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Multicomponent Diffusion Modeling in Clay Systems with Application to the Diffusion of Tritium, Iodide, and Sodium in Opalinus Clay

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The hydrogeochemical transport model PHREEQC was extended with options to calculate multicomponent diffusion in free pores and in the diffuse double layer (DDL). Each solute species can be given its own tracer diffusion coefficient. The composition of the DDL is calculated with the Donnan approximation. With these options, solute species can be transported in coexisting charged and uncharged regions as may exist in clays and membranes. The model was developed to simulate in-situ tracer diffusion experiments in Opalinus Clay with tritium, iodide, and sodium. Tritium gives the formation's tortuosity factor, which applies in principle for all the neutral species. Half of the porosity is not accessible for iodide due to anion exclusion, and assumed equal to the amount of DDL-water. With this assumption, the tortuosity factor for iodide is 1.4 times higher than that for tritium. The sodium data can be matched by reducing the tortuosity factor 1.6 times relative to tritium, and by distributing the cation exchange capacity over the DDL and fixed sites that are spread heterogeneously over the model domain. The physical origin of the variable tortuosity for differently charged species is discussed.

Introduction

Clays have rather ideal properties for waste containment in the field, but the transport processes are still difficult to quantify precisely. The dominant transport mode is diffusive and a function of the concentration gradient, activity corrections (activity coefficient and complexation), the mobility of the species in water, charging due to different mobilities or electrical current, the accessible porosity, the tortuosity (the length of the actual path over the straight line distance), and the retardation as a result of reactions such as sorption or ion exchange (*1*−*6*). Concentration data from diffusion experiments can be fitted with transport models that account for these variables, and the results provide effective diffusion coefficients for Fick's law

$$\frac{\partial}{\partial t}\left(c_i + s_i \frac{\rho_b}{\epsilon_{a,i}}\right) = D_{e,i}\frac{\partial^2 c_i}{\partial x^2} \quad (1)$$

where t is time (s), c_i is the concentration in accessible porewater (mol/L), s_i is the concentration in the solid (mol/kg), ρ_b is the bulk density (kg/L), $\epsilon_{a,i}$ is the accessible porosity (-), $D_{e,i}$ is the effective diffusion coefficient (m^2/s), and $\partial^2 c_i/\partial x^2$ is the divergence of the concentration-gradient of solute i (mol/m^5). The effective diffusion coefficient is related to the solute's tracer diffusion coefficient in "free" water by

$$D_{e,i} = \epsilon_{a,i} D_{p,i} = \epsilon_{a,i}\frac{D_{w,i}}{\theta_i^2} \quad (2)$$

where $\epsilon_{a,i}$ is the accessible porosity (-), $D_{p,i}$ is the porewater diffusion coefficient (m^2/s), $D_{w,i}$ is the tracer diffusion coefficient in water (m^2/s), and θ_i^2 is the tortuosity factor (-).

Most numerical models for calculating transport in clays assume that the diffusion coefficient, the accessible porosity, and the tortuosity factor are the same for all solutes. However, it is well-known that this is not the case (*6*−*25*). For example, porewater diffusion coefficients ($D_{p,i}$) from in-situ diffusion experiments in Opalinus Clay, a consolidated mudstone formation, are listed in Table 1 (*7*−*10*). Typical values are presented, and it should be noted that different models, with different accessible porosities and sorption, already give variations of 10−30% for the same experiment (*9*, *10*). Nevertheless, it is clear that cations, anions, and neutral species have unequal porewater diffusion coefficients. Furthermore, the accessible porosity is smaller for anions than for tritium and cations. Finally, the ratio D_w/D_p, expressing the tortuosity factor, is larger for anions than for tritium, but smaller for cations.

Commonly, the higher diffusivity of cations is attributed to surface diffusion (*15*−*18*) or to the diffuse double layer (DDL), where the concentrations of cations are increased (*19*−*23*). If the cations are at a higher concentration, their diffusion is enhanced since diffusional fluxes are coupled to concentrations as illustrated in Figure 1. However, this does not explain the smaller diffusivity of anions. If the accessible porespace is correctly determined, either by comparing concentrations in the porewater and in the contacting free solution (*13*, *24*), or by combining the transient and steady states in a laboratory diffusion experiment (*7*), the smaller diffusivity must be due to an increased tortuosity for anions. High tortuosities for anions have been reported often in clays and sediments (*12*, *13*, *15*, *25*). But, if the tortuosity can be higher for anions than for uncharged species, it could be smaller for cations, and thus explain the larger diffusivity by smaller tortuosity rather than by surface diffusion.

It is difficult to assess the major factor without a model that can calculate these processes independently. This provided stimulus to extend the geochemical transport code PHREEQC (*26*) with multicomponent diffusion, i.e., each solute can be given its own tracer diffusion coefficient. Diffusive transport is calculated separately for free porewater and the DDL (*27*, *28*). The developed model is able to calculate diffusion and chemical reactions (sorption, precipitation, etc.) of all the tracers together. We present the theory and examples, and apply the model to simulate diffusion experiments in Opalinus Clay. By comparing model and field data, aspects of diffusive transport in clay systems can be highlighted that were previously not well understood.

Theoretical Basis

Multicomponent Diffusion. Fick's laws calculate diffusion from concentration gradients and divergences. However, a more general equation would employ the electrochemical

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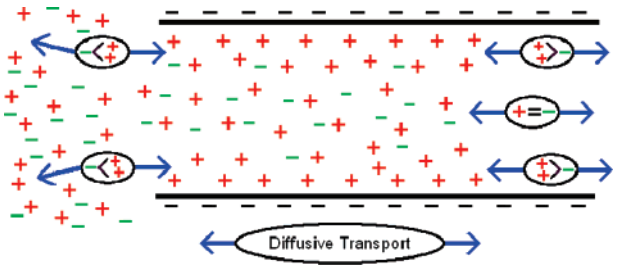

FIGURE 1. Pictorial simplification of solute diffusion in a (partly) charged pore connected with a free solution. Anions are excluded from the diffuse double layer at the negatively charged surface, cations are enriched there, and consequently, their diffusion is enhanced.

TABLE 1. Porewater Diffusion Coefficients (D_p), Accessible Porosities (ϵ_a) and Retardations ($R = 1 + (\rho_b)/(\epsilon_a)(ds)/(dc)$) in Opalinus Clay (*7*−*10*), Tracer Diffusion Coefficients in Water at 15 °C (D_w), and Tortuosity Factors ($\theta^2 = D_w/D_p$) in Opalinus Clay (Retardation for Cs^+ Is Variable)

	HTO	Na^+	Cs^+	I^-	Cl^-
$D_p/(10^{-11}$ m^2/s)	34	44	125	19	17
ϵ_a (-)	0.16	0.16	0.16	0.08	0.08
R (-)	1	3.5	variable	1	1
$D_w/(10^{-11}$ m^2/s)[a]	170[b]	102[c]	158[c]	153[c]	111[c]
θ^2	5.0	2.3	1.3	8.1	6.5

[a] Corrected to 15 °C by dividing the value at 25 °C by 1.32 (*35*). [b] From ref *42*. [c] From ref *36*.

potential, μ, rather than the concentration (*1*, *2*). The electrochemical potential of species i is

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \psi \tag{3}$$

where μ_i^0 is the standard (electrochemical) potential (J/mol), R is the gas constant (8.314 J/K/mol), T is the absolute temperature (K), a_i is the activity (-), z_i is the charge number (-), F is the Faraday constant (96485 J/V/eq), and ψ is the electrical potential (V). The activity is related to concentration by $a_i = \gamma_i c_i/c^0$, where γ_i is the activity coefficient (-) and c_i^0 is the standard state (1 mol/kg H_2O, assumed equal to 1 mol/L in the following).

The diffusive flux of i in solution as a result of chemical and electrical potential gradients is

$$J_i = -\frac{u_i c_i}{|z_i|F}\frac{\partial \mu_i}{\partial x} - \frac{u_i z_i c_i}{|z_i|}\frac{\partial \psi}{\partial x} \tag{4}$$

where u_i is the mobility (m^2/s/V). The gradient of the electrical potential ($\partial\psi/\partial x$) in eq 4 originates from different transport velocities of ions, which creates charge and an associated potential. This electrical potential may differ from the one used in eq 3, which comes from a charged surface and is fixed, without inducing electrical current.

If there is no electrical current, $\Sigma z_i J_i = 0$. This permits expression of the electrical potential gradient in eq 4 as (*2*, *4*, *29*, *30*)

$$\frac{\partial \psi}{\partial x} = -\frac{\sum_{j=1}^{n} \frac{u_j z_j c_j}{|z_j|F}\frac{\partial \mu_j}{\partial x}}{\sum_{j=1}^{n} \frac{u_j z_j^2 c_j}{|z_j|}} \tag{5}$$

where subscript j is introduced for species to show in subsequent equations that they stem from the potential term.

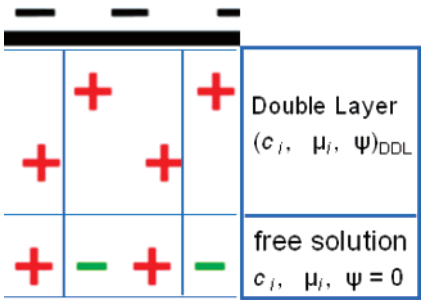

FIGURE 2. Discretization of a pore with a charge-free solution and a diffuse double layer that forms the basis for the multicomponent diffusion model in PHREEQC.

With eq 5 the electrical potential gradient can be eliminated from eq 4

$$J_i = -\frac{u_i c_i}{|z_i|F}\frac{\partial \mu_i}{\partial x} + \frac{u_i c_i z_i}{|z_i|}\frac{\sum_{j=1}^{n} \frac{u_j z_j c_j}{|z_j|F}\frac{\partial \mu_j}{\partial x}}{\sum_{j=1}^{n} \frac{u_j z_j^2 c_j}{|z_j|}} \tag{6}$$

The equation is also valid if the solution is not electrically neutral since any charge imbalance that may exist (notably in the DDL) is maintained by the condition $\Sigma z_i J_i = 0$.

Diffuse Double Layer. It has been suggested (*31*, *32*) that DDL properties can be neglected when calculating multicomponent diffusion in marine mud, because the DDL is very thin at seawater ionic strength and would occupy a very small part only of the pore. However, it is not the thickness of the DDL that determines the transport properties, but the distribution of a cation over the DDL and the pore solution, which depends on the cation exchange capacity (CEC) of the sediment. It can be calculated (*33*) that a marine mud with a porosity of 0.5 and a CEC of 0.3 eq/kg contains as much Na^+ in the cation exchange complex as in the pore solution. Since Na^+ forms an outer-sphere complex, probably most of the exchangeable Na^+ resides in the DDL. Moreover, it is likely that migration velocities of ions in the double layer and the free solution are similar (*34*).

The DDL can be incorporated in an arrangement shown in Figure 2. The porespace is condensed to a single pore, subdivided along its length in paired cells. One cell of each pair contains a charge-balanced solution, the other holds a charged surface and a DDL with a deficit of co-ions (with the same charge as the surface) and an excess of counterions. The solutes in the 2 cells are assumed to be in equilibrium according to Boltzmann's formula, with zero potential in the charge-free solution, and a potential in the other one that gives zero charge. The paired cells are aligned along the pore, and multicomponent diffusive transport is calculated by explicit finite differences (*33*) for each interface among the pairs of cells. It should be noted that the model can zoom in on the nm-scale suggested by Figure 2, but also uses it as the representative form for the cm-scale or larger.

In the DDL, the electrochemical potential is, similar to eq 3,

$$\mu_{i,\mathrm{DDL}} = \mu_i^0 + RT \ln a_{i,\mathrm{DDL}} + z_i F \psi_{\mathrm{DDL}} \tag{7}$$

At equilibrium, the electrochemical potential equals the chemical potential at infinite distance, where $\psi = 0$

$$\mu_{i,\mathrm{DDL}} = \mu_{i,\infty} \tag{8}$$

Thus, the activity in the DDL is

$$a_{i,\mathrm{DDL}} = a_{i,\infty} \exp(-zF\psi/RT) \quad (9)$$

Along the pore, the gradient of the electrochemical potential in the DDL is

$$\nabla(\mu_{i,\mathrm{DDL}}) = \nabla(RT\ln(a_{i,\mathrm{DDL}})) + \nabla(z_iF\psi) = 1/dx\,\{RT\,d(\ln(a_{i,\mathrm{DDL}})) + z_iFd(\psi)\} = 1/dx\,\{RT\,d(\ln(a_{i,\infty})) - z_iFd(\psi) + z_iFd(\psi)\} = \nabla(RT\ln(a_{i,\infty})) \quad (10)$$

Therefore, the electrochemical potential gradient in the DDL along the length of a pore is the same as the chemical potential gradient of the equilibrium solutions along the pore. This implies that eq 6 can be used for both the DDL and the free solution; only the concentrations (c_i and c_j in eq 6) are different in the free pore solution and the DDL.

