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NUMERICAL SOLUTION OF THE RADIONUCLIDE TRANSPORT EQUATION
NON-LINEAR SORPTION EFFECTS

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Vorwort

Abstract

A numerical solution of the one-dimensional geospheric radionuclide chain transport equation based on the pseudospectral method is developed. The advantages of this approach are flexibility in incorporating space and time dependent migration parameters, arbitrary boundary conditions and solute rock interactions as well as efficiency and reliability. As an application we investigate the impact of non-linear sorption isotherms on migration in crystalline rock. It is shown that non-linear sorption, in the present case a Freundlich isotherm, may reduce concentration at the geosphere outlet by orders of magnitude provided the migration time is comparable or larger than the half-life of the nuclide in question. The importance of fixing dispersivity within the continuum approach is stressed.

Zusammenfassung

Résumé

Une solution numérique de l'équation unidimensionnelle du transport dans la géosphère est développée, pour des chaînes de radionucléides, à l'aide de la méthode pseudospectrale. Cette méthode efficace et fiable, présente l'avantage de pouvoir tenir compte des points suivants: dépendance espace et temps des paramètres de migration: conditions aux limites et interactions nucléide roche quelconques. À titre d'application concrète, nous examinons l'effet des isothermes de sorption non-linéaires sur la migration dans les roches cristallines. Nous montrons, à l'aide des isothermes de Freundlich, qu'une sorption non-linéaire peut diminuer la concentration, à la sortie de la géosphère, de plusieurs ordres de grandeur, à supposé que les temps de transport soient comparables ou plus grands que les périodes de décroissance des nucléides considérés. Il est très important de fixer la dispersivité dans le cadre du milieu continu.
1. Introduction

High level radioactive wastes are planned to be deposited in deep-lying geologic formations. The objective of this disposal option is to guarantee that no or only acceptably small amounts of radionuclides reach the biosphere over time. It is generally agreed that transport by water through the geologic medium is the principal scenario since water access to the repository cannot be excluded and integrity of waste canisters and matrix cannot be assumed over thousands or even millions of years. The effect of the geologic barrier is twofold: it provides retardation mainly through sorption leading to - hopefully - sufficiently long travel times and dilution if substantial aquifers are present. Hence, radionuclide transport models are an important part in safety analyses for radioactive waste repositories.

Various models have been developed to be used in such a safety assessment and a wide range of algorithms has been chosen to solve the underlying transport equations. A rather comprehensive overview is provided by the INTRACOIN study /1/ which aims at model validation, code verification and at examining the quantitative impact of various modeling strategies on safety assessment. The objective of the present paper is first to present a flexible and efficient method to solve the geosphere transport equation. It is
based on the pseudospectral method. The ensuing computer code, RANCHN, has been verified /2,3/ within INTRACOIN. Second, we show the potential of this method by investigating the effects of non-linear sorption on migration analysis. Though the data base for non-linear isotherms is still scarce experimental results are accumulating *) indicating that these are the rule rather than the exception.

The paper is organized as follows: In section II we present the transport equation to be solved. In section III the pseudospectral method for numerical solution of the differential equations is given. In section IV we present results from a parameter study on non-linear sorption and give finally conclusions on its impact on migration analysis in section V. Code verification is discussed in the appendix.

*) See, for example, data from the International Sorption Information Retrieval System Project (ISIRS), OECD/NEA, Paris.
2. The System of Transport Equations

Let us assume that a chain of decaying radionuclides is transported by groundwater through a geologic medium. Let us further assume that we have a saturated medium with a single*) transporting water phase, only, and can define a representative elementary volume (REV). Then, by mass balance, the system of transport equations for the equivalent porous medium is given**) by

\[
\frac{\partial}{\partial t} (\varepsilon C^i_f + \delta C^i_s) = - \nabla \cdot (C^i_f \mathbf{v} - \mathbf{D} \nabla C^i_f) \\
- \lambda_i (\varepsilon C^i_f + \delta C^i_s) + \lambda_{i-1} (\varepsilon C^{i-1}_f + \delta C^{i-1}_s),
\]

\(i = 1, \ldots, M.\)

Here, we have defined the following macroscopic quantities (averaged over the REV):

\[C^i_f = \text{concentration of nuclide } i \text{ in water phase} \quad [\text{mol/m}^3]\]

\[C^i_s = \text{concentration of nuclide } i \text{ sorbed on rock surfaces} \quad [\text{mol/m}^2]\]

*) That is, we do not discuss diffusion into regions of stagnant water, at present.

**) See e.g. reference /4/.
\[ \varepsilon = \text{effective porosity [\(-\)]} \]

\[ \delta = \text{ratio of sorbing surface to total volume [\(m^{-1}\)]} \]

\[ v = \text{water velocity field [m/s]} \]

\[ D = \text{hydrodynamic dispersion tensor field [\(m^2/s\)]} \]

\[ \lambda_i = \text{decay constant of nuclide } i [\(s^{-1}\)] \]

\[ M = \text{total number of nuclides in a chain } 1 \rightarrow 2 \rightarrow \ldots \rightarrow M. \]

In addition to the mass balance, eq.(1), a relation between \(C_f^i\) and \(C_s^i\) has to be provided. Generally, sorption kinetics is believed to be of minor importance for safety analyses \(^1\) and we assume a sorption isotherm of the form

\[ \frac{C_s^i}{C_f^i} = f_i \left( C_f^i \right) \]  \hspace{1cm} (2)

independent of time. At this place we do not specify the function \(f_i\) but just mention that a fairly large number of isotherms, some purely empirical some theory based, can be found in the literature /5/, the standard for safety analyses being a linear relationship.

