

# MULTIPHASE-MULTICOMPONENT NONISOTHERMAL REACTIVE TRANSPORT IN PARTIALLY SATURATED POROUS MEDIA

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## ABSTRACT

A numerical model MULTIFLO is developed for describing reactive transport in a multiphase-multicomponent, nonisothermal, partially saturated porous medium. The model includes chemical reactions between aqueous, gaseous and solid phases. Reactions involving minerals are considered to be irreversible and described through appropriate kinetic rate laws. Homogeneous reactions within the aqueous phase and heterogeneous reactions between aqueous and gaseous phases are assumed to be reversible, their reaction rates controlled by transport and local equilibrium mass action relations. Flow of aqueous and gaseous phases is described by Darcy's law in a partially saturated porous medium. Solute transport includes contributions from advection, diffusion and dispersion. Enhanced binary diffusion of water vapor for transport in a two-phase system is taken into account. A sequentially coupled scheme is used to couple transport of water, air and heat to solute and minor gas components, and solids. Changes in porosity and permeability caused by chemical reactions are coupled to the flow field. Several options are available for solving numerically the transport equations including fully implicit, explicit and operator splitting methods. Mineral mass transfer equations are solved explicitly using the quasi-stationary state approximation. The coupled flow and transport model is applied to the proposed high-level nuclear waste storage facility located in unsaturated rock at Yucca Mountain, Nevada. A repository-scale model is used to calculate the redistribution of moisture, heat, and various chemical constituents caused by the thermal perturbation produced by the waste.

## INTRODUCTION

Of potentially fundamental importance to the longevity of a waste canister in a high-level waste (HLW) repository is the chemical composition of groundwater in the near-field region which could potentially come in contact with the container. This includes environmental variables defining the oxidation state, pH, chloride concentration, and other compositional variables of ingressing fluid which may impact the waste container and waste form. Depending on the composition of this fluid, the rate of corrosion and leaching of spent fuel could be greatly accelerated or inhibited.

A number of authors have presented model calculations of the redistribution of moisture resulting from the emplacement of nuclear waste at the proposed Yucca Mountain (YM) HLW site in Nevada [1, 9]. These calculations indicate that heat produced from the waste creates a dryout zone surrounding the repository with enhanced zones of saturation above and below the repository horizon caused by condensation of water vapor. The degree of

dryness and time to rewet the repository depends on the heat load of the radioactive waste and the hydraulic properties of the host rock.

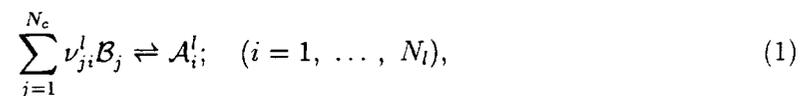
Unique to an unsaturated repository design concept is the possible increase in salinity of liquid water in the near-field region caused by continuous evaporation of water resulting from heat produced by the waste canisters. The amount of water that can be evaporated depends not only on the initial saturation of the pore spaces in the rock adjacent to the canisters, but also on the flow of water towards the waste packages resulting from capillary forces and gravity driven flow. Salts could form both on the waste package and in the near field as a result of evaporation [13]. Degradation of cement could result in the formation of hyperalkaline fluids which would react strongly with the silicate host rock producing calcium silicate hydrates and affect the sorption characteristics of the near field.

The purpose of this work is two-fold. The first is to present a general formulation of multicomponent–multiphase nonisothermal reactive transport model applicable to partially saturated porous media. The second is to apply the model to the proposed high-level nuclear waste storage facility at YM, Nevada.

