

## MIGRATION OF ACIDIC GROUNDWATER SEEPAGE FROM URANIUM-TAILINGS IMPOUNDMENTS, 3. SIMULATION OF THE CONCEPTUAL MODEL WITH APPLICATION TO SEEPAGE AREA A

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### ABSTRACT

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In this third paper of the series, the conceptual model for contaminant migration is coded into a family of computer programs named ADNEUT. Program framework, execution time and cost, efficiency, accuracy based on comparisons with other programs, and sensitivity of simulated results to input data provide insight into the benefits and limitations of ADNEUT.

Simulations with ADNEUT show that the neutralization zone is composed of a sequence of several sub-regions through which a theoretical step-function increase in pH and change in other aqueous constituents occur from the inner core to the outer zone. The pH, aqueous chemistry, and retardation of each sub-region are the result of the dissolution of, and buffering by, one of the minerals of the conceptual model. The behavior of a sub-region affects the behavior of all downgradient sub-regions, resulting in a complex scenario of dependence for sub-regions at a site. Depending on the information required from a simulation, ADNEUT can be used in its one-cell, two-cell or multi-cell mode. The use of ADNEUT in its one-cell mode demonstrates the limitations of laboratory batch tests, titration tests, and non-transport geochemical programs in evaluating contaminant migration.

ADNEUT is calibrated to current conditions at Seepage Area A at the Nordic Main impoundment in order to demonstrate the applicability of the conceptual model, to show specific limitations of the model, and to illustrate the measured data required for a reliable simulation. Following calibration, ADNEUT is used to examine probable past behavior of the contaminant plume prior to monitoring. The plume was likely more acidic in the past, apparently originates very close to or within the waste-rock impoundment dam, and began migrating out of the source area in 1966-1967. ADNEUT is then used to examine possible future behavior of the plume under the assumptions of continuation of current conditions, decreasing acidity, and increasing acidity through time, which can result in variations in retardation coefficients and in the number of sub-regions within the plume.

## 1. INTRODUCTION

The previous papers of this series (Morin et al., 1988 a, b) have presented a field study of contaminant migration from a uranium-tailings impoundment and have developed a conceptual model for contaminant migration. Major ions in the contaminant plume were found to be predominately regulated by precipitation-dissolution of the calcite-siderite solid solution, gypsum, Al-OH minerals, and Fe-OH minerals. Minor metals and non-metals and radionuclides are regulated by precipitation, coprecipitation, and absorption in such a complex manner that simulation along a groundwater flowpath cannot be easily accomplished. Consequently, the simulation of contaminant migration at the field site is currently limited to major ions.

Many computer programs designed to simulate contaminant migration in groundwater solve an advection-dispersion equation with solid-liquid interactions included through a retardation factor. In systems such as acid drainage where large amounts of precipitation-dissolution occur and aqueous speciation and pH are highly variable along a groundwater flowpath, the use of a species retardation factor may not provide accurate simulation. Thus, "cell" or "mixing cell" models in which chemical reactions take place within a cell before advection continues can be employed. This cell concept has already been used in this series of papers as "cell-and-streamtube" calculations through which simple mass-balance calculations were performed.

There are several computer programs currently available for simulating precipitation-dissolution, such as PHREEQE (Parkhurst et al., 1980), WATEGM-SE (Palmer, 1983), and MINTEQ (Felmy et al., 1984). However, when coupled to a cell-transport framework for acid-drainage simulation, these programs can be relatively time-consuming to execute for several reasons. First, they are generalized programs capable of precipitating-dissolving a large number of compounds. Second, these programs calculate concentrations for a large number of complexes and ion pairs, many of which are at insignificant levels in acid drainage. Third, many of the general programs construct a matrix and solve it by routines such as Gaussian Elimination. The matrix-solvers require good initial guesses of final results in order to obtain convergence and, thus, convergence to a solution is not always assured. The problem is that non-convergence at any one time in any one cell precludes any final results. Fourth, large amounts of computer time are needed by these programs to compute significant amounts of precipitation-dissolution, because small increments must be used otherwise convergence may not occur. Fifth, some of these matrix-solvers manipulate large, sparse matrices, resulting in unnecessary mathematical calculations. Consequently, where large amounts of precipitation-dissolution are to be simulated and convergence is always necessary, the generalized programs using matrix-solver methods are not often the cheapest and optimum approach. Morin (1985a) and Morin (1987) provide additional discussion on this topic.

## 2. THE ADNEUT COMPUTER PROGRAMS

In order to overcome the limitations of the generalized programs when applied to acid drainage, a family of relatively low-execution-cost, topic-specific programs were created to allow large, abrupt variations in pH, to efficiently accommodate large amounts of precipitation-dissolution, and to consistently converge to a solution. The benefit of low execution cost is intended for mainframe systems; however, the programs have been adapted to microcomputer systems and efficiency is now mainly relevant for execution time. The programs incorporate (1) only dominant aqueous species in acid drainage identified through calculations by WATEQ2 (Ball et al., 1979), (2) only the minerals of the conceptual model, and (3) flow of groundwater through a streamtube partitioned into cells. Dispersion is not simulated because it is expected to be unimportant in many cases of acidic-seepage neutralization (Morin et al., 1988a) and in many cases in general (Massman and Freeze, 1987, and references therein). The family name for the programs is ADNEUT, an acronym for Acid-Drainage NEUTralization, and the differences among the programs lie in specific details (Table 1). The difference between ADNEUT1 and ADNEUT2 lies in the inclusion of radionuclide speciation and sorption through a distribution coefficient ( $K_d$ ) in ADNEUT2. ADNEUT2 is not used for simulations in this paper because radionuclides in the contaminant plume at the field site are not regulated by simple sorption, but ADNEUT2 has been applied to other sites (Morin, 1983). ADNEUT3 was created after ADNEUT1 and ADNEUT2 to overcome major limitations preventing an acceptable simulation of the contaminant plume in Seepage Area A at the Nordic Main field site (Table 1).

