

AUG 10 1993

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Ray Wassel, Project Officer
Committee on Technical Bases
for Yucca Mountain Standards
National Academy of Sciences
Room 456
2001 Wisconsin Avenue, N.W.
Washington, D.C. 20007

Dear Mr. Wassel:

**SUBJECT: INFORMATION REQUESTED BY THE COMMITTEE ON TECHNICAL BASES FOR
YUCCA MOUNTAIN**

I have reviewed your letter of July 16 which outlines documents and information sought by the Committee as reflected in your notes from the May 27-29 meeting. As you have requested, we have compared your outline to our own analysis of notes taken from this meeting. We have found them to be largely in agreement with the contents of your letter. The items that have been requested are listed below (in bold typeface) along with the status of each item and clarifications of our understanding of the requests, where appropriate:

- (1) **NUREG/CR-3964:** We have recently transmitted the 8 copies that you requested. Volume I and Volume II of this NUREG/CR were both sent.
- (2) **Phase 2 Performance Assessment and document on the potential for large releases:** The Phase 2 work is scheduled for publication in April 1994. However, the NRC staff has made presentations about the development of this methodology which could be provided to the Committee. NUREG-1327, "Initial Demonstration of the NRC's Capability to Conduct a Performance Assessment for a High-Level Waste Repository," was published in May 1992 and describes the NRC staff's performance assessment capabilities at that time. We would be happy to provide copies of this report to the Committee, upon request.

NRC staff has identified one additional request related to performance assessment as follows:

Current results of the performance assessment modeling, as it pertains to C-14 releases: Presentation materials and a recent paper by Dr. Richard Codell on this subject are enclosed with this letter. We hope that this information will be sufficient.

- (3) **Effectiveness of Markers:** A list of references and a summary of the 10 CFR Part 60 regulatory history that relate to the persistence and effectiveness of institutional controls are currently being prepared. These can be provided to the Committee by early November.

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- (4) **10,000 year time period over which compliance must be demonstrated:** A summary of the Commission's previous comments to the Environmental Protection Agency about the time frame for compliance can be provided by the end of September.
- (5) **De minimis levels of Iodine:** Review of NRC staff notes do not indicate any committee requests for information from NRC in this area. We would appreciate clarification of the Committee's request related to this issue.
- (6) **ICRP-46 report:** Further information on this report has already been provided.
- (7) **Regulatory responsibility for waste transportation:** We understand that the summary of regulatory responsibility for transport of high-level waste may no longer be needed. We will take no additional action on this matter unless there is a request to do so.

We have outlined our understanding of the requests made to us by the Committee and have indicated their current status, including where appropriate, the schedule for providing the information. We will continue to do our best to meet the evolving needs of the Committee. If there are changes to the Committee's needs or if our interpretation of the requests differs from what is sought, please let me know.

Sincerely,



Margaret V. Federline, Chief
 Hydrology and Systems Performance Branch
 Division of High-Level Waste Management, NMSS

Enclosures:
 As stated

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- (6) **ICRP-46 report:** Further information on this report has already been provided. NRC staff have identified one additional request related to performance assessment as follows:

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MS

Margaret V. Federline, Chief
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Division of High-Level Waste Management, NMSS

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GEOCHEMICAL MODEL FOR ¹⁴C TRANSPORT IN UNSATURATED ROCK

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ABSTRACT

¹⁴C 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 ¹⁴C. A mechanistic interpretation of ¹⁴C 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 ¹⁴C transport. Repository heating is predicted to volatilize carbon from the liquid phase and to promote calcite precipitation. ¹⁴C transport is retarded principally by incorporation in the aqueous phase. A portion of early released ¹⁴C can be fixed in precipitated calcite for thousands of years.

INTRODUCTION

Under oxidizing conditions in a high-level nuclear waste repository, ¹⁴C in nuclear waste might be released as ¹⁴CO₂. 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.

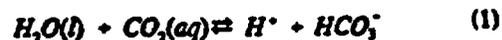
Several recent studies addressed ¹⁴C gaseous transport at the Yucca Mountain repository environment using simplified models of geochemical retardation^{1,2,3}. Accurate modeling of ¹⁴C transport requires coupling of relations between the source, heat flow, two phase fluid flow and the distribution of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

The ¹⁴C 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 ¹⁴C 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 ¹⁴C 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 CO₂ and H₂O, 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 Ampter 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-

ty 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.

