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Modeling the Hydrogeochemistry of Aquitards
using Radial Diffusion Experiments
By:
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MANAGEMENT PERSPECTIVE

This study was funded by the Swiss National Hydrological and Geological Survey (SNHGS), as part of an international cooperative effort to characterize the properties of potential host formations for the subsurface burial of nuclear waste material. In many parts of Canada similar formations play an important role in preventing the movement of contaminants to underlying groundwater resources, and for that reason their properties have long been studied by NWRI, under both the Nature and Clean Environment Issues.

The radial diffusion technique was developed by NWRI researchers (van der Kamp, Van Stempvoort and Wassenaar, 1996) as a new method to study the hydrogeological and chemical properties of clay and other geologic materials. Clay-rich formations have low permeability and occur in much of southern Canada. They play a critical role in protecting the groundwater in underlying aquifers from contamination. Thus it is important to have reliable methods for determining the properties of these formations, such as their ability to retard or degrade contaminants. The principal advantage of the radial diffusion method is that it allows laboratory characterization of the geochemical properties of intact samples of the material. By means of computer simulations, this paper shows that the chemical reactions induced within intact samples of clay and glacial by radial diffusion can be described by standard hydrogeochemical theory.

It had been suggested to the funding agency (SNHGS) by outside advisors that the radial diffusion technique developed at NWRI could provide useful information on the clay formation that they are studying. The results reported in this paper demonstrate that this method is a valuable tool for characterizing clay-rich formations. It is expected that in time the method will become a standard part of the hydrogeologist's "tool kit".

Additional testing will be conducted in 2000-01 to provide further information on the reactive behavior of ions in aquitards (clays and tills).

ModÉlisation de l'HydrogÉochimie des Aquitards
À l'aide d'expériences de Diffusion Radiale

Sommaire à l'intention de la direction

Cette étude était financée par le Service hydrologique et géologique national de la Suisse (SHGN), dans le cadre d'un effort de coopération internationale visant à caractériser les propriétés de formations hôtes pouvant servir à l'enfouissement de déchets nucléaires. Dans de nombreuses régions du Canada, des formations semblables jouent un rôle important en empêchant le déplacement des contaminants dans les ressources d'eaux souterraines sous-jacentes, et, pour cette raison, l'INRE étudie depuis longtemps leurs propriétés, dans le cadre des secteurs d'activité Nature et Environnement propre.

La technique de la diffusion radiale, développée par des chercheurs de l'INRE (van der Kamp, Van Stempvoort et Wassenaar, 1996), est une nouvelle méthode pour l'étude des propriétés hydrogéologiques et chimiques de l'argile et d'autres matières géologiques. Les formations riches en argile ont une faible perméabilité et on en trouve dans une grande partie du sud du Canada. Elles jouent un rôle essentiel en protégeant de la contamination l'eau souterraine des aquifères sous-jacents. Il est donc important d'avoir des méthodes fiables pour déterminer les propriétés de ces formations, par exemple leur capacité à dégrader les contaminants ou à retarder leur diffusion. Le principal avantage de la méthode de la diffusion radiale est de permettre la caractérisation en laboratoire des propriétés géochimiques d'échantillons intacts de matières. À l'aide de simulations sur ordinateur, cet article montre qu'on peut décrire par la théorie classique de l'hydrogéochimie les réactions chimiques provoquées par diffusion radiale dans des échantillons intacts d'argile et de till.

Des conseillers de l'extérieur ont déclaré à l'organisme qui assure le financement de l'étude (le SHGN) que la technique de diffusion radiale développée à l'INRE pourrait fournir des informations utiles sur les formations d'argile qu'il étudie. Les résultats présentés dans cet article démontrent l'utilité de cette méthode pour la caractérisation des formations riches en argile. On s'attend à ce que cette méthode devienne éventuellement un outil standard pour les hydrogéologistes.

On doit effectuer des essais supplémentaires en 2000-2001 afin d'obtenir des informations additionnelles sur le comportement réactif des ions dans les aquitards (argiles et tills).

Abstract

The radial diffusion method is a new technique that, among other applications, allows laboratory study of the chemistry of groundwater in intact aquitard materials. The computer model PHREEQC was used to simulate the changes in hydrochemistry observed in radial diffusion cells. A relatively small number of assumptions were required. In addition to using the mass measurements and the initial concentrations of aqueous species in the cells (after first addition of solution), equilibration of the aqueous solutions with the mineral calcite, and with a pool of exchangeable cations, was assumed for each step. For the majority of dilution steps, one or more of the following redox reactions were employed: oxidation of pyrite, oxidation of organic C, reduction of sulfate. The simulated trends in dissolved concentrations were close to the observed data. However, the simulated levels of exchangeable cations based on radial diffusion were lower than those determined by a conventional method.

Résumé

La méthode de la diffusion radiale est une nouvelle technique qui permet notamment l'étude en laboratoire de la chimie de l'eau souterraine à partir de matières intactes de l'aquitard. À l'aide d'un nombre relativement faible d'hypothèses, on a utilisé le modèle informatique PHREEQC pour simuler les changements hydrochimiques observés dans des cellules de diffusion radiale. En plus d'utiliser des mesures de masse et les concentrations initiales d'espèces aqueuses dans les cellules (après une première addition de solution), on a supposé, pour chacune des étapes, que les solutions aqueuses atteignaient un équilibre avec la calcite, ainsi qu'avec un ensemble de cations échangeables. Pour la plupart des étapes de dilution, on utilisait une ou plusieurs des réactions d'oxydo-réduction suivantes : oxydation de la pyrite, oxydation du carbone organique et réduction du sulfate. Les tendances simulées des concentrations de matières dissoutes étaient voisines des valeurs observées. Cependant, d'après les mesures de diffusion radiale, les teneurs simulées en cations échangeables étaient inférieures à celles déterminées par une méthode classique.

