Non-diagonal transport phenomena in deep disposal facilities: contribution of osmotic processes to the interpretation of the far-field water pressure in the Tournemire argillite

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Abstract:

This study aims at identifying and quantifyingthe contribution of each mechanism that may contribute to the excess hydraulic heads measured in the Toarcian/Domerianclayrockat Tournemire. Such excess heads are very close to those measured by Andrain the Callovo-Oxfordianargillite at the Bure URLand considered as a possible host rock for a HL-ILLL repository. A special focus is made on transport processes such as advection chemo-osmosis and thermo-osmosis, respectively responsible for a fluid flow under gradients of pressure, concentration and temperature. The quantification of their relative contribution has requiredto acquiretheir force gradients and their related parameters. A 1D modeling approach based on the application of continuity equation at steady state is proposed.A satisfactory reproduction of the measuredexcess-hydraulic head isachieved by coupling chemo-thermo-osmotic flows to advection. Those simulations also allowed comparing the characteristic times for diffusion to advection including non-diagonal osmotic flows.Results suggest thatdiffusion still remains the dominant transport phenomenon for solutes and therefore for RN at the formation scale. However, the introduction of thermo-osmotic flow in the calculations leadsto an increase of the specific discharge and to reverse the water movementswhich become directed upward.

1BACKGROUND

Excess-head pressures are frequently observed in aquitards such as shales and argillites compared to the theoretical hydrostatic profile deduced from hydraulic heads measured in their surrounding non-argillaceous aquifers. This is the case for the Callovo-Oxfordian argillite studied by Andra as a potential host rock for the repository of High Level and Intermediate Level Long-Lived radioactive wastes. This formation is known to develop an excess-head of about 50m in equivalent water level measured at the centre of the 150m-thick Callovo-Oxfordian(COx) formation and located at a mean depth of about 475m/bslin the vicinity of their deep Underground Research Laboratory (URL), located in theEast of France[**1**]. An excess-head of about 30m was also identified in the centre of the 250m-thick Toarcian/Domerian over-consolidated clayrockat the IRSN's URL in Tournemire (Figure 1), located in the South of France[2],[3]. Data reported in this figure are not affected by the tunnel or drifts influence[**2**] which tend to deplete the pore pressure and are therefore representative of the far-field water-pressure conditions.

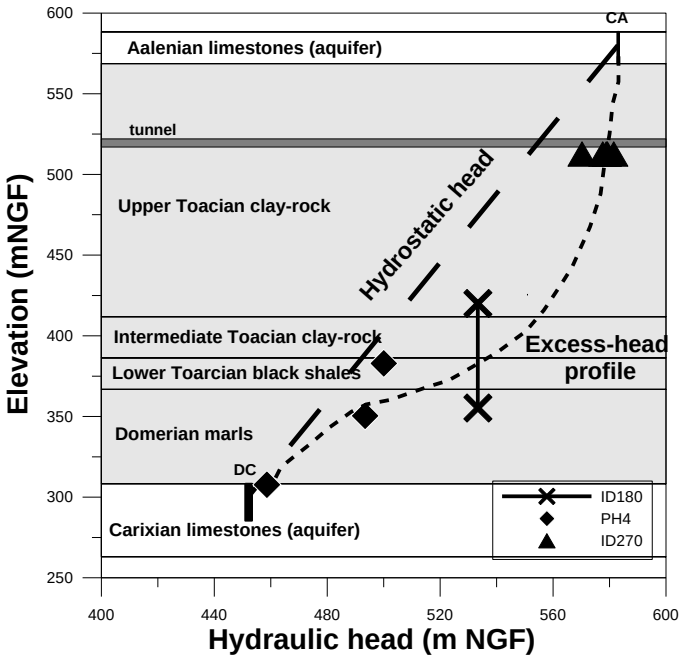

Figure 1: Hydraulic head profile at the Tournemire URL across the Toarcian/Domerianclayrock representative of far-field conditions with respect to the tunnel.

Several researchers [**4**], [**5**] agreed that excess-headsmay result from oneormore of the followingmechanisms related to: i) mechanical stresses such as compaction disequilibriumof the argillaceous formation or skeletondeformationof the sedimentunder tectonic stress, ii) diagenetic stresses during mineralogical transformation or neoformation, iii) changes in hydrodynamic boundary conditions, iv) hydromechanical processes including the visco-plastic behaviour of clays, and v) transport processes includingnon-diagonal one such as osmotic processes.

Andra firstproposed that thechemo-osmotic phenomenonalone wasable toexplain the excesshead [**1**] at their Bure site but decided to conduct a new study next to the assessment by IRSNthat the contribution of other processeswas likely[**6**]. The goal of this study wastoassess the relative contribution of osmotic processes to the measured overpressures. It also aimed at verifying whether thecouplingof transport processesinvolvinggradientsofhydraulic and chemicalpotentials on the water flux alone couldaccount forsuch an excess head. The conclusions based on in situ and lab experiments and also on a numerical approach of transport processes at steady state wereunambiguous. The chemicalosmotic effect estimated in the Callovo-oxfordien coupled to advection couldonly explain 10m out of the 20-50m of the measured excess heads[**7**].

During this study, the lab tests performed on remolded COx samples for determining their osmotic efficiency also showed the role of temperature on the pressure signal suggesting the participation of another transport process: Thermo-osmosis. This process was poorly characterized so that no satisfactoryexpression to calculate its contribution was available nor thermo-osmotic experiments performed on naturalshales, so far.

As there was no satisfactory model to explain the excess-head at the Bure site, IRSN decided to conduct its own research programme at the Tournemire URL with the goal of identifying and quantifying the contributionof each cause to the measured excess-head.The purpose of thisstudy wasto determine whether or not the osmotic phenomena may be considered as responsible forsuchpressure profile at the Tournemire site.