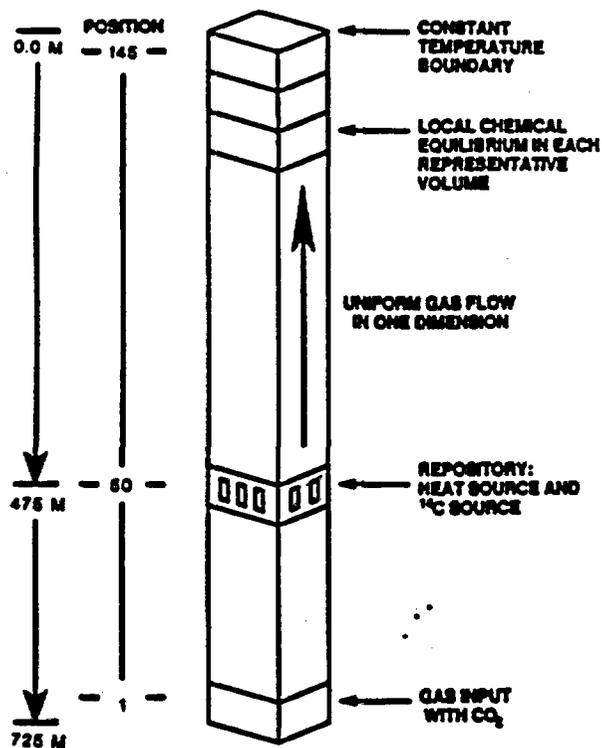


Figure 1 - One-dimensional Flow and Transport Model

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

A 12.5 cm²
 V 6250 cm³

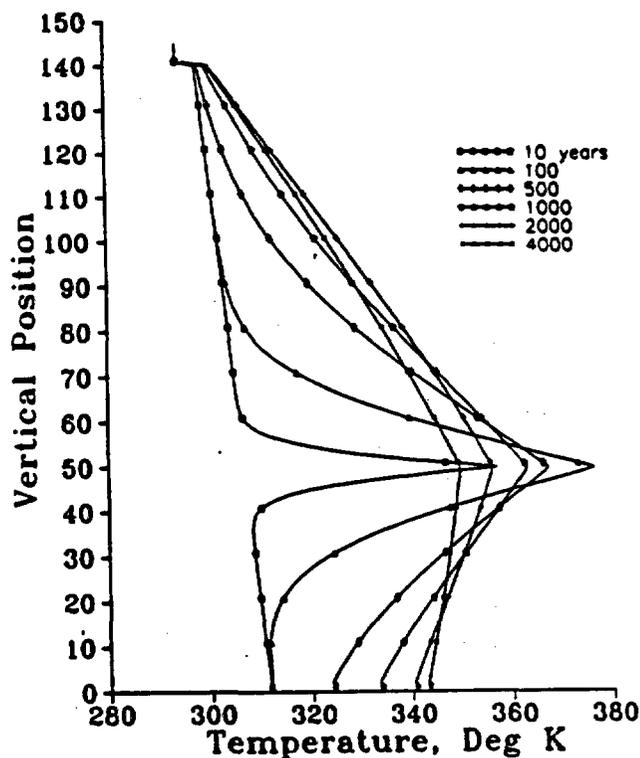


Figure 2 - Temperature Profiles for Example

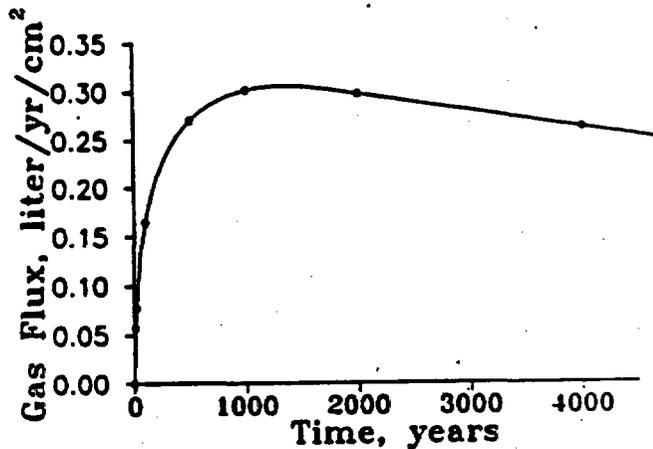


Figure 3 - Gas Flux for Example

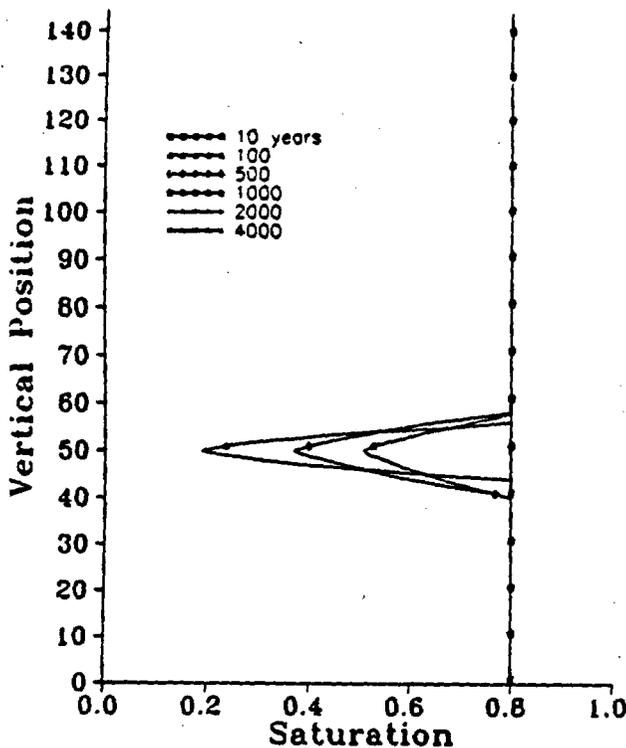


Figure 4 - Water Saturation for Example

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

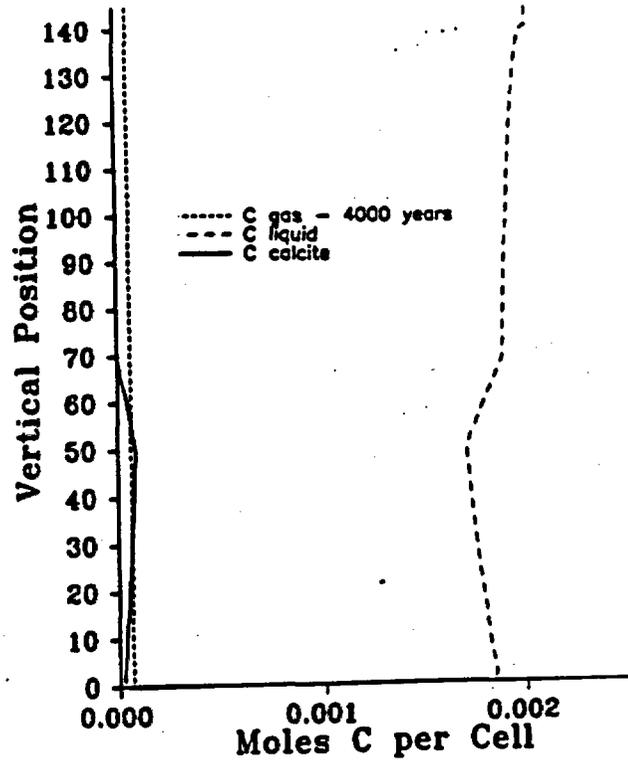
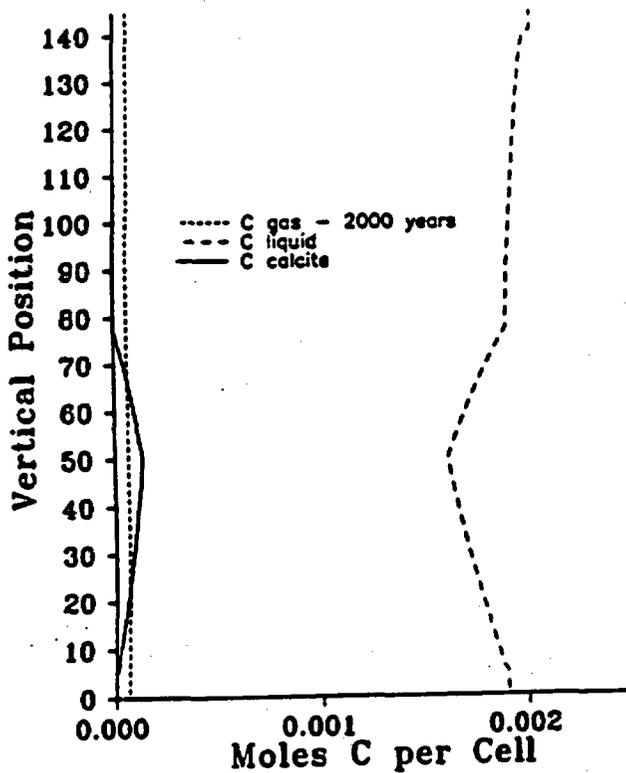
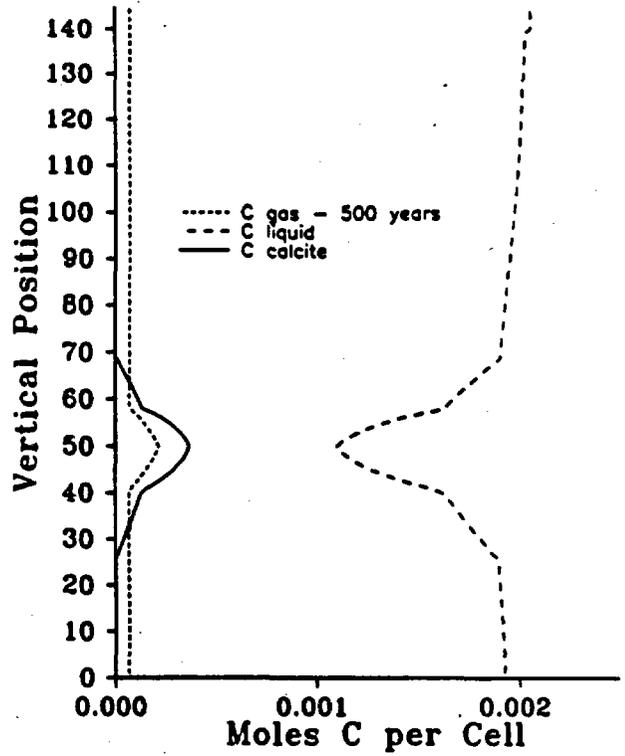
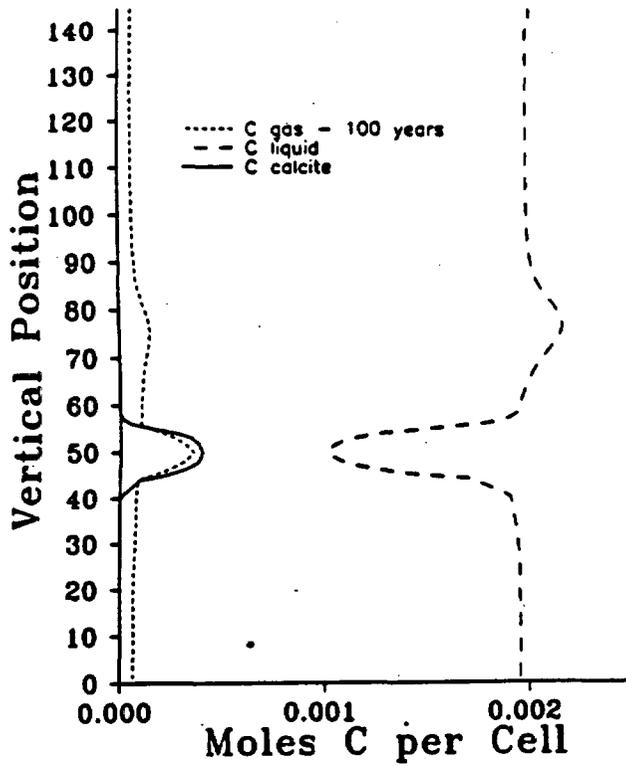


Figure 5 - Carbon content of gas, liquid and solid phases

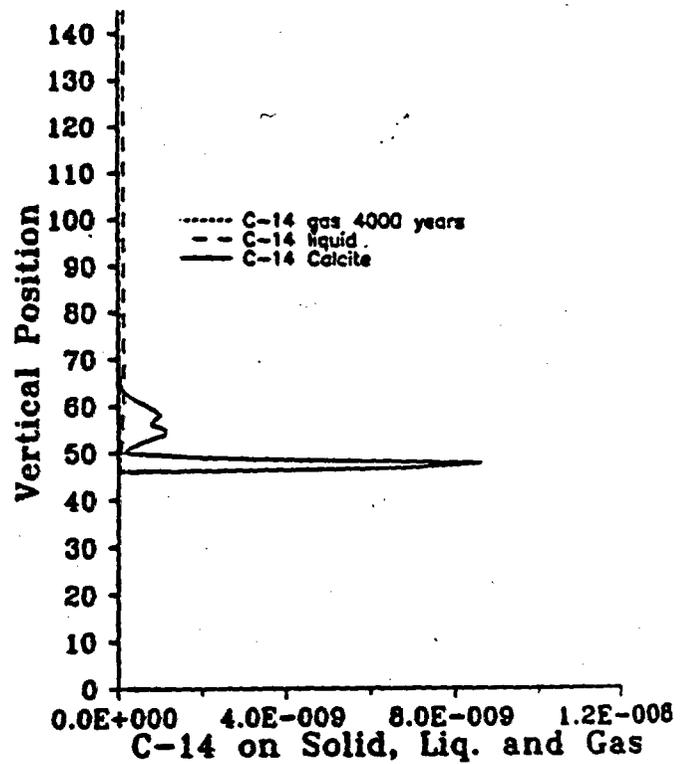
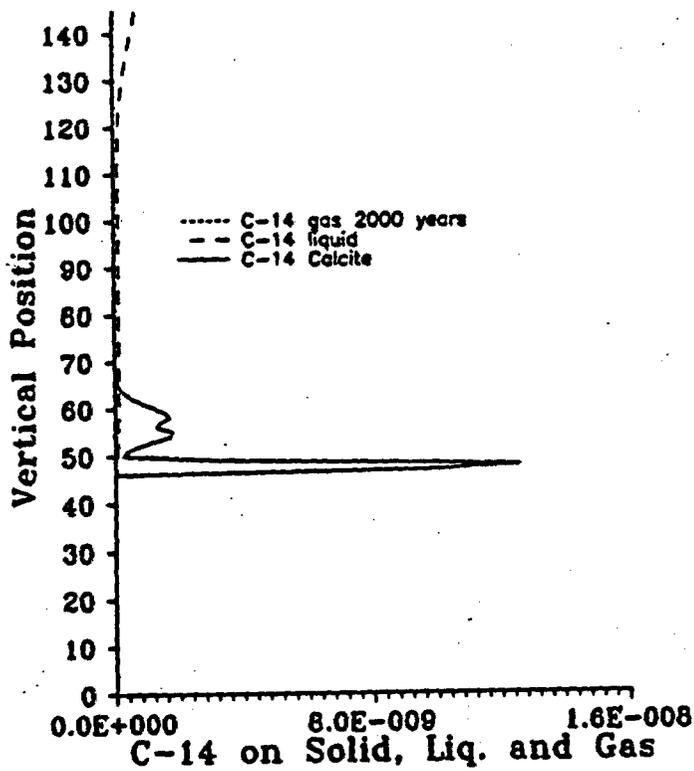
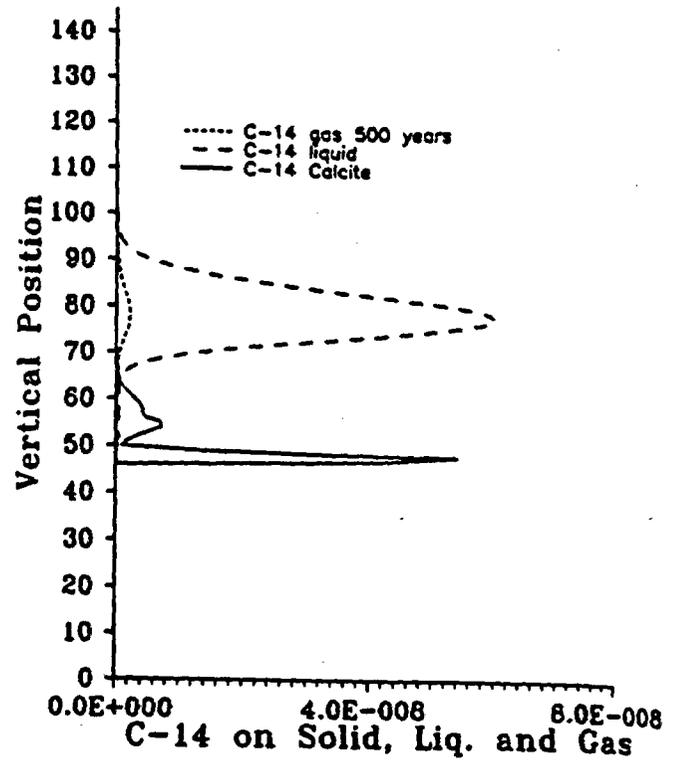
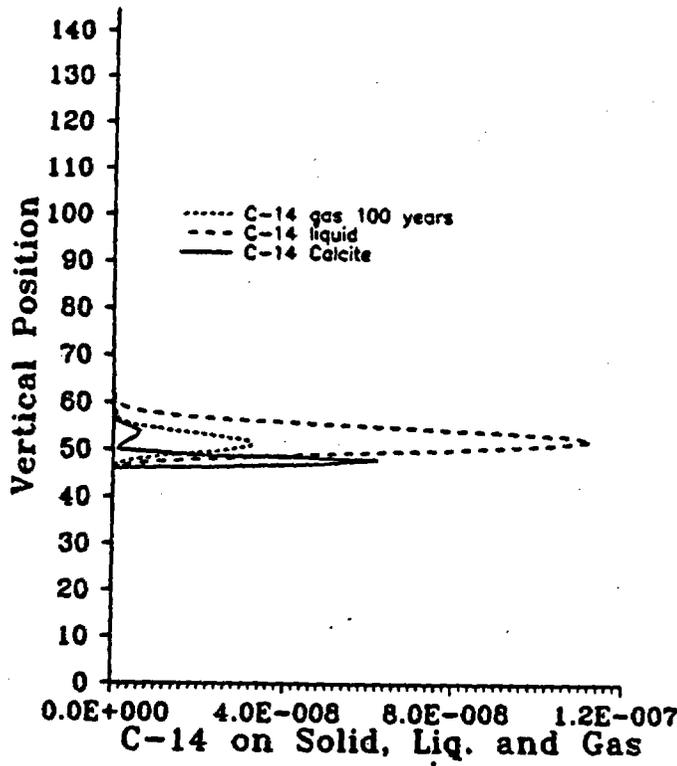


Figure 6 - ¹⁴C content of gas, liquid and solid phases
(NOTE: scales change)

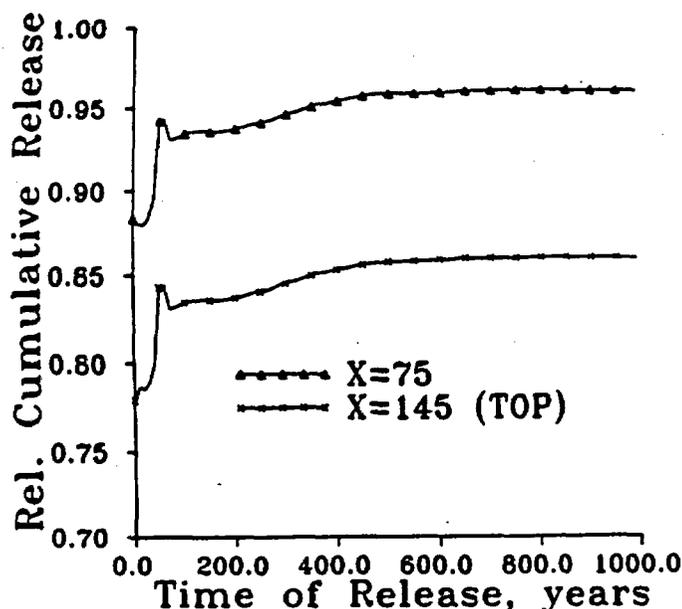


Figure 7 - Cumulative release by 1500 years as a function of when ¹⁴C was released

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 ¹⁴C 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.

References

1. S. Ampter, B. Ross, "Simulation of gas flow beneath Yucca Mountain, Nevada with a model based on freshwater head", Proceedings of the Symposium on Waste Management, Tucson, AZ, 2, 915 (1990)
2. W.B. Light, T.H. Pigford, P.L. Chambre, and W.W.L. Lee "Analytical models for C-14 transport in a partially saturated, fractured, porous media". FOCUS 89, Proceedings, Nuclear Waste Isolation in the Unsaturated Zone, American Nuclear Society, LaGrange Park, Illinois (1990)
3. R.B. Knapp, "An approximate calculation of advective gas-phase transport of ¹⁴C at Yucca Mountain, Nevada", J.Contaminant Hydrology, 5, 133 (1990)
4. J.J. Nitao, "Numerical modeling of the thermal and hydrological environment around a nuclear waste package using the equivalent continuum approximation: Horizontal Emplacement", UCID-21444, Lawrence Livermore National Laboratory (1990)

MODEL FOR RELEASE OF GASEOUS ^{14}C FROM SPENT FUEL

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(301)-504-2408

ABSTRACT

^{14}C is contained in cladding, intergrain boundaries and UO_2 in spent nuclear fuel, and can be released as gaseous $^{14}\text{CO}_2$ in an oxidizing environment. Approximately 2.5% of the inventory can be released quickly from gap, grain boundary and cladding surface. ^{14}C within cladding can be released upon oxidation of the metal, but is probably a minor source. Most ^{14}C is contained in UO_2 fuel, and can be released when the fuel oxidizes. Releases from fuel depend on diffusion of oxygen through the grain boundaries and a layer of U_3O_8 , and diffusion of $^{14}\text{CO}_2$ out through same two layers. A model of UO_2 oxidation was based on experimental data, and used in a model for ^{14}C release. This model is demonstrated on a hypothetical repository in an unsaturated environment, and shows a strong dependence on the time at which containers fail.