Introduction:

Aquitards are geologic units with low permeability that play important roles in limiting the mobility of contaminants in groundwater. Because of their low permeability, aquitards, such as till or clay units, are often used as hydraulic barriers to limit the subsurface movement of contaminants at disposal sites that contain hazardous wastes. Various aquitards, including salt formations, clays and crystalline rock are under investigation as potential storage media for radioactive wastes generated by the nuclear industry.

Not only do aquitards slow the migration of aqueous phase contaminants, they also react with them. These reactions, notably sorption and/or ion exchange, have strong effects on the mobility of contaminants. Thus, in addition to determining the physical hydraulic properties of aquitards, their complex hydrogeochemistry also has to be understood.

Various methods are employed to determine hydrogeochemical parameters of aquitard units. The installation of monitoring wells is a common procedure, but can be relatively expensive, and time-consuming if water level recoveries are slow. The dissolved ions measured in samples from such wells may be strongly affected by artifacts due to chemical interaction of groundwater and bentonite used to seal the annulus of the well (Rodvang, 1987; Remenda and van der Kamp, 1997) or oxidation of species exposed to oxygen (Wassenaar and Hendry, 1999). Squeezing techniques can be used in some cases to extract solutions from aquitards (Kalil and Goldhaber, 1973; Patterson et al., 1978), but this method is impractical for highly compacted clays/tills and rock samples, and the chemistry is affected by membrane filtration at high pressures. Monitoring wells and squeezing techniques generally do not yield some key hydrogeochemical parameters required in hydrogeological studies, such as sorption coefficients, effective diffusion coefficients and cation exchange capacity (CEC). To determine such parameters, a variety of methods have been devised that use intact core samples of aquitard materials (e.g., Barone et al., 1992; Maes et al., 1999) or batch tests with slurries of core samples (conventional CEC methods).

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A few years ago, a new non-destructive analysis technique for investigating the hydrochemistry of aquitards was introduced: the radial diffusion method (van der Kamp et al., 1996). This technique, which uses intact core samples, has been used to determine porewater composition, diffusion-accessible (effective) porosity and effective diffusion coefficients for conservative aqueous species in aquitard samples (van der Kamp et al., 1996; van der Kamp and Van Stempvoort, 2000). Along with monitoring wells, this method has recently been used to determine gradients of isotopic species in porewater of glacial till, thus yielding useful information on groundwater flow and the timing of geologic events (Wassenaar and Hendry, 1999). The advantage of this technique is that the diffusion-accessible porosity that is measured can be taken into account in the determination of the effective diffusion coefficient(s). Subsequently, both parameters can be used in mass transport calculations. Further, as discussed briefly in this paper, the approximate CEC and the concentrations of various exchangeable cations can also be determined by the radial diffusion technique.

The purpose of this paper is to examine some hydrochemical data that have been generated in radial diffusion tests. The test data considered in this study include aqueous concentrations of the following species: Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and for selected tests: alkalinity and Br^-. Specifically, this paper uses computer modeling to show how these data reflect the hydrogeochemistry of the aquitard materials that were tested.

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Materials and Methods:

<u>Aquitard Samples</u>

The data that were considered in this study were selected from various radial diffusion tests of aquitard samples that had been conducted over the period 1993 – 1997. The samples were collected as Shelby tube cores from boreholes at three sites in Canada: Warman, Saskatchewan, Luck Lake, Saskatchewan, and the Laidlaw Industrial Waste Disposal Facility near Sarnia, Ontario. Details of the individual cores are summarized in Table 1.

The till aquitard unit at Warman, Saskatchewan has been described by several investigators (Keller et al., 1989; Van Stempvoort et al., 1994; Remenda et al., 1996). It is a 70 m thick clayey till sequence, consisting of several till units (Keller et al., 1989). Previous analyses indicate that the till units contain approximately 5 % calcite, 0.5 - 1.5 % S and 0.5 to 1 % organic carbon (Van Stempvoort et al., 1994; unpublished data). Van Stempvoort et al. (1994) conducted laboratory weathering tests of initially unweathered core samples of the aquitard at Warman, Saskatchewan. They observed that 12 to 14 % of the reduced S (mainly pyrite) was oxidized to SO_4^{2-} over 2 weeks. Visible weathering of the aquitard at the site extends over a range from less than 3 m below ground to 8 m (Keller et al., 1989; Van Stempvoort et al., 1994). Test sample CD-10 was collected from within the unweathered zone at a depth of 21.9 m below ground surface on November 6, 1992. It was immediately sealed in plastic wrap and stored at 5°C, and placed in a radial diffusion cell on December 11, 1992.

The thick aquitard unit at Luck Lake, near Birsay, Saskatchewan has been described by Christiansen (1986), Remenda (1993) and Shaw and Hendry (1998). At the Luck Lake site where it was collected, it consists of 30 m of glacial till, weathered to a depth of 15 m, overlying 70 m of dark gray, non-calcareous silty marine clay, the Snakebite Member of the Cretaceous Bearpaw Formation. Previous analyses indicate that this unit contains only a trace (or non-detectable) of calcite, ~ 2 % S and ~ 1 % organic C (authors' unpublished data). Test sample CD-12 was collected in 1990 from the marine clay at a depth of 45 m below ground. At this depth the clay

contains some calcite plus reduced sulfur (probably mostly pyrite) and organic carbon (Table 1). This Shelby tube core was sealed with multiple layers of plastic wrap and tape, stored at 5°C, and prepared for radial diffusion testing on November 1, 1993.

