

GEOCHEMICAL MODEL FOR ^{14}C TRANSPORT IN UNSATURATED ROCK

Richard B. Codell
U.S. Nuclear Regulatory
Commission
Washington D.C. 20555
(301)-504-2408

William M. Murphy
Center for Nuclear Waste
Regulatory Analyses
San Antonio TX 78228
(512)-522-5263

ABSTRACT

^{14}C in a geologic nuclear waste repository could be released to the gaseous phase and escape to the accessible environment through partially saturated fractured rock. Interaction with the carbon system in the ground can lead to retardation of ^{14}C . A mechanistic interpretation of ^{14}C retardation and release is provided by a model that couples nonisothermal gas flow and water saturation, carbon distribution based on local equilibria among gas, liquid and solid phases, and C and ^{14}C transport. Repository heating is predicted to volatilize carbon from the liquid phase and to promote calcite precipitation. ^{14}C transport is retarded principally by incorporation in the aqueous phase. A portion of early released ^{14}C can be fixed in precipitated calcite for thousands of years.

INTRODUCTION

Under oxidizing conditions in a high-level nuclear waste repository, ^{14}C in nuclear waste might be released as $^{14}\text{CO}_2$. Any such gas escaping the engineered barrier will be incorporated in the existing carbon system of the geosphere, and be transported along with gaseous and dissolved carbon.

Several recent studies addressed ^{14}C gaseous transport at the Yucca Mountain repository environment using simplified models of geochemical retardation^{1,2,3}. Accurate modeling of ^{14}C transport requires coupling of relations between the source, heat flow, two phase fluid flow and the distribution of chemical species among solid, liquid, and gas phases. Interphase exchange of carbon could result in a significant retardation of released ^{14}C , thereby delaying its arrival at the accessible environment. This paper reports on a mechanistic model for the geochemical interaction of ^{14}C for a HLW repository in partially saturated rock.

The ^{14}C transport model consists of three parts:

- A geochemical model describing the state of all carbon species in the gas, liquid and solid phases for a representative volume of partially saturated rock;
- A flow and transport model for movement of total carbon through the system which consists of a number of connected volumes or "cells"; and
- A model of ^{14}C migration as a trace quantity in the general movement of total carbon.

GEOCHEMICAL MODEL

A carbon system geochemical model which incorporates all reactions of primary significance to ^{14}C transport in partially saturated fractured rock can be based on local chemical equilibrium and mass and charge conservation in a representative volume. Chemical reactions in the model comprise carbonate equilibria among aqueous species, dissociation of water, vapor-liquid equilibria for CO_2 and H_2O , and calcite dissolution and precipitation. In addition to the aqueous species in these equilibria, the present model includes Na^+ to represent other aqueous cations. The reactions represented in the present model are given below:



Local charge balance in the model aqueous phase is represented by equating sums of aqueous cation and anion equivalents. Local mass conservations for carbon and calcium are maintained within each cell, and the mass of sodium is conserved in the aqueous phase.

Given the total masses of C, Ca and other species, mass of water, and the temperature, pore volume and pressure of each cell, the above relationships lead to a set of nonlinear algebraic equations which are solved simultaneously to characterize local equilibrium in each cell for each time step. Equilibrium constants for reactions 1 to 5 are functions of temperature only at one bar pressure. Activity coefficients are functions of ionic strength, and are generated from an extended Debye-Hückel equation. Calcite is permitted to precipitate or dissolve, and the model solution becomes undersaturated with respect to calcite in its absence. The partial pressure of CO_2 is calculated from the activity of aqueous CO_2 assuming ideal gas relations.

TOTAL CARBON TRANSPORT MODEL

The calculation of transport of total carbon through the modeled system is performed by sequential iteration in the following steps:

- Local chemical equilibrium is calculated in each cell at time t using the geochemical model;
- Inputs and outputs to each cell are determined from an independent flow model for the next time step $t + \Delta t$. In the present model, only advective transport by gaseous flow is allowed. Therefore, the input of CO_2 to a cell is determined only by the partial pressure of CO_2 in the previous cell or upstream boundary and the flow of the transporting gas from that cell. Gaseous flow and condensation/evaporation of water is accounted for independently as part of the flow model and input to the chemical model.
- Mass distributions are revised in the cells for time step $t + \Delta t$ using the geochemical model with updated temperature and liquid saturation states.

