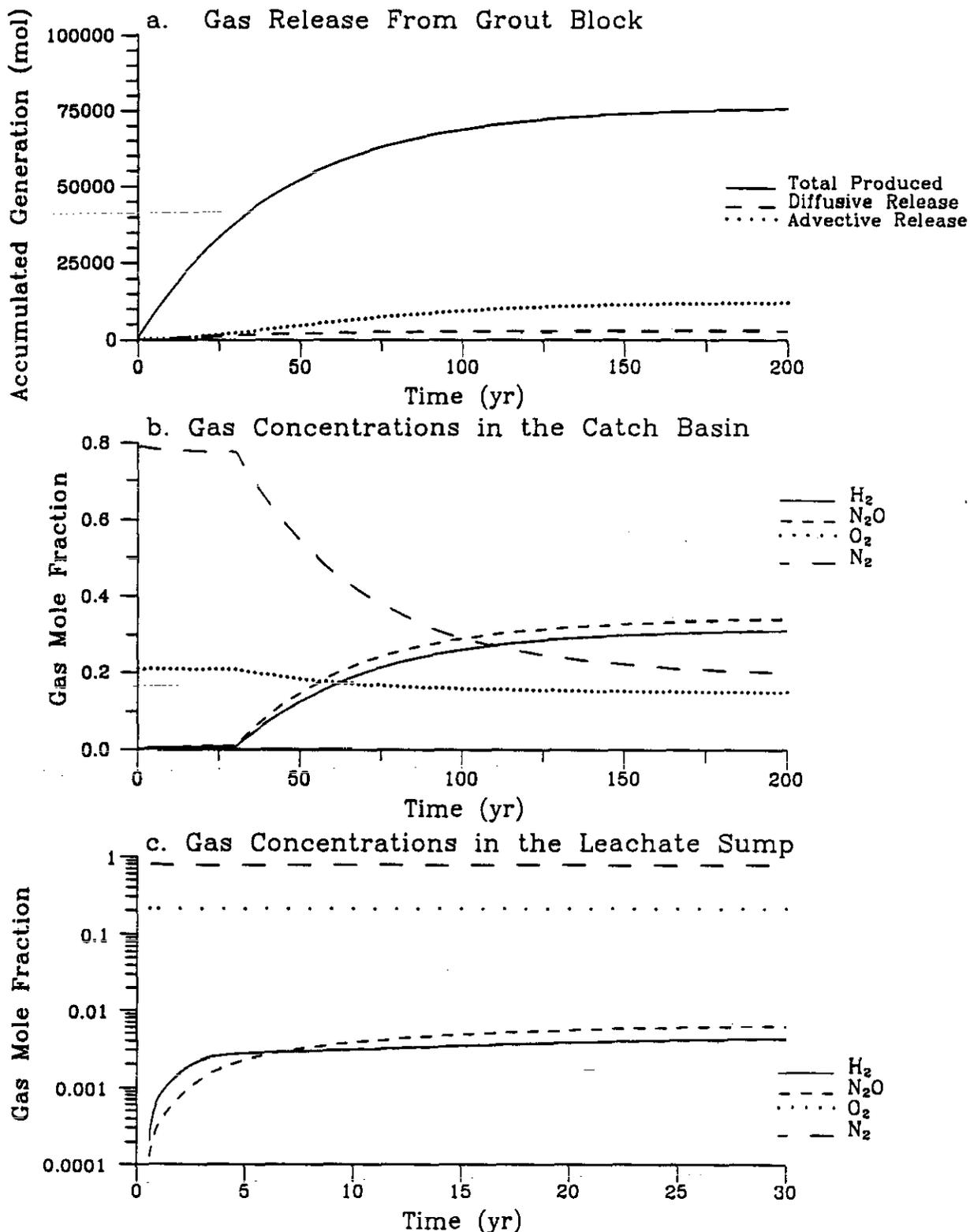
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Figure 5-11. Gas Release Source Term and Gas Concentrations--Mixture 3.
(Initial Gas Generation Rate = 0.1 mol/h.)



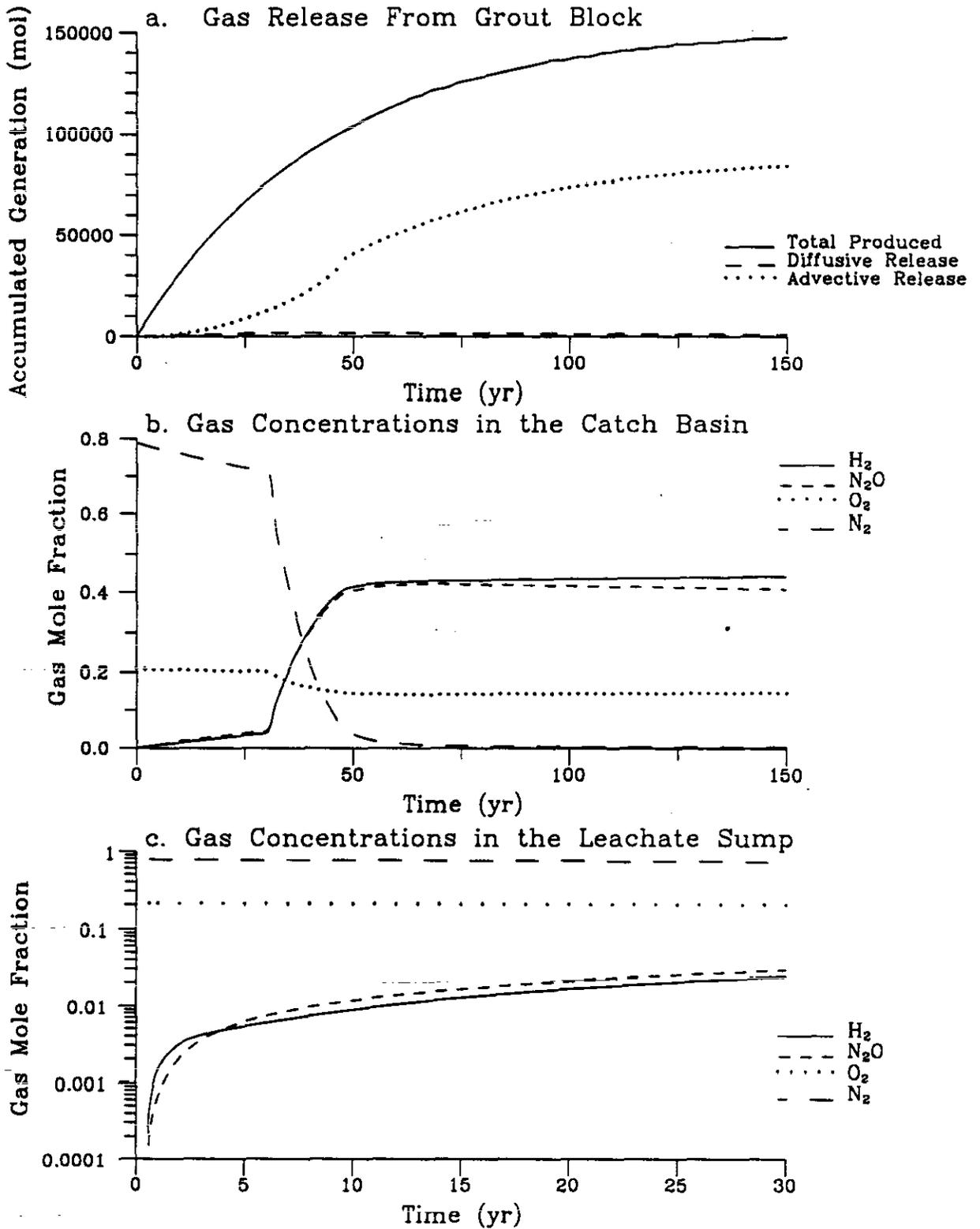
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Figure 5-12. Gas Release Source Term and Gas Concentrations--Mixture 3.
(Initial Gas Generation Rate = 0.2 mol/h.)



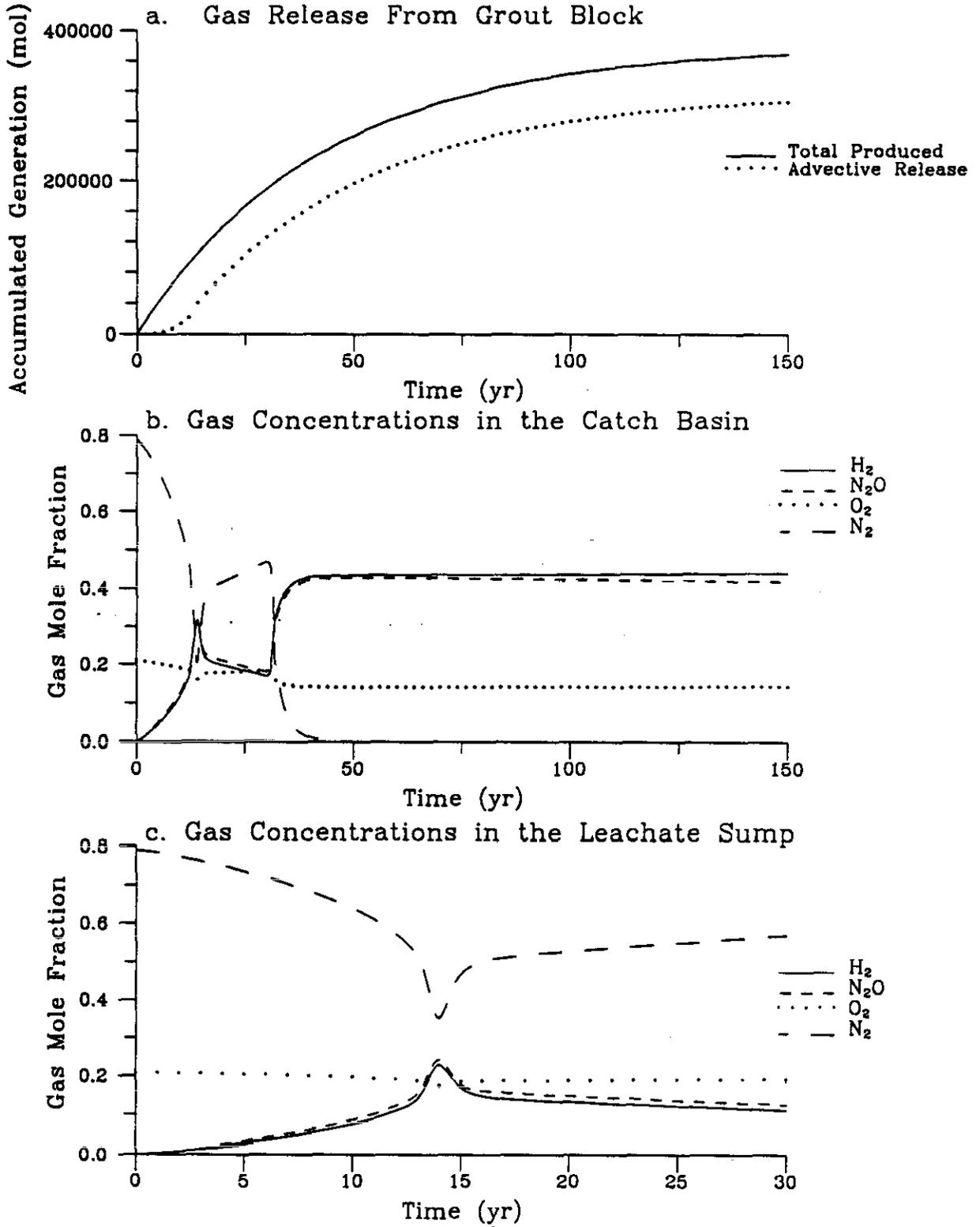
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Figure 5-13. Gas Release Source Term and Gas Concentrations--Mixture 3.
(Initial Gas Generation Rate = 0.4 mol/h.)



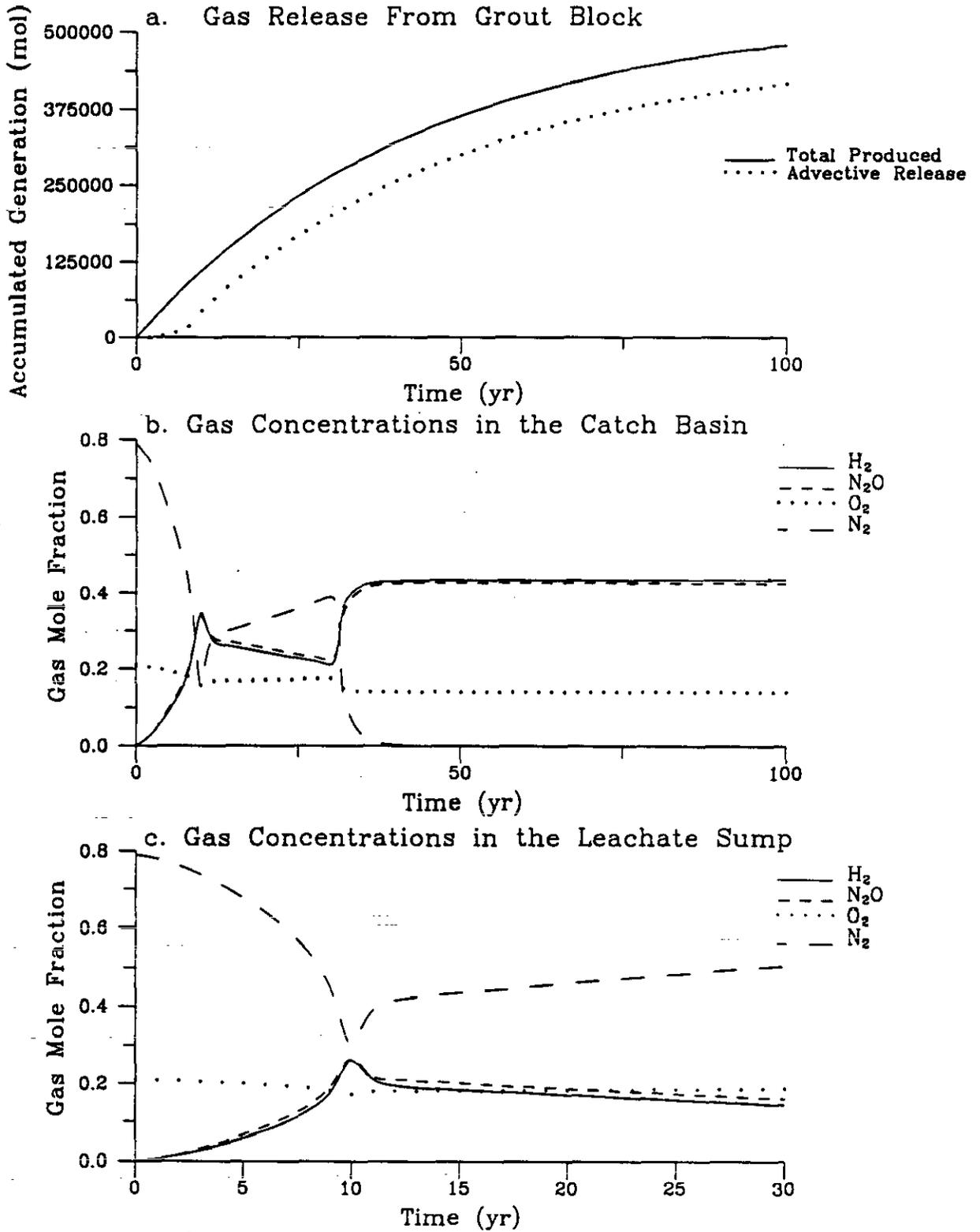
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Figure 5-14. Gas Release Source Term and Gas Concentrations--Mixture 3.
(Initial Gas Generation Rate = 1.0 mol/h.)



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Figure 5-15. Gas Release Source Term and Gas Concentrations--Mixture 3.
 (Initial Gas Generation Rate = 1.4 mol/h.)



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Table 5-2. Summary of Gas Release from Grout Block--Mixture 1
(29% H₂, 71% N₂O, 0% O₂).

Gas generation rate (mol/h)	Advection start time (yr)	Total gas release ^a					
		Diffusion (mol)			Advection (mol)		
		H ₂	N ₂ O	O ₂	H ₂	N ₂ O	O ₂
0.1	8	1.8 E+3	4.5 E+3	-9.2 E+1	3.2 E+2	7.9 E+2	1.4 E+1
0.2	4	1.2 E+3	4.9 E+3	-8.2 E+1	2.8 E+3	6.7 E+3	5.7 E+1
0.4	2	4.5 E+2	8.0 E+2	-4.7 E+1	2.6 E+4	6.1 E+4	2.1 E+2
1.0	0.7	2.2 E+2	-4.7 E+2	-3.4 E+1	9.3 E+4	2.2 E+5	2.7 E+2
1.4	0.5	1.6 E+2	-8.4 E+2	-2.8 E+1	1.4 E+5	3.3 E+5	2.7 E+2

Table 5-3. Summary of Gas Release from Grout Block--Mixture 2
(50% H₂, 50% N₂O, 0% O₂).

Gas generation rate (mol/h)	Advection start time (yr)	Total gas release ^a					
		Diffusion (mol)			Advection (mol)		
		H ₂	N ₂ O	O ₂	H ₂	N ₂ O	O ₂
0.1	6	2.2 E+3	2.8 E+3	-1.1 E+2	8.2 E+2	8.2 E+2	2.2 E+1
0.2	4	1.5 E+3	2.7 E+3	-8.7 E+1	5.8 E+3	5.7 E+3	7.1 E+1
0.4	1	5.3 E+2	2.5 E+2	-4.9 E+1	4.5 E+4	4.4 E+4	2.1 E+2
1.0	0.5	2.4 E+2	-5.2 E+2	-3.5 E+1	1.6 E+5	1.6 E+5	2.8 E+2
1.4	0.4	1.6 E+2	-7.4 E+2	-3.0 E+1	2.4 E+5	2.3 E+5	2.7 E+2

Table 5-4. Summary of Gas Release from Grout Block--Mixture 3
(43% H₂, 43% N₂O, 14% O₂).

Gas generation rate (mol/h)	Advection start time (yr)	Total gas release ^a					
		Diffusion (mol)			Advection (mol)		
		H ₂	N ₂ O	O ₂	H ₂	N ₂ O	O ₂
0.1	4	1.7 E+3	2.3 E+3	1.5 E+2	7.9 E+2	7.8 E+2	2.9 E+2
0.2	2	1.2 E+3	2.1 E+3	8.4 E+1	5.3 E+3	5.2 E+3	1.8 E+3
0.4	1	4.0 E+2	1.3 E+1	9.7 E+0	3.9 E+4	3.8 E+4	1.3 E+4
1.0	0.4	1.8 E+2	-5.0 E+2	-1.1 E+1	1.4 E+5	1.4 E+5	4.5 E+4
1.4	0.3	1.3 E+2	-6.8 E+2	-1.4 E+1	2.0 E+5	2.0 E+5	6.7 E+4

^aaccumulated releases at 300 years.

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Table 5-5. Compartment Gas Concentrations Versus Time--Mixture 1. (29% H₂, 71% N₂O, and 0% O₂). (sheet 1 of 2)

a. Initial Gas Generation Rate 0.1 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	2.5 E-3	3.5 E-3	2.1 E-1	7.9 E-1	1.5 E-3	2.2 E-3	2.1 E-1	7.9 E-1
30	2.0 E-3	5.4 E-3	2.1 E-1	7.8 E-1	1.2 E-3	3.4 E-3	2.1 E-1	7.9 E-1
100	7.7 E-2	2.2 E-1	1.5 E-1	5.6 E-1	--	--	--	--
200	1.1 E-1	3.3 E-1	1.2 E-1	4.5 E-1	--	--	--	--
300	1.3 E-1	3.7 E-1	1.0 E-1	3.9 E-1	--	--	--	--

b. Initial Gas Generation Rate 0.2 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	3.8 E-3	8.5 E-3	2.1 E-1	7.8 E-1	2.3 E-3	5.4 E-3	2.1 E-1	7.8 E-1
30	4.2 E-3	1.5 E-2	2.1 E-1	7.8 E-1	2.5 E-3	9.3 E-3	2.1 E-1	7.8 E-1
100	1.6 E-1	4.6 E-1	8.1 E-2	3.1 E-1	--	--	--	--
200	1.9 E-1	5.5 E-1	5.5 E-2	2.1 E-1	--	--	--	--
300	1.9 E-1	5.7 E-1	5.0 E-2	1.9 E-1	--	--	--	--

c. Initial Gas Generation Rate 0.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	8.6 E-3	2.6 E-2	2.0 E-1	7.6 E-1	5.1 E-3	1.7 E-2	2.1 E-1	7.7 E-1
30	2.4 E-2	6.7 E-2	1.9 E-1	7.2 E-1	1.4 E-2	4.3 E-2	2.0 E-1	7.5 E-1
100	3.0 E-1	6.9 E-1	2.1 E-3	4.6 E-3	--	--	--	--
200	3.2 E-1	6.8 E-1	1.7 E-3	3.4 E-3	--	--	--	--
300	3.3 E-1	6.6 E-1	1.7 E-3	3.5 E-3	--	--	--	--

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Table 5-5. Compartment Gas Concentrations Versus Time--Mixture 1.
(29% H₂, 71% N₂O, and 0% O₂). (sheet 2 of 2)

d. Initial Gas Generation Rate 1.0 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	7.1 E-2	1.9 E-1	1.6 E-1	5.9 E-1	4.5 E-2	1.3 E-1	1.7 E-1	6.5 E-1
30	1.1 E-1	3.0 E-1	1.2 E-1	4.7 E-1	7.5 E-2	2.1 E-1	1.5 E-1	5.7 E-1
100	3.0 E-1	7.0 E-1	7.7 E-5	1.5 E-4	--	--	--	--
200	3.0 E-1	7.0 E-1	4.4 E-5	8.7 E-5	--	--	--	--
300	3.1 E-1	6.9 E-1	4.2 E-5	8.4 E-5	--	--	--	--

e. Initial Gas Generation Rate 1.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.8 E-1	4.6 E-1	7.7 E-2	2.9 E-1	1.3 E-1	3.5 E-1	1.1 E-1	4.1 E-1
30	1.4 E-1	3.7 E-1	1.0 E-1	3.9 E-1	9.8 E-2	2.6 E-1	1.3 E-1	5.0 E-1
100	2.9 E-1	7.1 E-1	9.6 E-6	1.9 E-5	--	--	--	--
200	3.0 E-1	7.1 E-1	4.2 E-6	8.2 E-6	--	--	--	--
300	3.0 E-1	7.0 E-1	3.9 E-6	7.7 E-6	--	--	--	--

