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# A Stochastic Model for the Nuclide Migration in Geologic Media Using a Continuous Time Markov Process

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# 연속시간 마코프 프로세스를 이용한 지하매질에서의 통계적 핵종이동 모델

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## Abstract

A stochastic method using continuous time Markov process is presented to model the one-dimensional convective nuclide transport in geologic media, which have usually heterogeneous feature in physical/geochemical parameters such as velocity, dispersion coefficient, and retardation factor resulting poor description by conventional deterministic advection-dispersion model. The primary desired quantities from a stochastic model are the mean values and variance of the state variables as a function of time. The time-dependent probability distributions of nuclides are presented for each discretized compartment given the volumetric groundwater flux and the intensity of transition. Since this model is discrete in medium space, physical/geochemical parameters which affect nuclide transport can be easily incorporated for the heterogeneous media as well as remarkably layered media having spatially varied parameters. Even though the Markov process model developed in this study was shown to be sensitive to the number of discretized compartments showing numerical dispersion as the number of compartments are increased, this could be easily calibrated by comparing with the analytical deterministic model.

## 요 약

연속시간 마코프프로세스를 이용한 한 통계적방법에 의한 일차원 지하 핵종이동 모델이 제시되었다. 지하매질은 보편적으로 지하수속도, 분산계수 또는 지연계수 등 물리화학적 변수 등의 비균

질성을 보여 일반적인 결정론적 이류분산모델로는 잘 기술되지 않는다. 통계적 모델에서의 최종결과는 시간에 따른 함수로서의 기대값과 그 기대값의 분산도를 보여주는 분산치다. 매질이 균질하다고 생각될 정도로 나뉘어진 구획에 대한 핵종의 농도 분포를 구하여 결정론적인 해석해에 의한 농도분포와 비교하여 비균질 매질, 또는 현저하게 구분되는 다층매질의 경우에 대해서 유용할 것이라는 결론을 얻었다. 매질을 나눈 구획수가 수치적 분산에 민감한 것으로 나타났지만 해석적 모델에 의해 분산계수가 보정될 수 있었다.

## 1. Introduction

In case of simulating nuclide transport and groundwater flow through the geologic media around the repository in which radioactive wastes are disposed of, various approaches have been considered either in deterministic way or in stochastic way.

Groundwater flow and nuclide transport in natural geologic system have been found to be poorly described by the conventional deterministic advection–dispersion concept and equations. Furthermore, even the spatial variability of such system is comparatively well–known, it is often ignored when the deterministic models are formulated. It was reported that when deterministic approach is introduced, overlooking these heterogeneous features of the media may lead to incorrect predictions of the solute transport [1]. The spatially dependent physical/geochemical parameters (such as velocity, dispersion coefficient, and retardation factor) which govern the transport are accounted for in some stochastic approach by means of discretizing the medium[2], which is similar to the concept for multilayered media modeling.[3–4]

One stochastic process which has been successfully applied in various fields is the Markov process [5,6]. Using continuous time Markov process, the number of nuclides, or equivalent nuclide concentrations in heterogeneous geologic media can be modeled considering the nuclide distribution as a time–dependent random variable in a series of discretized compartments of such media : A nuclide could move from any present compartment in a given time interval (emigration process), could enter any compartment newly (immigration), and also could disappear from any present compartment due to radioactive decay (deaths). All these processes are conditional only on the present location of the nuclide regardeless of its present history utilizing the Markov conceptualization of the geologic system, which could be considered the geologic system as discretized serial geologic compartments. That is the reason why the Markov process can be applied to.

The objective of this research is to use the Markov process to describe one–dimensional convective transport of nuclides through the medium in the vicinity of the radioactive waste repository. The primary desired quantities from a stochastic model are the mean values and variance of the state variables as a function of time. To this end probability distributions of nuclides are presented for each discretized compartment given the volumetric groundwater flux as a source term and the intensity of transition as a sink term.

## 2. Continuous-Time Markov Process

When $\{X(t),\ t\geq 0\}$ is a continuous–time stochastic discrete process, it is a continuous–time Markov process if all $s$, $t\geq 0$, and for any non-negative integers, $s=i,\ j,\ i_{n-1},\ \cdots,\ i_0$

$$\Pr\{X(t_n)=j \mid X(t_{n-1})=i,\ X(t_{n-2})=i_{n-2},\cdots,X(t_0)=i_0\}=$$
$$\Pr\{X(t_n)=j \mid X(t_{n-1})=i\} \quad (1)$$

In other words, a continuous–time Markov process is a stochastic process having the Markov property that the conditional distribution of the future state $j$ at time $t_n$, given the present state $i$ at time $t_{n-1}$ and all past states depends only on the present state and is independent of the past history.

If, in addition, $\Pr\{X(t_n)=j \mid X(t_{n-1})=i\}$ is independent of $t_{n-1}$, then Markov process is said to have stationary or homogeneous transition probabilities.