INTRODUCTION

The release of ^{14}C from disposed nuclear waste at the partially saturated Yucca Mountain site is a potentially important regulatory issue because in the gaseous form it could migrate quickly to the atmosphere. Currently, Park¹ estimates that there will be about 78,000 curies of ^{14}C in the projected 70,000 MTHM of spent fuel in the repository, an order of magnitude greater than would be allowed to be released from the repository under present regulations².

Estimating the rate and quantity of release of ^{14}C to the accessible environment requires models for the release from the waste form, flow of gas and liquid through the geosphere, and interaction of the ^{14}C among water, air and rock³. The present paper reports on a model for gaseous release of ^{14}C from spent fuel, currently being used in NRC's total system performance assessment

for the Yucca Mountain repository.

Background

The main reservoirs for ^{14}C in spent fuel are the cladding, cladding/fuel gap, grain boundaries, and the fuel itself. Most of this ^{14}C must first oxidize to be released as gas. Although elemental carbon is generally stable at low temperatures, thermodynamics in air favors the formation of gaseous compounds such as CO_2 and methane. Ionizing radiation may also play a role in oxidation of carbon. Van Konynenburg⁴ noted that $^{14}\text{CO}_2$ was released from cladding in an oxidizing environment with a radiation level of 10,000 rad/hr and a temperature of 275°C. Kopp and Munzel⁵ however, showed $^{14}\text{CO}_2$ releases from ^{14}C -doped zirconium sheets at temperatures as low as 200°C, with virtually no radiation.

COMPONENTS OF MODEL

The model of ^{14}C release assumes that upon container failure, a portion of the ^{14}C inventory in the cladding/fuel gap, grain boundaries and cladding surface will be released quickly. ^{14}C will also be released from cladding, structural metals and spent fuel at rates controlled by oxidation of the substrates. The balance of this paper presents the bases for the assumed release mechanisms, and a demonstration of the model for a hypothetical repository situation.

Cladding Integrity

Protection of the fuel by the cladding has been ignored. While this is likely to be a pessimistic assumption, it may be difficult to prove to the contrary that the cladding would survive long periods of time. Factors that might lead to early cladding failures include; (1) a small number of undetected pinholes or cracks in stored fuel rods, generally considered to be lower than 1%, (2) swelling of fuel rods with consequent splitting of cladding when oxidized⁶, (3) hydride reorientation after removal from

reactor core, (4) fuel rod pressurization, and (5) mechanical breakage caused by handling errors, container buckling or earthquakes.

Prompt Release Fraction

Experiments on ruptured spent fuel indicate that upon cladding failure, 0.5 percent of the inventory may be released from the fuel/cladding gap⁷. In addition to this release, Smith and Baldwin⁸ showed that as much of 2 percent of the total spent fuel ¹⁴C inventory was released from zircaloy cladding heated to 350°C for 8 hours. The release rate is an Arrhenius relationship consistent with diffusion out of a thin oxide layer with an activation energy E of between 19 and 25 Kcal/mole. In argon with a trace of air, release rates were lower by a factor of about 10, indicating that the carbon was in a reduced state and had to oxidize before being released. Release of ¹⁴CO₂ from ¹⁴C-doped zirconium sheets showed a similar dependence on oxygen⁹. If the release of ¹⁴C from the cladding oxide layer is governed by diffusion of either oxygen or ¹⁴CO₂, it is possible to estimate the upper bound of release rate for the temperature range of interest, approximately 75°C to 350°C. One-dimensional molecular diffusion through the film of thickness L can be expressed by the partial differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where D is the diffusion coefficient, C is the concentration of oxygen or ¹⁴CO₂, and x is the distance measured from the edge of the cladding toward the center. Equation (1) can be solved analytically⁹ in terms of the dimensionless parameter Dt/L². The concentration profile, and hence fraction released at other temperatures, is related to this parameter. For a constant film thickness, time to reach an equivalent concentration profile is inversely proportional to the diffusion coefficient; i.e., t₂ = t₁D₁/D₂. The ratio D₁/D₂ can be related by the Arrhenius equation to be:

$$\frac{D_1}{D_2} = e^{-\frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (2)$$

where R is the gas law constant. Relying on experimental data of Smith and Baldwin⁸, the time for an equivalent release at temperature T₂ is illustrated in Table 1, assuming nearly all ¹⁴C is released in time t₁ = 8 hours at T₁ = 350°C. Results indicate that

for temperatures as low as 75°C, release of the ¹⁴C by diffusion out of the oxide film would be nearly complete within 10,000 years, and possibly much less time. In the present model, the entire quantity of ¹⁴C contained in the "prompt release fraction," 2.5 percent of the spent fuel inventory, is assumed to be released to the geosphere at the time of container failure.

Table 1 - Releases of ¹⁴C from Cladding Oxide

T-°C	t ₂ -yrs E=19 Kcal/m	t ₂ -yrs E=25 Kcal/m
350	.00091	.00091
250	.017	.043
150	1.3	13
75	169	7800

Release of ¹⁴C from Cladding Metal

The cladding oxidation layer is about 10 microns thick initially. The cladding metal itself is on the order of 0.6 mm thick, and contains the bulk of the ¹⁴C in the cladding. Upon oxidation, the ¹⁴C contained in the metal could be released as ¹⁴CO₂. Gazarelli¹⁰ presents several empirical formulas for the post-translational weight gain of zircaloy due to oxidation. The release model for cladding oxidation conservatively adopts the most pessimistic parameters. The fractional release of ¹⁴C contained in the cladding metal per year is:

$$\frac{\Delta m}{m} = 456.9 \times 10^{-11173/T} e^{-\lambda t} \quad (3)$$

where λ is the radioactive decay rate of ¹⁴C. The model additionally assumes that ¹⁴CO₂ is released at the rate that the metal oxidizes, and that other irradiated structural metal is included with the zircaloy cladding as a source of ¹⁴C.

Release of ¹⁴C from UO₂

The largest inventory of ¹⁴C is contained in the spent fuel. The exact form is unknown, but may be a solid solution of elemental carbon, carbides and oxycarbides with the UO₂¹¹. The model for release of ¹⁴C from spent fuel makes the following assumptions:

- UO₂ oxidizes at a rate controlled by the diffusion of oxygen through two barriers; the grain boundaries and a film of higher oxide of UO₂;

- The oxygen concentration at the oxide/fuel boundary is zero because all oxygen is being consumed by fuel oxidation;
- $^{14}\text{CO}_2$ will be released at the unoxidized fuel surface at the rate the spent fuel oxidizes;
- $^{14}\text{CO}_2$ must diffuse outward through the oxide film and grain boundaries, and;
- Concentration profiles for both oxygen and $^{14}\text{CO}_2$ are at steady state, although the position of the fuel/oxide boundary changes with time.

The present model assumes that the fuel mass can be represented by two concentric spheres as shown in Fig. 1. The outer sphere represents the grain-boundary diffusion barrier and has the equivalent spherical diameter of a fuel fragment, about 0.2 cm. The inner sphere represents the diffusion barrier through the oxide film on the surface of the fuel grain, with a diameter of about 20 microns. The boundary conditions for the model are zero oxygen concentration at the fuel/oxide interface and atmospheric oxygen concentration at the outer diameter.

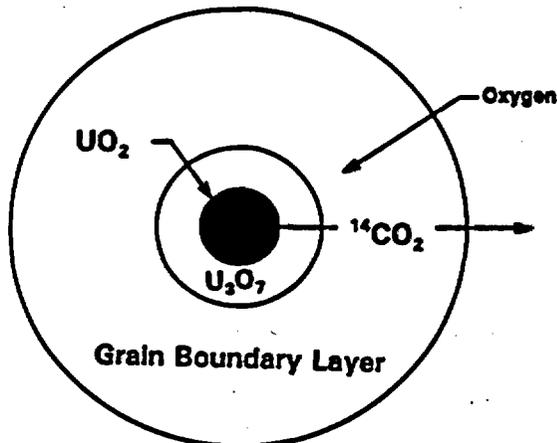


Figure 1 - Conceptual Model for UO_2 Oxidation

Diffusion of oxygen through the fuel grain will be governed by the following partial differential equation:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D \frac{\partial C}{\partial r} \right) \quad (4)$$

where C = oxygen concentration, t = time, r = radius from the center of the sphere, and D = diffusion coefficient. The diffusion coefficient D is a function of temperature,

and differs for the oxide layer and grain boundary layer. The boundary between the spent fuel grain and the oxide layer changes as the oxide layer grows, and is governed by the diffusion rate of oxygen at the interface:

$$\frac{\partial r'}{\partial t} = N_{\text{ox}} \frac{D}{\rho_{\text{ox}}} \frac{\partial C}{\partial r} \Big|_{r=r'} \quad (5)$$

where r' is the radius of the fuel/oxide interface and ρ_{ox} is the density of the oxide. The term N_{ox} is the conversion factor for UO_2 in terms of moles UO_2 oxidized per mole O reaching the boundary. For the temperature ranges likely to be encountered in the repository, most of the oxide formed will be U_3O_7 stoichiometrically¹². For the purposes of the present analysis, N_{ox} is taken to be 3, i.e., 3 moles of UO_2 will be oxidized by $1/2$ mole O_2 .

For steady state concentration of oxygen in both layers, Eqs. 4 and 5 reduce to:

$$\frac{dr'}{dt} = \frac{(C_0 - C_1) N_{\text{ox}}}{\left[\frac{1}{D_0} \left(\frac{1}{r'} - \frac{1}{R_0} \right) + \frac{1}{D_1} \left(\frac{1}{R_0} - \frac{1}{R_1} \right) \right] r'^2 \rho_{\text{ox}}} \quad (6)$$

where C_0 = the concentration at the interface between the UO_2 and U_3O_7 , taken here to be zero, and C_1 = concentration of oxygen at the surface of the fuel fragment, taken here to be the volumetric concentration in the atmosphere, 0.2 moles/22,400 cm^3 . R_0 is the initial grain radius and R_1 is the radius of the fuel particle. The rate of growth of the oxide layer depends on the diffusion coefficients D_0 and D_1 which are functions of fuel temperature. Between r' and R_0 , diffusion coefficient D_0 applies, and between R_0 and R_1 , D_1 applies. The temperature of the fuel is estimated externally with a transient heat conduction model.

Parameters for the UO_2 oxidation model were estimated from data collected on the degradation of unirradiated and spent fuel^{6,12,13,14,15,16,17,18}. Quantitative data on fuel oxidation in air was basically of four types; Thermal Gravimetric Analysis (TGA), dry bath analysis, ceramography and x-ray crystallography. Observations of ceramographic sections of spent fuel gave quantitative information about the sizes of fuel grains and the rate of growth of the oxide. In addition, ceramography gave qualitative information about the mechanisms of oxidation; e.g., the fact that the film of oxide appears to be growing at a consistent rate throughout the sample indicated

that diffusion of oxygen through grain boundaries and cracks probably was much faster than the diffusion across the oxide layer itself.

X-ray crystallography gave qualitative information on the chemical species of the oxide formed at different temperatures, useful for defining the conceptual model. Among the more interesting indications of x-ray crystallography was the observation that for temperatures below about 200°C, the oxide formed was primarily U₄O₉, even though it appeared to be U₃O₈, stoichiometrically¹². At higher temperatures (and possibly at lower temperatures for long periods of time) U₃O₈ was the oxidation product, and because of its lower density would swell the fuel rods and promote cladding failure⁴.

Data on sample weight gain from TGA and dry bath analysis and film thickness from ceramography at fixed temperatures were put into the form of "conversion fraction" of UO₂ to U₃O₈ versus time. Any conversion to U₃O₈ in the samples was ignored. Parameters of the model were then chosen that best matched conversion versus time for the 8 temperatures at which the data were available. The parameters allowed to vary were grain size, fragment diameters, D₀, D₁ at reference temperature T=200°C, and activation energy E (assumed to be the same for both layers). Parameters giving the best comparisons are shown in Table 2. The parameter identification did not explicitly take into account differences between fragment sizes, grain sizes or types of fuel, and the parameters represent the ensemble of all LWR fuel. Representative results of the model/data comparison are given in Fig.2.