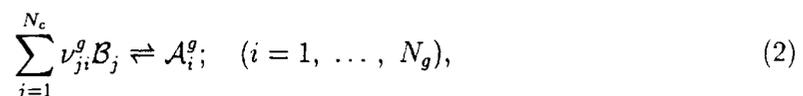
## REACTIVE MASS AND HEAT TRANSPORT IN HYDROTHERMAL SYSTEMS

In this section, equations are developed to describe flow and transport in a nonisothermal, multiphase–multicomponent system. Darcy's law is used to describe flow of liquid and gas phases in a partially saturated porous medium. Chemically reacting species may be present in the aqueous, gaseous or solid phases. The transport equations for solute and gaseous species include advection and diffusion/dispersion. Mineral reactions are assumed to be irreversible, described through a kinetic rate law. Homogeneous reactions within the aqueous phase and heterogeneous reactions between the aqueous and gaseous phases are assumed to obey conditions of local chemical equilibrium. Note that contrary to statements by White [14], the rates of reactions in local equilibrium do not vanish, but are governed by solute transport and appropriate mass action equations.

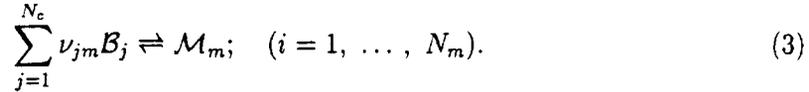
Chemical reactions taking place in the system consisting of  $N$  species are written in terms of a basic set of  $N_c$  independent species, or components, referred to as primary species denoted by the set  $\{\mathcal{B}_j; j = 1, \dots, N_c\}$ . The remaining  $N - N_c$  species are referred to as secondary species. The primary species may be aqueous or gaseous species depending on the phases present. For a general geochemical system consisting of  $N_l$  aqueous and  $N_g$  gaseous secondary species, and  $N_m$  minerals, the chemical reactions can be expressed in the canonical form [6]:



for aqueous species  $\mathcal{A}_i^l$ :



for gaseous species  $\mathcal{A}_i^g$ , and for minerals  $\mathcal{M}_m$ :

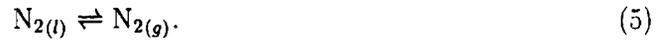


The matrices  $\nu_{ji}^l$ ,  $\nu_{ji}^g$ , and  $\nu_{jm}$  denote the stoichiometric reaction coefficients giving the number of moles of the  $j$ th primary species in one mole of the  $i$ th secondary species corresponding to aqueous, gaseous and mineral species, respectively. Each reaction is associated with a single secondary species with unit stoichiometric coefficient. A species is distinguished by its chemical formula and the phase to which it belongs. Reactions (1) and (2) are considered to be reversible representing conditions of local equilibrium. Reaction (3) is assumed to be irreversible with the reaction rate described through a kinetic rate law.

A special role is played by the solvent species  $\text{H}_2\text{O}$ , which is generally in much greater abundance than all other species (with notable exceptions). For the gas phase, both nitrogen (referred to here simply as air) and water vapor are considered to be the dominant gas species. Reactions involving water vapor and nitrogen are



representing a phase change of water from liquid to gas describing evaporation, condensation and boiling, and partitioning of air between the aqueous and gas phases:



The species water in the aqueous or gaseous phase ( $\text{H}_2\text{O}_{(l,g)}$ ) is always chosen as a primary species. The remaining primary species may be any independent set of species which conveniently characterize the chemical properties of the system under investigation. In what follows they are chosen to be a subset of the aqueous or gaseous species. Minerals are not used as primary species because any given mineral may not be present over the entire computational domain. Aqueous primary species are used for pure liquid and two-phase systems, and gaseous primary species for pure gas phase systems. For systems in which both single and two-phase regions are possible, basis switching is necessary at the boundary of a pure liquid or two-phase region and a pure gas phase region.