H₂ = Hydrogen
 N₂O = Nitrous oxide
 O₂ = Oxygen
 mol = Moles
 mol/h = Moles per hour
 yr = Years

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Table 5-6. Compartment Gas Concentrations Versus Time--Mixture 2.
(50% H₂, 50% N₂O, and 0% O₂). (sheet 1 of 2)

a. Initial Gas Generation Rate 0.1 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	3.6 E-3	2.7 E-3	2.1 E-1	7.9 E-1	2.2 E-3	1.7 E-3	2.1 E-1	7.9 E-1
30	3.0 E-3	4.0 E-3	2.1 E-1	7.9 E-1	1.8 E-3	2.5 E-3	2.1 E-1	7.9 E-1
100	1.2 E-1	1.6 E-1	1.5 E-1	5.7 E-1	--	--	--	--
200	1.7 E-1	2.3 E-1	1.3 E-1	4.8 E-1	--	--	--	--
300	2.0 E-1	2.6 E-1	1.1 E-1	4.3 E-1	--	--	--	--

b. Initial Gas Generation Rate 0.2 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	6.0 E-3	6.7 E-3	2.1 E-1	7.8 E-1	3.6 E-3	4.3 E-3	2.1 E-1	7.8 E-1
30	8.0 E-3	1.1 E-2	2.1 E-1	7.8 E-1	4.8 E-3	7.1 E-3	2.1 E-1	7.8 E-1
100	3.0 E-1	3.3 E-1	7.9 E-2	3.0 E-1	--	--	--	--
200	3.5 E-1	3.9 E-1	5.4 E-2	2.0 E-1	--	--	--	--
300	3.6 E-1	4.1 E-1	5.0 E-2	1.9 E-1	--	--	--	--

c. Initial Gas Generation Rate 0.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.7 E-2	2.1 E-2	2.0 E-1	7.6 E-1	1.0 E-2	1.3 E-2	2.1 E-1	7.7 E-1
30	4.5 E-2	5.1 E-2	1.9 E-1	7.1 E-1	2.8 E-2	3.3 E-2	2.0 E-1	7.4 E-1
100	5.1 E-1	4.9 E-1	2.0 E-3	4.4 E-3	--	--	--	--
200	5.3 E-1	4.7 E-1	1.6 E-3	3.3 E-3	--	--	--	--
300	5.4 E-1	4.5 E-1	1.6 E-3	3.3 E-3	--	--	--	--

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Table 5-6. Compartment Gas Concentrations Versus Time--Mixture 2.
(50% H₂, 50% N₂O, and 0% O₂). (sheet 2 of 2)

d. Initial Gas Generation Rate 1.0 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.3 E-1	1.4 E-1	1.5 E-1	5.7 E-1	8.6 E-2	9.8 E-2	1.7 E-1	6.5 E-1
30	2.0 E-1	2.1 E-1	1.3 E-1	4.7 E-1	1.3 E-1	1.5 E-1	1.5 E-1	5.7 E-1
100	5.1 E-1	4.9 E-1	6.9 E-5	1.4 E-4	--	--	--	--
200	5.2 E-1	4.8 E-1	4.0 E-5	7.9 E-5	--	--	--	--
300	5.3 E-1	4.7 E-1	3.8 E-5	7.6 E-5	--	--	--	--

e. Initial Gas Generation Rate 1.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	4.2 E-1	4.2 E-1	3.4 E-2	1.2 E-1	3.3 E-1	3.5 E-1	6.8 E-2	2.5 E-1
30	2.5 E-1	2.6 E-1	1.0 E-1	3.9 E-1	1.7 E-1	1.9 E-1	1.4 E-1	5.1 E-1
100	5.1 E-1	4.9 E-1	9.0 E-6	1.8 E-5	--	--	--	--
200	5.1 E-1	4.9 E-1	4.0 E-6	7.9 E-6	--	--	--	--
300	5.2 E-1	4.8 E-1	3.8 E-6	7.4 E-6	--	--	--	--

H₂ = Hydrogen
 N₂O = Nitrous oxide
 O₂ = Oxygen
 mol = Moles
 mol/h = Moles per hour
 yr = Years

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Table 5-7. Compartment Gas Concentrations Versus Time--Mixture 3.
(43% H₂, 43% N₂O, and 24% O₂). (sheet 1 of 2)

a. Initial Gas Generation Rate 0.1 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	2.9 E-3	2.4 E-3	2.1 E-1	7.9 E-1	1.7 E-3	1.5 E-3	2.1 E-1	7.9 E-1
30	2.5 E-3	3.5 E-3	2.1 E-1	7.9 E-1	1.5 E-3	2.2 E-3	2.1 E-1	7.9 E-1
100	1.0 E-1	1.4 E-1	1.8 E-1	5.8 E-1	--	--	--	--
200	1.5 E-1	2.0 E-1	1.6 E-1	5.0 E-1	--	--	--	--
300	1.7 E-1	2.2 E-1	1.5 E-1	4.6 E-1	--	--	--	--

b. Initial Gas Generation Rate 0.2 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	5.1 E-3	6.0 E-3	2.1 E-1	7.8 E-1	3.0 E-3	3.8 E-3	2.1 E-1	7.8 E-1
30	7.1 E-3	9.8 E-3	2.1 E-1	7.8 E-1	4.2 E-3	6.3 E-3	2.1 E-1	7.8 E-1
100	2.6 E-1	2.9 E-1	1.6 E-1	2.9 E-1	--	--	--	--
200	3.1 E-1	3.4 E-1	1.5 E-1	2.0 E-1	--	--	--	--
300	3.2 E-1	3.5 E-1	1.5 E-1	1.9 E-1	--	--	--	--

c. Initial Gas Generation Rate 0.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.5 E-2	1.9 E-2	2.1 E-1	7.6 E-1	8.9 E-3	1.2 E-2	2.1 E-1	7.7 E-1
30	4.0 E-2	4.6 E-2	2.0 E-1	7.1 E-1	2.5 E-2	3.0 E-2	2.1 E-1	7.4 E-1
100	4.3 E-1	4.2 E-1	1.4 E-1	4.3 E-1	--	--	--	--
200	4.5 E-1	4.0 E-1	1.5 E-1	3.2 E-1	--	--	--	--
300	4.6 E-1	3.8 E-1	1.5 E-1	3.2 E-1	--	--	--	--

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Table 5-7. Compartment Gas Concentrations Versus Time--Mixture 3.
(43% H₂, 43% N₂O, and 24% O₂). (sheet 2 of 2)

d. Initial Gas Generation Rate 1.0 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.2 E-1	1.3 E-1	1.9 E-1	5.7 E-1	7.6 E-2	8.7 E-2	2.0 E-1	6.4 E-1
30	1.7 E-1	1.8 E-1	1.8 E-1	4.7 E-1	1.1 E-1	1.3 E-1	1.9 E-1	5.7 E-1
100	4.4 E-1	4.2 E-1	1.4 E-1	1.3 E-4	--	--	--	--
200	4.4 E-1	4.1 E-1	1.5 E-1	7.5 E-5	--	--	--	--
300	4.5 E-1	4.0 E-1	1.5 E-1	7.2 E-5	--	--	--	--

e. Initial Gas Generation Rate 1.4 mol/h

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	3.5 E-1	3.4 E-1	1.6 E-1	1.6 E-1	2.6 E-2	2.7 E-1	1.7 E-1	3.0 E-1
30	2.1 E-1	2.2 E-1	1.8 E-1	3.9 E-1	1.5 E-1	1.6 E-1	1.9 E-1	5.1 E-1
100	4.3 E-1	4.2 E-1	1.4 E-1	1.7 E-5	--	--	--	--
200	4.4 E-1	4.2 E-1	1.4 E-1	7.7 E-6	--	--	--	--
300	4.5 E-1	4.1 E-1	1.5 E-1	7.1 E-6	--	--	--	--

H₂ = Hydrogen
 N₂O = Nitrous oxide
 O₂ = Oxygen
 mol = Moles
 mol/h = Moles per hour
 yr = Years

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The results in this study show the trend of release mechanisms of gas as initial generation rate increases. As discussed in Section 3.7.1, the relative quantity of gas released by advection is lower than that of diffusion for the lower gas generation rates. The total of fraction gas permanently retained in the grout block is also high. These trends reverse when the level of initial gas generation exceeds about 0.3 mol/h, which corresponds to a total gas generation volume equal to the assumed volume of unbound liquid. Diffusion releases from the grout block become less significant and gas release is characterized by pressure driven two-phase advection flow. The model allows diffusion to flow back to the grout. This condition is shown as negative values for the cases of high gas generation rates where advection is prominent. The accounting of total diffusion and advection flows are presented separately in the tables. In Table 5-2, the relatively high advection flow indicates a back diffusion flow by negative values at longer times.

Oxygen, like hydrogen, has a low solubility in the grout liquid. Its formation rate, if present, also enhances the advection flow of liquid and gas by about 20% above that of hydrogen because of its lower solubility. Nitrous oxide has a much higher solubility in the grout liquid and contributes to the advection flow of liquid and gas about 7% of that of hydrogen due to its higher solubility.

The higher release of gas by advection has an interesting effect on the compartment gas concentrations. The higher release rates of gases from the grout block go through the breakaway stage resulting in a rapid gas pressure, this pressure release displaces nitrogen and oxygen and lowers their concentrations. The breakaway point is identified by the increased slope of the advection curve in the part A of the figures. It occurs at about 50, 20, and 15 years, respectively for 0.4, 1.0, and 1.4 mol/h gas generation rates. After the gas release rate slows down and the outside air exchange in the sump region discharges some of the compartment atmosphere and introduces outside air that causes the nitrogen and oxygen levels to increase again. This exchange continues until the filtered vent to the outside air is closed. After that time, the concentrations of nitrogen and oxygen decrease in the leachate sump compartment because of diffusion mixing with the catch basin atmosphere through the drain line.

5.2 UNBOUND LIQUID FRACTION

The unbound pore liquid in the grout is discussed in Section 3.5.1. The unbound liquid volume is the volume of liquid in the pores that can be displaced by gas bubbles formed throughout the grout block. This sensitivity study investigates the effect of varying the unbound liquid volume on the gas release rate from the grout block.

The fraction of unbound liquid will vary with the following: (1) grout mixture specifications, (2) pore size and distribution, and (3) amount of liquid saturation. The reference case is based on a volume content of pores equal to 64%. Half the pore volume is assumed to be filled with capillary-bound liquid. The balance of the pore volume, 32%, is assumed to be filled with unbound liquid.

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The reference case initial gas generation rate of 0.043 mol/h was used for this study. The unbound liquid volume was investigated over a range from 20 to 40 vol%. No significant change in the gas release rate was determined in this study. Therefore, the release of gas from the grout block is not sensitive to the unbound liquid fraction for the gas generation level of the reference case.

5.3 DIFFUSIVITY OF GASES IN WET GROUT

A sensitivity study was conducted to determine the effects of diffusivity on gas release rates, compartment gas concentrations, and advection flow. The sensitivity study was based on the reference case with an initial gas generation rate of 0.043 mol/h. The sensitivity study used the upper and lower bound gas diffusivities listed in Table 3-2. The results of the lower bound and upper bound cases are shown in Figures 5-16 and 5-17, respectively, for the gas release from the grout, and gas concentrations in the catch basin and leachate sump, respectively. The gas releases and compartment concentrations are summarized in Table 5-8, part a, and parts b and c, respectively. The release of gas from the grout block is significantly affected by the value used for diffusivities.

5.4 GAS GENERATION RATE THRESHOLD

5.4.1 Advection Initiation

The mechanism of advection involves the buildup of gas pressure inside the grout material until a threshold pressure is reached that causes gas bubble formation and liquid displacement. The gas generation level corresponding to this occurrence is called advection initiation. This gas generation rate is affected by temperature distribution, gas solubilities, gas diffusion losses, liquid permeability, pore size, and static external pressure. The determination of this gas generation threshold requires more sophisticated modeling and supplemental validation measurements.

The simple model described in this report was used to find a representative gas generation rate that corresponds to the advection initiation threshold level. In this study, the relation of gas release to initial gas generation rate was modeled to show the increasing gas released due to advection as gas formation rate increases. The results of this study are shown in Figure 5-18. The threshold level is significantly affected by the fraction of less soluble gases such as hydrogen and oxygen in the generated gases. The threshold gas generation levels for advection initiation occurred in the range of 0.01 to 0.02 mol/h.

5.4.2 Advection Breakaway

A gas generation rate threshold for advection breakaway was described in Section 3.5.1. At this threshold level, a significant fraction of unbound liquid may be expelled and the fraction of gas released from the grout block increases significantly. The relationship of total gas release fraction versus gas generation rate is shown in Figure 5-19. Figure 5-19 indicates a threshold point in gas generation rate at which the release fraction of gas increases dramatically. This threshold gas generation rate defines the point that breakaway first occurs. The fraction of gas released from the grout block increases significantly for higher gas generation rates. The initial gas generation rate that corresponds to the breakaway threshold is 0.25 mol/h.

5.5 ASPHALT PERMEABILITY

A sensitivity study was made to determine the effect of asphalt permeability on pressure in the grout disposal facility internal regions. The sensitivity study was made to cover the contingency of a failure of the vent tubes located at the top of the leachate collection basin during phase III. In this sensitivity study, the equilibrium pressure inside the grout disposal facility was expressed by (Crank 1975):

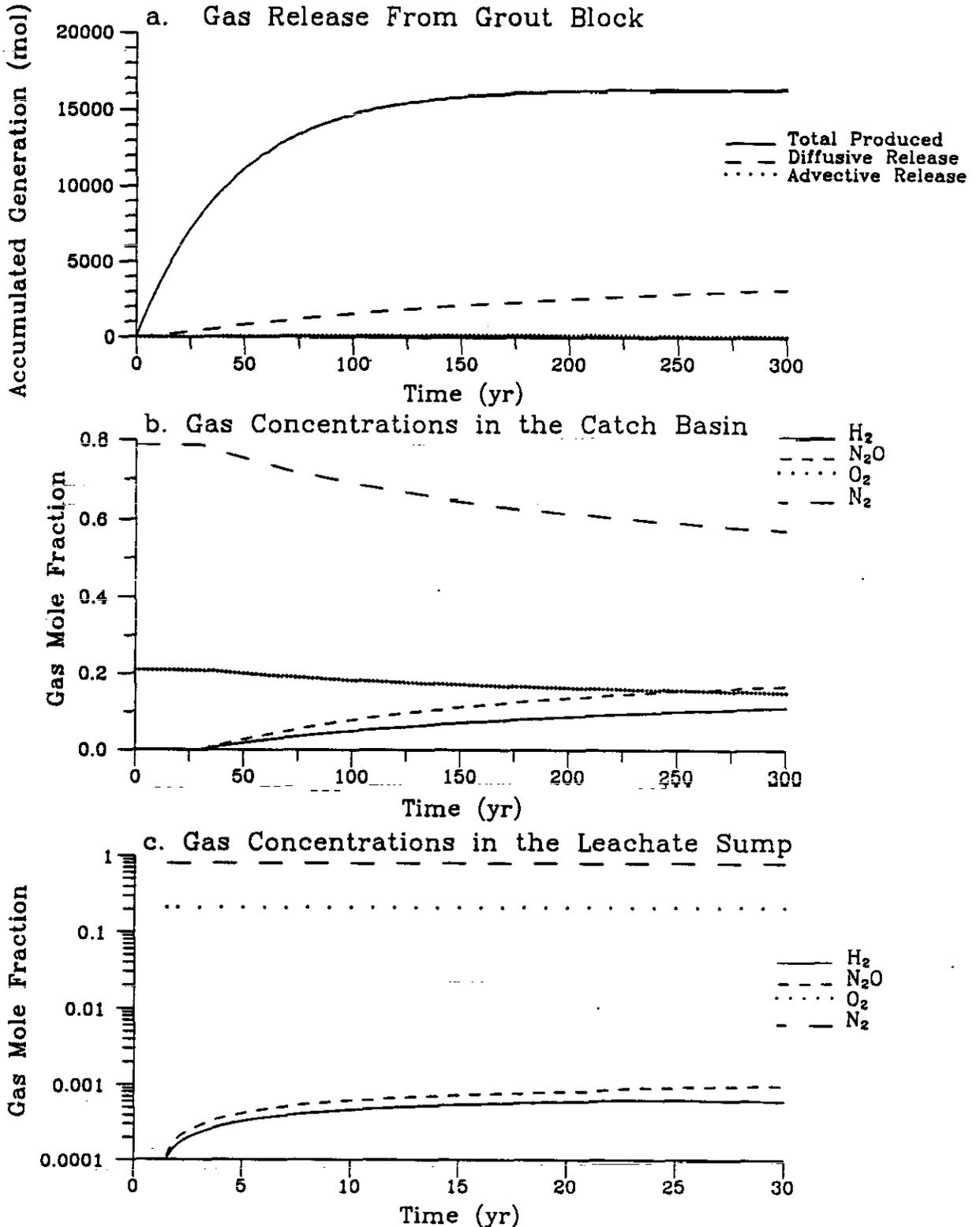
$$P = \frac{G \cdot T}{A \cdot \text{Perm}}$$

where G = gas generation rate, 0.043/3600 mol/s
 T = thickness, 122 cm
 A = area, 3.05 E+7 cm²
 Perm = permeability, mol/s-cm, and
 P = pressure, Pa

The relationship of the pressure drop across the asphalt wall versus asphalt permeability is shown in Figure 5-20. A reference value of the pressure difference of 1 lb/in² (6,895 Pa) corresponds to a permeability of 6.9 E-15 mol/s-cm-Pa.

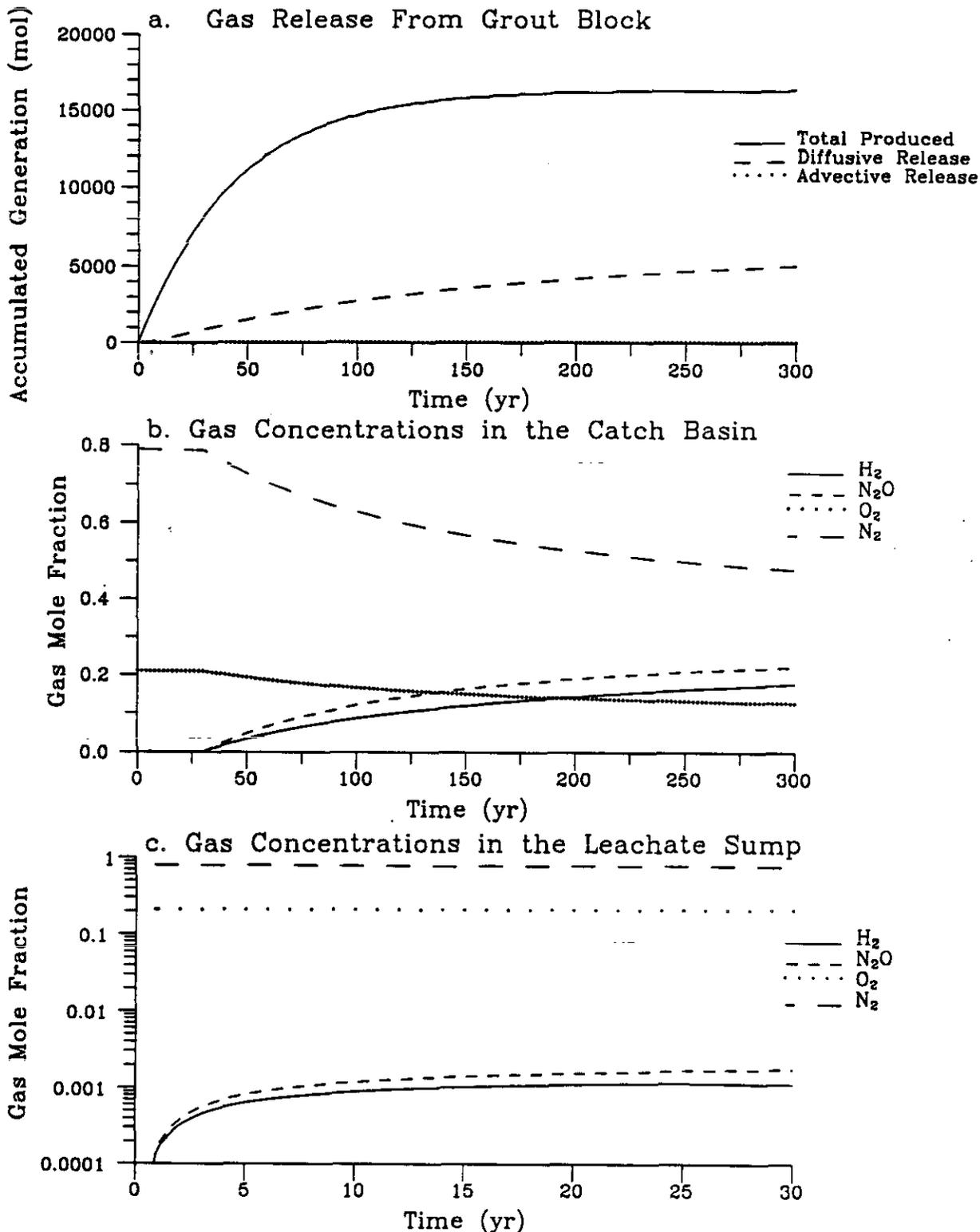
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Figure 5-16. Gas Release Source Terms and Gas Concentrations for Lower Bound Gas Diffusivities--Mixture 1 (29% H₂, 71% N₂O, 0% O₂). (Initial Gas Generation Rate = 0.043 mol/h.)



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Figure 5-17. Gas Release Source Terms and Gas Concentrations for Upper Bound Gas Diffusivities--Mixture 1 (29% H₂, 71% N₂O, 0% O₂). (Initial Gas Generation Rate = 0.043 mol/h.)