Introducing (2), eqs.(1) have to be solved with appropriate initial conditions.

\(^1\) The situation might be quite different for in-situ experiments and a fortiori for laboratory measurements on small scale.
\[ c_f (t=0) = 0 \] (3)

and boundary conditions. Before doing so, we cut the spatial dimensions down from three to one-dimensional transport along a water flow line. As a matter of fact this drastic approximation - though very common for safety analyses - is not always well founded. It draws its justification mainly from:

(i) too fragmentary a knowledge of especially the components of the dispersion tensor (transversal dispersion is believed to be much smaller than longitudinal one) and of the other relevant parameters,

(ii) the experience, e.g. within INTRACOIN, that one-dimensional approximations do perform reasonably well when compared to fully two-dimensional calculations,

(iii) the expenditure to numerically perform extensive parameter studies,

(iv) and especially for this paper that the salient features of non-linear isotherms can be exemplified in a one-dimensional model \(*\).

We are thus left with the simpler system of equations

\* Work is in progress to incorporate non-linear sorption into an existing two-dimensional transport code (RANCH2N).
\[
\frac{\partial c_i^L}{\partial t} = \frac{1}{R(c_f^L)} \frac{1}{\varepsilon} \frac{\partial}{\partial x} (\varepsilon a_L v \frac{\partial c_i^L}{\partial x} - \varepsilon v c_i^L)
\]  

(4)

where the coordinate \(x\) is taken along the flow line. We have neglected diffusion and we have defined the longitudinal dispersivity \(a_L\) in the conventional way, \(D = a_L v\). In addition we introduced the concentration dependent retention factor

\[
R(c_f^L) = 1 + \frac{\delta}{\varepsilon} \frac{df_i}{dc_f^L}
\]  

(5)

We remark that water conservation \(\nabla \cdot (\varepsilon v) = 0\) implies

\[
\frac{\partial}{\partial x} (\varepsilon v F) = 0
\]  

(6)

in the one-dimensional approximation, where \(F\) is the flow tube cross-section.

3. Numerical Solution of the Transport Equation

Analytic solutions to eq.(4) are available for very specific problems only, e.g. for a layered medium extending to infinity with piecewise constant parameters and linear sorption \(\delta/\varepsilon\). In order to overcome the inflexibility in
choice of parameters and boundary conditions and to allow for a consideration of more complex transport phenomena and extensions to more than one spatial dimension one has to resort to numerical solutions. Various methods, such as finite difference, finite element and random walk models have been used /3/ to numerically solve the relevant transport equations.

Although the focus of the present work is the numerical solution of the specific transport equation (4), the problem can be stated in a more general form: obtain a solution of

$$\frac{\partial C}{\partial t} = g(x,C,t) \frac{\partial^2}{\partial x^2} C(x,t) - h(x,C,t) \frac{\partial}{\partial x} C(x,t) + S(x,C,t),$$

with \( (x,t) \in [0,L] \times [0,T_e] \). \( g(x,C,t), h(x,C,t) \) and \( S(x,C,t) \) may represent any non-linear function in the variables \( x,t \) and the concentration \( C(x,t) \). From the mathematical point of view, the solution to eq. (7) is determined provided that both the initial and boundary conditions are specified. The initial condition can be

*) The contribution of a decaying precursor in a nuclide chain is incorporated in the term \( S \), that is the system of eqs. (4) is calculated consecutively starting with the parent nuclide.
defined as:

$$C(x,t=0) = C^0(x),$$

(8)

where $C^0(x)$ is an arbitrary function of space. Boundary conditions represent statements on mass or flux continuities at the boundary points $0,L$. They are described in the general case by inhomogeneous mixed Neumann and Dirichlet conditions

$$\alpha(x,t)C(x,t) + \beta(x,t) \frac{\partial}{\partial x} C(x,t)$$

(9)

$$= \gamma(x,t) , \ x = 0,L$$

where $\alpha, \beta$ and $\gamma$ are given functions depending on the physical problem at hand. In order to obtain a numerical solution of eq.(7) subjected to the conditions eqs.(8) and (9), in most approaches two basic steps must be undertaken. One is to identify the means for the approximation of the spatial derivatives and the other is to select the procedure for time integration. Spatial discretization techniques are used to convert the time varying partial differential equation into a set of ordinary differential equations. Using either classical finite difference or finite element as well as pseudospectral techniques, this discretization
produces a semi-discrete system of differential equations of the form

$$ A \frac{d\bar{C}}{dt} = -B(t,\bar{C}) \bar{C} + S(\bar{C}, t) $$

(10)

where $\bar{C}(t)$ is a vector valued function representing the concentration distribution at discretization points $k = 0, 1, \ldots, N$. $A$ and $B$ are $(N+1) \times (N+1)$ matrices depending on the discretization technique.