The carbon transport algorithm in the preceding steps simulates changes to the chemistry of each phase in the system as a function of time and space. The carbon transport model determines the quantities of CO_2 gas moving through the system of cells, as well as the exchange rates of carbon between the various phases.

^{14}C TRANSPORT MODEL

Any ^{14}C released from the waste will constitute only a small fraction of the total carbon in the surrounding rock. The ^{14}C transport model uses the state and evolution of total carbon speciation to simulate transport through the system of trace amounts of ^{14}C released instantaneously at a particular cell. Treating ^{14}C as a trace allows simple

formulation of the transport model and the use of linear superposition for more general, noninstantaneous source terms. ^{14}C is assumed to behave exactly in proportion to the total carbon, with no isotopic fractionation. However, radioactive decay removes ^{14}C from the solid, liquid and gas inventories. ^{14}C is removed from the liquid/gas phases if calcite precipitates from solution. It re-enters the system if previously ^{14}C -contaminated calcite dissolves. The model assumes that calcite dissolves first from the ^{14}C -contaminated calcite inventory before uncontaminated calcite redissolves. The model further assumes that the ^{14}C is distributed homogeneously within the contaminated calcite of each cell.

MODEL APPLICATIONS

The present geochemical transport model has been applied to simplified examples in order to demonstrate the range of possible phenomena associated with the release and transport of $^{14}\text{CO}_2$ in partially saturated fractured rock. The model domain is a one-dimensional column of 145 cells represented in Fig. 1, with constant hydraulic properties and cross section, passing through the center of a hypothetical repository plane, which is located at cell 50. Water, gas, and relevant mineral chemistries, as well as the geothermal gradient that resemble those observed at Yucca Mountain are provided as initial conditions. The system chosen for the example was simple in order not to confound the results of the geochemical transport model with other phenomena. For example, gas is assumed to flow in the upward direction only, even though thermal-hydraulic simulations indicate an initially outward gas flow in all directions from a heated repository in partially saturated tuff. Additionally, transport of ^{14}C is by advection in the gas phase only; there is no transport of ^{14}C by water flow or diffusion in gas or water.

Time-dependent temperature and gas flux used in the present example were generated from two-dimensional codes developed at NRC for predicting air flow through Yucca Mountain, and similar to those models developed by Amptner and Ross¹. Temperature, represented in Fig. 2, was calculated from a two-dimensional thermal conduction model which included the geothermal gradient. The thermal model assumed constant thermal conductivity and a uniform initial heat loading of 57 kilowatts per acre. Gas flux, shown in Fig. 3, varied with time, but was assumed to be uniform throughout the one-dimensional column.

Liquid saturation is shown in Fig. 4. The temperature and gas flow models did not include water saturation explicitly. Therefore, an approximate empirical model for saturation of the column was derived from the results of simulations of two-phase thermally induced circulation near repositories in tuff. The empirical model used in the example predicts that water saturation is 80% except within a zone of about 50 meters above and below the repository for a period of less than 2000 years. Other initial conditions and parameters of the example system are given in the table below. The input concentration of CO_2 was chosen so that gaseous CO_2 would be in equilibrium initial-

ly with the liquid and solid carbon concentrations. These conditions lead to an initial solution with pH = 7.2, moderately undersaturated with respect to calcite with the Q/K (saturation index/equilibrium constant) about 0.2 and partial pressures of CO₂ in the range 0.005 to 0.008 bar, depending on temperature.