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Table 5-8. Gas Release Source Term and Compartment Gas Concentrations--
Mixture 1. (29% H₂, 71% N₂O, and 0% O₂).
(Initial Gas Generation Rate 0.043 mol/h.)

a. Summary of Lower and Upper Bound Diffusivity Cases Gas Release

Sensitivity case	Advection start time (yr)	Total gas release ^a					
		Diffusion (mol)			Advection (mol)		
		H ₂	N ₂ O	O ₂	H ₂	N ₂ O	O ₂
Lower Bound Diffusivities	21	1.3 E+3	1.9 E+3	-4.9 E+1	2.7 E+1	7.0 E+1	2.5 E+0
Upper Bound Diffusivities	23	2.3 E+3	2.8 E+3	-6.4 E+1	1.7 E+1	4.6 E+1	1.8 E+0

b. Lower Bound Diffusivities Compartment Concentrations

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	7.9 E-4	9.8 E-4	2.1 E-1	7.9 E-1	4.7 E-4	6.2 E-4	2.1 E-1	7.9 E-1
30	1.0 E-3	1.5 E-3	2.1 E-1	7.9 E-1	6.1 E-4	9.7 E-4	2.1 E-1	7.9 E-1
100	5.0 E-2	7.8 E-2	1.8 E-1	6.9 E-1	--	--	--	--
200	8.7 E-2	1.4 E-1	1.6 E-1	6.2 E-1	--	--	--	--
300	1.1 E-1	1.7 E-1	1.5 E-1	5.7 E-1	--	--	--	--

c. Upper Bound Diffusivities Compartment Concentrations

Time (yr)	Catch basin (mol fraction)				Leachate sump (mol fraction)			
	H ₂	N ₂ O	O ₂	N ₂	H ₂	N ₂ O	O ₂	N ₂
10	1.5 E-3	1.9 E-3	2.1 E-1	7.9 E-1	8.9 E-4	1.2 E-3	2.1 E-1	7.9 E-1
30	1.9 E-2	2.8 E-3	2.1 E-1	7.9 E-1	1.1 E-3	1.8 E-3	2.1 E-1	7.9 E-1
100	8.6 E-2	1.2 E-1	1.7 E-1	6.3 E-1	--	--	--	--
200	1.4 E-1	1.9 E-1	1.4 E-1	5.3 E-1	--	--	--	--
300	1.8 E-1	2.2 E-1	1.3 E-1	4.8 E-1	--	--	--	--

^aaccumulated releases at 300 years.

- H₂ = Hydrogen
- N₂O = Nitrous oxide
- O₂ = Oxygen
- mol = Moles
- mol/h = Moles per hour
- yr = Years

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Figure 5-18. Advection Gas Release versus Initial Gas Generation Rate.

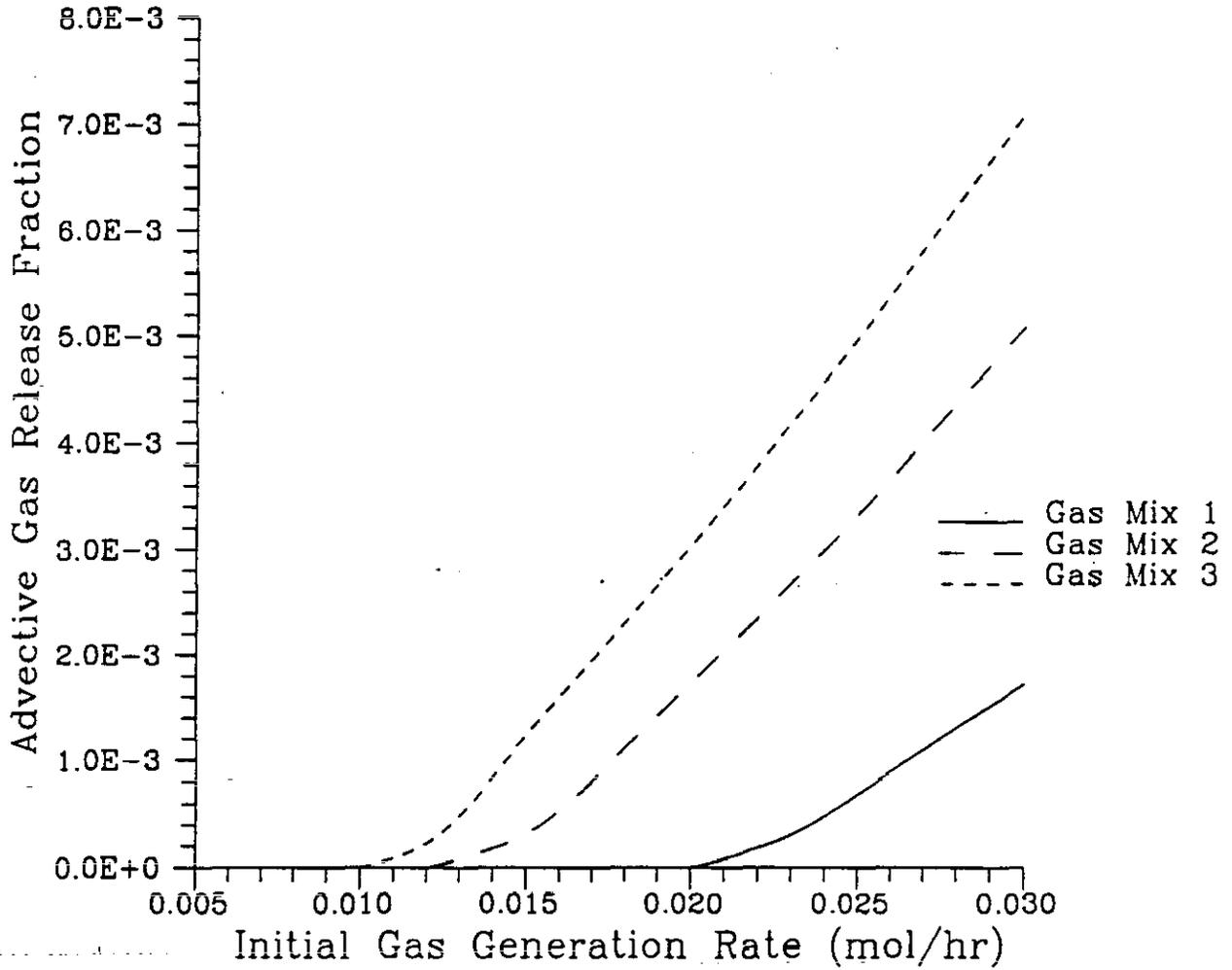


Figure 5-19. Gas Release Fraction versus Initial Gas Generation Rate.

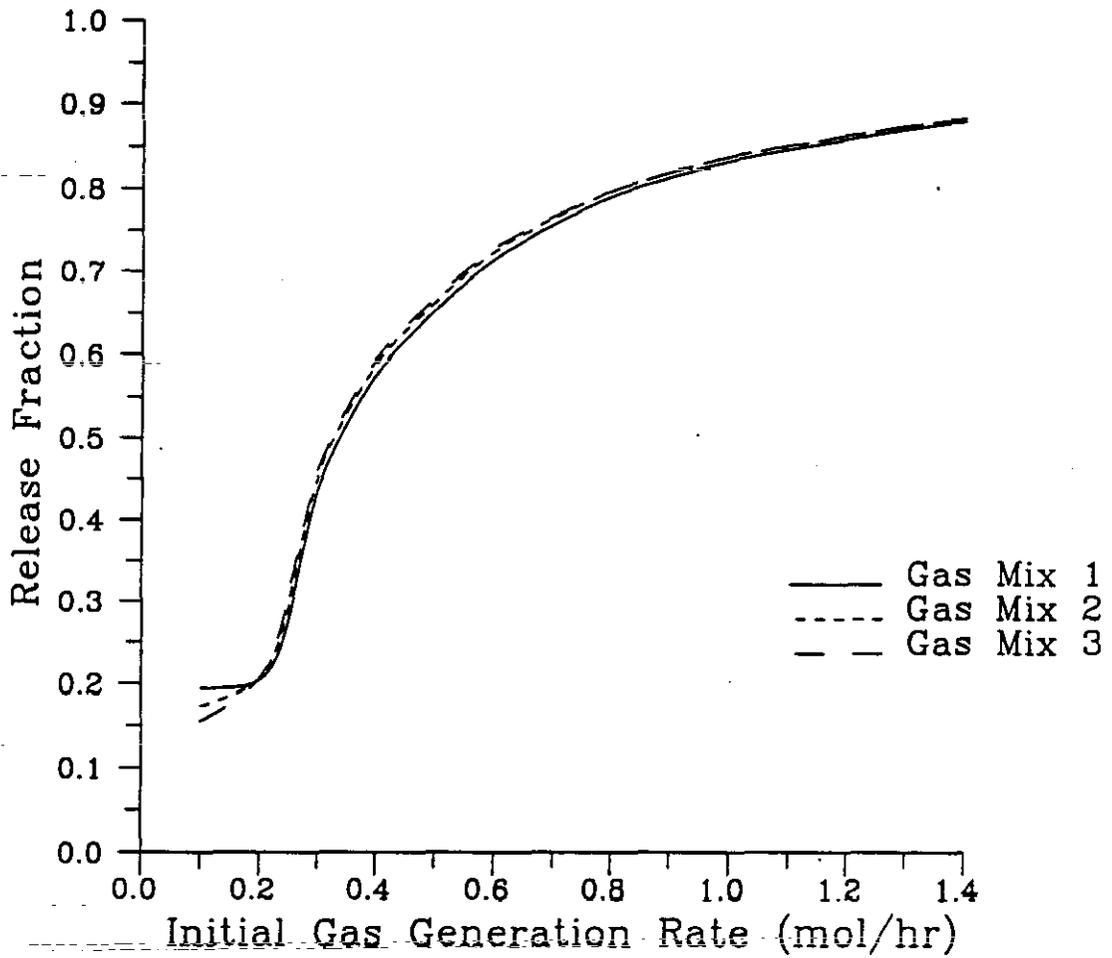
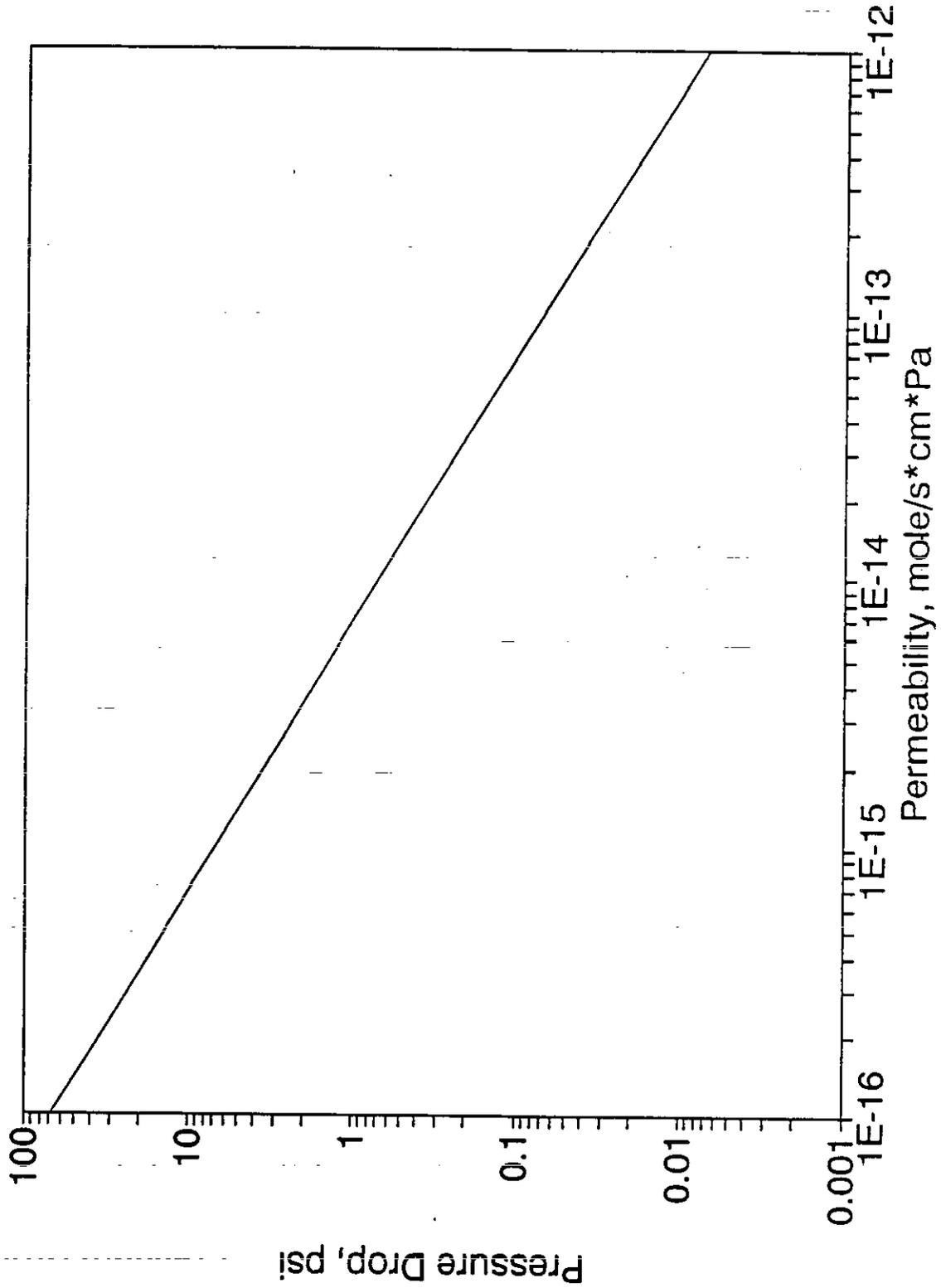


Figure 5-20. Vault Pressure Versus Asphalt Permeability at 0.043 g mol/h Generation Rate.



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6.0 RECOMMENDATIONS

The following recommendations are suggested from findings related to the analyses in this report.

6.1 GAS GENERATION RATES

The bounding gas generation rates assumed in this report for hydrogen, nitrous oxide, and oxygen represent a large upper range to demonstrate potentially adverse effects. These extreme effects are not representative of expected lower gas generation rates. To reduce conservatism, the bounding case should be reduced substantially by upgraded measurements and predictive modeling support. The extreme bounding gas generation rate assumption gives the impression that safety studies should be based on very restrictive assumptions rather than on less restrictive gas generation rates that could be justified by material specific measurements.

Predictive modeling of gas generation conversion factors are being developed for the waste tank characterization program. Predictive models and measurements consistent with the methods applied to the waste tank program characterization will provide better understanding of the gas formation mechanisms. These predictive models and measurements may provide justification to reduce the higher level of the gas generation rate range. Therefore, it is recommended that gas generation rates be validated with predictive modeling and measured data.

6.2 HYDROGEN MITIGATION SYSTEMS

If required, an active ventilation system would be the simplest solution to mitigation. The ventilation system could be made more effective by using an inert gas purge of the vault regions. The presence of an inert gas such as nitrogen would substantially lower the risk of flammability. An alternative mitigation system is the placement of a diffusion barrier on the inside surfaces of the grout vault sides and bottom. The potential of a diffusion barrier is discussed in Section 4.3. Its full evaluation will require further modeling and validation beyond the scope of this report.

6.3 VENT SYSTEM

The release rate and total release of gases from the grout block to the vault atmosphere for the reference case are at a level much lower than originally used in preliminary design of the facility (Whyatt 1989). Also, a potential gas release mechanism of permeability through the asphalt has been identified. For these reasons, the vent system that releases gas and pressure to the soil during phase III may not be needed to prevent unacceptable consequences of pressure buildup. Follow-on modeling of gas release and permeation through the barrier may result in acceptable internal pressures. The measurement program of the asphalt permeability should continue to determine an alternate gas release for the engineered vent system to avoid problems defending its design.

6.4 GAS HOLDUP AND RELEASE MODELING OF THE GROUT BLOCK

The model used to characterize gas holdup and release from the grout block is adequate to provide conservative results and trends in compartment gas concentrations for the safety studies. However, other concerns such as liquid expulsion and gas generation levels corresponding to advection initiation and breakaway were identified which cannot be quantitatively established by the simple one-dimensional model used in these studies. In addition, a three-dimension model may be needed to account for geometry affects on advection flow. A more sophisticated model that more rigorously accounts for two-phase flow of gas and liquid and temperature driving forces is needed. In addition, an adequate supply of quality data from a testing program is also needed to reduce uncertainties in data and to validate model predictions. Follow-on calculations should be made with these model improvements.

6.5 ESTABLISH GAS ADVECTION THRESHOLDS

Two thresholds have been identified in this report for the advection process. These thresholds are advection initiation and breakaway. A third and fourth threshold should be established which determines the gas generation rates that corresponds to an allowable level of liquid expulsion by advection and grout block swelling due to grout structure fracturing. These thresholds have been recognized in this report. They are needed to establish design criteria and processing limits. However, the gas generation rates corresponding to these thresholds cannot be quantitatively established with the present models and status of data. More sophisticated models and better defined data are needed to establish these threshold limits.

6.6 REABSORPTION OF LIQUID

The simplified models in this report did not address potential reabsorption of liquid in the catch basin, gravel fill, and concrete structures. The gravel fill and concrete structures of the vault and catch basin will perform as a blotter to liquid flow, depending on the degree of drying. The potential of reabsorption is high by this mechanism and may be used to absorb most or all of the liquid expelled from the grout block. Additional modeling and measurements should be performed to justify the quantity of liquid absorption available in the present design.

6.7 RETENTION OF LIQUID IN CATCH BASIN DURING PHASE III

During phase III, the sump will be grout filled and will no longer be used to remove liquid from the disposal facility. The liquid that may be expelled by advection or some other process will collect in the catch basin. The catch basin has a very large capacity to retain excess liquid in the void space in the gravel fill (about 16,800 L). The suitability of this holding capacity should be considered to retain liquid, if needed.

6.8 COLD CAP PERMEABILITY

This study assumed that the permeability of the cold cap material was the same as that of the grout material. If the cold cap permeability is considerably lower than the value used in the present calculation, more gases will be retained in the grout block. The follow on studies will incorporate an upgraded cold cap permeability, if applicable, to remove conservatism.

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7.0 CONCLUSIONS

The characterization of hydrogen, nitrous oxide, and oxygen transport in the grout vault was performed using models that employ the techniques of diffusion and mass transport, where appropriate. These models are sufficiently sophisticated to yield a conservative and defensible characterization of hydrogen and other gas flow rates and concentrations. These models can be used in safety analysis reports for the justification of the design from a hydrogen flammability safety standpoint and for specifying hydrogen mitigation systems. The time constraints of this study required that a simplified model be used for gas holdup and release from the grout block. It is desirable to validate these results with more sophisticated models and remove some of the conservatism imposed.

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The gas release rates and compartment concentration results of this modeling depend heavily on input data such as gas generation rates and material properties. The values of the materials property data used in the reference calculation of this report are based on best estimate values that are available from interpretation and application of data in the literature. Suggestions for upgrades in available data from the literature have been identified in this report for material-specific gas generation rates and asphalt permeability.

The permeability of gas through the asphalt diffusion barrier was investigated as an alternate method of release in place of the gas vents. A lower limit of the asphalt permeability was identified that may make this alternate release practical. The achievement of this permeability level will depend on measurement results of the quantity of interconnected pores that exist in the asphalt material.

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APPENDIX A
RECOMMENDATIONS FOR A RADIOLYTIC GAS FORMATION
FOR DOUBLE-SHELL SLURRY GROUTS

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Westinghouse
Hanford Company

Internal
Memo

From: Thermal Hydraulic Analysis
Phone: 6-3260 HO-33
Date: April 20, 1992
Subject: RECOMMENDATION FOR A RADIOLYTIC GAS FORMATION FOR DOUBLE SHELL
SLURRY GROUTS

To: W. J. Powell R4-03

cc: B. E. Bielicki	H5-72	S. P. Roblyer	H0-38
O. A. Halvorson	R3-10	J. E. Shapley	N1-38
D. G. Holcroft	P7-18	H. Toffer	H0-38
J. L. Homan	H5-72	J. B. Truitt	H5-56
M. J. Horhota	H4-16	J. A. Voogd	R4-03
R. M. Marusich	H5-32	M. P. Weis	L6-61
T. B. McCall	H0-33	G. H. Weissberg	R3-10
C. V. Mendoza	P8-44	J. H. Westsik	P7-19
C. J. Moore	H5-56	G. A. Whyatt	P7-19
A. L. Randle	N1-38	CAH LB/File	

SUMMARY

This memo contains the results of a literature survey of work concerning the radiolytic generation of gases from chemical systems that are related to the grouted double shell tank wastes, commonly called Double Shell Slurries (DSS). The memo makes recommendations about values for source terms for radiolytically generated hydrogen, nitrous oxide and oxygen gases in the presently designated grout formulation.

It is recommended that the two radiolytic gaseous source term cases be considered in all analytical work being performed on the Grout Vault System. Both of these recommended cases are shown in Table 1. The first case is the *Bounding Case*, that utilizes a very conservative source term that is expected to have a low probability of occurrence. This value leads to a total gas generation rate that can be used to size critical gas-handling systems. The second case is referred to as the *Nominal Case* or the expected case, and is based upon experimental evidence gathered from the literature.

Until a more complete understanding of the chemistry of the radiolytic formation of these gases is obtained, these recommended source term values should be used with caution. It is therefore recommended that the work toward an experimental determination of these values be continued. In addition, work should proceed toward the development of the analytical model of the radiolytic chemistry to accommodate future changes in grout formulations that may occur.

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Table 1
 Recommended Source Terms for
 Grout Vault Analyses

	BoundingCase		NominalCase	
	G-Value molec/100 eV	Q/t g mole/h	G-Value molec/100 eV	Q/t g mole/h
H ₂	0.23	0.64*	0.0043	0.012
N ₂ O	0.23	0.64	0.011	0.031
O ₂	0.07	0.19	0.0	0.0

Conversion Factor = 2.82 [g mole/hr]/[molec/100 eV] for 8.80E+06 kg grout.
 * Modified generation rate confirmed by GA Whyatt, PNL.

INTRODUCTION

The objective of this memo is to provide guidance to the analysts about the type and the amount of gases that may be produced by radiolytic decomposition of water, organics, and other chemical components contained within the grout. This information is needed to obtain realistic and bounding estimates of the consequences of the formation of flammable gases within the grout vault. The most probable gas to be generated is hydrogen, originating from the decomposition of water and associated organics that are contained in the liquid waste stream. Hydrogen gas is, of course, highly flammable when associated with an oxidizing environment. The oxidizing environment can consist not only of the oxygen in residual air within the vault structure, but also from the potential formation of nitrous oxide by radiolytic decomposition of the nitrates and/or nitrites that are present in the original liquid waste.

