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WS-B Experiment: Laboratory Measurement of Porosity, Pore Water Isotopic Composition and Effective Diffusivities of Opalinus Clay Core samples

By

G. Van der Kamp and D. R. Van Stempvoort

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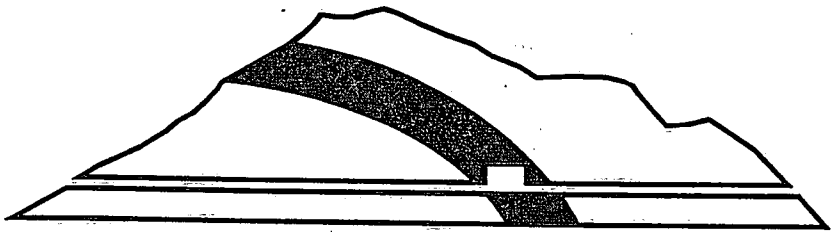

Mont Terri Project

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WS-B Experiment: Laboratory Measurement of Porosity, Pore Water Isotopic Composition and Effective Diffusivities of Opalinus Clay Core Samples

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1. Introduction

In clay-rich materials dissolved anionic species may not have access to the full pore volume because they are repelled away from the surface of the clay particles. Thus the masses of these dissolved ionic species that are present in a given volume of the material cannot be calculated reliably from measured concentrations only, but the accessible porosity for each species must also determined (Pearson, 1999). Modelling of pore water chemistry can then proceed, using the measured accessible porosity. Calculations of advective and diffusive transport also require determination of effective porosities.

The radial diffusion technique (van der Kamp et al. 1996) is a robust and practical method for determining diffusion-accessible (or effective) porosity. It is based on diffusion of dissolved species and of isotopically labelled water into or out of central fluid reservoirs that have been inserted along the axes of cylindrical core samples. Through measurement of the transient process of diffusion the effective diffusivities can be determined. The initial concentrations of water isotopes and of dissolved species in the pore water of the core sample can also be estimated by means of successive sampling and replacement of the fluid in the reservoir.

This report presents the results of radial diffusion testing for four samples of Opalinus Clay from the Mount Terri project in Switzerland.

2. Objective of the work

The purpose of the work was to measure the diffusion-accessible porosities, effective diffusivities, and initial concentrations of chloride and bromide, and of the isotopic water species $^{2}H\ ^{1}H\ ^{16}O$ and $^{1}H_2\ ^{18}O$ referred to "deuterium" and "oxygen-18" respectively in this report). Four core samples of Opalinus Clay were tested, (2 sandy species and 2 shaly species).

3. Experimental procedure

3.1 Sample preparation

Several core samples were provided by NAGRA. These were wrapped in air-tight aluminum foil that had been flushed with nitrogen to keep the samples as pristine as possible.

Four cells were prepared for radial diffusion testing of Opalinus Clay cores. A summary of cell information is given in Table 1. Cells N1 and N3 have core material from the sandy facies of the Clay and cells N2 and N4 have material from the shaly facies. The core pieces for cells N2 and N4 were taken from the same piece of core (Core No. WS-A5/H18) because no other intact pieces of shaly facies core were available.

The ends of the core pieces were trimmed and shaved to make them flat and the diameters of the pieces were reduced slightly by shaving so that they would fit into the PVC cylinders that form the walls of the diffusion cells. These PVC cylinders had been previously bored out to the appropriate inside diameter. Temporary end pieces were then bolted over each end of the cylinders to seal the samples. To minimize moisture losses during this procedure the sample preparation was carried out in the high humidity 5 ° C soil sample storage room of the Dept of Civil engineering at the University of Saskatchewan.

Trimming and shaving of the ends of the core pieces were done very carefully, but small pieces of core, a few cubic centimetres, did break away from the ends. The resulting small spaces left in the core were tamped full with shavings of the core material so as to minimize void spaces within the cells.

Water contents were estimated by oven-drying at 105°C of core material taken immediately above or below the pieces of core that were mounted in the cells.

A central cavity for accommodating the central reservoir was bored into each of the cell core samples through an opening in one of the temporary end plates, using an ordinary drill press. The temporary end plate kept the core material confined and minimized disturbance of the material during boring of the central hole. Previously saturated porous plastic tubes were inserted into the cavities, and a permanent end plate was then bolted in place. The porous plastic tubes (Porex® Technologies, X-5253) have a wall thickness of 2.2 mm, a porosity of about 0.45 and an approximate pore size of 60 microns. One end of the tubes was closed with a piece of porous plastic sheet (Porex® Technologies, X-4898) glued over the end. Access to the central reservoir was through a hole in the end plate which is closed with a threaded plug (Figure 1).

Throughout these procedures careful records were kept of the dimensions and masses of all materials that went to make up the cells, including the weight of the cell materials, the dry and wet weight of the porous tubes, the wet and oven-dried weight of the extra core samples, the weight of the cell core piece before and after drilling of the central cavity and the weight of the drill cuttings taken from the central cavity. These measurements allowed precise determination and double checking of the mass of core material in the cells, the initial mass of fluid in the cells, the mass of solids, the density of the solids and the initial porosity of the core samples in the cells.