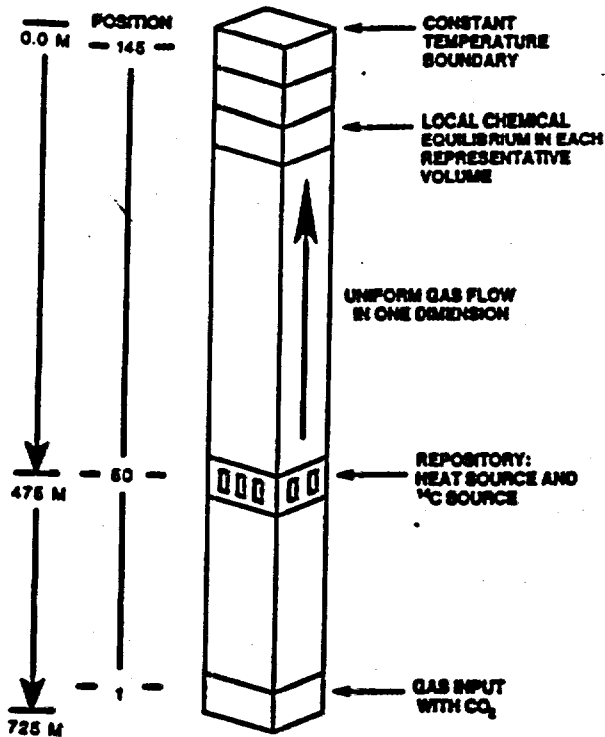


Figure 1 - One-dimensional Flow and Transport Model

Parameter	Value
Cell cross section	2 cm ²
Cell spacing	5 m
Volume of cell	6.25 m ³
Porosity	.2
Initial saturation	.8
Initial C/cell	.00202 mole/l
Na/cell	.001 mole/l
Ca/cell	.0004 mole/l
CO ₂ input gas	2.53E-4 mole/l

