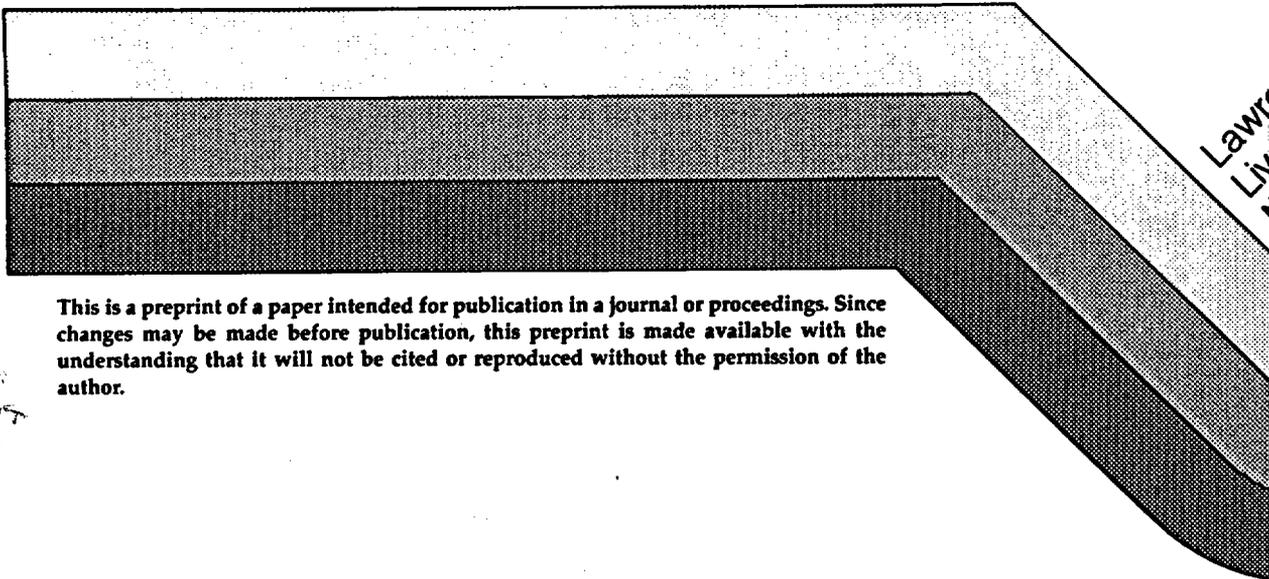


AN APPROXIMATE CALCULATION OF ADVECTIVE
GAS PHASE TRANSPORT OF ^{14}C At YUCCA
MOUNTAIN, NEVADA

Richard B. Knapp

Submitted to
Journal of Contaminant Hydrology

December 1987



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

HYDROLOGY DOCUMENT NUMBER 462

Lawr
Liv

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Prepared by Yucca Mountain Project (YMP) participants as part of the Civilian Radioactive Waste Management Program. The YMP project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. YMP Project work is sponsored by the DOE Office of Civilian Radioactive Waste Management.

AN APPROXIMATE CALCULATION OF ADVECTIVE GAS PHASE TRANSPORT OF ^{14}C AT YUCCA MOUNTAIN, NEVADA

R. B. Knapp

L-206, Earth Science Department, Lawrence Livermore National Laboratory, Livermore, California

ABSTRACT

A quasilinear partial differential equation, which describes gas phase transport of a ^{14}C kinematic wave through a porous media, is derived, its sensitivity to system variables is analyzed and it is applied to one possible release scenario at the proposed Yucca Mountain, Nevada high-level radioactive waste repository. Advection, isotope exchange between CO_2 in a flowing gas phase and HCO_3^- in a static aqueous phase, and radioactive decay are incorporated. Diffusion, dispersion, curvilinear pathlines, temporal and spatial variations in rock and fluid properties, and solid-fluid chemical interactions are not considered. The governing equation is solved analytically by the method of characteristics.

The mass fraction of ^{14}C in the gas phase, X_{14}^g , is controlled by radioactive decay. The relatively long half-life of ^{14}C , about 5,720 years, and the relatively shallow proposed burial depth of the radioactive waste, about 350 m, requires significant retardation of the ^{14}C wave velocity for significant reduction in X_{14}^g . ^{14}C wave velocity is most sensitive to temperature and pH which control the distribution of total carbon between the gas and liquid phase; the greater the partitioning of carbon into the liquid phase, the greater the retardation of the ^{14}C wave velocity and the greater the ultimate reduction in X_{14}^g from initial conditions. Partitioning of total carbon into the liquid phase is greatest at low temperatures, $<100^\circ\text{C}$, and high pH values, >8 . Increasing water saturation also tends to retard ^{14}C wave velocity but to a lesser extent. Retardation is expected to be greatest in the far-field region.

The governing equation has been applied using conditions that may possibly occur at the proposed Yucca Mountain repository. Temperatures, liquid saturations and gas velocities are arbitrarily chosen from the results of two-dimensional, finite difference modelling of heat and mass transfer at the proposed site. Conditions are for when sub-boiling temperatures are returned to at the radioactive waste containers, about 2,000 years after emplacement. An initial X_{14}^g value of 50 ppm is used; this is approximately 1% of the total ^{14}C content of a single container and it is assumed that this 1% is instantaneously discharged into the flowing gas phase. Liquid is assumed to be J-13 water in equilibrium with Topopah Springs Tuff. Calculations indicate that the ^{14}C wave takes about 5,900 years to reach the surface with a X_{14}^g equal to 25 ppm. Diffusion and dispersion are not of major importance for these conditions. These calculations are approximate due to the number of assumptions involved. Discharge of ^{14}C into the gas phase before the selected time would accelerate wave arrival and increase the amount of ^{14}C reaching the surface.

1. INTRODUCTION

It has been proposed to place high-level nuclear waste in the unsaturated zone at Yucca Mountain, Nevada. The presence of high-level waste will cause local heating, convective fluid circulation, and has the potential to cause release and transport of chemicals (Pruess, et al, 1985; Oversby and Wilson, 1985; Bates and Gerding, 1986). The radioactive isotope ^{14}C is among these chemicals. Transport of radionuclides from the engineered barrier system is restricted by NRC regulation and transport of radionuclides to the accessible environment is restricted by EPA regulation (Oversby, 1987). These regulations focus attention on at least three topics: the abundance of radionuclides in the waste packages, radionuclide transport away from the waste packages and chemical reactions along fluid pathways which may influence the abundance and rate of radionuclide transport.

The following is a brief investigation of transport and reaction, and provides estimates of ^{14}C abundance reaching the surface as a function of time. Calculated values are approximate due to the degree of simplification. Nevertheless, the approach can serve to elucidate some of the general transport processes. It may also provide some additional motivation for the acquisition and refinement of more sophisticated tools to address the transport of reactive chemicals in porous media.

We will first discuss the general processes expected to occur. The range of processes will be limited and their interactions simplified. A mathematical model is developed and solved analytically using reasonable ranges of values for properties and conditions at Yucca Mountain, Nevada. The equations are applied to one possible scenario at the potential site: instantaneous release of radionuclides when temperatures decrease below the boiling point of water at the radioactive waste containers. Finally, recommendations are made for more refined approaches.

2. CONCEPTUAL MODEL

High-level nuclear waste will cause significant variations in temperature, water saturation, fluid pathlines and ^{14}C abundance (Pruess et al, 1985; Smith et al., 1986; Green and Evans, 1987; Nitao, 1988). While the details of the behavior of these variables is still uncertain, some general conceptual statements can be made with confidence. High-level nuclear waste emplaced into the repository will serve as a transient heat source; heat will be dissipated by both conduction and convection. In the first few hundred years, isotherms will expand away from the waste contain-

ers; as the radioactive heat source decays isothermal movement reverses and isotherms eventually collapse back towards initial conditions. Boiling conditions are surpassed in a region around the containers with the size and duration of this steam region being largely a function of rock properties.