For $t_1<t_2$ the transition probability function is defined as

$$P_{ij}(t_1,t_2)=\Pr\{X(t_2)=j \mid X(t_1)=i\} \tag{2}$$

where $P_{ij}(t_1, t_2)$ does not depend on the values of X(t) for $t<t_1$.
Also $P_{ij}(t_1, t_2)$ satisfies

$$\sum_j P_{ij}(t_1,t_2)=1 \tag{3}$$

According to the Markov property, a set of differential equations for $P_{ij}(t_1, t_2)$, which may sometimes explicitly be solved, can be derived [5]. For homogeneous Markov process, since $P_{ij}(t_1, t_2)$ )depends only on the difference $(t_2-t_1)$,

$$P_{ij}(t_1,t_2)=P_{ij}(t_2-t_1), \tag{4}$$

which results in Chapman–Kolmogorov equation, by which the $P_{ij}(t_1, t_2)$ can be computed:

$$P_{ij}(t_1,t_2)=\sum_k P_{ik}(t_1,\tau)P_{kj}(\tau,t_2) \tag{5}$$

or equivalently for small time interval $\Delta t$

$$P_{ij}(0,t+\Delta t)=\sum_k P_{ik}(0,t)P_{kj}(0,\Delta t) \tag{6}$$

where the subscript $k$ represents an intermediate state between $i$ and $j$.

Let $\lambda_{ij}$ be the intensity of transition from compartment $i$ to compartment $j$ such that $\{\lambda_{ij}\ \Delta t+o(\Delta y)\}$ becomes the probability that the process makes a transition from $i$ to $j$ during $\Delta t$, where $o(\Delta t)$ represents higher–order terms which become insignificant as $\Delta t$ tends to zero.

Similarly $\eta_i\Delta t+o(\Delta t)$ is defined as the probability that the process leaves state $i$. Therefore the probability the process will remain at $t+\Delta t$ in $i$ without any transition is $\{1-[\Sigma_{j=1}\lambda_{ij}\Delta t+\eta_i\Delta t]+o(\Delta t)\}$, from which, if this probability is denoted by $\{1+\lambda_{ij}\Delta t+o(\Delta t)\}$,

$$\lambda_{ii}=-\left[\sum_{j\neq i}\lambda_{ij}+\eta_i\right],\ i=1,2,\cdots,n \tag{7}$$

By definition of derivative, Eq. (6) can be rewritten as

$$\frac{d}{dt}P_{ij}(0,t)=\sum_k P_{ik}(0,t)\lambda_{kj} \tag{8}$$

with the initial condition

$$P_{ij}(0,0)=\delta_{ij} \tag{9}$$

which is known as Kolmogorov forward differential equation and gives the relation between the rate of change of the transition probability and the intensity of transition.

In matrix notation.

$$\frac{d}{dt}\mathbf{P}(t)=\mathbf{P}(t)\ \Lambda=\Lambda\ \mathbf{P}(t) \tag{10}$$

and

$$\mathbf{P}(0)=\mathbf{I}\ \text{(the identity matrix)} \tag{11}$$

where

$$\mathbf{P}(t)=\begin{pmatrix} P_{11}(t) & P_{12}(t) & \cdots & P_{1n}(t) \\ P_{21}(t) & P_{22}(t) & \cdots & P_{2n}(t) \\ \vdots & & \ddots & \vdots \\ P_{n1}(t) & \cdots & \cdots & P_{nn}(t) \end{pmatrix} \tag{12}$$

and

$$\Lambda=\begin{pmatrix} \lambda_{11} & \lambda_{12} & \cdots & \lambda_{1n} \\ \lambda_{21} & \lambda_{22} & \cdots & \lambda_{2n} \\ \vdots & & \ddots & \vdots \\ \lambda_{n1} & \cdots & \cdots & \lambda_{nn} \end{pmatrix}. \tag{13}$$

A method to evaluate the transition probabilities corresponding to the transition intensity matrix $\Lambda$ are decribed briefly in Appendix [7,8]. Another method of obtaining transition probabilties without the eigenvectors is also available [e.g.7].

### 3. Transition Intensity

The porous medium through which nuclide migrates can be considered as a finite number of $n$

compartments with different processes occurring simultaneously within compartments. These processes include the advective transport of nuclides due to flow of groudwater, sorption of nuclides onto surface of soil or rock, radioactive decay, and so on.

Once, such geologic system is assumed to have Markov property, since the Markov process requires that only the present value of the time dependent random variable (i. e., time dependent number of nuclides or concentration in certain compartment) be known to determine the future value of the random variable, the nuclide migration in geologic media, which is divided by finite number of geologic compartments, can be modeled as a time continuous Markov process, which is continuous in time with respect to the individual transport processes but discrete in space.

The transition probability from a compartment, $i$ to another compartment, $j$ is affected by the intensity of transition as described in the previous section. These transition intensities are related to the processes involved. In this study only three processes such as transport due to groundwater flow, sorption and radioactive decay are assumed to be incorparated. However, diffusive transport of nuclide is assumed to be negligible compared to advective transport for the media having large Peclet number.