A modeling study is presently under way, where the generation and migration of the gases through the system are being analyzed. The source terms for these gases are one of the most important parameters required as input to the model. The generation rates affect the details of release and flow not only of gases, but possibly of liquids, through the spaces of the grout vault.

Another study is examining the consequences of a hydrogen burn, both in the catch basin and the sump. The energy released from this burn is dependent upon the local concentrations of the gaseous components. Those concentrations, in turn, are to be provided by the gas flow model that was discussed above.

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RECOMMENDATIONS

It is recommended that two radiolytic gaseous source term cases be considered in all analytical work being performed on the Grout Vault System. The first is the *BoundingCase*, a very conservative set of circumstances that is expected to have a low probability of occurrence. The second case is the *NominalCase* or the expected generation rates of gases.

The recommended *BoundingCase* is taken from a previous literature survey (Whyatt, 1991, see Attachment 1), where a G-value was recommended that yielded an initial gas generation rate of 0.62 gm-moles of gas/hr. The gas production rate is reduced over time as the radiation-producing components of the waste decay. This initial gas generation rate took into consideration the quantity of grout present and the expected starting radiation dose rates within the grout mass. It did not include an estimation for gases other than hydrogen. The G-value was taken from the work of Lewis and Warren, 1989 (see Attachment 1), as the highest measured rate of radiolytic H₂ generation in a grout, regardless of its chemical makeup. The measured G(H₂) of this work was 0.23 molecules of H₂/100 eV of absorbed radiation, as indicated in Table 1.

The *BoundingCase* for nitrous oxide generation has been chosen based on the observations in gas compositions from the SY-101 tank. It was stated in Fox, et al. (1990) that the gas composition for the 04/19/90 "burp" was 57% H₂ and 43% N₂O. For the *BoundingCase*, a N₂O quantity equal to the H₂ quantity was chosen. In addition, to be conservative, a quantity of O₂ was assumed to be formed that was equal to 30% of the amount H₂, as shown in Table 1.

The *NominalCase* is based upon the information obtained from the literature, and is offered based upon the analyses made in the following presentation. The recommended values for gaseous product source terms are contained in Table 1.

The recommended *NominalCase* is taken from the work of Friedman, et al., 1985, where the G-value was measured using a grout mix that was very similar in chemical makeup to the one presently in favor (see Table 3), and a liquid waste containing the important components that are present in the DSS tanks (see Table 4). The G-value derived from that work is a factor of more than 50 smaller than for the *BoundingCase*. The G(H₂) value derived from this work was 0.0043 molecules H₂/100 eV absorbed radiation. The equivalent gas yield from a vault of grout for this G-value is 0.012 moles of H₂/hr.

Also observed in the Friedman work, and incorporated into the recommended *NominalCase*, was a quantity of N₂O generated under irradiation that yielded a G(N₂O) of 0.011 molecules/100 eV. In addition, O₂ absorption was observed by Friedman for his primary grout composition for DSS wastes and gamma irradiations. (O₂ generation was observed in the case of alpha irradiation of grouts containing sludge waste materials, but not DSS wastes.)

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DISCUSSION

Table 2 presents a range of source term values measured for the generation of potential gases from both grout and aqueous solutions containing components that are anticipated to be included in the DSS grout and is presented without regard to the detailed technicalities of the experiments. To obtain the technical details of each of these studies, see the descriptive information in the summaries of Attachment 1, or consult the original references.

A number of factors have been investigated in the literature that influence the radiolytic formation rate of various gases. A listing of these factors includes: 1) presence and relative amounts of nitrate and/or nitrite ions in solution, 2) presence of blast furnace slag, particularly if it contains unoxidized sulfides, 3) the presence of an organic component in solution, 4) the external pressure of the gas under consideration, 5) the radiation dose and dose rate, 6) the type of radiation (alpha, beta or gamma), 7) other chemical additives (Fe_2O_3 , MnO_2 , Zircaloy, KCl , LiCl , NaIO_4 , Ag_2O , KMnO_4 , FeO , FeS , as the main chemical additives) and 8) water content.

The most influential factor in the reduction of the generation rate of H_2 appears to be the presence of NO_2^- and/or NO_3^- ions. This is shown in the work of Meisel, 1991, where two compositions of solutions were irradiated. The first solution, Solution P, contained NO_2^- and NO_3^- , and the "High Ionic Strength" contained no nitrite and a factor of almost 300 less nitrate. Other differences in composition existed between these two solutions, as can be seen in the summary of the work in Attachment 1. A $G(\text{H}_2)$ of 0.03 molecules/100-eV was measured for the nitrate/nitrite containing Solution P; 0.395 was measured for the other. Meisel concluded that $G(\text{H}_2)$ is strongly reduced by the NO_2^- ion, and is relatively independent of the NO_3^- ion.

Two influential factors relative to the generation of N_2O are the presence of a soluble organic "substrate" and the presence of NO_3^- and/or NO_2^- ions. In Meisel, 1991, no radiolytic N_2O was observed unless the solution contained an organic component. Likewise, no N_2O was formed unless there was either nitrate or nitrite present.

Organic molecules have been observed to suppress the formation of O_2 . The presence of blast furnace slag in a grout can also suppress the O_2 formation. A possible explanation of the mechanism for the gathering of the oxygen involves the oxidation of the sulfide or the organic. Another is the substoichiometric oxides of iron may provide a chemical sink for the oxygen. The most applicable experimentally determined source term information for radiolytically generated gases for the DSS grout can be extracted from work of Friedman, et al., (1985). The grout used in this study contains most of the components of our present "Formulation I" mix. Table 3 compares the grout mix used by Friedman to the presently in-favor Formulation 1.

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Table 2
 Summary of Measured G-Factors for Radiolytic
 Generation of Gaseous Species of Interest

G, Molecules of gas/100 eV of Absorbed Energy					
Reference	Radiation	H ₂	N ₂ O	O ₂	N ₂
Bibler (1978) Concrete		0.21		0.1	
			0.001 0.008		
Bibler (1980) Concrete		0.32	0.0	0.12	
		0.25	0.0	0.05	
		0.29	0.0	0.0	
		0.03	0.0	0.37	
		0.053	0.04	-0.08 (O ₂ Consumed)	
Friedman (1985) Grout		0.0043	0.011		
Kroth (1990) Cement Grout		0.086			
		0.013			
		1.64			
Lewis (1989) Mortar		0.23			
		0.16			
		0.02			
Meisel (1991) Aqueous solutions		0.031	0.0	0.08	
		0.033			
		0.395			
		0.46			
		0.08	0.3-1.2	-7 (O ₂ Consumed)	
		0.065	0.6-1.3		0.07-0.13

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Table 3
 Selected Grout Formulations
 Memo: Riebling to Voogd, 03/31/92

Grout Component	Friedman wt%	Formulation 1	
		Batching Info	Grout wt%
Cement	16.20	20 wt% dry	8.9
Fly Ash	16.20	66 wt% dry	29.3
Clay	9.68	14 wt% dry	6.2
Liquid Waste	57.92	8.7 #Solid/gal liquid	55.5

Sp Gravity liquid = 1.3

The simulated waste that was mixed with the grout dry mix in this work contains a chemical make-up of the Double-Shell Slurry that was "supplied by Rockwell Hanford Operations" and identified as DSS-Composition A-diluted 1.5. Since this experimental work was published in 1985, the compositions are not necessarily the same as the generic tank of today, for which there is not an equivalent compound concentration listing. The molar compositions given in the Friedman reference are converted to weight percents in Table 4 for an assumed specific gravity of 1.30 gm/cc.

A conversion of the anion/cation to compound compositions of the "generic" DSS tank contents listed in SD-WM-TI-355 is contained in Attachment 2.

Table 4
 Double Shell Slurry Simulated Compositions

Component	Molar	wt%	From SD-WM-TI-355 (see Attachment 2) wt%
NaAlO ₂	1.1	6.9	NA
NaOH	2.6	8.0	6.3
NaNO ₃	2.0	13.1	10.7
NaNO ₂	1.6	10.2	5.1
Na ₂ SO ₄	0.02	0.2	0.2
Na ₂ PO ₄	0.04	0.5	0.7
NaCrO ₄	0.04	0.5	NA
NaCl	0.08	0.4	0.4
NaF	0.02	0.1	0.1
TOC	4.8 g/L	0.4	0.2
Water	1000.0 cc	59.8	73.

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The measured quantities and composition of the gases formed during gamma radiation in this reference are detailed in the summary of the publication in the Attachment 1 of this memo. It was found that the implied $G(H_2)$ from this work is on the order of 2% of that used as our *BoundingCase* (Lewis & Warren, 0.23 molecules/100 eV):

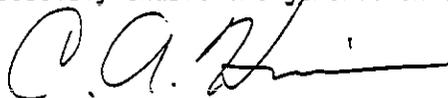
$G(\text{total}) = 0.018$ molecules/100 eV,
 $G(H_2) = 0.0043$ molecules/100 eV,
 $G(N_2O) = 0.01$ molecules/100 eV.

These values for source terms for H_2 and N_2O represent the best available experimentally-derived information in the literature for the present grout. However, the G-values have been found to be very sensitive to the compositions of the grout and the waste stream, with the NO_2^- and NO_3^- ions being most controlling. In addition, the blast furnace slag has been observed to change the character of the gases generated, most notably, in the scavenging of free O_2 that may be formed.

Almost all of the tanks contain significant amounts of NO_3^-/NO_2^- ions, both of which components have been observed to reduce the amount of H_2 in both aqueous solutions and in grout formulations. This is an indication that the $G(H_2)$ for DSS grouts will be less than the G that is being used presently.

In the "generic" tank waste composition, the Total Organic Carbon (TOC) is on the order of 0.5 to 2 wt%, larger than in the above simulated waste. The literature shows that this waste feed material may result in more H_2 being generated than was measured by Friedman. This level of TOC will presumably suppress any free O_2 formation. It may also enable the generation of N_2O .

For other potential grout formulations, the DSS feed will contain much less TOC than the above, e.g., while Tank AN-103 contains 0.5 wt% TOC, Tank AW-101 contains about 0.012 wt %. The lower concentrations will tend to reduce the amount of H_2 generated from their grouts, suppress the amount of N_2O and possibly enable the generation of small amounts of O_2 .

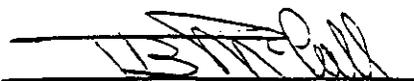


C. A. Hinman, Principal Science Engineer
Thermal Hydraulic Analysis

dsa

Attachments

CONCURRENCE:



T. B. McCall, Manager
Thermal Hydraulic Analysis

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The following is a listing of documents and contacts concerning the generation of gases in irradiated grout (H₂, O₂, N₂O). Compiled and interpreted by C. A. Hinman and G. A. Whyatt.

Ashby, EC, "Mechanistic Elucidation of the Chemistry in Tank 101-SY", Progress Report for 6 months 04/15 - 10/19/91, Georgia Tech, to GD Johnson, et al.

Progress report. Kinetic studies of gas evolution in simulated tank wastes. Chemical formation mechanisms (as opposed to radio-chemical mechanisms). Academic studies.

63 References.

Ashby, EC, "Progress Report for the Month of November, 1991", December 3, 1991, Letter report to GD Johnson.

Progress report. H₂ formation from formaldehyde. Thermal decomposition of organics.

Bibler, NE, "Radiolytic Gas Production During Long-Term Storage of Nuclear Wastes", DP-MS-76-51, 1976, Savannah River Laboratory.

Neat cement and cement containing Fe₂O₃ or MnO₂ to simulate waste were irradiated with ⁶⁰Co at rates of 1E+05 to > 1E+07 rad/h. H₂ was the only significant gas produced and reached an equilibrium pressure which was dependent on the dose rate. Seventy-five to 93% of the O₂ present was consumed. Results were consistent with observed pressurization of actual waste containers.

Bibler, NE, "Radiolytic Gas Production From Concrete Containing Savannah River Plant Waste", DP-1464, January 1978, Savannah River Laboratory.

This work is a continuation of the work described in Bibler (1976).

Pressure changes in closed containers containing the concrete specimens were measured during alpha (²⁴⁴Cm) and gamma (⁶⁰Co) irradiation. Gas composition was measured using gas chromatography. The concrete was made by mixing HighAlumina cement with simulated SRP wastes. Nominal composition of HiAlumina cement is:

Al ₂ O ₃	41 wt%
CaO	37
SiO ₂	9
Fe ₂ O ₃	6
MgO	2
Other oxides	5

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Total gas production was measured by monitoring pressure vs time. Steady-state pressures (SSP) were observed that depended upon dose rate and the chemistry of the grout. Water content didn't affect SSP.

One set of concretes contained simulated wastes consisting of 40 wt% Fe₂O₃ or MnO₂ (dry basis). For these concretes, H₂ was the only gas produced and O₂ was 60 to 80% consumed. SSP's for MnO₂ concrete ranged from 12 psi at 1E+05 rad/hr to 65 psi at 3E+07 rad/hr; for Fe₂O₃ concrete from 28 psi at 1E+05 rad/hr to 120 psi at 3E+07 rad/hr.

For concretes with no NO₃⁻/NO₂⁻, O₂ was 60-80% consumed, signified by pressure decreases during early stages of irradiation. N₂ was not significantly affected.

At low dose rates (8.9E+04 rad/hr), additions of 5 wt% NO₃⁻ caused small amounts of N₂O to be produced. Pressurization could be stopped by the imposition of 36 psi H₂. The gas produced was approximately:

5% N₂ and
95% H₂ with
O₂ consumed. N₂O:H₂ = 0.053.

An addition of 5 wt% NO₃⁻ and 2.5 wt% NO₂⁻ produced gas of:

20% N₂O and
80% H₂ with
O₂ consumed. N₂O:H₂ = 0.25.

At high dose rates (2.8E+07 rad/hr) O₂ was consumed in the absence of added NO₃⁻. O₂ was produced in NO₃⁻/NO₂⁻ concrete and SSP was not attained at 180 psi.

At high dose (8.0E+06 rads) O₂ was 92% consumed in the absence of NO₃⁻ but was increased by 43% when it was present.

For 1 wt% NO₃⁻, O₂ was produced in a ratio:

O₂:H₂ = 0.3 and
N₂O:H₂ = 0.008.

Addition of 1 wt% NO₂⁻ increases the N₂O production although a value was not given.

In concretes containing simulated SRP sludges (hydrous oxides of Fe⁺³, Al⁺³ and Mn⁺⁴), low dose rates produced H₂, consumed O₂ and produced N₂O:

N₂O:H₂ = 0.03.

At the high dose rate (gamma) the production was 34% O₂, 66% H₂ with no N₂O produced. No SSP was observed for alpha radiation:

O₂:H₂ = 0.52.

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At the low dose rate, the addition of 1.1 wt% ascorbic acid ($C_6H_8O_6$) to the simulated sludge grouts resulted in O_2 still being consumed. The imposition of 60 psi H_2 pressure did not affect the pressurization rate.

At high dose rate, the addition 1.7 wt% ascorbic acid prevented O_2 generation. A SSP of 150 psi was observed.

G-values were computed from information obtained in this work for cases where the production rate was not affected by pressure:

@5.0 wt% NO_3^- (<u>alpha</u>)	$G(H_2) = 0.21$	$G(O_2) = 0.1$	SSP = 60 psi
@5.0 wt% NO_3^- (<u>gamma</u>)	$G(N_2O) = 0.001$		
@2.5 wt% NO_2^- (<u>gamma</u>)	$G(N_2O) = 0.008$		SSP = 400 psi

21 References.

Bibler, NE, "Radiolytic Gas Generation in Concrete Made with Incinerator Ash Containing Transuranium Nuclides", Scientific Basis for Nuclear Waste Management, Vol 2, Editor, CJM Northrop, Jr., Plenum Press, 1980, pp 585-592.

This is a study of H_2 , N_2O and O_2 gas generation from alpha-radiation, using ^{238}Pu as the source in the concrete. It was shown that effect of NO_3^-/NO_2^- for both gamma $G(H_2)$ for concrete and alpha $G(H_2)$ for liquid water are the same.

Concrete used:

50 wt% cement,
20 wt% "ash",
30 wt% water,

and different amounts of ^{238}Pu to vary dose rate. The "ash" was derived from incinerating laboratory wastes, such as paper, plastics, etc. There was no organic content remaining in the ash. NO_3^-/NO_2^- additions were made to investigate their role in reducing $G(H_2)$.

Pressure increases and gas compositions were measured for two kinds of cements, Portland and HiAlumina. Two version of HiAlumina were tested: 1) simulated ash doped with ^{238}Pu , and 2) ash from incineration of waste contaminated with ^{238}Pu prior to burning.

H_2 was produced in all mixes. O_2 was produced in some. $G(H_2)$ was reduced by adding NO_3^- or NO_2^- ions (as sodium salts). $G(O_2)$ was increased by NO_3^- and decreased by NO_2^- .

	<u>$G(H_2)$</u>	<u>$G(O_2)$</u>	<u>$G(N_2O)$</u>
Portland	0.32	0.12	0.00
HiAluminal	0.25	0.05	0.00
HiAlumina2	0.29	0.00	0.00
"Concrete" + 6M NO_3^-	0.03	0.37	0.00
"Concrete" + 5M NO_2^-	0.053	-0.08	0.04

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Another topic that was covered was the reduction of H₂ generation by drying the concrete at 200°C and by "pressed" concrete (with 2 wt% water in a die at high pressure). Both worked.

9 References

Cooper, TD, "Hydrogen Generation in Tank 101-SY", letter of 02/25/91 to Babad, H.

A theoretical treatment of organic chemical mechanisms, such as "nucleophilic attack", "steric hinderance with alpha electron donors", etc.

Fox, GL, Himes, DA, Julyk, LJ, Mishma, J, Moore, CJ, Padilla, A, Winkel, BV, and Stepnewski, DD, "Response of Tank 241-SY-101 to a Postulated Hydrogen Burn", WHC-DS-WM-TI-426, May 1990.

Discusses gas composition of the 04/19/90 SY-101 "burp":

57% H₂,
43% N₂O.

This study used in the analysis of a burn a composition of 60% H₂/40% N₂O was assumed for the gas space above the crust of SY-101.

N₂O/H₂ = 0.75.

Friedman, HA, Dole, LR, Gilliam, TM, and Rogers, GC, "Radiolytic Gas Generation Rates From Hanford RHO-CAW Sludge and Double-Shell Slurry Immobilized in Grout", ORNL/TM-9412, 1985.

Simulated DSS was immobilized in a grout consisting of (by wt):

16.2% Type I-II-LA cement,
16.2% class F fly ash (Centralia WA),
3.24% Indian Red pottery clay,
6.44% Attapulgate clay (used as drilling mud),
14.04% DSS simulant solids, and
43.88% water.

The simulant DSS waste stream composition used was:

NaAlO ₂	1.1 M
NaOH	2.6 M
NaNO ₃	2.0 M
NaNO ₂	1.6 M
Na ₂ SO ₄	0.02 M
Na ₃ PO ₄	0.04 M
Na ₂ CrO ₄	0.04 M
NaCl	0.08 M
NaF	0.02 M
TOC	4.8 g/L (app 0.4 wt%)

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The grout samples were irradiated using two types of radiation sources, 2 samples for alpha irradiation from ^{244}Cu (presumably as an oxide) for a calculated dose rate of $5.67\text{E}+05$ rad/hr, and 3 samples for gamma irradiation from a ^{60}Co source at a rate of $8\text{E}+05$ rad/hr.

The average composition of the gas produced for three alpha-irradiated specimens was inconsistent between the 2 specimens, in one, N_2 appeared to be consumed, it was generated in the other; O_2 was generated in one, consumed in the other; there was a big difference between the H_2 and N_2O present in each. A small amount of CH_4 was found.

For the alpha-irradiated specimens, 2 average G(total) values were observed, one for the "early days" of the gas collection experiment, and a second for the "later days".

$$\begin{aligned} G(\text{total}) &= 0.046 \text{ Molecules/100 eV, "early",} \\ G(\text{total}) &= 0.12 \text{ "late".} \end{aligned}$$

The average compositions of the gas produced for three gamma-irradiated specimens were measured as:

$$\begin{aligned} 61\% \text{ } \text{N}_2\text{O,} \\ 24\% \text{ } \text{H}_2, \quad \text{N}_2\text{O}/\text{H}_2 = 2.5. \\ 15\% \text{ } \text{N}_2, \\ 0.15\% \text{ } \text{CH}_4. \end{aligned}$$

For the gamma irradiated specimens, the average G(total), based on the total pressure rise was calculated as 0.018 molecules of gas/100 eV. If it is assumed that production of gas is linear for each specie, then for:

$$G(\text{total}) = 0.018 \text{ molecules/100 eV,}$$

$$\begin{aligned} G(\text{H}_2) &= 0.0043, \\ G(\text{N}_2\text{O}) &= 0.011, \\ G(\text{N}_2) &= 0.0027, \text{ and} \\ G(\text{O}_2) &= \text{negative.} \end{aligned}$$

There is an indication of an initial gas retention phase for the grout in this work. For times between 30 and 60 hours after the irradiation was started, little radiolytically generated gas release was observed in the total pressure measurements.

There is also some indication of curvature in most of the plots of "Gas Volume, L/kg" vs time for both types of radiation, implying that the gas generation might be pressure sensitive. No discussion was found concerning this topic, or the values for pressures attained.

21 References.

9413222.0810

Henrie, JO, Flesher, DJ, Quinn, GJ, Greenborg, J., "Hydrogen Control in the Handling, Shipping and Storage of Wet Radioactive Waste", RHO-WM-EV-9 P, December 1985.

A discussion of radiolytically generated H₂. A section on GROUT, with NO₂ and N₂O generation. Refers to Friedman, 1985, for G-values.

21 References.

Henrie, JO, Barney, GS, Brown NN, Flesher, DJ, and Warrant, MM, "Gas Generation in TRU Wastes", February 1988, DRAFT, a report generated at the request of the Westinghouse Electric Corporation, Carlsbad NM.

A literature survey. Comparison of alpha and gamma radiolytic effects. Plastics, liquid organics, grouted wastes. Chemical and thermal decomposition.

83 References.

Kroth, K, Barnert, E, Brucher, PH, Lammertz, H, Niephaus, K., "Formation of Hydrogen and Radioactive Gases in Waste Packages with Cemented Intermediate Level Waste", Waste Management '90. "Working Towards a Cleaner Environment", Editor, Roy Post, 1990.