Thermal anomalies induced by the high-level nuclear waste cause horizontal fluid density perturbations which, in turn, initiate free convective circulation of both air and water (Pruess et al., 1985; Nitao, 1988). Fluid flow is generally away from the waste containers but fluid pathlines are curvilinear due to the transient nature of the heat source and the conservation of mass requirement (Norton and Knight, 1977; Norton, 1978). Fluid pathlines are generally not directly away from the waste containers to the surface; many fluid packets will instead initially rise towards the surface but then turn and recirculate downwards; pathlines can be quite tortuous on a macroscopic scale. A given packet will experience large variations in velocity, temperature and water vapor content. Fluid velocities will be greatest closest to the containers; Darcy gas velocities may exceed 5 km/yr (Nitao, 1988). Fluid velocities are least in the far field region, gas velocities being typically on the order of 1 m/yr. Gas velocities are usually much greater than liquid velocities; in the following mathematical development, the liquid phase will be assumed to be static. A gas fluid packet rapidly traverses the hot, low liquid saturation region and slowly traverses the more distal, cooler, higher liquid saturated region.

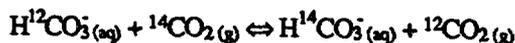
It is emphasized that fluid velocities and fluid pathlines are highly sensitive to the transport characteristics of the media. Transport in fractured media is much different than in porous media and in general the Yucca Mountain site is fractured. Studies to date (eg. Nitao, 1988) have been based upon the equivalent porous media concept and it is the results of these studies that are used for guidance in this report.

As a consequence of local heating and fluid flow, liquid water will be redistributed in the surrounding rocks by both liquid water flow and vapor phase transport. Vapor phase transport occurs by a sequence of boiling in the near-field region, humid air flow and condensation in the far-field region of the system. The region immediately around the waste containers first experiences a decrease in liquid saturation; desaturation to negligible values is possible. Near-field desaturation is followed by, after an uncertain amount of time, resaturation as isotherms collapse. More distal regions experience the reverse trend in liquid saturation; saturation initially increases as humid air flows into cooler regions and condenses; liquid saturation decreases as isotherms collapse.

^{14}C occurs naturally in the pore fluids at extremely small concentrations and is introduced into a repository with the high-level nuclear waste. For spent fuel, introduced ^{14}C is initially on the insides of fuel rods, on the interior of fuel assembly structural components and on the exterior of fuel assembly components (Van Konynenburg et al., 1985 and 1986). Eventually the package is breached and contacted by circulating air. External structural components are oxidized and ^{14}C enters the vapor phase as, predominantly, CO_2 ; apparently most of the ^{14}C to enter the gas phase originates from the external structural components. At 275 °C, the kinetics of the process are rapid and equilibrium is reached after several months and after about 1 - 2 mg of ^{14}C per assembly has been oxidized; kinetics are unknown at lower temperatures. With ^{14}C discharging into a flowing gas phase, the ^{14}C concentration profile will be a wave (figure 1) with the amplitude and wavelength dependent upon many parameters. These types of profiles have been called kinematic waves by Whitham (1974).

As a ^{14}C wave advects along a gas pathline, its amplitude, wavelength and velocity will be modified by physical and chemical processes. Dispersion and diffusion are the main physical processes and their combined quantitative effects are largely unknown. Diffusion in the gas phase has been studied by Tokunaga (1986), Smith et al (1986), and Green and Evan. (1987) whereas dispersion is largely unstudied. Qualitatively both processes decrease wave amplitude and increase wavelength, spreading ^{14}C over a larger porous volume; both processes are neglected in the mathematical model.

Isotopic exchange, radioactive decay, adsorption and water-carbonate mineral reactions are the main chemical modifying processes. Isotope exchange can occur between $\text{CO}_2(\text{g})$, $\text{HCO}_3^-(\text{aq})$ and $\text{CaCO}_3(\text{s})$ with ^{14}C , ^{13}C and ^{12}C the carbon isotopes which are involved in the exchange reactions. Of the possible exchange reactions at the Nevada site, the most important is



since ^{13}C is minor and $\text{CaCO}_3(\text{s})$ occurs primarily in vein fillings and fractures (Warren et al., 1984). The above exchange reaction occurs between air and adjacent liquid, is controlled by thermodynamic equilibrium constraints and is sensitive to temperature, saturation and concentrations.

Isotope exchange retards the progress of a ^{14}C wave due to the time it takes for ^{14}C to move from the gas to liquid phase, as the peak amplitude of the wave approaches a particular point, and then back again as the wave passes.

Radioactive decay directly affects the amplitude of the wave. Adsorption is potentially important but its quantitative effects are largely unknown; qualitatively it would retard the progress of a wave. Water-rock interaction is probably insignificant due to the low abundance of calcite at the Nevada site (Warren et al., 1984) and due to a prediction that calcite will not precipitate (Delany, 1985); however, should calcite precipitate it would form a long term sink for ^{14}C and reduce the amplitude of the wave. Isotope exchange and radioactive decay are included in the mathematical model while adsorption and solid-fluid reactions are excluded.

Transport of ^{14}C via aerosols is excluded in this study because work to date suggests aerosols will not form at the Yucca Mountain repository (Smith et al., 1986; Green and Evans, 1987).

In summary, a high-level nuclear waste package is proposed to be emplaced about 350 m deep into a fractured and porous media that is partially saturated with water. The waste is a transient heat source and will drive air and liquid water circulation; air circulation will be much faster than liquid circulation. As waste containers are breached, ^{14}C will discharge into the flowing gas and form a kinematic wave. A ^{14}C wave will follow a circuitous path and its progress will be retarded by isotope exchange with adjacent water. Dispersion, diffusion and radioactive decay will serve to decrease wave amplitude. Variables expected to influence wave velocity and amplitude are temperature, fluid saturations, liquid bicarbonate concentrations, porosity, gas phase velocity and path length.

A mathematical model is developed in the next section to quantitatively describe these processes and assess the relative importance of these variables. The model is highly simplified by assumptions which neglect dispersion, diffusion, adsorption and variations in rock and fluid properties, temperature and saturation. The focus is on the transport processes and questions concerning potential breaching of waste containers are not addressed. The objective is to obtain estimates of travel times and amplitudes of ^{14}C waves in the gaseous phase.

3. MATHEMATICAL MODEL

A macroscopic equation describing chemical transport in porous media is

$$\sum_{\alpha=1}^n \left\{ \frac{d[\phi \rho^{\alpha} S^{\alpha} X_{i4}^{\alpha}]}{dt} + \nabla \cdot [J_A^{\alpha} + J_D^{\alpha}] + R^{\alpha} \right\} = 0 \quad (1)$$

where

- J_A^{α} = advective flux in the α phase,
- J_D^{α} = diffusive/dispersive flux in the α phase,
- n = total number of phases,
- R^{α} = chemical reaction, source/sink term for the α phase,
- S^{α} = fluid saturation of the α phase,
- t = time,
- X_{i4}^{α} = mass fraction of ^{14}C in the α phase,
- α = phase indicator,
- ϕ = porosity and
- ρ^{α} = mass density of the α phase.

Neglecting nonadvective fluxes and fluid-solid chemical interactions and expanding the advective flux and source/sink term with respect to radioactive decay via

$$J_A^{\alpha} = v^{\alpha} \rho^{\alpha} X_{i4}^{\alpha} \quad (2)$$

$$R^{\alpha} = \lambda \phi \rho^{\alpha} S^{\alpha} X_{i4}^{\alpha}$$

then (1) becomes

$$\sum_{\alpha=1}^n \left\{ \frac{d[\phi \rho^{\alpha} S^{\alpha} X_{i4}^{\alpha}]}{dt} + \nabla \cdot [v^{\alpha} \rho^{\alpha} X_{i4}^{\alpha}] + \lambda \phi \rho^{\alpha} S^{\alpha} X_{i4}^{\alpha} \right\} = 0 \quad (3)$$

where

- v^{α} = Darcy velocity of the α phase and
- λ = radioactive decay constant of ^{14}C .