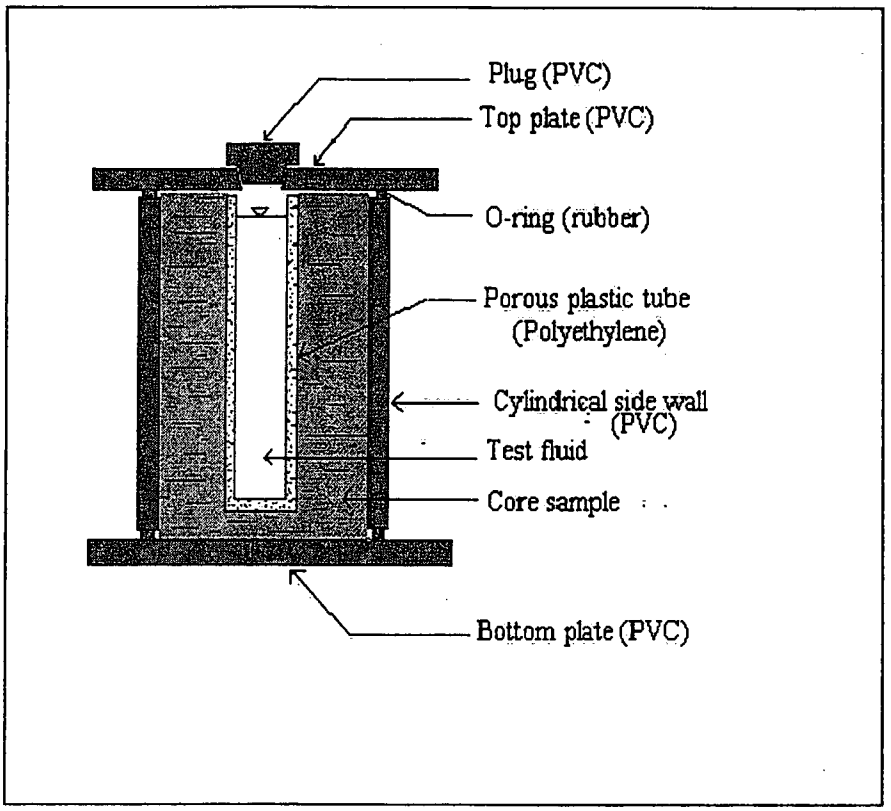

Figure 1. Cross-sectional diagram of a radial diffusion cell

3.2 Initial equilibration

The determination of effective diffusivities requires that the pore fluid in the cell must first be brought into equilibrium with the fluid in the central reservoir. This was done by filling the reservoir with fluid of known composition and leaving it to equilibrate with the surrounding core material by diffusion.

The properties of the core samples are likely to be dependent on the ionic strength of the pore fluid and its ionic composition. The initial ionic composition of the pore fluid in each of the cells was estimated from previous measurements of squeezed water and of borehole water, carried out during prior investigations (Pearson et al. *in press* Tables 6.2.1 and 6.2.3). The test fluid used for initial filling of the central reservoirs was brought to approximately the same ionic strength as the pore fluid by dissolving sodium chloride and a small amount of sodium bromide in the test fluid.

The composition of the test fluids is summarized in the Appendix . Isotope concentrations were determined by the stable isotope laboratory of the National Water Research Institute of

Environment Canada, and are reported relative to Standard Mean Ocean Water (SMOW). The concentrations of dissolved constituents were determined by the Central Analytical Laboratory of the National Water Research Institute. 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.

After initial filling of the reservoirs, topping up of the reservoirs was also necessary to allow for fluid uptake. Previous experience with similar measurements has shown that a small amount of fluid uptake by the core materials in the cells is inevitable, due to a combination of re-saturation of the (perhaps slightly desiccated) core samples, and swelling of the core samples into void spaces between the core and cell walls. In the case of the Opalinus Clay samples most of this fluid uptake took place within a few days and topping up was done 5 days after the initial filling.

To determine when equilibration was complete the electrical conductivity of the fluid in the reservoir was measured from time to time, until it appeared that no further changes were taking place. It was judged that complete equilibrium had been reached after about 150 days. At 198 days after initial filling the fluid in the central reservoir was removed for analysis and replaced with a new test fluid to initiate the diffusivity testing.

3.3 Determination of diffusion-accessible porosities

The radial diffusion technique allows a robust determination of accessible porosities for the species of interest (van der Kamp et al. 1996). It should be noted that the term "effective porosity" was used in the original paper. However, this term has been used in widely different ways and the term "diffusion-accessible porosity" (Pearson, 1999) is more descriptive and accurate.

The accessible porosity for the four species of interest was determined through three successive filling/equilibration/sampling cycles of the central reservoir, allowing the reservoir and pore fluid to come to complete equilibrium each time before final sampling. The accessible pore volume for a specific species can then be calculated by a simple mass balance based on the net mass added to the cell core sample and the change in concentrations, assuming that the concentration in the pore fluid is the same as the concentration in the reservoir. The accessible porosity was calculated as the ratio of accessible pore volume to the total volume of core material in the cell. The ration of accessible to total porosity was calculated as the ratio of accessible pore volume to total pore volume, determined on the basis of oven-drying results and measured fluid uptake. During each sampling and refilling procedure careful records were kept of the mass of the fluids that were removed from and added to the cell. The density of the fluid s was calculated on the assumption that the density was equivalent to that of a pure sodium chloride solution of the same ionic strength. The total weight of the cell before and after sampling and re-filling was also measured as an independent check on the fluid mass balance.

The accessible porosity is also one of the parameters that is required to determine the effective diffusivity. For the case of the diffusion tests the total mass of each species that was added to or removed from the cell core sample from the beginning to the end of the diffusion tests was used to calculate the accessible porosity. The diffusion tests represent the second of the three successive filling/equilibration cycles, with the proviso that the mass balance calculation includes the mass removed during sampling of the transient stage. The accessible porosity values used for the diffusion calculations thus may differ slightly from the values determined from an average of the three filling/equilibration/sampling cycles.