ADNEUT is programmed in three basic parts: a speciation routine, a precipitation-dissolution routine, and a transport routine. The speciation routine employs the Continuous-Fraction Method (e.g., Wigley, 1977), which is modified for more efficient use in ADNEUT (Morin, 1985a). The Continuous-Fraction Method has been found to converge consistently to a solution despite large one-step changes in concentrations. Thermodynamic data for ADNEUT are taken from WATEQ2 (Ball et al., 1979, 1980). Temperature adjustments of equilibrium constants are accomplished with the van't Hoff Equation and activity coefficients are calculated by the Davies Equation. The only redox couples

TABLE 1

The ADNEUT programs

	Radionuclide speciation- sorption	Variable velocity through the streamtube	Variable solubility through the streamtube	Changing input soln with time
ADNEUT1	no	no	no	no
ADNEUT2	yes	no	no	no
ADNEUT3	no	yes	yes	yes

currently in ADNEUT are  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ - $\text{Mn}^{3+}$ , although other couples can be added. However, an important conclusion on redox reactions in this study is that there are insufficient quantities of other oxidants in the contaminant plume to oxidize much  $\text{Fe}^{2+}$  (Morin, 1986; Morin et al., 1988a).

The speciation routine was tested against WATEQ2, from which it is derived. Comparison of calculated concentrations of five aqueous species in four acid-drainage waters shows a mean difference (calculated by  $[\text{ADNEUT VALUE} - \text{WATEQ2 VALUE}]/\text{WATEQ2 VALUE}$ ) of +0.0963 with a standard deviation of 0.1487. This disagreement is primarily attributed to the condition of electroneutrality, which is apparently appropriate in this study (Morin, 1988a), and is forced upon the initial input chemical analysis by ADNEUT by creating an unspecified species during speciation. This adjustment to electroneutrality results in a higher calculated ionic strength by ADNEUT which in turn results in differing activity coefficients and differing concentrations of species. The disagreement between ADNEUT and WATEQ2 can be particularly high for free  $\text{Al}^{3+}$  with differences up to an extreme factor of 3 noted. The cause of the disagreement may be related to the aforementioned reason of a higher ionic strength which could significantly affect the calculated activity of a 3+ ion.

The precipitation-dissolution routine in ADNEUT currently contains the five minerals of the conceptual model: calcite, siderite, gypsum,  $\text{Al}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_3$ . The treatment of calcite and siderite as separate minerals rather than a solid solution causes some degree of error, but cannot be overcome at this time (Morin and Cherry, 1986). The routine empirically precipitates or dissolves, if available, a predetermined amount of each mineral, occasionally changing the value of  $\log_{10} \text{SI}$  ( $\text{SI} = \text{ion activity product/solubility product}$ ) by more than 10, recalculates speciation, and checks for attainment of equilibrium which is arbitrarily set at  $-0.05 < \log \text{SI} < +0.05$ .

Only closed system dissolution of carbonate is currently simulated by ADNEUT. This lack of  $\text{CO}_2$  loss through gas transfer to the unsaturated zone is justified for Seepage Area A at the field site (Morin et al., 1988a, b) based on lack of significant ferric-iron precipitation by diffusion of oxygen through the unsaturated zone, stability of  $^{13}\text{C}$  values despite a significant change in pH, and general retention of  $^{222}\text{Rn}$  gas along the contaminant plume centerline.

To further evaluate the operation of ADNEUT, ADNEUT results were compared to results from PHREEQE (Parkhurst et al., 1980) for various data sets generally representative of acid drainage (Morin, 1983) using consistent thermodynamic data for mineral solubilities. Because of the limitation of internally allotted time in PHREEQE and the required large amount of mineral precipitation-dissolution, the comparisons were limited to only one or two minerals of the conceptual model. The disagreement in results between PHREEQE and ADNEUT were similar to those between WATEQ2 and ADNEUT, with the disagreement in pH-dependent species compounded by the difference in predicted pH. ADNEUT consistently predicted a pH after mineral reactions that was 0.03 to 0.05 pH units higher than the pH predicted by PHREEQE. This disagreement is probably

accounted for by the differing choice of species (valence 1, 2, or 3) used for forcing electroneutrality on the data set, often causing ADNEUT to calculate a higher ionic strength by about 10%. However, because execution time and costs for ADNEUT were less than 1/6 of those of PHREEQE, the relatively small differences are deemed acceptable.

Redox equilibrium is one major area of disagreement between ADNEUT and PHREEQE and the examination of this disagreement highlights problems in the simulation of redox reactions (see also Morin, 1986). At relatively high Eh around +700 mV, the two programs agree within 20 mV, but, at relatively low Eh around +100 mV near the important siderite-Fe(OH)<sub>3</sub> stability boundary, PHREEQE predicts values 100–150 mV higher than ADNEUT. The PHREEQE values do not reflect measured Eh values at the site. The inaccuracy in PHREEQE results is attributed to the fact that PHREEQE includes several "redox couples", such as SO<sub>4</sub><sup>2-</sup>-S<sup>2-</sup> (actually not a redox couple), which are probably not operative to a significant extent in Area A. The inclusion of the couples causes PHREEQE to allow more Fe<sup>2+</sup> to oxidize than ADNEUT, thus producing a higher Eh, and this effect of the couples is greater at lower Eh values where Fe<sup>2+</sup> is dominant.

The transport routine in ADNEUT is simply a cell approach by which water in a cell is passed to the adjacent downgradient cell at each time step. This approach is explained mathematically in Van Omman (1985).

The pH range which is reliably and efficiently simulated is about 1.5 to 7.5. Below pH 1.5, execution time increases greatly because gypsum precipitation-dissolution is calculated from the amount of SO<sub>4</sub><sup>2-</sup> rather than the dominant HSO<sub>4</sub><sup>-</sup> below pH 2. Acid drainage does not often attain a pH below 1.5 because of the pH-buffering capacity of the SO<sub>4</sub><sup>2-</sup>-HSO<sub>4</sub><sup>-</sup> couple around pH 2. Above pH 7.5, some neutral and anionic complexes not included in ADNEUT become important.