Table 2 - Numerical Values of ¹⁴C Model Coefficients

Model Parameter	Value
Grain rad. cm	0.001
Fragment rad., cm	0.1
Ref. oxide diff. coef. cm ² /yr	5.256x10 ⁻⁴
Ref. grain diff. coef. cm ² /yr	5.942x10 ⁻³
Reference T, °C	200
E, Kcal/mol	32

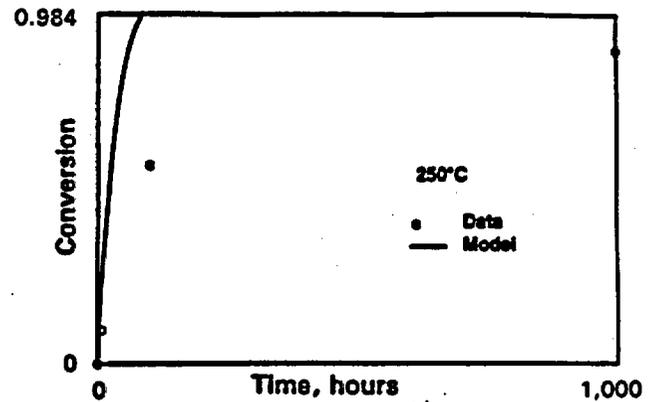


Figure 2a - Model/prototype comparison for UO₂ oxidation - 250°C

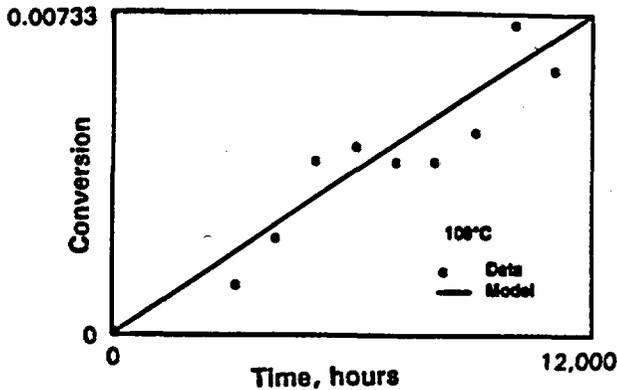


Figure 2b - Model/prototype comparison for UO_2 Oxidation - $109^\circ C$

The model for the release of $^{14}CO_2$ from the fuel matrix is similar to the UO_2 oxidation model. Diffusion of $^{14}CO_2$ through the fuel grain boundary layer and oxide layer will be governed by the following partial differential equation:

$$\frac{\partial C_c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D \frac{\partial C_c}{\partial r} \right) - \lambda C_c \quad (7)$$

where C_c = $^{14}CO_2$ concentration and λ is the decay coefficient for ^{14}C . The outer boundary condition sets the $^{14}CO_2$ concentration to zero at $r = R_1$. At the inner boundary r' , $^{14}CO_2$ enters the oxide layer from the just oxidized fuel. The gradient of $^{14}CO_2$ concentration C_c is set by the diffusive flux:

$$\left. \frac{\partial C_c}{\partial r} \right|_{r'} = \frac{3M}{4\pi R_1^3 D_0} \frac{dr}{dt} e^{-\lambda t} \quad (8)$$

where M is the initial inventory of ^{14}C . The ^{14}C diffusion model depends on the UO_2 oxidation model to provide the position of the moving boundary and the source flux of $^{14}CO_2$ at the inner boundary as the oxide layer grows. Release of $^{14}CO_2$ at the outer boundary of the fragment is calculated from the concentration gradient at that boundary:

$$q_{^{14}C} = 4\pi R_1^2 D_1 \left. \frac{\partial C_c}{\partial r} \right|_{R_1} \quad (9)$$

where q = the rate of release from the fragment, curies/year and D_1 = the diffusion coefficient in the grain-boundary layer.

The radial gradient of $^{14}CO_2$ is steady, but because of radioactive decay, less ^{14}C will leave the fuel fragment than emanated from the fuel/oxide interface. A similar model which includes ^{14}C decay was evaluated for parameter values likely to lead to the largest difference caused by neglecting radioactive decay. Results of this analysis led to the conclusion that effects of radioactive decay of ^{14}C on the flux can be ignored. Therefore the flux of ^{14}C from the fuel fragment is taken as the rate of release from the fuel/oxide interface.

OVERALL ^{14}C MODEL CONSERVATISM

The ^{14}C release rate model is probably conservative for the following reasons:

- Zircaloy is a highly corrosion resistant material, and it is likely that it would protect the fuel following container failure for a substantial period of time. Protection of the fuel even for a few hundred years would have a substantial impact on the calculated release rate because the greatest potential for release is the period during which the fuel temperature is highest.
- Most of the ^{14}C in the fuel, cladding and hardware is likely to be in a reduced state, and must first oxidize to be released in the gas pathway. While kinetic considerations might restrict the formation of gaseous compounds of the ^{14}C in the fuel, the model conservatively assumes that any ^{14}C available to be oxidized is converted to $^{14}CO_2$. A portion of the ^{14}C in the spent fuel may be in a chemical form that is not easily released. Experimental data in which spent fuel was heated to temperatures of up to $450^\circ C$ in oxygen indicated that up to half of the ^{14}C remained in the solid, and was not released as $^{14}CO_2$ ¹⁹.
- The model ignores resistance from the failed container; i.e., once $^{14}CO_2$ is released from the fuel fragment no credit is taken for diffusion through the long length of a failed fuel rod, or through very small holes in the container.

RESULTS OF ^{14}C RELEASE MODEL FOR A HYPOTHETICAL REPOSITORY

The model demonstrates the relative importance of the waste form compartments containing the ^{14}C , and the temperature at which waste package failure occurs. Figures 3 and 4 show release rates of ^{14}C calculated by the model for a hypothetical unsaturated repository. Release is calculated from 66 randomly placed spent fuel containers which are assumed to begin to fail once their temperatures fall below the boiling point of water. The two figures differ by the assumed lifetimes of the containers of either 200 ± 100 years or 1000 ± 300 years after cool-down,

normally distributed. The shorter container lifetime leads to greatly increased releases of ¹⁴C because of the dependence of the oxidation rates on temperature. Conversely, waste packages remaining intact for times closer to their design basis lifetimes have greatly reduced releases of gaseous ¹⁴C. The current EPA² limit for ¹⁴C release to the accessible environment is shown for reference, although the results presented here refer to releases from the waste packages to the geosphere only. In both cases, the UO₂ compartment was the largest contributor, while very little was released from the oxidation of cladding and metal.

PLANS FOR FURTHER MODEL DEVELOPMENT

The ¹⁴C source term model is based on an abstraction of several complex processes. The simplifying assumptions taken in the model are:

- The fuel is represented by concentric spheres, of a single set of dimensions; i.e., the irregular shape of the fragments and grains is not taken into account.
- No effects of the container or cladding on the diffusional processes are taken into account.
- The increase in surface area caused by oxidation of the grains is not taken into account.
- While there are some direct data on release of ¹⁴CO₂ from cladding and the grain/gap inventory, data on releases from the largest inventory in the fuel itself are lacking.

Future versions of the model will strive to relax some of the limitations in the present version. In particular, development will concentrate in two areas:

- Develop a transient model - The present model considers only steady state concentrations of oxygen and ¹⁴CO₂ in the fuel. Thermal gravimetric analysis data on some samples at relatively low temperature indicates a period of slow initial weight gain, followed by a substantially higher rate. This result has been interpreted as the transient diffusion of oxygen through the grain boundaries prior to oxidation of the grains. At high temperatures where diffusion coefficients are large, there is relatively little difference between the conversion of large fuel fragments and crushed samples, indicating that the grain boundary diffusion is fast. At lower

temperatures, the difference between whole and crushed samples is much more evident. While the steady state model appears to fit the data well, it may in fact be portraying the transient diffusion as a much slower rate of conversion, especially at lower temperatures. This could lead to inaccurate predictions of conversion rates at low temperatures for times much larger than the period of 12,000 hours in the longest experiment. A transient model for diffusion would alleviate this inconsistency.

- Incorporate variations of grain sizes and other material properties within samples - The present model assumes that the oxidizing fuel can be characterized by a single set of parameters. Actually, each sample of fuel oxidized in the laboratory consisted of grains of varying sizes, and material properties determined by the position of the sample in the fuel rod and distance from the pellet edge. Furthermore, the fuel would be expected to vary from one rod to the next in the same core, and from one set of spent fuel to another, depending on such factors as reactor type, burnup and fuel manufacturer. Variability in the fuel should be factored into the model to the degree possible.

CONCLUSIONS

A preliminary model has been developed for the release of ¹⁴C from spent fuel containers for a hypothetical repository for spent fuel in the unsaturated zone. This model includes phenomena responsible for the release of ¹⁴C from several compartments in spent fuel. Preliminary results indicate that the spent fuel itself would be the major source of ¹⁴C, with relatively minor amounts released from the other compartments. The ¹⁴C release model is being used in conjunction with a gas flow and transport model for NRC's Iterative Performance Assessment, Phase 2, to estimate potential releases of ¹⁴C to the accessible environment at the proposed Yucca Mountain repository.

DISCLAIMER

The contents of this paper are the sole opinions of the author, and do not represent the position of the Nuclear Regulatory Commission.

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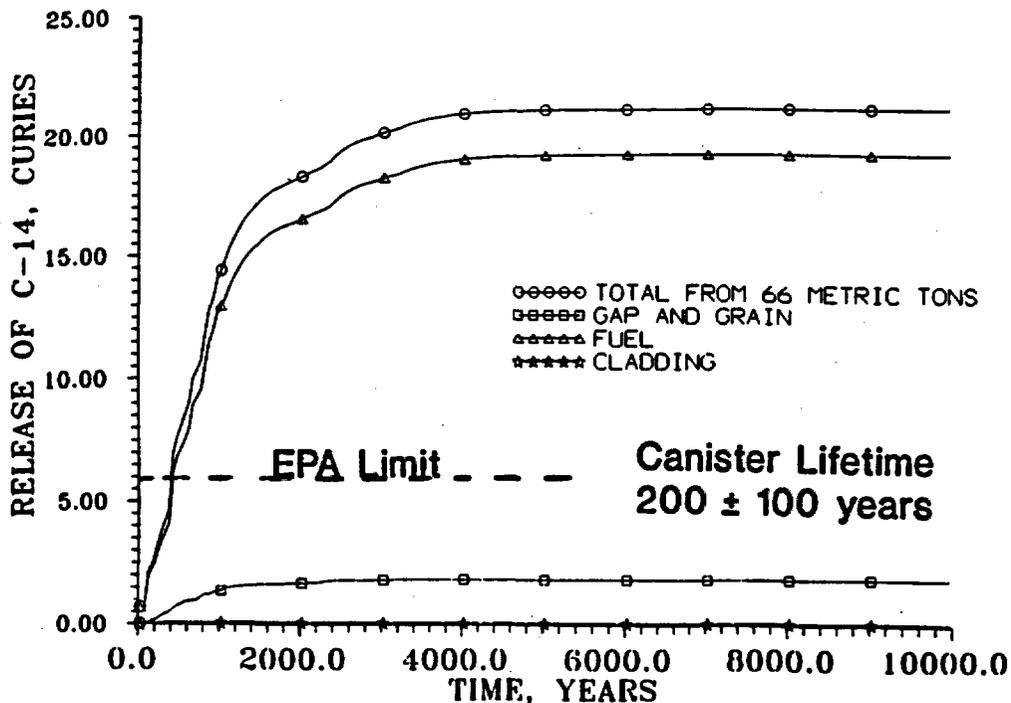


Figure 3 - Release of ¹⁴C from 66 randomly placed containers in a hypothetical repository in unsaturated tuff. Short Container Lifetime

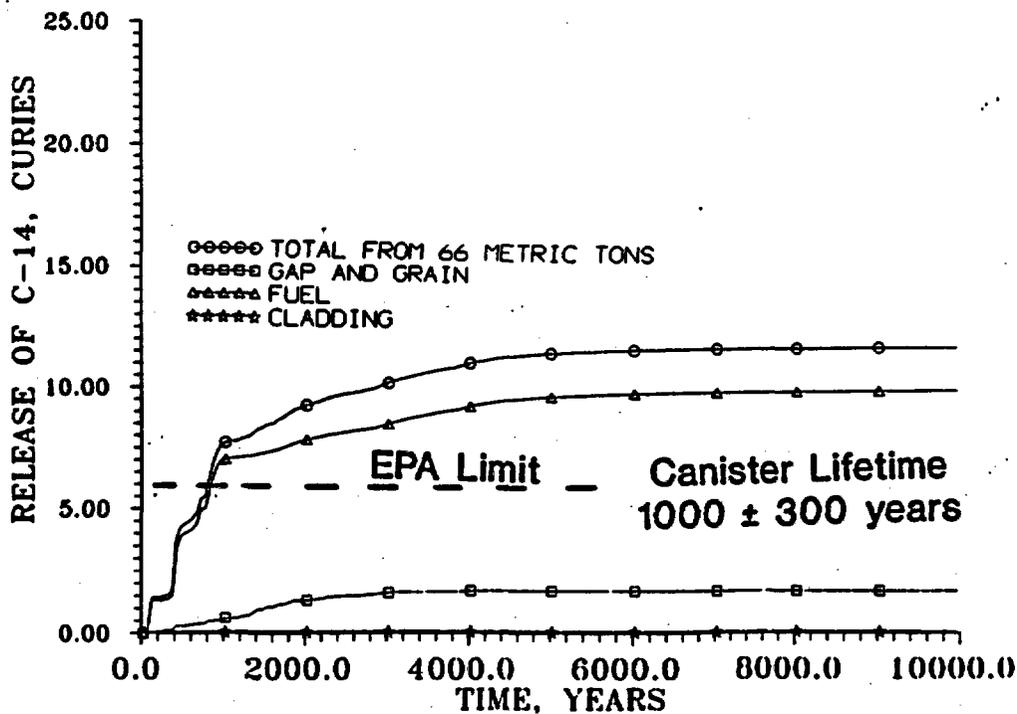


Figure 4 - Release of ¹⁴C from 66 randomly placed containers in a hypothetical repository in unsaturated tuff. Long Container Lifetime