3.4 Measurement of effective diffusivities

The first step in the determination of effective diffusivities with radial diffusion cells was carried out by allowing the fluid in the reservoir of each of the cells to come to full equilibrium with the pore water. The reservoir fluid was then sampled and analysed for its isotopic and chemical composition, and the reservoir was left empty (but sealed from air) until these analyses were completed. The reservoir was then re-filled with test fluid that had concentrations, for each of the species of interest, that were distinctly different from the equilibrium values. The reservoir fluid was again sampled and immediately re-filled during the transient stage of the diffusive exchange between the reservoir and pore fluid. Finally the reservoir fluid was again allowed to come to complete equilibrium with the pore fluid, and then sampled.

The approximate optimum time for sampling during the transient stage was determined by monitoring the electrical conductivity (EC) of the reservoir fluid. The final electrical conductivity that would occur if the reservoir were not sampled was estimated from mass balance estimates and the sampling was carried out when the EC of the reservoir was about halfway between the initial and estimated final values.

Diffusion testing can include several successive samplings during the transient stage of diffusion. Previous experience has shown however that little extra accuracy in the value of the effective diffusivities is gained in this way, and that the critical consideration is whether the sampling is done at the optimum time when the calculated diffusivity is least sensitive to analysis uncertainties in the concentrations of the diffusing constituents. Maintenance of accurate mass balances by means of precise determination of sample volumes and of solute concentrations is also important.

When all the analysis results were available, the effective diffusivities for the species of interest were determined by modelling the observed concentrations with the semi-analytical model for radial diffusion, RADIF2, (Novakowski and van der Kamp, 1996).

Although it is generally assumed that the diffusion is a single smooth process, it cannot be excluded a priori that slower diffusion processes (e.g. diffusive exchange with immobile water) may also play a role, resulting in continuing slow changes of concentrations. To check for this possibility, the third filling/equilibration/sampling stage was extended to a much longer duration than the previous two. A small fluid sample was taken at the time when equilibrium was

assumed to be complete, without further addition of test fluid to the reservoir. The remainder of the fluid was then sampled after approximately twice this duration. Both samples were analyzed, with duplicate blind samples, for the four constituents of interest, and the last sample was also analyzed for the other major inorganic species. The results for the first and second samples were compared to check for slow transients.

3.5 Determination of initial concentrations

The initial concentrations in the pore fluid, before any fluid was added , were calculated by extrapolating the measured equilibrium concentrations back to the value for zero net mass added to the cell core. Allowance was be made for the initial uptake of water by the cell core. The calculation was carried out by assuming that the uptake of fluid involved (a) the uptake of pure water with zero concentration of dissolved constituents and of isotopes (i.e. pure SMOW - Standard Mean Ocean Water), followed by (b) addition of the dissolved mass that was in the uptake fluid. Initial concentrations can be easily calculated for the case after uptake of water was complete, i.e. after step (a). Initial concentrations can also be calculated for the case before there was any uptake of water (i.e. prior to step (a) if it is assumed that the addition of uptake water resulted in dilution of the pore water. Which one of these two cases is most relevant depends on whether the water uptake was due to prior desiccation of the sample or to swelling of the sample.

4. Results

4.1 Total porosities and other cell parameters

Relevant parameters for the cells are summarized in Table 1, including dimensions, weights, water contents and porosities. The values for total porosity before and after fluid uptake were derived from the 105° C oven-drying of adjacent pieces of core. The oven-dry porosities before water uptake range from 0.156 to 0.163 with an average value of 0.158. It should be noted that the actual water content of the cells can be determined when all diffusion testing is completed, by drying the actual core material in each cell. However, such values are not reported here because it is foreseen that further testing of the cells may be desirable, and therefore the cells have been left intact.

Each of the cell cores took up water upon initial filling of the reservoir, with cell N1 taking up the largest amount, equal to 6 per cent of the total core volume or 37 per cent of the initial pore water volume. The water uptake for cells N2, N3 and N4 represents about 2 to 3 per cent of the total core volume and 12, 18 and 19 per cent respectively of the initial pore fluid volume. Thus the fluid uptake led to a significant increase of porosity, and to changes of pore water chemistry, with final porosity values ranging from 0.173 to 0.211 (Table 1).

It is likely that the water uptake was largely due to swelling of the core material into small void spaces between the core and cell walls. Probably the uptake was largest for cell N1

because this was the first one to be prepared and at one point during the preparation process the core cracked into several pieces along existing bedding planes. Dessication of the cores was probably not a major factor. It was noted that the wrapped cores lost no weight at all while they were stored in a cool room for several months prior to cell preparation. During cell preparation the core material lost 1 to 2 grams in weight, presumably by evaporation.

The density of the solids was calculated based on the volume of the core in the cell and its porosity and wet weight. The calculated density of the solids averages 2.75 g/cc.

4.2 Diffusion-accessible porosities

The results of total and accessible porosity determinations are summarized in Table 2. Table 2 (a) summarizes the results of the total porosity calculations, as reported in Table 1

Table 2 (b) summarizes the ratios of diffusion-accessible porosities to total porosity (i.e. porosity after water uptake) for each cell, as calculated from the mass balances for each constituent over three cycles of filling/equilibration/sampling [Appendix, Mass Balance calculations]. For these calculations the pore volume of the porous plastic tubes is included as part of the reservoir. The discrepancies and variability of the accessible porosities presumably reflect a combination of uncertainties in the mass balance calculations plus possible error in the determinations of oven-dry porosity. The average ratios of diffusion-accessible porosity to total porosity was 0.67 for chloride, 0.63 for bromide, 1.03 for deuterium and 1.14 for oxygen-18.