The gradient of the chemical potential is $\nabla(\mu_i) = \partial\mu_i/\partial c_i\,\nabla(c_i)$, where

$$\frac{\partial\mu_i}{\partial c_i} = RT\frac{\partial\ln(\gamma_i c_i)}{\partial c_i} = RT\left(\frac{\partial\ln(\gamma_i)}{\partial c_i} + \frac{\partial\ln(c_i)}{\partial c_i}\right) = \frac{RT}{c_i}\left(\frac{\partial\ln(\gamma_i)}{\partial\ln(c_i)} + 1\right) \quad (11)$$

and, with $D_{w,i} = u_iRT/(|z_i|\,F)$, eq 6 becomes

$$J_i = -D_{w,i}\left(\frac{\partial\ln(\gamma_i)}{\partial\ln(c_i)} + 1\right)\frac{\partial c_i}{\partial x} + D_{w,i}z_ic_i\frac{\sum_{j=1}^{n} D_{w,j}z_j\left(\frac{\partial\ln(\gamma_j)}{\partial\ln(c_j)} + 1\right)\frac{\partial c_j}{\partial x}}{\sum_{j=1}^{n} D_{w,j}z_j^2c_j} \quad (12)$$

The flux is calculated separately for the charge-free pore and the DDL, but the activity coefficients are assumed equal (which may not be true). Cross terms in diffusion are probably negligible in less than 1−2 molar solutions (*1*, *3*), but they may be incorporated in eq 12 (*31*).

By default, the concentrations in the DDL are calculated in PHREEQC by integration of eq 9 from the pore solution to the surface, while iteratively adapting the potential at the surface until the charge in the DDL counters the surface charge. This computer-intensive operation often fails. As an alternative, the code was extended with the Donnan approximation, which assumes a single potential for the DDL as an entity

$$c_{i,\mathrm{DDL}} = c_i \exp\left(\frac{-z_iF\psi_{\mathrm{DDL}}}{RT}\right) \quad (13)$$

and where the potential is optimized to achieve charge neutrality

$$\Sigma z_ic_{i,\mathrm{DDL}} + \sigma_{\mathrm{DDL}} = 0 \quad (14)$$

This simplification gives comparable results with the integration algorithm, as shown in the Supporting Information.

Implementation. Equation 12 was programmed in PHREEQC, calculating the fluxes for all the species separately in the free pore and the DDL, and then summing up for the interface between two model cells. Details and instructions for setting up input files are given in the Supporting Information.

Results

Numerical Example: A Diffusion Experiment with Opalinus Clay. We model first a hypothetical diffusion experiment with Opalinus Clay to illustrate how the various terms of multicomponent diffusion in the free pore and the DDL, and retardation by ion exchange, will modify the transport of 3 key solutes. PHREEQC input files are provided as Supporting Information. A 0.2 m diameter column of 0.5 m length is contacted for about 1 year with 0.8 L of porewater to which tritium, $^{22}Na^+$, and I^- are added as tracers at 1 μM. The porewater in the Opalinus Clay is a mixed (Na,Ca)Cl solution of 0.37 M ionic strength (*9*, cf. input files in Supporting Information).

First, a case with diffusion only, without retardation by ion exchange, was calculated with the multicomponent model with all species having the same tracer diffusion coefficient of 2.24×10^{-9} m^2/s of tritium and a tortuosity factor of 6.25 ($=1/\epsilon_w$). The resulting concentrations in the outer solution are identical for the 3 tracers (HTO, $^{22}Na^+$, I^-) and agree with PHREEQC's existing diffusion model (Figure 3a).

Second, a database was invoked with tracer diffusion coefficients for solute species (*36*−*38*). The results in Figure 3b, still without ion exchange or a DDL, show the strongest concentration decrease for HTO, less for I^-, and least for $^{22}Na^+$. Thus, HTO diffuses most quickly away in the clay and $^{22}Na^+$ is the slowest, in agreement with the order in the tracer diffusion coefficients (Table 1). If HTO is given the diffusion coefficient of $^{22}Na^+$, it shows exactly the same concentration decrease as $^{22}Na^+$, and with the diffusion coefficient of I^-, it follows I^-. This indicates that the current, generated by the different fluxes of Na^+ and I^-, is compensated by a slightly smaller flux of all the anions together and a somewhat larger flux of the cations (cf. eq 6). This is a fractional change; if ions are present at orders of magnitude greater concentrations than the tracers, and the current to be compensated is relatively small, the flux of the tracers is only little affected. However, this also depends on the initial and boundary conditions (cf. Supporting Information).

Third, a surface was added with a negative charge equal to the CEC of the Opalinus Clay (0.11 eq/kg or 1.6 eq/L porewater), and a DDL that occupies half of the pore (Figure 3c). HTO is not changed since it is a neutral species and not affected by potential differences. Iodide is rejected from the DDL, its overall diffusivity is therefore less and the concentration decrease is slower than that shown in Figure 3b. For $^{22}Na^+$, two lines are given for two extreme cases. One is calculated with the excess cations mobile in the DDL, the other is with the cations fixed on the surface. The fixed case is obtained by defining surface complexation reactions in the model (*20*, *39*, Supporting Information). The relative values for the constants (K_i) follow the order of the standard ion-exchange reactions of the PHREEQC databases. For example, with Su^- as the surface site

$$Su^- + Na^+ \leftrightarrow SuNa; \qquad K_{\mathrm{SuNa}} \quad (15)$$

$$Su^- + K^+ \leftrightarrow SuK; \qquad K_{\mathrm{SuK}} = 5 \times K_{\mathrm{SuNa}} \quad (16)$$

etc., for the other cations. The balance of the surface charge over the fixed sites (complexes) and the DDL depends on the value of K_{SuNa}. If $K_{\mathrm{SuNa}} = 1$, the DDL contains 35% of the surface charge. If $K_{\mathrm{SuNa}} = 10^5$ (the value used for Figure 3c), the charge of the DDL is less than 3×10^{-3}%.

In both cases, $^{22}Na^+$ in the outer solution decreases quicker than that shown in Figure 3b since its potential gradient is steepened by mass loss to the DDL or the exchanger. The

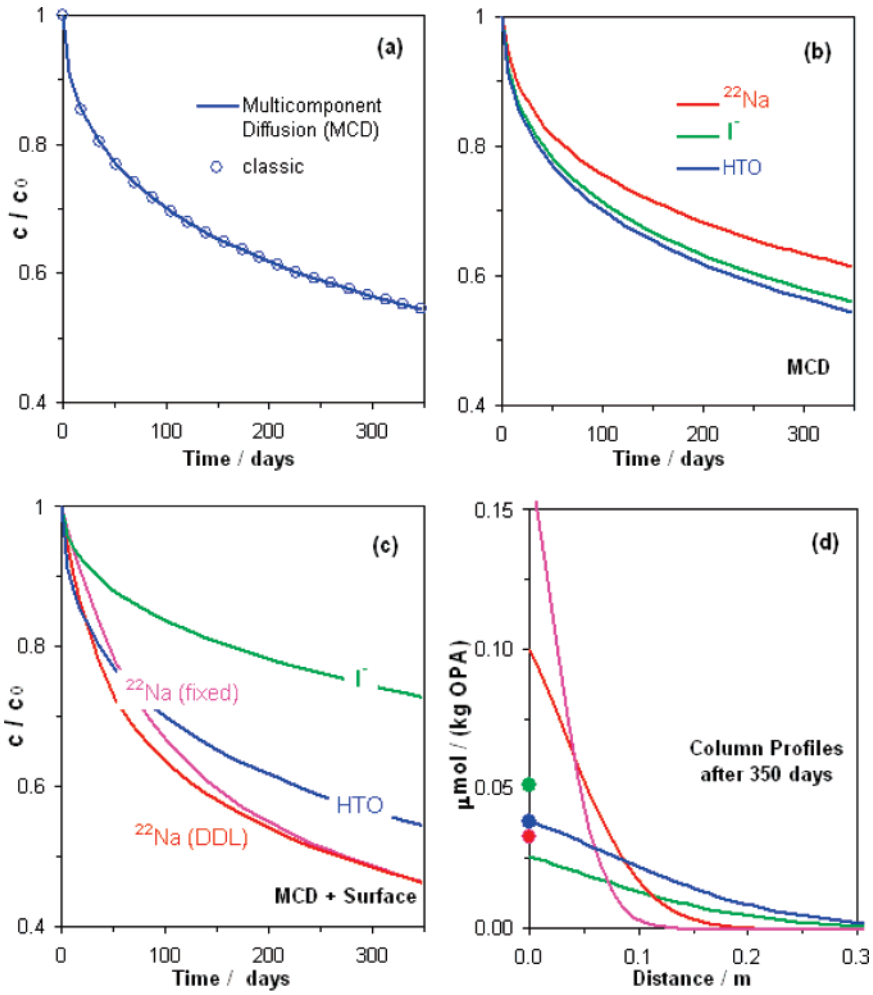

FIGURE 3. Model concentrations in the borehole fluid in contact with Opalinus Clay. (a) Comparing multicomponent diffusion (MCD) with identical tracer diffusion coefficients for all species, and "classical" PHREEQC. (b) MCD with different tracer diffusion coefficients for solute species. (c) and (d) MCD and a charged surface with a diffuse double layer (DDL) that excludes anions. In two models, $^{22}Na^+$ is assigned either to fixed surface sites (pink lines) or to the DDL (red lines). The latter option enhances transport in the clay. The concentrations in the column profiles (d) are given in μmol/kg Opalinus Clay; color coding follows (b), the circles indicate the concentrations in the borehole.

diffusivity with fixed sites increases more than with a DDL and to achieve equal concentration in the outer solution after 350 days (and thus an equal starting point for rock profiles discussed below), the tortuosity factor for the case with fixed sites was increased by 1.4.

The 2 lines for $^{22}Na^+$ have different curvatures. If excess $^{22}Na^+$ is mobile in the DDL, the concentration decreases initially quicker in the outer solution However, as the concentration builds up in the rock, the diffusivity diminishes. The different curvature indicates that it is possible to optimize the distribution of $^{22}Na^+$ over fixed sites and the DDL, together with the tortuosity factor.

Figure 3d shows the concentration profiles in the column after 350 days for Figure 3c, using the same color coding for the tracers. The concentrations in the borehole and porewater are expressed as μmol/kg by multiplying with the porosity/bulk-density factor ($\epsilon_w = 0.16$)/($\rho_b = 2.27$ kg/L). Tritium displays a regular diffusion profile with a smooth transition from the borehole (blue circle at $x = 0$) to the formation (blue line). Iodide shows the effect of anion exclusion in the downward concentration jump at the borehole perimeter. Since only half of the porespace contains I^-, the concentration in the rock (green line) appears to be halved compared to that in the borehole (green circle). On the other hand, the concentration of $^{22}Na^+$ jumps upward in the rock by sorption. As expected, the travel distance in the rock is larger for $^{22}Na^+$ when it resides in the DDL (red line), than on fixed sites (pink line). Thus, rock concentrations also enable finding the distribution over the fixed sites and the DDL, and were included in the optimizations of the real experiment.

Modeling the *in-Situ* Experiment. The physical situation of the actual experiment at Mont Terri (*8*, *9*) is more complicated than the previous (linear) column example. The borehole used for introducing the tracers intersects the bedding planes of the Opalinus Clay at an angle of 58°, which yields an elliptical perimeter for the contact surface. Since the diffusivity along the bedding plane is 5 times higher than perpendicular to it (*7*), a 3D elliptical grid was constructed that follows the outline of the main diffusion field (*10*). The porewater diffusion coefficient of tritium was optimized with PEST (*40*), and then multicomponent diffusion was introduced in the model as outlined before, with half of the porewater residing in the DDL, and balancing the surface charge over the DDL and the fixed sites by optimizing the value of K_{SuNa} (eq 15) and the tortuosity factor for $^{22}Na^+$.

Results are shown in Figure 4. The tritium data are fitted very well when a small, 2 cm zone around the borehole was given a 2.5 times higher diffusion coefficient than the rest of the formation. The tortuosity factor for tritium in the formation is 7.6 ($=\epsilon_w^{-1.11}$), which is somewhat higher than found in models that assumed a homogeneous formation right from the contact with the borehole (*8*, *9*, Table 1). The

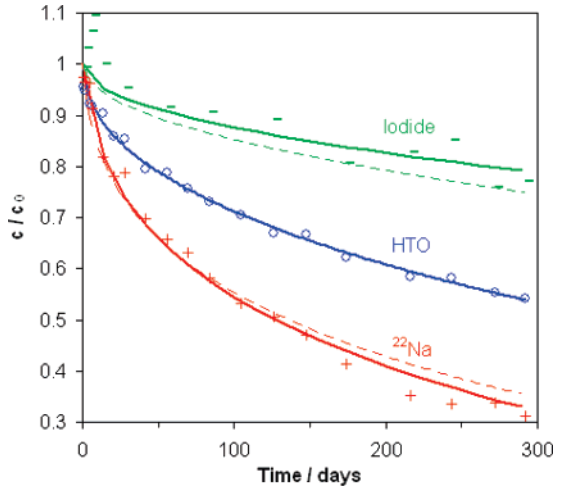

FIGURE 4. Observed iodide, tritium, and sodium in the borehole fluid during an *in-situ* diffusion experiment in Opalinus Clay (symbols) and model calculated concentrations (lines). The dotted line for iodide is obtained with the tortuosity of tritium; the solid line results when the tortuosity is increased by 1.2. The dotted line for ^{22}Na is obtained with the exchange sites distributed homogeneously; the solid line is for a patch-wise distribution of exchange sites (discussed in the text). In both cases, the tortuosity factor is about 1.6 times smaller than that of tritium.

dotted green line for I^- is obtained with the tortuosity factor of tritium, and is consistently below the data. The fit improves if the tortuosity factor is increased by 1.4 (solid green line). The dotted red line for $^{22}Na^+$ is obtained with 52% of the surface charge assigned to the DDL ($K_{SuNa} = 0.19$), and a tortuosity factor that is 1.6 times smaller than for tritium. However, the fitted line lies above the datapoints in the last 150 days, and the fit improves if the cation exchange capacity is distributed patchwise (solid red line), as discussed in the following.