One of the difficulties in solving the coupled ordinary differential equations (10) is that the set of equations usually behaves quite stiff. To show this let us assume that $A$ and $B$ are independent of time and $\bar{C}$ and that $S = S(t)$, then the solution to eq.(10) is given by

$$ \bar{C} = \exp\{-A^{-1} Bt\} \bar{C}(0) $$

$$ + \int_{0}^{t} \exp\{- (t-\tau) A^{-1} B\} A^{-1} S(\tau) \, d\tau. $$

Thus the time constants of the solutions can be defined as

$$ \tau_k \propto \frac{-1}{\text{Re}\{\lambda_k\}} $$

(12)

where, here, $\lambda_k$ are the eigenvalues of the Jacobi matrix
The ratio between the largest-modulus and smallest-modulus eigenvalue defines the stiffness of the problem and therefore the characteristic time step length for the numerical solution of eq.(7). Since the eigenvalue spectrum is unbounded an increasing number of discretization points (or increasing accuracy) simply exacerbates the stiffness problem. The occurrence of stiffness is mostly an artifact of the spatial discretizations and not a property of the governing physical equations. Consider for example the simple dispersion equation \( \partial C/\partial t = \partial^2 C/\partial x^2 \). If the space domain is discretized by a uniform mesh of \( N \) points in the unit interval and the second derivative is approximated by central differences, the resulting differential equation system has a maximum eigenvalue of the order of \(-4 N^2\), making it stiff for large \( N \).

For non-linear problems the situation is more complex since the eigenvalues depend not only on the discretization procedure but also on concentration \( C(x,t) \) and time \( t \). Thus care has to be taken when choosing the method for the time integration.
3.1 Pseudospectral method

As already mentioned above, a method must be devised to approximate the spatial derivatives occurring in the partial differential equation (7). In this paper we propose a pseudospectral method, novel in the context of geospheric radionuclide transport. Its advantage lies in combining flexibility and efficiency with reliability.

Pseudospectral methods have been applied with success to the solution of initial value problems in fluid dynamics and other problems where for complicated solutions /7,8,9/ high accuracy is desired. In a pseudospectral method, the solution is represented as an expansion into series of orthogonal functions which is then used to evaluate directly the spatial derivatives. Hence we look for a solution in the form

\[ C(x,t) = \sum_{k} a_k(t) \phi_k(x), \]  

(14)

where \( \phi_k(x) \) are orthogonal functions which have to be specified. Due to the minimax theory, the known theorems on convergence, and the fact of rapid convergence of the Chebyshev series /10/ we chose Chebyshev polynomials \( T_k \) which are orthogonal in the interval \([-1,1]\). Thus we transform the integration domain \([0,L]\) by
\[ x = \frac{L}{2} (1+y) \]  

into the interval \([-1,1]\) and write eq.(14) in the form

\[ C(y,t) = \sum_{k=0}^{N} a_k(t) T_k(y) \]  

The double prime indicates that both, the first and last terms are to be taken with a factor of one-half. The first and second spatial derivatives are then given by

\[ \frac{\partial}{\partial y} C(y,t) = \sum_{k=0}^{N} a_k(t) \frac{d}{dy} T_k(y) \]  
\[ \frac{\partial^2}{\partial y^2} C(y,t) = \sum_{k=0}^{N} a_k(t) \frac{d^2}{dy^2} T_k(y) \]

It should be mentioned, that the accuracy of the space derivatives is of infinite order as \(N \to \infty\), provided that all derivatives of \(C(y,t)\) are continuous. The continuous approximation (16) is now replaced by a discrete form introducing 'collocation points'

\[ y_k = \cos \frac{\pi k}{N}, \quad k = 0, \ldots, N \]
which means that the integration domain is discretized into
N+1 unequally distributed points. Using the orthogonality
condition for the Chebyshev polynomials the functions \( a_k(t) \)
in eq. (16) are then determined by

\[
a_k(t) = \frac{2}{N} \sum_{i=0}^{N} C(y_i, t) T_k(y_i) .
\]

Thus the first and second spatial derivatives are
approximated by the functional values \( C(y_k, t) \) at the
collocation points through

\[
\frac{\partial^2 C}{\partial y^2} \bigg|_{y=y_i} = \frac{2}{N} \sum_{k=0}^{N} C(y_k, t) \sum_{\ell=0}^{N} T_\ell(y_k) \frac{d^2}{dy^2} T_\ell(y_i) \tag{20a}
\]

= \sum_{k=0}^{N} C(y_k, t) \, D^{(1)}(y_i, y_k)

and

\[
\frac{\partial^2 C}{\partial y^2} \bigg|_{y=y_i} = \frac{2}{N} \sum_{k=0}^{N} C(y_k, t) \sum_{\ell=0}^{N} T_\ell(y_k) \frac{d^2}{dy^2} T_\ell(y_i) \tag{20b}
\]

= \sum_{k=0}^{N} C(y_k, t) \, D^{(2)}(y_i, y_k)

Since the Chebyshev polynomials are simply given by

\[
T_k(y_i) = \cos \frac{\pi y_i}{N}
\]

the matrices \( D^{(1)} \) and \( D^{(2)} \) can be evaluated analytically
leading to lengthy expressions not presented here.
Substituting eq. (20) into the partial differential equation (7) we obtain with the notation \( C_i = C(y_i, t) \) a set of coupled first order differential equations

\[
\frac{dC_i}{dt} = g(y_i, C_i, t) \frac{4}{L^2} \sum_{k=0}^{N} C_k D^{(2)}(y_i, Y_k) - h(y_i, C_i, t) \frac{2}{L} \sum_{k=0}^{N} C_k D^{(1)}(y_i, Y_k) + S(y_i, C_i, t) \quad i = 0, \ldots, N.
\]

The problem to be solved is now the numerical integration of eq. (22) which is conveniently written in matrix form

\[
\frac{d}{dt} \bar{C}(t) = V \bar{C}(t) \quad \text{(23)}
\]

where \( V \) is a \((N+1) \times (N+1)\) matrix, and we have denoted the vector of \( C_i \) by \( \bar{C} \).

