A Chemical Equilibria Model of Strontium-90 Adsorption and Transport in Soil in Response to Dynamic Alkaline Conditions

Brian P. Spalding* and Ian R. Spalding†
Environmental Sciences Division,
Oak Ridge National Laboratory‡
P.O. Box 2006
Oak Ridge, Tennessee 37831-6036

Abstract

Strontium-90 is a major hazardous contaminant of radioactive wastewater and its processing sludges at many Department of Energy (DOE) facilities. In the past, such contaminated wastewater and sludge has been disposed in soil seepage pits, lagoons, or cribs often under highly perturbed alkaline conditions (pH > 12) where $^{90}$Sr solubility is low and its adsorption to surrounding soil is high. As natural weathering returns these soils to near neutral or slightly acidic conditions, the adsorbed and precipitated calcium and magnesium phases, in which $^{90}$Sr is carried, change significantly in both nature and amounts. No comprehensive computational method has been formulated previously to quantitatively simulate the dynamics of $^{90}$Sr in the soil-groundwater environment under such dynamic and wide-ranging conditions. A computational code, the Hydrologic Utility Model for Demonstrating Integrated Nuclear Geochemical Environmental Responses (HUMDINGER), was composed to describe the changing equilibria of $^{90}$Sr in soil based on its causative chemical reactions including soil buffering,

*Corresponding author phone: (865)-574-7265; fax (865)-576-8543; e-mail: spaldingbp@ornl.gov.
† University of Tennessee, student, Department of Computer Sciences.
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pH-dependent cation exchange capacity, cation selectivity, and the precipitation/dissolution of calcium carbonate, calcium hydroxide, and magnesium hydroxide in response to leaching groundwater characteristics including pH, acid neutralizing capacity, dissolved cations, and inorganic carbonate species. The code includes a simulation of one-dimensional transport of $^{90}$Sr through a soil column as a series of soil mixing cells where the equilibrium soluble output from one cell is applied to the next cell. Unamended soil leaching and highly alkaline soil treatments, including potassium hydroxide, sodium silicate, and sodium aluminate, were simulated and compared with experimental findings using large (10 kg) soil columns which were leached with $^{90}$Sr-contaminated groundwater subsequent to treatment. HUMDINGER's simulations were in good agreement with dynamic experimental observations of soil exchange capacity, exchangeable cations, total $^{90}$Sr, and pH values of layers within the soil columns and of column effluents.

**Introduction**

One of the major and most hazardous fission products in U. S. Department of Energy (DOE) radioactive wastes is $^{90}$Sr. A common treatment practice in the recent past, for liquid radioactive wastes containing $^{90}$Sr, other fission products, and transuranic isotopes, was a modified lime-soda water softening process wherein highly alkaline (i.e., pH > 12) but variable-composition sludges were produced containing calcium carbonate, hydrous oxides of aluminum and iron, and frequently complex insoluble phosphates in which most of the radionuclides were coprecipitated ($I$). Waste sludge, excess wastewater, and often untreated wastewater were frequently disposed into unlined seepage trenches or lagoons from which contaminants adsorbed to surrounding soil or were allowed to dilute into groundwater while the entrained sludge retained most of the radionuclides. Thus, there are many highly alkaline (high pH and dissolved sodium) and radioactive waste inventories in such shallow subsurface
environments at DOE sites including Oak Ridge, Tennessee (2, 3), Hanford, Washington (4, 5, 6), and Savannah River, South Carolina (7, 8); the continued retention of radionuclides in these sludges depends on the maintenance of their highly alkaline condition. Throughout the first two half-lives of $^{90}\text{Sr}$ (i.e., the last 60 years), most of these waste pits, trenches, and/or lagoons have not resulted in major contamination of nearby surface water or major resource aquifers. However, the highly alkaline conditions on which their continued performance depends, cannot be viewed as stable in the longer term where continued groundwater leaching and natural acidic weathering (9) will solubilize many of their precipitated phases at some point. In general, $^{90}\text{Sr}$ is the radionuclide likely to pose the largest risk during future mobilization through a combination of its high intrinsic hazard and its environmental mobility; it becomes relatively mobile in soil as an exchangeable cation at or below neutral pH due to its chemical similarity to calcium and/or magnesium (10) which are the dominant exchangeable cations in most soils.

To predict the temporal dynamics of $^{90}\text{Sr}$ in and from such radioactive sludges and their intermixed and proximate soils, one must focus on several controlling chemical reactions (11, 12, 13). The chemical reactions for precipitating and dissolving phases containing Ca, Mg, and $^{90}\text{Sr}$ in both water and soil are fairly well understood as independent reactions as are the soil processes for cation exchange, cation selectivity, and pH-dependent cation exchange capacity (14, 15). The phases co-precipitating Ca, Mg, and $^{90}\text{Sr}$ at high pH include Ca(Mg)CO$_3$ (calcite), Mg(OH)$_2$ (brucite), and Ca(OH)$_2$ (portlandite); these and other insoluble phases can be described using solubility products (e.g., 16, 17) or, alternatively, more thermodynamic approaches, such as minimizing the Gibbs free energy function, coupled with the constraints of mass balance equations (18). However, the soil reactions for cation exchange, cation selectivity, and pH-dependent cation exchange capacity have mostly been formulated from empirical (e.g., solubility and ionization equilibria) rather than thermodynamic relationships. Thus, in attempting
to model a solid-solution composition and its temporal changes in soil, one is faced with merging many empirical functions with more defined chemical equilibria relationships. The solubility dynamics of $^{90}\text{Sr}$ in soil, from perturbed alkalinity condition (i.e., pH > 14) returning to a condition which is mildly acidic (e.g., pH ≈ 6), has posed significant challenges for combining hydrologic transport and chemical equilibrium models (12). Even the dynamics of major soil cations with only calcite precipitation/dissolution in an agricultural soil environment, within a considerably narrower pH range, has been challenging to simulate (19).