Discussion

Figure 5 gives a conceptual presentation of the Opalinus Clay at 2 microscopic scales. The nm-scale picture presents the water types in the clay mineral packages as either bound in the interlayer space of the illite/smectite intercalation, or as mobile between the packages. The interlayer water contains hydrated cations that compensate the structural charge of the smectite component and is devoid of anions. The mobile water type is subdivided in "not-bound" in the center of the pore and in "weakly bound" or "externally bound" near the mineral surface, which correspond to the model elements "free porewater" and "diffuse double layer water" in this paper. The nm-scale picture also illustrates how the pore may become filled entirely with a diffuse double layer when it narrows sufficiently. This constricts the passage of anions, and since the anions must circumnavigate the obstacle, they have greater tortuosity than tritium. This explains that a model with a tortuosity factor for iodide that is 1.4 times higher than for tritium better matches the data.

Both the interlayer and the diffuse double layer have higher cation/water ratios than free porewater. Thus, in interlayers and pore constrictions the cations pass in relatively larger amounts than in free porewater, and consequently, they have smaller tortuosity than tritium. On the other hand, exchange is partitioned over the diffuse double layer and exchange sites close to the surface where mobility is probably much less than in free porewater or in the DDL. The exchange sites can be visualized as bordering the "bound" interlayer water shown in Figure 5. In addition, the mm-scale picture of the Opalinus Clay in Figure 5 shows a heterogeneous texture with sandy–silty intercalations, and abundant secondary precipitates and concretions. The sandy lenses have a smaller exchange capacity than the clay minerals that form the bulk of the formation, implying that the retardation of $^{22}Na^+$ varies in space.

Model runs provided an optimum for $^{22}Na^+$ when (a) 85% of the exchange capacity of 1.6 eq/L was assigned to fixed sites and the remaining 15% was assigned to the diffuse double layer, (b) the heterogeneous texture was introduced in the model giving each uneven numbered cell 97.5% of the average exchange capacity of the formation, and each even numbered cell the remaining 2.5%, and (c) the tortuosity factor of $^{22}Na^+$ was reduced 1.6 times relative to tritium. The variables are highly correlated and the numbers are subject to large uncertainty ranges. However, the model is physically attractive and corresponds very well with the sodium data (solid red line in Figure 4).

Thus, the heterogeneous distribution of clay minerals in natural clays creates a spatially variable diffuse double layer

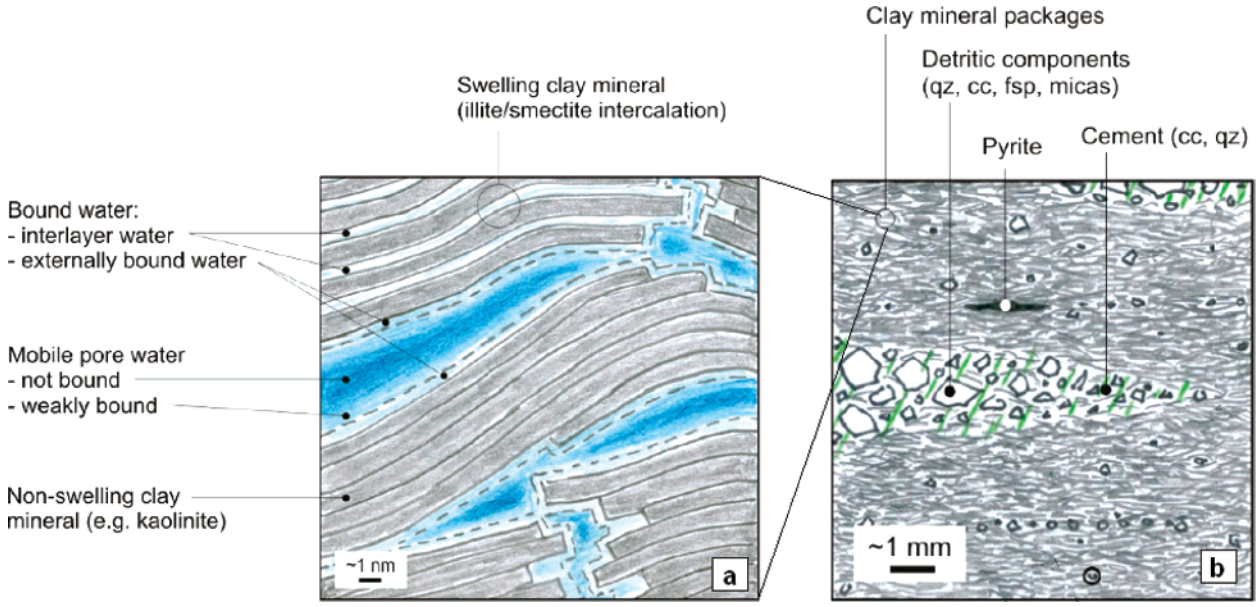

FIGURE 5. Texture of the Opalinus Clay, illustrating (a) the water properties in the clay mineral packages on the nm scale, and (b) the geochemical heterogeneity on the mm scale (*43*).

that blocks transport of the anions in pore constrictions where cations and tritium can continue to diffuse. Therefore, the tortuosity in a clay formation is larger for anions than for tritium. High tortuosities for anions have been reported often in clays and bentonites (*12*, *15*, *25*, *41*), although it is a property that can only be obtained correctly if also the exclusion volume is determined (*7, 15, 24*, example for I^- in the Supporting Information). Furthermore, when interconnecting pores are filled by a diffuse double layer and contain relatively more cations than the free pore solution, the diffusivity of the cations will be higher than that of water. Hence, cations will have smaller tortuosity than tritium. Properties of the porous medium are averaged in the tortuosity, but the physical background of this parameter implies that variations for different solutes will vanish if the model would be discretized to the nm-scale shown in Figure 5a.

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Supporting Information Available

New input options for MCD in PHREEQC are described. Input files are given for calculating Figures 3 and 4.

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Multicomponent diffusion modeling in clay systems with application to the diffusion of tritium, iodide and sodium in Opalinus Clay

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Contents:

(27 pages, 5 figures, 1 table)

Implementation

The multicomponent diffusion equation,

$$J_i = - D_{w,i}\left(\frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)}+1\right)\frac{\partial c_i}{\partial x} + D_{w,i} z_i c_i \frac{\sum_{j=1}^{n} D_{w,j} z_j \left(\frac{\partial \ln(\gamma_j)}{\partial \ln(c_j)}+1\right)\frac{\partial c_j}{\partial x}}{\sum_{j=1}^{n} D_{w,j} z_j^2 c_j} \quad (12)$$

was programmed in PHREEQC, calculating the fluxes for all the species individually both in the free pore and the DDL, and then summing up for the interface between two model cells. The diffusion coefficients are the tracer diffusion coefficients in water for individual species (D_w in m^2/s), corrected for temperature and viscosity (Atkins and dePaula, 2002), and recalculated to porewater diffusion coefficients (D_p) with the formula:

$$D_p = D_w \varepsilon_w^{\,n} \quad (S1)$$

where ε_w is the water filled porosity (-), and n is an empirical exponent ($\approx 0.9 - 1.2$, Grathwohl, 1998; Appelo and Postma, 2005). The fluxes found with Equation (12) are 1) multiplied with the interfacial surface $\varepsilon_w A$ (m^2) of 2 cells, taking the smallest ε_w in case the values are different for the 2 cells, 2) multiplied with the maximal permitted timestep for the solute with the highest diffusion coefficient (usually H^+), and 3) divided by the volume of the cell to obtain the concentration changes (mol/L) of all the individual solute species (ions, complexes) due to diffusion over the interface. The concentration changes of solute species are summed up as concentration changes of master species (components), which are speciated again by PHREEQC after each diffusive timestep.

New input options and structure of input files

The tracer diffusion coefficient in water at 25°C can be defined with identifier '-dw' under keyword SOLUTION_SPECIES:

```
SOLUTION_SPECIES
H+ = H+
      log_k 0.0; -gamma 9.0 0.0
      -dw   9.31e-9                      # tracer diffusion coefficient in water, 25oC, m2/s
```

A database (phreeqd.dat) with diffusion coefficients for individual solutes was constructed (Robinson and Stokes, 1959; Pikal, 1971; Jähne et al., 1987; Lasaga, 1998).

A new identifier '-multi_d' was added to keyword TRANSPORT:

```
TRANSPORT
 -multi_d true 1e-9 0.3 0.0 1.0          # [true/false] [default_Dw in m2/s] [porosity] [porosity
                                           limit] [n]
```

The [default_Dw] is the default tracer diffusion coefficient for species for which '-dw' has not been defined. The [porosity] is used, initially uniformly for all the cells in the model, to calculate the porewater diffusion coefficient and the effective surface area for diffusion (the porosity can be changed in a USER_ keyword, see below). If the porosity, by precipitation of solids or other reactions, falls below [porosity limit], diffusion stops for that cell. The exponent [n] is used for calculating the pore water diffusion coefficient according to Equation (S1). In the example, the porewater diffusion coefficient becomes $D_p = 0.3 \times 10^{-9} = 0.3 \times 10^{-9}$ m^2/s.

For mobile cells, PHREEQC can be run as usual, setting '-multi_d' true. For immobile cells, mixing factors among cells must be defined using keyword MIX, according to Equation (128) in the PHREEQC-2 manual:

$$mixf_{ij} = \frac{D_p \Delta t \, \varepsilon_w A_{ij}}{h_{ij} V_i} f_{bc} \qquad \text{(S2)}$$

where Δt is the timestep (s), A_{ij} is the shared surface area among cells i and j (m^2), h_{ij} is the distance between midpoints of the cells (m), V_i is the water volume in cell i for which the concentration change is calculated (m^3), and f_{bc} is a correction factor that equals 2 for constant concentration boundary cells and is 1 otherwise.

One and the same volume V_i = 0.001 m^3 must be used in Equation (S2) for all the immobile cells, but the amount of water in the SOLUTION's may be adapted to mimic volume variations among the cells. The pore water diffusion coefficient D_p in Equation (S2) must be tractable for PHREEQC from Equation (S1), $D_p = D_w \, \varepsilon_w^n$, and the porosity ε_w, the exponent n and the tracer diffusion coefficient D_w (used for calculating mixing factors) must be entered after identifier '–multi_d' in the input file. PHREEQC compares $D_{w,i}$ of solute species i with the default value and increases or decreases the mixing factor accordingly (while taking care that, overall, the zero charge flux is maintained). An interface should be defined only once since the concentration changes are calculated for both the cells on the interface (this contrasts with the default option, where mixing factors must be defined separately for each cell). If PHREEQC warns that negative concentrations are encountered in MCD, the timestep used for calculating the mixing factor must be decreased (and the number of shifts must be increased in proportion).

The following example input file calculates about 30 years diffusion of a NaCl solution, comparing multicomponent diffusion with the standard 'mixrun' option, while both calculations employ the same effective diffusion coefficient. Note how SOLUTIONs and MIXs are defined differently with MCD and mixrun. The calculated results are the same, except for the effect of the activity correction on diffusion that is applied in MCD.

```
SOLUTION 0; Na 0.1; Cl 0.1 charge
SOLUTION 1-2; pH 7 charge             # mobile cells, 1 L
SOLUTION 4-6; pH 7 charge; water 0.5  # Immobile cells. Note that MCD adds moles, 'water'
SOLUTION 8; pH 7 charge; water 0.25   #   is adapted to match the cell-volume differences
END

# Define mixf for 1 L volumes, and only once for interfaces (1,4), (4,6), (4,8), (2,5)
MIX 1; 4 0.03                         # Note to take small fractions if
MIX 4; 6 0.03; 8 0.03                 #   Dw(H+) = 10 * default_Dw
MIX 2; 5 0.02
END
USER_GRAPH
 -headings cell Na Cl pH
 -axis_titles Cell mol/L pH
 -axis_scale x_axis 1 8 1 1
 -init false
 -start
 10 graph_x cell_no
 20 graph_y tot("Na"), tot("Cl")
 30 graph_sy -la("H+")
 -end
TRANSPORT
 -cells 2
 -shifts 100 0; -punch_fr 100; -punch_c 1 4 6 8; -bcon 1 1
 -time 1e7
 -multi_d true 1e-9 0.3 0.0 1.0       # [default_Dw] [porosity] [porosity_limit] [n]
 -stag 3
END

# compare with 'normal' mixrun
SOLUTION 0; Na 0.1; Cl 0.1 charge
SOLUTION 1-6; pH 7 charge             # All the cells have 1 kg water (1 L)
SOLUTION 8; pH 7 charge
END

# define mixf's for each cell
```

```
MIX 1; 1 0.97; 4 0.03
MIX 4; 1 0.06; 6 0.06; 8 0.06; 4 0.82 # Note that cells 4 and 6 have half the volume of
MIX 6; 4 0.06; 6 0.94                 #   cell 1. Hence mixf is doubled, relative to cell 1
MIX 8; 4 0.12; 8 0.88                 #   Cell 8 has 1/4 of the volume of cell 1
MIX 2; 5 0.02; 2 0.98
MIX 5; 2 0.04; 5 0.96
END
TRANSPORT                              # other param's from previous simulation
 -diffc 0.3e-9
 -multi_d false
END
```

Two new special BASIC functions were added:

```
get_por(cell_no)              # returns the porosity in cell 'cell_no'
change_por(new_por, cell_no)  # modifies the porosity of cell_no to 'new_por'
```

Keyword SURFACE was extended with an identifier for Donnan calculations:

```
SURFACE 1-10
 -donnan 1e-8 viscosity 1             # [thickness (m) / debye_lengths (1/k)] [relative viscosity -]
```

or

```
-donnan debye_lengths 1.5 limit_DDL 0.45 viscosity 1       # [thickness (m) / debye_lengths (1/k)]
                                                             [limit DDL to fraction of bulk]
                                                             [relative viscosity -]
```

Option '-only_counter_ions' can be used with '-donnan'. However, when used in conjunction with the Donnan option, all the co-ions (with the same sign of charge as the surface) will be excluded from the DDL, and they will be given a concentration of (near) zero in the DDL ($c_{i,\,\mathrm{DDL}} = 0$). This contrasts with the combination of option '-diffuse_layer' and '-only_counter_ions', in which the co-ions are assigned the concentrations of the free solution ($c_{i,\,\mathrm{DDL}} = c_i$).