Hydrologic calculations suggest that liquid velocities are on the order of 0.1 m/yr while gas velocities are at least an order of magnitude greater (Nitao, 1988). Assuming negligible liquid velocities with respect to gas velocities,

then the one-dimensional equation for transport of ^{14}C in a partially saturated porous media with inert solid phases, two reactive fluid phases and constant gas velocity and fluid saturations is

$$\phi \rho^l S^l \frac{\partial X_{14}^l}{\partial t} + \phi \rho^g S^g \frac{\partial X_{14}^g}{\partial t} + \rho^g v^g \frac{\partial X_{14}^g}{\partial z} + \lambda \phi [\rho^l S^l X_{14}^l + \rho^g S^g X_{14}^g] = 0 \quad (4)$$

where the superscripts g and l denote the gas and liquid phases respectively.

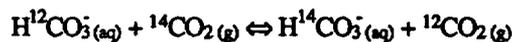
Diffusion and dispersion are potentially significant processes influencing the amplitude and wavelength of the ^{14}C wave as it propagates through the porous media. Neglecting their contributions diminishes the accuracy of the results and causes estimates of wave amplitude to approach maximum values. The assumptions of constant properties will be examined later in a sensitivity analysis.

Equation (4) is a first order partial differential equation with two dependent variables, X_{14}^g and X_{14}^l , and two independent variables, t and z. The remaining development is to reduce the number of dependent variables to one by writing X_{14}^l in terms of X_{14}^g .

Gas and liquid coexist as contiguous phases in the conceptual model; this permits interchange of all chemical species between the two phases constrained solely by thermodynamic equilibrium and reaction kinetics. Therefore, X_{14}^l can be written in terms of X_{14}^g .

$$\frac{\partial X_{14}^l}{\partial t} = \left[\frac{\partial X_{14}^l}{\partial X_{14}^g} \right] \left[\frac{\partial X_{14}^g}{\partial t} \right]_{X_{14}^g} \quad (5)$$

reducing the number of dependent variables by one. The relationship between X_{14}^l and X_{14}^g is imposed by isotopic equilibrium constraints. The isotope exchange reaction is expressed by



ignoring all other carbon isotopes. This reaction proceeds by a second order rate law (Stumm and Morgan, 1981)

$$\frac{\partial X_{14}^l}{\partial t} = k_f X_{12}^l X_{14}^g - k_r X_{14}^l X_{12}^g \quad (6)$$

where

k_f = forward reaction rate,

k_r = reverse reaction rate,

X_{12}^α = mass fraction of ^{12}C in the α phase and

X_{14}^α = mass fraction of ^{14}C in the α phase.

Equation (6) assumes the contribution of ^{13}C is negligible.

Applying the law of mass action

$$K = \frac{k_f}{k_r} \quad (7)$$

conservation of total carbon in the liquid phase

$$X_T^l = X_{12}^l + X_{14}^l \quad (8)$$

and conservation of ^{12}C in the fluid phases

$$X_{12}^F = \frac{X_{12}^l \rho^l S^l + X_{12}^s \rho^s S^s}{\rho^l S^l + \rho^s S^s} \quad (9)$$

to equation (6) gives

$$\frac{\partial X_{14}^l}{\partial t} = k_r \left\{ K X_T^l X_{14}^s + [A X_T^l - X_{12}^F (1 + A)] X_{14}^l - K X_{14}^l X_{14}^s - A [X_{14}^l]^2 \right\} \quad (10)$$

where

$$A = \frac{\rho^l S^l}{\rho^s S^s}$$

K = equilibrium constant for the exchange reaction

The first conservation equation, (8), is approximate since ^{14}C will decay to ^{17}N but the abundance of ^{14}C in the liquid is exceedingly small when compared with the abundance of ^{12}C and therefore (8) will be used. Equation (8) is not valid when the amplitude of the ^{14}C kinematic wave is large and when thermodynamic equilibrium requires a relatively large partition of carbon into the liquid phase. These two conditions are not likely to be simultaneously encountered at the Yucca Mountain repository. X_T^l is an initial condition.

The second conservation equation is consistent with the assumption that there is either a negligible carbonate mineral abundance or that isotopic exchange between the fluid phases and solid phases are small when compared to the liquid-gas exchanges (Warren et al., 1984).

Equilibrium according to the above exchange reaction is achieved on the order of 20 seconds (Stumm and Morgan, 1981). This is at least 8 orders of magnitude faster than the time scale of interest and so instantaneous equilibrium will be assumed. Consequently, equation (10) is equal to zero and can be rearranged to give, neglecting terms second order in X_{14}^1 ,

$$X_{14}^1 = \frac{K X_T^1 X_{14}^g}{B + K X_{14}^g} \quad (11)$$

where

$$B = X_{12}^F (1 + A) - X_T^1 A \quad (12)$$

The derivative of (11) can then be taken to yield

$$\left[\frac{\partial X_{14}^1}{\partial X_{14}^g} \right] = \frac{K X_T^1 B}{[B + K X_{14}^g]^2} \quad (13)$$

which can be substituted into (5) and the result substituted into (4) to give, ignoring second order terms,

$$\frac{\partial X_{14}^g}{\partial t} + v^* \frac{\partial X_{14}^g}{\partial z} + \lambda^* X_{14}^g = 0 \quad (14)$$

where

$$v^* = \left[\frac{v^g \rho^g}{\phi} \right] \left[\frac{C + D X_{14}^g(t)}{E + F X_{14}^g(t)} \right] \quad (15)$$

$$\lambda^* = \lambda \left[1 + \frac{G X_{14}^g(t)}{E + F X_{14}^g(t)} \right] \quad (16)$$

and

$$C = B^2$$

$$D = 2 B K$$

$$E = \rho^l S^l B K X_T^l + \rho^g S^g B^2$$

$$F = 2 \rho^g S^g B K$$

$$G = \rho^l S^l K^2 X_T^l$$

Equation (14) is a first order, quasilinear partial differential equation with one dependent variable, X_{14}^g , and two independent variables, t and z ; quasilinearity arises from the dependence of the coefficients, v^* and λ^* , on X_{14}^g . Many authors (eg. Ross, 1987) linearize the governing equations by ignoring this dependency. While this is attractive for very weak perturbations (on the order of a few ppm) and for early times in the history of wave transport, it invalidates the governing equation if the ^{14}C wave breaks and forms a shock front (Whitham, 1974); a breaking kinematic wave gradually steepens until a discontinuous concentration profile is formed. This effect and its importance will be examined in greater detail later.

Equation (15) is the expression for the velocity of the ^{14}C wave in the gas phase retarded by isotope exchange with aqueous bicarbonate species. As will be demonstrated later, v^* is directly proportional to X_{14}^g causing the kinematic wave to break. An effective decay constant, λ^* , is required because radioactive decay of ^{14}C occurs in both the liquid and aqueous phase whereas the governing equation, (14), is written solely in terms of the gaseous phase. The modification of λ does not appear in developments where a simple Henry's law relationship is used to describe gas-liquid equilibrium (Ross, 1987)

The governing equation, (14), can be solved by the method of characteristics (Whitham, 1974; Kevorkian, 1983).

Comparing the total differential operator

$$dX_{14}^g = \left[\frac{\partial X_{14}^g}{\partial t} \right]_z dt + \left[\frac{\partial X_{14}^g}{\partial z} \right]_t dz \quad (17)$$

with (14) gives two ordinary differential equations

$$\frac{\partial X_{14}^g}{\partial t} = -\lambda^* X_{14}^g \quad (18)$$

$$\frac{\partial z}{\partial t} = v^* \quad (19)$$

This transformation places the reference frame on a particular ^{14}C concentration, a characteristic, defined by the initial conditions

$$\begin{aligned} z(0) &= \xi \\ X_{14}^{\xi}(0) &= f(z) = f(\xi) \end{aligned} \tag{20}$$

Integrating (18) gives

$$\frac{[E + H X_{14}^{\xi}(t)]^I}{X_{14}^{\xi}(t)} = e^{\lambda t} \frac{[E + H X_{14}^{\xi}(0)]^I}{X_{14}^{\xi}(0)} \tag{21}$$

where

$$\begin{aligned} H &= F + G \\ I &= G / (F + G) \end{aligned}$$

Applying the binomial series expansion to $[E + H X_{14}^{\xi}(t)]^I$ and retaining the first three terms gives

$$\left\{ \frac{[I^2 - 1] E^{I-2} H^2}{2} \right\} (X_{14}^{\xi}(t))^2 + \left\{ I E^{I-1} H - e^{\lambda t} \frac{[E + H X_{14}^{\xi}(0)]^I}{X_{14}^{\xi}(0)} \right\} (X_{14}^{\xi}(t)) + E^I = 0 \tag{22}$$

with a remainder of

$$r_j = \sum_{j=4}^n r_{j-1} \left\{ \frac{H X_{14}^{\xi}(t) [I - j + 2]}{E [j - 1]} \right\} \tag{23}$$

$$r_3 = \frac{I [I - 1] E^{I-2} H^2 [X_{14}^{\xi}(t)]^2}{2} \tag{24}$$

The binomial series expansion converges when $E^2 > [H X_{14}^{\xi}(t)]^2$, which occurs for all temperatures and pH values in this study. Utilizing the first three terms ensures that the calculated $X_{14}^{\xi}(t)$ is at least 99.9% of the value attained by using $n \uparrow \infty$. Equation (22) is quadratic and is solved for $X_{14}^{\xi}(t)$ by using the negative root; the positive root produces unrealistic values in all cases. The distance a particular characteristic has travelled as a

function of time, $z(t)$, is obtained by substituting the negative root of (22) into (15), inserting the result into (19) and then integrating.