The Hydrologic Utility Model for Demonstrating Integrated Nuclear Geochemical Environmental Responses (HUMDINGER) is an attempt to address the need to couple soil empirical information and solubility equilibria functions into an integrated predictive model for the behavior of $^{90}\text{Sr}$ in soil under changing and wide-ranging pH conditions. A general empirical relationship for soil buffer capacity, pH-dependent cation exchange capacity, and monovalent-divalent cation exchange selectivity is proposed and techniques for measuring its required parameters for specific soils demonstrated; techniques to integrate these with the requisite solubility equilibria calculations are also proposed. All chemical equilibria are also coupled to a one-dimensional soil mixing-cell model to simulate the leaching of the common soil column. Model calibration and performance can be checked against the characteristics of any number of layers within a soil column subjected to alkaline or control treatments and leaching with $^{90}\text{Sr}$-contaminated groundwater. The model is entirely PC-based, requiring no supporting software other than the WINDOWS 95, NT, 98 or 2000® operating system, and contains integrated graphics and database outputs; alternate values for chemical constituents and equilibria constants can be selected. The code itself is readable within the model and the program can be downloaded at no cost from the Internet (http://www.ornl.gov/LANGMUIR/bpsintro.htm).
Equilibria model formulation

(a) soil acid-base buffering - Because highly alkaline conditions are generally favorable for the precipitation and adsorption of $^{90}$Sr in soil and subsequent leaching by acidic groundwater causes $^{90}$Sr to become soluble, the controlling process for predicting the adsorption and transport of $^{90}$Sr will be the acid-base buffering characteristic of soil. We have formulated the alkaline treatment-soil buffering-groundwater system as an acid-base buffer mixing problem; the simulated soil is limited to a closed system with respect to any CO$_2$ gas phase since an NaOH treatment solution, in an open system at any pCO$_2$ would form Na$_2$CO$_3$ at equilibrium. In mixing an alkaline chemical solution or groundwater with another solid-phase buffer like soil, the combined buffer capacity, i.e., acid neutralizing capacity (ANC), is conserved and is equal to the sum of the ANCs of the two mixed buffers (17). The dominant soluble buffering component in most groundwater arises from the carbonic acid equilibria with the result that groundwater ANC (equivalents/L) can be expressed as:

$$\text{ANC} = [\text{OH}^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{HCO}_3^-] - [\text{H}^+] \quad (1)$$

Groundwater ANC can be calculated or, more frequently, measured by acidimetric titration to some defined low pH where all three basic species in eq 1 are neutralized. The soluble ANC can be expressed as a function of the variables [H$^+$], total inorganic carbon concentration, and the constants: $K_{\alpha 1}$ and $K_{\alpha 2}$ (the two carbonic acid dissociation constants) and $K_w$ (the dissociation constant for water). Alkaline solutions, such as NaOH or Na$_2$CO$_3$ used for waste or soil treatment, can have their ANC expressed and measured using this same formula and constants.

The ANC arising from a soil's many solid phases can be formulated in the same manner. However, because soil buffering is composed of a complex mixture of solid chemical species and/or minerals, we have chosen to simulate soil buffering in a summary manner by formulating soil as a single mixed phase behaving as an insoluble quadraprotic weak acid (H$_4$X) with concentration in moles/L:
\[ [H_4X] \rightleftharpoons [H_3X^+] + [H^+] \rightleftharpoons [H_2X^2] + [H^+] \rightleftharpoons [HX^-] + [H^+] \rightleftharpoons [X^-] + [H^+] \]  

(2)

where each of the four equilibria is described by an ionization constant:

\[ K_1 = \frac{[H_3X^+] \cdot [H^+]}{[H_4X]} \]  

(3)

\[ K_2 = \frac{[H_2X^2] \cdot [H^+]}{[H_3X^-]} \]  

(4)

\[ K_3 = \frac{[HX^-] \cdot [H^+]}{[H_2X^2]} \]  

(5)

\[ K_4 = \frac{[X^-] \cdot [H^+]}{[HX^-]} \]  

(6)

This hypothetical soil polyprotic weak acid (H₄X) is implied to be a mixed hydrous oxide species where X can be -O-Si-, -O-Al-, -O-Fe-, or -O-Mn- phases or mixed phases on mineral surfaces. Typical values employed in HUMDINGER for pKᵢ - pK₄ were 3, 6, 9, and 11. The use of four independent ionization constants, coupled with the additional flexibility to specify a formula weight for H₄X (e.g. 10 kg/mole was typical) for soil, allows soil acid buffering to be fit to empirical titration data for almost any soil over wide pH ranges and buffering capacities. Thus, the total soil acid neutralizing capacity (SANC), including its component dissolved species, can be expressed as:

\[ \text{SANC} = [H_3X^+] + 2 \cdot [H_2X^2] + 3 \cdot [HX^-] + 4 \cdot [X^-] + [OH^-] + 2 \cdot [CO_3^{2-}] + [HCO_3^-] - [H^+] \]  

(7)

By mixing a soil (at a specified starting SANC) with an alkaline solution or groundwater (with its specified ANC), the resulting mixed SANC is calculated by summation; the equilibrium pH and the distribution of other solid and dissolved species can be solved with these equations; HUMDINGER solves eq 7 for [H⁺] by numerical iterations until convergence on the known value of SANC. In HUMDINGER, eq 7 is rewritten as a single fourth-order polynomial equation with terms containing only [H⁺], Ka₁, Ka₂, Kw, and K₁-K₄. Although usually not present prior to alkaline perturbation, other precipitated solid species, which contribute to the SANC such as CaCO₃, Ca(OH)₂, and Mg(OH)₂, can be and are included in the total SANC. For modeling transport in soil, only the dissolved species of the SANC (i.e., its sum of [OH⁻] + [CO₃^{2-}] + [HCO₃⁻] - [H⁺]) are allowed to flow out of a soil mixing cell.
as a new increment of groundwater or alkaline solution is added. In this manner, HUMDINGER can account for changing equilibrium soil pH and ANC speciation based on inputs and outputs of known and measurable solution chemical characteristics such as ANC, pH, total inorganic carbon, and/or alkalinity.