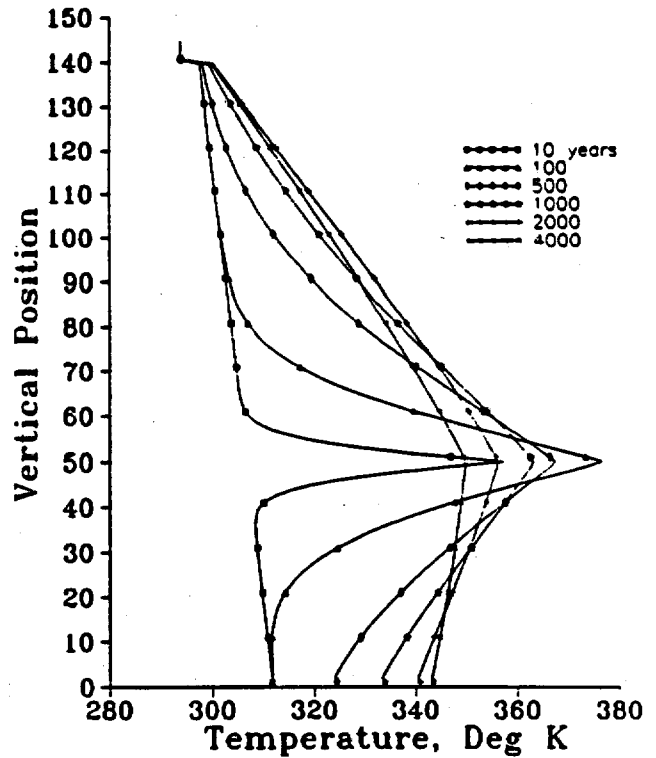


Figure 2 - Temperature Profiles for Example

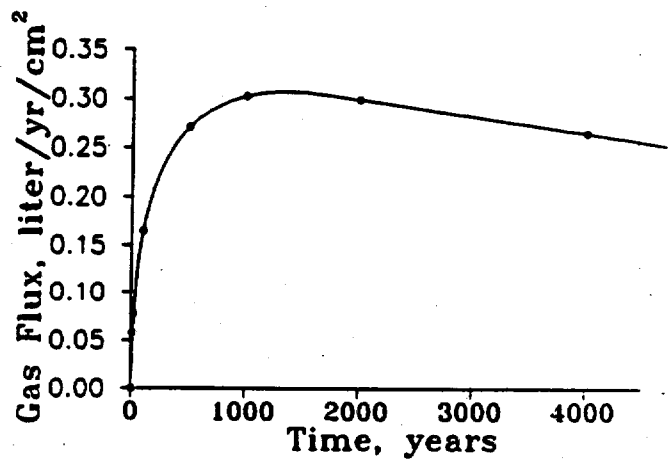


Figure 3 - Gas Flux for Example

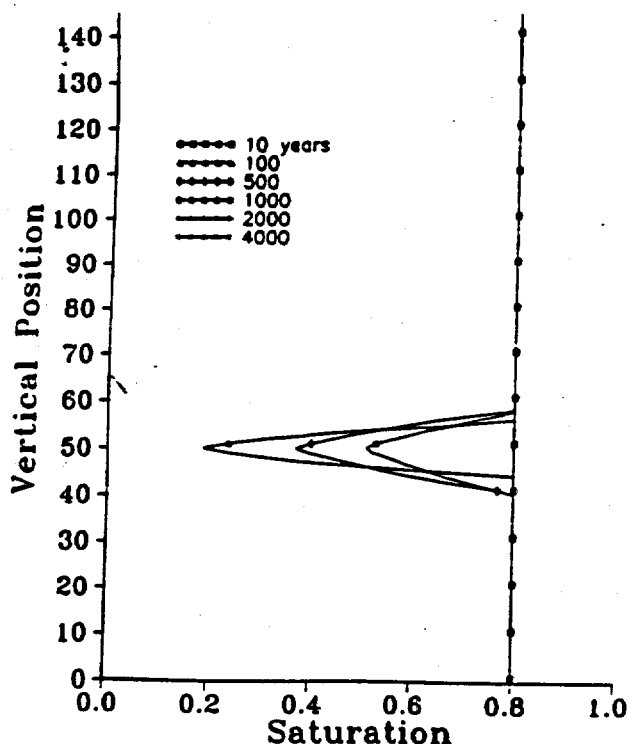


Figure 4 - Water Saturation for Example

Results for carbon model

Results for the carbon transport model are given in Fig. 5, which shows the distribution of carbon for each cell among the gas, liquid and solid phases for various times after repository closure. Initially, the carbon content decreases in the liquid phase and increases in the solid and gas phases near the repository level. Just above the repository, however, the carbon content of the gas and liquid phases increases, a reflection of gas transport of the pulse of CO_2 initially volatilized from the liquid near the repository and transported. Increasing temperature, decreasing solvent mass, and increasing pH due to CO_2 volatilization all promote calcite precipitation near the repository horizon.

At 500 years, the initially volatilized CO_2 pulse has been flushed out the top of the column. The calcite content continues to grow, spreading above and below the repository level as temperature increases. At 2000 and 4000 years the calcite progressively redissolves while the liquid content of carbon increases as the rock cools.

Results of ^{14}C model

Figure 6 shows the distribution of ^{14}C for each cell in the gas, liquid and solid phases at various times for 10^{-4} Ci of ^{14}C released 15 m below the assumed repository plane at time zero. The ^{14}C was released below the repos-

itory plane to account for gas circulation expected near the repository, and allows interaction of the contaminant below as well as above the engineered barrier.

At 100 years, most of the ^{14}C has redistributed to the liquid phase. The liquid and gas inventories of ^{14}C have moved above the repository plane because of gas transport, even though the fraction of ^{14}C in the gas phase is small. The ^{14}C in the calcite remains fixed until calcite redissolves. At 500 years, the gas and liquid inventories of ^{14}C have moved further above the repository plane. Some of the calcite near the repository plane redissolves, releasing its ^{14}C inventory, which in turn is partially captured by precipitating calcite further from the repository plane where temperature continues to increase.

By 2000 years, nearly all ^{14}C is swept from the column, except that which remains trapped in the calcite. By this time, calcite is redissolving everywhere, so the contaminated calcite acts as a long-term source of ^{14}C to the system. Some of this residual ^{14}C remains even at 4000 years.

Dependence on time of release

The model predicts that calcite starts to precipitate shortly after repository closure and then redissolves. Therefore, the timing of the release of ^{14}C from the waste is important to its ultimate fate. ^{14}C released after most calcite has precipitated will not be removed from the liquid and gas phases as effectively as ^{14}C released during the period of active calcite precipitation. Figure 7 shows the cumulative release (as a fraction of the amount released) at several locations in the column of ^{14}C over a 1500 years time period from repository closure, as a function of the time that the ^{14}C pulse was released. This figure demonstrates the interesting phenomenon that ^{14}C released at early times can arrive at the end of the column later than ^{14}C released subsequently.