Execution times for ADNEUT simulations are highly variable, depending on such factors as length of simulation, number of cells, amount of precipitation-dissolution in each cell, the number of times a "money saver" routine can be invoked (not applicable to ADNEUT3), and the number of time steps between output of intermediate results. Execution times for ADNEUT compiled under a WATFIV compiler on an IBM4341 mainframe were found to generally range from 0.1 to 2.0 CPU seconds (3 to 45 cents at 1984 research rates) per cell per time step during the course of this study. A large amount of execution time can be eliminated by using ADNEUT in the "two-cell mode" with an accompanying loss of spatial distributions as explained in Section 3. ADNEUT1 and ADNEUT3 are approximately 50 k-byte in size plus 1 k-byte array storage for each cell in the simulated streamtube; ADNEUT2 is about 75 k-bytes in size plus 1 k-byte for each cell. Additionally, up to several hundred k-bytes of disk storage are required for output if many intermediate results are stored. The source code and examples of input and output for ADNEUT1 and ADNEUT2 are listed in Appendix H of Morin (1983) and ADNEUT3 is presented in Cherry et al. (1984).

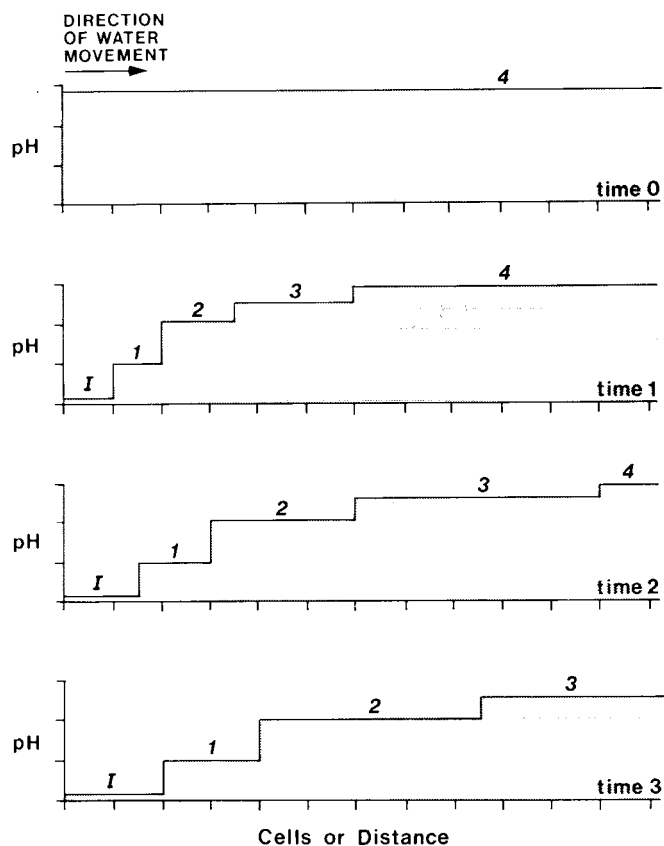
### 3. SIMULATION OF THE NEUTRALIZATION ZONE WITH ADNEUT

As described in the first paper of this series (Morin et al., 1988a), the neutralization zone is the transition region between the inner core and outer zone, where calcite dissolves and other minerals of the conceptual model precipitate. Results of the "cell-and-streamtube" calculations suggest that re-dissolution of precipitated minerals is important. ADNEUT simulations show that re-dissolution is indeed very important for understanding both the retardation of the inner core and the variable aqueous chemistry through the neutralization zone.

ADNEUT simulations indicate that the neutralization zone is divided into "sub-regions" and in each sub-region a particular mineral dominates the aqueous chemistry. An example based on a tailings impoundment in Wyoming (Morin, 1983; Morin, 1988b) illustrates the sub-region concept. These inner-core pH at the site is about 2.0 and outer-zone pH is 6.0. The here-defined "equilibrium pH" values for the minerals at the simulated site are:  $\text{Fe}(\text{OH})_3 = 3.5$ ,  $\text{Al}(\text{OH})_3 = 5.0$ ,  $\text{FeCO}_3 = 5.1$ , and  $\text{CaCO}_3 = 5.9$ . If solution pH is above a mineral's equilibrium pH, the mineral precipitates and, conversely, the mineral dissolves if solution pH is below its equilibrium pH, thereby raising solution pH up to equilibrium pH. This concept of equilibrium pH is consistent with that of Garrels et al. (1960) to describe the solubility of some carbonate minerals. It is important to note that equilibrium pH's are site-dependent values, varying with inner-core chemistry, solubility of minerals, and site conditions. When inner-core water at pH 2 at the simulated site first comes into contact with calcite (in the first simulated cell), the resulting pH after closed system dissolution is 5.9 and the other three minerals, whose equilibrium pH's are exceeded, as well as gypsum precipitate. After all calcite is removed from the first cell, the siderite formed by precipitation during calcite dissolution then dissolves into the acid drainage and the resulting solution pH is 5.1, causing  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , and gypsum to continue to precipitate. After all siderite is removed,  $\text{Al}(\text{OH})_3$  then dissolves and raises solution pH to 5.0, causing  $\text{Fe}(\text{OH})_3$  and gypsum to continue to precipitate, and so on. In this way, the neutralization zone is conceptually composed spatially of step-function sub-regions with unique pH's, aqueous chemistries, and migration rates (Fig. 1). Figure 1 is similar to the spatial profiles of Scrivner et al. (1986) for deep-well injection of high-iron acidic waste into dolomite.

The calcite sub-region is theoretically synonymous with the outer zone, but, in many actual cases, this equality only holds for the outer zone directly adjacent to the neutralization zone because the more distant outer zone is often affected by dilution with background water. Thus, a user of ADNEUT must determine the portion of the outer zone that is represented by the calcite sub-region. Also, the calcite and siderite sub-regions are not distinct entities because of their solid-solution relationship (Morin and Cherry, 1986) and the problems produced by their separate treatment are discussed in a later section.