(b) solubility of calcium-magnesium phases - As soil pH is raised by addition of alkaline solutions, several solid phases, containing calcium and magnesium which dominate the soluble and cation exchangeable phases of most soils, can precipitate and, thereby, co-precipitate $^{90}$Sr. Similarly, these same calcium and magnesium solid phases can dissolve as the natural weathering process proceeds where acidic groundwater titrates the alkali-amended soil. The calcium and magnesium phases precipitated at high pH include calcium/magnesium carbonate (calcite), magnesium hydroxide (brucite), and calcium hydroxide (portlandite) based on the dominant soluble anions (OH$^-$ and CO$_3^{2-}$) available in the soil. Solubility of these phases is calculated using their solubility products ($^{16, 17}$):

\[
[\text{Ca,Mg}^{++}] \cdot [\text{CO}_3^{2-}] \rightleftharpoons (\text{Ca,Mg})\text{CO}_3 \quad (\text{magnesian calcite, } pK_{s0} = -8.42 \text{ at } 25^\circ\text{C, } I = 0) \quad (8)
\]

\[
[\text{Ca}^{++}] \cdot [\text{OH}]^2 \rightleftharpoons \text{Ca(OH)}_2 \quad (\text{portlandite, } pK_{s0} = 22.8 \text{ at } 25^\circ\text{C, } I = 0) \quad (9)
\]

\[
[\text{Mg}^{++}] \cdot [\text{OH}]^2 \rightleftharpoons \text{Mg(OH)}_2 \quad (\text{brucite, } pK_{s0} = 16.84 \text{ at } 25^\circ\text{C, } I = 0). \quad (10)
\]

Ionic strength ($I = \frac{1}{2}\Sigma C_i z_i^2$) is calculated from all dissolved ionic species and was used to calculate conditional solubility products, as well as conditional carbonic acid and the soil quadraprotic acid dissociation constants; these conditional equilibria constants are functions of $I$ using the Güntelberg approximation method as recommended by Stumm and Morgan($^{17}$). The ionized solid phase species (e.g., $\text{H}_3\text{X}^-$, etc) were not considered in calculating $I$. HUMDINGER uses ion concentrations to calculate various ion concentration products (ICPs) and compare them to the conditional solubility and ionization products rather than compute activities explicitly to compare with unadjusted equilibria constants. Both methods correct for non-ideality identically but the use of ICPs in HUMDINGER is merely more efficient computationally for tracking the limited number of equilibria. In general, the most
oversaturated phase is then allowed to precipitate incrementally until its ICP equals the conditional solubility product as recommended by Morel and Morgan (16). Other phases are then similarly checked for equilibria once the first phase precipitation limitation is satisfied; the computational process is repeated until all phase solubility and cation exchange equilibria (discussed below) are satisfied. Analogously, if a solid phase is present in the soil and incremental leaching indicates that it becomes undersaturated, it is allowed to dissolve incrementally up to an ICP equal to its conditional solubility product. Mass balance constraints (for ANC, Ca, Mg, Na and/or K, and total inorganic carbon (TIC) ) are imposed and limit the total amount of each element or species in a soil cell; soil cells are closed with respect to CO$_2$ transfer to or from any gas phase. Although total SANC does not change with the precipitation or dissolution of CaCO$_3$, Ca(OH)$_2$, and Mg(OH)$_2$, the distribution of component species within the SANC (particularly the pH) does change and the model computes all component equilibria and species distribution. The SANC equation cannot be solved explicitly for [H$^+$], so HUMDINGER solves it iteratively using a narrowing approximation for [H$^+$] until the solution oscillates to a convergence within at least 1 part in 10,000 of the known value of SANC. Similar iterative solvers and convergence criteria are employed for the phase solubility equations, cation exchange capacity, and cation exchange distribution.

(c) soil cation exchange capacity versus pH - Soil cation exchange capacity generally increases with pH as surface hydrous oxides ionize and result in more negative charge on the soil mineral surfaces (14, 20). In addition to the conceptualization of soil as a polyprotic weak acid as a means to quantify its SANC and associated pH changes, HUMDINGER uses this empirical method to quantify and mathematically describe pH-dependent cation exchange capacity of soil. The soil cation exchange capacity can be expressed as the sum of all insoluble negative charge on this hypothetical soil species (in equivalents/L) at a given pH:
soil cation exchange capacity (CEC) = \([H_3X^-] + 2 \cdot [H_2X^{2-}] + 3 \cdot [HX^-] + 4 \cdot [X^-]\)  \(\text{(11)}\)

By this formulation of pH-dependent solid anionic charge (i.e., cation exchange capacity), selection of appropriate soil pK\(_a\)'s can be employed to match empirical cation exchange capacity measurements or the sum of exchangeable cations at various soil pH's. Selection of the value for a soil formula weight (e.g., \(H_4X = 10 \text{ kg/mole}\)) thereby sets a maximum soil CEC (e.g., 400 milliequivalents [-] / kg of soil) at a pH more than two units above its fourth ionization constant (e.g., pK\(_4\) = 11). Thus, HUMDINGER's techniques for computing SANC, pH, and component species distribution, are also used to compute the soil CEC. Although soils frequently exhibit fixed or non-pH-dependent cation exchange capacity, such fixed CEC is, in effect, maintained by selecting a low value for pK\(_1\) (e.g., 3) for the soil's quadruprotic acid because the range of model application is not intended to go below pH = 4; thus, the soil exhibits a minimum cation exchange capacity, at default conditions, of at least 100 milliequivalents/kg at any pH > 4.5. The cations that satisfy the soil's CEC are those species originally present (mostly Ca and Mg with lesser amounts of Na and K), plus any added with alkaline treatment (e.g., NaOH) or dissolved in groundwater subsequently used to leach the soil.