The thickness of the diffuse double layer (DDL) can be fixed (first example line) or vary with ionic strength in number of debye lengths (κ^{-1}) (second example line). The Debye length is defined as:

$$\kappa^{-1} = \sqrt{\frac{(\varepsilon_0 \varepsilon_w) R T}{2 F^2 I}} \qquad \text{(S3)}$$

where ($\varepsilon_0\varepsilon_w$) is the dielectric constant of water, and I is the ionic strength. The number (d) of Debye lengths can be defined in the input file, and PHREEQC calculates the thickness $r_d = d\,\kappa^{-1}$ as a function of the ionic strength. The maximal amount of DDL water can be fixed to a fraction of total water by 'limit_DDL' (default limit_DDL = 0.8). The viscosity of the DDL can be set relative to the viscosity of water ($\eta_{\,\mathrm{DDL}} / \eta_{\,\mathrm{H_2O}}$).

With the variable thickness option, a pore radius is calculated from the amount of water in the solution with which the initial surface is equilibrated (initial_surface) or from the total amount of water (the total of free solution and DDL water). In the first case, r is solved from the equation:

$$V_{aq} = \pi\,(r - r_d)^2\;\;(L \times \theta) \qquad \text{(S4)}$$

where V_{aq} is the volume of the solution (assuming 1 kg equals 1 dm^3), L is the cell-length (m) and θ is the tortuosity (-). The product of the latter 2 is implicitly available in the surface area A_s that is defined with each SURFACE in the input file, or:

$$A_s = 2\pi r\,(L \times \theta) \qquad \text{(S5)}$$

The volume water associated with the surface is now given by:

$$V_{surf} = \frac{r^2 - (r - r_d)^2}{(r - r_d)^2} V_{aq} \qquad \text{(S6)}$$

and the total volume of water is $V_{tot} = V_{aq} + V_{surf}$.

In the second case, r is solved simply from

$$V_{tot} = \pi r^2 \ (L \times \theta) \qquad \text{(S7)}$$

or

$$r = 2 V_{tot} / A_s \qquad \text{(S8)}$$

If, in any of the above cases, V_{surf} > limit_DDL × V_{tot}, then r_d is adapted to give V_{surf} = limit_DDL × V_{tot}.

It should be noted that PHREEQC's surface complexation model employs a potential term for a planar surface. Thus, the pore sizes written in the output file are only approximations.

Test examples

The zero charge flux condition regulates the diffusion of charged ions in the sense that faster ions are retarded and slower ions accelerated. Equation (12) can be shown to provide the Nernst equation for the overall diffusion coefficient of a single-salt solution (Cussler, 1979; Malusis and Shackelford, 2002):

$$D_{salt} = \frac{(z_+ - z_-) D_+ D_-}{z_+ D_+ - z_- D_-} \qquad \text{(S9)}$$

For example, an overall D_{NaCl} = 10^{-9} m^2/s is obtained for NaCl when D_{Cl} = 10^{-8} m^2/s, and D_{Na} = 5.26×10^{-10} m^2/s (these are example numbers, different from the actual values). The same overall

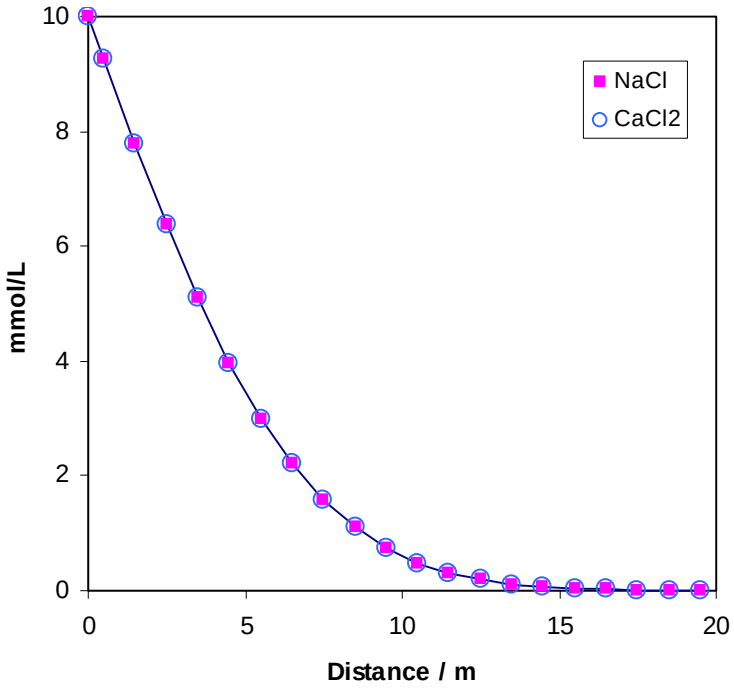

Figure S1. Cl^- concentration calculated for $D_{Na} = D_{Cl} = 10^{-9}$ m^2/s (line), and with different diffusion coefficients for Na^+, Ca^{2+} and Cl^-, adjusted to give the same overall D_{salt} = 10^{-9} m^2/s.

D_{salt} is obtained for $CaCl_2$ with the same D_{Cl}, when $D_{Ca} = 3.57 \times 10^{-10}$ m^2/s. Figure S1 compares the results for Cl^- when the ions have the same or different diffusion coefficients, and shows excellent agreement (the activity coefficients for the ions were made identical).

The results of the Donnan approximation and the complete integration of DDL concentrations are compared in Figure S2. Sodium from a 100 mM NaCl solution is replaced by equivalent proportions of Ca^{2+} and Al^{3+}. In each reaction step, the DDL composition of a small surface charge of 10 meq is calculated. The equivalent masses of the cations in the DDL are almost the same with the 2 calculation methods.

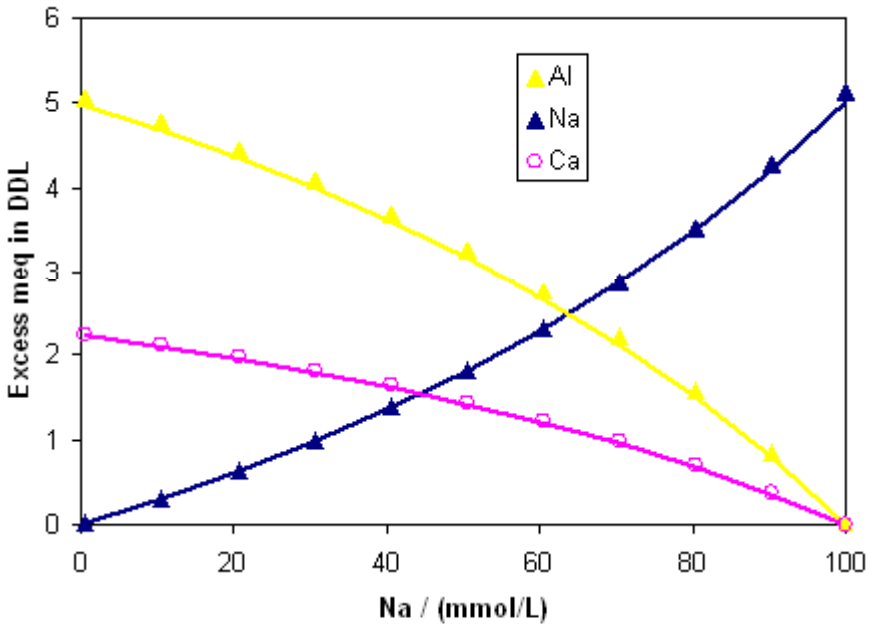

Figure S2. Excess cations in the DDL according to the PHREEQC integration (lines) and the Donnan approximation (symbols). Na^+ in a 100 mM NaCl solution (starting composition on the right side of the graph) is stepwise replaced by equivalent amounts of Ca^{2+} and Al^{3+} and the excess in the DDL is calculated in each step (the remaining surface charge of 10 meq is balanced by Cl^- deficit).

The accessible porosity of Iodide in Opalinus Clay

Figure S3 shows I^- in 3 rock profiles parallel to the bedding in the in-situ experiment, the extrapolated value at $x = 0$ cm (34 mg/kg), and the concentration in the borehole (outer solution) when the profiles were cored (970 mg/L). In the figure, the outer solution is expressed in mg/kg OPA assuming that all of the total porosity contains I^-: (I^- = 970 mg/L × (ε_w = 0.16) / (ρ_b = 2.27 kg/L) =) 68 mg/kg. The data can be used to assess if sorption of I^- occurs, as found by Van Loon et al. (2003).

The accessible porosity for I^- is $\varepsilon_{a(I^-)} = (34 / 970 - K_d) \times (\rho_b = 2.27$ kg/L).

If $K_d = 0$, $\varepsilon_{a(I^-)} = 0.08$ (50% of the total porespace).

If $K_d = 0.014$ L/kg (which is the highest experimental value for OPA in Mont Terri, Van Loon et al., 2003), $\varepsilon_{a(I^-)} = 0.045$ (28% of the total porespace). It seems rather unlikely that the accessible porosity for I^- is even smaller than for Cl^- (which has similar profiles), which shows that sorption of Iodide is not an issue in this experiment.

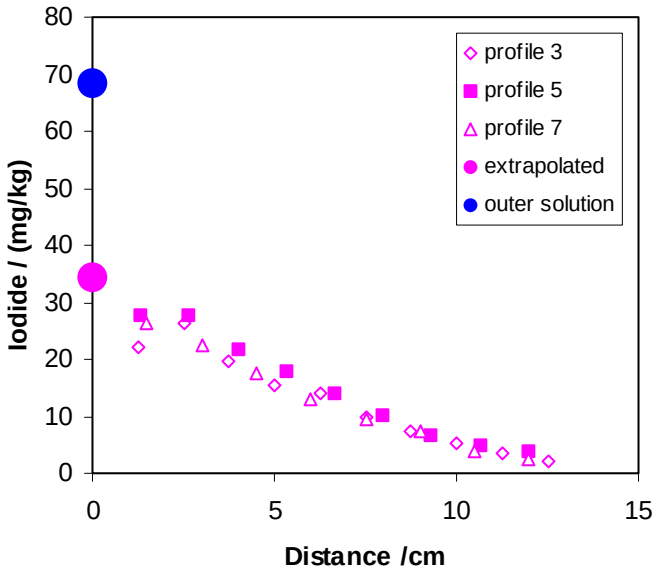

Figure S3. Observed Iodide in 3 rock profiles at the end of the DI A1 diffusion experiment, modeled in the paper. The concentrations in the rock are half of the concentrations in the outer solution in the borehole, which implies that $\varepsilon_{a(I^-)} = 0.5\ \varepsilon_w$.

PHREEQC input files for Figures 3a-d and Figure 4

The basic data for calculating the mixing factors with Equation (S2) for Figures 3a-d are listed in Table S1.

Table S1. Physical dimensions of the model of the column experiment with Opalinus Clay. V_{H_2O} is the volume of water in a cell, V_0 is the volume of the external solution with tracers that contacts the clay, the other parameters are explained with Equation (S2).

length / m	A_{ij} / m^2	D_w / (m^2/s)	ε	θ^2	Δt / s	h_{ij} / m	V_{H_2O} / L	V_0 / L
0.5	0.0314	2.24×10^{-9}	0.16	6.25	6×10^5	0.025	0.126	0.8

Input files are given in the appendix. If these are run with Vincent Post's PHREEQC for windows (download via links in www.xs4all.nl/~appt) the Figures 3a-d appear directly on screen.

It is of interest to run file Fig3b.phrq with the tracer diffusion coefficient of HTO adapted to the value of $^{22}Na^+$ or I^-, and see that the results are the same, independent of the charge of the tracer, as discussed in the paper. However, that is not the case if the porewater composition is changed to a 1 mM NaCl solution! Running this modification requires 10 times smaller mixing factors, thus 10 times smaller Δt and 10 times more shifts. Now the diffusion of $^{22}Na^+$ is higher than of HTO with the same tracer diffusion coefficient. In this case, the diffusion of a cation at trace concentration is enhanced by electrostatic repulsion by the major cations.