Accessible porosity results are also presented in Table 2 (c) as porosities. These values reflect the same results as in Table 2(b). However, these results are based on the determination of accessible pore volumes (Appendix 2) and on the total volume of core material in the cells (i.e. the total interior volumes of the cells minus the volume of the central reservoirs including the porous tubes). These results are therefore independent of the oven drying results.

For each of the cells the accessible porosity for bromide is slightly smaller than that for chloride and both of these are significantly smaller than the total porosity after water uptake. The accessible porosity results for bromide and chloride were remarkably consistent through the three cycles of filling/equilibration/sampling. (The individual results are expressed as ne/nt, the ratio of accessible to total porosity, in the detailed mass balance summaries [Appendix]. For example for bromide in cell N1 the ratio of accessible to total porosity was 0.67, 0.70, and 0.69 for each successive cycle. The long-term equilibrium test during the last cycle also showed that there were no significant changes of concentration of chloride and bromide between 110 and 225 days after filling of the reservoir (summary of laboratory analysis results, Appendix). Thus the accessible porosity results for chloride and bromide can be considered reliable and reproducible. However, it is not known how these results would differ if there had been no swelling of the core material in the cells. One might surmise that without swelling, the pores would likely be smaller and the ratio of accessible to total porosity would probably also be somewhat smaller.

The accessible porosity results for the isotopes of water are somewhat problematic. The results for oxygen -18 indicate higher porosity than for deuterium for all four cells, and the duplicate laboratory results suggest that the difference is not due to analysis errors. It may be that oxygen-18 is subject to slow diffusive exchange with hydrated water on the cations and on the clay surfaces. Such fractionation and exchange have been encountered by other investigators (e.g. Hsieh et al., 1998). The results for deuterium suggest that deuterium may have a diffusion-accessible porosity close to the total porosity, since the ratios of accessible to total porosity average 1.00 for cells N2, N3 and N4

The porosity results for cell N1 all indicate that the actual porosity of the core material in the cell is larger than the porosity determined from the adjacent pieces of core. Whether this is in fact the case cannot be determined until cell N1 is decommissioned and its actual water content determined. The core material in Cell N1 also swelled more than for the other cells, but the weight data show that there was definitely no additional undetected uptake of water.

With respect to the porosity results, there does not appear to be any obvious difference between the shaly and the sandy clay material.

4.3 Determination of initial pore fluid composition

The initial pore fluid compositions in the cell are summarized in Table 3, together with the compositions of water seeping into sealed sections of boreholes A-1 and A-3 (Pearson et al. *in press* Tables 6.2.1 and 6.2.3). The compositions after water uptake are calculated directly from the mass balance for each cell, by extrapolating the measured concentrations back to the point where zero net mass had been added to the core material, but after uptake of water. Due to the dilution by the uptake water these concentrations are probably too low as compared to actual in situ conditions.

If it is assumed that the uptake water (not including dissolved mass in the uptake water) diluted the pore water concentrations in proportion to the ratio of uptake water to total water in the cell, then the initial concentrations before uptake of water can also be calculated. The results of this calculation are given in section b of Table 3. This correction for water uptake is likely to be appropriate for the water isotopes, but is valid for the ions only if all the uptake water became part of the accessible pore volume. This assumption is not necessarily valid because the fraction of pore space that is accessible to the ions may change as the ionic strength of the pore fluid changes. The meaning of the results for the ions is therefore not well defined, but the original pore fluid concentration probably lies somewhere between the two quoted values.

Although the investigation was directed at the water isotopes, chloride and bromide, the results for the other ions are also included in Table 3, but it should be born in mind that these results are strongly influenced by various chemical reactions. Although pH was determined for the water samples taken from the cells [Appendix, Laboratory results] no attempt

was made to calculate the initial pH because the measured values are probably controlled by reactions in the cell. The strongest disruption of pore fluid chemistry during coring, storage, cell preparation and diffusion testing is likely due to oxidation of sulfides and dissolution of carbonates, as evidenced by the markedly higher concentrations of sulfate, calcium and magnesium in the cells as compared to the borehole water. Such reactions are commonly observed in testing of sulfide-rich clay materials.

The isotopic compositions of the pore fluid, corrected for water uptake, indicate perhaps slightly enriched oxygen-18 and deuterium in the cell cores as compared with the squeezed water. The computed concentrations for chloride are perhaps slightly lower than the concentrations reported for the squeezed water, but if the correction for uptake water is correct, then the chloride concentrations are in remarkably close agreement.

It may be noted that the core material in cells N2 and N4 were taken from the same piece of core, and one might therefore expect that the initial concentrations in the pore water would be the same for these two cells. The differences in the initial concentrations as determined from the radial diffusion tests therefore can be taken as in indication of the possible errors involved in the determination.

4.4 Determination of effective diffusivities.

The effective diffusion coefficients determined by modelling the experimental results with RADIF2, are summarized in Table 4. A plot of a typical test result and the modelled change of concentration with time (Chloride in cell N1) is shown in Figure 2. The plot shows both the actual changes of concentrations and the change of concentration that would have happened if the sampling and fluid replacement at 7 days had not resulted in a change in the concentration. For this case as for the other simulations, the first sample, at 7 days, was taken during the transient portion of the diffusion process and thus constrains the effective diffusivity. The second sample, taken after equilibrium conditions had been reached, constrains the accessible porosity. The fit is unique in that no other combination of accessible porosity and diffusivity can be made to fit the data.