Detailed Example of the IPA Process in a Specific Discipline: ^{14}C Carbon

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¹⁴CARBON RELEASES FROM YUCCA MOUNTAIN REPOSITORY

- **¹⁴Carbon associated with spent fuel**
- **Oxidized to carbon dioxide gas**
- **Transported in the gas phase in unsaturated rock**
- **Realistic assessment of impacts of ¹⁴Carbon requires coupling of source release, heat flow, two-phase fluid flow, and distribution of carbon among solid, liquid and gas phases**
- **Assessment of dose impacts**

RELEASES OF ¹⁴CARBON FROM SPENT FUEL

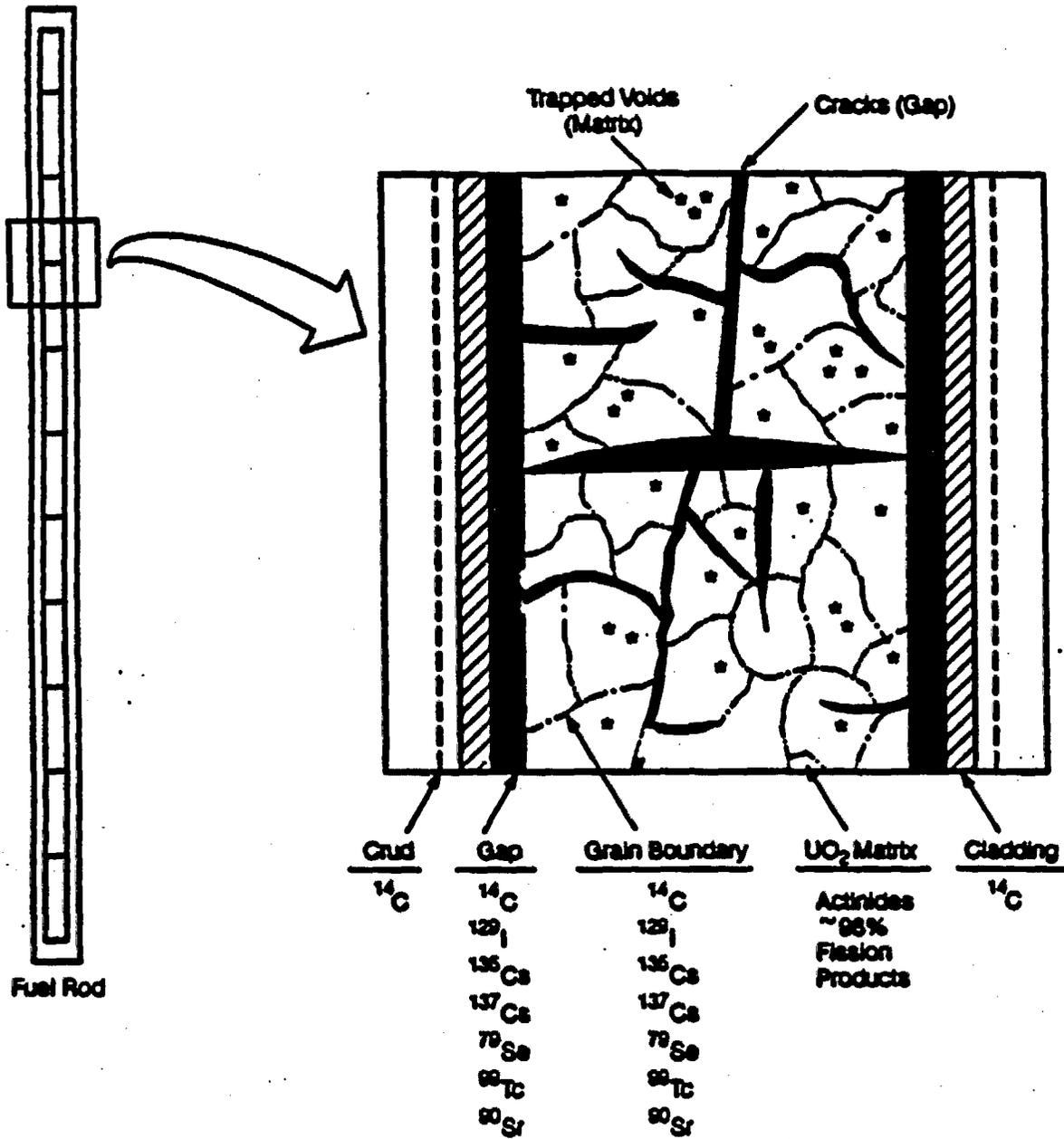
- Initial cladding oxide and crud
- Grain boundary and cladding gap
- Zircaloy oxidation
- Oxidation of fuel

ADJUSTED ¹⁴CARBON CONTENT IN SPENT FUEL (Ci/MTHM) (AFTER PARK, 1992)

Type	Burnup Mwd/MTHM	UO ₂	Zirc.	Hard- ware	Total
BWR	35,000	0.69	0.48	0.13	1.3
PWR	40,000	0.73	0.22	0.26	1.21
Average		0.72	0.31	0.21	1.24

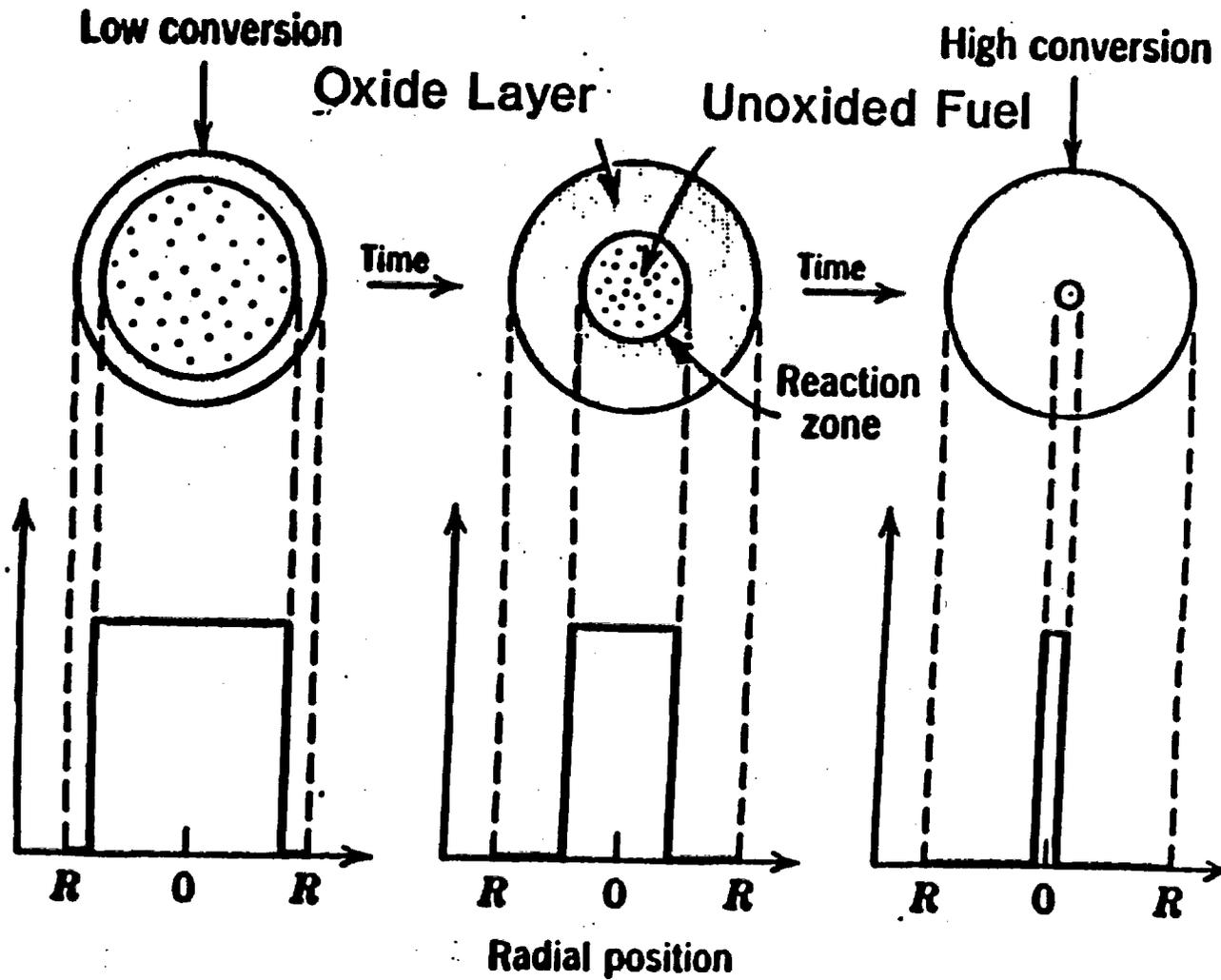
MODEL FOR RELEASE OF ¹⁴CARBON

- ¹⁴Carbon released quickly from grain boundaries, cladding/fuel gap, and initial zirconium oxide
- Minor releases from oxidation of cladding and other metals
- Major releasable inventory from UO₂ fuel



Location of Radionuclides in Spent Fuel and Potential Releases of C-14
 (Apted, et. al., 1989)