The aquitard at Sarnia, Ontario is a 40 m thick clay till unit (Quigley and Ogunbadejo, 1976; Desaulniers et al., 1981; Abbott, 1987; Rodvang, 1987; Ruland et al., 1991, McKay et al., 1993). At the Laidlaw Waste Disposal Facility site, this unit includes the following geologic units, from top to bottom: a thin veneer of glaciolacustrine clay, St. Joseph Till (10 to 15 m), lacustrine sandy silt to clay, followed by the Black Shale Till (Rodvang, 1987). The till units contain 10 - 25 % calcite, 5 - 8 % dolomite, and 0.05 to 0.7 % S (Rodvang, 1987; Abbott, 1987). At the Laidlaw site the aquitard is visibly weathered and fractured to a depth of approximately 6 m. Based on samples obtained by monitoring wells and squeezing, the weathered zone is marked by higher SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and HCO_3^-, compared to the underlying unweathered zone (Rodvang, 1987). Test samples LAI-1, LAI-3 and LAI-4 were collected from the weathered zone at depths of 2.8 to 4.5 m below ground on June 8, 1995, sealed and stored at 5°C and prepared for radial diffusion testing on November 7, 1995.

Rodvang (1987) and Abbott (1987) concluded that the SO_4^{2-} in the shallow subsurface at the Laidlaw site is a product of pyrite oxidation, and that this reaction, accompanied by carbonate dissolution, accounted for the higher dissolved ion concentrations in the weathered zone. Rodvang (1987) sometimes observed higher concentrations of SO_4^{2-} and other ions in squeezed samples from the unweathered zone, compared to monitoring wells, and concluded that this was due to aging (i.e., weathering) of the samples.

Assembly and operation of the radial diffusion cells

Details about the five cells used for the radial diffusion tests are provided in Table 1. Following the method described by van der Kamp et al. (1996), the five Shelby tube cores were cut to suitable lengths (Table 1), and then central reservoirs, liners and seals were installed (Figure 1). The cells used for the samples from the Warman and the Luck Lake sites (CD-10, 12)

were sealed with solid top covers that were removed each time the cells were sampled. The seals used for the Laidlaw site samples (LAI-1, 3, 4) had septa, which allowed sampling of the reservoir and addition of replacement fluids to be conducted without opening the cell. All of these diffusion cells were subjected to a series of dilution-diffusion steps. Deionized water or a salt solution (see Table 2) was placed in each reservoir and allowed to equilibrate via radial diffusion, generally over a period of 40 to 75 days, but up to 8 months. Then the reservoir fluid was withdrawn by syringe for analyses, and immediately replaced by approximately the same volume of deionized or dilute solution, allowed to equilibrate, and this process was repeated up to 10 times or more. During these procedures, a record was kept of the masses of the cells before and after sampling and the masses of fluid removed and added, to keep track of fluid additions, extractions, and any minor losses by evaporation. The water samples were analyzed for major and minor ions, and other selected hydrochemical parameters (e.g., pH, alkalinity). These analyses were conducted at the Central Analytical Laboratory of the National Hydrology Research Center in Saskatoon, Saskatchewan. Concentrations of chloride, bromide and sulfate were determined by ion exchange chromatography (Dionex 2000I), cation concentrations by flame atomic absorption spectroscopy (Elmer-Perkins), and pH and alkalinity with a Metrohm automated titrater using 0.01N sulfuric acid and titrating to endpoints of pH 4.5 and 8.5.

Simulation using PHREEQEC

The computer program PHREEQC (version 1.6: USGS, 1998) was used to simulate the observed changes in hydrochemistry that occurred during the dilution-diffusion steps. This program has been documented by Parkhurst (1995). It is based on the earlier, widely used program named PHREEQE (Parkhurst et al., 1980).

For each simulation, the radial diffusion cell was modeled as being a closed system, between the sequential reservoir fluid replacement episodes. The changes in the effective volume of the solution (i.e., "effective" pore volume in aquitard plus solution in reservoir) during each addition episode was calculated, using the mass measurements, combined with the

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sequential anion concentration data (Cl⁻ or Br⁻). Specifically the following conservation of mass relationships were employed:

$$V_2{}^*C_2 = C_1{}^*V_1 + C_a{}^*V_a \qquad (a)$$

and

$$V_2 = V_1 + V_a \qquad (b)$$

where V is effective volume of fluid, C is anion concentration, subscript 1 refers to equilibrated cell solution prior to addition of fluid, subscript 2 to equilibrated cell solution after addition, and subscript a to the added solution. The terms V_a, C_1, C_2 and C_a are measured quantities.

Combining (a) and (b):

$$(V_1 + V_a)C_2 = C_1{}^*V_1 + C_a{}^*V_a \qquad (c)$$

which can be rewritten as:

$$V_1 = (C_a{}^*V_a - C_2{}^*V_a)/(C_2 - C_1) \qquad (d)$$

The value obtained for V_1 was used, with the series of mass and density data, to calculate the effective volume of fluid for all aqueous species over time. These series of values were used in the modeling by PHREEQC. For the ionic species V_1 is generally significantly smaller than the total pore volume (van der Kamp et al., 1996).

The PHREEQC modeling was conducted as a series of steps that included solution mixing or dilution, reaction and equilibration (Figure 2). These components were chosen to simulate the reactive steps that were conducted for each cell. This modeling involved the

simulation of the changes in whole solution chemistry, rather than for various ions independently. The simulated results for the species were codependent, based on the various assumptions of PHREEQC, including aqueous speciation, mineral equilibria and ion exchange.