First, the transition intensity for the groundwater flow through some pore volume in porous medium can be written as

$$h_{ij} = \frac{Q_{ij}}{V_i}. \qquad (14)$$

Assuming that flow is well mixed with regard to groundwater and nuclides, transition probability due to advection can be written as

$$h_{ij}\,\Delta t + o(t) = \Pr\{\text{a nuclide in i at t will be in j at } (t+\Delta t)\}. \qquad (15)$$

Similarly, nuclide can be decayed out from compartment $i$ at a rate represented by decay constant. Therefore,

$$\lambda_d\,\Delta t + o(t) =$$
$$\Pr\{\text{a nuclide at t will be decayed out at } (t+\Delta t)\}. \qquad (16)$$

Under the assumption of linear isotherm sorption of nuclides in the medium can be introduced into the retardation of nuclide as $\lambda_{ij}/R_i$, where $R_i$, the retardation factor, is written for homogeneous compartment $i$ of porous medium as

$$R_i = \left(1 + \frac{\rho_b K_d^i}{\phi_i}\right). \qquad (17)$$

With these relatioship Eq. (7) can be rewritten as

$$\lambda_{ii} = -\left[\sum_{j\neq i} \frac{h_{ij}}{R_i} + \lambda_d\right],\ i = 1, 2, \cdots, n \qquad (18)$$

where $\lambda_{ii}$ is interpretted as the negative sum of all probabilities of exit from compartment $i$.

## 4. Nuclide Distributions

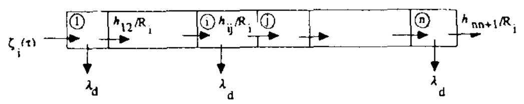


**Fig. 1. Schematic Representation of Discretized Compartments.**

Now let $X_i(t)$ be the random variable representing the number of nuclides in compartment $i$ at time $t$. For all $n$ compartments,

$$\mathbf{X}(t) = [X_1(t)\ X_2(t) \cdots X_n(t)]. \qquad (19)$$

Random vector $\mathbf{X}(t)$ is composed of $\mathbf{Y}(t)$ and $\mathbf{Z}(t)$,

$$\mathbf{X}(t) = \mathbf{Y}(t) + \mathbf{Z}(t), \qquad (20)$$

where

$$\mathbf{Y}(t) = [Y_1(t)\ Y_2(t) \cdots Y_n(t)] \qquad (21)$$

is the number of survived nuclides, which were originally in the system at t=0, and

$$\mathbf{Z}(t) = [Z_1(t)\ Z_2(t) \cdots Z_n(t)] \qquad (22)$$

is the number of nuclides that have entered the system during the time interval (0, t) and have survived in the respective compartment at $t$. Nuclides in **$Z(t)$** represent new additions and are not due to initial nuclides at $t=0$.

First, $m_i(0)$ denote the number of nuclides in i at $t=0$. At time t, each of the $m_i(0)$ must be either in one of the n compartments or disappear due to radioactive decay. Hence,

$$m_i(0)=\sum_{j=1}^{n} Y_{ij}(t)+D_i(t) \tag{23}$$

where $Y_{ij}(t)$ and $D_i(t)$ are random variables representing the number of nuclides in $j$ at $t$, which were in $i$ at time $0$, and the number of nuclides, which were in $i$ at time $0$, disappearing by time $t$ due to decay from the system, respectively.

For a given $m_i(0)$, the distribution of $Y_j(t)$, the remaining survived nuclides, at $t$ has multinomial distribution according to $\Sigma_j P_{ij}(t)=1$. It is easy to see that

$$Y_j(t)=\sum_{i=1}^{n} Y_{ij}(t). \tag{24}$$

The expected number and the variance of $Y_j(t)$ can be obtained by using familiar formulae of the multinomial distribution as

$$\mathrm{E}[Y_j(t)]=\sum_{i=1}^{n} m_i(0)P_{ij}(t) \tag{25}$$

and also,

$$\mathrm{Var}[Y_j(t)]=\sum_{i=1}^{n} m_i(0)P_{ij}(t)\{1-P_{ij}(t)\} \tag{26}$$

These expectation and variance allow us make statistical inference as to the predictive ability of the model.

Now at any time $\tau$ between time $0$ and $t$, suppose that nuclides flow into each compartment at rate of $\zeta_i(\tau)$ per unit time. $\zeta_i(\tau)$ is equal to the volumetric flow rate of nuclides into compartment $i$ and may be expressed as

$$\zeta_i(\tau)=Q_i C_i(\tau) \quad V_i \tag{27}$$

As soon as a freshly fed nuclide enter a compartment, it may begin to transfer to another compartment at once or may decay out. Therefore, vector $Z(t)$ is the outcome of sequences of events of input, transition between the compartments, and survival from the decay out.