German pilot reprocessing plant wastes, i.e., fuel hardware, cladding "hulls" and dissolver sludge were encased in a cement grout in sealed 200 liter (53 gallon) drums and pressure was monitored for about 3 years. Ordinary Portland cement (PZ45F) was used, water/cement = 0.45, app. 1% "concrete thinner" was added.

O₂ from the initial air in the drums was consumed within the first few months, exhibiting an initial pressure decrease. Part of the H₂ was thought to be absorbed by Zircalloy. H₂ formation rates

appeared to decrease with time. Some G-values were calculated in this work, and are considered to be of relatively low accuracy because of unspecified geometries and experimental errors:

	cc of gas/kJ	G(H ₂) Molec/100 eV
Hardware	0.2	0.086
ZrII Cladding	0.03	0.013
Sludge	3.8	1.64

[Conversion factor = 0.4305 (Molec/100 eV)/(cc/kJ)]

5 References..

180-7278-116

Lewis, MA, and Warren, DW, "Gas Generation From the Irradiation of Mortar", Argonne National Laboratory, CONF 890488-8, 1989.

Mortar samples were prepared using portland cement, ground granulated slag and class F fly ash in order to immobilize a high-chloride brine solution. Irradiation was performed at 0.1 to 0.5 Mrad/h using ⁶⁰Co.

In the presence of slag, only H₂ was produced.

In the absence of slag, O₂ was produced:

$$O_2:H_2 > 0.3.$$

The addition of 2 wt% FeS or CaS inhibited O₂ generation. Increasing concentration of chloride salts increased the H₂ generation rate at ambient temperature and decreased the rate at 120°C.

Lewis, MA, Warren, DW, "The Use of Additives for Reducing Hydrogen Yield in Mortar Containing Slag and Chloride Salts", Scientific Basis for Nuclear Waste Management, XII, Materials Research Society Symposium Proceedings, Vol. 176, pp. 53-60, CONF-891129-2, November 1989.

Grout containing slag, fly ash, portland cement, 27 wt% water and 10-wt%-salt (KCl-44 wt%-LiCl), and another grout without the slag with 6 wt% salt, were gamma irradiated. Measurements on the slag-grout gave:

G(H₂) = 0.227 ± 0.033 (6 samples @25°C),
 G(H₂) = 0.16 (@75°C),
 G(H₂) = 0.02 (@120°C),
 G(O₂) = negative for all slag-grouts,
 G(O₂) = negative for no-slag-grout w/FeS,
 G(O₂) = not negative for no-slag-grouts w/o FeS,
 G(N₂) = negative,
 G(N₂O) = ?

Additives (NaIO₄, Ag₂O, NaNO₃, KMnO₄, and FeO and FeS) had a secondary affect on H₂ generation. All slag-grouts consumed all the O₂ (in the air) and some of the N₂ (about 30-40%) present at beginning of irradiation.

Slag-grout containing 1 wt% NaNO₃ generated N₂O/H₂ at a ratio of 6.8/60.3, or 0.113. Experimental measurements indicated a "significant" reduction in H₂ formation due to the NO₃⁻ addition, but values G(H₂) and G(N₂O) could not be calculated. In addition, it was estimated that an excess of about 2X in N₂ was detected. None of the slag-grouts contained O₂ at the end of irradiation, (not analyzed to be a gain or loss over starting gases).

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Several specimens of no-slag-grout with similar compositions to the above were irradiated. The O₂ generating/absorption effects of two additives were investigated: FeO and FeS. End-of-irradiation gas compositional results:

	vol% H ₂	N ₂	O ₂	O ₂ /H ₂
No-Slag, No-Additive	75.4	13.3	10.9	0.145
No-Slag, 1 wt% FeO	75.5	9.4	15.0	0.199
No-Slag, 1 wt% FeS	85.6	13.8	non-detectible	

No attempt was made to calculate G-values from these results. No attempt was made to do a mass balance for the O₂ to see if any of it was consumed or generated for the first two specimens. Conclusion drawn: "Reduced sulphur species are more important in controlling the radiolysis mechanism than iron species in lower oxidation states."

14 References.

Meisel, D, Diamond, H, Horwitz, EP, Jonah, CD, Matheson, MS, Sauer, MC, Jr and Sullivan JC, "Radiation Chemistry of Synthetic Waste", ANL-91/40, November 1991, Argonne National Laboratory.

A literature survey of radiolytic chemistry of aqueous solutions of the kind in the waste tanks, particularly SY-101. This report is the product of SubTask 1 described in Meisel (ANL-91/41).

25% of observed H₂ in SY-101 can be accounted for by radiolysis. G(H₂) = 0.06 Molecules/100 eV, generating 37 moles/da or 1.5 moles/hr of H₂.

An increase of NO₃⁻ leads to a decrease in H₂ yields and an increase in O₂ yields, i.e., O₂ is produced as a direct effect of the radiation of the NO₃⁻ and NO₂⁻. The addition of organic solutes to NO₃⁻/NO₂⁻ solutions leads to the radiolytic production of N₂O. It is difficult to see how aluminate could directly interfere with any of the radiolytic processes. No effect of pressure should be present for the 0-2 atm expected in the tank.

93 References.

Meisel, D, Diamond, H, Horwitz, EP, Jonah, CD, Matheson, MS, Sauer, MC, Jr, Sullivan, JC, Barnabas, F, Cerny, E and Cheng, YD, , "Radiolytic Generation of Gases from Synthetic Waste, Annual Report, FY 1991", ANL- 91/41, December 1991, Argonne National Laboratory.

This report represents the best work encountered in this literature survey relative to the radiolytic generation of gases from water, organics and nitrites/nitrates in simulated wastes. Three tasks were reported on in this progress report for 1991, 1) literature survey, 2) laboratory tests, 3) analytical model development. Testing was done on simulated SY-101 liquids containing 75% of the inorganic components originally fed into

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SY-101. Sodium salts of organic compounds were added as a major variable. Two solutions were irradiated, each with controlled addition of several organic constituents:

<u>Component</u>	<u>"High Ionic Strength"</u>	
	<u>Solution</u>	<u>Solution</u>
NaOH	2.27 M	0.1 M
NaAlO ₂	0.86 M	
NaNO ₂	2.22 M	
NaNO ₃	2.79 M	1.0 mM
NaCl	0.0 M	1.0 M

H₂ & N₂O radiolytic generation rates were measured as functions of: 1) temperature (30° & 60°C), 2) dose and 3) dose-rate, 4) organic content, 5) NO₃⁻/NO₂⁻ ionic content.

For H₂: The observed G(H₂)'s were linear with dose, with concentration of each organic component, and with number of H-bonds in each organic molecule. G(H₂) is greater at 60°C than 30°C. The reactions that form H₂ from the organic were identified (primary reaction: H-abstraction from the organic molecule by an activated H⁺ atom) and related to chemical rate constants that were used to build a model for an organically derived G(H₂). A series of rate constants were measured or taken from the literature.

Inorganic effects: G(H₂) depends "strongly" on the concentration of NO₂⁻ ion, and is "relatively independent" of the concentration of NO₃⁻ ion. G(H₂) is decreased by NO₂⁻. (See G's for the two solutions listed below). Na₂CO₃ has slight to negligible negative effects upon G(H₂). Na₂S increases G(H₂).

For N₂O: No N₂O was detected in the Solution P without organic being present. The mechanism for formation was much more complex than for H₂ (possibly 2 competing pathways?, not well understood). G(N₂O) was not linear with dose rate, but was lower at higher dose rates. G(N₂O) was generally greater at 60°C than at 30°C. Isotopically labeled nitrogen was used to determine that the N in N₂O comes "overwhelmingly" from the inorganic NO₂⁻ or NO₃⁻ ions and not from the organic molecule.

For O₂: O₂ was detected only when there was no organic present. O₂ was consumed in at least one case by the organic.

For N₂: N₂ was observed at 60°C in several cases. It was immeasurable in most tests.

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Observed G-values (molecules/100 eV):

<u>Without Organics:</u>	<u>Solution P</u>	<u>"High Ionic Strength" Solution</u>
at 30°C:	G(H ₂) = 0.031 G(O ₂) = 0.08 G(N ₂ O) = 0.0	G(H ₂) = 0.395
at 60°C:	G(H ₂) = 0.033	G(H ₂) = 0.46
<u>With Organics:</u>		
at 30°C:	G(H ₂) to 0.08 G(N ₂ O) 0.3 to 1.2 G(-O ₂) = 7 (O ₂ consumed)	G(H ₂) to 0.9
at 60°C:	G(H ₂) to 0.065 G(N ₂ O) 0.6 to 1.3 G(N ₂) = 0.07 to 0.13	G(H ₂) to 1.0

In these experiments, whenever both H₂ and N₂O were detected, the ratio of N₂O/H₂ ≈ 10. In SY-101, that ratio was 1. They are investigating this discrepancy.

Thermal Production of Gases: N₂O production persisted from some samples after the irradiation had been terminated, but only at 30°C (no post-irradiation production of N₂O was observed at 60°C). The "post-irradiation effect" was not reproducible.

Some "irradiation enhanced thermal production" of both H₂ and N₂O was observed in a special mix containing three organic additives (solution POI) at 60°C. This occurred after a pre-irradiation step, followed by a de-gassing step, followed by a gas collection step (without radiation). Pre-irradiation caused a 20-25% increase in the radiolytic yield of H₂. This was called a "post-irradiation thermal generation of gases". "...pre-irradiation... caused the formation of relatively long-lived products that substantially enhance the thermal production of H₂ and N₂O". A much smaller amount of these gases were generated in an identical, non-irradiated blank of this solution.

An estimate was made that, if SY-101 behaved in a like manner (to Solution POI), 40% of the H₂ and 6% of the N₂O would be radiolytically generated, conversely, 60% of the H₂ and 94% of the N₂O would be by this "thermal" mechanism.

18 References.

Whyatt, GA, "Gas Generation and Release from Double-Shell Slurry Feed (DSSF) Grout Vaults", PNL-7644, March 1991.

A literature survey of radiolytic gas generation in grouts. Most references are included in the listings of this file. A radiolytic gas generation rate of 1.01 moles/hr was recommended, most of which is expected to be H₂, based upon the work of Lewis and Warren (1989).

15 References.

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Stoichiometry Balance of a Statistically Derived Table
(Chemistry Lost Out)
From Section 2.3 of SD-WM-TI-355

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Sorted on Concentration:		
Ionic Specie	mg/g	Mol Wt g/mole
H2O	730.	18.
Na+	100.	22.99
NO3-	78.	62.
NO2-	34.	46.
OH-	27.	17.
Al+++	12.	26.98
CO3-	7.9	61.
K+	7.	39.09
PO4---	4.2	96.97
Cl-	2.7	35.45
TOC	2.3	NA
SO4--	1.5	96.06
Cr+++	0.3	52.
F-	0.29	19.
Bi+++	0.076	208.98
Pb++	0.063	207.2
U++++	0.061	183.85
Sb+++	0.055	121.75
Si++++	0.049	28.09
Ta++++	0.043	180.95
Ca++	0.036	40.08
Zr++++	0.033	91.22
U++++	0.029	
As etc.	0.029	
Mo	0.026	
Se	0.022	
CN (total)	0.021	
Ni	0.021	
Fe	0.015	
Cd	0.012	
Ce	0.012	
Pd	0.0093	
Zn	0.009	
Mn	0.0072	
Hg	0.0071	
Be	0.0055	
V	0.0055	
B	0.0047	
Ba	0.0046	
Ti	0.0045	
Ag	0.0043	
Nd	0.0043	
Cu	0.0035	
Hg	0.0023	
Li	0.0019	
La	0.0001	
CN (free)	3.8E-06	

Cation	Cation wt%	moles/100 g	Assoc Moles	% Remain
Na+	10.0	0.43	0.03794	8.72%
Al+++	1.2	0.044		
K+	0.7	0.018		
Cr+++	0.03	0.00058		
Si++++	0.0076	0.000036		
Pb++	0.0063	0.000030		
W+6	0.0061	0.000033		
Sb+++	0.0055	0.000045		
Si+4	0.0049	0.000174		
Ta+5	0.0043	0.000024		
Ca++	0.0036	0.000090		
Zr+++	0.0033	0.000036		
SUM	11.97	0.4984		

Excess anion quantity = 28.9%

Anion	Anion wt%	moles/100 g
NO3-	7.80	0.13
NO2-	3.40	0.074
OH-	2.70	0.16
CO3-	0.79	0.013
PO4---	0.42	0.0044
Cl-	0.27	0.0076
SO4--	0.15	0.0016
F-	0.029	0.0015
SUM	15.56	0.3866

Compound	Compd wt%	moles/100 g
NaNO3	10.69	0.13
NaNO2	5.10	0.074
NaOH	6.35	0.16
NaCO3	1.09	0.013
Na3PO4	0.73	0.0044
NaCl	0.45	0.0076
Na2SO4	0.22	0.0016
NaF	0.09	0.0015
SUM	24.71	0.39

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APPENDIX B

**DISCUSSION AND CALCULATION OF GAS HOLDUP AND
RELEASE MODEL FROM GROUT BLOCK**

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B1.0 GROUT PROPERTIES AND BEHAVIOR

This discussion will be limited to the properties of grout that are important to the modeling of hydrogen, nitrous oxide, oxygen, and nitrogen and grout liquid mass transfer. A discussion of the hydrogen and other migration gases is given to establish an understanding of the mechanism. The material properties of the grout representing saturated and unsaturated liquid content are based on best estimates or measured data of similar materials. The grout properties important to our calculations are listed in Section B2.1.

The structure of grout-type solid on the microscopic scale is shown in Figure 3-3 of this document. The solid materials that contain liquid in the chemically bound state are represented by irregular shapes surrounding regions of pore liquid. The volumes in the intermediate pore regions contain liquid that is bound by capillary forces. The unbound liquid can be dried from the grout and accounts for the density change between wet and dried grout. The permeability for gaseous hydrogen flow is greatly enhanced by loss of this unbound pore liquid. Removing unbound pore liquid from the grout provides an interconnected path of partially liquid-filled pores in which hydrogen and other generated gases may flow with relative ease as compared to a saturated (liquid filled) pore space.

Hydrogen, nitrous oxide, and oxygen form within the liquid-filled pores. These gases will tend to migrate from the solid regions as they reach saturation limits. However, some holdup of gases is expected. For comparison purposes, the relative solubility ratios of four important gases in pure liquid at 60 °C are as follows: 1, 1.2, 15, and 23 for H₂, O₂, N₂O, and CO₂, respectively.

Carbon dioxide is dissolved in carbonated drinks and has the highest solubility. Nitrous oxide is relatively soluble in the liquid and much of it will be contained without large initial pressure buildup. Hydrogen, however, is relatively insoluble in liquid (see Section B2.2). The solubility of hydrogen is decreased by the presence of dissolved salts in the liquid. As a consequence, dissolved hydrogen and other gases will eventually form as a gas phase of small bubbles which build high pressures that can overcome resistive pressure and displace unbound liquid.

The time history of the grout liquid/gas flow is composed of three periods: (1) pressure buildup of dissolved gases, (2) movement of liquid out of the grout in a two phase flow with gas to allow gas to fill the unbound or moveable liquid regions, and (3) release of any pressurized gas of the liquid after the liquid ceases to move.

The dissolved gas will initially build pressure within the grout block until pressure builds to overcome static pressure and resistive pressure to liquid flow and form bubbles to displace liquid. As gas bubbles form within the liquid-filled pores, the liquid will be forced out of the grout and flow to the outer surfaces along a pressure gradient. Some of the gas bubbles will be carried with the liquid outside the grout. Other gas bubbles will form closed pockets of accumulated bubbles within the pore volumes.

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The permeability for gas and liquid flow increases as gas bubbles displace the unbound pore liquid and partially fill the intermediate pore volumes. The gas and liquid flow is represented by a two phase flow of gas bubbles and liquid containing dissolved gas. As flow progresses in time, the fraction of gas in the two-phase flow increases. For high gas generation rates, a state will be reached when the two-phase flow transitions to a single phase gas flow which is characterized by low flow resistance, low internal pressure in the grout material, and a lower fraction of generated gas held permanently in the grout block.

B2.0 TECHNICAL BASES FOR MASS TRANSPORT FROM GROUT

A model characterizing the release of gas and liquid from the grout block is discussed in this appendix. In this model (designated G³, meaning grout gas generation), the unbound liquid volume is separated into a single region at the top of the grout block with a gas volume at the bottom of the grout block in the bound liquid region. Liquid is not allowed to flow from the sides and bottom of the grout block because of the impermeable layer of the elastomer that blocks liquid flow in these directions. A pressure of 1 atmosphere above atmospheric pressure is assumed for the top grout surface to account for the weight of the grout ceiling and overburden. The top surface of the grout block is the bottom of a direct horizontal path to the drainage gap.

When dissolved gas pressure exceeds 1 atmosphere above atmospheric pressure, unbound liquid near the top surface will begin flowing up and out of the porous grout. This flow will seek a path out of the grout vault into the catch basin. The flow of liquid and dissolved gas will continue until the gas generation stops because of the decay of radioactive materials. If the gas generation were large enough, the free liquid will be expelled all the way from the bottom of the grout. The prototype G³ model assumed multiple layers moving in series, beginning with the top layer. However, if we assume that the free grout liquid moves as one layer, with gas forming below as a second layer, the time of liquid expulsion is delayed, but of the same order of magnitude. One layer for simplicity and calculation speed was chosen in the initial flow analysis.

The equations used in G³ for pressure buildup and liquid movement are discussed below. First, we examine the magnitude of the pressure buildup in the grout. Radiolysis produces three gases uniformly per unit volume in the grout pores and we relate the pore concentration in time for each gas *i* by

$$\frac{dc_i}{dt} = R_i \quad \text{--- (B-1)}$$

where:

- C_i = concentration of gas *i*
- R_i = rate of formation of gas *i*.

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Initially, these gases, if held in the liquid saturated pore matrix will go into solution with the concentration

$$C_i^* = \int_0^{t^*} R_i dt + C_{i0}^* \quad (B-2)$$

The pressure that this dissolved gas exerts to try to come out of solution is

$$P_i = H_i C_i^*(l) RT \quad (B-3)$$

where:

- H_i = Henry's Law solubility constant (Section B2.1)
- R = ideal gas law constant
- T = absolute temperature
- $C_{i(l)}^*$ = any dissolved "i" concentration.

Here H_i is the dimensionless ratio which is assumed to be independent of pressure if a gas and liquid phase existed in intimate contact.

$$H_i = C_i(g) / C_i(l) \quad (B-4)$$

This ratio is selected at a specific temperature and dissolved salt content.

$C_i(g)$ and $C_i(l)$ are the gas and liquid concentrations respectively. The relationship of dissolved and undissolved gases is exemplified by the closed volume V with gas i dissolved in both liquid phases and present in the gas phases, each having volumes V_l and V_g , such that $V = V_l + V_g$. Then by equation B-3, the distribution of i can be found. If the total mass of i is produced by radiolysis in the liquid producing M_i total moles, then $M_i = V_l C_i(l) + V_g C_i(g)$. If we know V_l , V_g , and M_i , then we can calculate $C_i(l)$ and $C_i(g)$, an essential activity for gas formation calculations. The pressure in the closed volume with many gases present is

$$P_T = P_{H_2O} + \sum P_i \quad (B-5)$$

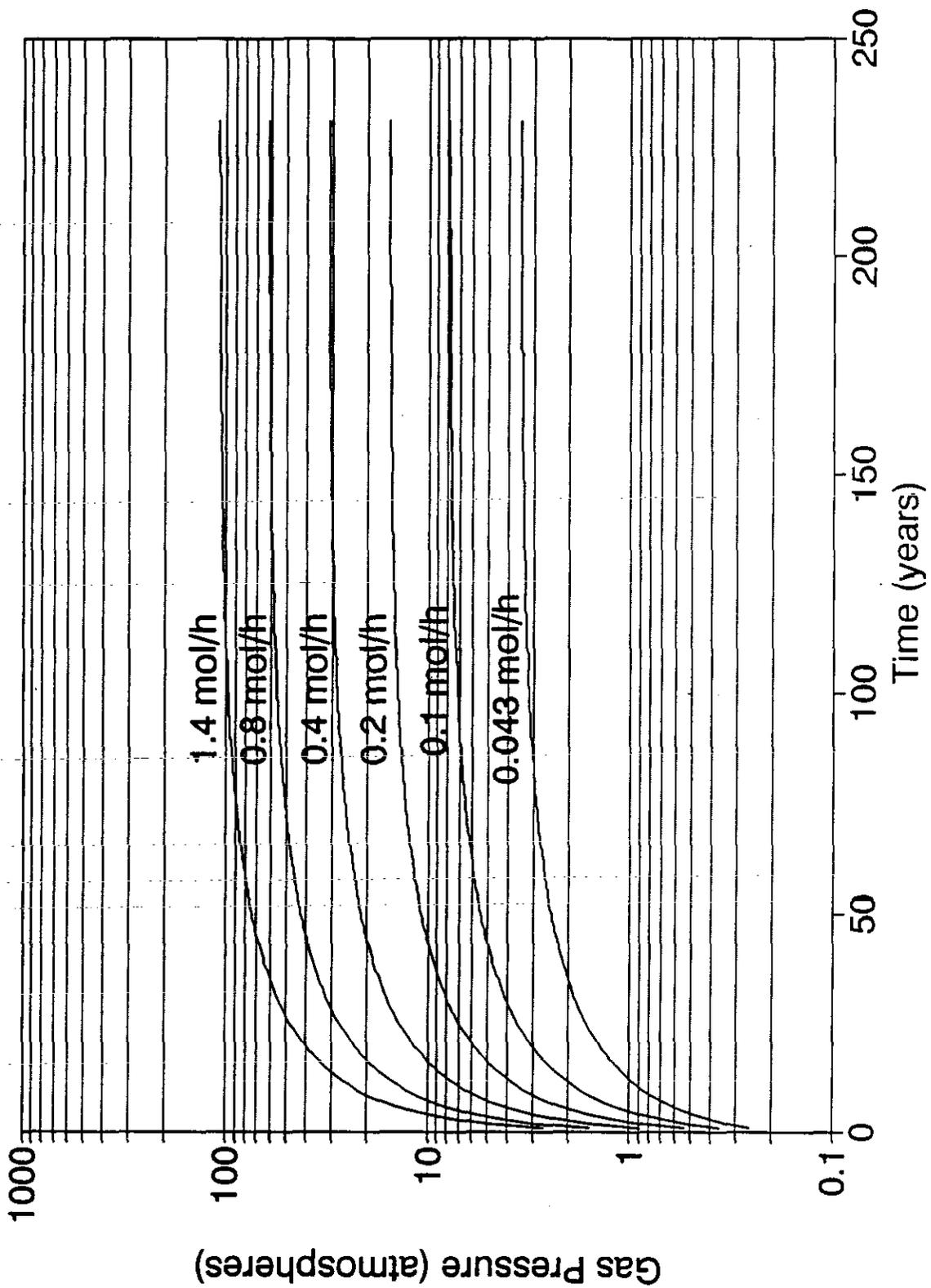
and

$$P_i = C_i(l) H_i RT \quad (B-6)$$

a variation on equation B-3.