A basic assumption of the modeling was that, for each sampling event, the chemical system comprised of the aqueous solution and the aquitard material was at steady state (cf., van der Kamp et al., 1996). Specifically, the cell solutions were assumed to be in chemical equilibrium with mineral-phase calcite, as well with exchangeable cations, using the ion exchange module. Equilibrium of the starting cell solution with calcite was either by adjusting the pH (CD-12, LAI series), or the dissolved CO_2 (CD-10). Each added solution was assumed to be in equilibrium with atmospheric CO_2.

For CD-12, the cell that apparently contained at most only a trace of calcite, a few simulations were tried in which the role of calcite dissolution was ignored. However, these simulations failed to provide a close fit to the observed data.
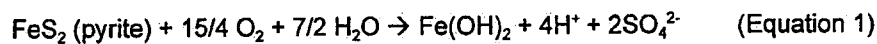
When the pH and dissolved carbonate concentrations of the 5 start-up cell solutions were adjusted to be in equilibrium with calcite, these cells were also found to be close to apparent equilibrium (saturation indices = 0.0 ± 0.21) with respect to dolomite ($CaMg(CO_3)_2$). However, because of sluggish kinetics, there is considerable disagreement regarding the solubility of dolomite. At low temperatures ($\sim 25°C$) it dissolves very slowly (e.g., Reardon et al., 1980), and it does not precipitate directly under laboratory conditions (Land, 1998). Accordingly, equilibration with dolomite was not employed in the PHREEQC simulations reported in this paper. This seems to be a reasonable assumption; when dolomite equilibration was included in preliminary simulations, large shifts in the simulated dissolved Ca^{2+} and Mg^{2+} concentrations resulted that did not correspond to observed data. In contrast, when dolomite equilibration was ignored, the resulting trends in Ca^{2+} and Mg^{2+} concentrations in the cell solutions closely fit the observed data (see results).

The EXCHANGE module was used to simulate cation exchange, using the Gaines-Thomas convention (Appelo and Postma, 1993: p. 156). Only one "exchanger" was defined and

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the cation exchange coefficients that were provided in the PHREEQC database (PHREEQC.DAT) were used without modification. For each cell, the total amount of exchangeable cations was fitted by calibration of the cation concentration series data. The fit criterion was minimizing the sum of the squares of the normalized errors ((observed - measured)/measured) for Ca^{2+}, Mg^{2+}, Na^+ and K^+. PHREEQC also included H^+ in the cation exchange calculations, based on the input pH values, and, in the case of CD-10, Fe^{2+}, based on the reported initial dissolved Fe value.

The CEC determined by PHREEQC calibration were compared to those obtained using a conventional soil analysis method. For each of the five cells tested, a subsample that had been removed during cutting of the Shelby tube core, or placement of the central reservoir in the cell, was analyzed for CEC using an ammonium acetate technique (McKeague, 1978).

During the modeling, it became apparent that the SO_4^{2-} data generally did not follow conservative, non-reactive behavior. Anomalies in the SO_4^{2-} data series (departures from ideal dilution) were compensated for by assuming that either a sulfate reduction or a sulfide (mineral) oxidation reaction had occurred within the aquitard material. The losses or gains in sulfate were quantified as reaction fluxes for each dilution step in the PHREEQC simulations. Redox reactions involving other species (O_2 or organic carbon) were assumed to have taken place (Equations 1, 2):

$$FeS_2 \text{ (pyrite)} + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_2 + 4H^+ + 2SO_4^{2-} \qquad \text{(Equation 1)}$$

or

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \qquad \text{(Equation 2)}$$

For the above reactions, stoichiometric quantities of aqueous products (H^+ or HCO_3^-, HS^-) were included as fluxes (gains) in the PHREEQC simulations. Note also that Equation 1 infers that an oxidation of Fe has also taken place, along with the sulfide oxidation. No net production of

Fe ions are inferred in this simplified reaction, given the low solubility of $Fe(OH)_2$ and similar phases under near neutral pH conditions. Accordingly, aqueous phase Fe reaction fluxes were not included in the PHREEQC simulations.

Often, in order to achieve calibration of the data, step-wise additions of CO_2, as reaction flux inputs, were also included. This was chosen to represent the oxidation of organic carbon by O_2 (Equation 3a to 3c):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(Equation 3a)}$$

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(Equation 3b)}$$

$$CH_3COOH + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad \text{(Equation 3c)}$$

For the reactions represented in Equations 1, 2 and 3a to 3c, the fluxes of O_2 were not entered into the PHREEQC model. Dissolved O_2 data were not available, but O_2 was likely present in the cells, mainly as trapped air introduced during each dilution step. For the purposes of the modeling, it was assumed that this O_2 was consumed instantaneously via the sulfide and/or organic carbon oxidation reaction(s). Thus, the O_2 was not included as a separate aqueous species.

Aqueous organic carbon species (Equations 2, 3a to 3c) were not included in the PHREEQC simulations, because dissolved organic carbon (DOC) concentrations were not available. Although dissolved organic species may effect the total aqueous concentrations of inorganic species via complexation, and also may participate in ion exchange reactions, the low levels of DOC that are typical of most groundwaters (< 10 mg/L) are generally ignored in hydrogeochemical modeling.

In one of the tests, step-wise degassing of CO_2 was inferred to have taken place, in order to achieve calibration:

$$CO_{2\,(aq)} \rightarrow CO_{2\,(g)} \qquad \text{(Equation 4)}$$

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CO$_2$ may have degassed into a trapped air pocket that was present in the upper portion of the reservoir of this cell during each step of the test, which would then have been released to the atmosphere during each sampling/addition episode.