(d) soil cation selectivity- Soil cation exchange selectivity, over the large range of alkaline chemical solution additions of interest for enhancing \(^{90}\text{Sr}\) adsorption, is dominated by cation selectivity differences between the alkaline earth elements (Ca and Mg) and alkali metal elements (Na and/or K). As a soil is modified by addition of NaOH or \(\text{Na}_2\text{CO}_3\) from an ambient condition of relatively low CEC, dominated by Ca and Mg cations, to a much higher CEC dominated by added Na, cation exchange selectivity may change in relation to pH or to the equivalent fraction of sites occupied by monovalent \(\text{Na}^+\)or \(\text{K}^+\). HUMDINGER formulates a general divalent (Ca&Mg) - monovalent (Na&K) cation exchange reaction using the Eriksson (21) selectivity coefficient (\(K_e\)) description as advocated by Buggenwert and Kamphorst (22):
\[
K_e = \frac{[\text{Na}^+ + \text{K}^+]^2 \cdot \{\text{ex. Ca}^{++} + \text{ex.Mg}^{++} / \Sigma(\text{exCations})\}}{[\text{Ca}^{++} + \text{Mg}^{++}] \cdot \{\text{ex. Na}^+ + \text{ex. K}^+ / \Sigma(\text{exCations})\}^2}
\]

where dissolved concentrations of cations are expressed in molarity and exchangeable cations are expressed as their equivalent fractions of the total CEC. Systematic variation of \(K_e\), following alkaline soil treatment, could conceivably be a function of pH, CEC magnitude, and/or equivalent loading of Na and/or K on the exchange sites. Obviously, there are differences in cation selectivity between Ca and Mg and also between Na and K; but, these are generally found to be small relative to selectivity differences between the divalent alkaline earth and monovalent alkali metal cations as groups (22).

(e) Strontium-90 behavior - Although HUMDINGER is largely composed of computational algorithms to couple empirical measurements and chemical equilibria formulations in modeling soil pH buffering and responses to added alkalinity, cation exchange capacity and selectivity, and the major precipitable alkaline earth solid phases, its primary intent is to simulate the behavior of \(^{90}\text{Sr}\) in soil as this radioisotope is carried, adsorbed, and coprecipitated with the soil's available Ca and Mg species (10). In the present test soil, as in most soils, ambient exchangeable stable Sr is present at only 0.001 mole fraction of the total soil exchangeable Ca&Mg&Sr (Table S1, Supporting Information) which situation makes both Sr and any \(^{90}\text{Sr}\) contaminant susceptible to being carried by Ca and Mg as co-precipitates or solid solutions of any insoluble Ca&Mg phases; this is similar to the well-studied situation in seawater where Sr solubility is maintained by a solid solution of Sr in CaCO\(_3\) rather than by equilibrium with SrCO\(_3\) (17). In HUMDINGER, \(^{90}\text{Sr}\) is carried proportionally among the dissolved, cation exchangeable Ca and Mg phases, and precipitated/dissolved to/from the (Ca,Mg)CO\(_3\), Mg(OH)\(_2\), and Ca(OH)\(_2\) phases; previous work with similar soils at ORNL and elsewhere found \(^{45}\text{Ca}\) and \(^{85}\text{Sr}\)
isotopic labels behaved identically during alkali and Ca-precipitating amendments of soil (20, 23, 24). Although $^{90}$Sr is in rapid equilibrium between the soil's dissolved and cation exchangeable phases, once co-precipitated with (Ca,Mg)CO$_3$, Mg(OH)$_2$, or Ca(OH)$_2$, it no longer equilibrates isotopically with either the dissolved or cation exchangeable phases until these precipitated phases redissolve (23, 24, 25). HUMDINGER keeps account of all transfers of $^{90}$Sr into these precipitated and unavailable phases by allowing a fraction of the total $^{90}$Sr activity, in the dissolved plus exchangeable phases, to precipitate in proportion to the fraction of Ca and/or Mg in the dissolved plus exchangeable phases which precipitates into one or more of these three insoluble forms. During dissolution, a fraction of the $^{90}$Sr activity in a particular phase is allowed to dissolve proportional to the amount of Ca and/or Mg in that phase which dissolves. Thus, HUMDINGER partitions $^{90}$Sr activity among five phases (soluble, cation exchangeable, calcite, brucite, and portlandite). Although HUMDINGER’s partitioning of $^{90}$Sr among only these five phases seems sufficient for many soil conditions, as has been generally observed both in soil waste disposal monitoring and in atmospheric fallout from nuclear weapons testing in the 1950’s and 1960’s (10), there are some situations, particularly in coarse-textured soils of very low cation exchange capacity, where specific adsorption on ferromanganous hydrous oxides can be a significant mechanism for $^{90}$Sr adsorption (26,27). Although not explicitly addressed in HUMDINGER, modeling strategies for possible specific adsorption of $^{90}$Sr (and/or the Ca and Mg with which it is carried) are discussed in the Supporting Information (section 3d, cation exchange selectivity).

To facilitate comparison with other models, HUMDINGER also calculates a distribution coefficient ($K_d$) for $^{90}$Sr activity, solely as a dependent variable which functions only as a descriptive statistic:

$$K_d = \frac{\sum (\text{Ca, Mg}\{^{90}\text{Sr}\}\text{CO}_3 + \text{Ca}\{^{90}\text{Sr}\}(\text{OH})_2 + \text{Mg}\{^{90}\text{Sr}\}(\text{OH})_2 + \text{ex. Ca}\{^{90}\text{Sr}\})}{\text{Ca, Mg}\{^{90}\text{Sr}\}\text{CO}_3 + \text{Ca}\{^{90}\text{Sr}\}(\text{OH})_2 + \text{Mg}\{^{90}\text{Sr}\}(\text{OH})_2 + \text{ex. Ca}\{^{90}\text{Sr}\}}}$$