First, a special attention is paid in section 2 to the definitions of individual flows in compacted clay rocks. This includes the darcy's flow and osmotic flows, i.e. the coupled fluid fluxes induced by chemical concentration, temperature and electrical gradients, in natural compacted clayrocks. Section 3deal with the modelling of the hydraulic head profile across the Tournemireclayrock, which includes the determination of force gradients and of coupled flow parameters profiles through the clayrock. The modelling of individual and coupled fluid flowsat steady state and comparison to the measured one, and to finish the contribution of coupled advective flows to the solute transport is assessed. At last the role of other possible processes such as transient hydromechanical to the excess head are also discussed.

Results presented inthis paper were mostly obtained in the PhD of J.Tremosa[**3**] who performed its thesis work at IRSNbetween 2008 and 2010.

2COUPLED FLUID FLOWS IN CLAYROCKS

2.1 Theory

Coupled-flows in clayrocks originate from the electrochemical interactionsoccuring at the pore scale between the charged surface of clay minerals andthe water and electrolytes. Due to isomorphic substitutions of cationsby others having a lower valence, in tetrahedral and octahedral layers, clayminerals present a surface charge, negative at natural pH, which inducesa non-uniform distribution of cations, anions and water molecules. Thesolutes distribution in the pore space results from the combination of theattraction by the charged surface and their diffusion towards the porecenter, where solute concentration is lower [**8**]. The ion distribution and the electrical potential can be described using double layer ortriple layer electrical models [8].

The Onsager's matrix (Table 1) summarizes the flows which candevelop under the different potential gradients[9],[10]. This includes fluxes related to theirnatural gradient, the diagonal flows, as well as the fluxesoccurring under the other potential gradients, i.e. the non-diagonal fluxes.

Table 1 also shows that the surrounded transport processes accounting for water flow are limited to Darcy flow and osmotic processes.

Flux	Gradients			
	Hydraulic head	Electrical	Chemical concentration	Temperature
Fluid	Darcy	Electro-osmosis	Chemical os-mosis	Thermo-osmosis
Current	Electrofiltration	Ohm	Membrane potential	Thermo-electricity
Ion	Ultrafiltration	Electrophoresis	Fick	Soret effect
Heat	Thermal filtra-tion	Peltier effect	Dufour effect	Fourier

Table 1: Onsager matrix with coupled-flows terminology

Coupling coefficients relating a flux to a driving force can be characterize through the principles of the irreversiblethermodynamics, based on the notion of entropy, and assumesa linear relation between the flows $J_i$and the gradients X_i, as follows [**11**]:

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \quad \text{Eq. 1}$$

where the subscripts i and j correspond to the various kinds of flows andgradients,respectively and L_{ij} are the phenomenological coefficients.The coefficients of the coupled flow matrix can then be obtained duringexperiments, i.e. measuring the flow associated to a force gradient.

When chemical osmosis, thermo-osmosis and electro-osmosis are considered together with the Darcy's flow, the fluid flow equation is extended and writes:

$$q = -\frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) + \frac{k_O}{\eta}\nabla \Pi - \frac{k_T}{\eta}\nabla \mathrm{T} + \beta\, \nabla \varphi \quad \text{Eq. 2}$$

where q is the pore fluid specific discharge (m s^{-1}),ηthe dynamic viscosity (Pa s), ρ_f the fluid density (kg m^3), g is the acceleration due to gravity (m s^{-2}),k, $k_O$andk_T denote the Intrinsicpermeability(m^2), the chemo-Osmoticpermeability (m^2) and the Thermo-osmoticpermeability ($m^2 s^{-1} K^{-1}$)respectively andβ is the electro-osmosis coefficient($m^2 s^{-1} V^{-1}$). $\nabla P, \nabla \Pi, \nabla \mathrm{T}, \nabla \varphi$represent the gradients of the pressure (Pa), osmotic pressure (Pa), temperature (°K), and current (A).The last three terms inEq. 2 can be considered as the non-diagonal transport phenomena and represent the osmotic contribution to the fluid flow.

2.2 Darcy flow

The contribution of the Darcy flow to the pore specific discharge may be deduced from Eq. 2:

$$q = -\frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) \quad \text{Eq. 3}$$

For a porous medium with a plane, parallel pore geometry, intrinsic permeability $k$can be obtained using a Poiseuilletypelaw:

$$k = b^2/3F \quad \text{Eq. 4}$$

where F, the formationfactoraccountingforthe tortuosity ofthe porousmedia, is defined as$F = \omega^{-m}$ with ω the porosity and m the cementation factor [**13**] which is rock dependent and must be defined for each case study. And *b* is the half-pore size (m) defined as:

$$b = \frac{\omega}{\rho_s A_s (1-\omega)} \qquad \text{Eq. 5}$$

with$\omega$the total porosity,ρ_s is the grain density(g m^{-3}) and $A_s$is the specific surface area(m^2 g^{-1}).It is worth noting that anion exclusion expression is applicable for both symmetric and nonsymmetricsolutions [**10**].

The fluid density ρ_f (kg m^{-3}) can be calculated from the Unesco equationof state which depends on salinity, temperature and pressure [**14**]. The dynamic viscosity of water (η in Pa·s) can be determined using the relation given in reference [**15**] as a function of temperature:

$$\frac{1}{\eta} = (5.38 + 3.8A - 0.26A^3) \times 10^3 \qquad \text{Eq. 6}$$

where$A = \frac{(T-150)}{100}$with T, the temperature, expressed in °C.

2.3 Osmotic flows

2.3.1 Chemical-osmosis

Chemical osmosis is the fluid flow across a material exhibiting a membrane behaviour induced by a difference of chemical potential. A membrane isa material whichlimits thetransport ofionic speciesbut notthe movement ofneutral speciessuch as water.Differences in concentration between two reservoirs induce a difference in osmotic pressure such as:

$$\Pi = -\frac{RT}{\Omega_w} \ln a_w \qquad \text{Eq. 7}$$

where Π is the osmotic pressure (Pa), R is the gas constant (8.32 x 10^{-3} $m^3PaK^{-1}mol^{-1}$), T is the temperature (K), $\Omega_w$is the molar volume of water (L mol^{-1}) and a_w is the water activity which depends on the aqueous concentration in the solution.