The assumption that equilibrium was reached before the second sample was taken was checked for each cell by means of electrical conductivity measurements. The assumption was also verified by repeating the test and taking two successive samples after equilibrium is supposed to have been reached, at 110 days and at 225 days. The results showed no significant change of concentration between 110 and 225 days, confirming that full equilibrium had been reached at 110 days.

Effective diffusivities in porous media are defined in two different ways in the literature. In one way (e.g. Novakowski and van der Kamp, 1996) porosity is not included in the effective diffusivity. In the other way (e.g. Pearson, 1999) porosity is included as part of the effective diffusivity, thereby giving lower values. In this report Pearson's terminology will be followed and the "effective diffusivity" of Novakowski and van der Kamp (1996) will be referred to as the "apparent diffusivity".

An additional difficulty is that the diffusion-accessible porosity, as determined by the mass balance calculations in this report, is not necessarily equal to the diffusion-area porosity which applies for diffusive transport (Pearson, 1999) The semi-analytical radial diffusion model of Novakowski and van der Kamp (1996) assumes implicitly that the two porosities are identical. The radial diffusion method does not allow independent measurement of the diffusion-area porosity. For mudstones such as the Opalinus Clay, in which dead-end pores are not likely to be important, the two porosities can probably be treated as identical (Pearson, 1999).

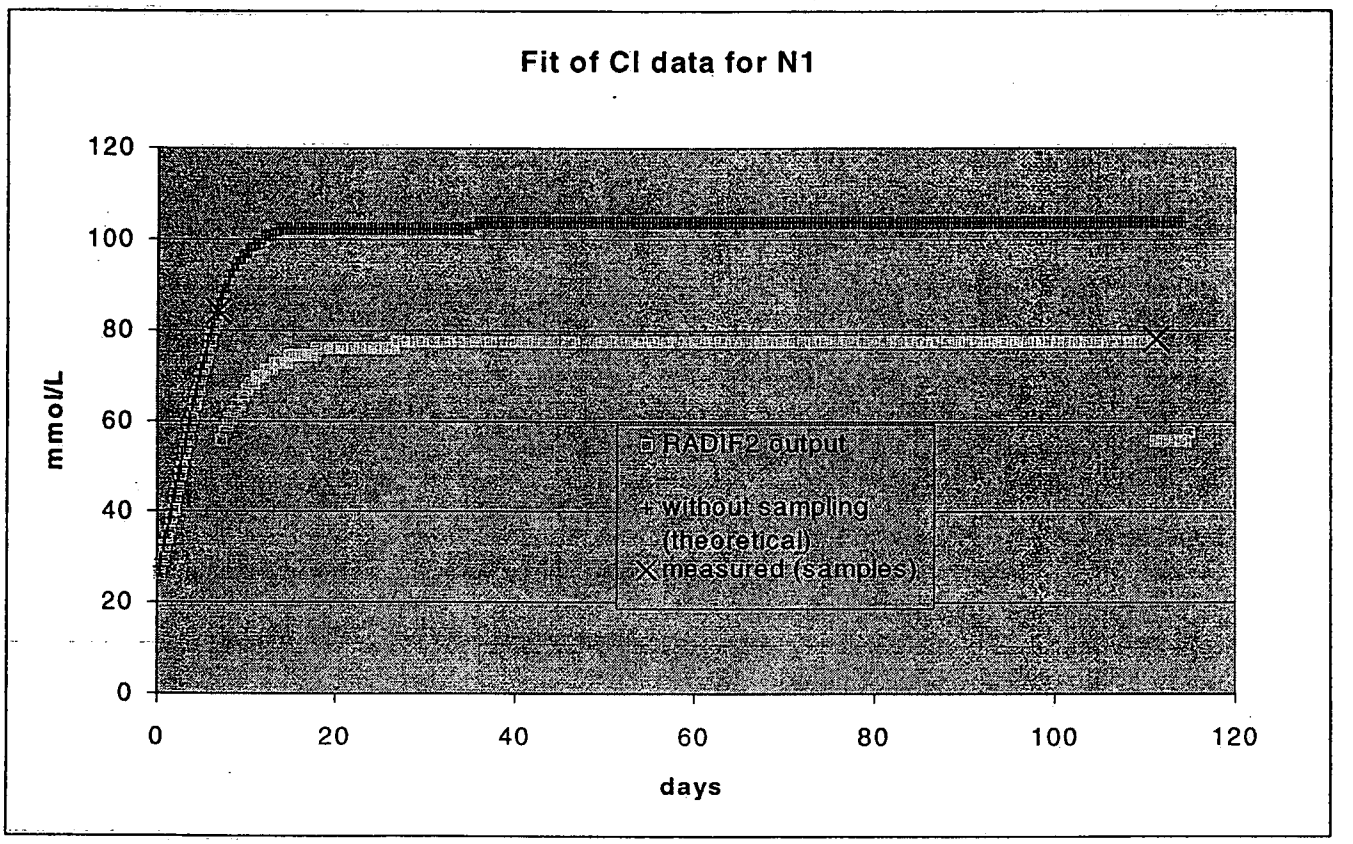

Figure 2. Plot of concentration changes as simulated by RADIF2 during diffusivity test, Cell N1, chloride.