(13)
Some comprehensive chemical equilibria models can compute dissolved and precipitated phases (or selected subsets of phases) in response to changing inputs at each iteration and, thus, can yield accurate descriptions of resulting equilibrium elemental distributions among various solid phases in response to changing inputs of various chemical species (13, 18). For elements such as Ca or Mg, descriptions of such changes can be quantitatively informative as to the dynamic processes occurring. However, such a process ignores and, thus, mixes any unique isotopic signature in the antecedent solid phases. For example, if $^{90}$Sr were initially present in the soil only in a Ca, Mg($^{90}$Sr)$\text{CO}_3$ phase, then redistributing $^{90}$Sr after each iteration among all phases in proportion to their Ca distribution, would lead to significant error in the distribution and description of $^{90}$Sr adsorption and movement. In a chemical model, the complete redistribution of an element like Ca after each incremental change, would have no effect because the new equilibrium Ca distribution among several phases would be independent and unaffected by the antecedent Ca distribution. HUMDINGER, however, adjusts $^{90}$Sr in a precipitated phase based on proportional Ca+Mg precipitation or dissolution from its antecedent distribution among those phases. This capability is essential for an isotopically-carried contaminant like $^{90}$Sr or if one were interested in simulating a stable isotopic distribution among phases whose initial stable isotopic signatures were different.

(f) transport computational capabilities - HUMDINGER simulates dynamic transport of soluble cations, $^{90}$Sr, and soluble ANC using a small incremental volume (default is 0.1 L) of treatment chemical or groundwater to mix within a soil cell volume (default is 0.928 L) containing a specified amount of soil and water. The previously computed dissolved chemical species in the water are allowed to flow out of that soil cell and, thus, become the input to the next soil cell (28). By default, the geometry of the 10 kg soil column is modeled as eight sequential soil mixing cells with column effluent
from the last cell. Only between 10 and 25% of the generated data is routinely saved to a database file so that graphical output can exhibit enough resolution to observe changes in soil parameters; complete data sets of dissolved output are temporarily saved during computations until the next soil cell calculations are completed. A default graphical display of soil exchangeable cations is provided after each soil cell is leached to the specified cumulative groundwater volume; additional graphical output can be viewed by selecting from any of 30 soil or groundwater parameters (including dissolved, exchangeable, and precipitated phases for Ca, Mg, Na and/or K, inorganic carbon, pH, ANC, and associated $^{90}$Sr species). After a short delay, HUMDINGER automatically proceeds with the next soil cell calculations if no user actions are taken; thus, large configurations of mixing cells can be completed unattended. Soil starting conditions, the number of identical soil cells, the volume and characteristics of the treatment solution, and total volume, incremental added volume, and characteristics of leaching groundwater can be specified. Although HUMDINGER stores its output data in a Microsoft Jet format (file type *.MDB), which can be used directly by many current database programs, HUMDINGER contains its own graphical and database subroutines to observe model performance and/or compare with data of previous model simulations. The user can set or change all model parameters through graphical input boxes; parameter values for the test soil reported herein are offered as defaults in these input boxes, which the user can change simply by entering new values, as can be done for all treatment solution and groundwater characteristics. All of HUMDINGER's computational code is available to inspect, read, analyze, print, and/or copy and paste from text boxes within sub-windows in the model. Although the program is freely available and can be downloaded from the Internet (www.ornl.gov\LANGMUIR\bpsintro.htm), the code itself is compiled and, thus, cannot be changed directly within HUMDINGER. But because the computational code is available as text files within
HUMDINGER, it can be read or copied from within the model. An overview of HUMDINGER's computational flow and transport strategy is depicted in Figure 1.

(g) limitation of applicable soil characteristics- The chemical equilibria in HUMDINGER address what we hypothesize to be the dominant processes and chemical reactions affecting the movement of $^{90}$Sr under most soil-groundwater scenarios. The model was constructed and tested for use in soils with pH greater than about 4; at pH < 4, exchangeable cations will become dominated by H, Al, Fe, Mn, which are not addressed by the model, and fixed soil cation exchange capacity may dominate the exchange process. The model also assumes that no chemical species, significant to either cation or $^{90}$Sr adsorption, dissolve at high pH; this implies a limitation to subsurface soils with low organic matter content which otherwise could solubilize at high pH. HUMDINGER presently encompasses only a closed CO$_2$ system where the total inorganic carbon content of both the added alkaline solution and/or subsequent groundwater to leach the treated soil must be specified; thus, there is no interaction with any gas phase with variable or fixed CO$_2$ partial pressure. HUMDINGER makes no calculation of aqueous dissolved Ca, Mg, or $^{90}$Sr speciation other than the total dissolved concentration. The model also does not address any kinetic constraints or their effects on dissolution or precipitation for the various phases. The model does not employ time explicitly as a controlling variable for its simulation of the one-dimensional linear configuration of soil cells (i.e., a soil column); only volume increments of treatment solution or groundwater are employed although time could be inferred under controlled or constant flow conditions. Hydrodynamic dispersion is addressed only indirectly through the selection of the incremental added volume relative to the volume of liquid in an individual soil-mixing cell; the default incremental volume was selected to simulate the hydrodynamic dispersion observed in the test soil columns as well as to minimize unnecessary computational time. The model also contains a
hypothetical non-adsorbing species (i.e., tritium) which can be followed graphically to observe elution peak broadening and numerical dispersion arising from mixing cell dilutions and configurations.