In order to evaluate sub-region migration and aqueous chemistry, ADNEUT can be used in "one-cell", "two-cell", and "multi-cell" modes. The multi-cell



- I** INNER CORE  
**1**  $\text{Fe}(\text{OH})_3$  SUB-REGION  
**2**  $\text{Al}(\text{OH})_3$  SUB-REGION  
**3** SIDERITE SUB-REGION  
**4** CALCITE SUB-REGION

Fig. 1. Multi-cell mode for ADNEUT simulations.

mode is the classical mode for cell models where a full string of cells is used in the simulation (Fig. 1). ADNEUT simulations have shown that the length of all sub-regions increase with time and the movement of a sub-region is less retarded than all upgradient sub-regions, i.e. a downgradient sub-region must migrate faster than upgradient sub-regions or it will be overtaken and disappear. The increase in length with time and the incorrect overtaking of a sub-region have implications on mass balance and validity of data, particularly site-specific mineral solubilities, which are discussed in detail in Morin (1983) and Cherry et al. (1984). A multi-cell-mode simulation yields both temporal and spatial information on the migration of sub-regions, but there are three major disadvantages to this mode. First, in order to obtain a realistic simulation of a well-established plume, data on past conditions such as past velocities and

date of acid-seepage commencement are required, but are not available if seepage began prior to monitoring. Second, the time and cost of a multi-cell simulation can be prohibitive. These problems can be overcome by using the two-cell mode if explicit spatial data is not important. Third, there is an error resulting from discretization at early times in the first cell where inner-core water comes into direct contact with calcite (outer zone), which in effect means no neutralization zone exists along the length of the first cell at early times. This error is propagated to a progressively lesser degree to following cells and vanishes as cell length decreases to zero to represent reality or as simulated time passes. Conversely, as cell length increases, the error increases as shown in Fig. 2. Simulation B has a cell length and associated time step that is 5 times larger than those of Simulation A. After an equivalent period of elapsed time (e.g. 75 time steps in Simulation A and 15 time steps in simulation B), the error in the coarser grid is apparent. On the other hand, the *patterns* in both simulations are identical after an identical number of time steps (see solid arrows in Fig. 2), indicating this equilibrium-based model is not sensitive to

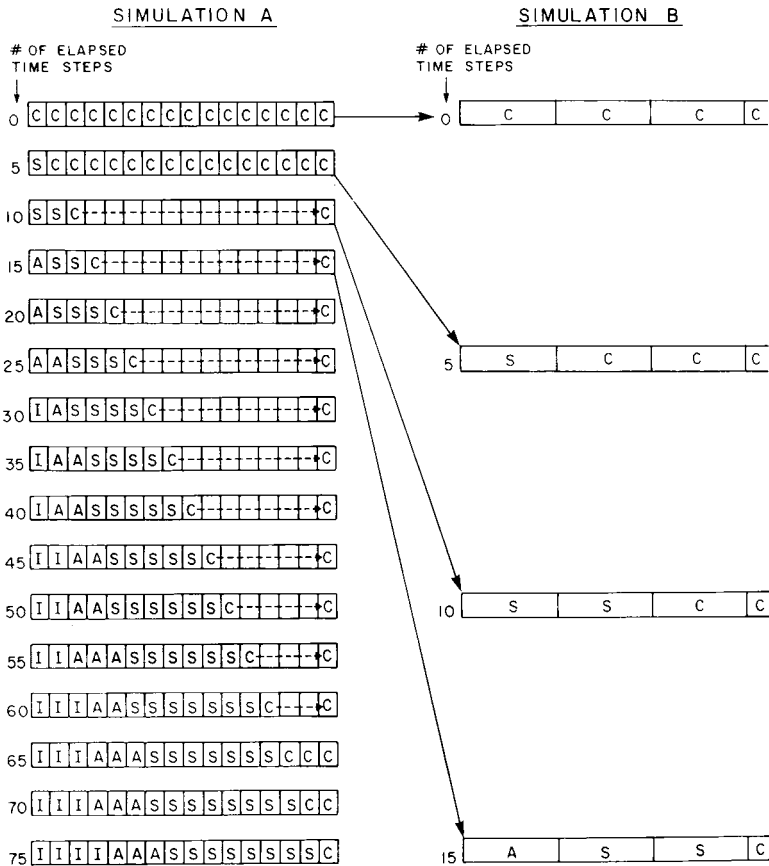


Fig. 2. Specific example of a multi-cell mode simulation.

elapsed real time, but is only sensitive to the number of elapsed time steps of any arbitrary length.

The one-cell mode (Fig. 3) is used where information on only equilibrium pH's and aqueous chemistries of the sub-regions are desired. Information on migration and retardation rates cannot be obtained, because inner-core water is always the input to the first and only cell. This error is related to the discretization problem discussed in the previous paragraph and to laboratory batch tests, which are essentially one-cell tests, on acid neutralization. The direct entry of inner-core water into a cell containing calcite will remove more calcite in one time step (less retardation) than is removed in reality when upgradient sub-regions partially neutralize the inner-core water before it reaches the calcite sub-region. Similarly, the direct entry of inner-core water into a cell containing siderite removes more siderite in a time step than is removed in reality when upgradient  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  sub-regions partially neutralize the inner-core water. In laboratory batch (static) tests, a predetermined volume of inner-core water is sometimes added to carbonate-containing material and the equilibrated pH and aqueous concentrations are measured. In terms of the sub-region concept, the equilibrium pH and concentrations in the

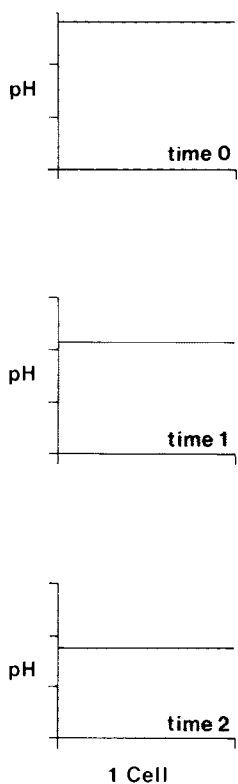


Fig. 3. One-cell mode simulation.

batch test depend on the solid: liquid ratio; the greater the proportion of inner-core water to solid, the greater the chance of an "upgradient" sub-region, e.g.  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$ , appearing. In this situation, a batch test simply represents a "snapshot" of the first cell at some unknown time with no evaluation of potential past and future conditions. In laboratory titration (dynamic) tests of carbonate material with inner-core water, the measured neutralization and the inferred retardation of movement in a groundwater system are subject to the same error as the one-cell mode. Simulations with non-transport geochemical programs used in the one-cell mode are also subject to the above errors (Morin, 1983).