The actual experiment at Mont Terri requires a 3D elliptical grid that follows the outline of the main diffusion field (Appelo, 2006). Again, diffusion is calculated with explicit finite differences, using mixing factors according to Equation (S2). A Pascal program was written that reads parameters from a file, and then prints the PHREEQC input file. By symmetry, only one quarter of the elliptical cylinder is modeled with the outline shown in Figures S4 and S5.

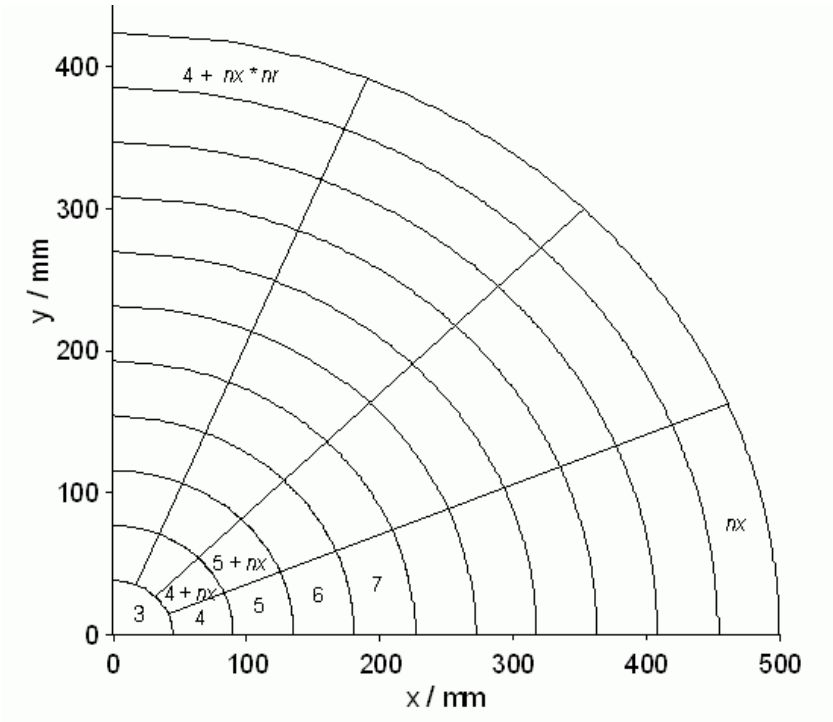

Figure S4. Example of the *x*-*y* outline of the elliptical grid for modeling diffusion in the Opalinus Clay with *nx* = 10 and *nr* = 4. The numbering of the cells is indicated, with cell 3 representing the borehole. For model checking, *nx* and *nr* were varied.

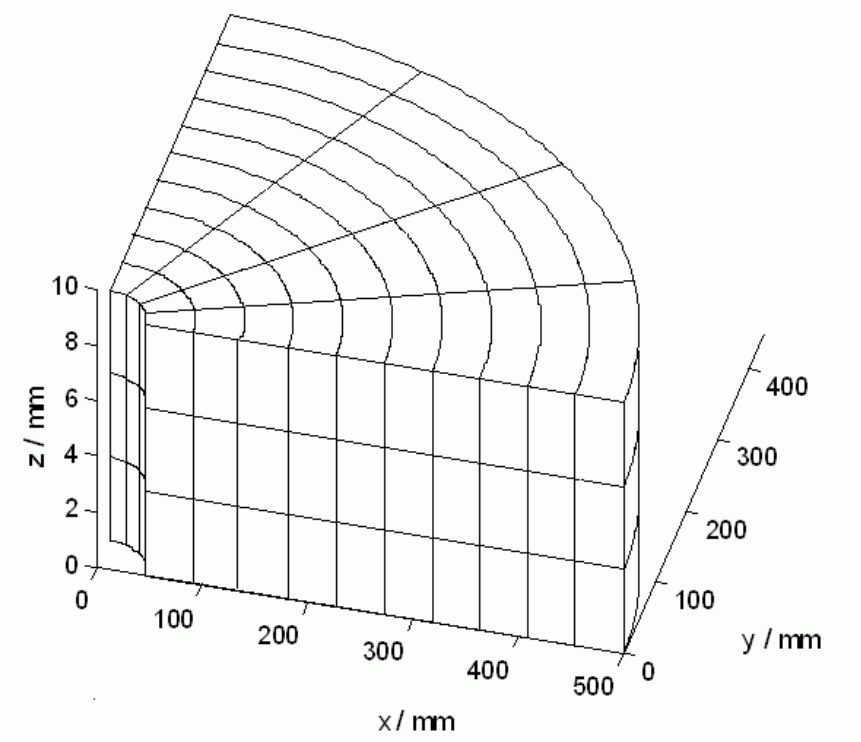

Figure S5. 3D view of an example grid, with *nx* = 10, *nr* = 4 and *nz* = 3. For model checking, *nx, nr* and *nz* were varied.

For the listed file, the model extends 0.44 m into the clay in the *x*-direction. The discretization can be adapted. The file is made with 3 sectors in the ellipse, each with 40 cells, and 1 layer in the *z*-direction, thus 120 cells in total. SOLUTION 3 is the borehole solution, SOLUTION 4-123 and SURFACE 4-123 are for the clay. The discretization along the outline of the grid is, in the *x*-direction 11 mm, in the *y*-direction 9.33 mm, and in the *z*-direction 9 mm. The cells have different water volumes, of which half is assigned to free porewater with identifier '–water' in keyword SOLUTION, and the other half by setting the surface area in keyword SURFACE with the thickness of the DDL with identifier '-donnan'. A scaling factor is applied to obtain water volumes that fall in a range (0.01 – 100 L) which facilitates convergence of the calculations. The surface charge is set homogeneously to 1.6 eq/L in the file, but it can be distributed heterogeneously over the cells to mimick the heterogeneities in the Opalinus Clay and improve the data-fit as is shown in the paper.

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Appendix

File for calculating Figure S1

```
SOLUTION_SPECIES
 Na+ = Na+;   log_k 0; -gamma 1e20 0;  -dw 5.2631578948e-10
 Ca+2 = Ca+2; log_k 0; -gamma 1e20 0;  -dw 3.5714285714e-10
 Cl- = Cl-;   log_k 0; -gamma 1e20 0;  -dw 1e-8
SOLUTION 0
 Ca 10  charge # or Na
 Cl 10
SOLUTION 1-20
 pH 7 charge
END
PRINT; -reset false
TRANSPORT
 -cells 20
 -shifts 15 0
```

```
 -bcon 1 1
 -punch_fr 15
 -time 3.15e9
 -multi_d true 1e-9 0.3 0.0 1.0       # [true/false] [default D_w] [porosity] [porosity limit] [n]
USER_GRAPH
 -head x Na/Ca Cl
 -start
 1 if step_no < 1 then goto 20
 10 graph_x dist
 12 if tot("Na") > 1e-90 then graph_y tot("Na")*1e3 else graph_y tot("Ca")*1e3
 14 graph_y tot("Cl")*1e3
 20 end
 -end
END
SOLUTION 0                             # compare with standard PHREEQC…
 Ca 10  charge # or Na
 Cl 10
SOLUTION 1-20
TRANSPORT
 -multi_d false
 -diffc 0.3e-9
END
```

File for calculating Figure S2

```
SOLUTION_SPECIES  # make Al+3 the only important Al species
Al+3 + H2O = AlOH+2 + H+; log_k -50.0
Al+3 + 2 H2O = Al(OH)2+ + 2 H+; log_k -100.1
Al+3 + 3 H2O = Al(OH)3 + 3 H+; log_k -160.9
Al+3 + 4 H2O = Al(OH)4- + 4 H+; log_k -220.7

SURFACE_MASTER_SPECIES
 Su Su-
SURFACE_SPECIES
 Su- = Su-; log_k 0
SOLUTION 1-2
 pH 6.0
 Na 1e2
 Cl 1 charge
SURFACE 1
 Su 1e-2 1e6 1
 -equil 1
 -donnan 1e-9
USER_GRAPH
 -head c_Na Na_Donnan Ca_Donnan Al_Donnan
 -axis_t "Na / (mmol/L)" "Excess meq in DDL"
 -axis_scale x_axis 0 100
 -axis_scale y_axis 0 6 1
 -start
 10 dl_Ca = (edl("Ca", "Su") - tot("Ca") * edl("water", "Su")) * 2
 12 dl_Al = (edl("Al", "Su") - tot("Al") * edl("water", "Su")) * 3
 20 dl_Na = (edl("Na", "Su") - tot("Na") * edl("water", "Su"))
 30 if (dl_Ca = 0 or tot("Na") = 0) then goto 60

 40 if cell_no = 1 then print 'Donnan' else print 'integration'
 42 print '. CB =', dl_Ca + dl_Na + dl_Al + tot("Cl") * edl("water") - edl("Cl", "Su") - mol("Su-")\
 * tot("water")

 50 graph_x tot("Na") * 1e3
 52 graph_y dl_Na*1e3, dl_Ca*1e3, dl_Al*1e3

 60 end
 -end
REACTION 1-2
 Na -10 Ca 2 Al 2
 1e-8 10*0.0020411
INCREMENTAL_REACTIONS
END

USER_GRAPH
 -head c_Na Na_Integrated Ca_Integrated Al_Integrated
SURFACE 2
 Su 1e-2 1e6 1
 -equil 2
```

```
 -diff 1e-9
USE solution 2
USE reaction 2
END
```

File for calculating Figure 3a

General for the files for Figure 3, SOLUTION 3 is for the outer solution, SOLUTION 4-23 are for 20 cells in the column.

```
SOLUTION_MASTER_SPECIES # define the tracers...
 Hto Hto 0 Hto 20
 Nat Nat+ 0 Nat 22
 I I- 0 I 126.9
SOLUTION_SPECIES
 Hto = Hto;    log_k 0; -gamma 1e10 0;# Dw 2.24e-9
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0;# Dw 1.33e-9
 I- = I-;   log_k 0; -gamma 1e10 0;# Dw 2.0e-9
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-23 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.125663706
END
PRINT; -reset false
# mixing factors for MCD
# interfaces need be defined only once...
MIX   3     ;  4       7.20606E-02
MIX   4     ;  5       3.60303E-02
MIX   5     ;  6       3.60303E-02
MIX   6     ;  7       3.60303E-02
MIX   7     ;  8       3.60303E-02
MIX   8     ;  9       3.60303E-02
MIX   9     ;  10      3.60303E-02
MIX   10    ;  11      3.60303E-02
MIX   11    ;  12      3.60303E-02
MIX   12    ;  13      3.60303E-02
MIX   13    ;  14      3.60303E-02
MIX   14    ;  15      3.60303E-02
MIX   15    ;  16      3.60303E-02
MIX   16    ;  17      3.60303E-02
MIX   17    ;  18      3.60303E-02
MIX   18    ;  19      3.60303E-02
MIX   19    ;  20      3.60303E-02
MIX   20    ;  21      3.60303E-02
MIX   21    ;  22      3.60303E-02
MIX   22    ;  23      3.60303E-02
END
USER_GRAPH
 -chart_title "Comparing MCD and Classic PHREEQC"
 -axis_t "Time / days" "c / c0"
 -axis_scale x_axis 0 350 50
 -axis_scale y_axis 0.4 1.0 0.1
 -head time/days HTO_mcd I_mcd 22Na_mcd
 -plot_c time
 -init false
 -start
 10 graph_x total_time / (3600 * 24)
 20 graph_y tot("Hto")*1e6, tot("I")*1e6, tot("Nat")*1e6
 -end
TRANSPORT
 -cells 1
 -bcon 1 2
 -shifts 60 0
 -punch_fr 1
 -punch_c 3
 -time 5e5
```

```
 -multi_d true 2.24e-9 0.16 0.0 1.0
 -stag 21
END

# Compare with classic PHREEQC...
USER_GRAPH
 -head time/days Reinitialize all solutions
SOLUTION 0-3
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water      1 # NOTE: define 1 L water in classic PHREEQC
SOLUTION 4-23
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      1
END
# Mixing factors for classic, repeat all interfaces for each cell...
MIX   3     ;  4       9.0076E-02     ;       3       9.0992E-01
MIX   4     ;  5       2.8672E-01     ;       3       5.7344E-01     ;       4       1.3984E-01
MIX   5     ;  6       2.8672E-01     ;       4       2.8672E-01     ;       5       4.2656E-01
MIX   6     ;  7       2.8672E-01     ;       5       2.8672E-01     ;       6       4.2656E-01
MIX   7     ;  8       2.8672E-01     ;       6       2.8672E-01     ;       7       4.2656E-01
MIX   8     ;  9       2.8672E-01     ;       7       2.8672E-01     ;       8       4.2656E-01
MIX   9     ;  10      2.8672E-01     ;       8       2.8672E-01     ;       9       4.2656E-01
MIX   10    ;  11      2.8672E-01     ;       9       2.8672E-01     ;       10      4.2656E-01
MIX   11    ;  12      2.8672E-01     ;       10      2.8672E-01     ;       11      4.2656E-01
MIX   12    ;  13      2.8672E-01     ;       11      2.8672E-01     ;       12      4.2656E-01
MIX   13    ;  14      2.8672E-01     ;       12      2.8672E-01     ;       13      4.2656E-01
MIX   14    ;  15      2.8672E-01     ;       13      2.8672E-01     ;       14      4.2656E-01
MIX   15    ;  16      2.8672E-01     ;       14      2.8672E-01     ;       15      4.2656E-01
MIX   16    ;  17      2.8672E-01     ;       15      2.8672E-01     ;       16      4.2656E-01
MIX   17    ;  18      2.8672E-01     ;       16      2.8672E-01     ;       17      4.2656E-01
MIX   18    ;  19      2.8672E-01     ;       17      2.8672E-01     ;       18      4.2656E-01
MIX   19    ;  20      2.8672E-01     ;       18      2.8672E-01     ;       19      4.2656E-01
MIX   20    ;  21      2.8672E-01     ;       19      2.8672E-01     ;       20      4.2656E-01
MIX   21    ;  22      2.8672E-01     ;       20      2.8672E-01     ;       21      4.2656E-01
MIX   22    ;  23      2.8672E-01     ;       21      2.8672E-01     ;       22      4.2656E-01
MIX   23    ;  0       0.0000E+00     ;       22      2.8672E-01     ;       23      7.1328E-01
END
USER_GRAPH
 -head time/days HTO_classic I_classic 22Na_classic
TRANSPORT
 -initial_time 0
 -multi_d false
END
```