The osmotic efficiency coefficient of a clayrock writes ε *and*rangesbetween 0 for non-membrane behavior and 1 for perfectmembrane behavior, where solute flux is totally inhibited.The pore fluid specific discharge (m s^{-1}) of the chemical-osmosis flow deduced from Eq. 2 thus writes:

$$q = -\frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) + \varepsilon \frac{k}{\eta} \nabla \Pi \qquad \text{Eq. 8}$$

Theεcoefficient can be determined experimentally (see [**3**] and references therein). The osmoticefficiency can also be computed in a predictive senseusing theoretical models that consider the electrical interactionsbetween the solution and the charged surface togetherwith the petrophysical properties of the porous media[**13**], [**16**], [**17**], [**18**]. Predictive models allow to have osmotic efficiency coefficients for a wide range of salinity and pore size conditions and more easily than from experiments. Experiments are however essential for model calibration and to demonstrate that the studied clayrock develops a membrane behaviour.The chemo-osmotic efficiencyis obtained from the Navier-Stokes equation integrating the chemical force [**11**]:

$$\varepsilon = \frac{\int_0^b \left(1 - \frac{\bar{C} - (x)}{C_f}\right)(2bx - x^2)dx}{\frac{2b^3}{3}} \quad \text{Eq. 9}$$

where $\bar{C} - (x)$ is the anion concentration at a distance x from the clay surface,Cf is the anion concentration in the equilibrium solution, and $2b$the pore size (m) defined for a plane, parallel pore geometry. However, overpressures predicted by this combined model (Eq. 8+Eq. 9) are systematically higher than the observed one[**19**]. This was attributed by [20]to two natural causes: the effect of the complex composition of naturalwaters, including both monovalent and divalent cations, on the osmotic efficiency and theresulting abnormal pressures, and the presence of steady state rather than transient-statesalinity distributions.

For this purpose, an electrical triple-layer model (TLM) accounting formulti-ionic solutions was developed and used to calculate the osmotic efficiency at differentproportions of monovalent and divalent cations (see Appendix A in [20]).The evolution of the chemo-osmotic efficiency coefficient calculated with the TLM as a function ofthe calcium index (CaI)is reported in Figure 2.

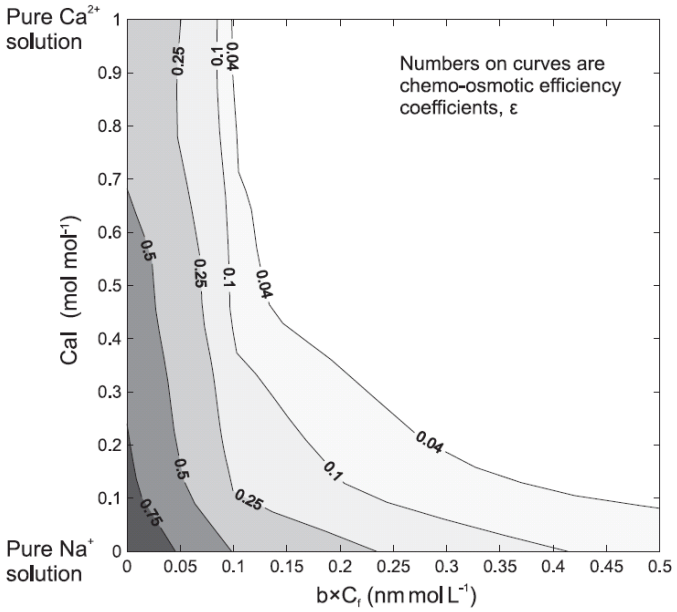

Figure 2: Evolution of chemo-osmotic efficiency coefficient calculated with the TLM as a function of the calcium index (CaI), 2xCa^{2+}/(Na^{+}+Ca^{2+}), and b xCf[20].

Figure 2 illustrates that ε decreases when the salinity(Cf) and/or the pore size (b) increase, and also when thecounterions are Ca^{2+} versus Na^{+}. At large pore size andfor high bulk concentration, the electrical double layer collapsesresulting in weak anionic exclusion.

2.3.2 Thermo-osmosis

Thermo-osmosis is a fluid flow driven by a temperature gradient.The macroscopic transportcoefficient for the thermo-osmotic permeability k_T was proposed from amicroscopicanalysisas $k_T = \frac{k\Delta H}{T}$[21]yielding to the following fluid specific discharge equation:

$$q = -\frac{k}{\eta}(\nabla P + \rho_f g \nabla z) - \frac{k}{\eta}\frac{\Delta H}{T}\nabla \mathrm{T} \quad \text{Eq. 10}$$

where q is theporefluidspecificdischarge(ms^{-1}), T is thetemperature(K)and ΔH is the macroscopic volume-averagedexcessspecificenthalpydueto fluid–solid interactions(J m^{-3}). This difference $\Delta H$is associated with an alteration of the hydrogen bond (HB) network of the water molecules and thus of the intermolecular bond energy due to fluid–solid interactions.A fully predictive theoretical expressions for k_T was developed bydirectly formalizing the enthalpy change ΔH due to hydrogen bonding modifications at the macro-scale[22].

2.3.3 Electro-osmosis

Electro-osmosis describes the flow of fluid due to an electrical potential gradient. However, in natural systems, themacroscopic current density is considered nil [**11**]and allows writing the electrical potential gradient as a function of the othergradients and coupling coefficients. This leads to an implicit integration of electro-osmosis in the flow coupling coefficients related to the pressure, chemical potential and temperature gradients [**11**] and which therefore turn as apparent coefficients.