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Figure B-1. Sealed System Gas Pressure Buildup.



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If no dissolved gas was allowed to leave the grout via diffusion or advection, then the internal grout "chemical" or vapor pressure, P_T , continues to buildup by radiolysis. Figure B-1 shows the hypothetical pressures as function of time for six (initial) gas generation rates. The pressure levels are directly proportional to the initial gas generation rates at any time point on the horizontal axis. Since the potential pressures are very large, something has to "give" along any possible flow path.

Even though molecular diffusion does relieve some of the pressure, we contend that liquid flow will commence upward toward the concrete cover block when P_T is greater than the overburden pressure, P_h ,

where:

$$P_h = P_o \text{ (weight of cover blocks + overburden)} \\ + \text{ hydrostatic head of liquid in grout}$$

when $P_T > P_h$, some fraction of the liquid will begin to move toward the concrete cap-grout plane along with pressure gradient via Darcy's Law (Bird 1960) with superficial velocity

$$v = - \frac{K}{\mu} \nabla P \tag{B-7}$$

$$= \frac{K}{\mu} \frac{(P_T - P_o)}{\Delta x} \tag{B-8}$$

where:

K = flow space intrinsic permeability

μ = liquid viscosity

Δx = grout vertical distance of liquid-saturated grout in the one-dimensional model, G^3

In Model G^3 , K is modified to include the inertia, or resistance to flow, of capillary forces. Here we ignore the viscosities of gases that are more than an order of magnitude smaller than the liquid.

The modification of K to include capillary or surface forces consists of a decrease in K in proportion to the fraction of energy expended on normal viscous flow (Darcy's Law) to the total energy expended in flow which includes the energy exposing new gas-liquid surfaces in the pores. The result of the modification shows that as the flow pore diameters decrease (at constant porosity) the effective permeability decreases.

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In the simple model that includes the surface forces $K' = cK$. The coefficient c is

$$c = \frac{-1 + (1 + 4b)^{1/2}}{2b}$$

$$b = \frac{dt K A_v \gamma}{\mu z^2}$$

dt = time step

z = vertical liquid column thickness

A_v = pore surface area per unit grout volume in which flow occurs

γ = liquid surface tension

This model assumes that a given free liquid surface area is produced in the time step dt while a vertical column of liquid is moved by pressure forces. The capillary pore diameter d_p is $4/A_v$. The coefficient c decreases as d_p decreases.

A two-layer model, one upper layer that contains moving liquid and a lower layer having the gas that displaced the upper liquid, approximates the rate of liquid loss because we have assumed that the unbound liquid free to move represents only 32% of the grout volume (1/2 the total pore liquid).

Model G^3 only approximately represents a more likely two-phase flow situation where both gas and liquid are simultaneously expelled. In G^3 , we calculate the liquid volumetric expulsion rate

$$Q = vA_p \tag{B-9}$$

where:

$A_p = 0.32 \times A_{grout}$, the pore cross-sectional area involved in flow
 A_{grout} = top surface area of grout volume.

We can account for the two-phase nature of the gas flow out of the grout by using the concentration of each gas that would be dissolved in the liquid phase if no gas phase existed, C_i' . (Implied liquid concentration if all gas is forced into the liquid)

where:

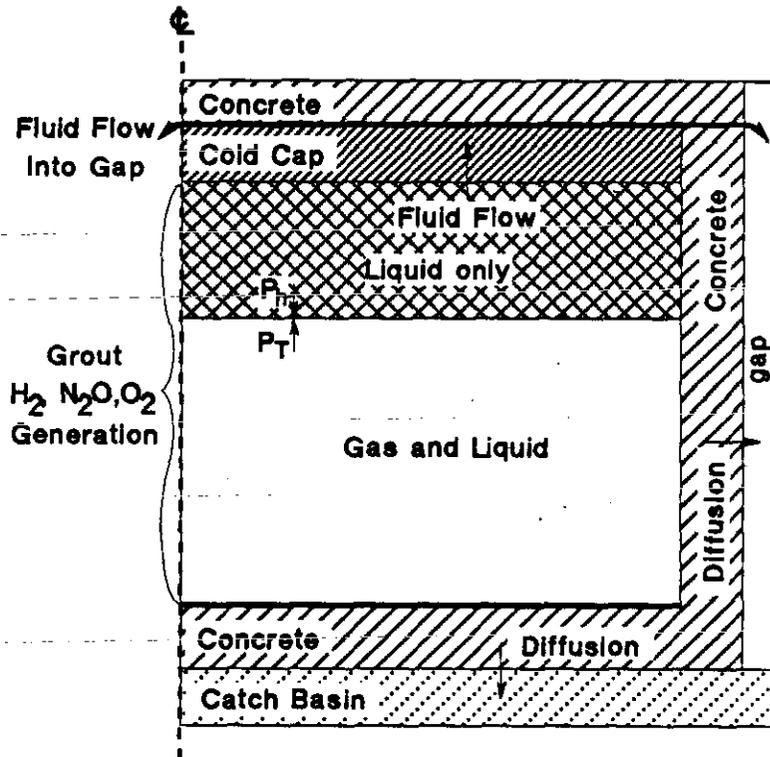
$$C_i' = M_i/V_i \tag{B-10}$$

and thus, the molar flow rate of i out of the grout due to liquid flow is

$$\dot{M}_i = QC_i' \tag{B-11}$$

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Figure B-2. Grout Vault Cross Section G³ Model Components.



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Loss of gases from the grout also occurs by molecular diffusion. The pathways assumed for diffusion are through the bottom of the grout to the catch basin and horizontally into the drainage gap along the outside concrete walls. Vertical diffusion upward was assumed to be important only during the filling period. After the cold cap is poured, the upward diffusion was ignored, because the upward path overall diffusion resistance is much larger due to its higher liquid content than the resistance of the horizontal and bottom paths. The rate equation used for diffusion flux of i is

$$N_i = K_i \Delta C_i \quad (B-12)$$

where:

K_i = a mass transfer coefficient

ΔC_i = gas phase concentration difference across the flow path

Equation B-12 assumes that a steady state concentration profile exists across the flow path. This conservative assumption is fairly close to reality, because the times of concern here are in years' duration. The assumption is conservative in that it ignores the delay time required for the flow path concentration to buildup. The mass transfer coefficient is defined

$$\frac{1}{K_i} = \frac{\Delta x_c H_i}{e_c (D_i)_c} + \frac{\Delta x_e}{(D_i)_e} + \frac{\Delta x_g}{e_g (D_i)_g} \quad (B-13)$$

Here, accounting for the combined gas solubility and diffusion resistance of the thin elastomer layer, a modified diffusion coefficient $(D_i)_e$ was used. The three parts of $1/K_i$ are the resistances of the concrete (c) the elastomer (e), and grout (g) to diffusion. Δx_c is the concrete wall thickness, and $(e_c D_i)_c$ are the concrete gas-filled porosity and gas phase diffusivity of i in the grout. Δx_e is the elastomer thickness and $(D_i)_e$ are the gas solubility-corrected diffusion coefficients. Similarly, $(e_g D_i)_g$ are the liquid porosity and liquid phase diffusivity of i on the grout. Because the diffusion barrier Δx_g in the grout in the unsteady state increases in time t , we have assumed that this growth can be expressed as (Carslaw and Jeager 1959)

$$\Delta x_g = 2\sqrt{D_i t} \quad (B-14)$$

Equation B-14 shows that the grout phase resistance to diffusion will become dominant at some time (usually within $t = 1$ year). Values used in equation B-13 are found in Section B2.1.

When Δx_g approaches the value of $\frac{1}{2}$ the grout depth (approximately 5 m), then Equation B-14 would cause a non-conservative reduction in the H_2 flux by diffusion. This would occur by 6×10^9 seconds or 190 years. However, since the three-dimensional overlap of five diffusion planes in that time frame is ignored as well, then one one-dimensional assumption opposes the non-conservatism of B-14.

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This completes the discussion of the technical basis of Model G³. Model G³ was made a subroutine of the C³ code. The G³ model is attached to this appendix. The C³ code and calculational results are discussed in Appendix E of this report. A subroutine of the C³ code, further discussions of C³, and results are found elsewhere.

B2.1 PROPERTIES OF GROUT USED IN G³ MODEL.

The following information is based on data received via Ryan Lokken, PNL.

The grout makeup is as follows:

- 1,080 g dry solids/liter waste,
- Final density = 1.61 g/cm³,
- Waste is 1.21 g/cm³ solution of NaNO₃ and other salts,
- Final solution density in pores is 1.23 g/cm³,
- 64% of grout space occupied by this solution (approximately 3N in ions as NaNO₃),
- Pore diameter where liquid can flow averages 10 micrometers diameter,
- Grout porosity equals 0.64,
- Concrete porosity equals 0.1, and
- Elastomer thickness equals 60 mil.

The diffusivities of the grout material, elastomer, and concrete are listed in Table B-1. These diffusivities include a viscosity correction for dissolved materials in the grout liquid corresponding to the reference grout mixture.

Table B-1. Diffusivities of materials in Grout Block and Vault Regions.

Material	Material Diffusivities (cm ² /s)			
	H ₂	N ₂ O	O ₂	N ₂
Saturated grout	1.15 E-5	2.46 E-6	2.89 E-6	3.09 E-6
Gas-filled concrete	9.50 E-4	1.90 E-4	2.54 E-4	2.54 E-4
Elastomer (includes gas solubility correction)	3.49 E-8	5.34 E-9	1.58 E-8	5.34 E-9

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B2.2 SOLUBILITY OF GASES IN GROUT SOLUTION AT EQUILIBRIUM

Values tabulated are a Henry's Law constant, H_i , equal to the gas phase concentration/liquid phase concentration.

Values for pure H₂O at 60 °C (assumed grout temperature, calculated from Handbook of Chemistry and Physics, 59th edition, 1978-1979) are as follow:

$$\begin{array}{cccc} \text{gas } i = & \text{H}_2 & \text{N}_2\text{O} & \text{O}_2 & \text{N}_2^* \\ H_i = & \frac{\quad}{44.2} & \frac{\quad}{3.14} & \frac{\quad}{41.2} & \frac{\quad}{78.4} \end{array}$$

Solubility is reduced by solutes, therefore, H_i 's are increased (based on lower temperature values in International Critical Tables, Vol. III, 1928, McGraw-Hill, New York, New York.)

Values for grout solution at 60 °C are as follow:

$$\begin{array}{cccc} \text{gas } i = & \text{H}_2 & \text{N}_2\text{O} & \text{O}_2 & \text{N}_2^* \\ H_i = & \frac{\quad}{84.6} & \frac{\quad}{6.19} & \frac{\quad}{100.8} & \frac{\quad}{191.7} \end{array}$$

B3.0 RESULTS

The C³ model was used to determine the release of gases to the vault sides space and the catch basin compartments. The release of gases to the vault vapor space is shown in Figure 4-5, part a, and Table 4-2, part a. The release of gases to the catch basin compartment is shown in Figure 4-1, part a, and case A of Table 4-1, part a.

*N₂ values with pure H₂O are calculated from information in Lange, N.A., 1952, *Handbook of Chemistry*, Handbook Publishers, Inc., Sandusky, Ohio.

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```

C      Grout Gas Generation
      Subroutine G3(giadv,gidif,TT,DT,nT,liqdot,totliq,iopt,Tmolpro)

      Real kgr,DZg,Zp,TT,DT,Tmolpro,
+Phyd,mu,giadv(7,4),gidif(7,4),pfrac,
+totserg,totliq,liqdot,difsum,diffac,Rdotgo,Rgmdot
      integer iopt,nT,jflag
      COMMON/region1/DZg,Zm,tprint,jflag,
#          totsgr,pfrac(4),epsf,Po,Tg,kgr,dpore,
#          epso,Av,Zp,Rgmdot(4),Rdotgo(4),
#          henry(4),mu,gam,rho,grav,RT,pH2O,Pdisgas,difsum(4)

c      read in data first time through, initialize constants
      if(TT .le. DT)then
          OPEN(UNIT=1,FILE='tfg.d',STATUS='OLD') !input file
c      total source generation rate (mol/hr),H2percent,O2pct,N2Opct,
c      grout porosity, flow (wet) porosity, overburden pressure (atm),
c      grout temp (C), intrinsic permeability m2, pore diameter m*e-6,
c      dummy, parametric diffusion factor
          READ(1,805)totsgr,pfrac(1),pfrac(3),pfrac(2),epso,epsf,Po,Tg,
#      kgr,dpore,henpar,diffac
c      calculate production rate of hydrogen, NO2, and oxygen
          pfrac(4) = 0. !N2 is never produced
          do k=1,4
c      Rgmdot(k)=pfrac(k)/100.*totsgr
c      Rgmdot=2.8,max; 0.14 best estimate; 0.007, min.
c      Rdotgo in gmoles/m**3/s in pore space
          Rdotgo(k)=(30./34.)*Rgmdot(k)/5300./3600./epso
          enddo
c      Henry's Law constants at 60 C:
          henry(1)=84.6
          henry(2)=6.19
          henry(3)=100.8
          henry(4)=191.7
          mu=4.665E-4 !water viscosity in grout, kg/m/s, at 60 C
c      multiplier of viscosity due to high ionic strength is 1.25 for
c      NaNO3 solutions around 20% w/w.
          mu=mu*1.25
c      gam = water surface tension, SI units (N/m), at 20 C. Elevated
c      temperatures should be counteracted by solute effect on gam.
          gam=7.2E-2
          rho=1230. !grout liquid density kg/m**3
c      rho is a composite mean from C. Hinman (out of a report).
          grav=9.8 ! accel of gravity m/s2
          Tabs=333.16 !grout temp, K
    
```

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Rgas=8.3147 !Rgas in m**3-Pa/gmole/K
 RT=Rgas*Tabs
 pH2O=1.994E+4 ! pure water vapor pressure, Pa
 pH2O=pH2O*(760.-68.1)/760.!cor for vapor press depress by solute
 pdisgas=1.013e+05-pH2O !pressure dissolved gas

```

c*****
c      calcs Av= area of pores created during voiding/volume of grout
      Call PRR(dpore,epsf,Av)
c *****
c      height of grout in feet
      Zft=34.
c      Zm grout thicknesses, m.
      Zm=0.3048*Zft
c      Position of trailing(lower) edge of liquid layer, Zp
      Zp=Zm
c      DZg thickness of gas layer.
c      initialized to 1.e-10 first time.
      DZg=1.e-10
      endif
c      Hydrostatic pressure at Zp, Pa (0-Tinit).
c      hydrostatic pressure (Pa) =
c      density (kg/m3)*gravity (m/s2) * height (m)+
c      overburden P.(atm) * conversion factor atm to Pa
      Phyd= rho*grav*Zp + Po*1.01325E+5
c *****
      Call MOVE(DT,TT,Phyd,Tmolpro,nT,iopt,gidif,
      #      liqdot,totliq,giadv,diffac)
c *****
c      increment counter
      nT=nT+1
      805 format(8(F9.4,/),E8.3/,3(F9.4,/))

      return
      end
c*****
    
```

Subroutine MOVE(DT,TT,Phyd,Tmolpro,nT,iopt,gidif,
 # liqdot,totliq,giadv,diffac)

Real kgr,DZg,Zp,gidif(7,4),giadv(7,4),
 +Phyd,mu,DXa,totliq,liqdot,TT,DT,ggen(4),Rdotg(4),
 +surface(6),mastrans(7,4),c,diffc,
 +Tmolg,egd,dehe,ecdc2,diffac,gdot(4),flxg(4),
 +molwt,ecdc3,Tmolpro,pfrac,concc(4),difsum,
 +netmol,nmol(4),concg(4),concl(4),nmolg(4),nmoll(4),

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```

delxe=0. !elastomer thickness (cm),ignore, true thick=0.1524 cm
c initialize total moles produced (including gas dissolved in
c grout at time of mixing)
  Tmolg(1)=0.
  Tmolg(2)=0.
  Tmolg(3)=netmol(3)
  Tmolg(4)=netmol(4)
c initialize total moles escaped
  Tmolx(1)=0.
  Tmolx(2)=0.
  Tmolx(3)=0.
  Tmolx(4)=0.
endif
c calculate intermediate values for mass transfer coefficients
ecdc2(2)=(diffc(2,2)/diffc(2,1))*ecdc2(1)
ecdc2(3)=(diffc(2,3)/diffc(2,1))*ecdc2(1)
ecdc2(4)=(diffc(2,4)/diffc(2,1))*ecdc2(1)
ecdc3(2)=(diffc(3,2)/diffc(3,1))*ecdc3(1)
ecdc3(3)=(diffc(3,3)/diffc(3,1))*ecdc3(1)
ecdc3(4)=(diffc(3,4)/diffc(3,1))*ecdc3(1)
c calculate mass transfer coefficients, only interested in
c compartments 2 and 3, all 4 gasses
do k=1,4
  mastrans(2,k)=1./(henry(k)*2.*sqrt(TT*egd(k)/epso)/egd(k) +
# delxe/dehe(k) + delxc2/ecdc2(k))
enddo
do k=1,4
  mastrans(3,k)=1./(henry(k)*2.*sqrt(TT*egd(k)/epso)/egd(k) +
# delxe/dehe(k) + delxc3/ecdc3(k))
enddo
c calculate radioactive decay factor
decay=a1+a2*EXP(-b1*TT)
c adjust gas source term for radioactive decay
do k=1,4
  Rdotg(k)=Rdotgo(k)*decay
c calculate the moles produced in this time step
  nmol(k)=DT*void*Rdotg(k)
enddo
c update total mole production
Tmolpro = 0.
do k=1,4
  if(pfrac(k) .gt. 1.E-10)then
    Tmolg(k)=Tmolg(k)+nmol(k)
    Tmolpro=Tmolpro+Tmolg(k)
  endif

```

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```

+Rdotgo,Rgmdot,henry
integer iopt,nT
COMMON/region0/conc(7,4),diffc(7,4)
COMMON/region/i,Tmolg(4),Tmolx(4),
#      egdg(4),dehe(4),ecdc2(4),ecdc3(4),molwt(4),
#      delxe,delxc2,delxc3,netmol(4)
COMMON/region1/DZg,Zm,tprint,jflag,
#      totsgr,pfrac(4),epsf,Po,Tg,kgr,dpore,
#      epso,Av,Zp,Rgmdot(4),Rdotgo(4),
#      henry(4),mu,gam,rho,grav,RT,pH20,Pdisgas,difsum(4)
a1=.00023      ! constants that add =1. to fit
a2=.99977      ! normalized hydrogen formation curve
b1=7.30467E-10 ! 1/s, decay factor
Agrout=579.4   !area of bottom of grout, m2
V1=Zp*eps0     !volume of void per square meter of bottom of vault
void=Zm*eps0*Agrout !total volume of void space in grout, m3
vliq0=void*1.E+6 !total volume of void space in grout, cm3
Tday=TT/(24.*3600.) !time in days
surface(2)= 1.10E+07 !cm2 area of grout sides
surface(3)= 5.794E+06 !cm2 area of grout bottom
c initialize constansts first time through time loop
if(nT.eq.1)then
  data molwt/2.,44.,32.,28./ !molecular weight, h2,n2o,o2,n2
  data dehe/3.486E-08,5.34e-09,1.578e-08,5.34e-09/
  liqdot=0.      ! flow rate of liquid, gal/hr
  totliq=0.      ! total liquid produced, gal
  netmol(1)=0.
  netmol(2)=0.
c assume O2 and N2 dissolve frac same as atmosphere frac
  netmol(3)=.21*pdisgas*vliq0/(RT*1.e+06)/henry(3)
  netmol(4)=.79*pdisgas*vliq0/(RT*1.e+06)/henry(4)
c constants for calculating mass transfer coefficients
  egdg(1)=1.1552E-05*diffac ! diffus factor for sensitivity stdy
  egdg(2)=sqrt(molwt(1)/molwt(2))*egdg(1) !changed 06/30/92
  egdg(3)=sqrt(molwt(1)/molwt(3))*egdg(1)
  egdg(4)=sqrt(molwt(1)/molwt(4))*egdg(1)
  ecdc2(1)=9.5E-04
  ecdc3(1)=9.5E-04
  if(jflag .eq. 1)then
    delxc2=91.4      !concrete thickness (cm) sides
    delxc3=137.2    !concrete thickness (cm) bottom
  else
    delxc2=.1
    delxc3=0.
  endif
endif

```

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```

        enddo
c       if no holdup specified set flow into compartment 3 equal to
c       the entire source term, in moles per second and skip rest
c       of calculation
        if(iopt.eq.1)then
            do k=1,4
                giadv(3,k)=nmol(k)/DT      !mol/sec
                Tmolx(k)=Tmolx(k)+DT*giadv(3,k)
            enddo
            goto 610
        endif
c       calculate the moles remaining in grout
        if(jflag .eq.1)then
            do k=1,4
                netmol(k)=netmol(k)+nmol(k)- (giadv(2,k)+giadv(3,k)+
#                 gidif(2,k)+gidif(3,k))*dt
            enddo
        else
            do k=1,4
                netmol(k)=netmol(k)+nmol(k)- gidif(2,k)*dt
            enddo
        endif
        vgas=(DZg/Zm)*(epsf/epso)*vliq0
        vliq=vliq0-vgas
        do i=1,4
            if(vgas .gt. 0.)then
                nmolg(i)=netmol(i)/(1.+ (1./henry(i))*(vliq/vgas))
                concg(i) = nmolg(i)/vgas
            else
                nmolg(i)=0.
                concg(i)=(netmol(i)/vliq)*henry(i)
            endif
            nmoll(i)=netmol(i)-nmolg(i)
            concl(i) = nmoll(i)/vliq
        enddo
c       diffusion calc into compartments 2-3
        if(iopt .eq. 2 .or. iopt.eq.4)then
            do k=1,4
                gidif(2,k)=mastrans(2,k)*surface(2)*(concg(k)-conc(2,k))
            enddo
            if(jflag .eq. 1)then
                do k=1,4
                    gidif(3,k)=mastrans(3,k)*surface(3)*(concg(k)-conc(3,k))
                enddo
            endif
        endif