The two-cell model (Fig. 4) yields information on sub-region migration through retardation coefficients (ratio of sub-region velocity to groundwater velocity). Sometimes complex calculations must be used with the coefficients to obtain spatial data, such as distances travelled and lengths of sub-regions after an elapsed time period, which are explicitly supplied by the multi-cell mode.

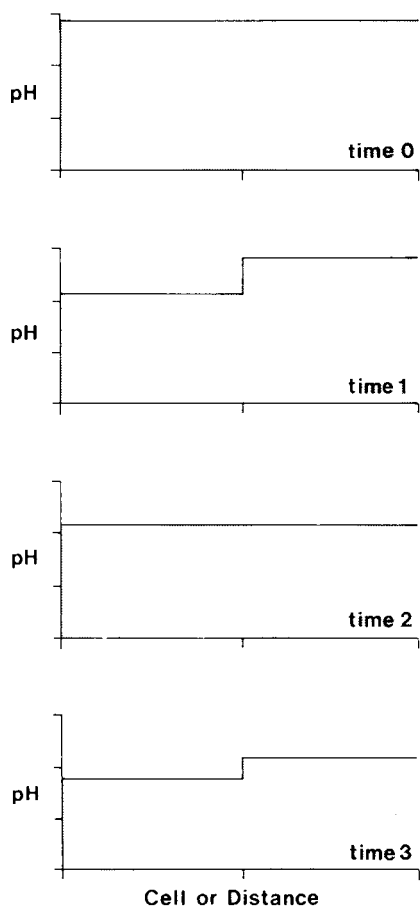


Fig. 4. Two-cell mode simulation.

However, in light of the savings of execution time and cost, the two-cell mode may often be more desirable. The two-cell mode does not involve simulation from commencement of seepage like the multi-cell mode and, thus, past conditions prior to monitoring of contaminant plumes are not critical for the simulation of current conditions.

Retardation coefficients are obtained from the two-cell-mode simulations by noting the amount of a mineral removed at each time step in the second cell when a lower pH (different sub-region) is present in the first cell. For example, both cells initially contain calcite as inner-core water enters the first cell. As previously explained, calcite is removed unrealistically fast from the first cell, as the second cell remains dormant. After all calcite is removed in the first cell, siderite dissolves and raises solution pH to its equilibrium pH (time 1 in Fig. 4). At this point, calcite begins to dissolve in the second cell to complete the neutralization. If the second cell initially contains 20 wt.% calcite and 2 wt.% is removed at each time step, the resulting retardation coefficient for the upgradient edge of the calcite sub-region is the reciprocal of  $(20/2) + 1$ , or 9.1% of groundwater velocity.

#### 4. SENSITIVITY OF ADNEUT SIMULATIONS TO INPUT DATA

This section examines the changes in simulated results upon changes in input data of velocity, cell size, concentrations of minerals, pH, Eh, concentrations of aqueous species, and solubilities of minerals. The effects of varying the first three factors are not site-dependent and, thus, are easily described. The effects of varying the remaining factors are site-dependent and are discussed here only through data from Seepage Area A. The effects of varying the last four factors are not proportional to the variation, do not display regular and easily predicted trends, and are different for each sub-region.

For the effect of changing groundwater velocities on simulation results, sub-regions migrate at 1/2 the previous rate and sub-region lengths are shorter after an equivalent period of time when a simulation is made at 1/2 the groundwater velocity of a previous simulation. Retardation coefficients obtained from two-cell-mode simulations are independent of velocity.

Because ADNEUT simulates "plug flow", the size of cells essentially affects only the smoothness of simulated movement. If velocity is 1 m/yr and cell length is 5 m, sub-regions remain stationary for 5 years then jump 5 m downgradient, whereas a cell length of 1 m would produce movement every year. There must be a compromise between cell length and smoothness of movement in order to obtain acceptable execution time and costs. An additional problem with cell length is the error in the first cell which is propagated to a proportionally lesser degree to each downgradient cell at early times as explained in the previous section. As the length of the first cell increases, the portion of the streamtube affected by the error increases.

Variations in input concentrations of initial mineral content has a linear effect. For example, if 1/2 of a previous amount of calcite is used in a

simulation, then the calcite maintains its equilibrium pH and aqueous chemistry for 1/2 the previous length of time. As a result, the values of the retardation coefficients and the migration rate of the sub-region increase by a factor of 2.

The effect of changing input inner-core pH on final results varies from negligible to extreme. Varying the input pH by a few tenths of a pH unit would normally not be significant; however, as each mineral has an equilibrium pH, changes in input pH from less than to greater than a particular equilibrium pH will greatly alter the results of a simulation. Consequently, there is no simple trend from varying input pH.

The effect of changing input Eh is similar to that of pH. For example, when  $\text{Fe}(\text{OH})_3$  is highly unstable (i.e., Eh is very low), there are negligible effects upon varying input Eh by a few tens of millivolts. However, if Eh places the water near the siderite- $\text{Fe}(\text{OH})_3$  stability boundary, a small change in Eh could eliminate one of the minerals from the system.

Effects of varying input concentrations of aqueous species depend on which species are varied. If input sodium concentrations, for instance, are varied by several tens-of-percent among otherwise identical simulations, the effects on simulated results would be small because sodium does not engage in mineral reactions in ADNEUT. Additionally, sodium often comprises a small percentage of total cations in acid drainage so that changes in concentration do not greatly affect activity coefficients. On the other hand, the effect of halving input inner-core concentrations of the major ions, iron and sulfate, varies with sub-region. In the  $\text{Al}(\text{OH})_3$  sub-region adjacent to the inner core, the effect is minor. On the other hand, the value of the retardation coefficient in the siderite sub-region is approximately doubled because less siderite is initially formed from the lower iron concentrations and a higher percentage of the siderite must therefore dissolve to reach saturation. In the calcite sub-region of Area A, equilibrium pH decreases by 0.15 pH units, iron and calcium concentrations decrease by approximately 30%, sulfate decreases by 50%, and the value of the retardation coefficient decreases by 25%.