The number of new nuclides that have entered a compartment is $\zeta_i(\tau)d\tau$. If we let $\zeta_i$ be the number of nuclides that have successfully entered compartment $i$, then it has a respective probability of $P_{ij}(t-\tau)$ either entering or remaining there. Therefore a binomial distribution can be formed for these new nuclides. Letting $Z_i(t)$ represent a random variable which is the number of nuclides available for entry to compartment i in the time interval $(\tau,\ t)$,

$$\Pr\{Z_i(t)=z_i\}=\frac{[\zeta_i(\tau)\,d\tau]!}{\{[\zeta_i(\tau)\,d\tau]-z_i\}!z_i!}P_{ij}(t-\tau)^{z_i}[1-P_{ij}(t-\tau)]^{[\zeta_i(\tau)\,d\tau-z_i]} \tag{28}$$

For large value of $\zeta_i(\tau)d\tau$ the binomial distribution is approximated to Poisson distribution.

$$\Pr\{Z_i(t)=z_i\}=\exp\{\zeta_i(\tau)\,d\tau P_{ij}(t-\tau)\}\frac{\{\zeta_i(\tau)\,d\tau P_{ij}(t-\tau)\}^{z_i}}{z_i!} \tag{29}$$

where $\zeta_i(\tau)d\tau\ \ P_{ij}(t-\tau)$ is the expected number of nuclides in $j$ at time $t$ that have entered from $\zeta_i(\tau)d\tau$ nuclides. Statistically, since nuclides could enter through any compartment and each of these events is independent of each other for distinct $\tau$, the Poisson distribution is a good approximation. For Poisson distribution mean and variance of $Z_i(t)$ are commonly expressed as

$$\mathrm{E}[Z_j(t)]=\mathrm{Var}[Z_j(t)]=\int_0^t\sum_{i=1}^{n}\zeta_i(\tau)\,d\tau P_{ij}(t-\tau)\,d\tau. \tag{30}$$

Finally we can get, from Eqs. (20, 25–26, 30), the distribution of $X_j(t)$, the number of nuclides remaining in each compartment that have survived, as the convolution of the two independent distributions, $Y_j(t)$ and $Z_j(t)$ :

$$\mathrm{E}[X_j(t)]=\sum_{i=1}^{n} m_i(0)P_{ij}(t)+\int_0^t\sum_{i=1}^{n}\zeta_i(\tau)P_{ij}(t-\tau)\,d\tau \tag{31}$$

$\mathrm{Var}[X_j(t)] =$

$$\sum_{i=1}^{n} m_i(0)P_{ij}(t)\{1-P_{ij}(t)\} + \int_{0}^{t} \sum_{i=1}^{n} \zeta_i(\tau)P_{ij}(t-\tau)\,d\tau \quad (32)$$

Therefore, the mean and variance of $C_j(t)$, concentration of nuclides in $j$ at time $t$ are. respectively,

$$E[C_j(t)] = \frac{E[X_j(t)]}{V_j} \quad (33)$$

$$\mathrm{Var}[C_j(t)] = \frac{\mathrm{Var}[X_j(t)]}{V_j} \quad (34)$$

where $V_j$ is the pore water volume of compartment $j$.

### 5. Numerical Illustration

To demonstrate the use of the present stochastic model using Markov process and to verify the stochastic model by comparing with the deterministic model, two specific simple calculations of nuclide profiles for a column packed with homogeneous porous soil and also for a two--layered column packed with two different, but homogeneous porous soils are presented. As is seen in Fig. 2, let's consider a special case of the $n$ serial discretized compartments of equal size in which complete mixing takes place. Nuclides enter the system only through the first compartment and leave it through the last compartment.

For the first example, the expression of the mean and variance of the concentration of a nuclide is formulated and computed.

The assumed column data are listed in Table 1.

For simplicity, several assumptions were introduced to the specific example : first, the groundwater flow is constant and is saturated for all column region ; second, the groundwater flow and nuclide transport are considered to be made only

**Table 1. Column Data Values Used.**

| Soil column | Value |
|---|---|
| Dimension | 10 $cm^{\phi}$ ×90 $cm^{L}$ |
| Volumetric flow rate, Q[$cm^3$/y] | 185.6 |
| Porosity of soil, $\phi$ [$cm^3/cm^3$] | 0.36 |
| Bulk density of soil, $\rho_b$[g/$cm^3$] | 1.6 |
| Number of discretized compartments, n | 18 |

between adjacent soil compartments without upward flow ; and finally, both of decay out (for firsr example) and sorption of nuclide are negligible, which do not affect the validity of the model.