3MODELLING THE CLAYROCKPOREWATER HEADS

3.1 Modelling concept

The aim of these calculations is to establish the effect of the osmotic flowson the head profile in the clayrock (Figure 1). The individual and coupled effectsof chemical osmosis and thermo-osmosis were studied assuming that electro-osmosis flow is negligible.Calculations were made in 1D, along the *z*-axis, in the Toarcian/Domerian layers usingthe pressure, temperature conditions determined for the Carixian and Aalenianaquifers asboundary conditions and the concentration profile determined for the clayrock. These calculations allowed obtaining a pressure profileacross the argillaceous formation and, after transformation as a hydraulichead, comparing it to the hydraulic head monitored in the formation and reported in Figure 1.In the present calculations, a pressure build-up was calculated for a given profile of concentration and temperature, considering that at a given time, themodeled system is in pseudo-equilibrium, so that the variations of pressurewith time can be assumed nil. This simplification can be made becauseof the very low hydraulic diffusivity and diffusion coefficient of the Tournemireclayrock[20]. The election of steady-state conditions for the calculationspresents the interest to avoid performing a reconstruction of the basin evolutionincluding the flows and transfers in the clayrock, requiredfor transient-state calculations. An assessment of such hypothesis is discussed in section 3.4.4.

The pressure field in the formationis finally calculated by solving the pressure - diffusion equation including osmoticcoupled flows at steady-state:

$$\frac{\partial}{\partial z}\left(\rho_f \frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) - \rho_f \varepsilon \frac{k}{\eta}\nabla \Pi + \frac{k}{\eta}\frac{\Delta H}{T}\nabla \mathrm{T}\right) = 0 \quad \text{Eq. 11}$$

with, from left to right in the left-hand-side term, the contributionsof the Darcy's flow, the chemical osmosis flow and thethermo-osmosis flow.

3.2 Gradients

Figure 3 presents the hydraulic head, concentration and temperature conditions used for the calculations. It includes: i) the heads measured in aquifers surrounding the clayrock[**2**], ii) the concentration profile of the clayrockporewater expressed in molal unit and calculated by geochemical modeling [23], iii) the temperature profile established at the Tournemire URL and obtained by direct measurement of temperature across the clayrock[24]. The occurrence of a 5Mavolcanic dyke at a distance of about 2km from the Tournemire URL likely explains the surprisingly high gradient, almost twice the normal geothermal gradient.

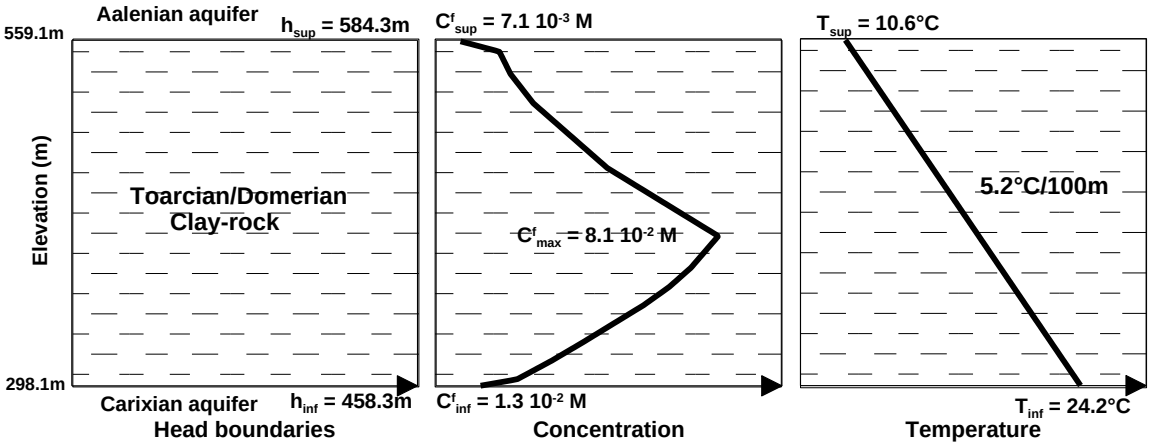

Figure 3: Hydraulic head boundary conditions with temperature and salinity profiles used for calculating the head profile in Tournemireclayrock.

3.3 Coupled flow parameters

Additional parameters are needed in the calculations (Eq.11): the dynamic viscosity of water (η), the fluid density(ρ_f), the intrinsic permeability (k), the chemo-osmotic efficiencyε, the thermo-osmotic permeability (k_T). Their variations across the formation are thus required.

The dynamic viscosity of water (η in Pa s) was calculated from Eq. 6across the formation and displays values ranging between 8.95 x 10^{-4} Pa s and 1.27 x 10^{-4} Pa s, for the highest and the lowest temperature, respectively. The fluid density was determined from the Unesco equation of state [14] and provided computed fluid density in between 998.5 and 1002.3 kg m^{-3}, with the highest values linked to the most saline porewaters in the centre of the clayrock formation.The intrinsic permeability profile was calculated from Eq. 4using petrophysicalresultsobtained across the whole clayrock[25]. The cementation factor $m$was fitted to a value of 2.3for natural clayrockpermeabilities and diffusion coefficients[3]. The calculated values range between 10^{-21} and 10^{-20} m^2 (Figure 4) and are of the same order of magnitude as values deduced from pulse tests performed in equipped boreholes [3].

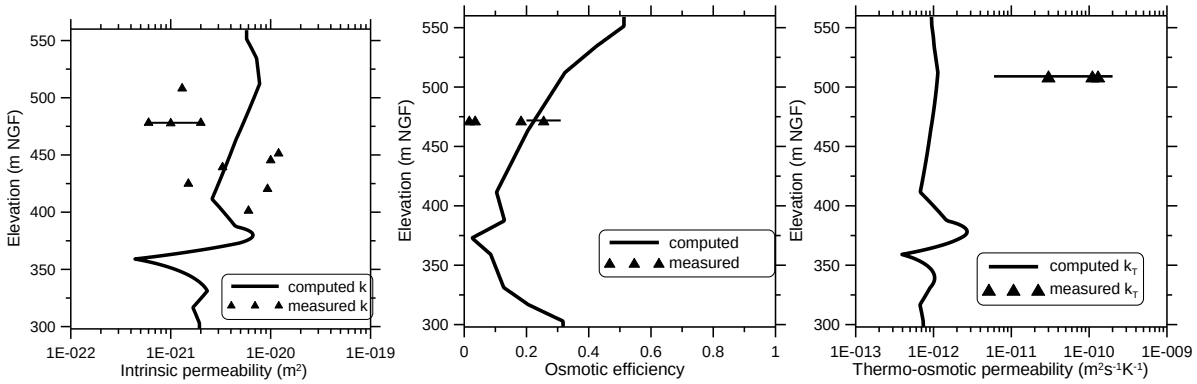

Figure 4: Profiles of measured and computed intrinsic permeability (***k***), chemical osmosis efficiency (ε) and thermo-osmotic permeability (k_T) compared to the measured values.