The reported pH data were not used for calibration, given the fact that the samples were possibly affected by active degassing prior to pH analyses. However, the reported alkalinity data were used for calibration of some of the tests.

Results:

Results of the modeling are provided in Figures 3 through 8. Details about the assumptions of the simulations for each cell are provided in Table 2.

Figures 3 through 7 indicate that, in general, the simulated hydrochemical changes based on PHREEQC closely match the observed changes in the hydrochemistry of the aqueous solutions in the radial diffusion cells. This observation applies to the conservative anions (Cl$^-$, Br$^-$), non-conservative SO$_4^{2-}$ and alkalinity, and also the cations (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$). By incorporating cation exchange, the PHREEQC simulations were able to reproduce the steeper declines in the concentrations of divalent cations, Ca^{2+} and Mg^{2+}, compared to monovalent cations, Na$^+$ and K$^+$. This is due to the preferential adsorption of the higher valence ions during dilution: the "concentration effect of heterovalent exchange" (p. 462 in Appelo and Postma, 1993). Note, for example, the cross-over in the concentrations of Mg^{2+} and K$^+$ during dilution in CD-10 (Figure 3). The increases in concentrations of cations due to introduction of sodium chloride and/or bromide solutions were closely simulated, including the ion exchange induced increases of the other cations (Figures 5 through 7).

The calibration of the PHREEQC simulations presented in this paper represent a new method for determining the approximate concentrations of exchangeable cations in aquitard materials (Table 3). For cell CD-10, the modeled amount of exchangeable cations was 21.3

meq/100 g (per dry solids), similar to the amount based on the conventional ammonium acetate method (16.8 meq/100 g, same borehole at 22.5 m). In contrast, the other four PHREEQC simulations yielded lower CEC than the ammonium acetate technique. Based on PHREEQC, the CEC for sample CD-12 was initially 1.3 meq/100 g (first dilution step), and appeared to increase with the later addition of NaCl (7.7 meq/100 g for step 10). These values are much lower than the amount (30.3 meq/100 g) determined by the ammonium acetate test. For the Laidlaw site samples (LAI-1, 3, 4) the concentrations of total exchangeable cations based on PHREEQC were 4.5, 4.3 and 3.1 meq/100 g, whereas the levels determined by the ammonium acetate technique were 5.4, 7.4 and 5.6 meq/100 g.

Although the modeled changes in SO_4^{2-} and alkalinity involved various other hydrochemical species, the reactions represented by Equations 1 through 4 can be described briefly as a gain (1) or loss (2) of SO_4^{2-}, or a gain (3a to 3c) or loss (4) of dissolved CO_2 (Figure 8). Based on the PHREEQC simulations, for the Saskatchewan samples, CD-10 and CD-12, there was generally a net gain of SO_4^{2-} during the step-wise diffusion testing. The gain in SO_4^{2-} was non-steady, decreasing over time. This suggests that the hydrochemistry of these diffusion cells became more reducing over time, thus less favourable to sulfur oxidation. Perhaps an excess of O_2 was available in the first dilution step, due to previous exposure of the core to the atmosphere. Based on Table 2, the amounts of O_2 required to account for the gains in SO_4^{2-} are small, consistent with the hypothesis that the O_2 was mainly derived from small amounts of air that were trapped during the opening and reclosing of the cells for these tests.

For the samples from the Ontario site (LAI series) non-steady losses of SO_4^{2-} were required for PHREEQC calibration, rather than gains, as above (CD series). This may largely reflect the fact that the diffusion cell constructions for the two series were different. The cells that contained the Saskatchewan samples (CD series) may have incorporated larger amounts of trapped air during each dilution step, because the seals were removed each time. The three Ontario (LAI) cells were sampled via septa, probably resulting in less introduction of O_2.

The nonsteady fluxes in SO_4^{2-} additions and/or losses required for calibration of the PHREEQC simulations indicates that SO_4^{2-} cannot be modeled closely simply by choosing an alternative, unique effective porosity, in contrast to that observed for Cl^- (see van der Kamp et al., 1996). Based on these results, we conclude that redox reactions within the aquitard samples have affected the SO_4^{2-} concentrations in these cells during the radial diffusion tests.

The utility of the CO_2 production reaction (Equation 3), which was used to fit some of the data for four cells (CD-10, LA-1, LAI-3), suggests that inadvertent addition of O_2 and consequent microbial oxidation of organic carbon (perhaps largely dissolved organic matter) may have been an important process in the cell experiments. For cell CD-10, it appears that organic carbon oxidation became more important than sulfur oxidation after step 2 of the radial diffusion testing (Figure 8). This may have been partly related to an overall decline in the redox potential (Eh) of the cell solution over time. The Eh of the CD-10 porewater might have been relatively high at the beginning of the experiment, since this core had been exposed to the atmosphere prior to diffusion cell testing.

Based on the model reaction fluxes, the marine clay sample in the CD-12 cell had apparently experienced a net loss or degassing of CO_2 over time, although the inferred flux of this gas declined over time, based on Figure 8. The reason why this cell exhibited apparent CO_2 loss is unknown. We speculate that perhaps this cell had a relatively large headspace or a relatively high partial pressure of CO_2 in equilibrium with the dissolved CO_2. Perhaps the CO_2 had built up as a non-aqueous gas phase during the relatively long storage period, between sampling (1990) and cell construction (1993).

Discussion:

As indicated above, the radial diffusion cell data were closely simulated using PHREEQC. This suggests that the modeling assumptions employed were adequate representations of the major factors that control the hydrochemistry of these aquitards. These assumptions included the

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aqueous species equilibria incorporated in PHREEQC, calcite saturation, no precipitation or dissolution of dolomite, cation exchange, and also, non-steady redox reactions involving S and C.