3.2 Time integration

For the numerical integration of the ordinary coupled differential equations (23) we use Gear's \cite{11, 12, 13} method which is well suited for stiff systems. Local error estimates, variable time steps and variable order
approximations are possible. Time discretization errors are
typically much smaller than are spatial discretization
errors since the time steps are frequently restricted in
size by explicit stability conditions.
To discuss the principles of the method let us denote by
\( \bar{C}_n \) the functional values *) of \( \bar{C}(t_n) \) at time \( t = t_n \).
Then Gear's method requires the solution of the following
equations

\[
\frac{d\bar{C}}{dt} \bigg|_{t=t_n} = \frac{-\bar{C}_n}{\Delta t_n} - \frac{1}{\Delta t_n} \left( -\alpha_{n,0} \bar{C}_n - \sum_{m=1}^{q} \alpha_{n,m} \bar{C}_{n-m} \right)
\]

(24)

where the step size \( t_n - t_{n-1} \) is denoted by \( \Delta t_n \), \( q \) is
the order of the method ( \( q < 5 \) ) and \( \alpha_{n,m} \) are order
dependent constants. \( \bar{C}_{n-1} \), ..., \( \bar{C}_{n-q} \) are previously
calculated values. Eq. (24) may be solved in an iterative
way. Let \( \bar{C}_n^{(0)} \) and \( \bar{C}_n^{(0)} \) be some predicted values of \( \bar{C}_n \)
and \( \bar{C}_n \), respectively. These values satisfy

\[
\frac{-\bar{C}_n^{(0)}}{\Delta t_n} = \frac{1}{\Delta t_n} \left( -\alpha_{n,0} \bar{C}_n^{(0)} - \sum_{m=1}^{q} \alpha_{n,m} \bar{C}_{n-m} \right)
\]

(25)

but it is not expected that \( \bar{C}_n^{(0)} \) will agree with eq. (23).
Thus we will have residuals

*) We stress that in this subsection the lower index
signifies time discretization.
\[
0 = \frac{C_n}{\alpha_n} - \frac{C_n}{\alpha_n}^{(0)} + \frac{\Delta t_n}{\alpha_n^{0}} \left\{ V(\bar{C}_n, t_n) - \frac{\bar{C}_n}{\alpha_n}^{(0)} \right\}
\]

(26)

from which it is seen that the computation of \( \bar{C}_n \) is equivalent to finding the zeros of

\[
Q(Y) = Y - \frac{C_n}{\alpha_n} + \frac{\Delta t_n}{\alpha_n^{0}} \left\{ V(Y, t_n) - \frac{\bar{C}_n}{\alpha_n}^{(0)} \right\} .
\]

(27)

This is done iteratively by Newton's method in the form

\[
P_n \left( Y_{m+1} - Y_m \right) = -Q(Y_m)
\]

(28)

\[
Y_{m+1} = Y_m - P_n^{-1} Q(Y_m)
\]

\[m = 0, \ldots, M-1,\]

where \( M \) is the number of iterations. The matrix \( P_n \) is defined as

\[
P_n = I + \frac{\Delta t_n}{\alpha_n^{0}} J
\]

(29)

\( J \) being the Jacobian and \( I \) the identity matrix. Since the iteration process is strongly convergent as long as

\[
\left| \frac{\Delta t_n}{\alpha_n^{0}} J_{ij} \right| < 1
\]

(30)
P_n does not need to be known with much precision, so that P_n has not to be evaluated at every time step.

The effectiveness of the Gear algorithm is closely related to the efficiency with which the evaluation of the Jacobian and the inversion of the matrix J, or the equivalent linear equation solution is performed. Although the Jacobian can be evaluated analytically leading to

\[
J_{ij} = \delta_{ij} \left\{ \frac{4}{L^2} \sum_{k=0}^{N} C_k D^{(2)} (y_i, y_k) \frac{3}{\partial C_i} g(y_i, C_i, t) \right. \\
- \frac{2}{L} \sum_{k=0}^{N} C_k D^{(1)} (y_i, y_k) \frac{3}{\partial C_i} h(y_i, C_i, t) \\
+ \frac{2}{3C_i} S(y_i, C_i, t) \right\} + \frac{4}{L^2} g(y_i, C_i, t) D^{(2)} (y_i, y_j) \\
- \frac{2}{L} h(y_i, C_i, t) D^{(1)} (y_i, y_j),
\]

the system of equations (28) has to be solved at every time step. One possibility to reduce the amount of computation is a banded approximation of the Jacobian or in the extreme case a diagonal approximation with the possible disadvantage of a rather slow convergence.