The predictedchemical osmosis efficiency profile across the clayrock(Figure 4) was obtained either by the Bolt expression (Eq. 9after [**11**])in agreement with rock properties and solution composition or through the triple-layer electricalmodel (TLM)describing the interactions between the charged solid surfaceof a clayrock and theporewater and taking into accountthe interactions of adjacent diffuse layers and both monovalent and divalentcounter-ions[20]. This profile is compared to values obtained on a clayrocksample. The experiments consisted in inducing a fluid flow through thesample upon a salinity gradient [**3**]. Efficiency values rangingbetween 0.014 and 0.31 as a function of the salinity were obtained duringthese experiments and are in the range of the predicted osmotic efficiencies.

As for the chemical osmotic efficiency, the thermo-osmotic permeabilityof the Tournemireclayrock was obtained by both predictive calculationsand experimental measurements. Predictions of the thermo-osmotic permeability were obtained by a model calculating the excess specific enthalpy in the pore spaceresponsible of the occurrence of thermo-osmosis by molecular interaction considerations[3], [22].Model input are a set of petrophysical parameters (porosity,specific surface area and cation exchange capacity) and the salinity of thebulk porewater. Taking into consideration the variations of these parametersacross the Toarcian/Domerian argillaceous formation, a profile of $k_T$is proposed (Fig. 4).The thermo-osmotic permeability of the Tournemireclayrock was also measuredduring in situ experiments, in an equipped borehole by inducing a temperature gradient between test section of the borehole and the clayrock[24]. A temperature gradient was induced. The inversion of the pressureevolution in the chamber allowed identifying a range of thermo-osmotic permeabilities with $k_T$values ranging between 6 10^{-12} and 2 10^{-10} m^2 s^{-1} K^{-1} (Figure 4).In this figure, the measured thermo-osmotic permeabilitiesare one order of magnitude greater than the predicted one, likely underestimated.

3.4 Contribution of flows to head profile

The contribution of each individual transport phenomena to the fluid pressure is evaluated by solving the pressure - diffusion equation at steady-state (Eq.11). Results are reported in Figure 5.

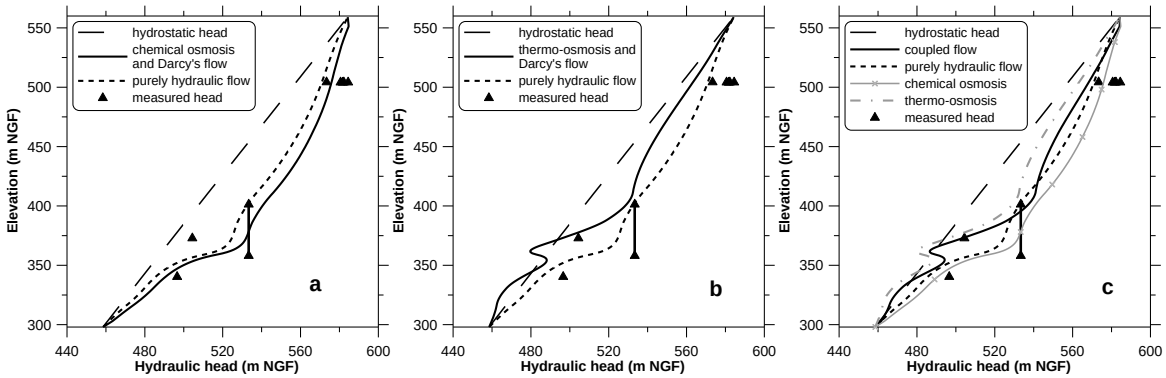

Figure 5: Contribution of the chemical-osmosis(a) and thermo-osmosis(b), and fully-coupled flows (c) to the head profile compared to a pure hydraulic flow.

3.4.1 Darcy flow

For a pure hydraulic flow eq.11 becomes:

$$\frac{\partial}{\partial z}\left(\rho_f \frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right)\right) = 0 \qquad \text{Eq. 12}$$

And σ , the deviation between the measured and calculated head, is estimated from:

$$\sigma = \frac{|\Delta h_{data} - \Delta h_{model}|}{\Delta h_{data}} \times 1000 \qquad \text{Eq. 13}$$

Eq.12gives alinear hydraulic head profile when the hydraulic parameters are taken constant across the clayrock (k = $10^{-21}m^2$, η = 10^{-3} Pa s, ρ_f= 10^3 kg m^{-3}), thus providing access to the hydrostatic head profile. The computed head profile displays spatial variations with a deviation of 24 %compared to the measured heads when hydraulic parameters areallowed to vary (Figure 4). The effect of the intrinsic permeability is the most significanton the head profile, although the variations of the fluid viscosity arealso non-negligible. The specific discharge $q$is -1.3 10^{-14} m s^{-1}, the negative value indicating a water movement directed downward.

3.4.2 Chemical osmosis

The head profile across the formation induced by chemicalosmosis is calculatedfrom (Eq. 11) which is restricted to Darcy's flow andchemical osmosis so that the solved equation becomes:

$$\frac{\partial}{\partial z}\left(\rho_f \frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) - \rho_f \varepsilon \frac{k}{\eta}\nabla \Pi\right) = 0 \qquad \text{Eq. 14}$$

Addition of chemical osmosis to the Darcy's flow leads to increase of 8 m the excess-heads at the centre of the clayrock(Figure 5a) compared to those obtained with Darcy's flow alone. The calculated hydraulic head profile is close to the measuredone, so that a deviation of 16 % is found between the model and the measured data, thus chemical osmosis does not induce significant changes on the head profile which is likely due to the weak porewater concentration profile across the Toarcian/Domerian clayrock. The specific discharge is of-1.4 10^{-14} m s^{-1} with a water movement still directed downward.