Results and Discussion

The default soil for HUMDINGER was characterized as described in the section on experimental measurement of soil characteristics (see Supporting Information). The experimental techniques for measuring the default soil model parameters and the comparisons between this default soil column leaching performance after alkaline chemical treatments and without treatments and HUMDINGER simulations are also expanded in the Supporting Information. Prior to discussing the similarities of HUMDINGER’s simulations and the empirical observations of the soil column responses, HUMDINGER’s simulations of the underlying soil reactions serve to illustrate how $^{90}\text{Sr}$ solubility in soil is controlled under various alkaline conditions. After a layer of soil is treated with a small volume of NaOH (or KOH) solution and subsequently leached with a substantial volume of a typical hard (i.e., Ca+Mg > 0.002 M) groundwater, HUMDINGER simulates all the changing exchangeable cation conditions (Figure 2). Because of the pH-dependent charge generated at the NaOH-perturbed condition (i.e., pH >14), the soil CEC increases rapidly from its starting CEC of 147 meq/kg to 400 meq/kg with practically all of that CEC composed of $\text{Na}^+$. The original exchangeable Ca and Mg in the soil reacts to form $\text{Ca(OH)}_2$ and $\text{Mg(OH)}_2$ precipitate at the imposed high pH and these exchange sites also become saturated with Na. There always remains some small amount of soluble and exchangeable Ca and Mg to satisfy both the cation exchange selectivity equilibrium and the equilibrium solubility of portlandite and brucite. After excess/unreacted NaOH solution has percolated through a soil layer, groundwater leaching begins and is continued until the final volume selected. The default groundwater contains relatively little Na, compared to Ca and Mg, which are usually in the bicarbonate form as is the case with most hard (dissolved Ca+Mg > 0.002 M) groundwater; the groundwater is undersaturated with
respect to calcite. Thus, the large amount of exchangeable Na in the soil after NaOH treatment is gradually exchanged for dissolved Ca and Mg in the groundwater and eventually results in complete replacement of the induced exchangeable Na after about 125 L of cumulative leaching (Figure 2).

The replacement of this exchangeable Na is also accelerated by the rapidly dropping soil pH which, in turn, lowers the soil CEC ultimately to some new equilibrium determined by the pH and dissolved cations in the groundwater. The soil pH is adjusted downward due to mixing with its dissolved acidity (or base neutralizing capacity) which is composed mostly of bicarbonate and carbonic acid species. By default, HUMDINGER assumes that 98.5% of the groundwater's dissolved cations are balanced by bicarbonate/carbonate anions; however, this percentage can be set at any value with the implication that any additional anionic species required for charge balance are inert to buffering (e.g., chloride or sulfate). As the pH continues to fall during leaching, the solubility limits of both portlandite and brucite become greater and both of these phases dissolve completely by about pH=10. However, this dissolving Ca and Mg can react further with carbonate anion converted from the percolating bicarbonate and carbonic acid in the groundwater. Thus, during the continued pH decline, Ca(Mg)CO$_3$ (calcite) precipitates in the soil while both brucite and portlandite dissolve (see Figure S3 in Supporting Information). Ultimately, when the groundwater becomes undersaturated with respect to calcite, this secondary calcite will dissolve as its ultimate stability in the soil is set by the pH and hardness of the leaching groundwater.

The leaching groundwater pH can be varied in HUMDINGER and lower pH values will lead to more rapid calcite dissolution. HUMDINGER also allows selection of an alkaline treatment with Na$_2$CO$_3$ instead of NaOH. Although the initial pH is not as high when Na$_2$CO$_3$ is employed, the large amounts of carbonate introduced by this treatment lead directly to formation of calcite rather than relying on the dissolved inorganic carbon to build up slowly with the subsequent leaching groundwater.
The ratio of carbonate to hydroxide in the treatment solution can be altered in HUMDINGER to explore such potential effects.

The predictions of HUMDINGER can be compared to two general responses of the alkali-treated and control soil columns: 1) the observed column effluent characteristics and 2) the final distribution of soil characteristics (exchangeable cations and total $^{90}$Sr) within the columns after completing an equivalent degree of leaching. In general, treated soil columns were subjected to a cumulative leaching volume with $^{90}$Sr-contaminated groundwater roughly equal to that of the controls where $^{90}$Sr activity breakthrough approached 10% of the average applied activity. This breakthrough threshold criteria was selected to yield a good resolution of $^{90}$Sr distribution within the eight depth layers employed and to compare with the distributions after an equivalent degree of leaching of the chemically-treated soil columns. Both of the oxalate-treated columns and one of the aluminate-treated columns clogged during development and could not be leached to this degree. Flow in each column was maintained at the same rate to avoid possible differences in depth distributions resulting from differing hydrodynamic dispersion. In general, depth distribution of a contaminant within a soil column is more powerful in calibrating or testing a model than are column effluent characteristics alone. Column effluent characteristics focus on only one spatial position in the column, albeit with temporal resolution, whereas depth distribution characterization requires a model to predict behavior at many positions within the column with each successive layer undergoing an increasing degree of leaching.

A comparison of HUMDINGER's calculated distributions of total $^{90}$Sr in the soil layers for both the control and KOH-treated columns after leaching with the specified groundwater, are presented in Figure 3. The agreement seems quite good providing some confidence that HUMDINGER's computational approach and assumptions are adequate to predict the behavior of $^{90}$Sr over the widely differing conditions from highly alkaline treatment to relatively unperturbed control conditions with near
neutral calcium-magnesium bicarbonate-type groundwater. As predicted by HUMDINGER, the KOH-treatment resulted in a much sharper contaminant distribution front within the column than the control-treatment; this resulted from the highly favorable conditions for \(^{90}\text{Sr}\) adsorption and precipitation after alkali treatment when soil CEC is large and highly saturated with \(K^+\), and when \(^{90}\text{Sr}\)-coprecipitable species (portlandite, brucite, and calcite) can form. The contrast between the final characteristics of the KOH-treated and untreated soil columns would have been much greater had groundwater leaching been terminated at much earlier stage; the NaAl(OH)\(_4\)-treated soil column, which had clogged and, thus, was leached with only 124 L of groundwater (Figure 3), illustrates how the \(^{90}\text{Sr}\) accumulates in the topmost layers in earlier stages of development in an alkaline-treated soil. The other alkaline treatments (Na\(_2\)SiO\(_3\) and NaAl(OH)\(_4\)) yielded \(^{90}\text{Sr}\) depth distributions very similar to those of the KOH-treatments; their similarities to KOH treatments suggests that soil mineral dissolution (i.e., increased solubility of Si and/or Al) under highly alkaline conditions does not directly affect the movement of Ca, Mg, or \(^{90}\text{Sr}\).