CONCLUSIONS

Numerical experiments with a flow and transport model that includes coupled nonisothermal geochemistry, provide insights to the behavior of ^{14}C in a partially saturated geologic repository for nuclear waste. Applications have been made to a system resembling the proposed repository at Yucca Mountain, Nevada. Model results show a significant redistribution of autochthonous carbon among solid, liquid and gas phases, even in areas remote from the repository plane. Carbon remains predominantly in the aqueous solution, in spite of the fact that near-field heating results in a reduction of liquid saturation, abundant calcite precipitation, and increased equilibrium fractionation of CO_2 into the gas phase.

While not shown explicitly in this paper, transport of ^{14}C released from the repository would be generally retarded by a factor of approximately 30 to 40 because of immobilization in the liquid phase. In addition, ^{14}C released early during the period of solid calcite precipitation can be

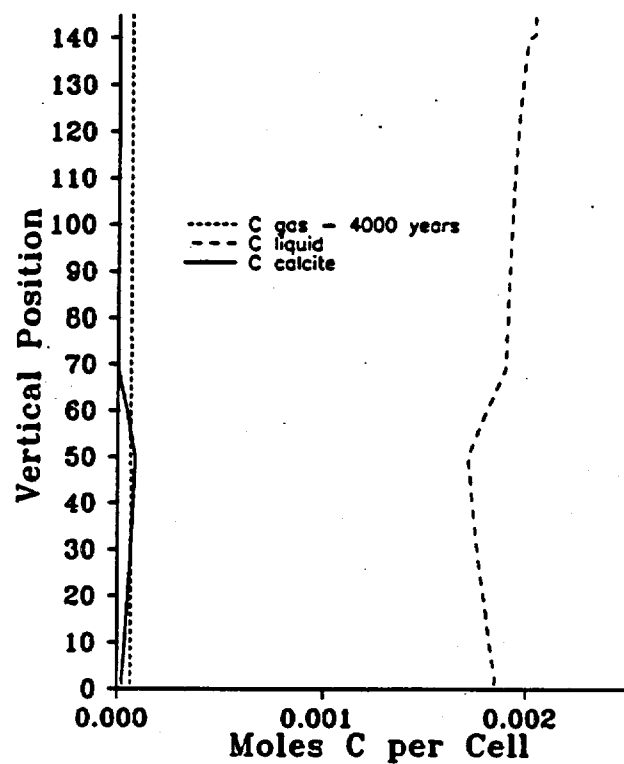
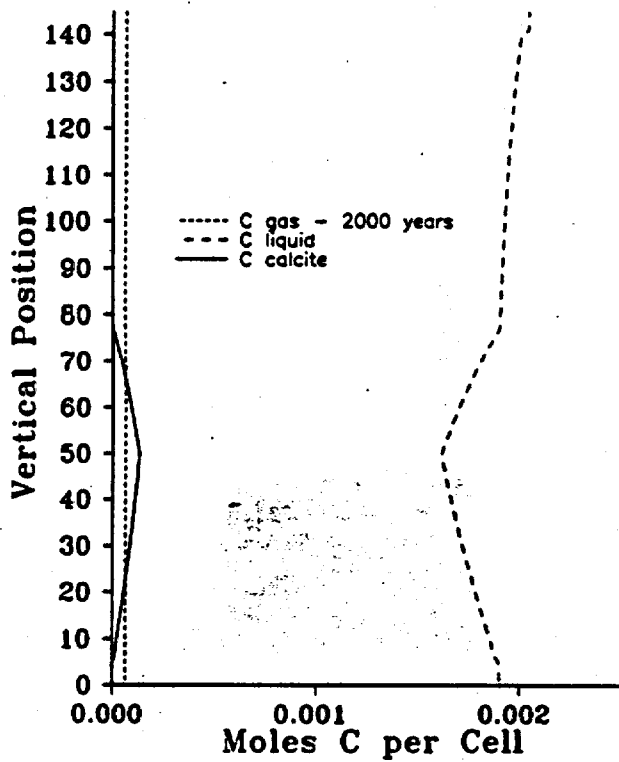
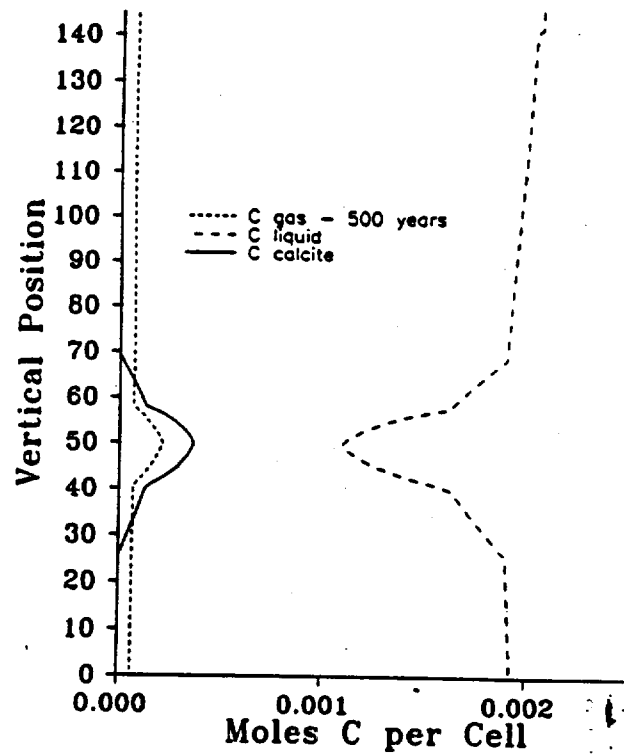
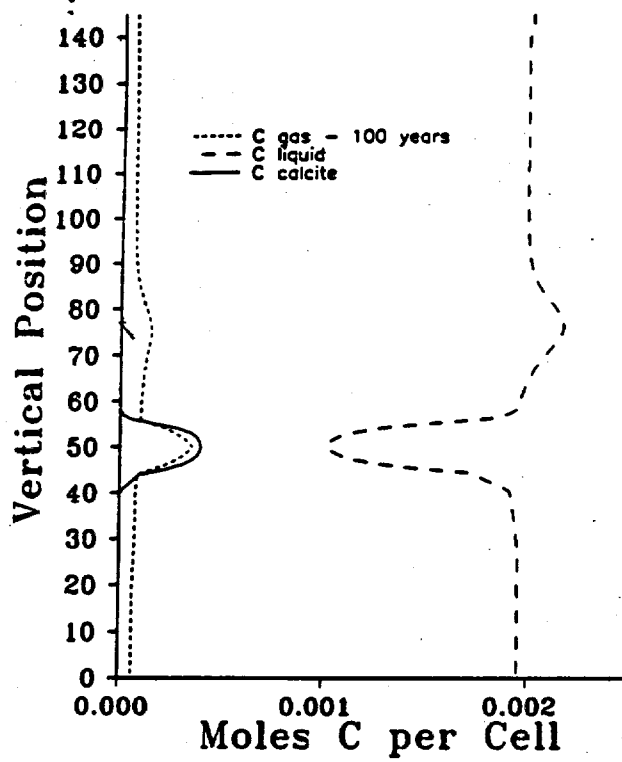