3.4.3 Thermo-osmosis

Considering only thermo-osmosis and Darcy's flows, Eq. 11becomes:

$$\frac{\partial}{\partial z}\left(\rho_f \frac{k}{\eta}\left(\nabla P + \rho_f g \nabla z\right) + \frac{k}{\eta}\frac{\Delta H}{T}\nabla \mathrm{T}\right) = 0 \qquad \text{Eq. 15}$$

The introduction of thermo-osmosis, together with the Darcy's flow, leadsto a hydraulic head lower than the one calculated with a purely hydraulicflow (Figure 5b). The resulting head profile is between 10 and 15 m less for the upper Toarcian and up to 35 m less in the lower Toarcian. In the deepest part of the formation, the head is even slightly lower than the hydrostatichead. It results in a higher deviation (84 %). The specific discharge is of 3.3 10^{-14} m $s^{-1}$and its positive value indicates an upward water movement attributed to the thermo-osmotic flow.

3.4.4 All coupled flows

Coupling all flows by applying Eq. 11provides a maximum excess head of 25 m at the clayrock centre and an excess-head almost nil below (Figure 5c). A deviation of 59 % to the measured hydraulic head profile is found.The influence of the thermo-osmosis on the trend of the calculated hydraulichead with coupled flows is obvious.When both chemo- and thermo-osmosis and Darcy's flow are considered, aspecific discharge of 3.2 10^{-14}m $s^{-1}$is computed, close to the one calculated forthermo-osmosis and Darcy's flow, and indicates an upward water movement.

Steady-state conditions were postulated in Eq. 11because ofuncertainties on the conditions that constrain the calculations of evolutionof the flows and transfers at geological time-scales. Nevertheless, because ofthe transient conditions of the concentration profile, two simple calculationsat transient-state were performed. One of these calculations considerschemical osmosis and Darcy's flow and the second one gathers chemicalosmosis, thermo-osmosis and Darcy's flow. The diffusion scenario for the Tournemire argillaceous formation [25],[26] was reproduced in these calculations and a Fick's diffusion was involved from a seawater salinityto a salinity profile close of the present-day profile using a diffusion coefficientin the range of those measured at Tournemire.

At final transient-state, thehydraulic head profiles and specific discharges are very close tothose calculated assuming a quasi-steady-state. This observation allowsasserting that the hypothesis of a pseudo-equilibrium of fluid flow for agiven concentration profile is valid.
The steady-state conditions can then beassumed with confidence and the calculations results are very likely realistic.

3.5 Contribution of coupled flows to mass transport of RN

The modification of the fluid movement caused byosmotic processes was shownto turn upward when thermo-osmosis is introducedin the calculations.The real interest of the fluid flow direction lies in its potentialimpact on advection mass transport. For this purpose, the Peclet number wascalculated for estimating the advection vs. diffusion contribution to the mass transport. The Peclet number,Pe, can be establishedas the ratio of the characteristic times for diffusion $\tau_D = \frac{L^2}{D_p}$toadvection $\tau_a = \frac{L}{u}$, where $L$is the thickness(m) of the porous medium crossed by the solute, $D_p = \frac{D_e}{\omega_{anions}}$, $D_p$and $D_e$stand forthe pore and effective diffusion coefficients, respectively ($m^2\ s^{-1}$) and $\omega_{anions}$is the anions accessible porosity. $u$is thepore fluid velocity ($m\ s^{-1}$) related to the specific discharge q by the relation$u = q/\omega_k$, where ω_k is the kinematic porosity or porosity accessible to flow. The Peclet number thus writes:$Pe = Lq/D_p\omega_k$.

The Peclet numbers for the Tournemire argillaceous formation were determinedfor Cl^-, as ^{36}Cl is one of the most mobile radionuclide, at the center of the 250 m thick formation(L = 125 m), using an effective diffusion coefficient for $Cl^-$of 4 10^{-12} m^2 s^{-1}[25] and the specific discharges reported previously.

The kinematic porosity value ranges between the total porosity and theaccessible porositywhich are 8.8 % and 6.6 % for Cl^-, respectively [25]. Calculationuses the total porosity as kinematic porosity. The resulting Peclet number is 0.28for the purely hydraulic flow, 0.30 for chemical osmotic and Darcy's flows,0.71 for the thermo-osmotic and Darcy's flows and 0.69 for all coupledflows. These calculatedPeclet numbers slightly lower than 1 suggest that diffusion is dominantbut the advective flow is not negligible for mass transport at the formationscale. Advection has also to be taken into consideration for mass transportespecially if thermo-osmosis is considered, because of the underestimationof the modeled thermo-osmotic permeability compared to the measuredvalues. This is in contradiction with the general assumption that solute transportin a compacted clayrock is mainly controlled by diffusion.

3.6 Contribution of hydromechanical processes to head profile

3.6.1 Viscoplastic behaviour of clays

The visco-plastic behavior of clayrocksresults in a delayed deformation.Here, our interest to the visco-plastic behaviour of clays is limitedto the time dependent volumetric deformation (one rock deformation mechanism) and can lead to a persistence of overpressures during large geologicaltime scales. The macroscopic volumetric creep of the rock, or compactioncreep, can result from granular mechanisms like pressure dissolution, in carbonatesand sandstones, or sliding and rotation of grains and platelets leadingto an aggregate deformation, in clays.