4. Numerical Examples

The choice of parameters should reconcile two requirements: first, relevance for a specific disposal option and, second, definite statements on the impact of non-linear sorption on safety assessment. In the Swiss - and other countries’ -
context this means granitic rock as a geologic medium and long-lived radionuclides for which experimental data on non-linear sorption are available. These points limit the selection of radionuclides considerably. For example, Plutonium shows such high a sorption \( /\text{15} / \) that it decays to insignificance during geospheric migration, on the other hand, Uranium has such a long-lived isotope that a properly defined, concentration independent, retention factor is a good approximation for the migration parameters considered below.

4.1 Choice of the Isotherm

A fair amount of data exists on sorption of Cesium on granite. For this reason we have chosen the long-lived nuclide \( ^{135}\text{Cs} \) (half-life of \( 2.3 \times 10^6 \text{ yr} \)) as an example. Experiments \( /\text{16}, \text{17}, \text{18} / \) can be fitted nicely with a Freundlich isotherm

\[
\tilde{C}_S = K_1 C_f^{K_2} \quad (32)
\]

where \( \tilde{C}_S \), here, is the volume based concentration of nuclide \([\text{mol/kg}]. \) For one experiment \( /\text{16} / \) the fit extends over 10 orders of magnitude in \( C_f \). The Freundlich exponent varies in a narrow range \(^*) \), \( 0.5 < K_2 < 0.7 \). For definiteness we fix \(^**) \) it at \( K_2 = 0.7 \) in the calculations. The constant \( K_1 \) varies over several orders of magnitude.
depending on solid phase characterization (e.g. weathering, crushing, contact time). For our base case we fix it at 
\[ K_1 = 1.15 \cdot 10^{-2} \text{ mol}^{1-K_2} \text{ m}^{3K_2} \text{ kg}^{-1} \]. What we actually need is the isotherm for surface based concentrations, eq.(2),

\[ C_s = K_1 C_f^{K_2} \]  \hspace{1cm} (33)

here the constant is given by

\[ K_1 = \frac{M}{S} \bar{K}_1 \]  \hspace{1cm} (34)

where M/S is the mass to surface ratio as measured in the experiments. This ratio, again, varies strongly, especially with the experimental method for its determination. Four our base case we have fixed S/M = 500 m
\[^2/kg\] yielding 
\[ K_1 = 2.3 \cdot 10^{-5} \text{ [mol}^{0.3} \text{ m}^{0.1}] \]. Taking into account part of these variabilities we have also performed calculations with 
\[ K_1 = 2.3 \cdot 10^{-4} \text{ [mol}^{0.3} \text{ m}^{0.1}] \]. This might correspond to a reasonable upper bound; on the other hand much lower values do not yield new information as will shortly become clear.

*) Interestingly enough, this is the case for other solid materials, also.

**) In the last section we give results for varying K_2 keeping all other parameters fixed.
4.2 Choice of other migration parameters

We first fix the ratio $\delta / \varepsilon$ corresponding to the ratio of sorbing surface to volume of transported water. In a model with parallel fracture we would have $\delta / \varepsilon = 2/a$ where $a$ is the fracture aperture. Since $a = 3 \cdot 10^{-5}$ m is a reasonable value /19/ for deep-lying granite we fix $\delta / \varepsilon = 6.7 \cdot 10^4$ m$^{-1}$, certainly conservative a value.

The water velocity is taken to be $v = 1 m/yr$ and migration distances of $x = 3000$ m or, for some parameter variations, $x = 1000$ m are considered.

For the longitudinal dispersivity we have chosen two values, namely $a_L = 100$ m and $a_L = 300$ m. Unfortunately this is largely a free parameter, but experiments /19/ and the suggested dependence on migration distances /20/ seem to indicate such (or even higher) values.

For non-linear sorption the migration time is strongly dependent on the input concentration. Therefore we have varied this in a broad range. We fix an upstream boundary condition by

$$C_f (x=0,t) = C_0 e^{-\lambda t} u(T-t), \quad (35)$$

where $u(t)$ is the unit step function, the leach duration $T = 10^5$ yr, and
\[ C_0 = \frac{I_0}{QT} \]  \tag{36}

As a standard value we have chosen \( I_0 = 1.6 \) mol corresponding to the inventory of a glass canister /21/ and the water flow \( Q = 0.5 \text{m}^3/\text{yr} \), yielding \( C_0 = 3.2 \cdot 10^{-5} \) mol/m\(^3\). We have varied \( C_0 \) by two orders of magnitude up and down.

Downstream we have fixed \( C_f = 0 \) at \( x = 4000 \) m. This essentially corresponds to an infinite medium.