```

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```

else          !no diffusion case
  do i=2,3
    do k=1,4
      gidif(i,k)=0.
    enddo
  enddo
endif
do k=1,4
  difsum(k)=difsum(k)+dt*(gidif(2,k)+gidif(3,k))
enddo
c calc gas pressure in the grout
pchem=(RT*1.E+06)*(concg(1)+concg(2)+concg(3)+concg(4)) +pH2O
c DP= driving pressure for movement of liquid. N/m2
DP=pchem-Phyd

if(Zp.gt.0.)then  !if water level drops to 0 then goto else 555
  if(DP.gt.0.)then
    DPDZ=DP/Zp
    beta=DT*kgr*DPDZ/mu ! s * m2 * N/m3 * m*s/kg = m
    alfa=Av*gam/Zp/DP ! 1/m * N/m * 1/m * m2/N = 1/m
c move DX (superficial), DXa(actual)
DX=(-1.+SQRT(1.+4.*beta*alfa))/2./alfa
DXa=DX/epsf
c adjust height of water by DXa
Zp=Zp-DXa
c add DXa to DZg
DZg=DZg+DXa
if(Zp .le. 0.)then
  Zp = 0.
  DZg = Zm
endif
c velocity of liquid leaving the grout
veliq=DX/DT !m/s
flxliq=veliq*3600. !m/hr
c rate of liquid leaving the bottom of the grout
liqdot=flxliq*Agrout !m3/hr
liqdot=liqdot*264.17 !gal/hr
c total liquid ejected from grout
totliq=totliq+(dt/3600.)*liqdot !gal
else
  flxliq=0.
endif
c concc models a 2-phase flow approximation of concentration
do k=1,4
  concc(k) = netmol(k)/vliq

```

```

..... flxg(k)=flxliq*concc(k)/1.0e-6
..... gdot(k)=flxg(k)*Agrout
..... enddo
555 else !!!! Zp le 0 , all liquid expelled
c compute gas advection rates after liquid expulsion.
visgas=2.E-5
DZt=Zm
permg=2.5E-15
if(DP.gt.0.)then
velgas=permg*DP/visgas/DZt/2.
else
velgas=0.
endif
c new method for calculating gas fluxes
flxgas=pchem*velgas/RT
do k=1,4
..... flxg(k)=flxgas*(1.E+06*RT*concg(k)/pchem)
..... gdot(k)=flxg(k)*Agrout*3600.
..... ggen(k)=Rdotg(k)*Zm*epso*Agrout*3600.
..... enddo
c correction for inaccuracy in flow driving force:
do k=1,4
if(ggen(k).gt.gdot(k))then
flxg(k)=ggen(k)/Agrout/3600.
gdot(k)=ggen(k)
endif
enddo
endif
if(iopt .ne. 2)then
do k=1,4
Tmolx(k)=Tmolx(k)+DT/3600.*gdot(k)
enddo
endif
c calculate advective flow mol/s
if(iopt.eq.3 .or. iopt.eq.4)then
do k=1,4
giadv(2,k)=gdot(k)/3600.
enddo
else
Ino advective flow specified
do k=1,4
giadv(2,k)=0.
enddo
endif
599 continue
610 if(mod(TT,tprint) .eq. 0. .or. TT .le. DT)then

```

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```

      Twrite=TT/3600./24./365.
c     t(yr),accumulated mol diffused and advected of ea of 4 gasses
      write(25,'(9(lpe9.2,lx))')Twrite,(difsum(k),k=1,4),
      #(Tmolx(k),k=1,4)
      endif

      return
      end
c*****
      Subroutine PRR(dpore,epsf,Av)
c     This subroutine returns the area of pores created during the voiding
c     per unit volume of grout.

      dp=dpore*1.E-6
      Vp=epsf
      elp=Vp/dp/dp
      Ap=3.14159*dp*elp
c     Ap assumes round pores.
      Av=Ap/Vp
c     Av in 1/m

      return
      end
c*****

```

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APPENDIX C

DISCUSSION OF HYDROGEN AND NITROUS OXIDE BUOYANCY

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Stagnant regions of hydrogen gas are not likely to form in upper regions of the compartments because the hydrogen/nitrous oxide mix is near the air density and its mixing by diffusion is high when compared to the generation rate. The hydrogen generated by the grout is mixed with equimolar or more quantities of N_2O , a gas that is heavier, i.e., more dense than air. The density of a gas is directly proportional to its molecular weight (MW).

$$\text{MW (air)} = 29$$

$$\text{MW (H}_2\text{, pure)} = 2$$

$$\text{MW (N}_2\text{O)} = 44.$$

A 1:1 liquid mixture of H_2 and N_2O has an average MW of 23, slightly less than air. A 1:2.5 mixture of H_2 and N_2O has an average molecular weight of 32 (same as pure O_2). We can conclude that the proposed mixtures of H_2 and N_2O gases generated by the grout (1:1 to 1:2.5) will range from either slightly buoyant to slightly negatively buoyant. These minor (\pm) buoyancies will not allow significant pockets of generated gas to exist separate from diluting gases. Diffusion will effectively dilute stagnant unmixed gas pockets.

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APPENDIX D
CALCULATION OF TIME-DEPENDENT GAS CONCENTRATIONS
IN THE GROUT DISPOSAL FACILITY REGIONS

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D1.0 ASSUMPTIONS

1. Compartment temperatures are 60 °F
2. Diffusivities of hydrogen, nitrous oxide, oxygen, and nitrogen are treated separately.
3. All gas pressures are at 1 atmosphere in the compartments (assumes gas vent operational)
4. The operating periods are:
- | | |
|---------|--|
| Phase 1 | 0 to 1 yr. Vault space open, no cold cap |
| Phase 2 | 1 to 30 yr. Sump vent open |
| Phase 3 | > 30 yr. Sump vent grout filled, gas vented through vent tube in side of barrier |
5. Gas generation rate in grout is:
- | | |
|---------------|-------------|
| hydrogen | 0.012 mol/h |
| nitrous oxide | 0.031 mol/h |
| oxygen | 0.0 mol/h |
6. Significant holdup of the gases in the grout block will occur due to the low diffusivity of grout and surrounding vault materials. Gas sources are determined in Appendix B.
7. Barometric pressure variation provides a volumetric gas exchange rate of 2.4 volumes per yr. This exchange rate is introduced into the sump vent volume during phase I and II. It no longer exists during phase III.

D2.0 REFERENCE

Garfield, J. S., 1975, *Maximum Anticipated H₂ Concentrations in Underground Tank Atmospheres from Radiolysis of Water*, ARD-CD-267.

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D3.0 CALCULATIONS

D3.1 A GENERIC COMPARTMENT MODEL

The objects of these calculations are to describe an engineering model of the grout disposal facility compartments and their arrangement and interaction with the environs. Figure D-1 shows a generic compartment and the sources, sinks, and flows to and from interconnected compartments.

- where
- $G_{i,K}$ = rate of flow from compartment i of gas K
 - $G_{i,K} = \frac{D_{i,K} A_i}{DX_i} (C_{i,K} - C_{i+1,K})$ (1)
 - $D_{i,K}$ = diffusivity of gas K.
 - K = 1; 2; 3; and 4 for hydrogen, nitrous oxide, oxygen, and nitrogen, respectively
 - A_i = cross section area of path connecting compartment i with i+1
 - DX_i = diffusion length between compartment i and i+1 (nodal model)
 - $GI_{i,K}$ = input rate of gas K into compartment i
 - $GO_{i,K}$ = sink rate of gas K from compartment i
 - $C_{i,K}$ = concentration of Gas K in compartment i

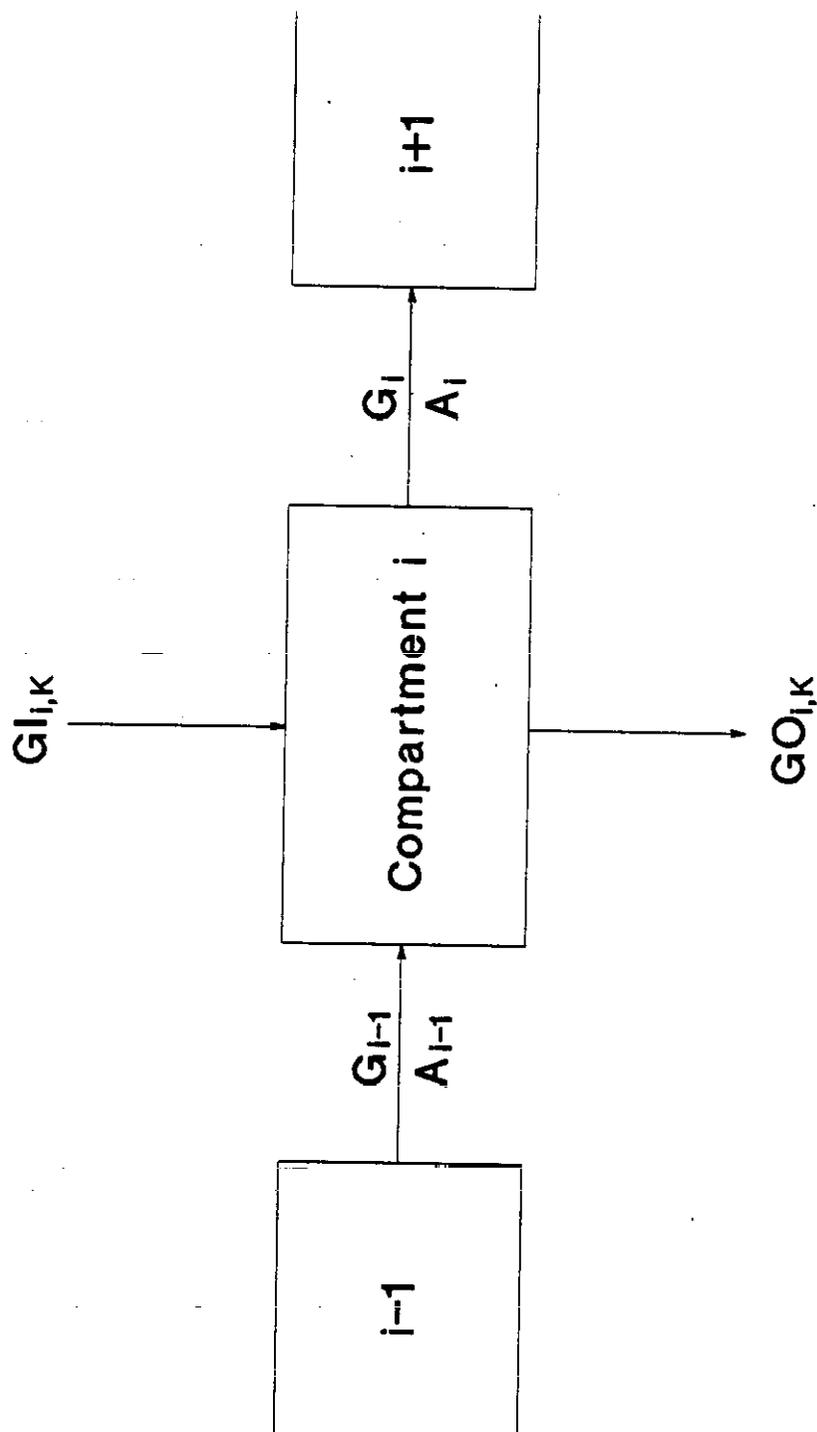
The diffusion calculation is first determined for the unit cell during a time increment as described above. The rates for the source and loss terms are determined by

$$M_{i,K}' = M_{i,K} + dt \times (GI_{i,K} + G_{i-1,K} - GO_{i,K} - G_{i,K}) \quad (2)$$

where $M_{i,K}$ is the moles of gas K in compartment i, and dt is the differential time step.

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Figure D-1. Generic Grout Disposal Facility Compartment.



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The updated $M_{i,k}'$ values are found for each gas type in each compartment. These values represent an intermediate value that must be corrected by a slug flow that represents a displacement of the gas that was diffused or affected by source and loss terms. The values of $M_{i,k}'$ are summed in each compartment to give:

$$M_{t,i}' = \sum_{K'=1}^4 M_{i,K}' \quad (3)$$

$$X_{i,K}' = \frac{M_{i,K}'}{M_{t,i}'} \quad (4)$$

$$C_{i,K}' = \frac{M_{i,K}'}{V_i} \quad (5)$$

where $M_{t,i}'$ is the total intermediate moles in compartment i,
 and $X_{i,K}'$ is the intermediate mole fraction of gas K in compartment i,
 and V_i = volume of compartment i.

The displacement flow correction is determined by the amount of $M_{t,i}'$ that is either above or below the moles of gas that can be held in a compartment of volume V_i at 1 atmosphere pressure.

From the gas law,

$$n = \frac{PV}{RT} \quad (6)$$

where n = number of moles
 P = pressure (1 atmosphere)
 R = gas constant, and
 T = absolute temperature

the number of moles in excess (or deficit) is:

$$dm_i = M_{t,i}' - n \quad (7)$$

If dm_i is positive, the number of moles of each gas transmitted by displacement to the next compartment is:

$$MS_{i,K} = dm_i \times X_{i,K} \quad (8)$$

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The compartment this displacement flow is transmitted to depends on the position of the active vent. If the sump vent is not capped, the flow will be in that direction. If the sump vent is capped, the flow will be towards the vent at the side of the vault walls.

The moles in each compartment will be corrected by:

$$M_{i,k} = M_{i,k} - MS_{i,k} \quad (9)$$

$$M_{i+1,k} = M_{i+1,k} + MS_{i,k} \quad \text{if the active vent is at a compartment number higher than } i \quad (10)$$

$$M_{i-1,k} = M_{i-1,k} + MS_{i,k} \quad \text{if the active vent is at a lower compartment number than } i \quad (11)$$

If dm_i is negative, the compartment i will draw displacement flow from the adjacent compartment between compartment i and the active vent. If the active vent is at a compartment number higher than i ;

$$MS_{i,k} = dm_i \times X_{i,k} \quad (12)$$

$$M_{i,k} = M_{i,k} - MS_{i,k}, \text{ and} \quad (13)$$

$$M_{i+1,k} = M_{i+1,k} + MS_{i,k} \quad (14)$$

If the active vent is at a compartment number lower than i ,

$$MS_{i,k} = dm_i \times X_{i,k} \quad (15)$$

$$M_{i,k} = M_{i,k} - MS_{i,k}, \text{ and} \quad (16)$$

$$M_{i-1,k} = M_{i-1,k} + MS_{i,k} \quad (17)$$

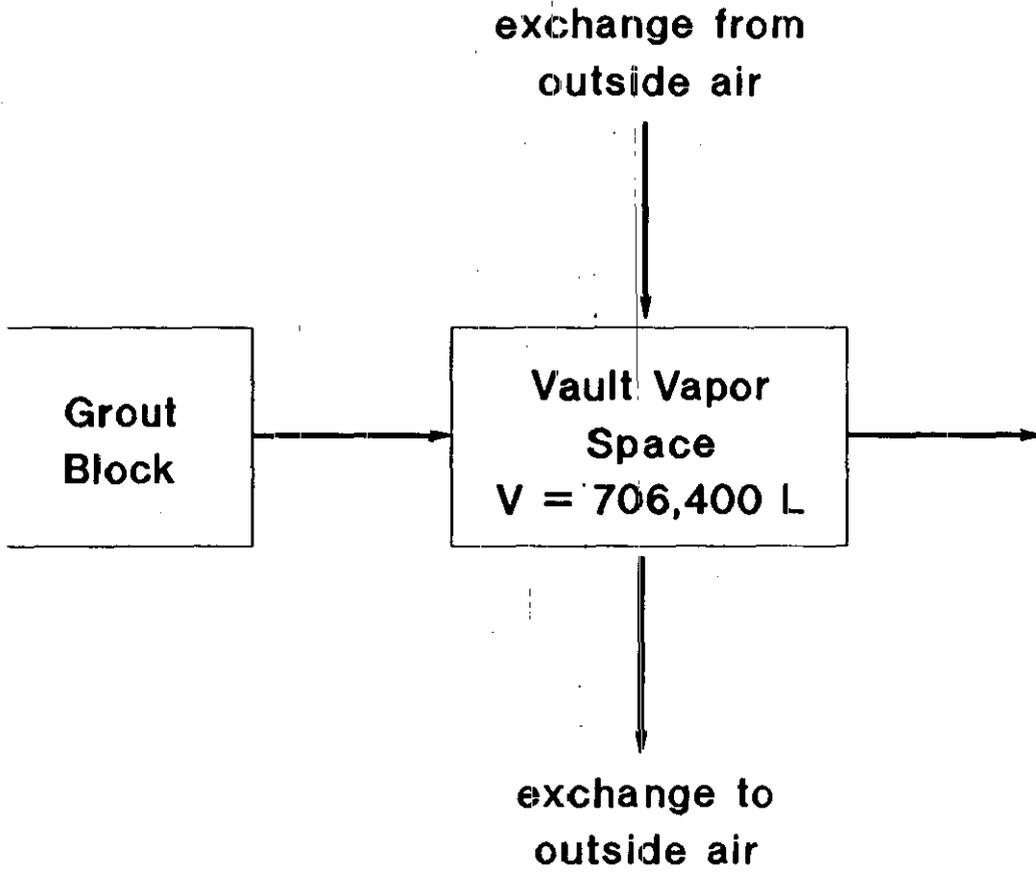
at the end of this step, after the total moles in all compartments have been adjusted to 1 atmosphere pressure and their masses conserved by slug flow, final values of total moles and concentrations are determined by formulas 3, 4, and 5, and the interaction step proceeds to the next cycle.

D3.2 Grout Disposal Facility Compartments

The grout disposal facility compartments are shown in Figure D-2. The compartments of interest include the vault vapor space (this is filled with cold cap grout during phases II and III), vault sides, leachate collection basin, drain line, sump, and sump vents. These compartment arrangements will be discussed for the vault vapor space and catch basin in the following sections.

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Figure D-2. Vault Vapor Space Compartments.



D3.2.1 Vault Vapor Space

The compartment arrangement and interconnecting flow paths of the vault vapor are shown in Figure D-2.

The release to the vault vapor space is the simplest arrangement. This case involves the release of gas from the top of the grout into the vault vapor space. The vault vapor space was assumed to be equal to the cold cap volume which is the smallest volume that will occur during filling. The results will be conservative due to this assumption. This volume is equal to:

$$\begin{aligned}
 V &= 4.0 \text{ ft} \times 50.5 \text{ ft} \times 123.5 \text{ ft} & (18) \\
 &= 24,947 \text{ ft}^3 \\
 &= 706,400 \text{ l}
 \end{aligned}$$

The vault vapor space volume is connected to the ventilation inlet port in addition to other penetrations. The volume of the ventilation inlet port is:

$$\begin{aligned}
 V &= \pi \times 1 \text{ ft}^2 \times 11 \text{ ft} & (19) \\
 &= 34.6 \text{ ft}^3 \\
 &= 980 \text{ l}
 \end{aligned}$$

The arrangement of these volumes is shown in Figure D-3.

An outside air exchange exists due to atmospheric pressure variations. Garfield (1975) gave an average exchange rate of 660 ft³/day in a 100,000 ft³ tank space due to measured pressure variations. The exchange rate per year is

$$\begin{aligned}
 \text{Vol change} &= \frac{660 \text{ ft}^3/\text{d} \times 365 \text{ d/y}}{100,000 \text{ ft}^3} & (20) \\
 &= 2.4 \text{ changes per year.}
 \end{aligned}$$

The exchange rate of air is

$$\begin{aligned}
 \text{flow rate} &= \frac{(706,400 + 980) \text{ l} \times 2.4 \text{ yr}^{-1}}{365 \text{ d/yr} \times 24 \text{ h/d} \times 3,600 \text{ S/h}} & (21) \\
 &= 0.054 \text{ cm}^3/\text{s}
 \end{aligned}$$

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D3.2 Catch Basin and Leachate Sump Compartments

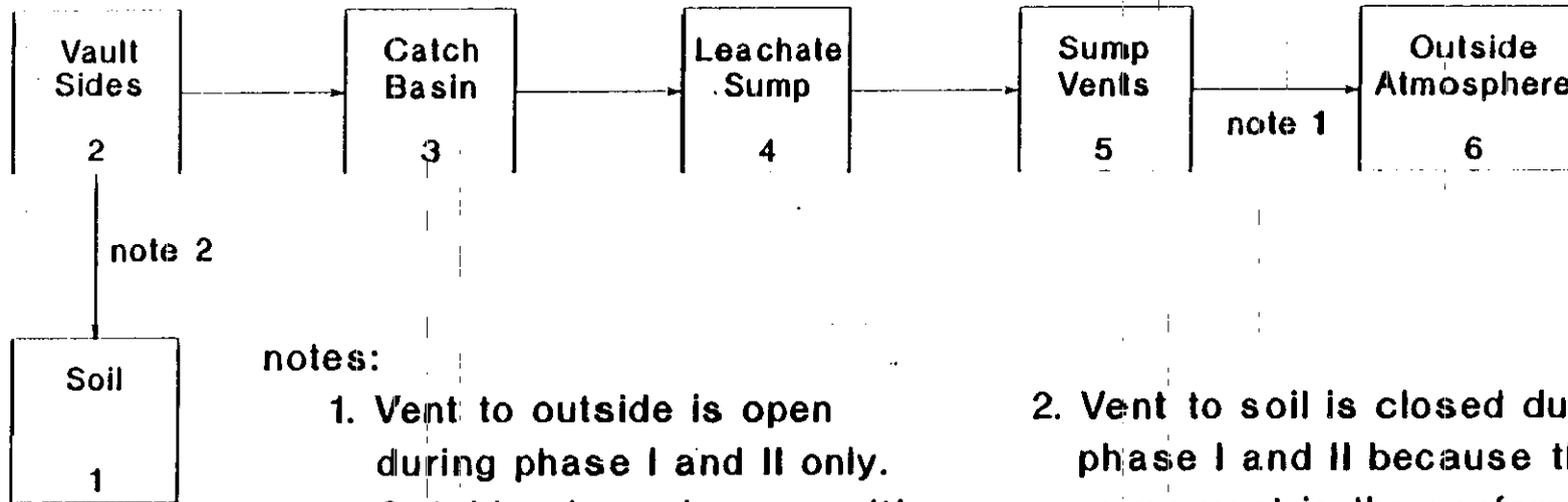
A diagram of the compartment arrangements and interconnecting flow paths of the catch basin, leachate sump, and vault sides, drain line and vents used in this calculation, are shown in Figure D-3. The outside air exchange rate in the sump vents was determined by applying the barometric volumetric exchange to the combined compartment volumes as done in formula 21.