The results of the diffusivity testing are relatively consistent, with the water itself as measured by means of the isotopes having a slightly higher effective diffusivity than the bromide and chloride. There is some indication that the effective diffusivities for the sandy facies (cells N1 and N3) may be slightly higher than the diffusivities for the shaly facies (cells N2 and N4). Overall the effective diffusivities are in the general range of 2×10^{-11} to 10×10^{-11} m^2/sec. The

average values of effective diffusivity (in 10^{-11} m^2/sec) were 4.3 for chloride, 3.7 for bromide, 6.7 for deuterium and 7.0 for oxygen-18 .

The diffusion was radial, perpendicular to the axes of the cores, and more or less parallel to the bedding planes. It is possible that for diffusion perpendicular to the bedding planes the diffusivity may be lower. The core samples in the cells had all been subject to some degree of swelling, leading to a significant increase in the porosity and presumably in the average pore size. Thus the effective diffusivity is likely to be somewhat higher for these core samples as compared to the same material under in situ conditions. The results reported here do not allow an estimate of the magnitude of this effect.

Summary

No obvious difference could be discerned between the shaly facies and the sandy facies of the Opalinus Clay with regard to porosity and diffusivity.

The oven-dry porosities before water uptake, determined by oven-drying of adjacent pieces of core, range from 0.156 to 0.163 with an average value of 0.158.

The average ratios of diffusion-accessible porosity to total porosity after swelling were 0.67 for chloride, 0.63 for bromide, 1.03 for deuterium, and 1.16 for oxygen-18. There is an indication that the results for oxygen-18 were influenced by slow exchange with bound water.

The isotopic compositions of the pore fluid, corrected for water uptake, indicate perhaps slightly enriched oxygen-18 and deuterium in the cell cores as compared with water collected from boreholes. The computed concentrations for chloride are slightly lower than the concentrations reported for the borehole water, but if the correction for uptake water is appropriate, than the chloride concentrations are in remarkably close agreement.

The average values of effective diffusivity (in 10^{-11} m^2/sec) were 4.3 for chloride, 3.7 for bromide, 6.7 for deuterium and 7.0 for oxygen-18. The effective diffusivities for the sandy species appear to be slightly higher than for the shaly species. No slow component of diffusion in the cells was observed: the aqueous concentrations of dissolved species and of the isotopes of water were virtually identical at 110 and 225 days after filling of the reservoir.

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Cell No.	N1	N2	N3	N4
Core No.	WS-A3/C27	WS-A5/H18	WS-A3/C30	WS-A5/H18
Depth of core (m)	20.5	4.9	26.71	4.9
Location	Mt Terri, CH	Mt Terri, CH	Mt Terri, CH	Mt. Terri, CH
Geologic material	Opalinus Clay, sandy	Opalinus Clay, shaly	Opalinus Clay, sandy	Opalinus Clay, shaly
Date of coring	96/dec	97/dec	96/dec	97/dec
Date of cell preparation	13-Jan-98	21-Jan-98	16-Jan-98	21-Jan-98
O.D. of core sample (cm)	7.2	7.2	7.2	7.2
Length of sample (cm)	12	9	8.99	9
Mass of dry porous tube (g)	10.99	8.42	7.31	8.18
Mass of saturated porous tube (g)	19.22	14.27	12.91	14.3
Mass of permanent cell fittings	1158.02	1054.67	1050.21	1054.34
Diameter of bored hole (cm)	2.70	2.70	2.70	2.70
Length of bored hole (cm)	11.00	7.60	7.60	7.60
Initial mass of wet soil in cell (g)	981.85	786.80	778.29	781.06
Initial water content (w)	0.071	0.067	0.067	0.067
Initial water in soil (cm3)	65.40	49.60	49.10	49.30
Water uptake after filling of cell (cm3)	24.41	6.30	8.46	9.81
Water volume in soil after water uptake (cm3)	89.81	55.90	57.56	59.11
Initial porosity before water uptake	0.163	0.157	0.156	0.157
Final porosity after water uptake	0.211	0.173	0.178	0.183
Volume of soil (cm3)	426	323	323	323
Volume of solids (cm3)	336	267	265	264
Density of solids (g/cm3)	2.73	2.76	2.75	2.77

Table 1. Summary of core and cell parameters

	N1	N2	N3	N4
Core No.	WS-A3/C27	WS-A5/H18	WS-A3/C30	WS-A5/H18
Depth of core (m)	20.5	4.9	26.71	4.9
Location	Mt Terri, CH	Mt Terri, CH	Mt Terri, CH	Mt. Terri, CH
Geologic material	Opalinus Clay, sandy	Opalinus Clay, shaly	Opalinus Clay, sandy	Opalinus Clay,shaly
Date of coring	96/dec	97/dec	96/dec	97/dec
Range of pore fluid ionic strength	0.273 to 0.119	0.469 to 0.219	0.225 to 0.333	0.472 to 0.176
(a) Total porosities				
"Oven-dry" porosity	0.163	0.157	0.156	0.157
Porosity after water uptake	0.211	0.173	0.178	0.183
(b) Ratio of accessible porosities to porosity after water uptake				
Choride	0.72	0.60	0.68	0.68
Bromide	0.69	0.59	0.58	0.66
Deuterium	1.12	0.99	1.00	1.01
Oxygen-18	1.17	1.07	1.13	1.20
(c) Diffusion-accessible porosity				
Chloride	0.152	0.104	0.121	0.124
Bromide	0.146	0.102	0.103	0.121
Deuterium	0.236	0.171	0.178	0.185
Oxygen-18	0.247	0.185	0.201	0.220