A calculation of the excess pressure caused by the visco-plastic behavior of the Tournemireclayrockwas made to assess the possible contributionof creep to the present measured pressure profile. This calculation was madefor a 1D geometry, along the *z* axis and the equation to be solved is:

$$K\frac{\partial P}{\partial z} = S_s\frac{\partial P}{\partial t} - \rho_f\frac{\sigma}{\eta_s(t)} \qquad \text{Eq. 16}$$

Where $K$is the hydraulic conductivity ($m\ s^{-1}$), S_s is the specific storativity (m^{-1}), $\sigma$the total stress (Pa), and $\eta_s(t)$is the volumetric viscosity coefficient of the porous medium (Pa s).

A relation describing the viscosity coefficient evolution with time was obtained from an inversion of the volumetric deformation measured on the Toarcian clay [27]and writes:

$$\eta_s(t) = 3.5\ 10^{11} \times t^{0.9} \quad \text{Eq. 17}$$

This time dependent relationship gives a $\eta_s(t)$value of $6\ 10^{23}$ Pa s after 1 Maof creep.

The main uncertainty in the calculation input lies in fixing time since thepresent total stress conditions are established. A calculation was performed assuming that the present-day total stress of $4 \pm 1\ MPa$ has not changed since 34 Ma which corresponds to the end of the Pyrenean orogeny, the last noticeable tectonic event [28]. Two other times were tested as they likely have modified the total stress: 5 Ma ago, at the end of the valley incision, and at 2 Ma, the start of the glacial period.

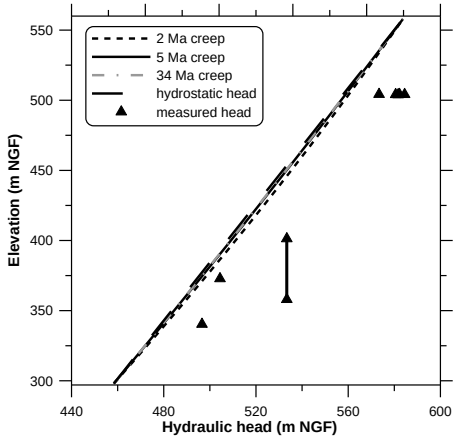

Figure 6: Calculated contribution of creep on the hydraulic head profile in Tournemireclayrock.

Calculations were made for constant K = 10^{-14}m s^{-1}, Ss =$10^{-6}m^{-1}$, σ = 4 MPa and the time-dependent variable $\eta_s(t)$from eq. 17. The results shownin Figure 6 indicate a very limited influence ofthis phenomenon on the pressure profile.The excess head, related to thehydrostatic head, is of few meters and tends to decrease with time withoutcompletely vanishing. Indeed, after 2 Ma of viscous behavior an excesshead around 3.7 m is calculated while after 5 Ma the excess head is around1.6 m and around 1.3 m after 34 Ma.

3.6.2 Other possible processes

Other possible causes for an excess-head are erosion unloading, lateral tectonic compression and compaction disequilibrium. All these processes are unlikely due i) to the exceptional over-consolidated nature of the clayrock acquired a very long time ago since the Cretaceous times when more than 1000 meters of sediments were eroded, ii) the long delay since the last tectonic event (about 34 Ma).

4 CONCLUSIONS

In very impervious clayrocks, like the Callovo-Oxfordian(COx) studied by Andra as a potential host rock for the disposal of HL-ILLL radioactive wastes, pore pressure,and their related hydraulic heads, frequently show excess-heads with respect to the theoretical hydrostatic head profile driven by the surrounding aquifers. The origin of such excess head was still a subject of controversy since it may result from many processes including transport and hydromechanicalprocesses. An overpressure of 30m is being measured in the Toarcian/Domerianclayrock at Tournemire URLwhereas it is of about 50m for the COxcentre at the Bure URL.

This paper aimed at identifying and quantifying the contribution of each cause to the excess-head measured at Tournemire and their possible contribution to the transport of radionuclides.A special focus was made on transport processes and especially on advection, the diagonal transport process, and on chemo-osmosis and thermo-osmosis, the non-diagonal one, respectively responsible for a fluid flow under gradients of pressure, concentration and temperature.

Osmotic processes are expected to develop due to the small pore size and the electrostatic interactions related to the charged surface of clay minerals. The quantification of their relative contribution has required the acquisition of their force gradients and of their related parameters hereinafter referred permeabilities. The force gradients for P,T,C were obtained by direct measurements (P,T) at Tournemire and indirectly by geochemical modeling (C). Darcy permeability was deduced from petrophysical measurements. Chemo-osmotic and themo-osmotic permeabilities were obtained from on-site and lab experiments and by theoretical models with petrophysical parameters and medium conditions (porewater composition and temperature) as input parameters.

A 1D modeling approach based on the application of continuity equation at steady state was proposed to assess the individual or coupled contribution of flow transport processes. A satisfactory reproduction of the measuredexcess-hydraulic head was achieved by coupling chemical osmosis,thermo-osmosis and advection which alone are able to generate, in the present-day conditions, an excess-headin Tournemireclayrock.

The contribution of hydromechanical processes (e.g., the visco-plastic behaviour of clays, erosion unloading, lateral tectonic compression and compaction disequilibrium) was also assessedbut their contribution to the measured excess-head looks very unlikely. To conclude, onlythe transport processes, related to the intrinsic permeability variation acrossthe formation coupled to non-diagonal osmotic processes can explain the pressure field in theToarcian/Domerian formation at the Tournemire URL. Those calculations also allowed a comparison of the characteristic times for diffusion and advection. Results suggest that diffusion still remains the dominant transport phenomenon for solutes and therefore for RN at the formation scale, so far, but the contribution of advection cannot be neglected as the Peclet number is 0.7, not that far from 1. This indicates that the coupled fluid flows also have to be taken into account for mass transport. This isespecially true if thermo-osmosis is considered because of the underestimationof the modeled thermo-osmotic permeability compared to the measuredvalues and also because its introduction in the calculations leadsto an increase of the specific discharge and to inverse the water movementswhich become directed upward.