Figure 5 - Carbon content of gas, liquid and solid phases

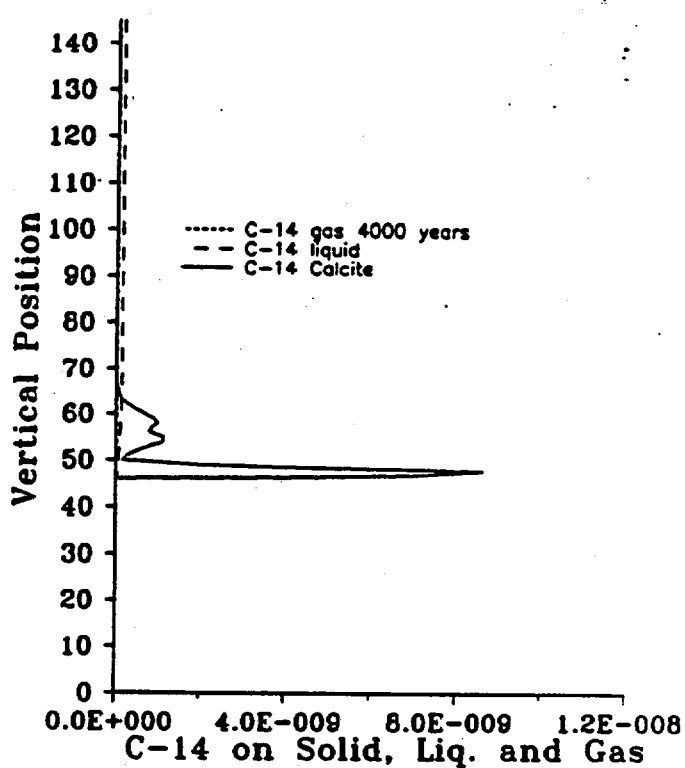
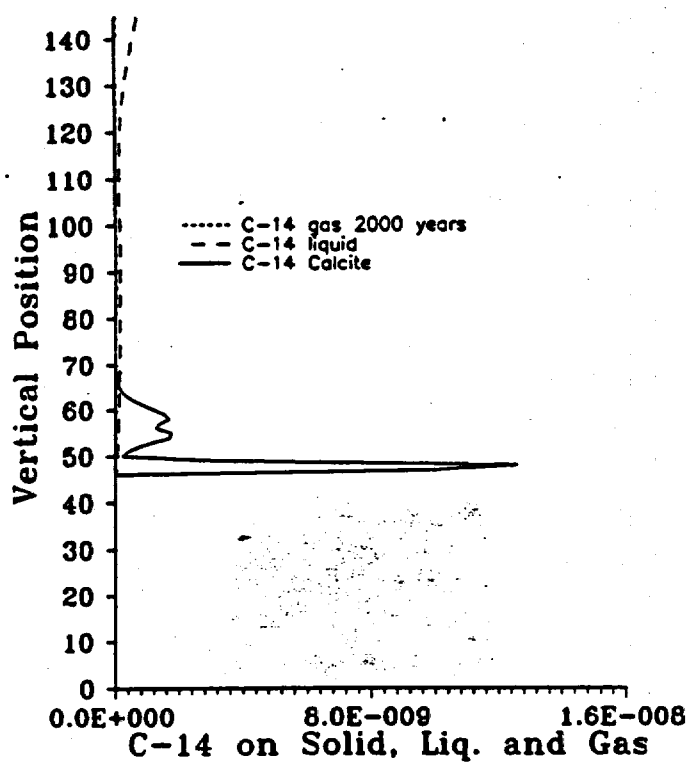
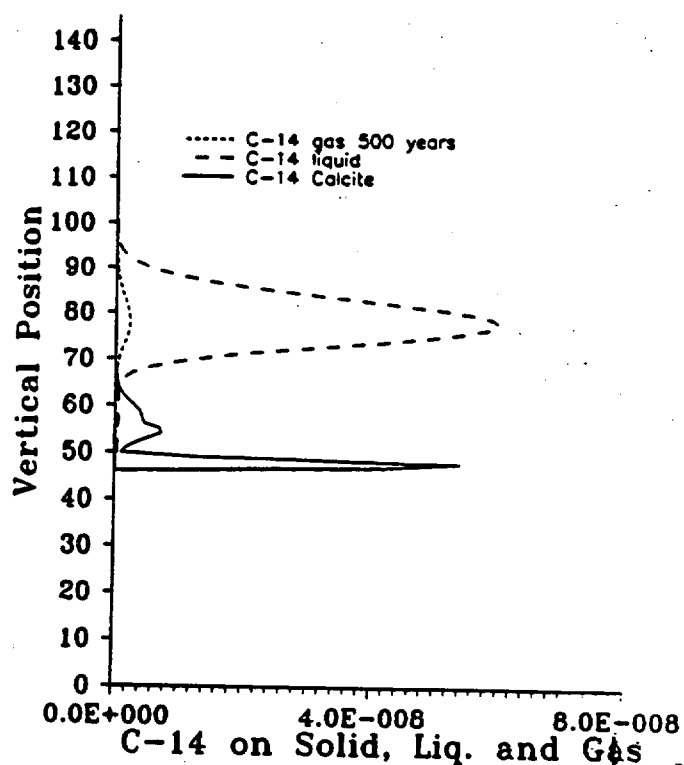
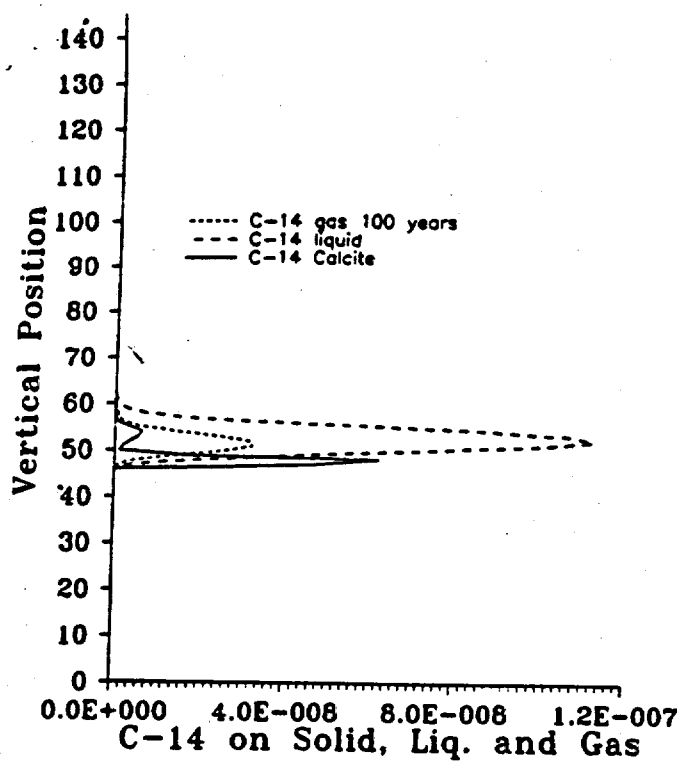