HUMDINGER has a tremendous degree of freedom in selecting the characteristics of the leaching groundwater (pH, Ca, Mg, K, and Na, and inorganic carbon), the buffering of the soil (4 pK\(_a\)'s and a maximum CEC), and characteristics of the treatment solution (pH, Na, Ca, Mg, and inorganic carbon). Model characteristics can interact in far too numerous combinations to test all possible scenarios; minor changes in one parameter, like groundwater pH, will yield significant differences in model predictions.

HUMDINGER also predicts the observed distribution of soil exchangeable cations in both the alkali-treated (Figure 4) and control columns. The residual effects of the KOH treatment can still be observed in Figure 4 in the elevated exchangeable Na/K within the bottom three layers of this soil column concomitant with its minimum in exchangeable Ca+Mg in the bottom layer; this minimum was, as expected, near the soil's starting and uniformly-distributed exchangeable Ca+Mg (i.e., 143 meq/kg). In addition, the increase in soil CEC caused by the KOH treatment was still evident in the upper layers.
of the soil column where the exchangeable cations far exceeded their starting amounts; deeper in the column, the breakthrough front for K-Ca&Mg cation exchange preceded the $^{90}\text{Sr}$-breakthrough front (Figure 3) by one layer in the same soil column. Similar results were observed with the sodium silicate- and sodium aluminate-treated soil columns consistent with the similar behavior of Na and K in the general monovalent-divalent cation exchange process within these soil columns.

With HUMDINGER's capability to simulate the dynamics of both exchangeable Ca and Mg and their precipitated phases throughout a wide pH range (4-14), it now becomes possible to understand quantitatively the linked behavior of $^{90}\text{Sr}$ in alkaline-treated soil columns. In the NaOH-treatment scenario modeled in Figure 2 and S3 (Supporting Information), $^{90}\text{Sr}$ was not initially present in the soil or in the chemical treatment solution but was introduced subsequently with the leaching groundwater; notably, the default groundwater activity was not constant but varied with the cumulative groundwater volume following a measured linear relationship for both $^{90}\text{Sr}$ activity and hardness (Ca+Mg); HUMDINGER allows a constant groundwater activity and hardness. Again selecting only the top soil layer for illustration, the forms of $^{90}\text{Sr}$ among dissolved, cation exchangeable, and precipitated phases (portlandite, brucite, and calcite), coincident with the dynamics discussed above, are depicted in Figure 5. A logarithmic vertical scale is employed in Figure 5 because of the wide range in magnitude of the various phases during leaching. Relatively little $^{90}\text{Sr}$ is precipitated as either portlandite or brucite simply because little $^{90}\text{Sr}$ had been introduced when these phases were forming or before they had fully dissolved. However, these phases would determine the behavior of $^{90}\text{Sr}$ under an alternative scenario where a soil, already contaminated with $^{90}\text{Sr}$, is treated with alkaline chemicals and subsequently leached with groundwater; here, almost all of the $^{90}\text{Sr}$ would coprecipitate with both portlandite and brucite and its subsequent leaching behavior would be significantly retarded by these phases (20, 25). However, in the present scenario, although some $^{90}\text{Sr}$ activity is precipitated with portlandite and
brucite, the dominant phase for its retention in the soil layer is as a co-precipitate with calcite and as an exchangeable cation. The breakthrough of dissolved $^{90}\text{Sr}$ (Figure 5) from the soil layer is retarded until about 100 L cumulative leaching where calcite begins to dissolve and exchangeable Ca and Mg become larger than exchangeable Na (Figure 2). The dissolved activity of $^{90}\text{Sr}$ becomes slightly elevated while calcite (and its coprecipitated $^{90}\text{Sr}$) is dissolving and drops off to a slightly lower activity once this source is depleted. Once the soil reaches equilibrium with the leaching groundwater (i.e., near 500 L in Figures 2, and 5), dissolved $^{90}\text{Sr}$ activity is maintained solely by its cation exchangeable phase; this partition between dissolved and exchangeable phases is, in turn, maintained by the Ca and Mg cation exchange equilibria. In untreated soil, the Ca and Mg cation exchange equilibria is not perturbed significantly and $^{90}\text{Sr}$ breakthrough in various layers is determined by its relatively constant partition between dissolved and cation exchange sites within each soil layer.

Notably, the dominant precipitated phase sequestering $^{90}\text{Sr}$ in soil is calcite. This phase should remain stable as long as the soil solution remains at or near saturation with respect to calcite. Leaching with calcite-saturated or supersaturated groundwater would allow this phase to grow or, at least, remain constant once formed by an alkaline treatment. Alternately, leaching with low pH and/or calcite-undersaturated groundwater will hasten its dissolution; HUMDINGER allows the simulation of volume of any specific groundwater which must leach a treated soil (or how long the alkaline treatment will last if groundwater velocities were employed) to dissolve the $^{90}\text{Sr}$-immobilized phases. Precipitation of calcite in soil seems to be an excellent phase to immobilize $^{90}\text{Sr}$ as has been observed previously (23, 25, 29, 30) and HUMDINGER represents a research tool to calculate conditions under which a $^{90}\text{Sr}$-calcite co-precipitated phase can form and persist.

Although HUMDINGER has some significant limitations in the range of soil characteristics to which it can presently be applied (as discussed previously), it is able to simulate many subsurface soil
conditions and $^{90}$Sr-contamination scenarios. In particular, it can address a wide range of pH-dependent CEC and initial soil exchangeable cation conditions. It can also address a wide range of alkaline chemical treatment variables (pH, carbonate, hydroxide, major cation concentrations, and treatment volumes). HUMDINGER can also accommodate a large range of characteristics for leachate or groundwater (pH, inorganic carbon, dissolved cations, and volumes) to simulate long-term performance of alkaline soil treatments. HUMDINGER can be configured as a soil column with any number of layers to simulate any desired resolution within a soil column or dissolved phase characteristics within any or all layers of that column. It can also address the scenario where a soil, previously contaminated with $^{90}$Sr, is treated with alkaline solutions and subsequently leached with either uncontaminated or contaminated groundwater. This latter scenario can be used to test hypotheses concerning $^{90}$Sr-contaminated soil surrounding buried radioactive waste (29, 30).