#### Multiphase-Multicomponent Mass Transport Equations

Taking into account chemical reactions in the form represented by Eqns.(1), (2) and (3), the mass and energy transport equations have the following form for the  $\text{H}_2\text{O}$  component ( $w$ )

$$\begin{aligned} \frac{\partial}{\partial t} [\phi (s_l n_l X_w^l + s_g n_g X_w^g)] + \nabla \cdot (\mathbf{q}_l n_l X_w^l + \mathbf{q}_g n_g X_w^g - D_g^{\text{eff}} n_g \nabla X_w^g) = \\ - \sum_{m=1}^{N_m} \nu_{wm} I_m + Q_w, \end{aligned} \quad (6)$$

for the air component ( $a$ ):

$$\begin{aligned} \frac{\partial}{\partial t} [\phi (s_l n_l X_a^l + s_g n_g X_a^g)] + \nabla \cdot (\mathbf{q}_l n_l X_a^l + \mathbf{q}_g n_g X_a^g - D_g^{\text{eff}} n_g \nabla X_a^g) = \\ - \sum_{m=1}^{N_m} \nu_{am} I_m + Q_a, \end{aligned} \quad (7)$$

and for the energy balance equation:

$$\begin{aligned} \frac{\partial}{\partial t} [\phi (s_l n_l U_l + s_g n_g U_g)] + \nabla \cdot (\mathbf{q}_l n_l H_l + \mathbf{q}_g n_g H_g) \\ + \frac{\partial}{\partial t} [(1 - \phi) C_p^{\text{rock}} \rho_{\text{rock}} T] - \nabla \cdot \kappa \nabla T = Q_e. \end{aligned} \quad (8)$$

In these equations  $n_{l,g}$  denotes the density of liquid and gas phases, on a molar basis, and  $X_{w,a}^{l,g}$  the mole fraction of water and air in the liquid and gas phases, respectively, and  $\phi$  denotes the porosity of the porous medium. The quantities  $Q_{w,a}$ , and  $Q_e$  added to the right hand sides of the transport equations represent source terms in addition to the chemical reaction terms. Diffusion of water in the aqueous phase is neglected. The liquid ( $l$ ) and gas ( $g$ ) phases occupy fractions  $s_l$  and  $s_g$ , respectively, with

$$s_l + s_g = 1. \quad (9)$$

The velocity of phase  $\pi$ ,  $\mathbf{q}_\pi$ , is determined by Darcy's law:

$$\mathbf{q}_\pi = -\frac{k k_{r\pi}}{\mu_\pi} \nabla (p_\pi - \rho_\pi g z), \quad (10)$$

where  $k$  refers to the saturated permeability of the porous medium,  $p_\pi$  refers to the pressure,  $k_{r\pi}$  represents the relative permeability, and  $\mu_\pi$  the viscosity of phase  $\pi$ ,  $g$  denotes the acceleration of gravity, and  $z$  the vertical height. The temperature is denoted by  $T$ ,  $U_\pi$  represents the total internal energy and  $H_\pi$  the total enthalpy of the  $\pi$ th fluid phase,  $C_p$  the heat capacity, and  $\kappa$  the thermal conductivity. Heat produced by chemical reactions is ignored. The effective binary gas diffusion coefficient is defined in terms of temperature, pressure and material properties by

$$D_g^{\text{eff}} = \omega \tau \phi s_g D_g^0 \frac{p_0}{p_g} \left[ \frac{T + T_0}{T_0} \right]^\theta, \quad (11)$$

where  $\theta$  is an empirical constant,  $D_g^0$  represents the binary gas diffusion coefficient at the reference pressure  $p_0$  and temperature  $T_0$ ,  $\tau$  denotes the tortuosity, and  $\omega$  is an enhancement factor [7]. The enhancement factor is inversely proportional to the gas saturation  $s_g$  which thus cancels from the expression for the effective gas diffusion coefficient.