A major point discussed in Morin et al. (1988a) and in Morin and Cherry (1986) is the variable solubilities of minerals in the conceptual model excluding gypsum. While other input data for ADNEUT are easily measured, the site-specific and sub-region-specific solubilities are not easily defined and the assistance of a speciation model is required. The sensitivity studies show that the effects of varying solubilities between simulations do not display simple, predictable trends because of the dependence that exists among the sub-regions. In other words, results of simulation of the calcite sub-region depend on all mineral solubilities in the calcite sub-region as well as on aqueous concentrations passed from the siderite sub-region. In turn, the aqueous concentrations in the siderite sub-region which are passed to the calcite sub-region depend on all mineral solubilities in the siderite sub-region as well as on aqueous concentrations passed from the  $\text{Al}(\text{OH})_3$  sub-region, and so on. A sensitivity analysis of this type of dependence is complex and only simple

analyses are presented here based on Seepage Area A which does not have a  $\text{Fe}(\text{OH})_3$  sub-region. More complex analyses are given in Cherry et al. (1984) and Morin (1983).

The sensitivity of results in the  $\text{Al}(\text{OH})_3$  sub-region, which is adjacent to the inner core in Area A, is examined first. To evaluate the potential sensitivity of results to gypsum solubility, the log SP (solubility product) of gypsum was changed from  $-4.63$  to  $-4.53$ , causing aqueous calcium to increase by 23%, aqueous sulfate to increase by 2% equal to the molal increase in calcium, and ionic strength to increase by 1.5%. This change in log SP gypsum does not affect the retardation of the  $\text{Al}(\text{OH})_3$  sub-region, but the consumption of gypsum over one time step doubles. By changing log SP  $\text{Al}(\text{OH})_3$  from  $-32.11$  to  $-33.11$  (i.e., from amorphous to more crystalline  $\text{Al}(\text{OH})_3$ ), aqueous aluminium and the value of the retardation coefficient decrease by almost one order of magnitude, i.e. the migration rate of the sub-region and consumption of  $\text{Al}(\text{OH})_3$  decrease, because the degree of neutralization of inner core water is less. However, this causes an increased consumption of siderite in the downgradient siderite sub-region.

In order to examine the sensitivity of the siderite sub-region to variations in aluminum, the log SP  $\text{Al}(\text{OH})_3$  in the siderite sub-region was varied as all other conditions in the siderite and in the upgradient  $\text{Al}(\text{OH})_3$  sub-regions remained constant. Results are presented in Table 2 and it is interesting to note that, while a decrease in  $\text{Al}(\text{OH})_3$  solubility in the  $\text{Al}(\text{OH})_3$  sub-region (previous paragraph) causes additional retardation of that sub-region, a decrease in  $\text{Al}(\text{OH})_3$  solubility in the siderite sub-region causes less retardation. The reason for this event is that  $\text{Al}(\text{OH})_3$  dissolves (consumes  $\text{H}^+$ ) in the  $\text{Al}(\text{OH})_3$  sub-region and precipitates (produces  $\text{H}^+$ ) in the siderite sub-region requiring additional siderite dissolution for neutralization. Consequently, variations in  $\text{Al}(\text{OH})_3$  solubility in the two sub-regions produce opposite effects. Also, variations in  $\text{Al}(\text{OH})_3$  solubility in the siderite sub-region produce minor but noticeable changes in Eh, Fe, and retardation in the calcite sub-region.

In the calcite sub-region, two tests involved (1) a change only in log SP calcite from  $-9.98$  to  $-9.73$  and (2) a change in log SP calcite from  $-9.98$  to

TABLE 2

Variation in conditions within the siderite sub-region with a change in log SP  $\text{Al}(\text{OH})_3$

Change from log SP $\text{Al}(\text{OH})_3$ = 33.61	Change from original condition				
	Change in pH (pH units)	Change in Eh (pe units)	Change in DIC <sup>1</sup> (%)	Change in Al (%)	Change in ret. coeff. (%)
-0.5	+0.02	-0.05	-7	-45	-15
-1.0	+0.05	-0.10	-19	-125	-38
-1.5	+0.14	0.33	-41	+277	-80

<sup>1</sup>DIC = dissolved organic carbon.

-9.73 with a change in log SP  $\text{Al}(\text{OH})_3$  from -32.61 to -34.11. Results (Table 3) highlight the complex and dramatic response of aqueous chemistry to mineral solubility.

##### 5. APPLICATION OF ADNEUT TO SEEPAGE AREA A

As explained in the first paper of this series, the conceptual model that is simulated by ADNEUT is general in nature, based on data from several acidic uranium-tailings sites and acid drainage in general (Morin, 1983, 1988b). Before ADNEUT can be used to simulate probable past or future contaminant migration at a site, it must be calibrated to current conditions at a site using groundwater velocity, inner-core chemistry, initial concentrations of relevant minerals, and mineral solubilities. Proper calibration requires predicted retardation of sub-regions to equal observed retardation and predicted concentrations in the sub-regions to equal observed concentrations. Because site-specific solubilities of minerals are rarely measured directly at sites and/or initial concentrations of relevant minerals are not always measured, calibration involves the changing of these parameters until similar predicted and observed retardation and chemistries are obtained. This section contains a description of the calibration of ADNEUT to Seepage Area A, providing important insights into the quantity and quality of input data required for the proper use of ADNEUT as well as the limitations of ADNEUT. Following calibration, ADNEUT is used to determine the anticipated future behavior and the probable past behavior of the plume prior to monitoring, including the probable source area of the plume within the impoundment which could not be located through drilling and piezometer installation.