Equation (22) combined with equation (15) and the integral of (19) describe the magnitude, rate of movement and location of points on a ^{14}C kinematic wave. However, (15) is valid only for early times and an alternative expression must be used at later times. This characteristic is caused by the proportionality between v^* and $X_{14}^{\#}(t)$; points on the wave (fig. 1) with greater amplitudes travel faster than points with smaller amplitudes. This causes the wave to break forward, ie. gradually steepen until a discontinuous shock front is formed (fig. 2); (15) becomes invalid at this point. After the wave breaks it travels at a rate of (Whitham, 1974)

$$v_s^* = \frac{[v^* X_{14}^{\#}(t)]_2 - [v^* X_{14}^{\#}(t)]_1}{[X_{14}^{\#}(t)]_2 - [X_{14}^{\#}(t)]_1} \quad (25)$$

The subscripts on the square brackets denote location with respect to the discontinuity: 1 indicates values ahead of the shock and 2 indicates values behind the shock. The problem now reduces to including discontinuities into (15) and (19) so that the shock condition, (25), is satisfied. In the present case (25) can be approximated by

$$v_s^* = \left(\frac{v^s \rho^s}{2 \phi} \right) \left(\frac{[D E + C F] X_{14}^{\#}(t) + 2 C E}{E E + E F X_{14}^{\#}(t)} \right) \quad (26)$$

since $[X_{14}^{\#}(t)]_1 \rightarrow 0$. Substituting the negative root of (22) into (26) and integrating the result with respect to time, using Simpson's rule with 21 points, gives the distance the kinematic wave has travelled after a shock front has developed. The time required for a shock to develop is the half wavelength times the difference between the peak amplitude velocity and the minimum amplitude velocity. In the present study, the initial wavelength is relatively small so the shock front is considered to be established instantaneously; all references to velocity and distance will imply the use of (26).

4. ANALYSIS

Equations (22), (26) and (19) describe the movement of a decaying kinematic gas wave through a porous media where there is instantaneous isotopic equilibrium between $\text{CO}_2(\text{g})$ and $\text{HCO}_3^-(\text{aq})$. It has been assumed that:

- 1) the liquid phase is stationary,
- 2) diffusion and dispersion are negligible,
- 3) ^{13}C has a negligible influence,
- 4) ^{12}C is the dominant C isotope in the liquid phase,
- 5) solid carbonate phases are insignificant and
- 6) rock and fluid properties are constant along a pathline.

Though these assumptions restrict the applicability of the model, insight into important processes at Yucca Mountain can still be gained. In the following, reasonable ranges in variables will be used to examine their relative importance and to elucidate the overall advective/exchange process.

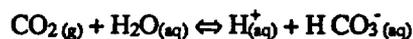
$X_{14}^g(t)$, λ^* , v^* and $z(t)$ are functions of the mass distribution of carbon between liquid and gas. This control is exerted through the coefficients in the governing equations. The coefficients themselves are functions of the more primitive variables temperature (T), pH, saturation, initial carbon isotope concentrations and porosity. Values for these primitive variables are expected to vary widely at the Yucca Mountain site but ranges have been selected from the literature (Table 1).

J-13 water analyses are used for X_T^l . The peak value of 50 ppm for $X_{14}^g(0)$ selected for the characteristic represents 1% of the total inventory per container, 14 mg, (Van Konyenburg et al., 1985 and 1986) instantaneously discharged into a gas occupying the space between the container and borehole wall ($3.4 \times 10^5 \text{ cm}^3$). This number appears to be a maximum because the release will not be instantaneous and air will be flowing at a high rate past the container.

$X_{14}^g(t)$ decays exponentially, as can be seen from the governing equation (22), is sensitive to temperature and pH (figure 3) and is insensitive to saturation changes. Temperature and pH influence the equilibrium distribution of total carbon between the gas and liquid phase,

$$\log \left[\frac{X_T^g}{X_T^l} \right] = 1.538 - \log K_{eq}(T) - \text{pH} \quad (27)$$

which originates from



and

$$K_{eq}(T) = \frac{a_{H^+} a_{HCO_3^-}}{f_{CO_2} a_{H_2O}}$$

assuming unit activity of water, unit activity coefficients and a total pressure of 1 MPa. The value of 1.538 in equation (27) results from converting partial pressure and molality to mass fractions. Equilibrium constants from Stumm and Morgan (1981) have been used.

As temperature increases the more volatile phase is favored and X_T^g increases at the expense of X_T^l (figure 4); X_T^g is also favored at lower pH as H_2CO_3 becomes the dominant aqueous species. Temperature and pH control the rate of decay through λ^* (16); λ^* increases as carbon is increasingly partitioned into the liquid phase (figure 5). The change in λ^* is a consequence of writing the governing equation with respect to the gas phase only; radioactive decay of ^{14}C in the liquid phase must then be included through a modified decay constant.

The velocity of a particular characteristic on the ^{14}C kinematic wave has a large influence on X_{14}^g because the ^{14}C half-life is relatively long, about 5,700 years, and the distance from radioactive waste container to the surface is relatively small, about 350 m; slower velocities cause longer transit times and greater radioactive decay. The velocity of a particular characteristic, (15), is retarded from the true gas velocity due to isotope exchange between the gas and liquid phase. Movement of ^{14}C from the gas to the liquid and back again slows wave progress and the greater the amount of carbon in the liquid phase, the greater the retardation (figures 6 and 7). Kinematic wave velocity is most sensitive to the distribution of carbon between the two phases; velocity is greatest at high temperatures and low pH.

Wave velocity is most sensitive to saturation in the low liquid saturation regime (figures 6 and 7). Increasing S^l in this regime causes velocity to decrease because the mass of carbon in the liquid phase is increasing with respect to the mass of carbon in the vapor phase.

Wave velocity is greatest at high temperatures and low liquid saturations; these conditions are anticipated in the near-field region. The near-field region is also where gas velocities can exceed 1 km/yr. Therefore a ^{14}C wave is expected to traverse the region near high-level radioactive waste containers very rapidly. Wave velocity is slowest in the low temperature, high liquid saturation regime; these conditions are anticipated in the far-field regime. Therefore a ^{14}C wave will traverse the far-field region relatively slowly. This slow passage will permit greater loss of ^{14}C due to radioactive decay and result in lower emissions to the accessible environment. The exact concentrations depend on site particulars and will be investigated in greater detail later.

Wave velocity is only slightly sensitive to the amount of ^{14}C in the gas phase (figure 8). Wave velocity increases about 3.5 cm/yr for every 50 ppm increase in X_{14}^g ; this is the rate at which the wave breaks. The small difference between peak velocity and shock velocity and the probable small initial wavelength of the kinematic wave serve to justify the use of shock velocity in the calculations.

Assuming a straight pathline, then the time to reach the accessible environment can be estimated using the shock velocity (figure 9). These estimates are very approximate due to the number of assumptions involved and due to the large variations in temperature and saturation as a wave moves from source to surface. In the next section, the equations will be applied to one possible scenario at the proposed Nevada repository.