Figure 6 - ^{14}C content of gas, liquid and solid phases
(NOTE: scales change)

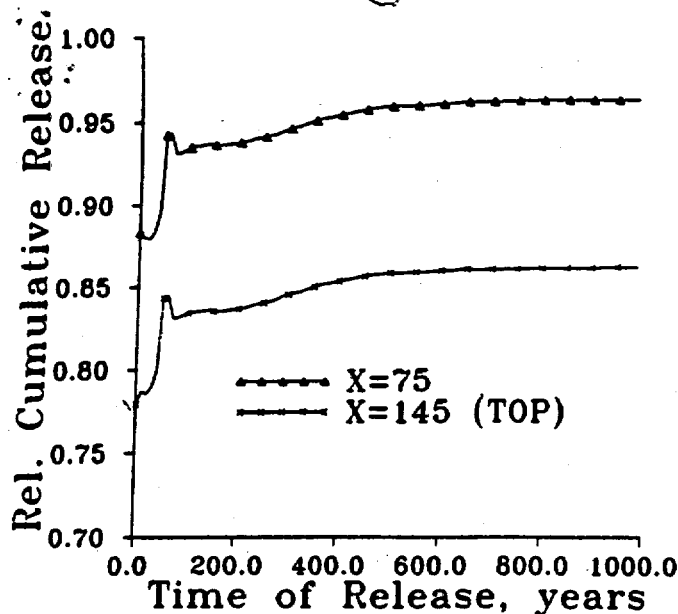


Figure 7 - Cumulative release by 1500 years as a function of when ^{14}C was released

fixed for a long period before repository cooling leads to redissolution of the calcite.

Although simplified, the model demonstrates the complex nature of the geochemical processes affecting ^{14}C transport. Results of the simulation depend strongly on model assumptions, and retardation would change under different conditions of chemistry, hydrology, temperature or gas flow. We contemplate coupling geochemistry and carbon transport models with more realistic two or three dimensional treatments of heat and mass transfer near a repository in partially saturated tuff, which would include transport in the gas and liquid phases and allow for molecular diffusion.

DISCLAIMER

The contents of this paper are solely the opinions of the authors, and do not necessarily constitute the official positions of either the U.S. Nuclear Regulatory Commission or the Center for Nuclear Waste Regulatory Analyses.

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