Under the assumption made above, the transition intensity matrix in Eq. (13) becomes

$$\Lambda = \begin{pmatrix} -h & h & & 0 \\ & -h & h & \\ & & \ddots & \ddots \\ & & & \ddots & h \\ 0 & & & & -h \end{pmatrix} \quad (35)$$

which has single eigenvalue of $-h$ with multiplicity n and from which the transition probability $\{P_{1j}(t),$ j=1, ···, n$\}$ can be obtained through Eq. (10) as follows [see Appendix] :

$$P(t) = Q \begin{pmatrix} e^{-ht} & & 0 \\ & e^{-ht} & \\ & & \ddots & \\ 0 & & & e^{-ht} \end{pmatrix} Q^{-1} \quad (36)$$

Furthermore, according to Eq. (19),

$$X_i(0) = 0 \quad (37)$$

Also, if nuclides are fed to the first compartment of the system at a constant rate of $\zeta_i$,

$$\zeta(\tau) = [\zeta_1\ 0 \cdots 0]_, \quad (38)$$

For the second example, assuming fundamental column data are the same as those listed in Table 1. except the inclusion of the radioactive decay term as a sink, $^{90}Sr$ was considered as a nuclide. However, some variation was made to demons-

**Table 2. Variation of the Volumetric Flow Rate for Second Layer.**

| No. runs | Begining no. of second layer | Volumetric flow rate [cm$^3$/y] | |
|---|---|---|---|
| | | 1$^{st}$ Layer | 2$^{nd}$ Layer |
| 1 | 6 out of 18 | 185.6 | 185.6×0.5 |
| 2 | 6 out of 18 | 185.6 | 185.6×0.75 |
| 3 | 6 out of 18 | 185.6 | 185.6 |

trate the sensitivity of such main parameters as volumetric flow rate of groundwater and decay constant, as listed in Table 2.

Also in this example the soil column was considered to have two separately layered media, each of which has homogeneous volumetric groundwater flow rate and is discretized into $n_i$ layers. In this study $n_I=6$ and $n_{II}=12$ were used.

By means of the same procedure given previously in the first case, the transition intensity matrix may be written

$$\Lambda = \begin{pmatrix} \begin{array}{ccc|ccc} -h_1-\lambda_d & h_1 & & & & \\ & -h_1-\lambda_d & h_1 & & 0 & \\ & & \ddots & \ddots & & \\ \hline & & & -h_2-\lambda_d & h_2 & \\ & 0 & & & -h_2-\lambda_d & \end{array} \end{pmatrix} \tag{39}$$

which has two eigenvalues of $-h_1-\lambda_d$ and $-h_2-\lambda_d$ with multiplicity of discretized number of each layer.

Therefore, the transition probability $\{P_{1j}(t),\ j=1, \cdots, n\}$ can be obtained as follows [see Appendix]

$$\mathbf{P}(t) = \mathbf{Q}\begin{pmatrix} \mathbf{E}_1(t) & 0 \\ 0 & \mathbf{E}_2(t) \end{pmatrix}\mathbf{Q}^{-1} \tag{40}$$

Meanwhile, for layered semi-infinite column, 1-dimensional advection-dispersion equation for $\ell$th layer is

$$R_l\frac{\partial C}{\partial t} - \frac{q_l}{\phi_l}\frac{\partial C}{\partial x_l} - D_l\frac{\partial^2 C}{\partial x_l^2} - \lambda_d R_l C = 0 \tag{41}$$

with the initial- and boundary conditions for first layer

$$C(x_1, 0) = 0 \tag{42}$$

$$C(0, t) = C_0 e^{-\lambda t} \tag{43}$$

$$C(\infty, t) = 0 \tag{44}$$

An analytical solution for the first layer, subject to Eqs. (42–44), is available :

$$\frac{C(x_1,t)}{C_0} = \frac{1}{2}\exp(-\lambda t)\left\{\mathrm{erfc}\left(\frac{x_1 - q_1/(\phi_1 R_1)t}{\sqrt{4D_1/R_1 t}}\right)\right.$$
$$\left. + \exp\left(\frac{q/(\phi_1 R_1)x_1}{D_1/R_1}\right)\mathrm{erfc}\left(\frac{x_1 + q_1/(\phi_1 R_1)t}{\sqrt{4D_1/R_1 t}}\right)\right\} \tag{45}$$

In the second layer, the boundary conditions are the same to Eq. (44) and at $x_2=0$

$$C(x_2=0, t) = C(x_1=L_1, t) \tag{46}$$

The initial condition for second layer is again

$$C(x_2, 0) = 0 \tag{47}$$

For second layer, a solution, subject to the above initial- and boundary conditions, is [4]

$$C(x_2, t) = \int_0^t C(x_1 = L_1, \tau)\, k(x_2, t-\tau)\, d\tau \tag{48}$$

where

$$k(x_2, t) = \frac{x_2}{\sqrt{4\pi D_2 t^3}}\exp\left(\frac{q/(\phi_1 R_1)x_1}{2D_1/R_1}\right)$$
$$\times\exp\left\{-\frac{[q/(\phi_1 R_1)]^2 t}{4D_1/R_1} - \frac{x_2^2}{4D_1/R_1 t}\right\} \tag{49}$$

A plot of normalized concentration as a function of distance in the soil column is shown in Fig. 2, in which standard deviation, $\sigma$, nonnegative sqare root of the variance, which is one of the most important moments of a distribution, is used as a measure of the dispersion of a distribution about its mean value.