Diffusion has not been considered in the above analysis even though it has been studied in this context (Smith et al, 1986; Green and Evans, 1987). The focus has instead been upon advection and velocity reduction caused by isotope exchange with a liquid phase. But when a shock wave forms, the relative importance of diffusion needs to be further examined because concentration gradients at the shock front are infinite. If diffusion is important then the step from background ^{14}C concentrations to peak values will occur over a finite distance instead of discontinuously at the shock front. If the size of this transition zone is significant with respect to the scale of the problem, then diffusion must be included in a rigorous analysis. The width of a transition zone, δ , is on the order of (Whitham, 1974)

$$\delta \propto \frac{\mathcal{D}^*}{\Delta v^*} \quad (28)$$

$$\mathcal{D}^* = \rho^g S^g \frac{[C + B X_{14}^g(t)]}{[D + E X_{14}^g(t)]} \mathcal{D} \quad (29)$$

where

\mathcal{D} = dispersion coefficient + effective dispersion coefficient of ^{14}C in gas phase

$\approx 500 \text{ m}^2/\text{yr}$

Δv^* = velocity difference between peak and background portions of ^{14}C wave

$\approx 0.035 \text{ m/yr}$

\mathcal{D} becomes of comparable importance to advection at higher temperatures, higher pH values and higher saturations (figure 10). This combination is expected to be uncommon in the proposed repository.

5. EXAMPLE

The governing equations can be applied using results from two-dimensional, finite difference heat and mass transfer modelling done specifically for the proposed Yucca Mountain repository (Nitao, 1988). The finite difference model predicts temperature, saturations and gas velocities as a function of time and space. Conditions at the time temperatures fall below the boiling point, about 2,000 years after emplacement (figure 11), are arbitrarily used for the calculations; it is assumed that the waste package is breached at this time and 50 ppm of ^{14}C is instantaneously discharged into the flowing gas phase. Carbon concentrations in the liquid, $X_{\text{T}}^{\text{L}} = 25\text{ppm}$ and $\text{pH} = 8.0$, have been chosen to be J-13 water (Delany, 1985). We emphasize that these results are preliminary and may not represent conditions actually achieved at Yucca Mountain; they are used only as estimates of one possible scenario.

Equation (26) is applied to each grid point in the finite difference model and v_{T}^* is calculated. Incremental transit times between grid points are calculated and summed to give elapsed times; this value is used in (22) to calculate X_{14}^{G} at each grid point. This incremental approach is very approximate but required by the current development.

Results for this scenario indicate that the ^{14}C wave reaches the surface after about 5,850 years with an amplitude, about 25 ppm, about half that of the initial amplitude (figure 12). The key factor is the relatively slow gas velocity in the high liquid saturation regime near the surface; large retardations permit radioactive decay to reduce wave amplitude.

It is emphasized that the model and calculations are highly approximate. Specifically, temperatures, saturations and gas velocities will change from the chosen conditions as the ^{14}C wave takes over 5,000 years to reach the surface. In addition, we have assumed the pathline to be straight from the waste packages to the surface whereas in reality they will be curvilinear. However, both factors are expected to delay the arrival of the kinematic wave, making the present calculations minimum arrival times. Faster arrivals with greater ^{14}C concentrations would occur if the radioactive waste packages were to be breached earlier when temperatures would be hotter, liquid saturations gen-

erally lower in a large region around the containers and gas velocities much greater. The timing of package breaching is a very important variable.

Diffusion and dispersion do not appear to be important processes for this scenario since transition zone widths (28) are less than 1.5 m.

6. CONCLUSIONS

Equations describing the movement of a decaying ^{14}C kinematic wave from radioactive waste containers to the surface have been derived assuming:

1. advection is the dominant physical transport process,
2. isotope exchange between flowing gas and static liquid is the dominant chemical process,
3. the amplitude of the initial ^{14}C wave is small,
4. chemical equilibrium between gas and liquid,
5. a straight pathline from container to surface,
6. constant conditions along the pathline and
7. a porous media.

It has been shown that the amplitude of the ^{14}C wave is controlled by the transit time, or the wave velocity. Wave velocity is most sensitive to the relative distribution of total carbon between the gas and liquid phase; this is controlled by thermodynamic equilibrium constraints. Velocities are greatest at high temperatures and low pH values where partitioning favors the gas phase. Velocities are least at low temperatures and high pH values where equilibrium favors the liquid phase. Wave velocities are also sensitive to liquid saturation and aqueous bicarbonate concentration; velocities are slowest at high liquid saturations and high bicarbonate concentrations.

Application of the governing equations to one potential release scenario indicates that transit time from containers to surface takes about one half-life. The scenario assumes that there is release of ^{14}C into the gas phase from the waste only when temperatures at the containers return to sub-boiling levels causing large scale condensation. Earlier release would result in much faster transit times and much greater concentrations at the surface.

These calculations are highly approximate due to the degree of simplification but they do serve to provide initial estimate of the impact of high-level nuclear waste disposal on ^{14}C release at the surface. It is recommended that more sophisticated approaches be developed and applied. Specifically, full dynamic coupling between chemical and physical processes covering a range in conditions should be applied. In addition, more information is required on the variation of key porous media variables as pathlines extend from containers to the surface. Finally, it is important that the fluid composition in equilibrium with the rock at all predicted conditions be known or estimated. Application of the transport problem with these more sophisticated tools and more complete knowledge of the media could generate greater confidence in predicted ^{14}C release rates.

7. REFERENCES

- Bates, J. K. and T. J. Gerding, 1986. One-year results of the NNWSI unsaturated test procedure: SRL 165 glass application. Argonne National Laboratory, ANL 85-41, 78 pp.
- Delany, J. M., 1985. Reaction of Topopah Spring Tuff with J-13 water: A geochemical modelling approach using the EQ3/6 reaction path code. Lawrence Livermore National Laboratory, UCRL 53631, 46 pp.
- Faure, G., 1977. Principles of Isotope Geochemistry. J. Wiley and Sons, Inc., 464 pp.
- Friedman, I. and J. R. O'Neil, 1977. Data of geochemistry, Chapter KK, Compilation of stable isotope fractionation factors of geochemical interest. USGS Prof. Paper 440-KK, 110 pp.
- Green, R. T. and D. D. Evans, 1987. Radionuclide transport as vapor through unsaturated fractured rock. NUREG/CR-4654, 163 pp.
- Kerrisk, J. F., 1987. Groundwater chemistry at Yucca Mountain, Nevada, and Vicinity. Los Alamos National Laboratory, LA-10929-MS, 118 pp.
- Kevorkian, J., 1983. First-order partial differential equations *in* Handbook of Applied Mathematics, C. E. Pearson, ed., Van Nostrand Reinhold Co., Inc., 378-447.
- McKenzie, W., 1987. personal communication.

Nitao, J., 1988. Numerical modeling of the thermal and hydrological environment around a nuclear waste package using the equivalent continuum approximation: horizontal emplacement. Lawrence Livermore National Laboratory, UCID 21444, 72 pp.

Norton, D. and J. Knight, 1977. Transport phenomena in hydrothermal systems: cooling plutons. *Amer. Jour. Sci.*, 277: 937-981.

Norton, D., 1978. Sourcelines, source regions, and pathlines for fluids in hydrothermal systems related to cooling plutons. *Econ. Geol.*, 73: 21-28.

Oversby, V. and C. N. Wilson, 1985. Derivation of a waste package source term for NNWSI from the results of laboratory experiments. Lawrence Livermore National Laboratory, UCRL 92096, 10 pp.

Oversby, V. M., 1987. Important radionuclides in high-level nuclear waste disposal: determination using a comparison of the U.S. EPA and NRC Regulations. *Nuc. and Chem. Waste Mgt.*, 7: 149-161.

Pruess, K., Y. W. Tsang and J. S. Y. Wang, 1985. Modelling of strongly heat-driven flow in partially saturated fractured porous media. *Proc. Int'l. Assoc. Hydrogeol.*, 17th Int'l. Congress, Tucson, AZ, 17: 486-497.

Ross, B., 1987. Governing equations for gas-transport of ^{14}C at Yucca Mountain. Sandia National Laboratory, 29 pp.