The applicability of the redox reactions represented by Equations 1 through 3 was not anticipated. In particular, the fact that sulfur oxidation and/or reduction reaction(s) were required to calibrate the SO_4^{2-} series data for most of the radial diffusion tests is a key finding. This indicates that SO_4^{2-} did not behave as a conservative anion in the radial diffusion tests, but was a reactive component. The sulfide oxidation reactions inferred for the two Saskatchewan aquitard tests (CD-10, 12) are apparently typical of aging or weathering of such samples (Rodvang, 1987; Van Stempvoort et al., 1994). It is possible that S-oxidizing microorganisms were active during these tests. In contrast, it appears that sulfate-reducing microorganisms played an active role in the Sarnia site samples. The PHREEQC simulation results that indicate sulfate reduction support the interpretation that oxidation of organic carbon (in this case coupled with S reduction) was an important process during the radial diffusion test(s).

Our model results indicating that redox processes have affected the cell solutions may prove useful for future (re)design of radial diffusion experiments. If the radial diffusion method is employed to determine the pristine chemistry of groundwater in aquitards within the anaerobic zone, it will be necessary to employ techniques that prevent introduction of O_2 and subsequent oxidation in the cells. For example, the aquitard samples could be immediately transferred in the field to airtight containers with anaerobic atmospheres (e.g. argon), and the subsequent sampling and handling of the cells within similar atmospheres (e.g., glove box) during the dilution steps. Such procedures should eliminate artifacts produced by oxidation reactions. However, the impact of such techniques on the level of dissolved CO_2 and carbonate species, and other gases (e.g. methane) would still have to be considered, as well as the effects of any changes in pressure and temperature, between the field and laboratory. The evolution of the CO_2 system could be closely monitored by sampling the headspace of the diffusion cell.

The insight into the role of redox reactions provided by this study suggests that there may be other, related applications of the radial diffusion technique. This method may be useful for the

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study of reactions that occur when various dissolved redox species are introduced to aquitards by advection and/or diffusion (e.g. O_2, nitrate, labile organic compounds), or to track the sorption and/or bioremediation of contaminants within aquitard units.

Based on our initial results, we suggest that the radial diffusion-based method has several advantages, when compared to conventional techniques, for the determination of the CEC of aquitards. The role of secondary reactions, such as the dissolution of calcite can be taken into consideration. Disturbance by oxidation reactions is minimized, though not eliminated. Disturbance of the structure of the aquitard material being tested is also minimal. Conventional batch slurry techniques may be subject to artifacts related to artificially high solution to solids ratios (i.e., the solids effect: O'Connor and Conolly, 1980).

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Figure Captions

Figure 1. Schematic of a radial diffusion cell. The top and bottom plates are clamped together to prevent fluid loss.

Figure 2. Schematic Diagram of computer modeling process by PHREEQC for simulation of step-wise changes in hydrochemistry of the cell solution, as sampled from the reservoir for each dilution/diffusion step.

Figure 3. Observed and simulated changes in aqueous ion concentrations, CD-10. Note that the the first sample was collected before the first dilution/diffusion step, and subsequent samples were collected after each step. For this reason, there are 10 samples corresponding to 9 steps.

Figure 4. Observed and simulated changes in aqueous ion concentrations, CD-12.

Figure 5. Observed and simulated changes in aqueous ion concentrations, LAI-1.

Figure 6. Observed and simulated changes in aqueous ion concentrations, LAI-3.

Figure 7. Observed and simulated changes in aqueous ion concentrations, LAI-4.

Figure 8. Reaction fluxes of SO_4^{2-} and CO_2 (g) included with each simulation step. Note that concurrent with the SO_4^{2-} reactions, fluxes of H^+ or HCO_3^- and HS^- were based on Equations 1 or 2. Fluxes in CO_2 (g) were based on Equation 3 or 4.

Table 1. Details about the five aquitard samples used in the radial diffusion tests.

Cell	CD10	CD12	LAI-1	LAI-3	LAI-4
Depth of core (m)	21.9	45	4.4-4.5	4.3-4.4	2.75-2.85
Location	Warman, SK	Luck Lake, SK	Laidlaw site, ON	Laidlaw site, ON	Laidlaw site, ON
Formation	Warman Formation, Sutherland Group	Snakebite Member, Upper Colorado Group	St. Joseph Till	St. Joseph Till	St. Joseph Till
Lithology	till	shale	till	till	till
Date of coring	6-Nov-92	1990	8-Jun-95	8-Jun-95	8-Jun-95
Date of cell preparation	11-Dec-92	01-Nov-93	07-Nov-95	07-Nov-95	07-Nov-95
O.D. of core sample (cm)	7.1	7.1	6.94	6.94	6.94
Length of sample (cm)	11.9	12.1	11.9	11.7	11.8
Diameter of bored hole (cm)*	2.86	2.86	2.54	2.54	2.54
Length of bored hole (cm)*	10.00	10.00	10.80	10.70	10.80
Volume of sediment (cm^3)	407	437	395	388	392
Porosity	0.336	0.483	0.343	0.326	0.332
Volume of porewater in cell (cm^3)	148	221	138	130	136
Mass (dry) of sediment in cell (g)	783	633	712	723	742

*bored to form cell reservoir (Figure 1)

Table 2. Details on data and assumptions used for PHREEQC simulations.