The transport equations for aqueous and gaseous primary species, taking into account local equilibrium of homogeneous reactions within the aqueous and gaseous phases and heterogeneous reactions between these phases, have the form

$$\frac{\partial}{\partial t} (\phi \Psi_j) + \nabla \cdot \Omega_j = - \sum_{m=1}^{N_m} \nu_{jm} I_m, \quad (12)$$

and mineral mass transfer equations are given by

$$\frac{\partial \phi_m}{\partial t} = \bar{V}_m I_m. \quad (13)$$

The generalized concentration  $\Psi_j$  and flux  $\Omega_j$  appearing in the primary species transport equations are defined by

$$\Psi_j = s_l \Psi_j^l + s_g \Psi_j^g, \quad (14)$$

and

$$\Omega_j = \Omega_j^l + \Omega_j^g, \quad (15)$$

with

$$\Psi_j^l = \delta_{\pi,j,l} C_j^l + \sum_{i=1}^{N_c^l} \nu_{j,i}^l C_i^l, \quad \Psi_j^g = \delta_{\pi,j,g} C_j^g + \sum_{i=1}^{N_c^g} \nu_{j,i}^g C_i^g, \quad (16)$$

and

$$\Omega_j^l = \delta_{\pi,j,l} \mathbf{J}_j^l + \sum_{i=1}^{N_c^l} \nu_{j,i}^l \mathbf{J}_i^l, \quad \Omega_j^g = \delta_{\pi,j,g} \mathbf{J}_j^g + \sum_{i=1}^{N_c^g} \nu_{j,i}^g \mathbf{J}_i^g, \quad (17)$$

where  $\pi_j = l, g$  depending on whether the  $j$ th primary species belongs to the liquid or gas phase. The kronecker delta function  $\delta_{\pi,j,\pi}$  appears in Eqns.(16) and (17) because any particular primary species can belong to only one phase. Here  $C_i^\pi$  and  $\mathbf{J}_i^\pi$  denote the concentration and flux of the  $i$ th species in the  $\pi$ th phase,  $\phi_m$ ,  $\bar{V}_m$ , and  $I_m$  denote the volume fraction, molar volume and reaction rate, respectively, of the  $m$ th mineral. The liquid flux  $\mathbf{J}_j^l$  appearing in these equations is defined by

$$\mathbf{J}_i^l = -\phi \tau s_l D_l \nabla C_i^l + \mathbf{q}_l C_i^l, \quad (18)$$

and the gas flux by the equation

$$\mathbf{J}_i^g = -\phi \tau s_g D_g \nabla C_i^g + \mathbf{q}_g C_i^g, \quad (19)$$

where  $D_\pi$  denotes the diffusion coefficient in phase  $\pi$  assumed to be the same for each species in a particular phase. For species-independent diffusion coefficients the solute flux  $\Omega_j^\pi$  simplifies to the expression

$$\Omega_j^\pi = (-\tau \phi s_\pi D_\pi \nabla + \mathbf{q}_\pi) \Psi_j^\pi, \quad (20)$$

involving directly the generalized concentration  $\Psi_j^\pi$ .

These equations are completely general and include both the solvent and solute species, and gases. Solving the solute and gas mass conservation equations provides not only the concentrations of both primary and secondary species, but also the mineral reaction rates. Combined with mineral mass transfer equations, an energy balance equation, constitutive relations for rock properties, kinetic rate laws and mass action relations, and finally initial and boundary conditions, they completely describe the system.

### Constitutive Relations

*Rock Properties.* Capillary pressure and relative permeability are related to saturation by the van Genuchten relations [11]. The equivalent continuum model is used to account for highly fractured rock such as characterizes Yucca Mountain tuff [2]. Vapor pressure lowering is taken into account which may raise the temperature at which liquid water is stable considerably above 100°C at 1 bar.

By relating permeability to porosity, it is possible to couple changes in porosity resulting from mineral precipitation and dissolution to the flow field and transport of solutes. One possibility is a simple power law relation of the form

$$k = k_0 \left( \frac{\phi}{\phi_0} \right)^n. \quad (21)$$

Porosity and mineral volume fractions in turn are related by an equation of the form

$$\phi = 1 - \sum_{m=1}^{N_m} \phi_m. \quad (22)$$

However, this expression is not completely general and may be deceptively simple because no distinction is made between connected and total porosity. Other forms relating porosity and permeability are also possible. However, very little data is available to better constrain the change in permeability with changes in porosity.