Smith, D. M., C. D. Updegraff, E. J. Bonano and J. D. Randall, 1986. Assessment of radionuclide vapor-phase transport in unsaturated tuff. NUREG/CR-4693, SAND86-1598, 42 pp.

Stumm W. and J. J. Morgan, 1981. *Aquatic Chemistry*, J. Wiley and Sons, Inc., 780 pp.

Tokunaga, T., 1986. Diffusive transport of gaseous radionuclides. *in Critical Parameters for a High-Level Waste Repository*, v. 2: Tuff, E. P. Binnall, S. M. Benson, L. Tsao, H. A. Wollenberg, T. K. Tokunaga and E. M. Didwall editors, NUREG/CR-4161, Vol. 2, UCID-20092, Vol. 2, p.A1-A8.

Van Konynenburg, R. A., C. F. Smith, H. W. Culham and C. H. Otto, 1985. Behavior of ^{14}C in waste packages for fuel in a repository in tuff. *Mat. Res. Soc. Symp. Proc.*, 44: 405-412.

Van Konynenburg, R. A., C. F. Smith, H. W. Culham and H. D. Smith, 1986. ^{14}C in waste packages for spent fuel in a tuff repository. Lawrence Livermore National Laboratory, UCRL 94708, 12 pp.

Warren, R. G., Byers, F. M. and Caporuscio, F. A., 1984. Petrography and mineral chemistry of units of the Topopah Spring, Calico Hills and Crater Flat Tuffs and older volcanics units with emphasis on samples from drill

hole USW G-1, Yucca Mountain, Nevada Test Site. Los Alamos National Laboratory, Los Alamos, NM, LA-10003-MS.

Weast, R. C., M. J. Astle and W. H. Beyer, 1986. CRC Handbook of Chemistry and Physics, CRC Press, FL.

Weeks, E. P. and W. E. Wilson, 1984. Preliminary evaluation of hydrologic properties of cores of unsaturated tuff, test well USW H-1, Yucca Mountain, Nevada. USGS Water Resources Invest. Report 84-4193, 30 pp.

Whitham, G. B., 1974. Linear and Nonlinear Waves. J. Wiley and Sons, Inc., 636 pp.

TABLE 1

Variable	Range	Selected	Reference
S^l	0.0 - 1.0	0.1 - 0.9	Nitao, 1988
T (°C)	10 - 200	25 - 200	Kerrisk, 1987; Nitao, 1988
v^g	0 - 6,000 m/yr	1 m/yr	Nitao, 1988
X_T^l	5 - 130 ppm	25 ppm	Kerrisk, 1987
$X_{14}^g(0)$?	50 ppm	this study
pH	6.5 - 9.2	7 - 9	Kerrisk, 1987
λ	1.22×10^{-4} /yr	1.22×10^{-4} /yr	Faure, 1977
ϕ	10-50%	10%	Weeks and Wilson, 1984
ρ^g (T)		look-up tables	Weast et al, 1986
ρ^l (T)		look-up tables	Weast et al, 1986

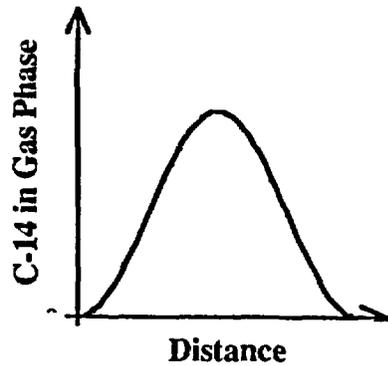


Fig. 1. Schematic of ^{14}C wave in circulating air shortly after a spent fuel assembly has been contacted by flowing air. The amplitude and wavelength of the wave is a function of the amount of ^{14}C in the assemblies that is accessible to air, the rate that ^{14}C is oxidized and gas velocity.

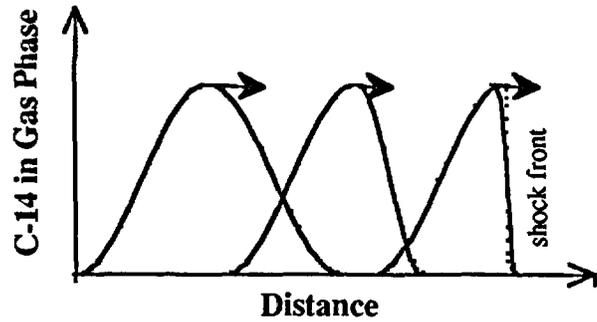


Fig. 2. Schematic snapshots of a breaking kinematic wave. A shock front is caused by a positive relationship between velocity and concentration; more concentrated portions of the wave move faster and eventually catch up with the less concentrated portions forming a discontinuity in concentration. Special jump conditions, equation (25), need to be satisfied when this occurs. In natural systems, dispersion and diffusion tend to reduce the importance of shock fronts in kinematic waves.

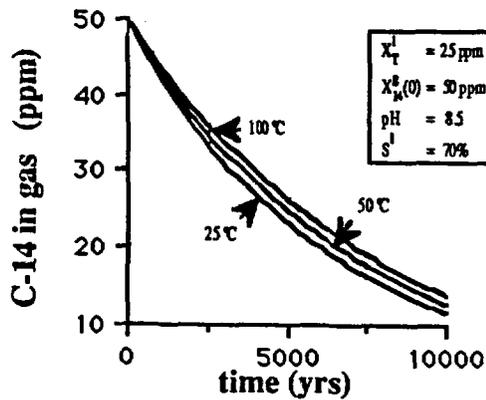


Figure 3. X_{14}^g at the peak amplitude as a function of time and temperature. Temperature and pH influence the concentration through thermodynamic equilibrium between the gas and liquid phases, (27). X_{14}^g is not sensitive to saturation changes.

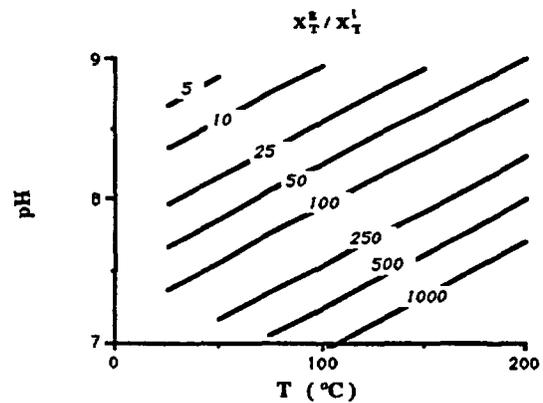


Figure 4. Equilibrium distribution of carbon between gas and liquid phases calculated from (27) and assuming unit activity coefficients, unit water activity and a total pressure of 10 MPa. The selected pH range is in a region where the bicarbonate ion is the predominate aqueous species.

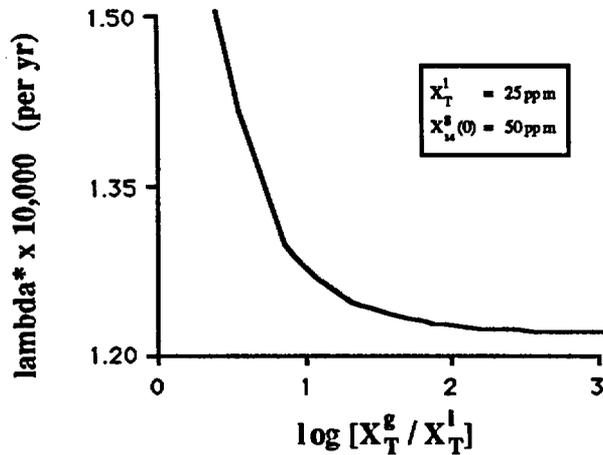


Figure 5. Modified decay constant as a function of the distribution of total carbon between the gas and liquid phases. λ is modified because the governing equation, (14), is written with respect to the gas phase whereas radioactive decay occurs in both the gas and liquid phase. The distribution of carbon is controlled by equilibrium between $\text{CO}_2(\text{g})$ and $\text{HCO}_3^-(\text{aq})$; it is a function of temperature and pH, (27).