Also, from Fig. 3, it is known that the Markov process model presented here is well agreed to analytical solution of Eq. (45) with some calibration of value of dispersion coefficient, even though, as shown in Eq. (48), numerical integration procedure to evaulate the concentration for the second layer might be accompanied with some truncation error. For integration of Eq. (48), Gaussian quadrature scheme was used. The Markov process model presented in this study were found to be sensitive to the number of compart-

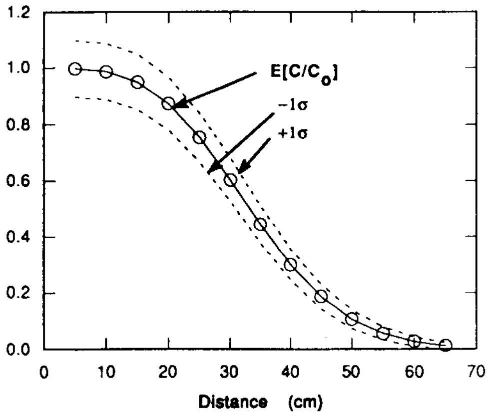


Fig. 2. Expectancy and Variance of the Normalized Concentration Profiles of a Nuclide at Time =5 hrs.

ment, which results in change of length of compartment for fixed column length. In this figure the effect of the model due to change of the compartment size through 9 cm to 3.6 cm resulting in the change of number of compartments through n= 10 to n=25 is shown. As known from the figure increasing the number of compartment from 10 to 25 decreases the dispersion. With calibrated dispersion coefficient the concentration profiles were investigated by increasing time from t=1 hr to $10^5(\simeq\infty)$ hrs, some of whose results are illustrated in Fig. 4. Although compartment size or number of compartments introduces numerical dispersion, however, with small compensating of dispersion coefficient, the model agrees well to exact analytical solutions.

Fig. 5 is a plot of normalized concentration profiles for $^{90}Sr$ concentration for double-layered column when the volumetric flow rate of groundwater is varied as listed in Table 2. The predicted points denoted by filled symbols represent an estimated mean concentration of $^{90}Sr$ as calculated

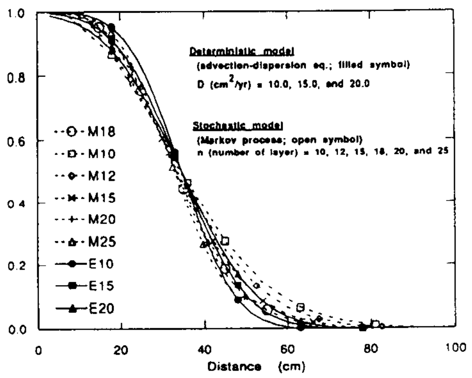


Fig. 3. Expectancy of the Normalized Concentration Profiles of a Nuclide at Time=5 hrs Computed by Markov Process Model with Varying Number of Compartments, Compared with Advection-Dispersion Model with three Arbitrary Values of Dispersion Coefficients [Eq.(45)].

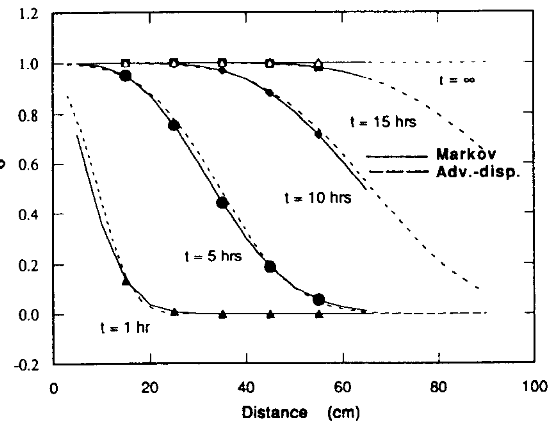


Fig. 4. Expectancy of the Normalized Concentration Profiles of a Nuclide Computed by Markov Process Model (n =15) with Varying Times Lapsed, Compared with Advection-Dispersion Model with Dispersion Coefficient of 15.0 [Eq.(45)].