In Table I we summarize the variations of those parameter combinations entering eq.(4) and the boundary conditions. With these variations the important ratio of nuclide migration time to half-life covers over four orders of magnitude.

\begin{table}[h]
\centering
\begin{tabular}{l|c|c|c|c|c}
I & Parameter & Values chosen & I & I & I \\
\hline
1 & \((\delta/\varepsilon) K_1\) & 1.53 & 15.3 & I & I \\
1 & \(a_L\) & 100 & 300 & I & I \\
1 & \(C_0\) & 3.2 E-3 & 3.2E-5 & 3.2E-7 & I \\
1 & \(x\) & 1000 & 3000 & I & I \\
\hline
\end{tabular}
\caption{Table I: Matrix of parameter variations.}
\end{table}

The units are those given in the text.
4.3 Results

In order to visualize the impact of non-linear sorption we compare the results with those calculated from a linear isotherm. For a single measurement of solute-rock distribution at the given initial solute concentration \( C_0 \) and making the linear ansatz \( C_s = K C_0 \), the constant \( K \) is related to those of the non-linear isotherm by \( K = K_1 C_0^{K_2-1} \). For comparison purposes we define, consequently, a constant retention factor by

\[
R = 1 + \frac{\delta}{C} K_1 C_0^{K_2-1}.
\]

(37)

The corresponding values are indicated in the figures. It is interesting to note that by defining /22/ a retention factor

\[
R_f = 1 + \frac{2}{a} K_a
\]

(38)

and taking the recommended range /23/ of the distribution constant \( K_\alpha \) one arrives at \( 400 < R_f < 3300 \), roughly in accordance with the numbers calculated by eq. (37). Figures 1 to 13 show the results of the present calculations in form of concentration at a given distance versus time.
Calculations with linear sorption isotherm, eq.(37), are represented by dashed lines those with a non-linear isotherm by full lines.

The effect of the non-linear isotherm is *) to steepen the rising part and to smear out the trailing part of the curves.

Let us define a nuclide transition time by

\[ t_0 = \frac{x}{v} R \tag{39} \]

then, for \( t_0 \lambda \ll 1 \) the effect of non-linearity can essentially be neglected, see figures 1, 2, 4, 5, 7 and 10.

This is rather independent of the choice of dispersivity as can be seen when comparing fig. 1 to fig. 4, fig. 2 to fig. 5 and fig. 7 to fig. 10.

The situation becomes very different when transition times are large, i.e. \( t_0 \lambda \gg 1 \), figs. 8, 9, 11 and 12. In the case of constant retention factor, due to dispersion, the fast running part of contamination survives radioactive decay and the maximum is reduced and shifted to times less than \( t_0 \). For the case of non-linear sorption the leading part of migrating nuclides is retarded stronger, decay playing a much more pronounced effect. This is, of course, strongly dependent on the value of dispersivity: compare

*) This holds generally for \( K_2 < 1 \).
fig. 9 to fig. 12, where a decrease of dispersivity by a factor of three yields a reduction of maximum concentration by five orders of magnitude. A further decrease to $a = 50$ m would lead to essentially total decay of Cesium along the migration path. The impact of dispersivity and the building up of large differences between the linear and non-linear sorption models can be nicely seen when going from the pair of figures 3 and 6, to figures 8 and 11, to figures 9 and 12.

5. Conclusions

We have given a solution of the one-dimensional geospheric radionuclide transport equation within the framework of the spectral method. As underlying orthogonal polynomials we have chosen the Chebyshev polynomials. This choice has the advantage that the collocation points are optimally distributed, that is the discretization points are denser in the interesting regions of geospheric inlet and outlet. Advantages of the spectral method are:

(i) The transport equation is solved without generating numerical dispersion.

(ii) The rate of convergence to stable results in function of grid points is, in general, much faster than for conventional finite difference methods.

(iii) As a consequence the spectral method is efficient.
Few degrees of freedom are required to achieve moderate accuracy. In addition the attractiveness of spectral methods increases with increasing accuracy requirements.

(iv) Boundary conditions can be implemented in a natural way as defined by the differential equations.

Applying the pseudospectral method to a simple geospheric transport problem with constant migration parameters we have investigated the impact of a non-linear Freundlich isotherm describing solute-rock interactions. In order to be specific we have selected parameters from existing experiments. The conclusions, however, are more general;

(i) If transport times are very small compared to half-life the constant retention factor approach is a reliable approximation.

(ii) If transport times begin to approach half-life a tailing of the chromatographic curve builds up.

(iii) If transport times are around or larger than half-life non-linear sorption becomes important and yields a reduction in peak concentration by orders of magnitude. This is, of course, dependent on the Freundlich exponent. In order to show this, we have varied - as a purely numerical exercise - the exponent $K_2$, keeping all other parameters fixed (figure 13).

(iv) The importance of dispersion has to be stressed especially for the last mentioned case.
The need for improving data on isotherms and the knowledge on dispersion becomes clearly obvious. This is especially true if one aims at a comprehensive safety analysis for nuclear waste repositories. Several topics in connection with non-linear sorption are not investigated in this work:

(i) The effect of a nuclide source along the migration path due to precursor decay and due to other isotopes of the same element, mainly because of lack of relevant sorption data.

(ii) the quantitative influence of dilution by freshwater along the migration path in the one-dimensional approximation. The effect is clearly recognized in retarding nuclides more strongly.

(iii) The influence of transverse dispersion in multi-dimensional transport models. It seems evident that the effect might be as large as that from longitudinal dispersion.

Work along these lines is in progress.

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Appendix

Based on Gear's algorithm for the integration of ordinary differential equations a computer code RANCHN has been developed. The generalized transport equation (7) together with initial and boundary conditions eqs. (8) and (9) is solved in the pseudospectral formulation in the form of eq. (22). The algorithms used in the program have been tested rigorously. The time integration of the ordinary differential equations is handled by a modified version of the IMSL subroutine DGEAR /13/. The choice of time step size is done automatically and controlled by the requested accuracy. Care has to be taken, only, of the choice of order of Chebyshev polynomials N or, equivalently, the number of discretization points. Since there exists no rigorous mathematical criterion on convergence with respect to the order of Chebyshev expansion, statements about the accuracy can be done only by

(i) comparing numerical results with analytically solvable models and

(ii) performing calculations with varying order of Chebyshev polynomials in order to prove convergence.