Table 2. Summary of diffusion-accessible porosities

		Cell N-1	Cell N-3	BGS water sample	Cell N-2	Cell N-4	BGS water sample
Core No.		WS-A3/C27	WS-A3/C30	A-3	WS-A5/H18	WS-A5/H18	A-1
Depth of core (m)		20.5	26.71	21.9-28.1	4.9	4.9	13.2-20.0
Opalinus Clay facies		Sandy	Sandy	-	Shaly	Shaly	-
Date of coring		96/dec	96/dec	18 Jun, 1997	97/dec	97/dec	18 Jun, 1997
Initial porosity before swelling		0.163	0.157		0.156	0.157	
Final porosity after swelling		0.211	0.173		0.175	0.183	
Pore fluid composition in cell after water uptake							
Ca	(meq/L)	44.4	19.4	14.6	74.2	82.5	29.8
Mg	(meq/L)	45.6	19.9	13.3	85.5	100.4	33.4
Na	(meq/L)	126.2	141.8	128.0	243.5	237.1	245
K	(meq/L)	2.7	1.9	1.1	4.7	4.2	1.5
SO4	(meq/L)	58.2	59.3	23.0	72.9	85.6	27.2
Choride	(meq/L)	84.5	97.4	133.0	253.2	222.7	287
Bromide	(meq/L)	0.3	0.3	0.19	0.36	0.63	0.46
HCO3	(meq/L)	11.6	21.5	5.2	5.93	6.88	0.7
Deuterium	(o/oo)	-48	-38	-64	-39	-33	-56
Oxygen-18	(o/oo)	-6.5	-6.5	-9.1	-6.8	-6.9	-8.5
Pore fluid composition in cell before water uptake							
Ca	(meq/L)	65	23	14.6	84	99	29.8
Mg	(meq/L)	67	23	13.3	96	120	33.4
Na	(meq/L)	184	166	128	274	284	245
K	(meq/L)	4	2	1.1	5	5	1.5
SO4	(meq/L)	85	70	23	82	103	27
Choride	(meq/L)	123	114	133	285	267	287
Bromide	(meq/L)	0	0.4	0.19	0.4	0.8	0.46
HCO3	(meq/L)	17	25.2	5.2	6.7	8.2	0.7
Deuterium	(o/oo)	-70	-45	-64	-44	-40	-56
Oxygen-18	(o/oo)	-9	-7.6	-9.1	-7.7	-8.3	-8.5

Table 3. Summary of initial concentrations

Effective diffusivities (1.0E-11 m2/s)				
	N1	N2	N3	N4
Cl	5.6	1.8	5.2	4.4
Br	4.5	1.7	4.1	4.3
Deuterium	8.4	5.1	7.9	5.6
Oxygen-18	10.0	5.6	7.4	5.9

Table 4. Summary of effective diffusivity results

N4 Mass Balance

			N4 BALANCE SHEET			
		N4-0	N4-1	N4-2	N4-3	N4-4A/4B
Date Filled		13-fevr-98	16-fevr-98	09-oct-98	16-oct-98	04-fevr-99
Time Filled		13:45	13:38	14:35	13:46	16:34
Date Sampled			02-sept-98	16-oct-98	04-fevr-99	17-sept-99
Time Sampled			11:52	13:36	16:30	16:40
Contact Time	(Days)		197,926	6,959	111,114	225,004
Type of Fluid Added		NACL/BR10K-MQ1	NACL/BR20K-MQ1	INV1	INV1	MQ1
Density of Fluid Added	(g/ml)	1,007	1,013	1,000	1,000	1,000
Fluid Added	(Grams)	6,120	31,370	25,140	26,880	27,000
Volume of Fluid Added	(mls)	6,077	30,967	25,132	26,872	26,992
Evaporation Losses	(Grams)	0,000	0,900	0,200	1,000	0,100
Density of Fluid Removed	(g/ml)	1,000	1,015	1,007	1,007	1,005
Fluid Removed	(Grams)	0,000	20,560	24,460	25,170	27,030
Volume of Fluid Removed	(mls)	0,000	20,256	24,290	24,995	26,896
Net Volume of Fluid Added	(mls)	6,077	6,077	6,719	7,596	7,592
Ca:						
Conc. Added	(Meqs/L)	0,11	0,21	0,00	0,00	0,00
Mass Added	(Meqs)	0,00	0,01	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		41,17	15,07	16,37	10,23
Mass Removed	(Meqs)	0,00	0,87	0,37	0,43	0,28
Net Mass Added	(Meqs)	0,00	-0,86	-1,23	-1,66	-1,93
Mass in Free Fluid	(Meqs)		0,25	0,10	0,12	0,08
Net Mass Added to Soil	(Meqs)		-1,11	-1,33	-1,78	-2,01
Initial concentration	(Meqs/L)				82,48	
Mg:						
Conc. Added	(Meqs/L)	0,01	0,01	0,00	0,00	0,00
Mass Added	(Meqs)	0,00	0,00	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		49,94	17,52	20,16	11,76
Mass Removed	(Meqs)	0,00	1,06	0,43	0,52	0,32
Net Mass Added	(Meqs)	0,00	-1,06	-1,49	-2,01	-2,33
Mass in Free Fluid	(Meqs)		0,30	0,12	0,15	0,09
Net Mass Added to Soil	(Meqs)		-1,36	-1,60	-2,16	-2,42
Initial concentration	(Meqs/L)				100,38	
Na:						
Conc. Added	(Meqs/L)	178,99	347,98	0,00	0,00	0,00
Mass Added	(Meqs)	1,09	10,78	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		308,35	150,33	160,42	120,27
Mass Removed	(Meqs)	0,00	6,52	3,68	4,17	3,25
Net Mass Added	(Meqs)	1,09	5,34	-1,66	-2,51	-5,76
Mass in Free Fluid	(Meqs)		1,87	1,01	1,22	0,91
Net Mass Added to Soil	(Meqs)		3,47	0,65	-3,73	-6,67
Initial concentration	(Meqs/L)				237,09	
K:						
Conc. Added	(Meqs/L)	0,63	1,22	0,00	0,00	0,00
Mass Added	(Meqs)	0,00	0,04	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		3,27	1,74	1,72	1,33
Mass Removed	(Meqs)	0,00	0,07	0,04	0,04	0,04
Net Mass Added	(Meqs)	0,00	-0,03	-0,07	-0,11	-0,15
Mass in Free Fluid	(Meqs)		0,02	0,01	0,01	0,01
Net Mass Added to Soil	(Meqs)		-0,05	-0,08	-0,13	-0,16
Initial concentration	(Meqs/L)				4,18	