TABLE 3

Variation in conditions within the calcite sub-region with changes in solubilities

Parameter	Change from original conditions	
	Change in log SP calcite from -9.98 to -9.73	Change in log SP calcite from -9.98 to -9.73 and in log SP $\text{Al}(\text{OH})_3$ from -32.61 to -34.11
pH (pH units)	0.03 unit increase	0.09 unit increase
Eh (pE units)	0.08 unit increase	0.33 unit increase
Ionic strength	6% decrease	39% decrease
Fe	19% decrease	60% decrease
Ca	30% decrease	15% decrease
Al	40% decrease	7% decrease
$\text{SO}_4$	7% decrease	45% decrease
DIC	4% decrease	4% increase
Ret. coeff. value	14% increase	283% increase

ADNEUT was calibrated to Area A using measured data from 1980 to 1984. Using ADNEUT's two-cell mode, the calibration primarily involved the adjustment of mineral solubilities in each sub-region and the best-match solubilities are listed in Table 4. While arbitrary solubilities can be used as a simple tool to force a match of retardation at a site, anomalous solubilities will generally not provide a match to observed concentrations in the sub-regions. The results of the best-match simulation and comparisons with measured data show generally good agreement and some discrepancies (Table 5). The discrepancies arise from the irregular, natural annual variations in inner-core chemistry which cannot be simulated, from the difficulty in selecting a piezometer to represent a sub-region each year (Morin et al., 1988a), and from weaknesses in ADNEUT. The problems with natural variation and piezometer selection can be seen by comparing annually measured data for each parameter in Table 5. The major weaknesses with ADNEUT lie in the calcite sub-region and are probably the result of simulating the calcite sub-region as a distinct entity when it likely forms a continuum with the siderite sub-region. Although this problem indicates DIC (dissolved inorganic carbon) in, and retardation of, the calcite sub-region cannot often be exactly simulated, it does not affect the remaining sub-regions that are upgradient. Additionally, aqueous aluminum in both the calcite and siderite sub-regions is significantly overestimated by ADNEUT and this may be the result of either the precipitation of additional Al minerals in the plume such as allophane (Morin et al., 1988a, b) which are not included in ADNEUT or the aluminum speciation error discussed in an earlier section. In any case, this difficulty in properly simulating aluminum has also been noted elsewhere (Senes Consultants, 1986). For Area A, overestimation of aqueous Al has not prevented calibration to other concentrations and to retardation.

The best-match simulation of Area A can be summarized as containing three sub-regions: the  $\text{Al}(\text{OH})_3$  sub-region with an equilibrium pH of 5.02 and a retardation coefficient of 0.20% of groundwater velocity, the siderite sub-region with an equilibrium pH of 5.27 and a retardation of 0.46%, and the calcite sub-region with an equilibrium pH of 5.73 and a retardation of 14.0%. The pH and concentration plateaus are not clearly evident in aqueous profiles through Area A (e.g. Fig. 11 of Morin et al., 1988a) for one or more of the

TABLE 4

Solubilities providing best-match calibration for Area A

Sub-region	Mineral				
	Calcite	Siderite	$\text{Al}(\text{OH})_3$	$\text{Fe}(\text{OH})_3$	Gypsum
Calcite	9.98	-9.34	-33.61	*	-4.63
Siderite	*	-10.34	-33.11	*	-4.63
$\text{Al}(\text{OH})_3$	*	*	-33.71	*	-4.63

\* The mineral does not exist in the sub-region.

TABLE 5

Comparison of measured and ADNEUT3-predicted data

(I = inner core, used as input; meas = measured; pred = predicted; calc = calculated; concentrations as millimolar)

	Sub-regions <sup>1</sup>			
	I	Al(OH) <sub>3</sub>	Siderite	Calcite
pH meas (1980)	4.40	4.90	4.86(?)	5.80
pH meas (1981)	4.24	-	5.22	5.65
pH meas (1982)	4.60	5.18	5.43	5.75
pH meas (1983)	4.4	5.0	5.5	5.4
pH meas (1984)	4.69	4.75	5.50	5.94
pH pred	4.40	5.02	5.27	5.73
Fe meas (1980)	100.8	85.1	39.2	35.8
Fe meas (1981)	91.6	-	60.1	37.7
Fe meas (1982)	89.3	83.2	55.8	36.0
Fe meas (1983)	102.2	65.9	63.0	47.3
Fe meas (1984)	97.5	57.9	56.0	52.2
Fe pred	93.1	93.1	94.7	41.6
Ca meas (1980)	8.9	9.0	7.9	11.0
Ca meas (1981)	10.8	-	12.8	12.3
Ca meas (1982)	10.0	10.2	11.6	10.2
Ca meas (1983)	13.9	13.9	13.7	14.0
Ca meas (1984)	11.9	9.7	11.9	11.8
Ca pred	10.0	12.5	12.5	12.6
Al meas (1980)	7.0	3.5	0.4	0.04
Al meas (1981)	8.1	-	0.7	< 0.01
Al meas (1982)	5.1	2.9	0.3	0.05
Al meas (1983)	4.9	0.08	0.1	0.03
Al meas (1984)	2.7	1.4	0.03	0.1
Al pred	7.0	7.3	6.8	0.90
SO <sub>4</sub> meas (1980)	139.3	-	67.2	60.7
SO <sub>4</sub> meas (1981)	128.5	-	92.4	64.1
SO <sub>4</sub> meas (1982)	124.9	116.2	85.7	61.5
SO <sub>4</sub> meas (1983)	136.4	102.1	99.1	68.9
SO <sub>4</sub> meas (1984)	129.9	74.1	77.1	76.1
SO <sub>4</sub> pred	132.0	132.0	132.0	71.5
DIC calc (1980)	5-10	5-10	5-10	5-10
DIC calc (1981)	5-10	5-10	5-10	5-10
DIC meas (1982)	7.2	5.8	5.8	-
DIC calc (1983)	-	-	-	-
DIC calc (1984)	5-10	5-10	5-10	5-10
DIC pred	8.0	8.0	9.6	19.5
Ret. fact. meas		0.27%	0.27%	2-6%
Ref. fact. pred		0.20%	0.46%	14.0
				%

<sup>1</sup>Inner core as defined by piezometer M1; the Al(OH)<sub>3</sub> sub-region by piezometer M8 and M16; the siderite sub-region by piezometer M17, M18, and M19; the calcite sub-region by M9 and M27.

following reasons: lengths of the sub-regions relative to piezometer spacing, seasonal erratic behavior not detected in yearly summer samples (suggested by November 1984 data in Morin, 1985b), and reaction kinetics. If near attainment of equilibrium requires 1 to 2 days, for example, the contact between two sub-regions in Area A will be a diffuse zone 1 to 4 meters long at a groundwater velocity of 1 to 2 m a day. Longer, more distinct sub-regions can be seen in other case studies (Morin, 1983, 1988b).