The importance of $^{90}$Sr-coprecipitated phases in immobilizing $^{90}$Sr in soil becomes apparent with modified HUMDINGER simulations. For example, if the portlandite, brucite, and/or calcite solubility/precipitation subroutines in HUMDINGER are disabled, then NaOH treatment of a $^{90}$Sr-contaminated soil is simulated to cause rapid leaching of the soil’s $^{90}$Sr, Ca, and Mg; even with the large increase in pH-dependent CEC caused by the NaOH treatment, a large of excess of dissolved Na would remain available to exchange Ca and Mg which, under these simulated conditions, have no precipitated phases to constrain their solubilities. Such rapid leaching of $^{90}$Sr following treatment of soil with NaOH is not observed experimentally and, to the contrary, researchers frequently observe greatly elevated $K_d$'s for $^{90}$Sr or $^{85}$Sr in laboratory measurements (6, 8, 23, 31); this has also been observed in the batch adsorption studies supporting HUMDINGER development (Table S3, Supporting Information). Thus, the precipitation of portlandite, brucite, and calcite are controlling processes in the adsorption of $^{90}$Sr in soil at elevated pH and must be included in predictive models.
HUMDINGER does not address all the chemical reactions determining the behavior of $^{90}\text{Sr}$ in soil. It simply provides a computational tool to ask questions about the controlling and interdependent simultaneous reactions which occur in soil under dynamic pH conditions. Many of the stimulating "what if" and "suppose" type conjectures, which are the basis for all scientific insights and engineering designs for environmental remedies, can now be asked with more than rhetorical intent. Obvious important potential applications exist to simulate the leaching of $^{90}\text{Sr}$ at many DOE sites including the alkaline waste trenches in Oak Ridge, Tennessee ($3, 11$), leaking storage tanks in Hanford, Washington ($5, 6, 31, 32$), or waste sludge lagoons in Savannah River, South Carolina ($7, 8$). The conceptual approach in HUMDINGER, where empirically measured soil pH-dependent CEC is simulated as a polyprotic weak acid, may also be useful in assessing other environmental and geological reactions where mixing of buffers is a likely controlling process including the weathering of primary or secondary carbonates in soil ($18$), leaching effects of acidic deposition on soil ($9$), and management of alkaline soils under agriculture ($19$).

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**Supporting Information Available**

Detailed descriptions of experimental methods and results; test soil chemical characteristics (Table S1); large soil column construction and development techniques and characteristics (Table S2); radioisotope distribution coefficient measurements (Table S3); chemical treatment effects on soil exchangeable cations (Table S4); pH-dependent soil cation exchange capacity results(Figure S1); soil cation exchange selectivity measurements (Figure S2); model simulations of portlandite, brucite, and calcite precipitation
and dissolution (Figure S3); model simulations comparisons to effluent $^{90}\text{Sr}$ and pH from control and alkali treated soil columns (Figures S4 and S5); and dynamics of the distribution coefficient of $^{90}\text{Sr}$ in soil during leaching (Figure S6).

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Figure 1. Summary of input variables, output variables, and computational flow of HUMDINGER for describing the adsorption and transport of $^{90}\text{Sr}$ in soil under dynamic alkaline conditions.

Figure 2. Simulated response of soil exchangeable cations after NaOH treatment and exhaustive leaching with a calcium-magnesium bicarbonate groundwater at pH=7.

Figure 3. A comparison of model-predicted and observed distribution of $^{90}\text{Sr}$ in depth layers of large soil columns after leaching with $^{90}\text{Sr}$-contaminated groundwater.

Figure 4. Exchangeable cations in depth layers of a soil column treated with KOH and leached with $^{90}\text{Sr}$-contaminated groundwater.

Figure 5. Dynamics of $^{90}\text{Sr}$ phases in soil treated with NaOH and subsequently leached with $^{90}\text{Sr}$-contaminated groundwater as simulated by HUMDINGER.
One-Dimensional Soil Mixing Cell Model Coupled With "HUMDINGER" $^{90}$Sr Chemistry

User-Specified Chemical Treatment:
- NaOH, $Na_2CO_3$ or None
- Dissolved Cations and $^{90}$Sr Activity
- Treatment Volume (TVOL)

User-Specified Groundwater Leaching:
- $^{90}$Sr Activity
- Dissolved Cations, Inorganic Carbon, pH
- Total Volume (ENDVOL)

User Must Specify or Use Default Values For:
- Soil "Acid" $pK_a$'s and capacity (MAXCEC)
- Starting $^{90}$Sr, Soil Cations, and pH
- Soil Physical Parameters (Bulk density and volume)
  (Usually Identical For All Cells)
- Incremental Flow Volume ($dV$)
- Number of Soil Mixing Cells and Total Groundwater Flow/Leach Volume (ENDVOL)

Final Groundwater Observation Point

Final Groundwater Observation Point

Model Generates Database File (*.MDB) For All Soil Mixing Cells Containing Dissolved and Adsorbed $^{90}$Sr and Cations (Ca, Mg, Na, K) And Displays Results Graphically Versus Total Flow/Leach Volume
The graph shows the distribution of $^{90}$Sr (Bq/kg) in different soil column layers. The different treatments and models are indicated as follows:

- **KOH Treatment $^{90}$Sr** (dashed blue line with square markers)
- **Control Treatment $^{90}$Sr** (dashed red line with triangle markers)
- **Control Model, pH=7** (solid blue line with circle markers)
- **NaOH Model, pH=7** (solid red line with square markers)
- **NaAl(OH)4 Treatment** (solid pink line with circle markers)

The x-axis represents the soil column layer, while the y-axis represents the concentration of $^{90}$Sr (Bq/kg).
Soil Column Layer

Exchangeable Cations (meq/kg)

Starting Ca+Mg (143 meq/kg)

Starting K+Na (4 meq/kg)