5REFERENCES

[1] Andra (2005) – Dossier argile 2005 - http://www.andra.fr/download/site-principal/document/editions/269.pdf

[2] Matray, J.-M., Savoye, S., and Cabrera, J. (2007) Desaturationandstructurerelationshipsarounddriftsexcavated in the well-compactedTournemire'sargillite (Aveyron, France). Engineering Geology 9, p1-16.

[3] Tremosa, J. (2010), Influenceofosmoticprocesses on theexcess-hydraulicheadmeasured in theToarcian/DomerianargillaceousformationofTournemire, Ph.D. thesis, Universite´ Pierre et Marie Curie, Paris 6, France.

[4] GonçalvèsJ., Violette,S., Wendling,J. (2004) Analytical andnumericalsolutionsfor alternative overpressuringprocesses: applicationtotheCallovo-Oxfordiansedimentarysequence in the Paris basin, France. J.Geophys.Res.109, B02110.1–B02110.14.

[5] Neuzil, C. E. (1995), Abnormal Pressures as Hydrodynamic Phenomena, American journal of Science, 295, 742-786.

[6] IRSN (2005) – Avis de l'IRSN sur le Dossier 2005 Argile - http://www.irsn.fr/FR/expertise/rapports_expertise/Documents/surete/IRSN_rapport_2005_argile.pdf.

[7] Rousseau-Gueutin, P. (2008) Les processus couplés dans les argilites du Callovo-Oxfordien sur le site de Bure : implications pour les mouvements de fluide et de solutés. PhD thesis, Université Pierre et Marie Curie, Paris VI, 2008.

[8] Mitchell, J. K., and K. Soga (2005) Fundamentals of Soil Behavior, 3rd ed., 558 pp., John Wiley, N. Y.

[9] Onsager, L, (1931a) Reciprocal relations in irreversible processes. I. Phys. Rev. 37, 405.

[10] Onsager, L.,(1931b) Reciprocal relations in irreversible processes. II.Phys. Rev. 38, 2265.

[11] Bolt, G. H. (1979) Soil Chemistry, B. Physicochemical Models, 480 pp.,Elsevier, Amsterdam, Netherlands.

[12] A. Katchalsky, P.F. Curran, Nonequilibrium Thermodynamics in Biophysics, Harvard University Press, Cambridge, Massachusetts, 1967.

[13] Revil and Leroy, 2004Revil, A., and P. Leroy (2004), Constitutive equations for ionic transport in porous shales, J. Geophys. Res., 109, B03208, doi:10.1029/2003 JB002755.

[14] Unesco (1980) Tenth report on the joint panel on oceanographic tables and standard. Sidney, BC, Canada. 1-5 september 1980. Unesco technical paper in marine science 36, 1981. http://unesdoc.unesco.org/images/0004/000461/046148eb.pdf

[15] Mercer, J. W., Pinder, G. F., and Donalson, I. G. A (1975) Galerkin-finite element analysis of the hydrothermal system at Wairakei, New-Zealand. Journal of Geophysical Research 80, 2608-2621.

[16] Bresler, E. (1973) Anion exclusion and coupling effects in nonsteady transport unsaturated soils: I. Theory, Soil Sci. Soc. Am. Proc., 37(5), 663–669.

[17] Fritz, S. J. (1986) Ideality of clay membranes in osmotic processes: A review, Clays Clay Miner., 34(2), 214–223.

[18] Gonçalvès, J., P. Rousseau-Gueutin, and A. Revil (2007) Introducing interacting diffuse layers in TLM calculations. A reappraisal of the influence of the pore size on the swelling pressure and the osmotic efficiency of compacted bentonites, J. Colloid Interface Sci., 316, 92–99.

[19] Neuzil, C. E., and A. M. Provost (2009) Recent experimental data may point to a greater role for osmotic pressures in the subsurface, Water Resources Research, 45, W03,410,doi:10.1029/2007WR006,450.

[20] Tremosa,J., Gonçalvès, J., Matray, J.M. (2012) Natural conditions for more limited osmotic abnormal fluid pressures in sedimentary basins. Water Resources Research, Vol. 48, W04530, doi:10.1029/2011WR010914.

[21] Gonçalvès, J.,Tremosa,J. (2010). Thermo-osmosis in clayrocks: I theoretical insights. J.Colloid Interface Sci. 342,166–174.

[22] Gonçalvès, J., de Marsily G., Tremosa, J. (2012) Importance of thermo-osmosis for fluid flow and transport in clay formations hosting a nuclear waste repository Earth and Planetary Science Letters 339–340 1–10, http://dx.doi.org/10.1016/j.epsl.2012.03.032

[23] Tremosa, J., Arcos D., Matray J.M., Bensenouci F., Gaucher E.C., Tournassat C., Hadi J. (2012) Geochemical characterization and modelling of the Toarcian/Domerian porewaterat the Tournemire underground research laboratory. Applied Geochemistry 27 1417–1431 doi:10.1016/j.apgeochem.2012.01.005

[24] Tremosa, J., Gonçalvès, J., Matray, J.M., Violette,S. (2010) Thermo-osmosis in clay-rocks: II in-situ experimental approach. J.Colloid Interface Sci. 342, 175–184.

[25] Bensenouci, F. (2010) Apport des traceurs naturels á la compréhension des transferts au sein des formations argileuses compactées. Ph.D. thesis. Univ. Paris-Sud 11.

[26] Savoye, S., Michelot, J. L., Bensenouci, F., Matray, J. M., and Cabrera, J. (2008) Insight given by stable isotope profiles in pore-water for understanding transfers through Toarcian/Domerian argillaceous rocks over large space and time scales. Physics and Chemistry of the Earth 33, S67-S74.

[27] Fabre, G., and Pellet, F. (2006) Creep and time-dependent damage in argillaceous rocks. International Journal of Rock Mechanics and Mining Science 43, 950-960.

[28]Cabrera, J., Beaucaire, C., Bruno, G., De Windt, L.,Genty, A., Ramambasoa, N., Rejeb, A., Savoye, S., andVolant, P. (2001) Projet Tournemire. Synthèse des programmes de recherche. Rapport DPRE/SERGD 01-19, IRSN.