Name Of Test	# Steps Simulated	Total Water (g) In Cell Assumed	Solution(s) Added*	mL Soln. Added/Step	Dry Mass (g)	Exchangeable Cations (eq.) in model	Reactions Included	mmol O_2 consumed/step (assuming Eqn. 1, 3a,b,c)
CD-10	9	106.4 to 119.3	A	25.3 to 45	783	0.167	1, 3	0.11 to 0.27
CD-12	6	146 to 166	A	24.1 to 43.78	633	0.008**	1, 2, 3, 4	0.08 to 0.53
LAI-1	4	151.6 to 153.8	B, C	34.42 to 36.6	712	0.032	2, 3	0 to 0.16
LAI-3	4	138.4 to 142.3	B, C, D	32.65 to 34.9	723	0.0309	2, 3	0.08 to 0.1
LAI-4	4	147.6 to 149.4	B, C	32.25 to 34.44	742	0.023	2	0

*Hydrochemistry of added solutions in mmol/L: A - deionized water, B - 0.23 Ca, 0.09 Mg, 0.11 Na, 0.06 K, 0.67 Cl; C - 25.84 Na, 16.45 Cl, 9.51 Br; D - 0.14 Ca, 0.10 Mg, 4.26 Na, 0.07 K, 5.14 Cl.
**assuming constant CEC over time (cf. Table 3).

Table 3. Comparison of CEC values by PHREEQC to those by a conventional ammonium acetate test.

sample	CEC by CH_3COONH_4 (meq/100 g)	CEC by PHREEQC* (meq/100 g)		
CD-11	16.8	CD-10	21.3	± 0.07
LAI-1	5.4		4.5	± 0.01
LAI-3	7.4		4.3	± 0.02
LAI-4	5.6		3.1	± 0.13
CD-12	30.3	step 1	1.3	± 0.12
		step 10**	7.7	± 0.16

*based on above best fit criterion, the ± correspond to the equivalent increments in CEC tested.
**not shown on Figure 4.

Figure 1.

rubber septum
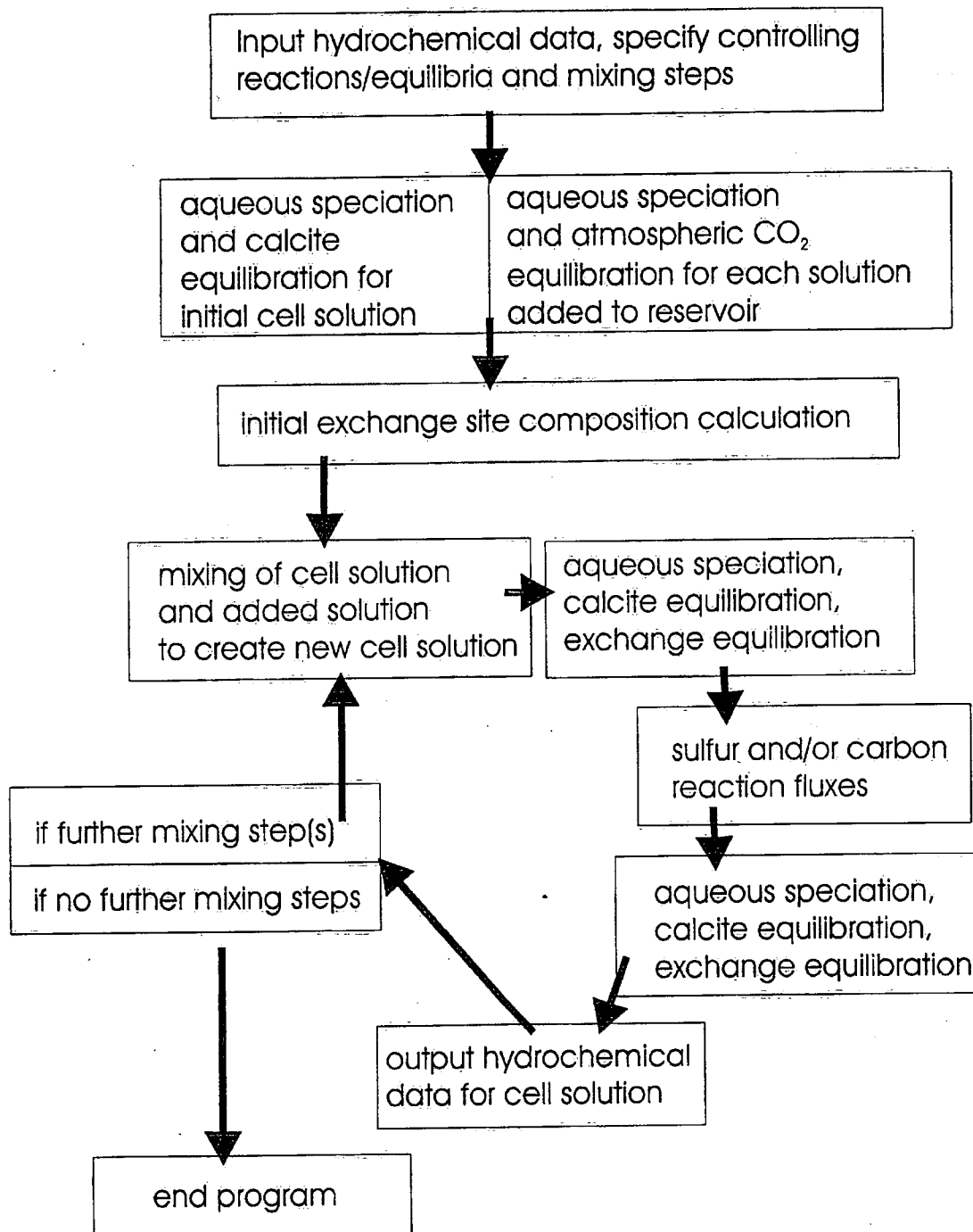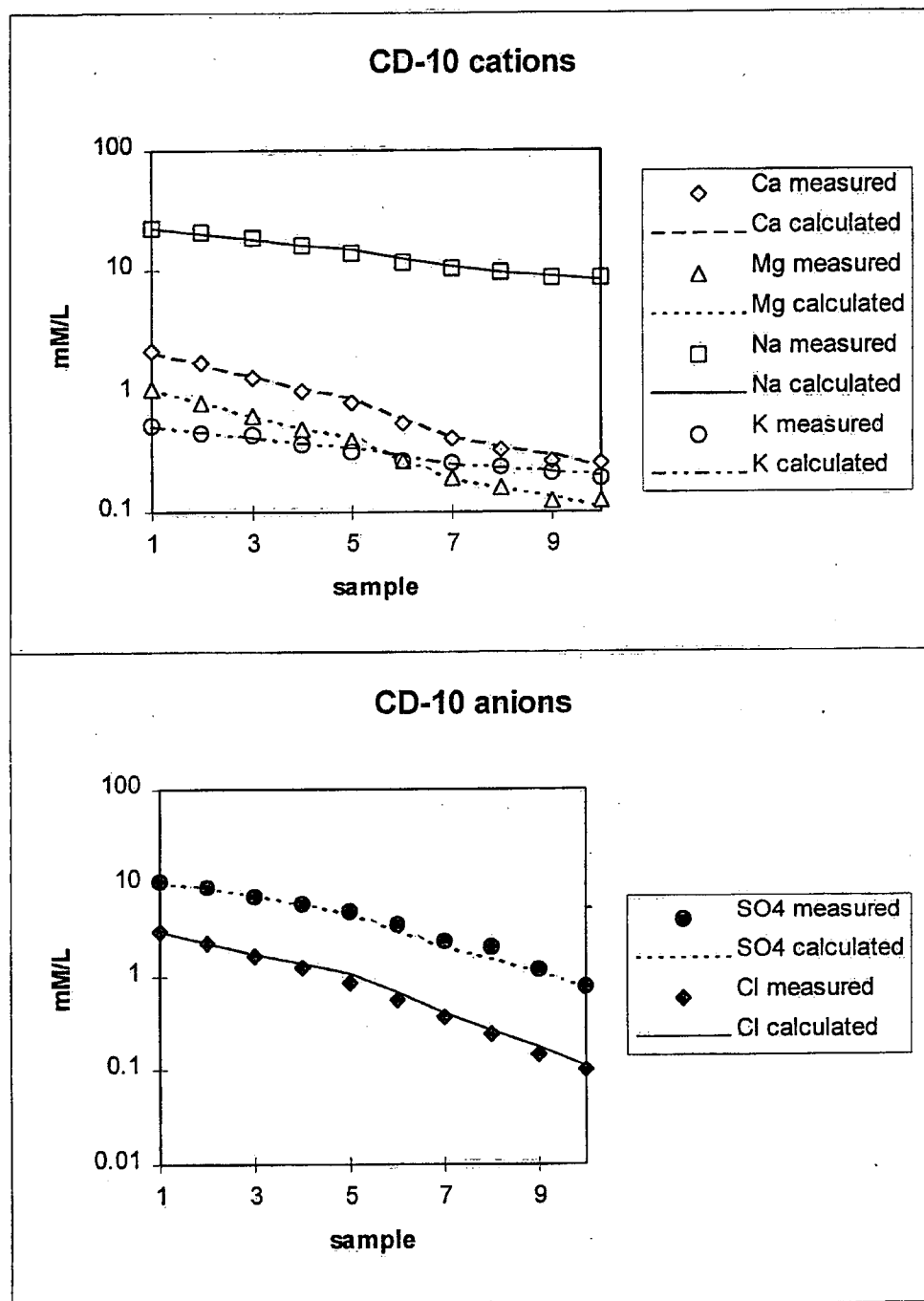(optional)