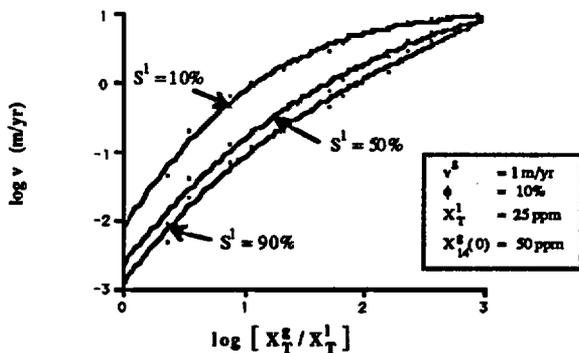


Figure 7. Velocity of peak amplitude on kinematic wave as a function of the distribution of total carbon between the gas and liquid phase. Retardation from true gas velocity, v^g/ϕ , is greatest where temperature and pH favor high relative concentrations in the liquid phase; saturation has less influence on velocity. Points represent computed data through which lines have been graphically fit.

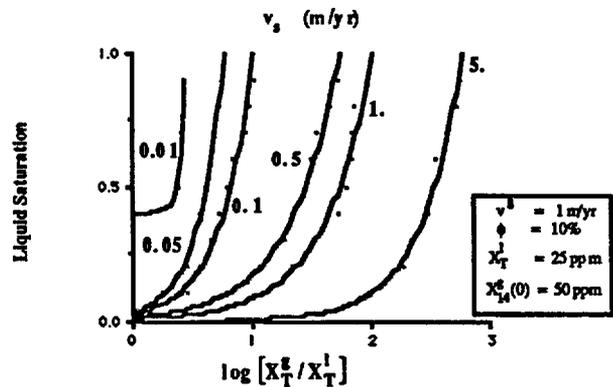


Figure 6. Velocity of peak amplitude on the ^{14}C wave. The velocity is most sensitive to the relative distribution of carbon between the liquid and gaseous phase (figure 4) and only sensitive to saturation at low temperatures and high pH. A ^{14}C wave traverses the near field region rapidly (high temperature, low liquid saturation) but traverses the far field region much more slowly (lower temperature, higher liquid saturation). This has a potentially great impact on the amount of ^{14}C reaching the accessible environment. Points represent computed data through which lines have been graphically fit.

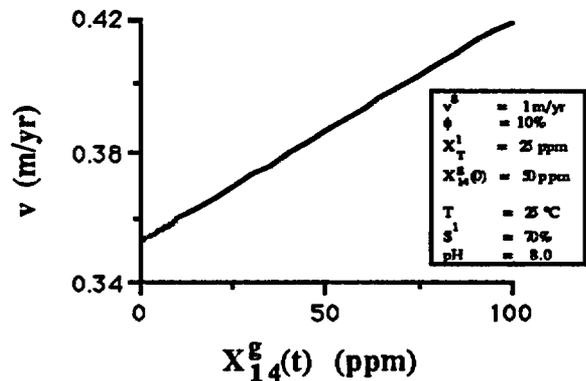


Figure 8. Kinematic wave velocity as a function of the amount of ^{14}C in the gas phase. The rate of increase is about 0.67 mm/yr/ppm . This dependency, though small, causes the wave to break forward and form a shock front, which at the chosen conditions travels at a velocity of about 40 cm/yr .

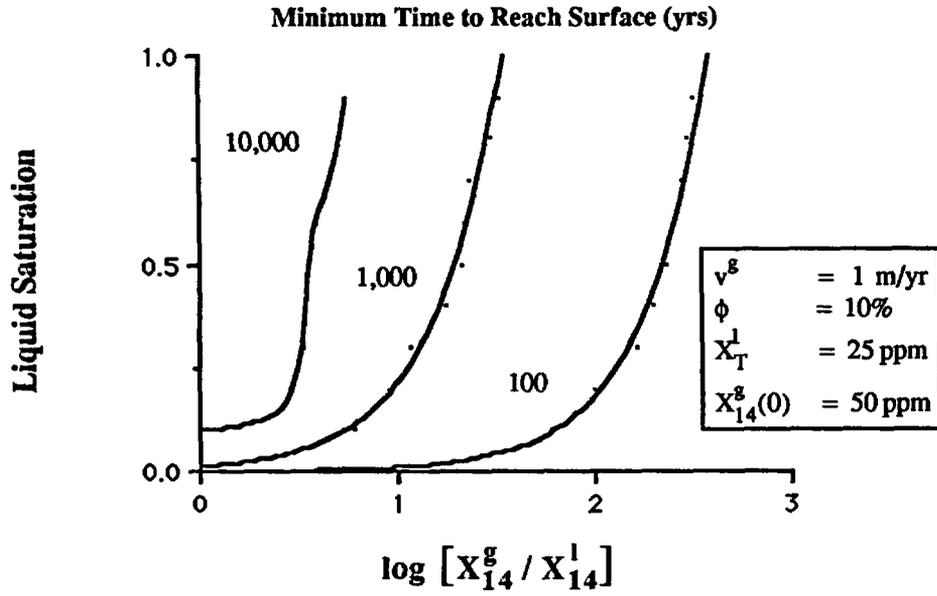


Figure 9. Times required for a ^{14}C wave to move in a straight line from radioactive waste containers, buried at a depth of 350 m, to the surface. The wave is expected to encounter a range of saturations and temperatures, which would influence the mass distribution of carbon (figure 4). The contours are plotted assuming constant saturation and mass distributions for the entire pathline; these assumptions amount to holding wave velocity constant. Points represent computed data through which lines have been graphically fit.

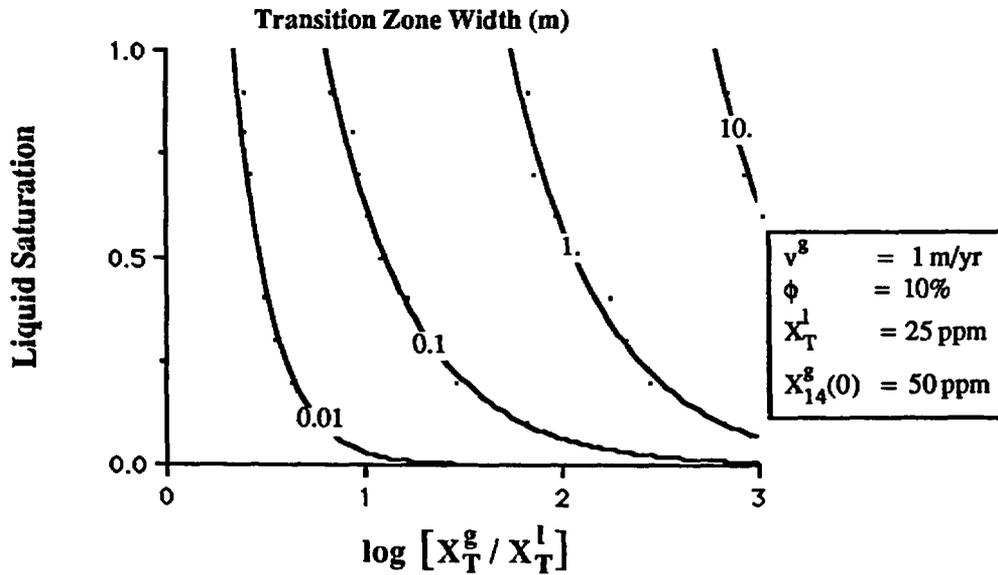


Figure 10. Width of transition from peak to background concentrations in a breaking kinematic wave. The transition zone is comparable to the scale of the current problem, 350 m., only at higher temperatures and lower pH values (figure 4); this is the regime where diffusion must be considered in the transport problem and where the current analysis is deficient. Points represent computed data through which lines have been graphically fit.