A.1 Linear sorption case

For linear sorption and constant migration parameters
analytical solutions exist for the first nuclide /4/ and semianalytical solutions /6/ for piecewise constant parameters for daughter nuclides. For various parameter variations the computer code RANCHN has been verified within the INTRACOIN study /3/. Agreement in the range of < .1% was found when comparing analytical with numerical results. It has been shown that the principal advantage of spectral methods for the solution of the advective-dispersive equation lies in the ability to achieve accurate results with substantially fewer grid points than required by typical finite difference methods /14/.

A.2 Non-linear Partial Differential Equations

For non-linear partial differential equations exactly solvable problems exist in form of the Burger, sine-Gordon and Korteweg-de-Vries equations. We have studied the Burger equation which results from eq. (7) when setting

\[ g(x,C,t) = 0.003 \\
\[ h(x,C,t) = C(x,t) \\
\[ S(x,C,t) = 0 \\
\]

yielding

\[ \frac{\partial C}{\partial t} = 0.003 \frac{\partial^2 C}{\partial x^2} - C \frac{\partial C}{\partial x} . \]
The exact solution of this problem with appropriate initial 
and boundary conditions is

\[ c^{\text{ex}}(x,t) = \frac{0.1e^{-A} + 0.5e^{-B} + e^{-C}}{e^{-A} + e^{-B} + e^{-C}} \]  

(3)

with

\[ A = \frac{50}{3} (x - 0.5 + 4.95t) \]

(4)

\[ B = \frac{250}{3} (x - 0.5 + 0.75t) \]

\[ C = \frac{500}{3} (x - 0.375) \]

and represents a shock-wave, one overtaking another. We 
have solved numerically this problem in the interval \( x,t \in \) 
\([0,0.75] \times [0,1] \) with initial and boundary conditions as

\[ c(x,0) = c^{\text{ex}}(x,0) \]

(5)

\[ c(x,t) = c^{\text{ex}}(x,t), \quad x = 0, 0.75. \]

Results from the numerical solution are shown in figs. 14 
and 15 for the order of Chebyshev polynomials \( N = 30 \) and 
\( N = 40 \), respectively. The concentration \( C(x,t) \) is plotted 
as a function of time for various \( x \) values. It is seen that 
the numerical values (dashed lines) reproduce very well the 
exact solution (continuous lines) with only 31 grid points. 
The small oscillations around the asymptotic value of 1
disappear with a total number of 41 points (accuracy better than .1%). Again, the number of grid points is considerably smaller than for a finite difference solution /14/ with comparable accuracy.

A.3 Non-linear Sorption Case

For non-linear sorption with a Freundlich isotherm analytical solutions are unknown. Thus we are limited to consistency and convergence tests. Consistency tests with a Freundlich exponent of $K_2 = 1$ lead to the corresponding linear sorption case. Freundlich exponents around 1 show the same behaviour as the linear sorption case. As a typical example for convergence we show in Fig. 16 for the parameter variation

$$a_L = 100 \text{ m}$$
$$K_1 = 2.3 \times 10^{-5}$$
$$K_2 = 0.7$$
$$C_0 = 3.2 \times 10^{-7}$$

results for various numbers N of Chebyshev polynomials. The concentration $C(3000, t)$ is plotted as a function of time for $N = 15, 25, 35$ and 45, as indicated in the figure. Besides some small oscillations for $N = 15$ and 25 at time $t = 300000$ yr the different order approximations agree very well. In
Table II we show for the same set of N values the maximum concentration $C_{\text{max}}$ and values at a fixed time (around the 10% level) at the front of the time distribution.

<table>
<thead>
<tr>
<th>N</th>
<th>$C_{\text{max}}$</th>
<th>$T_{\text{max}}$</th>
<th>$C_{\text{10%}}$</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>6.566E-7</td>
<td>492000</td>
<td>8.195E-8</td>
<td>374000</td>
</tr>
<tr>
<td>25</td>
<td>6.562E-7</td>
<td>492000</td>
<td>7.405E-8</td>
<td>374000</td>
</tr>
<tr>
<td>35</td>
<td>6.563E-7</td>
<td>492000</td>
<td>7.013E-8</td>
<td>374000</td>
</tr>
<tr>
<td>45</td>
<td>6.563E-7</td>
<td>492000</td>
<td>7.014E-8</td>
<td>374000</td>
</tr>
</tbody>
</table>

Table II: Maximum concentration values and values around the 10% level at the front of the time distribution for different order of Chebyshev polynomials.

It is seen that the maximum concentrations virtually agree in all cases whereas the 10% values have converged at $N = 35$ approximately. This is the general behaviour for all our parameter variations considered. Maximum concentration values are reproduced with a few numbers of polynomials. However, in order to get the front part of the concentration distribution accurately, the number of Chebyshev polynomials has to be increased.
A.4 Limitations of the Method

As every approximation also the pseudospectral method has its limitations. Here, they stem from the oscillating character of orthogonal polynomials. By the very fact of a finite expansion of the solution into Chebyshev polynomials oscillating concentrations are created well ahead of the migrating contamination front throughout the geosphere. For the orders \( N (N \leq 40) \) of expansion considered in this paper these are on the relative level of \( 10^{-8} \) to \( 10^{-10} \) (compared to the maximal boundary concentration \( C_0 \)). If now the nuclide concentration at an observation point has decreased more than 8 to 10 orders of magnitude the method fails: The concentration peak disappears in the "noise" giving evidence, only, of the fact that contamination has decreased below this limit.