*Mass Action Equations.* Constitutive relations in the form of mass action equations are required for aqueous and gaseous species. The concentration of aqueous and gaseous secondary species are related to the concentrations of primary species by the equation

$$C_i^\pi = (\gamma_i^\pi)^{-1} K_i^\pi \prod_{j=1}^{N_c} (\gamma_j^\pi C_j^\pi)^{\nu_{ji}^\pi}, \quad (23)$$

where  $\gamma_i^\pi$  denotes the activity coefficient, and  $K_i^\pi$  the equilibrium constant associated with phase  $\pi$ . The equilibrium constants  $K_i^\pi$  are in general functions of temperature and pressure.

*Kinetic Rate Law.* Mineral reactions are assumed to be irreversible, their reaction rates described through a kinetic rate law. For simplicity and because of lack of knowledge of detailed reaction mechanisms, mineral reactions are represented by an overall reaction between the solid and aqueous solution. The form of the reaction rate is based on transition state theory. Precipitation or dissolution may occur depending on the sign of the affinity  $A_m$  of the reaction, defined by

$$A_m = -RT \ln K_m Q_m, \quad (24)$$

with equilibrium constant  $K_m$ , gas constant  $R$ , and  $Q_m$  the ion activity product defined by

$$Q_m = \prod_{j=1}^{N_c} (\gamma_j C_j)^{\nu_{jm}}. \quad (25)$$

The mineral reaction rate  $I_m$  has the form

$$I_m = \begin{cases} -k_m s_m \left[ \prod_i a_i^{n_i} \right] (1 - e^{-A_m/RT}), & \text{if } \phi_m > 0, \text{ or if } \phi_m = 0 \text{ and } A_m < 0, \\ 0, & \text{otherwise,} \end{cases} \quad (26)$$

where  $k_m$  denotes the kinetic rate constant,  $s_m$  denotes the mineral surface area participating in the reaction,  $a_i$  represents the activity of the  $i$ th species, and  $n_i$  is a constant. This form of the rate takes into account the moving boundary nature of the transport-reaction problem. The rate has units of moles per unit time per unit volume of bulk porous medium and is taken as positive for precipitation and negative for dissolution. Thus it represents the average rate taken over a REV. The rate law given by Eqn.(26) should really be referred to as a pseudo-kinetic rate law. Because it refers to the overall mineral precipitation/dissolution reaction, it generally does not describe the actual kinetic mechanism by which the mineral reacts. Nevertheless, it provides a useful form to describe departures from equilibrium. Close to equilibrium the rate becomes proportional to the chemical affinity. The temperature dependence of the kinetic rate constants may be calculated from the expression:

$$k_m(T) = \frac{T k_m^0}{T_0} \exp \left[ - \left( \frac{1}{T} - \frac{1}{T_0} \right) \frac{\Delta H_m^\ddagger}{R} \right], \quad (27)$$

where  $k_m^0$  denotes the rate constant at  $T_0$  and  $\Delta H_m^\ddagger$  denotes the enthalpy of activation. For a typical activation energy of 35 kJ mole<sup>-1</sup> corresponding to the kinetic rate constant for feldspar, a 100°C increase in temperature implies an increase in the rate constant by more than one and a half orders of magnitude from its value at 25°C.