N4 Mass Balance

SO4:						
Conc. Added	(Meqs/L)	0,00	0,00	0,00	0,00	0,00
Mass Added	(Meqs)	0,00	0,00	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		68,69	32,31	50,11	41,34
Mass Removed	(Meqs)	0,00	1,45	0,79	1,30	1,12
Net Mass Added	(Meqs)	0,00	-1,45	-2,24	-3,55	-4,66
Mass in Free Fluid	(Meqs)		0,42	0,22	0,38	0,31
Net Mass Added to Soil	(Meqs)		-1,87	-2,46	-3,93	-4,98
Initial concentration	(Meqs/L)				85,59	
Cl:						
Conc. Added	(Meqs/L)	173,17	332,92	0,00	0,00	0,00
Mass Added	(Meqs)	1,05	10,31	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		298,11	142,45	145,53	87,21
Mass Removed	(Meqs)	0,00	6,31	3,49	3,78	2,35
Net Mass Added	(Meqs)	1,05	5,06	1,57	-2,22	-4,57
Mass in Free Fluid	(Meqs)		1,81	0,96	1,11	0,66
Net Mass Added to Soil	(Meqs)		3,24	0,61	-3,32	-5,23
ne/nt					0,73	0,68
Initial concentration	(Meqs/L)				222,73	
Br						
Conc. Added	(Meqs/L)	9,87	18,77	0,00	0,00	0,00
Mass Added	(Meqs)	0,06	0,58	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		10,02	4,74	4,64	2,89
Mass Removed	(Meqs)	0,00	0,21	0,12	0,12	0,08
Net Mass Added	(Meqs)	0,06	0,43	0,31	0,19	0,11
Mass in Free Fluid	(Meqs)		0,06	0,03	0,04	0,02
Net Mass Added to Soil	(Meqs)		0,37	0,28	0,16	0,09
ne/nt			0,62		0,66	0,66
Initial concentration	(Meqs/L)				0,63	
HCO3: (Calculated)						
Conc. Added	(Meqs/L)	0,04	0,03	0,00	0,00	0,00
Mass Added	(Meqs)	0,00	0,00	0,00	0,00	0,00
Conc. Removed	(Meqs/L)		6,16	5,26	5,04	14,95
Mass Removed	(Meqs)	0,00	0,13	0,13	0,13	0,40
Net Mass Added	(Meqs)	0,00	-0,13	-0,26	-0,39	-0,79
Mass in Free Fluid	(Meqs)		0,04	0,04	0,04	0,11
Net Mass Added to Soil	(Meqs)		-0,17	-0,29	-0,43	-0,91
Initial concentration	(Meqs/L)				6,88	
Ionic Strength			**472,76**	**217,18**	**245,32**	**176,66**
Deuterium						
Conc. Added	(0/00)	-139	-139	-218	-218	-139
Mass Added	((0/00) x L)	-0,845	-4,304	-5,479	-5,858	-3,752
Conc. Removed	(0/00)	-139,000	-84,00	-141,00	-146,00	-142,00
Mass Removed	((0/00) x L)	0,00	-1,777	-3,453	-3,795	-3,833
Net Mass Added	((0/00) x L)	-0,845	-3,372	-5,398	-7,461	-7,379
Mass in Free Fluid	((0/00) x L)		-0,510	-0,947	-1,109	-1,078
Net Mass Added to Soil	((0/00) x L)		-2,862	-4,451	-6,352	-6,301
ne/nt					0,95	1,01
Initial concentration	((0/00) x L)				-33,16	
d 18O						
Conc. Added	(0/00)	-17,9	-17,9	-28,8	-28,8	-17,9
Mass Added	((0/00) x L)	-0,109	-0,554	-0,724	-0,774	-0,483
Conc. Removed	(0/00)	-17,900	-12,10	-18,80	-19,30	-18,50
Mass Removed	((0/00) x L)	0,00	-0,256	-0,460	-0,502	-0,499
Net Mass Added	((0/00) x L)	-0,109	-0,407	-0,671	-0,943	-0,926
Mass in Free Fluid	((0/00) x L)		-0,074	-0,126	-0,147	-0,140
Net Mass Added to Soil	((0/00) x L)		-0,334	-0,544	-0,796	-0,786
ne/nt					1,09	1,20
Initial concentration	((0/00) x L)				-6,91	

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