With a satisfactory calibration to 1980–1984 data except for retardation of the calcite sub-region, ADNEUT was used in the multi-cell mode to evaluate probable past behavior of the plume prior to monitoring, particularly (1) the year that acidic seepage began, (2) the distance to the source area of acid generation, and (3) the past acidity (pH). Some field data suggest the plume was wider and more acidic in the past. ADNEUT3 was employed several times for simulations up to 1983 with variations in the three aforementioned characteristics and the best match to present conditions was obtained with (1) acidic seepage initially leaving the source area around 1966–1967, (2) the source area located approximately 6 m upgradient of M1 which is within the waste-rock impoundment dam, and (3) inner-core water somewhat more acidic in the past (Cherry et al., 1984). Interestingly, the more acidic, past inner-core water used in the best-match scenario had a pH of 3.6 and Fe and  $\text{SO}_4$  concentrations twice the current levels which produced a faster moving, reverse sequence of sub-regions: a siderite sub-region with an equilibrium pH of 5.27 and an  $\text{Al}(\text{OH})_3$  sub-region with an equilibrium pH of 5.31. According to the results of simulations, the present inner-core water probably began flowing from the source area around 1970, after approximately 3 years of the more acidic inner-core water, and the sub-regions reversed to their present sequence, resulting in the relatively short, less developed sub-regions currently observed.

After this examination of past conditions, ADNEUT3 was used in the multi-cell mode to examine possible future migration (Cherry et al., 1984). If all conditions in Area A remain constant for hundreds of years, the sub-region movement slows because of slower groundwater velocities far from the impoundment dam, with a total movement of 240 m from the dam requiring about 1050 years for the siderite sub-region (the contact of the siderite and  $\text{Al}(\text{OH})_3$  sub-regions) and 1625 years for the  $\text{Al}(\text{OH})_3$  sub-region (the contact of the  $\text{Al}(\text{OH})_3$  sub-region and inner core). Other simulations indicate that as acid generation decreases the number of sub-regions in Area A and their migration rates generally decrease with temporary perturbations (a few hundred years) in aqueous chemistries as the minerals re-equilibrate to the changing input chemistry. If acid generation increases, the migration rates of the present sub-regions increase and, if inner-core pH decreases below 3, a  $\text{Fe}(\text{OH})_3$  sub-region may form between the inner core and the  $\text{Al}(\text{OH})_3$  sub-region.

ADNEUT was also used to simulate acidic-groundwater migration within the Nordic Main tailings pile (Dubrovsky, 1986). ADNEUT accurately simulated effluent from laboratory column studies, but could not accurately simulate

tailings porewater chemistry primarily because of the importance of Al-SO<sub>4</sub> minerals, which are not present in ADNEUT.

## 6. CONCLUSION

This third paper in the series describes the ADNEUT family of computer programs which simulate the conceptual model for contaminant migration from acidic uranium tailings. The program framework, execution time and cost, efficiency, and sensitivity of simulated results to input data are examined in detail. Comparisons with other programs indicate ADNEUT has acceptable accuracy, particularly in light of ADNEUT's significant reduction in execution time and cost.

Simulations with ADNEUT show that the neutralization zone consists of several sub-regions which are defined by the dissolution of one mineral of the conceptual model. Each sub-region of the neutralization zone has a unique equilibrium pH, aqueous chemistry, and retardation coefficient, which are site-dependent. The sub-regions at a site commonly form a subset of the following sequence from the inner core to the outer zone: the Fe(OH)<sub>3</sub> sub-region (equilibrium pH 3.0–3.7), the Al(OH)<sub>3</sub> sub-region (equilibrium pH 4.3–5.0), the siderite sub-region (equilibrium pH 5.1–6.0), and the calcite sub-region (equilibrium pH 5.5–6.8) which is often synonymous with the upgradient portion of the outer zone. Gypsum rarely forms an independent sub-region, but, when it does, produces an aqueous chemistry and retardation coefficient close to those of an adjacent sub-region. Each sub-region affects the behavior of downgradient sub-regions.

ADNEUT can be used in the multi-cell, two-cell, and one-cell modes, and each mode has benefits and limitations. The one-cell mode highlights the limitations of laboratory batch tests, titration experiments, and non-transport geochemical programs in evaluating contaminant migration.

The calibration of ADNEUT to Seepage Area A at the Nordic Main impoundment requires the adjustment of mineral solubilities, which cannot not be made simply in order to obtain a good match but must reproduce observed concentrations in the sub-regions. The calibration highlights the applicability of the conceptual model, some specific exceptions, and the data required for reliable simulation.

In light of the annual natural variability in input inner-core data, calibration to 1980–1984 data was generally successful except for retardation of the calcite sub-region and aluminum concentrations in the siderite and calcite sub-regions. Following calibration, ADNEUT was used in the multi-cell mode to determine that the plume was likely more acidic in the past, that acidic seepage likely began in 1966–1967, and that the source area of the plume is apparently located within the waste-rock impoundment dam. ADNEUT was then used to determine possible future behavior of the plume such as an increase or decrease in the number of sub-regions under steady-state conditions and under the assumptions of increasing and decreasing acidity.

Application of ADNEUT to other uranium-tailings sites (Morin, 1983 and 1988b) provides additional evidence for the general applicability of the conceptual model and ADNEUT, and highlights the quality and quantity of data needed for ADNEUT simulations. Initial steps have also been taken for the application of the conceptual model to groundwater contamination from other types of tailings (Morin, 1988c).

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