File for calculating Figure 3b

```
DATABASE phreeqd.dat
SOLUTION_MASTER_SPECIES # define the tracers...
 Hto Hto 0 Hto 20
 Nat Nat+ 0 Nat 22
 I I- 0 I 126.9
SOLUTION_SPECIES
 Hto = Hto;    log_k 0; -gamma 1e10 0; Dw 2.24e-9
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0; Dw 1.33e-9
 I- = I-;   log_k 0; -gamma 1e10 0; Dw 2.0e-9
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-23 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.125663706
END
PRINT; -reset false
# mixing factors for MCD
```

```
# interfaces need be defined only once...
MIX   3     ;  4       7.20606E-02
MIX   4     ;  5       3.60303E-02
MIX   5     ;  6       3.60303E-02
MIX   6     ;  7       3.60303E-02
MIX   7     ;  8       3.60303E-02
MIX   8     ;  9       3.60303E-02
MIX   9     ;  10      3.60303E-02
MIX   10    ;  11      3.60303E-02
MIX   11    ;  12      3.60303E-02
MIX   12    ;  13      3.60303E-02
MIX   13    ;  14      3.60303E-02
MIX   14    ;  15      3.60303E-02
MIX   15    ;  16      3.60303E-02
MIX   16    ;  17      3.60303E-02
MIX   17    ;  18      3.60303E-02
MIX   18    ;  19      3.60303E-02
MIX   19    ;  20      3.60303E-02
MIX   20    ;  21      3.60303E-02
MIX   21    ;  22      3.60303E-02
MIX   22    ;  23      3.60303E-02
END
USER_GRAPH
 -chart_title "MCD: using actual Dw's"
 -axis_t "Time / days" "c / c0"
 -axis_scale x_axis 0 350 50
 -axis_scale y_axis 0.4 1.0 0.1
 -head time/days HTO_mcd I_mcd 22Na_mcd
 -plot_c time
 -init false
 -start
 10 graph_x total_time / (3600 * 24)
 20 graph_y tot("Hto")*1e6, tot("I")*1e6, tot("Nat")*1e6
 -end
TRANSPORT
 -cells 1
 -bcon 1 2
 -shifts 60 0
 -punch_fr 1
 -punch_c 3
 -time 5e5
 -multi_d true 2.24e-9 0.16 0.0 1.0
 -stag 21
END
```

File for calculating Figure 3c

```
DATABASE phreeqd.dat
SOLUTION_MASTER_SPECIES # define the tracers...
 Hto Hto 0 Hto 20
 Nat Nat+ 0 Nat 22
 I I- 0 I 126.9
SOLUTION_SPECIES
 Hto = Hto;    log_k 0; -gamma 1e10 0; Dw 2.24e-9
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0; Dw 1.33e-9
 I- = I-;   log_k 0; -gamma 1e10 0; Dw 2.0e-9
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-23 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.062831853
END
SURFACE 4-43;  -equil 4;      Su     0.20106193     1.00E+05       1
 -donnan    6.28E-10
 -only_co
SURFACE_MASTER_SPECIES; Su Su-
SURFACE_SPECIES;       Su- = Su-;     log_k 0
END
```

```
PRINT; -reset false
# mixing factors for MCD
# interfaces need be defined only once...
MIX   3     ;  4       7.20606E-02
MIX   4     ;  5       3.60303E-02
MIX   5     ;  6       3.60303E-02
MIX   6     ;  7       3.60303E-02
MIX   7     ;  8       3.60303E-02
MIX   8     ;  9       3.60303E-02
MIX   9     ;  10      3.60303E-02
MIX   10    ;  11      3.60303E-02
MIX   11    ;  12      3.60303E-02
MIX   12    ;  13      3.60303E-02
MIX   13    ;  14      3.60303E-02
MIX   14    ;  15      3.60303E-02
MIX   15    ;  16      3.60303E-02
MIX   16    ;  17      3.60303E-02
MIX   17    ;  18      3.60303E-02
MIX   18    ;  19      3.60303E-02
MIX   19    ;  20      3.60303E-02
MIX   20    ;  21      3.60303E-02
MIX   21    ;  22      3.60303E-02
MIX   22    ;  23      3.60303E-02
END
USER_GRAPH
 -chart_title "MCD: different Dw's and Surface"
 -axis_t "Time / days" "c / c0"
 -axis_scale x_axis 0 350 50
 -axis_scale y_axis 0.4 1.0 0.1
 -head time/days HTO I 22Na_ddl
 -plot_c time
 -init false
 -start
 10 graph_x total_time / (3600 * 24)
 20 graph_y tot("Hto")*1e6, tot("I")*1e6, tot("Nat")*1e6
 -end
TRANSPORT
 -cells 1
 -bcon 1 2
 -shifts 60 0
 -punch_fr 1
 -punch_c 3
 -time 5e5
 -multi_d true 2.24e-9 0.16 0.0 1.0
 -stag 23
END

# Compare with exchange on fixed sites...
# Decrease Dp of Nat to get the same final conc...
SOLUTION_SPECIES
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0; Dw 0.8e-9 # 1.33e-9 * 0.6
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-23 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.062831853
END
SURFACE 4-43;  -equil 4;      Su      0.20106193     1.00E+05       1
 -donnan    6.28E-10
 -only_co
SURFACE_MASTER_SPECIES; Su Su-
SURFACE_SPECIES;       Su- = Su-;     log_k 0
Na+ + Su- = NaSu;      log_k                  5
Nat+ + Su- = NatSu;    log_k                  5
K+ + Su- = KSu;        log_k                  5.7
Ca+2 + 2Su- = CaSu2;   log_k                  10.8
Mg+2 + 2Su- = MgSu2;   log_k                  10.7
Sr+2 + 2Su- = SrSu2;   log_k                  10.91
END
USER_GRAPH
 -head time/days 22Na_fixed
```

```
 -start
 10 graph_x total_time / (3600 * 24)
 20 graph_y tot("Nat")*1e6
 -end
TRANSPORT
 -initial_time 0
END
```

File for calculating Figure 3d

```
DATABASE phreeqd.dat
SOLUTION_MASTER_SPECIES # define the tracers...
 Hto Hto 0 Hto 20
 Nat Nat+ 0 Nat 22
 I I- 0 I 126.9
SOLUTION_SPECIES
 Hto = Hto;    log_k 0; -gamma 1e10 0; Dw 2.24e-9
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0; Dw 1.33e-9
 I- = I-;   log_k 0; -gamma 1e10 0; Dw 2.0e-9
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-43 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.062831853
END
SURFACE 4-43;  -equil 4;      Su     0.20106193     1.00E+05       1
 -donnan    6.2832E-10
 -only_co
SURFACE_MASTER_SPECIES; Su Su-
SURFACE_SPECIES;       Su- = Su-;     log_k 0
END
PRINT; -reset false
# mixing factors for MCD
# interfaces need be defined only once...
MIX   3     ;  4       7.20606E-02
MIX   4     ;  5       3.60303E-02
MIX   5     ;  6       3.60303E-02
MIX   6     ;  7       3.60303E-02
MIX   7     ;  8       3.60303E-02
MIX   8     ;  9       3.60303E-02
MIX   9     ;  10      3.60303E-02
MIX   10    ;  11      3.60303E-02
MIX   11    ;  12      3.60303E-02
MIX   12    ;  13      3.60303E-02
MIX   13    ;  14      3.60303E-02
MIX   14    ;  15      3.60303E-02
MIX   15    ;  16      3.60303E-02
MIX   16    ;  17      3.60303E-02
MIX   17    ;  18      3.60303E-02
MIX   18    ;  19      3.60303E-02
MIX   19    ;  20      3.60303E-02
MIX   20    ;  21      3.60303E-02
MIX   21    ;  22      3.60303E-02
MIX   22    ;  23      3.60303E-02
END
USER_GRAPH
 -chart_title "MCD: column profiles"
 -axis_t "Distance / m" "umol / kg OPA"
 -axis_scale x_axis 0 0.5 0.1
 -axis_scale y_axis 0 0.15 0.05
 -head dist HTO I 22Na_ddl
 -plot_c x
 -init false
 -start
 10 if cell_no = 3 then graph_x 0 else graph_x (cell_no - 3.5) * 0.025
 20 if cell_no = 3 then ew = 0.8 else ew = tot("water") * 2
 30 c_f = 0.16 / (2.7 * 0.84) * 1e6 / ew # convert from mol/L to mol/kg
 40 graph_y sys("Hto")*c_f, sys("I")*c_f, sys("Nat")*c_f
```

```
 -end
TRANSPORT
 -cells 1
 -bcon 1 2
 -shifts 60 0
 -punch_fr 60
 -punch_c 3-23
 -time 5e5
 -multi_d true 2.24e-9 0.16 0.0 1.0
 -stag 21
END

# Compare with exchange on fixed sites...
# Decrease Dp of Nat to get the same final conc in the borehole...
SOLUTION_SPECIES
 Nat+ = Nat+;  log_k 0; -gamma 1e10 0; Dw 0.8e-9 # 1.33e-9 * 0.6
SOLUTION 0-3 # Outer solution with 1 uM tracers...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 Hto 1e-3;  Nat 1e-3;  I 1e-3
 water 0.8 # NOTE: define actual L water in MCD
SOLUTION 4-23 # Opalinus Clay porewater...
 pH 7.09
 Na 239;    K 1.54;    Mg 17.2;       Ca 25.9;       Sr 0.500
 Alkalinity 2.5; S(6) 12.6;   Cl 304 charge
 water      0.062831853
END
SURFACE 4-43;  -equil 4;      Su     0.20106193     1.00E+05       1
 -donnan    6.2832E-10
 -only_co
SURFACE_MASTER_SPECIES; Su Su-
SURFACE_SPECIES;       Su- = Su-;     log_k 0
Na+ + Su- = NaSu;      log_k                  5
Nat+ + Su- = NatSu;    log_k                  5
K+ + Su- = KSu;        log_k                  5.7
Ca+2 + 2Su- = CaSu2;   log_k                  10.8
Mg+2 + 2Su- = MgSu2;   log_k                  10.7
Sr+2 + 2Su- = SrSu2;   log_k                  10.91
END
PRINT; -reset false
USER_GRAPH
 -head time/days 22Na_fixed
 -init true
 -start
 2 if step_no = 0 then goto 50
 10 if cell_no = 3 then graph_x 0 else graph_x (cell_no - 3.5) * 0.025
 20 if cell_no = 3 then ew = 0.8 else ew = tot("water") * 2
 30 c_f = 0.16 / (2.7 * 0.84) * 1e6 / ew # convert from mol/L to mol/kg
 40 graph_y sys("Nat")*c_f
 50 end
 -end
TRANSPORT
 -initial_time 0
END
```