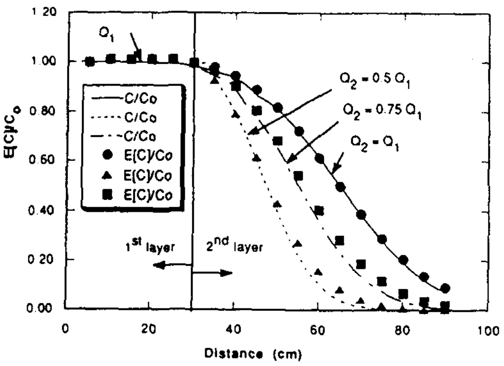


**Fig. 5. Expectancy of the Normalized Concentration Profiles of Sr-90 Computed by Markov Process Model for Double-Layered Porous Media at Time t=10 yrs with Varying Volumetric Flow Rates of the 2nd Layer by Factors of 0.5, 0.75, and 1.0 with Respect to the 1st Layer, Compared with Advection-Dispersion Model with Three Arbitrary Values of Dispersion Coefficients [Eqs.(45 and 48)].**

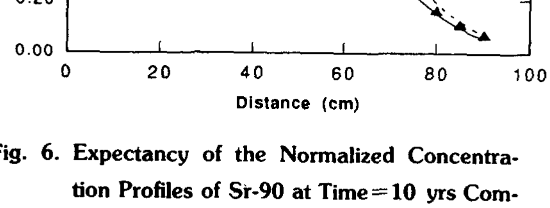


**Fig. 6. Expectancy of the Normalized Concentration Profiles of Sr-90 at Time=10 yrs Computed by Markov Process Model Including the Radioactive Decay Term(half-life=30.2 yrs), Compared with Advection-Dispersion Model with Three Arbitrary Values of Dispersion Coefficients [Eqs.(48 and 51)].**

by Markov process model, while the lines represent the concentration by the exact analytical solutions (Eqs. (45,48–49)).

Also, for the case that radioactive decay is included as a sink term, a sample calculated profile is shown compared with the analytical result is as shown in Fig. 6.

## 6. Conclusions

Through this study a stochastic modeling approach using a continuous-time Markov process for the one-dimensional convection transport of nuclides through the medium around the repository has been carried out. By calculating the time-dependent transition probability of nuclide from the transition intensity between, into, and/or from the compartments utilizing Chapman-Kolmogorov equation, the expectation of distribution of nuclide concentration can be obtained as well as the variance of the concentration.

Since this model is discrete in medium space, physical/geochemical parameters including velocity, dispersion coefficient, and retardation factor, which effect nuclide transport can be easily incorporated for the heterogeneous media as well as remarkably layered media having spatially varied parameters.

Even though the Markov process model developed in this study were shown to be sensitive to the number of discretized compartment showing numerical dispersion as the number of compartments is increased, this could be easily calibrated by comparing with the anaytical deterministic model.

Therefore, using this model statistical distribution of the nuclide within the discrete compartment of heterogeneous media around the repository could be well modeled by discretizing the media considering the degree of variation of the parameters.

## Notation

$C_i(t)$ nuclide concentration in the feeding flux $Q_i$.

$C_i(t)$ nuclide concentration in compartment i at time $t$.

$D_i$ dispersion coefficient in compartment $i$, cm/year.

$D_i(t)$ random variable representing the number of nuclides in state $i$ at time $0$, disappearing by time $t$.

$E[X_i(t)]$ expectancy of $X_i(t)$.

$h_{ij}$ transition intensity from compartment $i$ to compartment $j$ due to groundwater flow.

$k$ kernel used in Eq. (48).

$K_d$ distribution coefficient of a nuclide of compartment $i$, cm$^2$/g.

$m_i(0)$ number of nuclides in compartment $i$ at time $0$.

$\boldsymbol{P}(t)$ transition probability matrix.

$P_{ij}(t)$ transition probability that a nuclide in state $i$ at time $0$ will be in state $j$ at time $t$.

$P_{ij}(t_1, t_2)$ transition probability that a nuclide in state $i$ at time $t_1$ will be in state $j$ at time $t_2$.

$\mathbf{Q}$ eigen raw matrix.

$\mathbf{Q}^{-1}$ inverse of eigen raw matrix.

$q_i$ Darcy velocity of groundwater in compartment $i$, cm/year.

$Q_i$ volumetric flow rate of feeding groundwater to compartment $i$.

$Q_{ij}$ volumetric flow rate from compartment $i$ to compartment $j$.

$R_i$ retardation coefficient in compartment $i$.

$s$, $i$, $j$ state or compartment of the geologic system.

$Var[X_i(t)]$ variance of $X_i(t)$.

$V_i$ volume of compartment $i$.

$X(t)$ random variable at time $t$.

$X_i(t)$ random variable representing the number of nuclides in compartment $i$ at time $t$.

$Y_i(t)$ random variable representing the number of survived nuclides in compartment $i$ at time $t$, which were originally in the system at time $0$.

$Y_{ij}(t)$ random variable representing the number of nuclides in state $j$ at time $t$, which were in state $i$ at time $0$.

$Z_i(t)$ random variable representing the number of nuclides in compartment $i$ at time $t$, which have entered the system during $(0, t)$.

### Greek Letters

$\beta_k$ left eigen vector of $\Lambda$ corresponding to the eigenvalues $\rho_k$.

$\delta_{ij}$ Kronecker delta function.

$\phi_i$ porosity of compartment $i$.

$\Lambda$ intensuty matrix.

$\lambda_d$ radioactive decay constant.