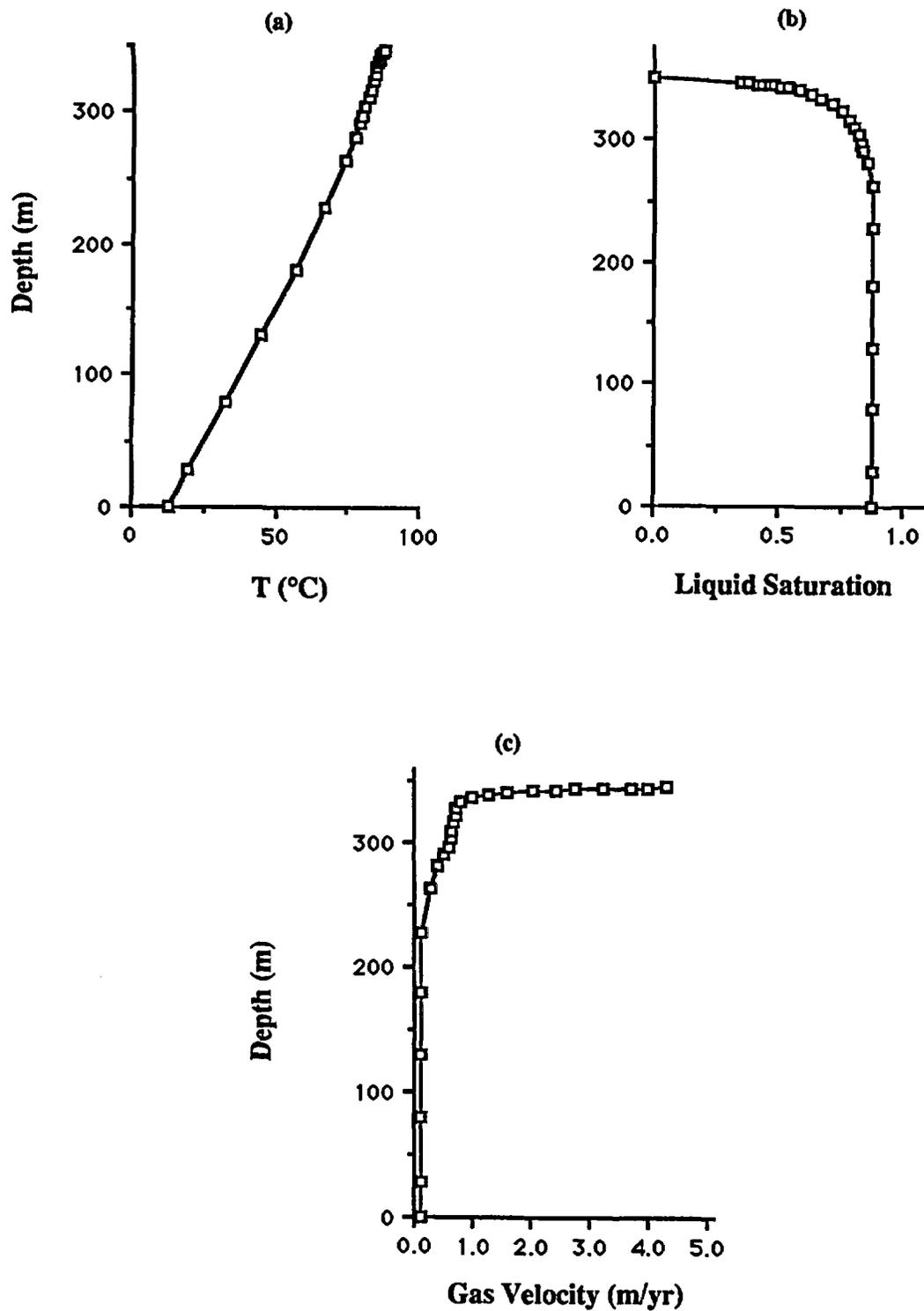


Figure 11. Temperature (a), liquid saturation (b) and gas velocity (c) calculated from a two-dimensional, finite difference heat and mass transfer model of the proposed Yucca Mountain repository (Nitao,1988). Conditions are when sub-boiling temperatures are returned to, about 2,000 years after emplacement. Open squares denote finite difference grid-points.

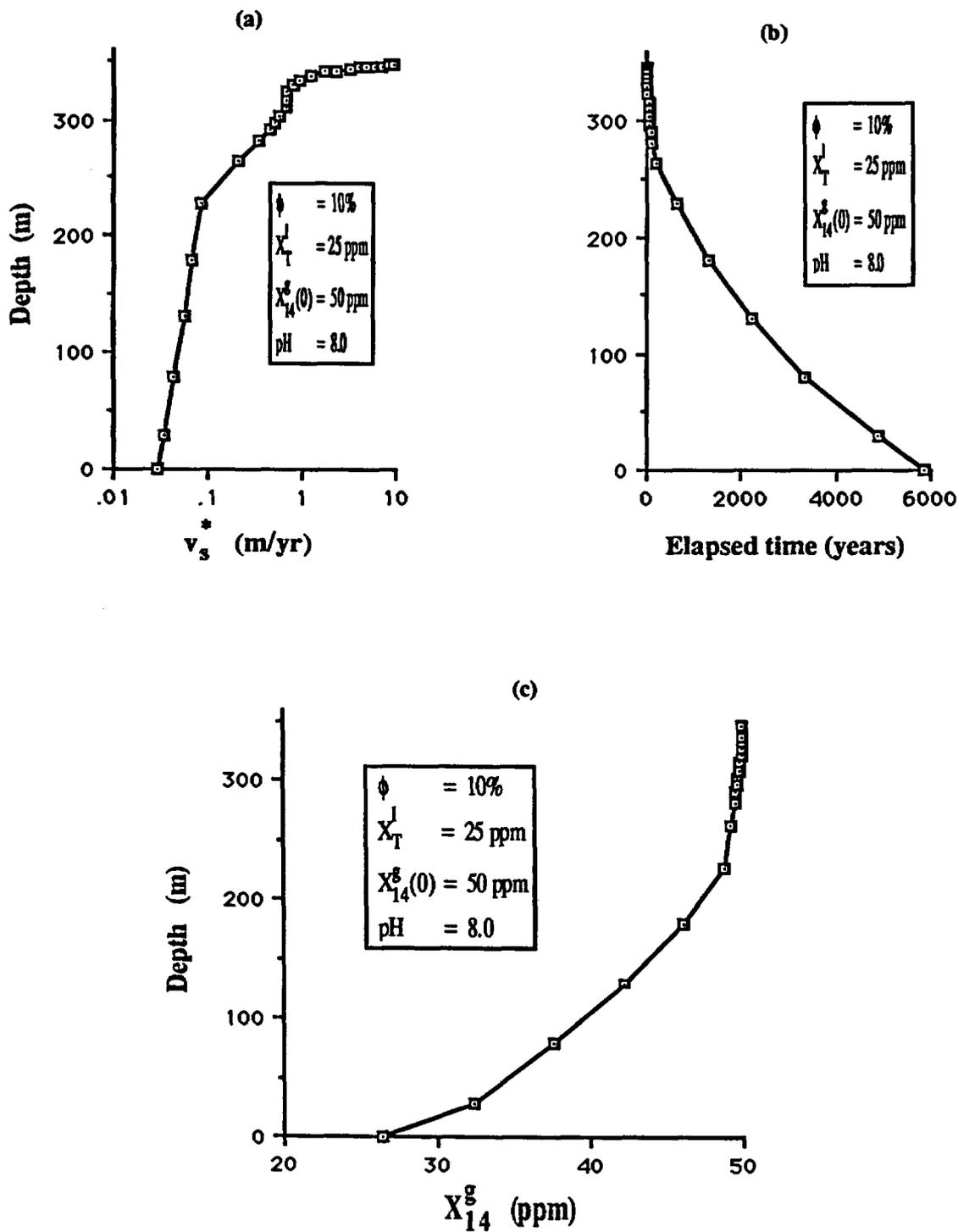


Figure 12. ^{14}C wave velocity (a), transit time (b) and ^{14}C concentration in gas phase (c) are calculated using conditions shown in figure 11, applying equations (22) and (26) in an incremental fashion, and assuming $X_T^l = 25 \text{ ppm}$, $X_{14}^g(0) = 50 \text{ ppm}$, $\text{pH} = 8.0$ and $\phi = 10\%$. X_{14}^g is about half the initial value when the wave reaches the surface because slow gas velocities through high liquid saturated regions greatly retard wave velocity; this permits radioactive decay to reduce total ^{14}C content. These calculations are highly approximate due to the number of assumptions involved.

Technical Information Department · Lawrence Livermore National Laboratory
University of California · Livermore, California 94550