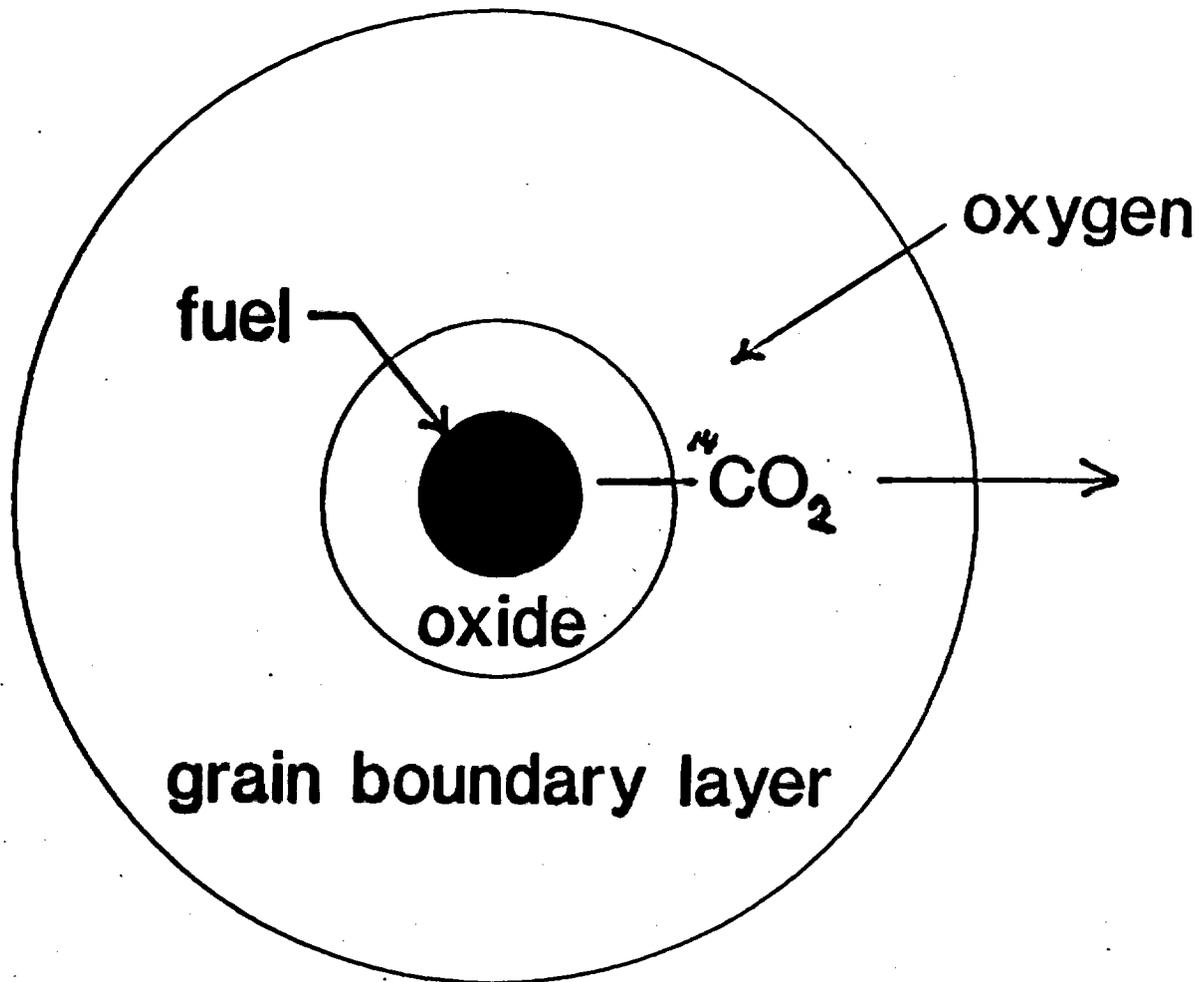
SHRINKING CORE MODEL FOR FUEL OXIDATION



ACNW WORKING GROUP MEETING ON PERFORMANCE ASSESSMENT
DECEMBER 16, 1992
DIVISION OF HIGH-LEVEL WASTE MANAGEMENT

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C-14 Gaseous Release Model



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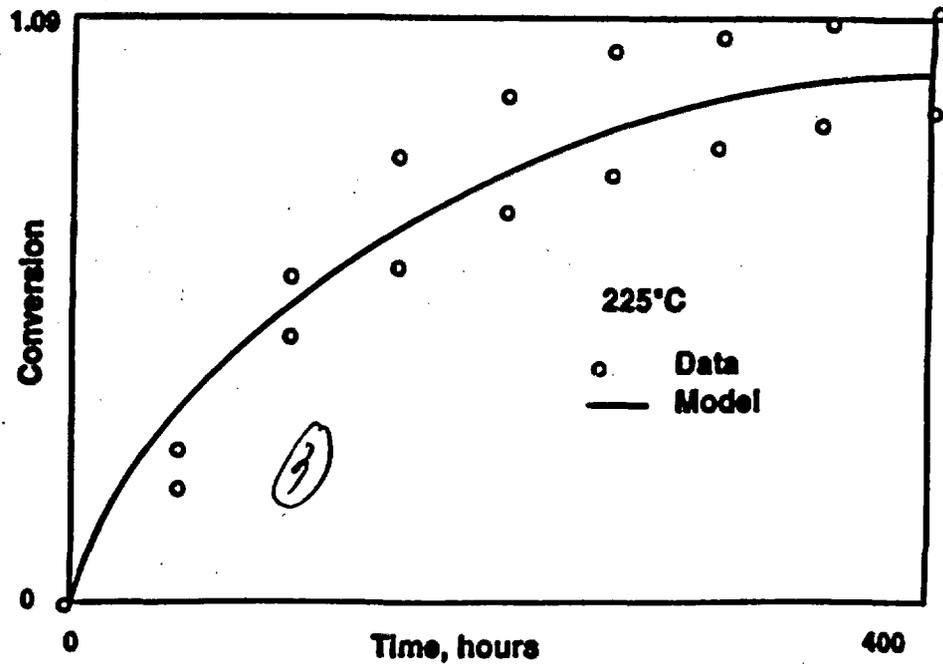
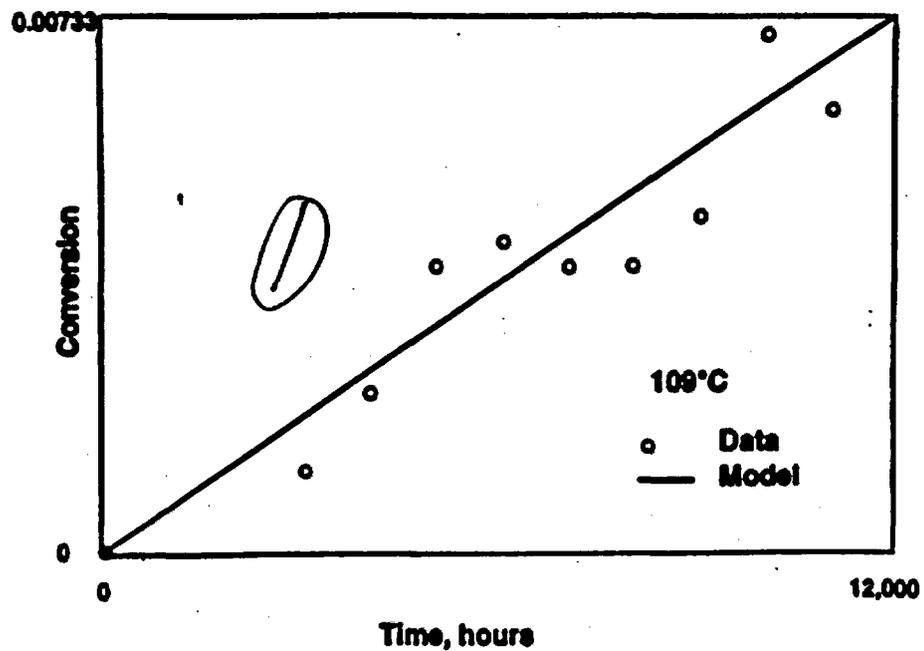
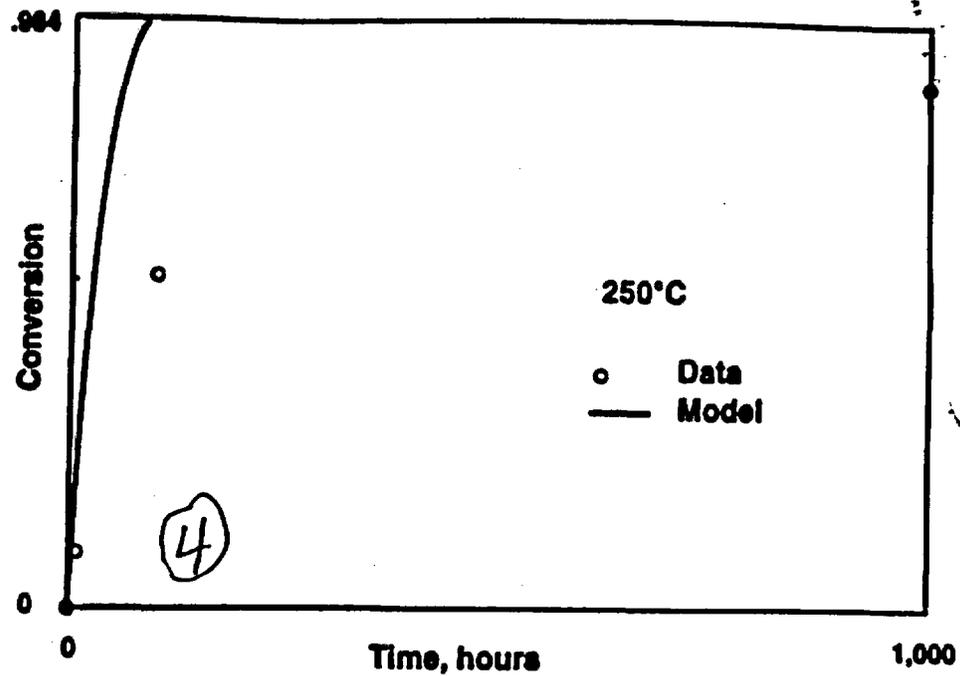
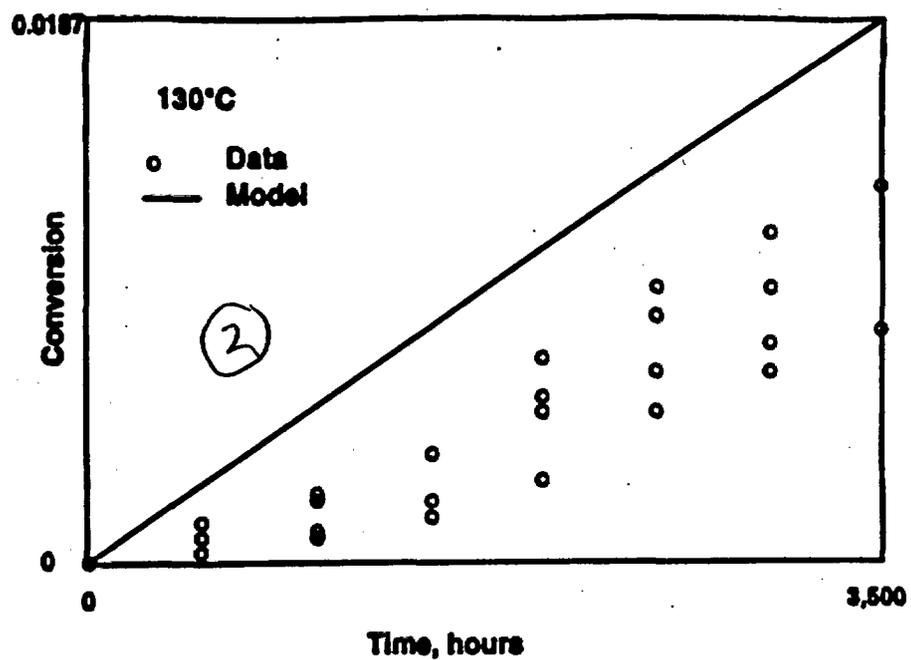
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FUEL OXIDATION MODEL ASSUMPTIONS:

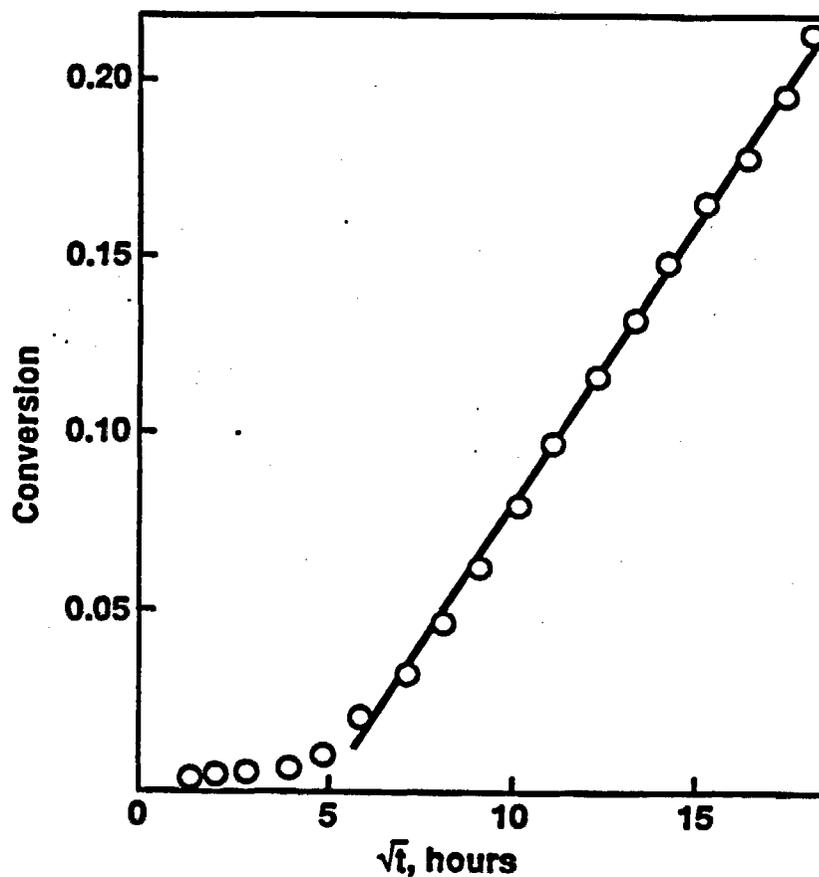
- **No oxidation until canister fails**
- **No protection of fuel by cladding**
- **Oxygen diffuses through two layers:**
 - **outer layer representing grain boundaries**
 - **inner layer representing oxidized fuel**
- **Oxide is U_3O_7 stoichiometrically**
- **Oxygen concentration zero at inner boundary**
- **Oxygen profiles in layers are at steady state**