$\lambda_{ij}$ transition intensity from state $i$ to state $j$.

$\eta_i(t)$ transition intensity of exit from state/compartment $i$ at time $t$.

$\rho_b$ bulk density of compartment $i$.

$\rho_k$ eigenvalue of $\Lambda$.

$\xi_b$ right eigen vector of $\Lambda$ corresponding to the eigenvalues $\rho_k$.

$\zeta_i(\tau)$ feed rate of nuclides into compartment$i$

## Appendix

### Evaluation of P(t)

If the eigenvalues of $\Lambda$, $\rho_1$, $\rho_2$, $\cdots$, $\rho_n$, are real and distinct, then $\Lambda$ has eigen row matrix $\mathbf{Q}$, each column in which is the right eigenvector $\xi_k$ (as defined in Eq. (A2)) of $\Lambda$ corresponding to the eigenvalue $\rho_k$, and $\Lambda$ has another eigen column matrix $\mathbf{Q}^{-1}$, whose raws are the left eigenvector $\beta_k$ (as defined in Eq. (A3)) of $\Lambda$ corresponding to the eigenvalue $\rho_k$,, the solution of Eq. (10) is [9]

$$\mathbf{P}(t) = e^{\Lambda t} = \mathbf{Q}\,\mathbf{E}(t)\,\mathbf{Q}^{-1} \tag{A1}$$

The right eigenvectors, $\xi_k$ and left eigenvectors $\beta_k$ are defined by following Eqs. (A2) and (A3), respectively :

$$\Lambda\xi_k = \rho_k\xi_k,\ k=1,\cdots,n \tag{A2}$$

$$\beta_k^T\Lambda = \rho_k\beta_k^T,\ k=1,\cdots,n \tag{A3}$$

where

$$\mathbf{Q} = (\xi_1\ \xi_2 \cdots \xi_n), \tag{A4}$$

and

$$\mathbf{Q}^{-1} = \begin{pmatrix} \beta_1^T \\ \beta_2^T \\ \vdots \\ \beta_n^T \end{pmatrix} \tag{A5}$$

which result the diagonal matrix whose elements are the eigenvalues of $\Lambda$ :

$$\mathbf{Q}^{-1}\Lambda\mathbf{Q} = \begin{pmatrix} \rho_1 & & & 0 \\ & \rho_2 & & \\ & & \ddots & \\ 0 & & & \rho_n \end{pmatrix} \tag{A6}$$

and

$$\mathbf{E}(t) = \exp(\mathbf{Q}^{-1}\Lambda\mathbf{Q}) = \begin{pmatrix} e^{\rho_1 t} & & & 0 \\ & e^{\rho_2 t} & & \\ & & \ddots & \\ 0 & & & e^{\rho_n t} \end{pmatrix} \tag{A7}$$

If $\Lambda$ has repeated eigenvalues, $\rho_1$, $\rho_2,\cdots$, $\rho_a$ with respective multiplicities $n_1$, $n_2$, $\cdots$, $n_a$ such that $\Sigma_{i=1}^{a} n_i=n$, then it does not have $n$ linearly independent eigenvectors. In this case it is not posiible to find $\mathbf{Q}$ and $\mathbf{Q}^{-1}$, which diagonalize $\Lambda$. However, a form is possible which is almost diagonal called the Jordan canonical form. In this case, instead of eigenvectors, supplimentary vectors, which are required to form a nonsingular matrix: For example, suppose the eigenvalue, $\rho_1$ has multiplicity $n_k$. Since there are no sufficient eigenvectors to constitute $\mathbf{Q}$, $n_i-1$ more independent vectors are required. The supplementary vectors $g_j$ can be found with the only eigenvector, $\xi_k$ initially as following procedure:

$$(\Lambda - \rho_k\mathbf{I})\,\mathbf{g}_1 = \xi_k \tag{A8}$$

and

$$(\Lambda - \rho_k\mathbf{I})\,\mathbf{g}_j = \mathbf{g}_{j-1},\ j = 2,\cdots,n_k-1 \tag{A9}$$

And the transition probability for $\Lambda$ having multiple eigenvalues is

$$\mathbf{P}(t) = \mathbf{Q}\ \mathrm{Diag}\ \{\mathbf{E}_1(t)\ \mathbf{E}_2(t)\cdots\ \mathbf{E}_a(t)\}\ \mathbf{Q}^{-1} \tag{A10}$$

where

$$\mathbf{E}_k(t) = \begin{pmatrix} e^{\rho_k t} & \frac{t}{1!}e^{\rho_k t} & \cdots & \frac{t^{n_k-1}}{(n_k-1)!}e^{\rho_k t} \\ & e^{\rho_k t} & \cdots & \frac{t^{n_k-2}}{(n_k-2)!}e^{\rho_k t} \\ & & \ddots & \vdots \\ 0 & & & e^{\rho_k t} \end{pmatrix},\ k=1,\cdots,a \tag{A11}$$

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