File for calculating Figure 4

Note how mixing factors for the interfaces among the cells are defined only once with option –multi_D. For example, cell 44, the cell in the 2nd sector that borders the borehole, is mixed with the borehole solution (defined in MIX 3), with cell 4 (MIX 4), and with cells 45 and 84 (MIX 44).
This file is used for optimizing parameters, and must be run with the UNIX or DOS version of PHREEQC. It writes in file Fig4.txt the concentrations of HTO, ^{22}Na and I^- in the borehole solution. Tritium and ^{22}Na are corrected for decay.

```
database phreeqd.dat
SOLUTION_MASTER_SPECIES
 Hto Hto 0 Hto 1
 Nat Nat+ 0 Nat 23
 I I- 0 I 126.9
SOLUTION_SPECIES
```

```
 Hto = Hto;      log_k 0;  Dw 2.24e-9; -gamma 1e10 0
 Nat+ = Nat+;    log_k 0;  Dw   2.11557527299990E-0009; #-gamma 1e10 0
 I- = I-;        log_k 0;  Dw   1.40000000000000E-0009; #-gamma 1e10 0
SURFACE_MASTER_SPECIES; Su Su-
SURFACE_SPECIES; Su- = Su-; log_k 0
Na+ + Su- = NaSu; log_k -7.24012489999950E-0001
Nat+ + Su- = NatSu; log_k -7.24012489999950E-0001
K+ + Su- = KSu; log_k -2.40124899999500E-0002
Ca+2 + 2Su- = CaSu2; log_k  7.59875100000500E-0002
Mg+2 + 2Su- = MgSu2; log_k -1.24012489999950E-0001
Sr+2 + 2Su- = SrSu2; log_k  1.85987510000050E-0001
SOLUTION 0-1500; END
RATES
 Tritium
 -start; 10 save -1.787E-09 * sys("Hto") * time; -end
 Na_22
 -start; 10 save -8.45367E-09 * sys("Nat") * time; -end
KINETICS 3-1500
 Tritium; -formula Hto
 Na_22; -formula Nat 1; #-cvode
END
END; MIX 1; 1 1
MIX 3; 4 6.58269485279561E-0002; 44 7.56074498598309E-0002; 84 8.69555246487153E-0002
SOLUTION 3
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
 Hto 1e-3;      Nat 1e-3;       I 1e-3
 water  2.52199999999925E+0001
MIX 4; 44 1.62551916725704E-0003; 5 4.09933263218250E-0002;
SURFACE 4; -equil 4; Su  5.66158505167550E-0001 4.71798754306316E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 4; -water  1.76924532864859E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 5; 45 1.33386908829323E-0003; 6 3.40498978166011E-0002;
SURFACE 5; -equil 5; Su  6.89948898019065E-0001 5.74957415016174E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 5; -water  2.15609030630958E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 6; 46 4.38492600049045E-0004; 7 2.21593315216921E-0002;
SURFACE 6; -equil 6; Su  8.13739290869853E-0001 6.78116075724602E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 6; -water  2.54293528396829E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 7; 47 3.80594518172117E-0004; 8 2.52920464079409E-0002;
SURFACE 7; -equil 7; Su  9.37529683721368E-0001 7.81274736433983E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 7; -water  2.92978026162928E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 8; 48 3.36202672592023E-0004; 9 2.84247593781686E-0002;
SURFACE 8; -equil 8; Su  1.06132007657288E+0000 8.84433397144318E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 8; -water  3.31662523929026E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 9; 49 3.01084734242707E-0004; 10 3.15574733064068E-0002;
SURFACE 9; -equil 9; Su  1.18511046942440E+0000 9.87592057853699E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 9; -water  3.70347021695125E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 10; 50 2.72609393389089E-0004; 11 3.46901885486659E-0002;
SURFACE 10; -equil 10; Su  1.30890086227446E+0000 1.09075071856117E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 10; -water  4.09031519461223E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 11; 51 2.49054818239358E-0004; 12 3.78229011628832E-0002;
SURFACE 11; -equil 11; Su  1.43269125512597E+0000 1.19390937927246E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 11; -water  4.47716017226412E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 12; 52 2.29246943506922E-0004; 13 4.09556150910930E-0002;
SURFACE 12; -equil 12; Su  1.55648164797749E+0000 1.29706803998184E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 12; -water  4.86400514992965E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 13; 53 2.12357673041197E-0004; 14 4.40883290193028E-0002;
SURFACE 13; -equil 13; Su  1.68027204083046E+0000 1.40022670069122E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 13; -water  5.25085012759519E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 14; 54 1.97786204187977E-0004; 15 4.72210465248963E-0002;
SURFACE 14; -equil 14; Su  1.80406243368052E+0000 1.50338536140060E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 14; -water  5.63769510525162E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 15; 55 1.85086055374128E-0004; 16 5.03537568757793E-0002;
SURFACE 15; -equil 15; Su  1.92785282653349E+0000 1.60654402211189E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 15; -water  6.02454008291716E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 16; 56 1.73918482001412E-0004; 17 5.34864708040459E-0002;
SURFACE 16; -equil 16; Su  2.05164321938355E+0000 1.70970268281937E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 16; -water  6.41138506057359E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 17; 57 1.64021855176522E-0004; 18 5.66191847323125E-0002;
SURFACE 17; -equil 17; Su  2.17543361223361E+0000 1.81286134352875E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 17; -water  6.79823003823003E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 18; 58 1.55190913278780E-0004; 19 5.97518189766788E-0002;
SURFACE 18; -equil 18; Su  2.29922400508658E+0000 1.91602000423813E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 18; -water  7.18507501589556E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 19; 59 1.47262281097582E-0004; 20 6.28846125887321E-0002;
SURFACE 19; -equil 19; Su  2.42301439793664E+0000 2.01917866494751E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 19; -water  7.57191999355200E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 20; 60 1.40104433918253E-0004; 21 6.60173315183101E-0002;
SURFACE 20; -equil 20; Su  2.54680479078961E+0000 2.12233732565689E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 20; -water  7.95876497122663E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 21; 61 1.33610149100782E-0004; 22 6.91500404452654E-0002;
SURFACE 21; -equil 21; Su  2.67059518363967E+0000 2.22549598636627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 21; -water  8.34560994887397E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 22; 62 1.27691257957530E-0004; 23 7.22827543734184E-0002;
SURFACE 22; -equil 22; Su  2.79438557648973E+0000 2.32865464707565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 22; -water  8.73245492653041E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 23; 63 1.22274540012235E-0004; 24 1.34962976378347E-0001;
SURFACE 23; -equil 23; Su  2.91817596934270E+0000 2.43181330778503E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 23; -water  9.11929990419594E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 24; 64 3.02535036754392E-0004; 25 2.02590334882871E-0001;
SURFACE 24; -equil 24; Su  3.04196636219276E+0000 2.53497196849442E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 24; -water  9.50614488185238E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 25; 65 2.90705038716155E-0004; 26 1.46175540734703E-0001;
SURFACE 25; -equil 25; Su  3.16575675504573E+0000 2.63813062920380E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 25; -water  9.89298985951791E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 26; 66 1.08470447236542E-0004; 27 8.48136165117239E-0002;
SURFACE 26; -equil 26; Su  3.28954714789870E+0000 2.74128928991699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 26; -water  1.02798348371834E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 27; 67 1.04536586086645E-0004; 28 8.79463173519071E-0002;
SURFACE 27; -equil 27; Su  3.41333754074876E+0000 2.84444795062256E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 27; -water  1.06666798148399E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 28; 68 1.00878073389765E-0004; 29 9.10790448427861E-0002;
SURFACE 28; -equil 28; Su  3.53712793359882E+0000 2.94760661133194E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 28; -water  1.10535247924963E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 29; 69 9.74669802856099E-0005; 30 9.42117590083171E-0002;
SURFACE 29; -equil 29; Su  3.66091832644888E+0000 3.05076527204132E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 29; -water  1.14403697701528E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 30; 70 9.42790223356305E-0005; 31 9.73444584245726E-0002;
SURFACE 30; -equil 30; Su  3.78470871929894E+0000 3.15392393275070E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 30; -water  1.18272147478092E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 31; 71 9.12930116410138E-0005; 32 1.00477187339720E-0001;
SURFACE 31; -equil 31; Su  3.90849911214900E+0000 3.25708259345627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 31; -water  1.22140597254656E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 32; 72 8.84903326074493E-0005; 33 1.03609885806350E-0001;
SURFACE 32; -equil 32; Su  4.03228950499906E+0000 3.36024125416565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 32; -water  1.26009047031221E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 33; 73 8.58546145936501E-0005; 34 1.06742615670555E-0001;
SURFACE 33; -equil 33; Su  4.15607989785494E+0000 3.46339991487885E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 33; -water  1.29877496807967E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 34; 74 8.33713719671003E-0005; 35 1.09875313188240E-0001;
SURFACE 34; -equil 34; Su  4.27987029070500E+0000 3.56655857558823E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 34; -water  1.33745946584531E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 35; 75 8.10277361432021E-0005; 36 1.13008044001731E-0001;
SURFACE 35; -equil 35; Su  4.40366068355506E+0000 3.66971723629379E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 35; -water  1.37614396361096E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 36; 76 7.88122579565176E-0005; 37 1.16140758167262E-0001;
SURFACE 36; -equil 36; Su  4.52745107641094E+0000 3.77287589700699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 36; -water  1.41482846137842E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 37; 77 7.67147075466212E-0005; 38 1.19273454260906E-0001;
SURFACE 37; -equil 37; Su  4.65124146925518E+0000 3.87603455771255E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 37; -water  1.45351295914224E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 38; 78 7.47259203147443E-0005; 39 1.22406186498324E-0001;
SURFACE 38; -equil 38; Su  4.77503186211106E+0000 3.97919321842575E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 38; -water  1.49219745690971E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 39; 79 7.28376432384437E-0005; 40 1.25538881642797E-0001;
SURFACE 39; -equil 39; Su  4.89882225496112E+0000 4.08235187913513E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 39; -water  1.53088195467535E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 40; 80 7.10424415898636E-0005; 41 1.28671614829727E-0001;
SURFACE 40; -equil 40; Su  5.02261264781700E+0000 4.18551053984833E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 40; -water  1.56956645244281E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 41; 81 6.93336006637679E-0005; 42 1.31804328995031E-0001;
SURFACE 41; -equil 41; Su  5.14640304066124E+0000 4.28866920055389E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 41; -water  1.60825095020482E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 42; 82 6.77050370115673E-0005; 43 1.34937022715349E-0001;
SURFACE 42; -equil 42; Su  5.27019343351712E+0000 4.39182786126709E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 42; -water  1.64693544797228E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 43; 83 6.61512304849232E-0005;
SURFACE 43; -equil 43; Su  5.39398382636718E+0000 4.49498652197266E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 43; -water  1.68561994573975E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 44; 84 1.38005180995293E-0003; 45 4.70840667710490E-0002;
SURFACE 44; -equil 44; Su  5.66158505167550E-0001 4.71798754306316E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 44; -water  1.76924532864859E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 45; 85 1.13244335819473E-0003; 46 3.91090111787662E-0002;
SURFACE 45; -equil 45; Su  6.89948898019065E-0001 5.74957415016174E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 45; -water  2.15609030630958E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 46; 86 3.72276469309440E-0004; 47 2.54517390654883E-0002;
SURFACE 46; -equil 46; Su  8.13739290869853E-0001 6.78116075724602E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 46; -water  2.54293528396829E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 47; 87 3.23121462957232E-0004; 48 2.90499079628717E-0002;
SURFACE 47; -equil 47; Su  9.37529683721368E-0001 7.81274736433983E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 47; -water  2.92978026162928E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 48; 88 2.85433188980733E-0004; 49 3.26480845735091E-0002;
SURFACE 48; -equil 48; Su  1.06132007657288E+0000 8.84433397144318E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 48; -water  3.31662523929026E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 49; 89 2.55618333846641E-0004; 50 3.62462457576385E-0002;
SURFACE 49; -equil 49; Su  1.18511046942440E+0000 9.87592057853699E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 49; -water  3.70347021695125E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 50; 90 2.31443023088929E-0004; 51 3.98444146550219E-0002;
SURFACE 50; -equil 50; Su  1.30890086227446E+0000 1.09075071856117E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 50; -water  4.09031519461223E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 51; 91 2.11445386539566E-0004; 52 4.34425835524053E-0002;
SURFACE 51; -equil 51; Su  1.43269125512597E+0000 1.19390937927246E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 51; -water  4.47716017226412E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 52; 92 1.94628681947151E-0004; 53 4.70407524497887E-0002;
SURFACE 52; -equil 52; Su  1.55648164797749E+0000 1.29706803998184E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 52; -water  4.86400514992965E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 53; 93 1.80289836276515E-0004; 54 5.06389213471721E-0002;
SURFACE 53; -equil 53; Su  1.68027204083046E+0000 1.40022670069122E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 53; -water  5.25085012759519E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 54; 94 1.67918784334731E-0004; 55 5.42371158720698E-0002;
SURFACE 54; -equil 54; Su  1.80406243368052E+0000 1.50338536140060E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 54; -water  5.63769510525162E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 55; 95 1.57136448894235E-0004; 56 5.78352591419389E-0002;
SURFACE 55; -equil 55; Su  1.92785282653349E+0000 1.60654402211189E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 55; -water  6.02454008291716E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 56; 96 1.47655287926973E-0004; 57 6.14334622682691E-0002;
SURFACE 56; -equil 56; Su  2.05164321938355E+0000 1.70970268281937E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 56; -water  6.41138506057359E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 57; 97 1.39253148892315E-0004; 58 6.50315607028915E-0002;
SURFACE 57; -equil 57; Su  2.17543361223361E+0000 1.81286134352875E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 57; -water  6.79823003823003E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 58; 98 1.31755735669614E-0004; 59 6.86298040726570E-0002;
SURFACE 58; -equil 58; Su  2.29922400508658E+0000 1.91602000423813E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 58; -water  7.18507501589556E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 59; 99 1.25024427756415E-0004; 60 7.22278944880372E-0002;
SURFACE 59; -equil 59; Su  2.42301439793664E+0000 2.01917866494751E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 59; -water  7.57191999355200E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 60; 100 1.18947459880658E-0004; 61 7.58261458770448E-0002;
SURFACE 60; -equil 60; Su  2.54680479078961E+0000 2.12233732565689E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 60; -water  7.95876497122663E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 61; 101 1.13433878512303E-0004; 62 7.94243167790682E-0002;