#### SEQUENTIALLY COUPLED TWO-PHASE FLOW AND TRANSPORT

A sequentially coupled methodology is used to solve the multidimensional, multiphase, multicomponent fluid and solute flow and transport equations in a partially saturated porous medium. In this approach, heat, air-water vapor, and solvent mass conservation equations are solved separately from solute mass conservation equations. Thus at each new time step, first the heat and mass flow equations are solved simultaneously to obtain the temperature, pressure, saturation and flow field as functions of distance. Second, chemically reacting solutes are transported using the results obtained from solving the heat and solvent mass conservation equations. As a third step, mineral concentrations are calculated enabling changes in porosity, tortuosity and permeability to be computed which can then alter the flow field. This three-step approach can be justified based on the different time scales of the processes involved. Thus, alteration of rock properties through chemical reactions proceeds much more slowly compared to changes in the aqueous solution composition and flow and temperature fields caused by decay of the radioactive waste form. Another way to put it, the system adjusts quasi-statically to chemical alteration of the host rock [4, 5]. The sequentially coupled approach is expected to be a good approximation for sufficiently dilute solutions in which density corrections are not important. To carry out this scheme, the code MULTIFLO was developed. MULTIFLO consists of two modules: METRA (Mass and Energy TRANsport) and GEM (General Electrochemical Migration). METRA is similar to other two-phase codes such as TOUGH [8]. The code GEM [6] consists of the reactive transport part of the MULTIFLO code.

The code METRA uses a fully implicit finite difference scheme with upstream weighting. The jacobian is computed analytically. Several solution schemes are possible including a D4 ordered direct solver and the WATSOLV conjugate gradient solver [12]. The time-stepping algorithm used in GEM involves different strategies depending on the dimensionality of the problem. For 1D systems, a fully implicit time-stepping algorithm is used with dynamically

computed adaptive time steps. For 2D and 3D problems, an operator splitting algorithm is employed in which flow and transport time steps are decoupled from the chemical algorithm.

A Leonard-TVD scheme is used for describing high Peclet number flows. Several different solver options are available for inverting the sparse jacobian matrix. For 1D problems, a block tridiagonal solver is used, and for 2D and 3D problems, the conjugate gradient solver WATSOLV is used. MULTIFLO employs efficient dynamic memory allocation providing reduced storage requirements.

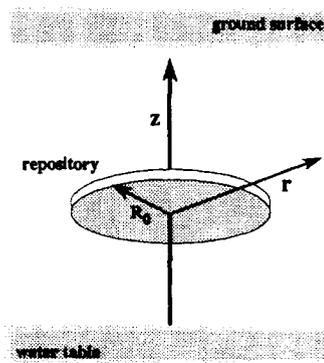


Figure 1: Liquid saturation profile.

### APPLICATION TO THE PROPOSED NUCLEAR WASTE REPOSITORY AT YUCCA MOUNTAIN, NEVADA

In this section the two-phase reactive transport equations are applied to the proposed Yucca Mountain repository. A moderate heat loading of 80 kW acre<sup>-1</sup> is assumed in the calculations. With this heat load a liquid phase is always present and complete dryout does not occur following emplacement of the waste. The Yucca Mountain host rock is modeled in these preliminary calculations as pure amorphous silica with 10% porosity. This assumption is considered reasonable for the purpose of the calculations presented here which is to estimate the change in salinity caused by evaporation and condensation process. The kinetic rate law proposed in [10] was used in the calculations. The initial fluid composition is taken to have pH 6.9, log P<sub>CO<sub>2</sub></sub> = -1.627, and total concentrations of Cl<sup>-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and SiO<sub>2</sub> of 0.18, 0.1, 2.0, 0.29, and 1.1 mmol L<sup>-1</sup>, respectively, corresponding to J-13 groundwater sampled from YM.

#### Results

Preliminary results are presented of a 1D calculation using the computer code MULTIFLO along the vertical through the centerline of the repository located 375 m below the ground-surface and 225 m above the water table, as indicated schematically in Fig. 1. Near the center of the repository a 1D calculation has been demonstrated to accurately represent the behavior of the system. The temperature profile plotted as a function of depth below the ground surface is shown in Fig. 2 for times of 10, 25, and 50 years. The maximum temperature obtained for this heat load is approximately 130°C, which occurs after an elapsed time of about 50 years. The liquid saturation profile is shown in Fig. 3. Above and below the repository horizon the pore spaces become almost fully saturated during the dryout period. This saturation state is a dynamic condition caused by continuous evaporation of liquid drawn toward the repository by capillary forces and condensation further away in cooler regions, as shown in Fig. 4. The resulting pH profile is shown in Fig. 5 and the chloride concentration in Fig. 6. In the region in which evaporation occurs, the pH dramatically increases as CO<sub>2</sub> degasses from the liquid phase. Likewise the chloride concentration increases by approximately a factor of 4. By contrast, in the condensation zones the pH and chloride concentration decrease from their ambient values as expected since the condensing liquid is devoid of dissolved salts.