PARAMETER IDENTIFICATION AND MODEL VERIFICATION

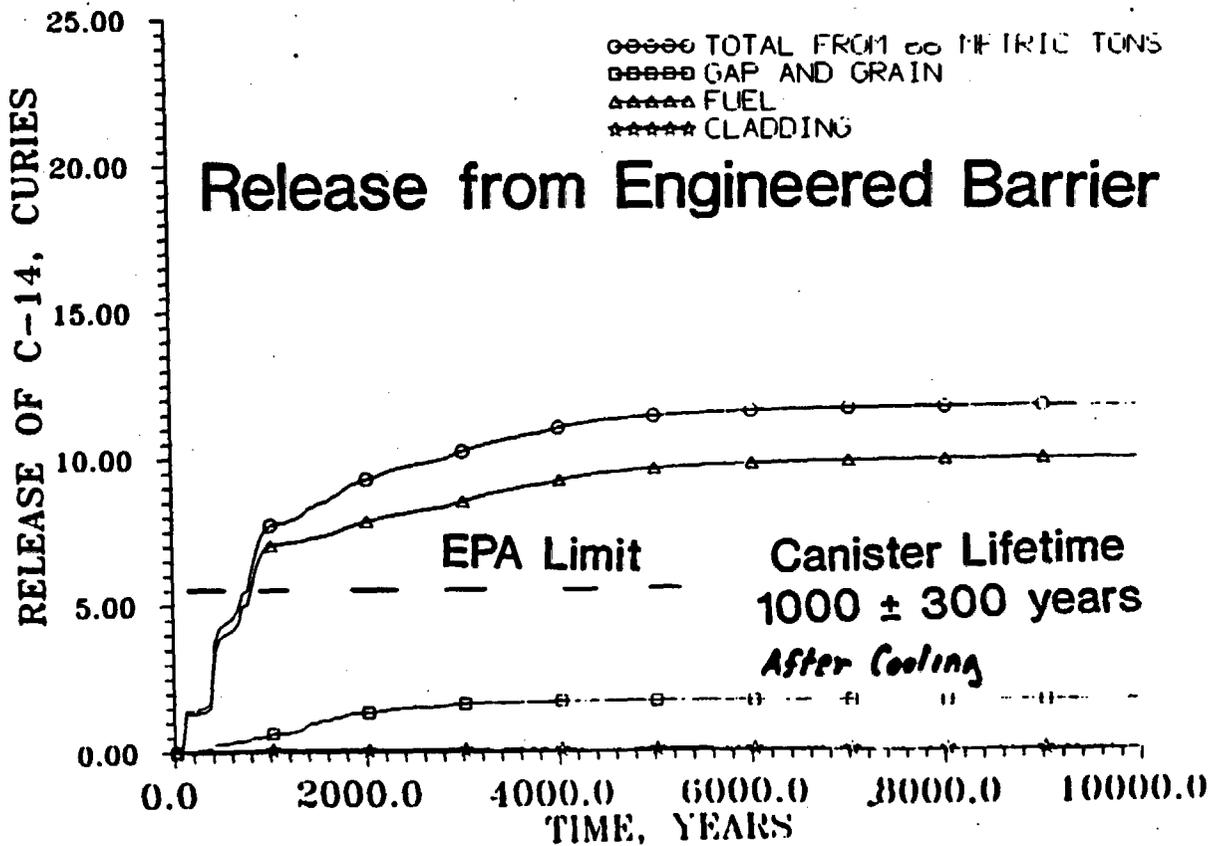
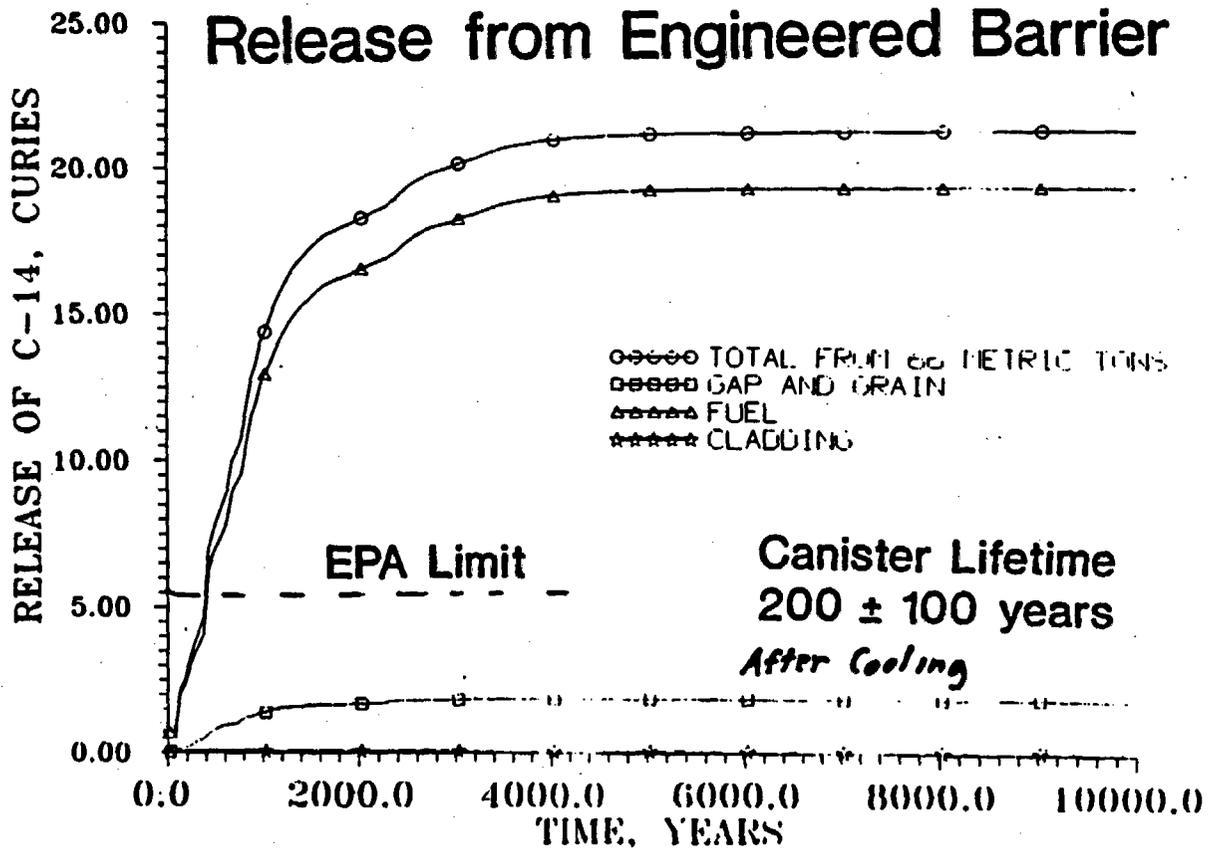
- **Grain diameter from micrographs of fuel (20 microns)**
- **Outer layer diameter taken as fragment size (2mm)**
- **Weight gain from thermal gravimetric analysis and dry bath experiments between 110 and 250 degrees C (PNL)**
- **Activation energy and diffusion coefficients adjusted for best fit to oxidation data on fuel fragments in 8 temperature ranges**
- **Little data found on ¹⁴Carbon releases from fuel oxidation**



Transient Oxidation Effects

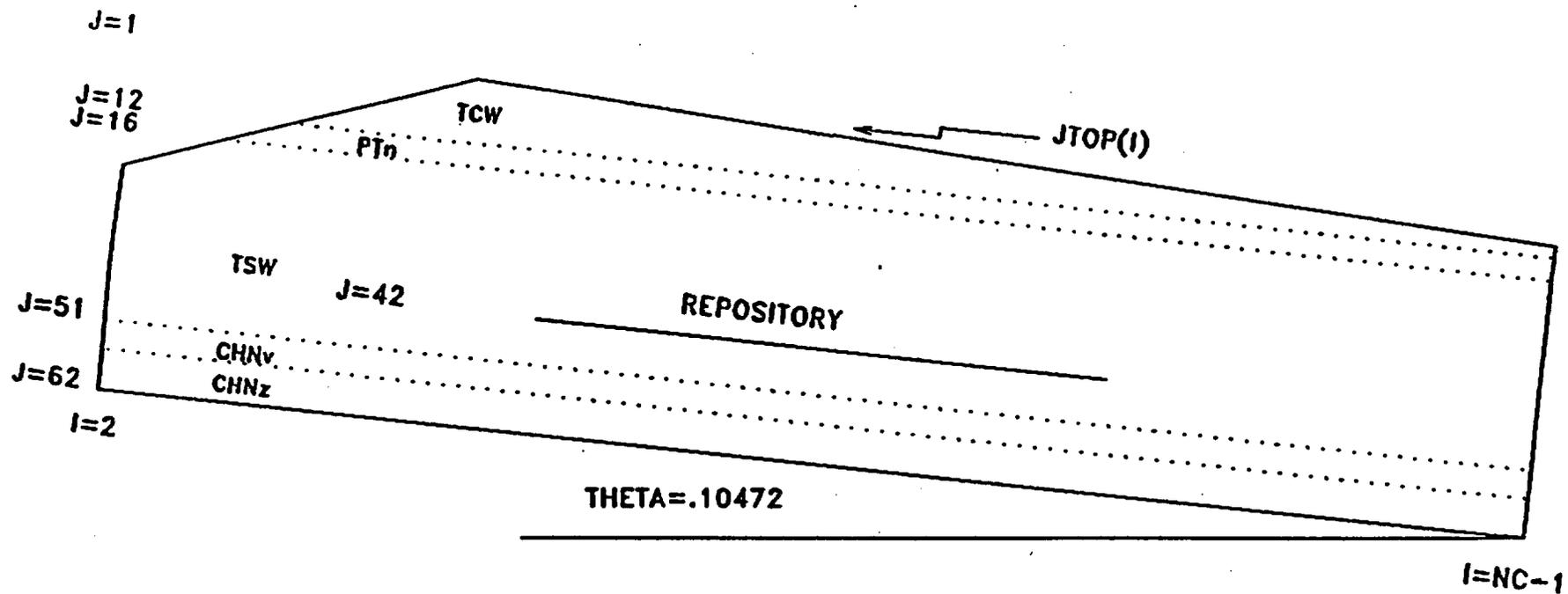


Not included in fuel oxidation model

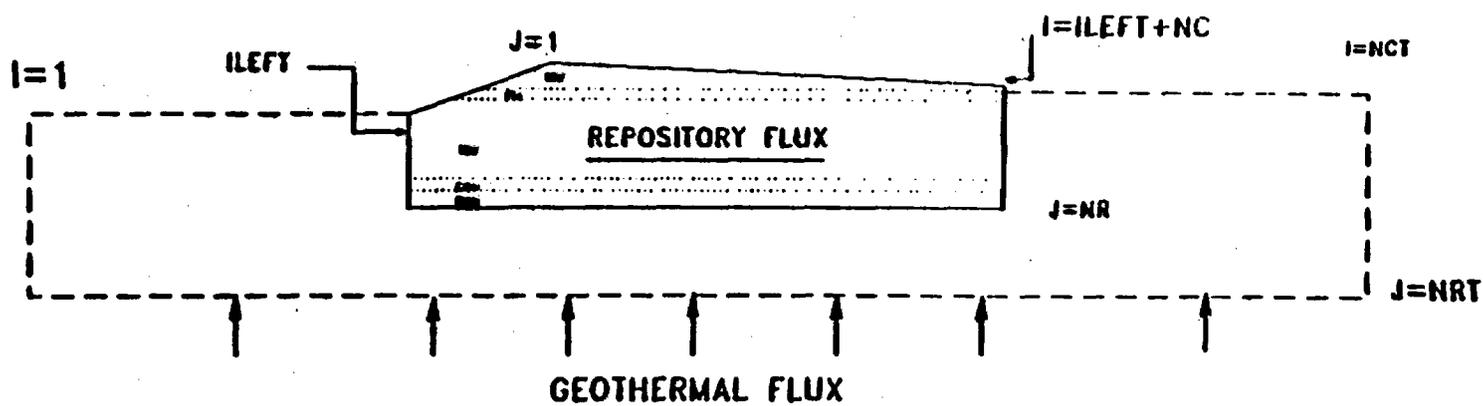


GAS FLOW AND ¹⁴CARBON TRANSPORT MODEL

- **Based on model of Ross *et al.* (TGIF)**
- **2-D Finite difference model**
 - **Quasi steady state; transient temperature field but steady gas flow**
- **Equivalent porous medium combines fractures and matrix**
- **Single phase -- water-saturated gas only**
- **¹⁴Carbon transport by advection with retardation factor**