SURFACE 61; -equil 61; Su  2.67059518363967E+0000 2.22549598636627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 61; -water  8.34560994887397E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 62; 102 1.08408802396198E-0004; 63 8.30223951656990E-0002;
SURFACE 62; -equil 62; Su  2.79438557648973E+0000 2.32865464707565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 62; -water  8.73245492653041E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 63; 103 1.03810041757946E-0004; 64 1.55015703827985E-0001;
SURFACE 63; -equil 63; Su  2.91817596934270E+0000 2.43181330778503E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 63; -water  9.11929990419594E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 64; 104 2.56849692903671E-0004; 65 2.32690840093255E-0001;
SURFACE 64; -equil 64; Su  3.04196636219276E+0000 2.53497196849442E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 64; -water  9.50614488185238E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 65; 105 2.46806108212638E-0004; 66 1.67894383712564E-0001;
SURFACE 65; -equil 65; Su  3.16575675504573E+0000 2.63813062920380E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 65; -water  9.89298985951791E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 66; 106 9.20904800961964E-0005; 67 9.74150627361041E-0002;
SURFACE 66; -equil 66; Su  3.28954714789870E+0000 2.74128928991699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 66; -water  1.02798348371834E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 67; 107 8.87506627452517E-0005; 68 1.01013342192346E-0001;
SURFACE 67; -equil 67; Su  3.41333754074876E+0000 2.84444795062256E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 67; -water  1.06666798148399E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 68; 108 8.56446193249205E-0005; 69 1.04611396521136E-0001;
SURFACE 68; -equil 68; Su  3.53712793359882E+0000 2.94760661133194E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 68; -water  1.10535247924963E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 69; 109 8.27486246398834E-0005; 70 1.08209683996506E-0001;
SURFACE 69; -equil 69; Su  3.66091832644888E+0000 3.05076527204132E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 69; -water  1.14403697701528E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 70; 110 8.00420812663738E-0005; 71 1.11807730306396E-0001;
SURFACE 70; -equil 70; Su  3.78470871929894E+0000 3.15392393275070E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 70; -water  1.18272147478092E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 71; 111 7.75069786463689E-0005; 72 1.15406025801121E-0001;
SURFACE 71; -equil 71; Su  3.90849911214900E+0000 3.25708259345627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 71; -water  1.22140597254656E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 72; 112 7.51275386042138E-0005; 73 1.19004196703031E-0001;
SURFACE 72; -equil 72; Su  4.03228950499906E+0000 3.36024125416565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 72; -water  1.26009047031221E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 73; 113 7.28898379970033E-0005; 74 1.22602094363174E-0001;
SURFACE 73; -equil 73; Su  4.15607989785494E+0000 3.46339991487885E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 73; -water  1.29877496807967E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 74; 114 7.07815732447159E-0005; 75 1.26200538507646E-0001;
SURFACE 74; -equil 74; Su  4.27987029070500E+0000 3.56655857558823E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 74; -water  1.33745946584531E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 75; 115 6.87918483918359E-0005; 76 1.29798709409897E-0001;
SURFACE 75; -equil 75; Su  4.40366068355506E+0000 3.66971723629379E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 75; -water  1.37614396361096E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 76; 116 6.69109303101045E-0005; 77 1.33396880311921E-0001;
SURFACE 76; -equil 76; Su  4.52745107641094E+0000 3.77287589700699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 76; -water  1.41482846137842E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 77; 117 6.51301356340284E-0005; 78 1.36995180677104E-0001;
SURFACE 77; -equil 77; Su  4.65124146925518E+0000 3.87603455771255E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 77; -water  1.45351295914224E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 78; 118 6.34416692922635E-0005; 79 1.40592908778217E-0001;
SURFACE 78; -equil 78; Su  4.77503186211106E+0000 3.97919321842575E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 78; -water  1.49219745690971E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 79; 119 6.18385283742029E-0005; 80 1.44191393018446E-0001;
SURFACE 79; -equil 79; Su  4.89882225496112E+0000 4.08235187913513E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 79; -water  1.53088195467535E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 80; 120 6.03144190185922E-0005; 81 1.47789563920696E-0001;
SURFACE 80; -equil 80; Su  5.02261264781700E+0000 4.18551053984833E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 80; -water  1.56956645244281E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 81; 121 5.88636307686130E-0005; 82 1.51387734822720E-0001;
SURFACE 81; -equil 81; Su  5.14640304066124E+0000 4.28866920055389E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 81; -water  1.60825095020482E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 82; 122 5.74810001809922E-0005; 83 1.54985560310251E-0001;
SURFACE 82; -equil 82; Su  5.27019343351712E+0000 4.39182786126709E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 82; -water  1.64693544797228E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 83; 123 5.61618220086046E-0005;
SURFACE 83; -equil 83; Su  5.39398382636718E+0000 4.49498652197266E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 83; -water  1.68561994573975E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 84; 85 5.41510049746421E-0002;
SURFACE 84; -equil 84; Su  5.66158505167550E-0001 4.71798754306316E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 84; -water  1.76924532864859E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 85; 86 4.49789503542775E-0002;
SURFACE 85; -equil 85; Su  6.89948898019065E-0001 5.74957415016174E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 85; -water  2.15609030630958E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 86; 87 2.92718294341228E-0002;
SURFACE 86; -equil 86; Su  8.13739290869853E-0001 6.78116075724602E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 86; -water  2.54293528396829E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 87; 88 3.34100761278933E-0002;
SURFACE 87; -equil 87; Su  9.37529683721368E-0001 7.81274736433983E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 87; -water  2.92978026162928E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 88; 89 3.75483047828311E-0002;
SURFACE 88; -equil 88; Su  1.06132007657288E+0000 8.84433397144318E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 88; -water  3.31662523929026E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 89; 90 4.16865289782891E-0002;
SURFACE 89; -equil 89; Su  1.18511046942440E+0000 9.87592057853699E+0005  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 89; -water  3.70347021695125E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 90; 91 4.58247236734906E-0002;
SURFACE 90; -equil 90; Su  1.30890086227446E+0000 1.09075071856117E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 90; -water  4.09031519461223E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 91; 92 4.99629788617426E-0002;
SURFACE 91; -equil 91; Su  1.43269125512597E+0000 1.19390937927246E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 91; -water  4.47716017226412E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 92; 93 5.41012114667865E-0002;
SURFACE 92; -equil 92; Su  1.55648164797749E+0000 1.29706803998184E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 92; -water  4.86400514992965E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 93; 94 5.82394381377185E-0002;
SURFACE 93; -equil 93; Su  1.68027204083046E+0000 1.40022670069122E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 93; -water  5.25085012759519E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 94; 95 6.23776179126594E-0002;
SURFACE 94; -equil 94; Su  1.80406243368052E+0000 1.50338536140060E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 94; -water  5.63769510525162E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 95; 96 6.65159335868566E-0002;
SURFACE 95; -equil 95; Su  1.92785282653349E+0000 1.60654402211189E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 95; -water  6.02454008291716E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 96; 97 7.06540650323859E-0002;
SURFACE 96; -equil 96; Su  2.05164321938355E+0000 1.70970268281937E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 96; -water  6.41138506057359E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 97; 98 7.47922885922208E-0002;
SURFACE 97; -equil 97; Su  2.17543361223361E+0000 1.81286134352875E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 97; -water  6.79823003823003E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 98; 99 7.89306214586531E-0002;
SURFACE 98; -equil 98; Su  2.29922400508658E+0000 1.91602000423813E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 98; -water  7.18507501589556E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 99; 100 8.30687357117768E-0002;
SURFACE 99; -equil 99; Su  2.42301439793664E+0000 2.01917866494751E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 99; -water  7.57191999355200E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 100; 101 8.72069592717253E-0002;
SURFACE 100; -equil 100; Su  2.54680479078961E+0000 2.12233732565689E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 100; -water  7.95876497122663E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 101; 102 9.13453201796983E-0002;
SURFACE 101; -equil 101; Su  2.67059518363967E+0000 2.22549598636627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 101; -water  8.34560994887397E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 102; 103 9.54834063912813E-0002;
SURFACE 102; -equil 102; Su  2.79438557648973E+0000 2.32865464707565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 102; -water  8.73245492653041E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 103; 104 1.78282105764993E-0001;
SURFACE 103; -equil 103; Su  2.91817596934270E+0000 2.43181330778503E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 103; -water  9.11929990419594E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 104; 105 2.67616314988118E-0001;
SURFACE 104; -equil 104; Su  3.04196636219276E+0000 2.53497196849442E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 104; -water  9.50614488185238E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 105; 106 1.93093617992645E-0001;
SURFACE 105; -equil 105; Su  3.16575675504573E+0000 2.63813062920380E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 105; -water  9.89298985951791E-0001
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 106; 107 1.12036469090413E-0001;
SURFACE 106; -equil 106; Su  3.28954714789870E+0000 2.74128928991699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 106; -water  1.02798348371834E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 107; 108 1.16174524190569E-0001;
SURFACE 107; -equil 107; Su  3.41333754074876E+0000 2.84444795062256E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 107; -water  1.06666798148399E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 108; 109 1.20312747750290E-0001;
SURFACE 108; -equil 108; Su  3.53712793359882E+0000 2.94760661133194E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 108; -water  1.10535247924963E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 109; 110 1.24450971310239E-0001;
SURFACE 109; -equil 109; Su  3.66091832644888E+0000 3.05076527204132E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 109; -water  1.14403697701528E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 110; 111 1.28589164324694E-0001;
SURFACE 110; -equil 110; Su  3.78470871929894E+0000 3.15392393275070E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 110; -water  1.18272147478092E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 111; 112 1.32727817573368E-0001;
SURFACE 111; -equil 111; Su  3.90849911214900E+0000 3.25708259345627E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 111; -water  1.22140597254656E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 112; 113 1.36865641989743E-0001;
SURFACE 112; -equil 112; Su  4.03228950499906E+0000 3.36024125416565E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 112; -water  1.26009047031221E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 113; 114 1.41003865549465E-0001;
SURFACE 113; -equil 113; Su  4.15607989785494E+0000 3.46339991487885E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 113; -water  1.29877496807967E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 114; 115 1.45142089109186E-0001;
SURFACE 114; -equil 114; Su  4.27987029070500E+0000 3.56655857558823E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 114; -water  1.33745946584531E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 115; 116 1.49280312669134E-0001;
SURFACE 115; -equil 115; Su  4.40366068355506E+0000 3.66971723629379E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 115; -water  1.37614396361096E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 116; 117 1.53418997595509E-0001;
SURFACE 116; -equil 116; Su  4.52745107641094E+0000 3.77287589700699E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 116; -water  1.41482846137842E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 117; 118 1.57556722362642E-0001;
SURFACE 117; -equil 117; Su  4.65124146925518E+0000 3.87603455771255E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 117; -water  1.45351295914224E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 118; 119 1.61694983348298E-0001;
SURFACE 118; -equil 118; Su  4.77503186211106E+0000 3.97919321842575E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 118; -water  1.49219745690971E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 119; 120 1.65833206908474E-0001;
SURFACE 119; -equil 119; Su  4.89882225496112E+0000 4.08235187913513E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 119; -water  1.53088195467535E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 120; 121 1.69971430468195E-0001;
SURFACE 120; -equil 120; Su  5.02261264781700E+0000 4.18551053984833E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 120; -water  1.56956645244281E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
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 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 121; 122 1.74110177618104E-0001;
SURFACE 121; -equil 121; Su  5.14640304066124E+0000 4.28866920055389E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 121; -water  1.60825095020482E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
MIX 122; 123 1.78247877587637E-0001;
SURFACE 122; -equil 122; Su  5.27019343351712E+0000 4.39182786126709E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 122; -water  1.64693544797228E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge

SURFACE 123; -equil 123; Su  5.39398382636718E+0000 4.49498652197266E+0006  1
-donnan  3.74999999999975E-0010 v  1.00000000000000E+0000; -only_co
SOLUTION 123; -water  1.68561994573975E+0000
 pH 7.09; #pe 14 O2(g) -2
 Na 239;        K 1.54;         Mg 17.2;        Ca 25.9;        Sr 0.500
 Alkalinity 2.5; S(6) 12.6;     Cl 304 charge
END;  PRINT; -reset false; # -user_pr true
TRANSPORT; -war true; -flow diff; -cells 1; -bcon 1 2; -stag 121
-shifts 1168; -time  2.16000000000000E+0004
-punch_c 3 #27 29 31 34 36
 -punch_fr 4
-multi_D true 2.24e-9 0.16 0 1.0
SELECTED_OUTPUT; -file Fig4.txt; -reset false; -high_pr true
USER_PUNCH; -head days HTO Na I #dist DD(Bq/g); -start
 10 if cell_no = 3 then punch total_time / (24*3600), tot("Hto") * 1e6 tot("Nat") * 1e6,\
 tot("I") * 1e6
 20 if step_no < 1168 then goto 50
 30 x = (((cell_no - 23.5) *  4.20951775601977E-0003)^2 + ((cell_no - 23.5)\
 *  8.61843706486951E-0003)^2)^0.5; 32 c = 0.165 * exp(-20.0 * x)
 40 if cell_no > 3 then punch total_time/(24*3600), tot("Nat")*1e6, x, c - sys("Nat") * 2.018e6 / 16
 50 end; -end
END
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