The source of gas was determined by the engineering G³ model described in Appendix B. A summary of the variables used in the compartment calculation is given in Table D-1.

Table D-1. Variables Used in Vault Vapor Space Gas Concentrations.

	<u>Vapor Space</u>	<u>Ventilation Inlet Ports</u>
Volume (cm ³)	7.06 x 10 ⁸	9.80 x 10 ⁵
exit area (cm ²)	2919	2919
diffusion length (cm)	335	335
outside air (cm ³ /s)	0.0	0.054
initial source terms in grout		
hydrogen (mol/h)	0.012	0.0
nitrous oxide (mol/h)	0.031	0.0
oxygen (mol/h)	0.0	0.0
grout surface (cm ²)	5.79 x 10 ⁶	0.0

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notes:

1. Vent to outside is open during phase I and II only. Outside air exchanges with sump vent atmosphere by diffusion and volumetric exchanges caused by atmospheric pressure variations.

2. Vent to soil is closed during phase I and II because the sump vent is the preferred path. Open only during phase III.

3. This figure applies to the time after the grout block is filled and the cold cap is in place. The situation of the vault vapor space is shown in Figure D2

Figure D-3. Vault Compartments

Table D-2. Summary of Parameters Used in Compartment Model of Grout Disposal Facility.

	Vault side regions <u>2</u>	Catch basin <u>3</u>	Sump <u>4</u>	Sump vents <u>5</u>
Volume (cm ³)	3.73 E+7	1.668 E+8	2.00 E+7	5.10 E+6
discharge area (cm ²)	2.95 E+4	74.2	3550	3550
diffusion length (cm)	633	1140	671	671
barometric driven volume exchange (cm ³ /s)	2.83	15.5	17.0	17.4
Initial source terms in grout				
hydrogen (mol/h)	0.012	0.012	N/A	N/A
nitrous oxide (mol/h)	0.031	0.031	N/A	N/A
oxygen (mol/h)	0.0	0.0	N/A	N/A
surface area of grout (cm ²)	1.10 E+7	5.79 E+6	0	0
elastomer thickness (cm)	0.152	0.152	0	0
concrete thickness (cm)	91.4	137.2	0	0
advection flow from grout block	Yes	No	N/A	N/A
diffusion flow from grout block	Yes	Yes	N/A	N/A

D3.2 Release Source Terms from Grout Block

The Gas release source terms from the grout block were determined in Appendix B for the reference case of initial 0.043 mol/h generation rate. One source term, for the vault vapor space calculation was direct diffusion of gas from the grout block without its cold cap cover. The other source term, involving diffusion of gas through the vault walls and advection of gas and liquid through the top of the grout, used for the catch basin and leachate sump calculations. The compartment concentrations were determined accordingly by the C³ model.

D4.0 RESULTS

D4.1 Vault Vapor Space Gas Concentrations

The results of the vault vapor space compartment concentrations during phase I are shown in part b of Figure 4-5 and Table 4-2 in the main text.

D4-2. Catch Basin and Leachate Sump Gas Concentrations

The results of the catch basin and leachate sump compartment gas concentrations are shown in Figure 4-1 and Table 4-1 in the main text.

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~~Listing of C³, Compartment Concentration Calculation~~

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```

Program C3          ! Compartment Concentration Calculation
C   Define M(i,k) as gmoles j in compartment i, conc(i,k) as the concentration,
C   X(i,k) as the mole fraction, diffc(i,k) as the diffusivity, G(i,k) as the
C   molar flow rate from i to i+1, GI(i,k) as a source rate, GO(i,k) as a
C   sink rate, and V(i) as compartment volume. DX(i) = diffusion length
C   between i and i+1, and A(i) is the cross sectional area for diffusion.
C   giadv(i,k) is the advection source rate, gidif(i,k) is the diffusion
C   source rate, liqdot is the liquid flow rate out of the grout.
c   input files: flog.d, tfg.d
C
C   FULL GROUT MODEL: _____ (jflag=1)
C   Compartment 1 = Dummy (Soil)
C   Compartment 2 = Vertical Wall Gap
C   Compartment 3 = Catch Basin
C   Compartment 4 = Sump
C   Compartment 5 = Sump Vent Pipes
C   Compartment 6 = Outside
C
c   VAPOR SPACE MODEL: _____ (jflag=2)
C   Compartment 1 = Dummy
C   Compartment 2 = Vapor Space
C   Compartment 3 = Vent Pipe
C   Compartment 4 = Outside
C
C   Component 1 = H2
C   Component 2 = N2O
C   Component 3 = O2
C   Component 4 = N2
C
C   DT = time step , seconds.
C   tcap = time of capping off system, years.
C
C   Real M(7,4), C, X(7,4), diffc, G(7,4), gi(7,4), GO(7,4),
C   +V(7), DX(7), A(7), Nm(7,4), Mt(7), Madd,Xtmp(4),
C   +Dmx(4),GIsum(4),Msum(4),totliq,liqdot,gidif(7,4),giadv(7,4),
C   +Tmolpro,TT,DT,molwt,netmol,diftot,kgr,mu,vt(6),
C   +pfrac,advtot,grttot,DZg,totsgr,Zp,difsum,Rgmdot,Rdotgo,henry
C   integer iopt,nT,jflag,ihicmpt,capped
C   COMMON/region0/conc(7,4),diffc(7,4)
C   COMMON/region/i,Tmolg(4),Tmolx(4),
C   #       egdg(4),dehe(4),ecdc2(4),ecdc3(4),molwt(4),
C   #       delxe,delxc2,delxc3,netmol(4)
C   COMMON/region1/DZg,Zm,tprint,jflag,
C   #       totsgr,pfrac(4),epsf,Po,Tg,kgr,dpore,
C   #       epso,Av,Zp,Rgmdot(4),Rdotgo(4),

```

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```

#      henry(4),mu,gam,rho,grav,RT,pH2O,Pdisgas,difsum(4)
c      initialize mole fractions and concentrations
      data X/28*0./
      data conc/28*0./
      data gidif/28*0./
      data giadv/28*0./
      data difsum/4*0./
c      initialize the source terms and diffusion flows
      data GI/28*0./
      data G/28*0./
      data GIsun/4*0./
      data vt/4*0./
c      initialize the sink terms
      data GO/28*0./
      OPEN(unit=1,file='flog.d',status='old') !input file
c      option flag: iopt = 1/2/3/4 = no holdup/diffusion only/
c      advection only/ both diffusion and advection
c      jflag=1 for total grout model, jflag=2 for vapor space model
c      time step(sec),time cap(yr),time stop(yr),ioption,jflag
      Read(1,705)DT,tcap,Tstop,iopt,jflag
      if(jflag .eq. 1)then
        write(6,*)' Full Grout Model (jflag=1) '
        OPEN(unit=2,file='basin.dat',status='unknown')
        OPEN(unit=11,file='sump.dat',status='unknown')
      else
        write(6,*)' Vapor Space Model (jflag=2) '
        OPEN(unit=2,file='vap.dat',status='unknown')
      endif
      OPEN(unit=9,file='gen.dat',status='unknown')
      OPEN(unit=10,file='liq.dat',status='unknown')
      if(iopt .eq. 1)write(6,*)' No Holdup '
      if(iopt .eq. 2)write(6,*)' Diffusion Only '
      if(iopt .eq. 3)write(6,*)' Advection Only '
      if(iopt .eq. 4)write(6,*)' Diffusion & Advection (normal) '
      write(25,*)'Twrite,(difsum(k),k=1,4), Tmolx (1-4)'
      write(9,*)' T Tmolpro Diftot Advtot grttot'
      write(10,*)' T liqdot liqtot '
      write(12,*)'Twrite,(M(i,1),i=1,6),'
      write(13,*)'Twrite,(M(i,2),i=1,6),'
      write(14,*)'Twrite,(M(i,3),i=1,6),'
      Tstop=Tstop*365.*24.*3600. !sec
      tcap=tcap*365.*24.*3600. ! time that sump is capped (s)
      pressure=1.
      TempK=288.8 ! temp of air in grout system (K)
      Rconst=82.06 ! cm3-Atm/mol-K

```

```
pRT=pressure/(Rconst*TempK)
diftot=0. ! total gas that has diffused out of grout (moles)
advtot=0. ! total gas that has advected out of grout
grttot=0. ! total gas that remains in the grout
Tmolpro=0. ! total mol gas produced in grout+those init dissolv
nT=1 ! loop counter
```

```
c initialize areas and volumes of the compartments
if(jflag .eq. 1)then
  A(1) = 0.
  A(2) = 2.95E+04 ! gap between vault and asphalt
  A(3) = 74.2 ! pipe draining catch basin to sump
  A(4) = 3550. ! sump exhaust pipe(s) (avg) to outside
  A(5) = A(4)
  A(6) = A(5)
  V(1) = 1.
  V(2) = 3.73E+07 ! gap between vault and asphalt
  V(3) = 1.668E+08 ! catch basin 40% void space
  V(4) = 2.00E+07 ! sump
  V(5) = 5.10E+06 ! sump exhaust
  V(6) = 1.
c initialize the diffusion lengths (cm)
  DX(1) = 30.
  DX(2) = 633.0 ! half height of gap between vault and asphalt
  DX(3) = 1140. ! full length of pipe from basin to sump
  DX(4) = 671. ! half length of sump exhaust
  DX(5) = 671.
  DX(6) = 1.
  ncomp = 6 !number of compartments in model
c high compartment number that diffusion or advection may
c directly enter from grout, assumes that they may enter
c compartments 2 through ihicmpt.
  ihicmpt=3
  tprint=63072000. !period between print statements
else
  A(1) = 0.
  A(2) = 2919. ! inlet pipe from outside (cm2)
  A(3) = A(2)
  A(4) = A(2)
  A(5) = A(4)
  A(6) = A(5)
  V(1) = 1.
  V(2) = 7.064E+08 ! vapor space (cm3)
  V(3) = 1.6E+06 ! inlet pipe
  V(4) = 1.
```

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```

V(5) = 1.
V(6) = 1.
c initialize the diffusion lengths (cm)
DX(1) = 1.      ! assume inlet pipe is 18ft long, diameter=2ft
DX(2) = 335.   ! half height of inlet pipe + 2ft for HEPA filt
DX(3) = 335.
DX(4) = 1.
DX(5) = 1.
DX(6) = 1.
ncomp = 4
ihicmpt=2
tprint=3153600. !time interval (sec) between data writes
endif
c initially at atmospheric conditions
Do i=1,ncomp
X(i,3)=0.21
X(i,4)=0.79
conc(i,3)=pRT*X(i,3)
conc(i,4)=pRT*X(i,4)
if(i .eq. 1 .or. i .eq. ncomp)goto 78
M(i,3)=V(i)*conc(i,3)
M(i,4)=V(i)*conc(i,4)
78 continue
enddo
do i=1,ncomp
do k=1,4
Gisum(k)=Gisum(k)+M(i,k)
enddo
c initial values for diffusion coef
diffc(i,1)=.8
diffc(i,2)=.2
diffc(i,3)=.3
diffc(i,4)=.3
enddo
c calculate total volume of system
Do i=2,(ncomp-1)
vt(i)=vt(i-1)+v(i)
enddo
C The following establish breathing caused by atmospheric pressure
C fluctuations throughout the year.
if(jflag .eq. 1)then
c Assume breathe 2.4*totvol/yr
gi(5,3)=(0.21*vt(5)*pRT/(365.*24.*3600.))*2.4
gi(5,4)=(0.79*vt(5)*pRT/(365.*24.*3600.))*2.4
else

```

```

c      Assume .054 cm3/s breathing rate
      gi(3,3)=(.21*.054*22.4/1000.*270./TempK)
      gi(3,4)=(.79*.054*22.4/1000.*270./TempK)
endif

c      set initial time to 0
      TT=0.

c      no cap initially
      capped=0

C      Start marching in time
c      %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
      100 continue                               ! start of time loop
c      increment time
      TT=TT+DT      !sec
c      *****
c      calculate time dependent source term
      Call G3(giadv,gidif,TT,DT,nT,liqdot,totliq,iapt,Tmolpro)
c      *****
c      Atmospheric breathing effects extended into all compartments:
c      if sump not capped then compartment i breathes from i+1 a volume
c      of gas equal to the sum of v(2)+v(3)+...+v(i). The gas it
c      breathes consists of the proper concentrations of each gas for
c      the compartment from which it takes its gas. Pressure driven
c      displacement flow should correct for any gas buildup due to this
c      "backward" flow:
      if(capped .le. 0)then
        if(jflag .eq. 1)then
          do i=2,(ncomp-2)
            do k=1,4
              gi(i,k)=(X(i+1,k)*vt(i)*pRT/(365.*24.*3600.))*2.4
            enddo
          enddo
        else
          do i=2,(ncomp-2)
            do k=1,4
              gi(i,k) = 0.
            enddo
          enddo
        endif
      else
        do i=2,(ncomp-2)
          do k=1,4
            gi(i,k) = 0.
          enddo
        enddo
      endif
endif

```

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```

endif
c combine diffusive & advective flow into compt. 2
do i=2,ihicmpt
do k=1,4
c add advective flow to source term
c if no advection specified then skip this step
if(iopt.ne.2)then
gi(i,k)=gi(i,k)+giadv(i,k) !add gi to giadv,for new breathe
endif
c add diffusive flow to source term
c if no diffusion specified then skip this step
if(iopt.lt. 3 .or. iopt.gt. 3)then
gi(i,k)=gi(i,k)+gidif(i,k)
endif
enddo
enddo
if(iopt.ne.3)then
c calc accum generation (mol) due to diff into both compt 2&3
do i=2,ihicmpt
do k=1,4
if(pfrac(k).gt. 1.E-10)then !test to see if gas is produced
diftot=diftot+gidif(i,k)*DT
endif
enddo
enddo
endif
if(iopt.ne.2)then
c calc accum generation (mol) due to advect into both compt 2&3
do i=2,ihicmpt
do k=1,4
if(pfrac(k).gt. 1.E-10)then
advtot=advtot+giadv(i,k)*DT
endif
enddo
enddo
endif
grttot = 0.
do k=1,4
if(pfrac(k).gt. 1.E-10)then
grttot=grttot+netmol(k) !tot num mol remaining in grout
endif
enddo
667 continue

c when time > tcap shut off breathing in cell 5 and

```

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```

c      diffusion from cell 6
      if((TT.ge.tcap).and.(capped.le.0))then
        gi(5,3)=0.
        gi(5,4)=0.
        A(3)=0.  !sump is filled with concrete in order to "cap" it
        A(4)=0.  !therefore no gas is allowed past catch basin
        A(5)=0.
        capped=1
      endif

c      initialize variables for calculation of diffusion coeffs.
      do i=1,ncomp
        do k=1,4
          Xtmp(k)=X(i,k)
          G(i,k)=0.
        enddo
c *****
c      calculate diffusion coefficients
      call DMIX(Xtmp,Dmx)
c *****
      do k=1,4
        diffc(i,k)=Dmx(k)
      enddo
    enddo

c calculate diffusion flow
    DO 215 I=2,(ncomp-1)
      do kj=1,4
        Nm(I,kj)=diffc(I,kj)*(conc(I,kj)-conc(I+1,kj))/DX(I)
        G(I,kj)=A(I)*Nm(I,kj)  !mole flow rate from comp i to i+1
      enddo
    215  CONTINUE

c      update moles, total moles, and mole fractions for each cell
      do i=2,ncomp
        Mt(i)=0
        do k=1,4
          M(i,k)=M(i,k)+DT*(G(i-1,k)+gi(i,k)-G(i,k)-GO(i,k))
          Mt(i)=Mt(i)+M(i,k)
        enddo
        do k=1,4
          if(Mt(i) .le. 0.)goto 222
          X(i,k)=M(i,k)/Mt(i)
        enddo
    222  continue
      enddo

```

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```

enddo

```

```

c do slug flow
c time < tcap ; flow from cell 2 towards 6
  if(TT.lt.tcap)then
    do i=2,(ncomp-1)
c      determine the difference between the number of moles in the
c      cell and the number that should be there at atmospheric
c      pressure. Adjust accordingly. Update total moles and mole
c      fractions.
      dm=Mt(i)-prt*V(i)
      Mt(i)=0.
      Mt(i+1)=0.
      do k=1,4
        M(i,k)=M(i,k)-dm*X(i,k)
        M(i+1,k)=M(i+1,k)+dm*X(i,k)
        Mt(i)=Mt(i)+M(i,k)
        Mt(i+1)=Mt(i+1)+M(i+1,k)
      enddo
      do k=1,4
        X(i,k)=M(i,k)/Mt(i)
        X(i+1,k)=M(i+1,k)/Mt(i+1)
      enddo
    enddo
  else ! time >= tcap ; flow from cell 5 towards 1
    do i=(ncomp-1),2,-1
c      determine the difference between the number of moles in the
c      cell and the number that should be there at atmospheric
c      pressure. Adjust accordingly. Update total moles and mole
c      fractions.
      dm=Mt(i)-prt*V(i)
      Mt(i)=0.
      Mt(i-1)=0.
      do k=1,4
        M(i,k)=M(i,k)-dm*X(i,k)
        M(i-1,k)=M(i-1,k)+dm*X(i,k)
        Mt(i)=Mt(i)+M(i,k)
        Mt(i-1)=Mt(i-1)+M(i-1,k)
      enddo
      do k=1,4
        X(i,k)=M(i,k)/Mt(i)
        X(i-1,k)=M(i-1,k)/Mt(i-1)
      enddo
    enddo
  endif

```

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```

c   update concentrations for cells 2-5, leave 1 and 6 at
c   atmospheric conditions
do i=2,(ncomp-1)
  do k=1,4
    conc(i,k)=M(i,k)/V(i)    !conc
  enddo
enddo

C   Write results
Twrite=TT/3600./24./365.
if(mod(TT,(tprint/2.)).eq.0. .or. TT.le.DT)then
  if(jflag .eq. 1)then
c   sump is filled w/concrete when capped
    if((TT.le.tcap).or.(capped.le.0))then
c   time(yr),mole fraction in sump, gas 1-4
      write(11,700)Twrite,(X(4,k),k=1,4) !changed 7/7
    endif
  endif
endif
if(mod(TT,tprint) .eq. 0. .or. TT .le. DT)then
  if(jflag .eq. 1)then
c   time(yr),mole fraction in catch basin, gas 1-4
    write(2,700)Twrite,(X(3,k),k=1,4)
  else
c   time(yr),mole fraction in vapor space, gas 1-4
    write(2,700)Twrite,(X(2,k),k=1,4)
  endif
c tim(yr),tot mol produced + orig dissolv,tot diff,tot adv,remain grout
  write(9,700)Twrite,Tmolpro,diftot,advtot,grttot
c tim(yr),rate of liq expulsion (gal/hr), accumulated liq release
  write(10,'(3(1pe9.2,1x))')Twrite,liqdot,totliq
c t(yr), Number of moles currently in each of 6 compartments for ea gas
  write(12,702)Twrite,(M(i,1),i=1,6)
  write(13,702)Twrite,(M(i,2),i=1,6)
  write(14,702)Twrite,(M(i,3),i=1,6)
  endif
  liqdot=0.    !reset liquid flow to zero
700 format(5(1x,1pe9.2))
701 format(4(1x,1pe9.2))
702 format(7(1pe9.2,1x))
705 format(3(F9.3,/),2(I2,/))

  if(TT.lt.Tstop)goto 100    ! Time LOOP *****
999 continue

```

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```

c Bell to alert interactive user of normal completion of program
do i=1,5
  write(6,*)char(7)
enddo
stop
end

```

```

c endENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDENDEND

```

SUBROUTINE DMIX(X,Dm)

```

C
C DMIX provides a gas diffusivity for each component of a quaternary
C mixture of hydrogen(H2), nitrous oxide(N2O), oxygen(O2), and nitrogen(N2).

```

```

C Input requirements are absolute temperature T, (K), absolute pressure P,
C atm, and mole fractions of each gas, X(i), i=1,4, in the order above.

```

```

Real X(4), MW(4), D(4,4), Omeg(4,4), Sigg(4,4), Ekk(4,4), Dm(4),
+ek(4), sig(4)

```

```

C The output values are Dm(i) in cm**2/s.

```

```

Data MW/2.016,44.02,32.,28.02/
Data ek/38.,220.,113.,91.5/
Data sig/2.915,3.879,3.443,3.681/
Pressure=1.
Tempk=288.8

```

```

Do 100 i=1,4
  do k=1,4
    Sigg(i,k)=0.5*(sig(i)+sig(k))
    Ekk(i,k)=sqrt(ek(i)*ek(k))
    Omeg(i,k)=0.7075+0.7341*Ekk(i,k)/TempK
  C Above fit from NUREG/CR-5765
    sg2=Sigg(i,k)**2.
    cik=1./MW(i) + 1./MW(k)
    D(i,k)=0.0018583*(TempK**1.5)*(cik**0.5)/Pressure/sg2/Omeg(i,k)
  enddo

```

```

100 continue

```

```

-----DO 1=1,4
  xd=0.
  do m1=1,4
    xd=xd+X(m1)/D(1,m1)
  enddo
  if(X(1).eq.1.)then
    Dm(1)=D(1,1)

```

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```
else
  xd=xd-X(1)/D(1,1)
  Dm(1)=(1./xd)*(1.-X(1))
endif
endDO
```

C Method from Bird,R.B., W.E.Stewart, and E.N.Lightfoot. 1960. "Transport
C Phenomena". John Wiley & Sons, NY.

```
return
end
```

C*****

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