top plate
(aluminum)

rubber o-ring
seal

Shelby tube
(steel)

porous PVC
tube (liner)

reservoir fluid

core sample

rubber o-ring
seal

bottom plate
(aluminum)

Figure 2.

Input hydrochemical data, specify controlling reactions/equilibria and mixing steps

aqueous speciation and calcite equilibration for initial cell solution

aqueous speciation and atmospheric CO_2 equilibration for each solution added to reservoir

initial exchange site composition calculation

mixing of cell solution and added solution to create new cell solution

aqueous speciation, calcite equilibration, exchange equilibration

sulfur and/or carbon reaction fluxes

if further mixing step(s)

if no further mixing steps

aqueous speciation, calcite equilibration, exchange equilibration

output hydrochemical data for cell solution

end program

Figure 3.

CD-10 cations

CD-10 anions

Figure 4.

CD-12 cations

CD-12 anions

Figure 5.

LAI-1 cations

Legend:
- ◇ Ca measured
- --- Ca calculated
- △ Mg measured
- ······ Mg calculated
- □ Na measured
- — Na calculated
- ○ K measured
- ·-·-· K calculated

LAI-1 anions

Legend:
- ● SO4 measured
- ······· SO4 calculated
- ◆ Cl measured
- ·-·-· Cl calculated
- ▲ HCO3-Alk measured
- — HCO3-Alk calculated
- ■ Br measured
- ·-·-· Br calculated

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Figure 6.

LAI-3 cations

LAI-3 anions

Figure 7.

LAI-4 cations

Ca measured
Ca calculated
Mg measured
Mg calculated
Na measured
Na calculated
K measured
K calculated

LAI-4 anions

SO4 measured
SO4 calculated
Cl measured
Cl calculated
HCO3-Alk measured
HCO3-Alk calculated
Br measured
Br calculated

Figure 8.