REPOSITORY CROSS SECTION FOR GAS FLOW MODEL

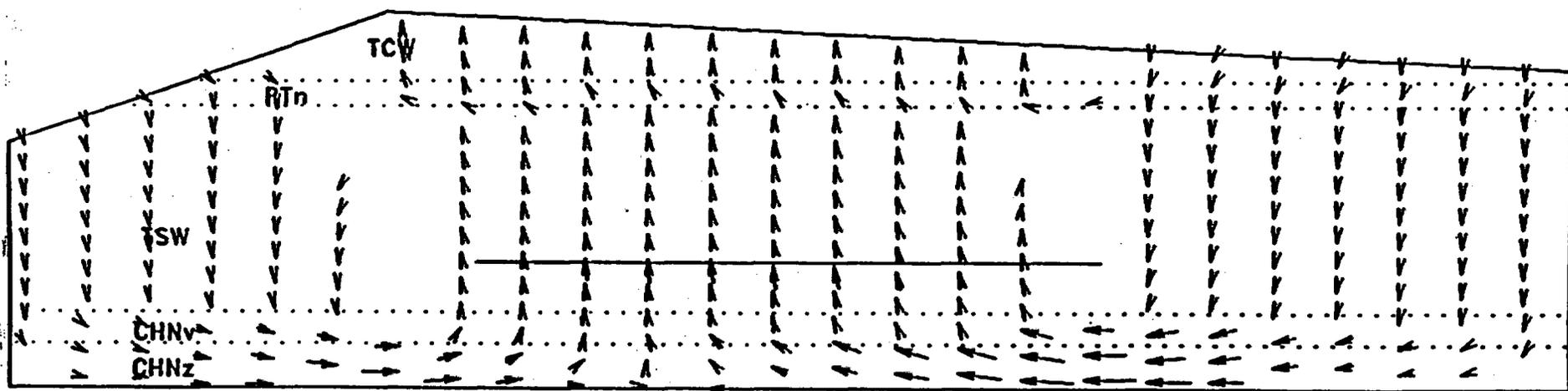


REPRESENTATION OF REPOSITORY X-SECTION FOR HEAT TRANSFER

18

TYPICAL X-SECTION 500 YRS

.001 M/YR
→



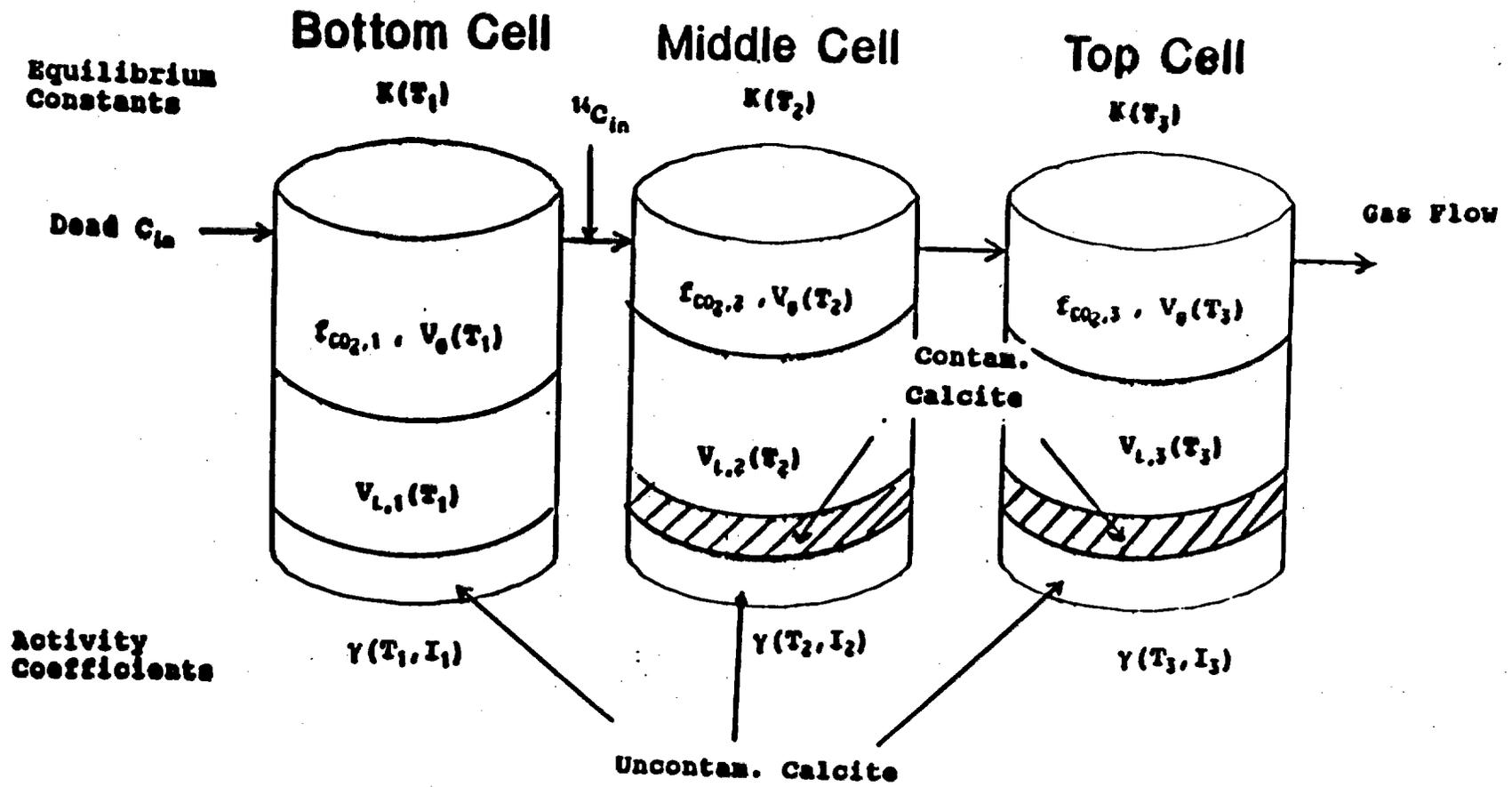
WEAKNESSES OF ¹⁴CARBON FLOW AND TRANSPORT MODEL

- **Does not include 2-phase flow**
- **2-D Steady state only -- Cannot include third dimension or time**
- **Retardation coefficient may not adequately capture interaction of ¹⁴Carbon with water and rock**

GEOCHEMICAL MODEL FOR TOTAL CARBON

- Calculate chemical equilibrium in each tank
- Determine output from tank to next tank in gaseous phase (no water moves)
- Sum new inventories of carbon and recompute coefficients
 - Eq. Coefficients function of T
 - Activity coefficients function of T and ionic strength
- Repeat calculations of chemical equilibrium for next time step

Mixed-Tank Model for C and C-14



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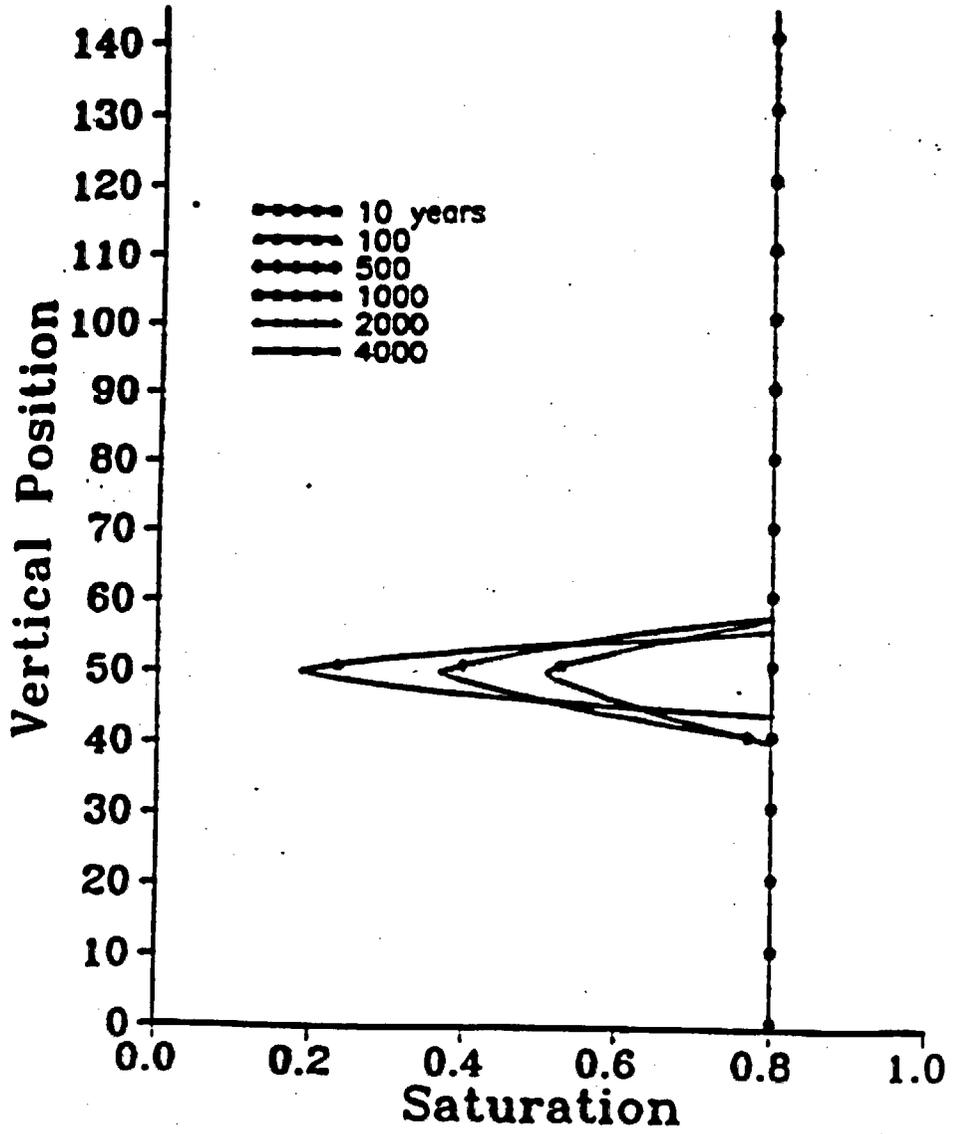
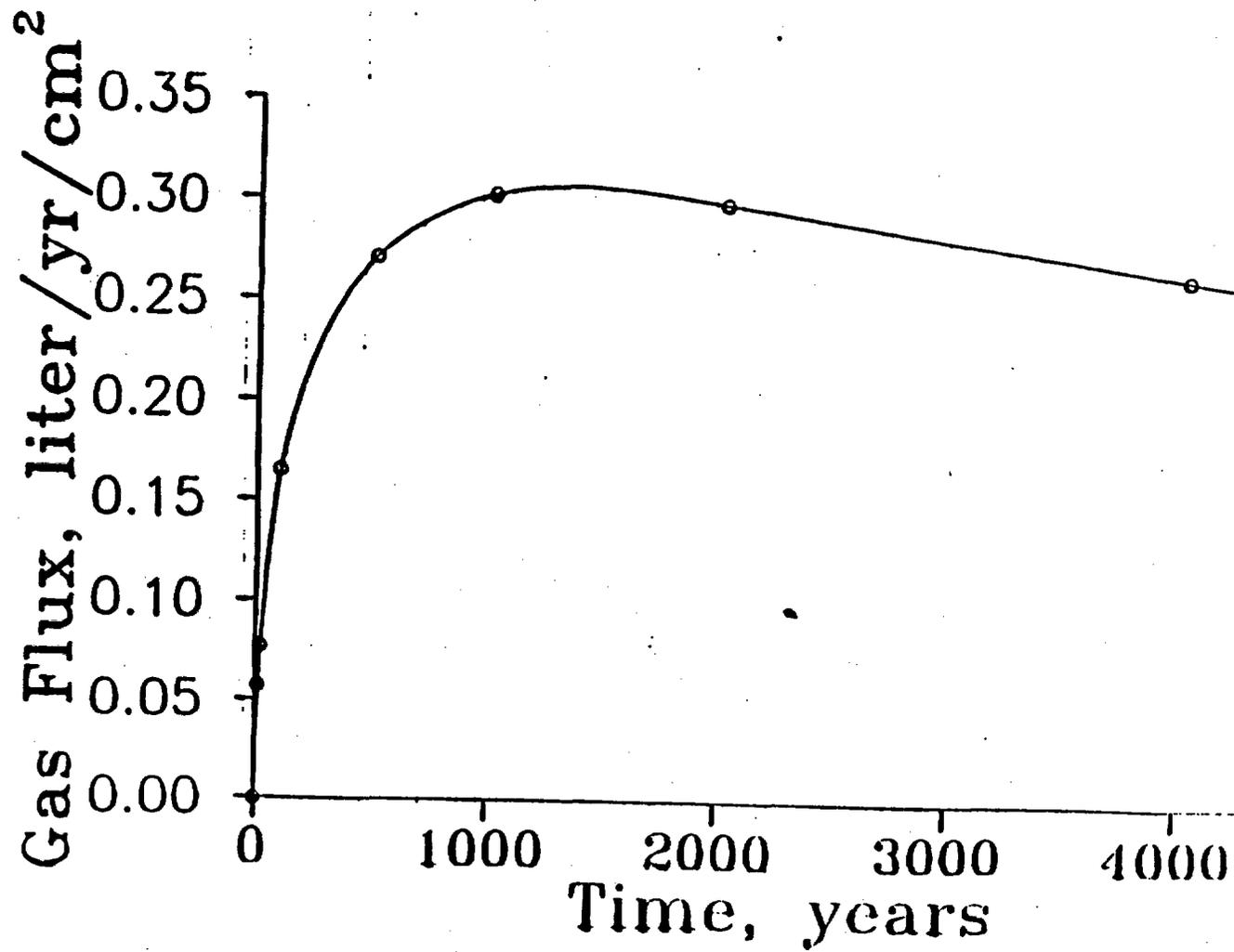


Figure 4 - Water Saturation for Example



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IMPACT OF ¹⁴CARBON RELEASE

- **Cumulative Release at Accessible Environment**
- **Lifetime doses to regional and global populations, and average dose to individuals**
 - **Near field concentrations in air**
 - **Water from Wells**

SUMMARY

- **NRC is developing a suite of models for the release and transport of ^{14}C Carbon**
 - **Release from waste form**
 - **Gas flow and advective transport**
 - **Geochemical interaction of ^{14}C Carbon**
- **Models are simplified and preliminary, but allow experimentation with parameter variations to determine sensitivities**

TENTATIVE CONCLUSIONS

- **Significant concerns exist about likely size of gaseous ¹⁴Carbon releases and the uncertainty in estimates of those releases**
- **Even after substantial research and analysis, the remaining uncertainties may make it difficult to evaluate compliance with EPA's ¹⁴Carbon release limit**
- **Direct exposure to airborne ¹⁴Carbon probably insignificant dose**