Such is exactly the case for the parameters considered in figure 9 (non-linear sorption). For this reason we have performed the calculation of this curve using the method of lines and a Taylor expansion to third order with 121 discretization points /24/. This method does not exhibit the oscillating structure. Its disadvantage is, however, slow convergence and, consequently, higher computing time.

We do not consider this production of oscillating structure a serious drawback since in realistic safety analyses one will rarely be interested in concentrations at such a low level.
Figure Captions

Figure 1: Concentrations at distances of $x = 1000$ m and $x = 3000$ m as a function of time. The broken line is for linear sorption, the full line for a Freundlich isotherm. The variable parameters are specified, for those which have been fixed throughout the calculations see section 4. The effect of non-linear sorption is negligible for this parameter set.

Figure 2: See caption to figure 1.

Figure 3: See caption to figure 1. For $x = 3000$ m the effect of non-linearity is seen, the parameter $t_0$ being 0.12.

Figure 4: See caption to figure 1. The lower plateau for $x = 3000$ m is a result of fixing the downstream boundary condition at 4000 m. The effect of non-linear sorption is negligible for this parameter set.

Figure 5: See caption to figure 1. The effect of non-linearity is negligible for this parameter set.
Figure 6: See caption to figure 1. For \( x = 3000 \) m the effect of non-linearity is seen. As in figure 3, \( t_0 = 0.12 \).

Figure 7: See caption to figure 1. The effect of non-linearity is small.

Figure 8: See caption to figure 1. For \( x = 3000 \) m the effect of non-linear sorption is the reduction of maximum concentration by a factor of 3.7, the parameter \( t_0 \) being 0.31.

Figure 9: See caption to figure 1. A strong effect of non-linear sorption is seen; \( t_0 = 1.23 \). For the sake of perspicuity we have omitted the curves for \( x = 1000 \) m where the reduction in peak concentration is a factor of 6.

Figure 10: See caption to figure 1. The effect of non-linear sorption is small for \( x = 3000 \) m and negligible for \( x = 1000 \) m.

Figure 11: See caption to figure 1. The effect of non-linearity is reduction in peak concentration by a factor of 1.6 for \( x = 1000 \) m and a factor of 3.8 for \( x = 3000 \) m, respectively. The parameter \( t_0 \) is 0.10 and 0.31, respectively.
Figure 12: See caption to figure 1. A strong effect of non-linearity is seen; \( t_0 = 1.23 \). We have omitted curves for \( x = 1000 \) m where peak reduction is a factor of 4. For the impact of dispersivity compare to figure 9.

Figure 13: Concentration at \( x = 3000 \) m as a function of time. Shown is the dependency on the Freundlich exponent \( K_2 \) as indicated in the figure. The other parameters are kept fixed at the values given. For \( K_2 = 0.6 \) radionuclides do not survive geosphere transport.

Figure 14: Comparison of exact (solid lines) and numerical (dashed lines) solution of Burger's equation. The concentrations are plotted as a function of time for various collocation points \( x \) as indicated in the figure. The order of Chebyshev expansion is \( N=30 \).

Figure 15: The same as figure 14 but for Chebyshev expansion of order \( N=40 \). Note the change of collocation points \( x \) and the rapid convergence when comparing to the previous figure.

Figure 16: Shown is the convergence of results with increasing Chebyshev order \( N \) as indicated in the figure. The parameter are those of figure 3.
**Fig. 1**

- **Linear sorption**
  - $R = 9.6$

- **Non-linear sorption**
  - $K_1 = 2.3 \times 10^{-5}$

- $a_L = 100 \text{ m}$
- $c_0 = 3.2 \times 10^{-3}$

- *10$^{-2}$

- $C(x, T)$

- $T \cdot 10^6 \text{ yr}$
Fig. 2
linear sorption $R=137$

non-linear sorption $K_1=2.3 \cdot 10^{-5}$

$s_L = 100 \text{ m}$

c$0 = 3.2 \cdot 10^{-7}$

Fig. 3
Fig. 4
Fig. 5
linear sorption \( K=137 \)
non-linear sorption \( K_f=2.3 \cdot 10^{-5} \)

\( a_L = 300 \) m
\( c_0 = 3 \cdot 10^{-7} \)

**Fig. 6**
Fig. 7
Fig. 8
Fig. 9
Fig. 10

--- linear sorption \( R = 86.6 \)

--- non-linear sorption \( K_i = 2.3 \times 10^{-4} \)

\[ a_L = 300 \, \text{m} \]
\[ c_0 = 3.2 \times 10^{-3} \]
Fig. 11
Fig. 12
non-linear sorption

\[ K_1 = 2.3 \times 10^{-5} \]

\[ a_L = 100 \, m \]

\[ C_0 = 3.2 \times 10^{-7} \]

Fig. 13
Fig. 14
Fig. 15
Fig. 16