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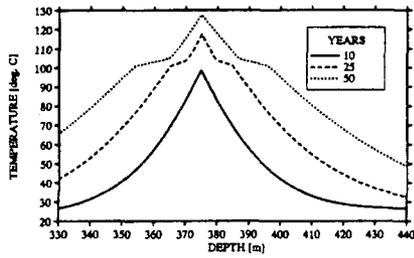


Figure 2: Temperature profile.

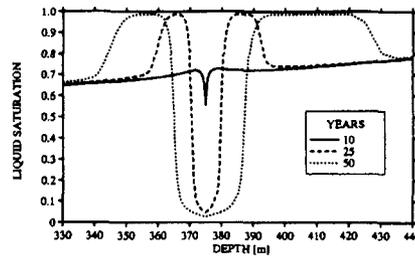


Figure 3: Liquid saturation profile.

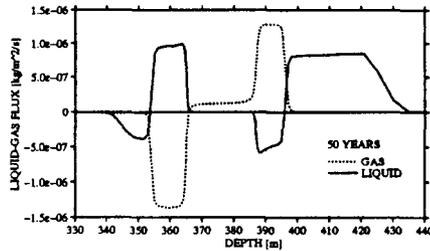
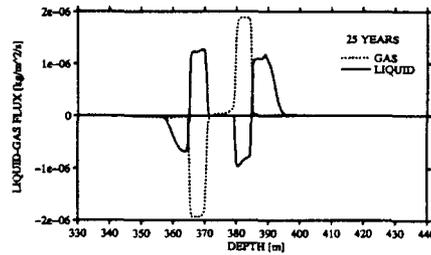
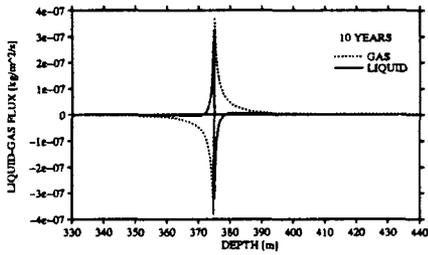


Figure 4: Liquid and gas fluxes plotted as a function of depth for the indicated times.

## CONCLUSION

This work investigated the effects of liquid evaporation and condensation on the possibility of brine formation in the near-field region of a HLW repository located in a partially saturated host rock. This work provided the conceptual and mathematical framework for such an endeavor. Such calculations involve two-phase fluid transport coupled to multicomponent solute and gas transport and fluid/rock interaction. Results showed that significant changes in pH and salinity could occur with moderate thermal loading of the repository.

This work was funded by the U.S. Nuclear Regulatory Commission. This paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

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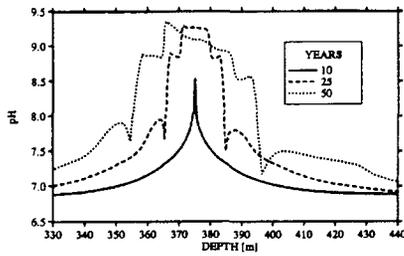


Figure 5: Computed pH profile.

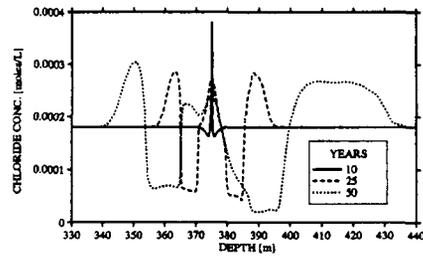


Figure 6: Chloride concentration.

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